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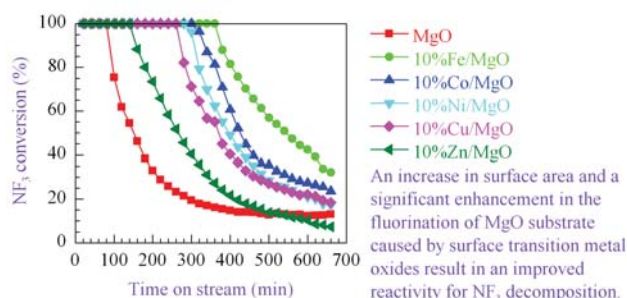
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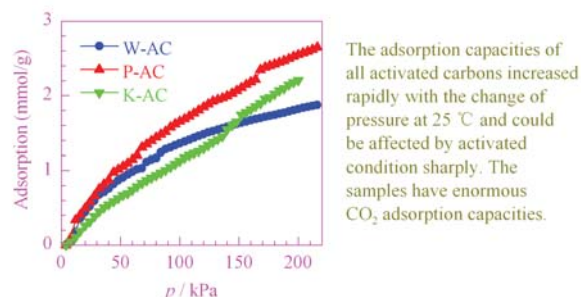
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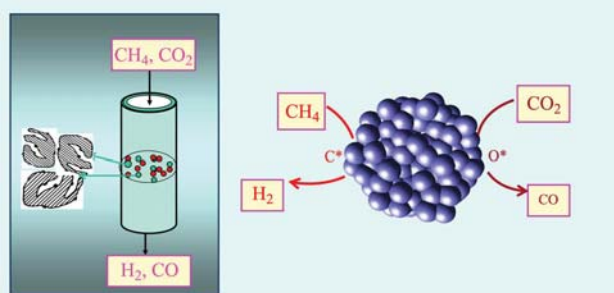
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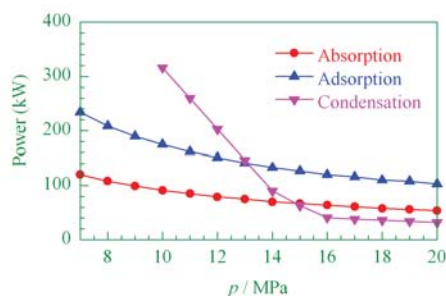
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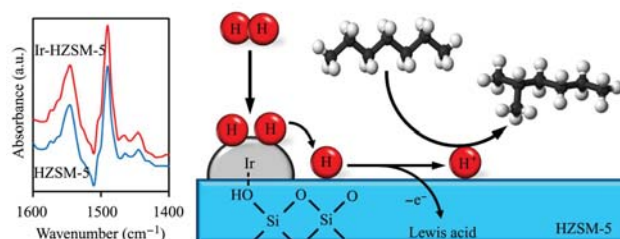
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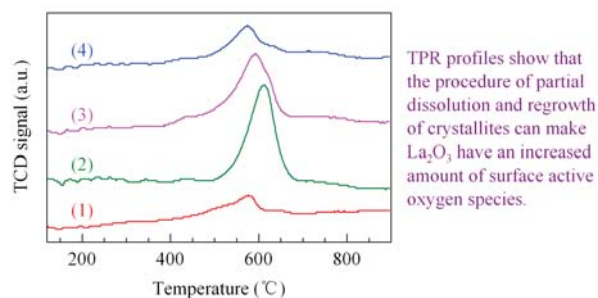
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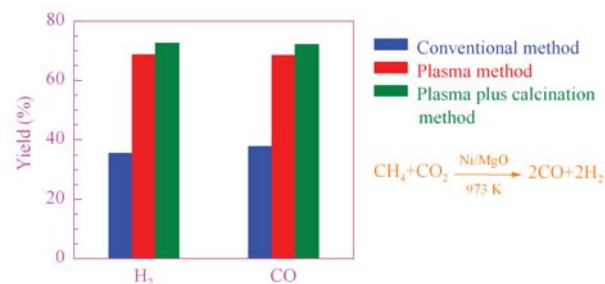
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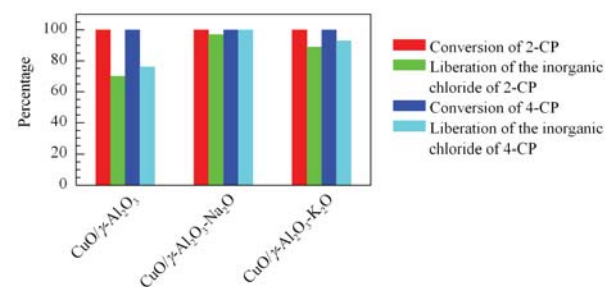
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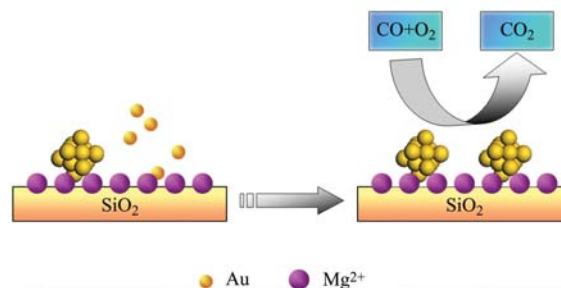
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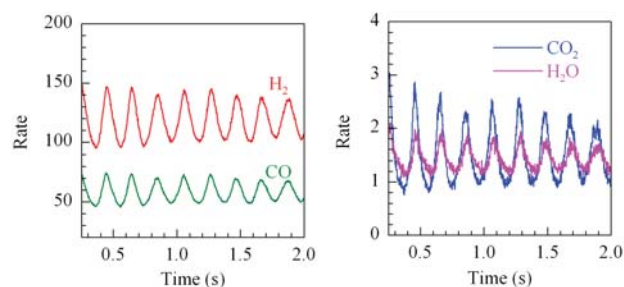
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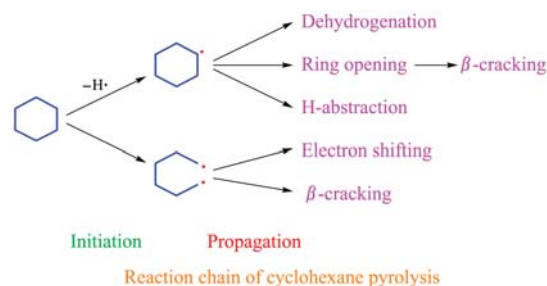
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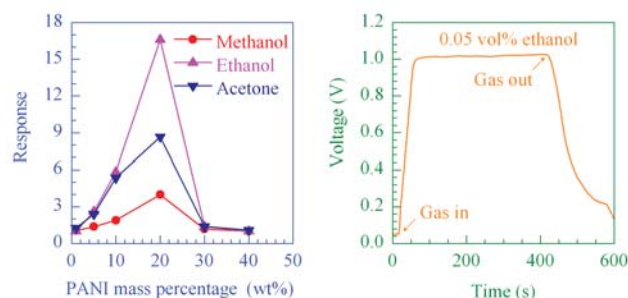
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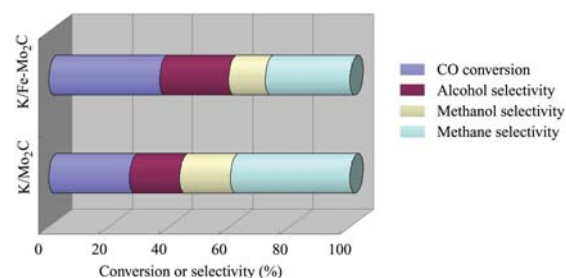
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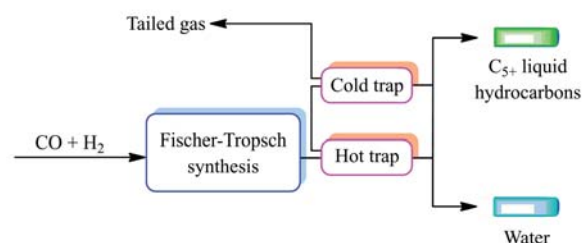
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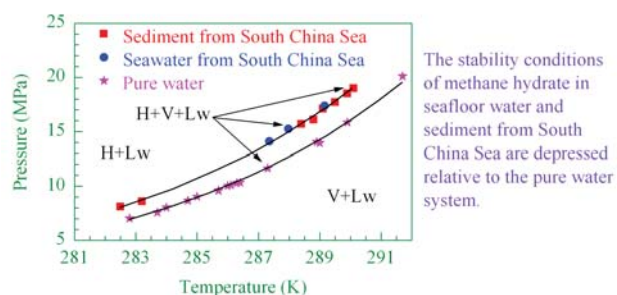
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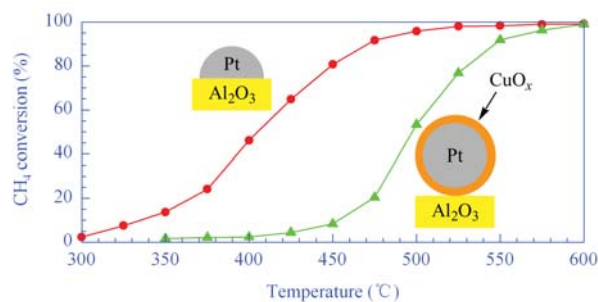
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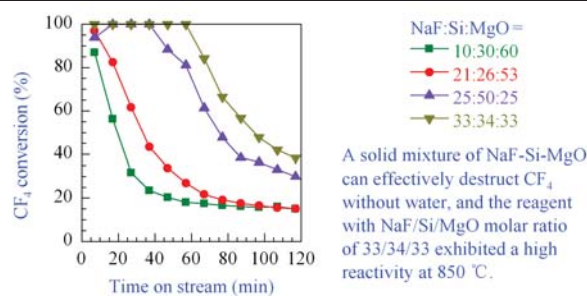
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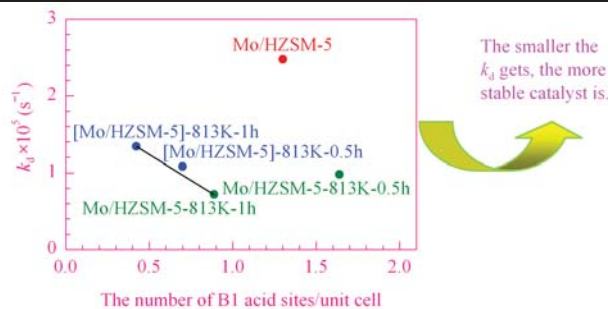
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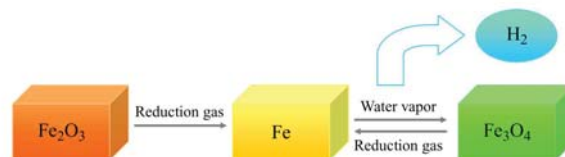
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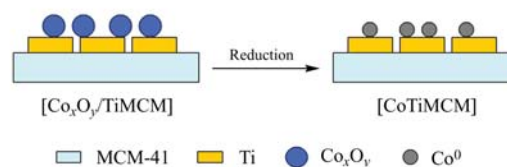


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Ti-Si composite oxide-supported cobalt catalysts for CO₂ hydrogenation

- Role of Ti: (i) Facilitate the reduction of Co_xO_y (TPR)
 (ii) Prevent the formation of silicate compounds (XPS)
 (iii) Inhibit the RWGS reaction (CO₂ hydrogenation)



Jakrapan Janlamool, Piyasan Praserttham, Bunjerd Jongsomjit

Ti-Si composite oxide-supported cobalt catalysts for CO₂ hydrogenation

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Abstract

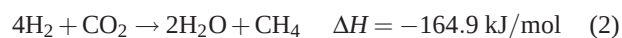
In the present work, different silica-based supported cobalt (Co) catalysts were synthesized and used for CO₂ hydrogenation for methanation. Different supports, such as SSP, MCM-41, TiSSP and TiMCM were used to prepare Co catalysts with 20 wt% Co loading. The supports and catalysts were characterized by means of N₂ physisorption, XRD, SEM/EDX, XPS, TPR and CO chemisorption. It is found that after calcination of catalysts, Ti is present in the form of anatase. The introduction of Ti plays important roles in the properties of Co catalysts by: (i) facilitating the reduction of Co oxides species which are strongly interacted with support, (ii) preventing the formation of silicate compounds, and (iii) inhibiting the RWGS reaction. Based on CO₂ hydrogenation, the CoTiMCM catalyst exhibits the highest activity and stability.

Key words

CO₂ hydrogenation; titania-silica; cobalt catalysts; methanation

1. Introduction

Recently, global warming, which is caused by CO₂ emission into the atmosphere, has become a serious problem all over the world. Among various types of methods for recovering, chemical fixation of emitted CO₂ is also expected to help the conservation of fossil fuels. Hydrogenation of CO₂ to methane is important for the purification of ammonia feedstocks, methanation of coal-derived gases and the production of process heat from reusable waste streams containing carbon dioxide [1]. Development of catalysts for CO and CO₂ hydrogenation is the key technology of gas to liquid (GTL) process. The catalytic hydrogenation of carbon monoxide and carbon dioxide produces a large variety of products ranging from methane and methanol to higher molecular weight alkanes, alkenes and alcohols [2–5]. The methanation of CO₂ is reported to proceed with a lower activated energy than the methanation of CO [6]. The lower exothermicity of the overall reaction of CO₂ as compared with CO makes temperature control in a catalytic reactor easier as shown in Equations (1) and (2) [7].



Transition metal oxides are generally regarded as good hydrogenation catalysts. Furthermore, Weatherbee and Bartholomew [8] studied the specific activities of various Group VIII metals catalysts supported on SiO₂ on the methanation of CO₂ at 177–377 °C and 140–1030 kPa and they found that the activities decreased in order of Co > Ru > Ni > Fe. The Co and Ni-based catalysts were preferred because they required considerably milder operating pressures (about 1 atm) than the high pressure for Fe catalyst [9]. Supported cobalt catalysts were the preferred catalysts for CO₂ hydrogenation because of lower cost compared with Ru [10]. Moreover, the catalytic activity of metal towards carbon deposition was found to decrease in order of Ni > Co > Fe [11,12]. Previous researches revealed that supports, such as Al₂O₃, SiO₂, ZrO₂, TiO₂ and CeO₂ can efficiently affect activities and selectivities of cobalt catalysts for CO and CO₂ hydrogenation [13–16]. Recently, Ti-Si composite represents a novel class of materials that was attractively used as catalysts and supports for a wide variety of catalytic reactions. It was reported that the photocatalytic activity of Ti-Si is 3-fold

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higher than that of the corresponding TiO_2 [17–19]. Furthermore, heterogeneous catalysts such as SiO_2 -supported TiO_2 and Ti-Si composite are known to be effective for selective oxidation reaction [20]. The Ti-Si composite supports exhibit novel properties that are not found in single oxide supports. In addition, mesoporous SiO_2 , such as MCM-41 and hexagonal mesoporous silica (HMS), exhibits sufficiently large surface area, high thermal stability, excellent mechanical strength and uniform pore sizes [21]. Ti-Si composite is generally synthesized through flame hydrolysis [22], impregnation [23], coprecipitation [24] and sol-gel [25] methods by adding titanium precursor into silica framework. The titanium distribution in Ti-Si composite depends on the method of preparation [26]. The sol-gel hydrolysis is widely used because of its capability in controlling the textural and surface properties of the mixed oxides [21].

The present research focused on the application of Ti-Si composite used as support for cobalt catalysts. First, the mesoporous silicas, such as spherical silica particle (SSP) and MCM-41 were prepared. Then, titanium isopropoxide was introduced into the silica framework by hydrolysis to obtain Ti-Si composite. The cobalt catalysts were prepared by direct impregnation of cobalt precursor into different supports. The characteristics and catalytic behaviors via CO_2 hydrogenation were investigated and further discussed in more detail.

2. Experimental

2.1. Materials

Chemicals as follows were used: titanium isopropoxide (TiPOT, 97%, Aldrich), tetraethyl orthosilicate (TEOS, 98%, Aldrich), ammonia (30%, Panreac), ethanol (99.99%, J. T. Baker), cetyltrimethylammonium bromide (CTAB, Aldrich), isopropanol (QReC), cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%, Aldrich).

2.2. Support and cobalt catalyst preparation

The mesoporous silica supports were synthesized by sol-gel method. The composition of the synthesized gel was as follows: molar ratio of 1 TEOS : 0.3 CTAB : 11 NH_3 : x ethanol : 144 H_2O . Molar ratio of ethanol addition was adopted 0 for MCM-41 and 58 for SSP, respectively [27]. The mixture was further stirred for 2 h at room temperature. White precipitate was then collected by filtration and washed with deionized water. The dried sample was calcined at 550 °C for 6 h with a heating rate of 10 °C/min in air.

The desired amount of titanium isopropoxide (ca. 25 wt% of Ti) was dissolved in isopropanol (1 : 3 w/w). SSP or MCM-41 was then added into the mixed solution and stirred for 1 h. Hydrolysis was performed by addition of ammonia ($\text{H}_2\text{O} : \text{TiPOT} = 4 : 1$). The sol was further stirred for 20 h at room temperature. Then, the sample was dried at 110 °C for 24 h. Finally, the sample was calcined at 850 °C for 2 h in a muffle furnace.

The cobalt catalysts loading 20 wt% Co were prepared by incipient wetness impregnation using aqueous solution of cobalt (II) nitrate hexahydrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$]. The catalysts were dried at 110 °C for 12 h, and then calcined in air at 500 °C for 4 h.

Nomenclature of samples were given as follows: SSP and MCM referred to spherical silica and MCM-41, respectively. Furthermore, TiSSP and TiMCM referred to titania spherical-silica composite and titania-MCM-41 composite, respectively. For catalysts samples, CoX referred to cobalt catalyst supported on the X support as mentioned above.

2.3. Catalysts characterization

Various supports and cobalt catalysts were characterized by several techniques as follows:

N_2 physisorption: N_2 physisorption (N_2 adsorption at –196 °C in a Micromeritics ASPS 2020) was performed to determine surface areas of various supports and cobalt catalysts.

X-ray diffraction (XRD): XRD was used to determine the phase composition of different supports and catalysts using SIEMENS D 5000 X-ray diffractometer with $\text{Cu } K_\alpha$ radiation with Ni filter in the 2θ range of 20°–80° with resolution of 0.04°.

Temperature-programmed reduction (TPR): TPR was used to determine the reducibility and reduction temperature of cobalt catalysts. Approximately, 0.05 g catalyst sample was used in the operation and temperature ramped from 35 °C to 800 °C at 10 °C/min. The carrier gas was 10% H_2 in Ar. A thermal conductivity detector (TCD) was used to measure the amount of hydrogen consumption. The calibration of hydrogen consumption was performed with bulk cobalt oxide (Co_3O_4) under the same condition.

CO chemisorption: Static CO chemisorption at room temperature on the reduced catalysts was used to determine the number of reducible surface cobalt metal atoms. CO chemisorption was carried out following the procedure using a Micromeritics Pulse Chemisorb 2750 instrument. Prior to chemisorption, the catalysts were reduced at 350 °C for 3 h after ramping up at a rate of 10 °C/min. After that, 30 μL CO was injected into catalyst bed and repeated until the desorption peaks were constant at room temperature. Amounts of CO adsorption on catalysts are proportional to the number of active sites.

Scanning electron microscopy (SEM) and dispersive X-ray spectroscopy (EDX): SEM (JEOL mode JSM-5800LV) and EDX (Link Isis Series 300) were used to determine the morphology and elemental distribution of the catalyst particles. The particle sizes and cobalt distributions of catalyst samples were observed using JEOL-JEM 200CX transmission electron microscope operated at 100 kV.

X-ray photoelectron spectroscopy (XPS): XPS analysis was performed originally using an AMICUS spectrometer equipped with a $\text{Mg } K_\alpha$ X-ray radiation. For a typical analysis, the source was operated at a voltage of 15 kV and a current

of 12 mA. The pressure in the analysis chamber was less than 10^{-5} Pa.

2.4. Reaction test

CO₂ hydrogenation was performed to determine the overall activity and selectivity of the catalysts. Typically, 0.1 g catalyst was packed in a fixed-bed microreactor. The catalyst sample was reduced in situ in flowing H₂ (50 mL/min) at 350 °C for 3 h. After reduction, a flow rate of Ar = 8 mL/min and H₂ (including 8.8% CO₂) = 22 mL/min was fed into the reactor. The CO₂ hydrogenation was carried out at 220 °C at 1 atm. The product gas samples were taken in 1 h interval and analyzed by gas chromatography. The steady state was reached within 6 h.

3. Results and discussion

3.1. Characteristics

The surface areas of the different supports and catalysts are shown in Table 1. The surface areas of the mesoporous silicas (SSP and MCM-41) were remarkably large as expected. However, with the addition of Ti into the silica framework, it was found that the surface areas of Ti-Si composites (TiSSP and TiMCM) were much lower than that of the corresponding mesoporous silica. As seen, the surface areas of TiSSP and TiMCM which were calcined at 850 °C, were dramatically low ca. 385 and 137 m²/g, respectively. This can be attributed to the distribution of Ti in the silica framework. The surface areas of cobalt catalysts deposited on SSP and MCM-41 were much smaller than those of their supports, whereas CoTiSSP and CoTiMCM only had slight effect. This can be attributed to the larger pore sizes of CoSSP and CoMCM. The phase identification was carried out on the basis of data obtained from XRD. The XRD patterns for all support samples are shown in Figure 1. As seen, SSP and MCM-41 exhibited broad peak at 20°–30° indicating amorphous silica. The Ti-Si composites of TiSSP and TiMCM showed that titania was present in the anatase form (2θ of 25°, 38°, 48°, 54°, 55° and 75°). The XRD patterns of the calcined Co catalysts are shown in Figure 2. All catalyst samples exhibited almost identical XRD patterns of Co₃O₄ at 31°, 37°, 45°, 59° and 65° [28]. It can be

observed that the XRD peaks of anatase TiO₂ at 2θ of 25.3° were less apparent due to the strong intensity of Co₃O₄ peaks, which disturbed the observation of anatase peaks.

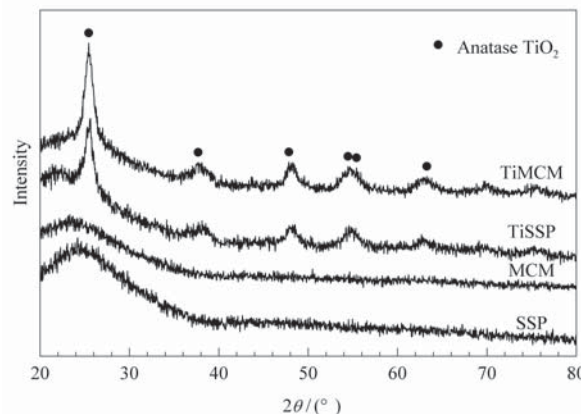


Figure 1. XRD patterns of different supports

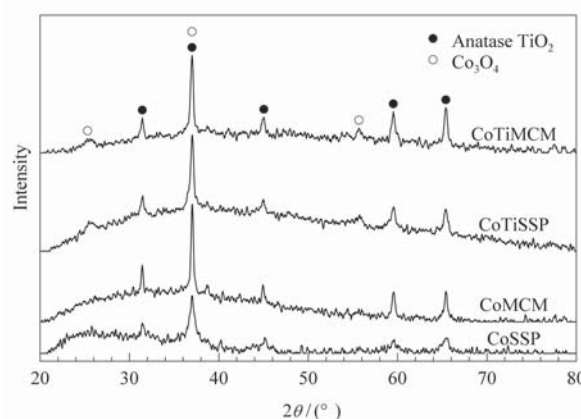
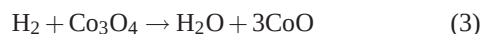


Figure 2. XRD patterns of different cobalt catalysts

TPR was performed in order to determine the reduction behaviors. The TPR profiles of all catalysts are shown in Figure 3. The reduction temperatures for all calcined catalysts were located between ca. 200 to 600 °C. One broad reduction peak with shoulder was observed for all catalysts. This can be generally assigned to the overlap of two reduction steps of Co₃O₄ to CoO and then to Co⁰. The two reaction steps (Equations (3) and (4)) may be whether or not observed depended upon the TPR conditions, such as ramping rate of temperature, feed gas flow rate and amount of samples.



The reduction temperature and reducibility results are summarized in Table 2. The reduction temperatures of CoSSP and CoMCM were located at ca. 210–330 °C and 210–360 °C, respectively. For CoTiSSP and CoTiMCM, the reduction temperatures were shifted to broad ranges (220–610 °C for CoTiSSP and 220–600 °C for CoTiMCM),

Table 1. BET surface areas, pore volumes and pore diameters of supports and cobalt catalysts

Samples	A_{BET} (m ² /g)	V_p (cm ³ /g)	D_{BJH} /nm
SSP	927	0.8135	2.04
MCM	1187	1.0287	2.13
TiSSP	385	0.1587	3.23
TiMCM	137	0.1371	4.57
CoSSP	637	0.4898	2.26
CoMCM	583	0.2134	2.58
CoTiSSP	380	0.2117	2.82
CoTiMCM	126	0.1004	4.24

indicating the existence of larger number of reduced cobalt atoms. The higher reduction temperature represented the cobalt oxide species strongly interacted with the supports, which are reducible. Therefore, the addition of Ti into the silica framework apparently facilitated the reduction of cobalt strongly interacted with the support. Without introduction of Ti, the higher reduction peak was absent as seen for CoSSP and CoMCM samples. The strong interaction between cobalt and supports was reported following the order of $\text{Al}_2\text{O}_3 > \text{TiO}_2 > \text{SiO}_2$ [29]. In addition, the reducibility of CoTiSSP and CoTiMCM catalysts was higher than that of CoSSP and CoMCM catalysts due to the reduction of strongly interacted cobalt oxide species as mentioned earlier. It was also reported that using TiPOT for the preparation of Ti-Si composite also resulted in increased reducibility of nickel catalysts [26].

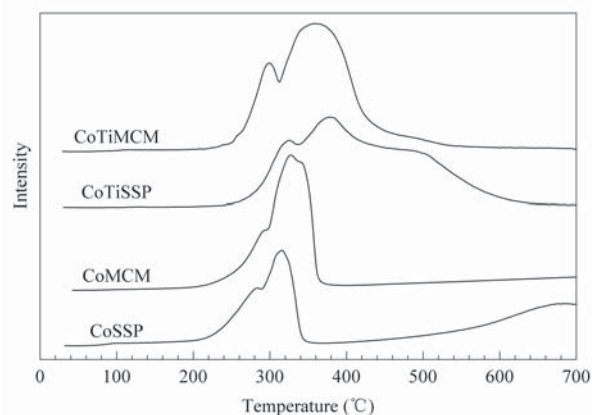


Figure 3. TPR profiles of different cobalt catalysts

Table 2. Maximum temperatures, reducibility from TPR profiles and Co dispersion of cobalt catalysts

Catalysts	Reduction temperature (°C)	Reducibility (%) ^a	Total CO chemisorption ($\mu\text{mol}_{\text{CO}}/\text{g}_{\text{cat}}$)	Dispersion of cobalt (%) ^b
CoSSP	210–330	30.3	28	0.84
CoMCM	210–360	21.2	37	1.10
CoTiSSP	220–610	45.4	21	0.61
CoTiMCM	220–600	45.5	19	0.56

^a Determined by TPR analysis; ^b Determined by CO chemisorption

CO chemisorption was conducted on samples reduced in hydrogen flow at 350 °C for 3 h. The amounts of carbon monoxide adsorbed on the catalysts were determined in order to obtain the number of reducible cobalt metal atoms. The adsorbed amounts of CO were directly proportional to the amounts of active sites. The amounts of CO adsorbed on the catalytic phase were ranged from 19 to 37 $\mu\text{mol}_{\text{CO}}/\text{g}_{\text{cat}}$ as shown in Table 2. It can be observed that in this case, the TPR and CO chemisorption results did not relate with each other due to different conditions applied. The CO chemisorption results showed that the number of reducible cobalt metal atoms slightly decreased with the addition of titania into the support. This was in accordance with the decreased number of cobalt atoms with increasing the amounts of titania in the mixed oxide supports [30]. Furthermore, the acidic property of titania-silica was quite different from that of either pure titania or pure silica, since pure titania only possesses Lewis acidity while silica has neither Brönsted nor Lewis acidity. However, new Brönsted acid sites are created when titania and silica form Ti–O–Si chemical bonds [31–33]. One possible reason for the lower CO chemisorption amounts of CoTiSSP and CoTiMCM can be explained that the electron donor additives like alkali metals enhance chemisorption, while electron acceptors inhibit chemisorption [34–36]. It should be noted that the results of CO chemisorption were different from those of TPR due to differences in measurement conditions for both techniques.

SEM and EDX were also conducted in order to study the morphologies and elemental distributions of the catalysts, respectively. The typical external surface granules and EDX mappings of the calcined cobalt catalysts are shown in Fig-

ure 4. It can be observed that the cobalt oxide species exhibited good distribution. The white spots on the external surfaces represent high concentrations of Co. The EDX analysis is not a bulk technique, but rather a surface analytical tool based on the fact that it gives information down to a depth of approximately 1 μm from the surface that makes the information obtained from EDX comparable to atomic absorption [37]. Table 3 summarizes the element quantities of cobalt catalysts based on EDX and XPS analyses. It should be mentioned that EDX only measures the concentrations in a layer less than 1 μm from the surface. The EDX results revealed that Ti loadings were 17.4 wt% and 23.1 wt% for CoTiSSP and CoTiMCM, respectively. In addition, Co loadings for all catalysts were ranged from 22.1 wt% and 30.8 wt%. The element compositions of surface and subsurface layers (depth of XPS analysis is about ten angstroms) indicated that the amounts of Ti were 42.6 wt% and 30.6 wt% for CoTiSSP and CoTiMCM, respectively. The amounts of Ti from XPS analysis were larger than those obtained from EDX analysis. This was due to the titania accumulation on the external surface of silica supports. Moreover, the amounts of Co for CoMCM, CoTiSSP and CoTiMCM from XPS analysis were distinctly larger than those from EDX analysis, indicating that most cobalt oxides distributed on the external surface. In contrast, the amount of Co for CoSSP from XPS measurement was remarkably smaller than that obtained from the EDX analysis, confirming that most cobalt oxides dispersed in the bulk of silica particles.

Besides the determination of surface concentration, XPS is one of the most powerful techniques used to identify the binding energy (BE) of elements. According to the BE results

obtained from XPS as shown in Table 3, it can be observed that the Co 2*p* core level spectra of Co₃O₄ were present at the BE of 780–782 eV and 795–796 eV for 2*p*_{3/2} and 2*p*_{1/2}, respectively for all the catalyst samples. These values were in agreement with the reported work [38]. On the other hand, there was no change in BE for Co 2*p* core level with the addition of Ti. However, CoSSP and CoMCM exhibited the BE at 95.1 eV and 94.6 eV for former, 104.2 eV and 103.5 eV for latter. In fact, the BE at 95.1 eV and 94.6 eV were assigned to the formation of silicate compounds as reported by Wagner et al. [39] and Arnby et al. [40]. Previous reports

suggested that the formation of surface cobalt silicates during preliminary steps of catalyst preparation or even during reduction, was considered as a reason for partial reduction of the total cobalt presenting at the temperatures normally above 500 °C [41]. However, the presence of Ti in CoTiSSP and CoTiMCM apparently resulted in the absence of BE for silicate compound. These results were in accordance with those obtained from TPR.

TEM micrographs for all the catalysts are shown in Figure 5. The dark spots represented cobalt oxide patches dispersing on the supports after calcinating the catalysts.

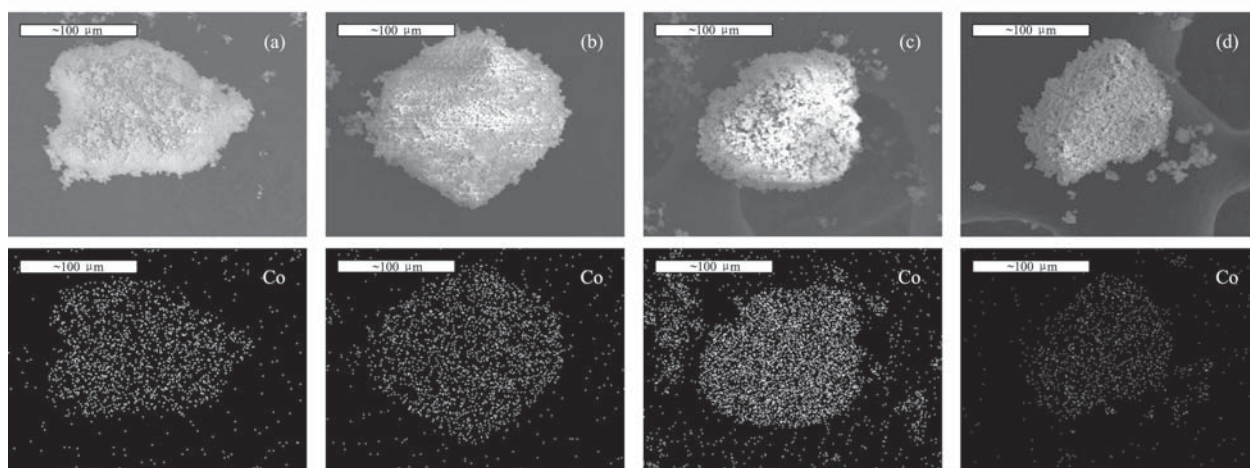


Figure 4. SEM micrographs and EDX mappings of cobalt catalysts. (a) CoSSP, (b) CoMCM, (c) CoTiSSP, (d) CoTiMCM

Table 3. XPS data and EDX analysis of cobalt catalysts

Catalysts	Binding energy (eV)			Amount of elements on surface (wt%) ^a			Amount of elements in bulk (wt%) ^b		
	Si 2 <i>p</i>	Ti 2 <i>p</i>	Co 2 <i>p</i>	Si	Ti	Co	Si	Ti	Co
CoSSP	95.1	—	781.0	90.7	—	9.3	75.5	—	24.3
	104.2	—	795.8						
CoMCM	94.6	—	780.2	59.8	—	40.2	69.6	—	30.4
	103.5	—	795.3						
CoTiSSP	103.7	460.1	781.0	19.8	42.6	37.6	60.5	17.4	22.1
		465.7	796.6						
CoTiMCM	103.4	459.7	780.4	34.0	30.6	35.4	46.1	23.1	30.8
		465.6	795.4						

^a Determined by XPS analysis; ^b Determined by EDX analysis

Figure 5 (a) and (c) shows that the cobalt oxide species exhibited good distribution in CoSSP and CoTiSSP catalysts, respectively. Figure 5 (b) reveals that cobalt oxide species were agglomerated in CoMCM catalyst. In contrast, Figure 5 (d) displays the cobalt oxide species having good distribution in CoTiMCM catalyst. TEM micrographs demonstrated that the titania particles on the MCM-41 can improve the dispersion of cobalt oxide. This phenomenon was also observed with the presence of Ti in Ni catalyst [26].

3.2. Reaction study

CO₂ hydrogenation over different cobalt catalysts at 220 °C under methanation condition was investigated. The

reaction results are summarized in Table 4. Methane was a major product for all catalyst samples. It was found that the CoTiMCM sample exhibited the highest activity among all the samples. The selectivity to CO also decreased with the addition of Ti into MCM-41 due to the increased acidity by increasing the amount of Ti in the supports [26]. This is in agreement with the increased amount of absorbed CO₂ by increasing the basicity of the alkali metal oxides, which might be related to the influence on the local electron density of neighboring metal species [7]. In addition, the stability of catalyst was found to increase with the addition of Ti when compared the conversion of initial and steady states. The obtained products for methane and CO indicate that CO₂ hydrogenation over these catalysts occurred via a consecutive mechanism as

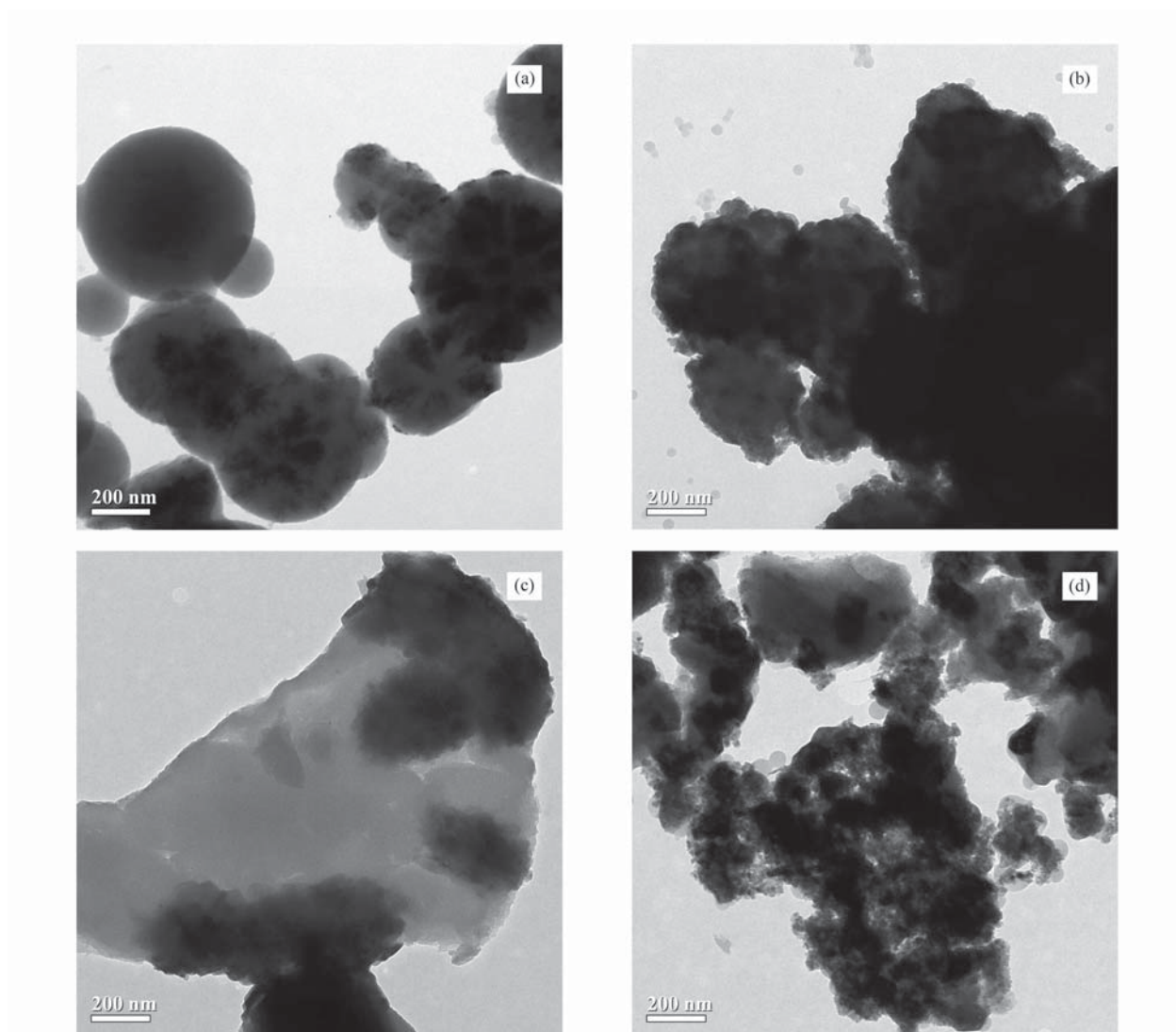


Figure 5. TEM micrographs of cobalt catalysts. (a) CoSSP, (b) CoMCM, (c) CoTiSSP, (d) CoTiMCM

shown in Equations (5) and (6). CO_2 is first converted to CO by reverse water gas-shift (RWGS) reaction, and then CO was hydrogenated to methane.



For CO_2 hydrogenation, the operating temperature must

be rather high because of the equilibrium constraint for the reverse CO shift reaction, which limits the application of temperature in the low range for Fischer-Tropsch conversion [7]. In this study, the activities of cobalt catalysts were not related to the cobalt dispersion based on CO chemisorption. This was in accordance with the methanation turnover rate in Fischer-Tropsch synthesis which was also independent of cobalt dispersion on supported catalysts and surface orientation on Co single crystals [42].

Table 4. Activity and product selectivity of cobalt catalysts

Reaction temperature ($^{\circ}\text{C}$)	Catalysts	Conversion ^a		Rate ^c ($\times 10^2 \text{ g}_{\text{CH}_4} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$)	Product selectivity (%) ^c	
		initial ^b	steady state ^c		CH_4	CO
220	CoSSP	38	27	16.5	89.5	10.5
	CoMCM	35	28	18.1	91.4	8.6
	CoTiSSP	17	16	10.0	92.1	7.9
	CoTiMCM	35	34	22.3	94.9	5.1

^a CO_2 hydrogenation was carried out at 1 atm, and molar ratio of $\text{H}_2/\text{CO}_2/\text{Ar} = 20/2/8$, $F/W = 18 \text{ L} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$; ^b After running the reaction for 5 min;

^c After running the reaction for 6 h

4. Conclusions

In summary, the addition of Ti into SSP and MCM-41 can alter the characteristics and catalytic properties of CoTiSSP and CoTiMCM catalysts. It is found that the presence of Ti can facilitate the reduction of cobalt oxide species which are strongly interacted with the support, resulting in the appearance of high temperature reduction peak. Based on XPS analysis, it is observed that the formed silicate is disappeared with the presence of Ti. It is worth noting that CoTiMCM catalyst exhibits the highest activity for CO₂ hydrogenation due to increased reducibility. The addition of Ti also inhibits the RWGS, leading to a decrease in the selectivity to CO.

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LLDPE synthesis via SiO₂–Ga-supported zirconocene/MMAO catalyst

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ABSTRACT

In this present study, the linear low-density polyethylene (LLDPE) was synthesized via ethylene/1-octene copolymerization with the zirconocene/MMAO catalyst by *in situ* impregnation of different silica (SiO₂) supports. The SiO₂ supports used were small-pored (SP) and large-pored (LP) sizes with and without Ga modification. It was found that the SP-SiO₂ support exhibited higher polymerization activity (~1.5 times) than that obtained from the LP-SiO₂ one. This can be attributed to the lower amount of MMAO being present inside the SP-SiO₂ support resulting in higher content of MMAO at the external surface. The higher activity in ethylene/1-octene copolymerization was also found with the supported catalyst having Ga modification onto both SP- and LP-SiO₂ supports. The results demonstrated that the introduction of Ga may improve ability of supports to immobilize metallocene catalyst. Based on ¹³C NMR measurement, it indicated that all synthesized polymers were typical LLDPE having random distribution of comonomer.

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1. Introduction

The linear low-density polyethylene (LLDPE) is very attractive polymer because of its excellent mechanical property, high thermal stability and good resistance for chemicals. Therefore, it has been widely used for various applications, especially in film and packaging industries. LLDPE is the copolymer synthesized from copolymerization of ethylene and 1-olefin [1–4]. For commercial production, it is usually produced with a catalytic system, such as Ziegler–Natta, metallocene, and metal-oxide catalysts [5]. However, the use of metallocene catalyst together with methylaluminoxane (MAO) as cocatalyst have been found to be very effective to produce polymer with high catalytic activity and give narrow molecular weight distribution. Moreover, synthesis of copolymer by using solid support as carrier has been proven to solve some disadvantages of homogeneous catalyst [6,7], including reactor fouling, low bulk density of polymer, and unable to polymerize in slurry and gas polymerization process. The most widely used supports in metallocene system are inorganic materials including silica [8,9], alumina [10], titania [11], MCM-41 [12] and zirconia [13].

In this work, we used silica with different pore sizes as a support due to the fact that pore sizes may have effects on copolymerization activity and incorporation of olefin comonomer. We also extended this study into the influence of support acidity according

to Rahiala et al. [12]. They demonstrated that the use of acidic Al seems advantageous to formation of active centers resulting in high activity compared with unmodified support. Hence, the improvement of acidic material is considered as an interesting path for better heterogeneous system. Experimentally, the copolymerization of ethylene/1-octene with *rac*-Et[Ind]₂ZrCl₂/MMAO system via *in situ* impregnation over different pore sizes of silica support was performed to produce LLDPE. The Ga modification onto the support was conducted in order to increase acidity. At the end, effects of SiO₂ pore size and Ga modification on properties of the LLDPE produced are elucidated by means of density and ¹³C NMR measurements.

2. Experimental

2.1. Materials

All chemicals and polymerization were manipulated under an argon atmosphere, using a glove box and/or Schlenk techniques. Toluene was dried over dehydrated CaCl₂ and distilled over sodium/benzophenone before use. The *rac*-ethylenebis(indenyl) zirconium dichloride (*rac*-Et[Ind]₂ZrCl₂) was supplied from Aldrich Chemical Company, Inc. Modified methylaluminoxane (MMAO) in hexane was donated by Tosoh (Akso, Japan). Trialkylaluminum (TMA, 2 M in toluene) was supplied by Nippon Aluminum Alkyls, Ltd., Japan. Ultrahigh purity argon was further purified by passing it through columns that were packed with BASF catalyst R3-11G (molecular-sieved to 3 Å), sodium hydroxide (NaOH), and phosphorus pentoxide (P₂O₅) to remove traces of oxygen and

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moisture. Ethylene gas (99.96% pure) was donated by the National Petrochemical Co., Ltd., Thailand. 1-Octene ($d = 0.715$) was purchased from Aldrich Chemical Company, Inc.

2.1.1. Preparation of Ga-modified silica support

The Ga modification on the silica supports was prepared by the incipient-wetness impregnation method according to the procedure described previously [11]. The Ga source in this case was $\text{Ga}(\text{NO}_3)_3$. Ga was impregnated onto different pore-sized silica gels having 1.0 wt.% of Ga. The support was dried in oven at 383 K for 12 h, and then heated in vacuum at 673 K for 2 h.

2.2. Polymerization procedure

0.2 g of the support obtained above was allowed to contact with 1.14 ml of MMAO ($[\text{Al}]_{\text{MMAO}}/[\text{Zr}]_{\text{cat}} = 1135$) for 30 min, in reactor with magnetic stirring. After this period of time, the suspension was undergone the clarified liquid test to confirm that all MMAO was immobilized on the support. About 1 ml of the clarified liquid was injected into the polymerization reactor, where the desired amount of zirconocene was already present. If any noticeable amount of polymer was formed, it means that this clarified liquid still contains MMAO. Therefore, the fixation of cocatalyst onto support was not complete. To ensure that MMAO was completely impregnated onto support, the MMAO/support ratio was then decreased until no polymer was formed [14]. After this test, the suspension was mixed with desired amount of *rac*- $\text{Et}[\text{Ind}]_2\text{ZrCl}_2$ and TMA ($[\text{Al}]_{\text{TMA}}/[\text{Zr}]_{\text{cat}} = 2500$). In fact, the high ratio of $[\text{Al}]_{\text{TMA}}/[\text{Zr}]_{\text{cat}}$ was employed as a scavenger due to the ethylene fed was obtained from the plant containing some impurities. From an industrial point of view, it is preferable to use TEA or TIBA in place of TMA. Then, toluene (to make a total volume of 30 ml) was introduced into the reactor. The reactor was frozen in liquid nitrogen to stop reaction, and then 0.018 mol of 1-octene was injected into the reactor. The reactor was evacuated to remove argon. Then, it was heated up to polymerization temperature (343 K) and the polymerization was started by feeding ethylene gas (total pressure 50 psi in the reactor) until the consumption of ethylene at 0.018 mol was reached (6 psi was observed from the pressure gauge). The reaction of polymerization was completely terminated by addition of acidic methanol. The reaction time was recorded for purpose of calculating the activity. The precipitated polymer was washed with methanol and dried at room temperature prior to characterization.

2.3. Supports characterization

2.3.1. X-ray diffraction (XRD)

XRD was performed to determine the bulk crystalline phases of sample. It was conducted using a SIEMENS D-5000 X-ray diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.54439 \times 10^{-10}$ m). The spectra were scanned at a rate 2.4 degree/min in the range of $2\theta = 20$ –80 degrees.

2.3.2. N_2 physisorption

Measurement of BET surface area, average pore diameter and pore size distribution of silica support were determined by N_2 physisorption using a Micromeritics ASAP 2000 automated system.

2.3.3. Scanning electron microscopy (SEM)

Scanning electron microscopy was used to determine the morphologies and elemental distribution throughout the sample granules, respectively. The SEM of JEOL mode JSM-6400 was applied.

2.3.4. NH_3 -temperature programmed desorption (TPD)

Temperature programmed desorption (TPD) of NH_3 was performed in a Micromeritics ChemiSorb 2750 automated system attached with ChemiSoft TPx software. The amount of NH_3 adsorbed on the surface was determined by temperature programmed desorption.

2.4. Polymer characterization

2.4.1. ^{13}C NMR spectroscopy

^{13}C NMR spectroscopy was used to determine the 1-octene incorporation and copolymer microstructure. Chemical shifts were referenced internally to the CDCl_3 and calculated according to the method described by Randall [15]. Each sample solution was prepared by dissolving 50 mg of copolymer in 1,2,4-trichlorobenzene and CDCl_3 . ^{13}C NMR spectra were taken at 373 K using a BRUKER AVANCE II 400 operating at 100 MHz with an acquisition time of 1.5 s and a delay time of 4 s.

2.4.2. Scanning electron microscopy (SEM)

SEM was performed to study morphologies of polymer produced. The same equipment as mentioned above was employed.

2.4.3. Densimeter

Polymer density was measured with an electronic densimeter (Mirage SD-120L) in the temperature range 298–313 K.

3. Results and discussion

In our research, we synthesized LLDPEs over inorganic materials with different pore-sized silica, where the large pored-silica denoted as SiO_2 (LP) and the small pored-silica denoted as SiO_2 (SP). In addition, we modified silica with 1.0 wt% of Ga to increase acidity of support. The XRD patterns (not shown) exhibit only a broad peak between ca 20° and 30° for both SiO_2 (LP)

Table 1
BET surface area and pore diameter of Ga-modified silica supports.

Support	BET surface area (m^2/g)	Pore diameter ($\text{\AA}$)
SiO_2 (LP)	71	146
SiO_2 (LP)–Ga-1.0%	69	148
SiO_2 (SP)	217	138
SiO_2 (SP)–Ga-1.0%	170	138

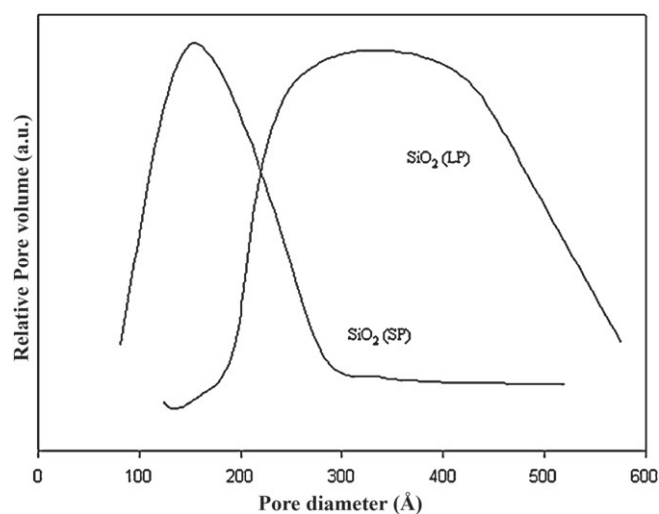


Fig. 1. Pore size distribution of different SiO_2 -based supports.

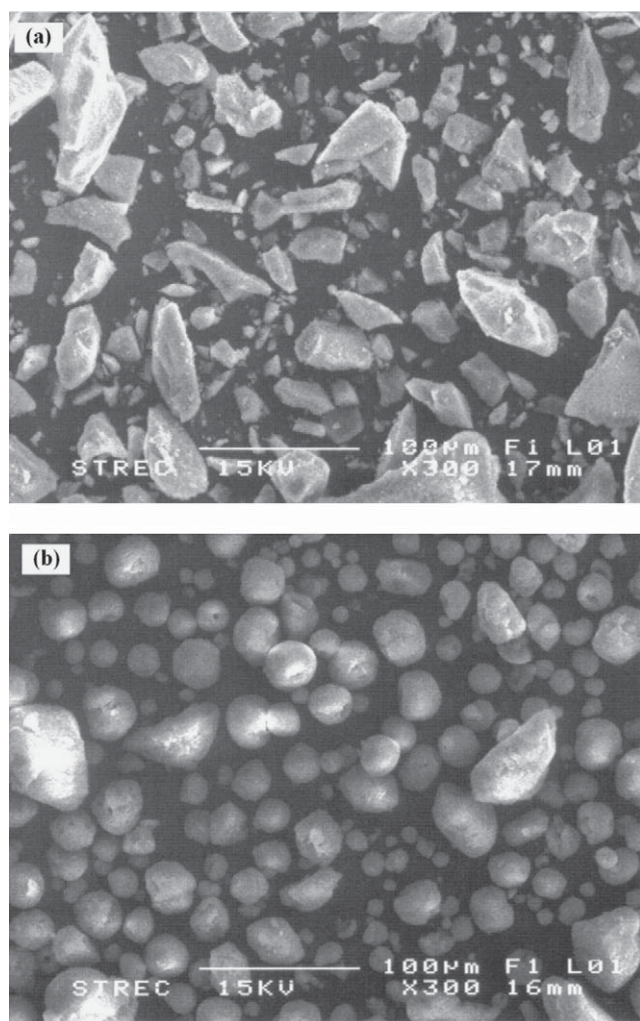


Fig. 2. SEM micrograph of Ga-modified silica (LP) and silica (SP) supports; (top) SiO_2 (LP), (bottom) SiO_2 (SP).

and SiO_2 (SP) supports. As very well-known, the broad peak is due to scattering from non-crystalline area of silica. However, it does not show the Ga peak because only small amount of Ga was introduced onto the support. Moreover, Ga present on SiO_2 was in the highly dispersed form.

Table 2

Catalytic activities of various silica-supported zirconocene/MMAO catalysts via *in situ* impregnation method.

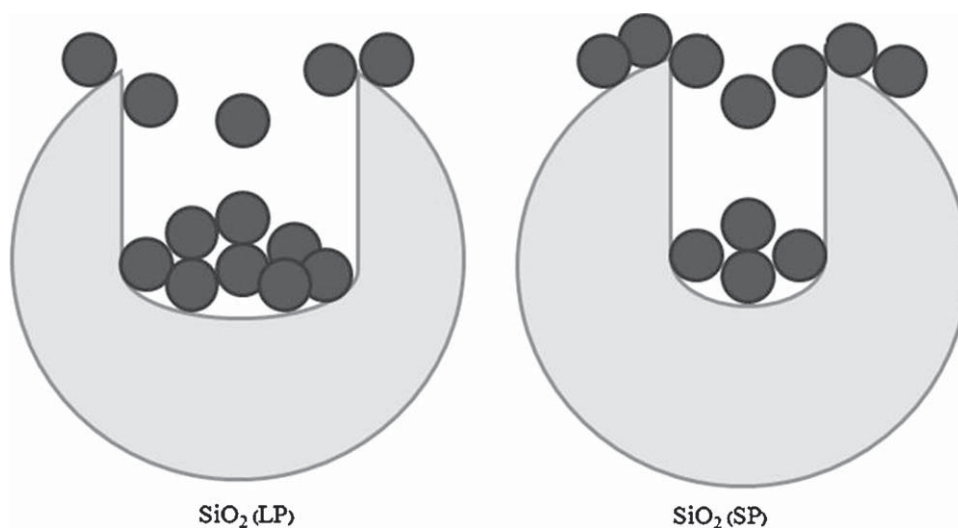
Samples	Polymerization yield ^a (g)	Polymerization times (s)	Catalytic activity ^b (kg of pol/mol Zr h)
Homogeneous	1.534	123	29,803
SiO_2 (LP)	1.495	88	40,405
SiO_2 (LP)–Ga-1.0%	1.756	76	55,329
SiO_2 (SP)	1.798	80	53,411
SiO_2 (SP)–Ga-1.0%	2.036	74	66,214

^a The polymer yield was fixed [limited by ethylene fed and 1-octene used (0.018 mole equally)].

^b Activities were measured at polymerization temperature of 343 K, [ethylene] = 0.018 mole, [1-octene] = 0.018 mole, [Al]_{MMAO}/[Zr] = 1135, [Al]_{TMA}/[Zr] = 2500, in toluene with total volume = 30 ml, and [Zr] = 5×10^{-5} M.

The BET surface areas determined by N_2 physisorption of supports are shown in Table 1. It indicates that SiO_2 (SP) exhibits higher surface area than SiO_2 (LP). It is also found that the addition of Ga leads to a slight decrease in the surface area for SiO_2 (LP), but a remarkable decrease for the SiO_2 (SP) due to the pore blockage with Ga. As seen in Fig. 1, it can be observed that the SiO_2 (LP) support exhibits the large pore size distribution while the SiO_2 (SP) support shows the small pore having narrow size distribution. SEM was used to determine particle morphology. The SEM micrographs of SiO_2 (LP) and SiO_2 (SP) supports are shown in Fig. 2. It can be observed that SiO_2 (LP) has jagged shape, whereas the SiO_2 (SP) has the shape of spheroid.

Table 2 displays the ethylene/1-octene copolymerization activity and activity of homogeneous system for comparison. It was found that the heterogeneous system exhibited higher catalytic activity than the homogeneous one. Based on the work done by Jungling et al. [16], a good bulk density can improve the distribution of active site. In addition, it can reduce reactor fouling, which is resulted from the adhesion of polymer to the reactor. Here, the heterogeneous system exhibited higher bulk density than the homogeneous system under this specified reaction condition. Meanwhile, it can be proposed that the SiO_2 support might inhibit the formation of $\text{ZrCH}_2\text{CH}_2\text{Zr}$ species [17,18], which can be formed via a bimolecular process as it minimizes the steric hindrance effect of the system. It indicated that catalytic activity of SiO_2 (SP) support was ~ 1.5 times higher than that obtained from SiO_2 (LP) one. It results from the fact that, for SiO_2 (LP), MMAO cocatalyst can reach into its pore leading to lower MMAO present in the bulk, and hence less active species in the system. On the



Scheme 1. Location of active site over different supports.

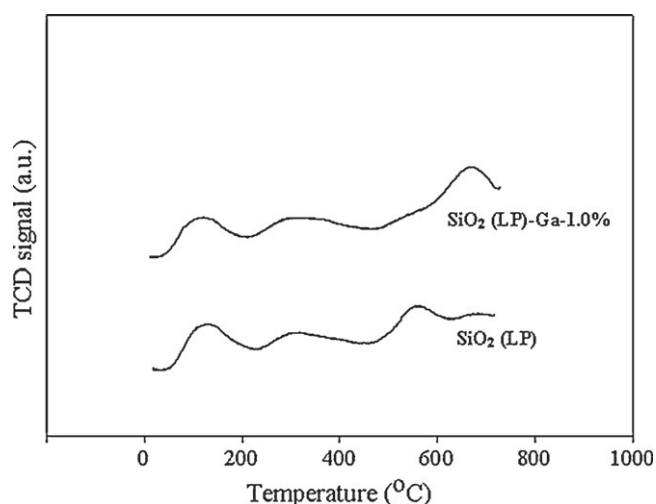


Fig. 3. NH_3 -TPD profiles of Ga-modified SiO_2 support.

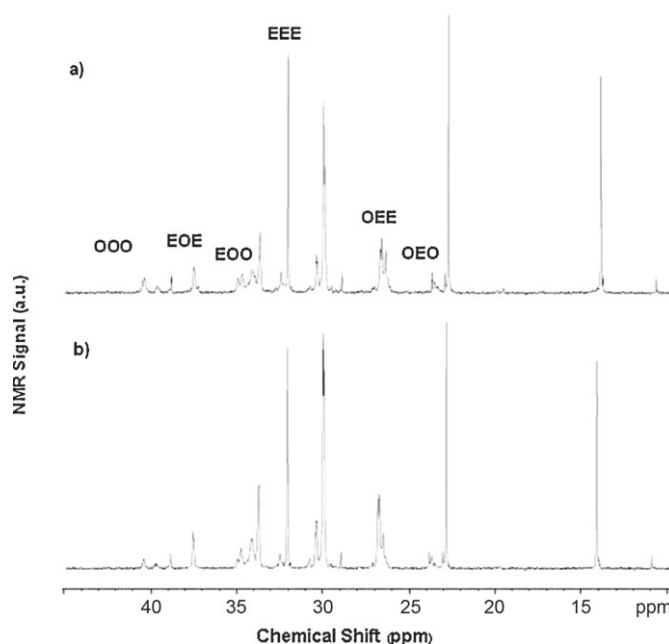


Fig. 4. Typical ^{13}C NMR spectra of copolymers obtained with (a) SiO_2 (LP) and (b) SiO_2 (SP) support.

of the propagation rate for polymerization. This result is consistent with Yamamoto [21], whose work revealed that SiO_2/MgO had strongly acid sites which helped enhance the propylene polymerization activity. Moreover, the obtained copolymers were further characterized using ^{13}C NMR to determine the comonomer distribution. The triad distribution and % incorporation of 1-octene comonomer are shown in Table 4 which is evaluated according to Randall [15]. From Table 4 it is apparent that only the random copolymers were produced in this system.

In addition, the ^{13}C NMR spectra are shown in Fig. 4. They revealed that Ga-modification had no effect on microstructure of copolymer. However, when considered the insertion of comonomer, it can be observed that SiO_2 (SP) gives higher 1-octene insertion than that of SiO_2 (LP) support due to most of the active is present on the external surface for SiO_2 (SP) leading to decreased steric hindrance. The obtained result is also consistent with Shan et al. [22].

Fig. 5 shows the SEM image of copolymer produced using support. It can be seen that after copolymerization, the support was covered with copolymer. Particles size of polymer is 20 μm , which are about 1.5 times larger than supports. Polymer density measured by the densimeter, was about 0.89–0.91 g/cm^3 for all polymer produced indicating the typical LLDPE obtained. However, the measured density was slightly lower than the commercial LLDPE (~ 0.92 – 0.93 g/cm^3). The lower density is probably due to higher insertion (>10 mol%) of 1-octene comonomer having low crystallinity [23].

Table 3
Acidity of Ga-modified SiO_2 support obtained from NH_3 -TPD.

Support	Acid site ($\mu\text{mol H}^+/\text{g}$)
SiO_2 (LP)	593
SiO_2 (LP)-Ga-1.0%	624

contrary, the higher activity was observed for SiO_2 (SP) support due to lower amount of MMAO in its pore. This makes MMAO remain highly in the bulk, and hence enhance the activity of polymerization (Scheme 1). Considering the effect of support modification with Ga, it was found that the polymerization activity increased with Ga loading. An increase in catalytic activity is probably due to improved ability of supports to immobilize metallocene catalyst. According to the work done by Campos et al. [14], they found that the characteristic peaks of Lewis acid center at 1457, 1492 and 1621 cm^{-1} in the case of Ga-MCM-41, while MCM-41 does not exhibit these peaks. FTIR analysis result suggested that the interaction between zirconocene and the Lewis acid centers derived from the introduction of Ga in the support seems to play an important role in the formation of the active species and the optimization of Ga of the MCM-41 support. In addition, it can be seen from NH_3 -TPD method that modifying support with Ga resulted in more active site being present in the system, as shown in Fig. 3 and Table 3. All the samples exhibited two main desorption peaks around 140–170 $^\circ\text{C}$ and 330–340 $^\circ\text{C}$, which were corresponding to weak and medium acid sites, respectively [19]. Additional peak at around 500–700 $^\circ\text{C}$ indicates the presence of strong acid sites of the supports [20]. The more Ga added, the more amount of acid site measured. Moreover, another reason for the higher activity of acid support is probably due to the higher efficiency of zirconocene cation generation and/or the improvement

Table 4
 ^{13}C NMR analysis of ethylene/1-octene copolymer.

System	Triad distribution of copolymer						1-Octene insertion (mol%)
	EEE	EEO	EOE	EOO	OEO	OOO	
Homogeneous	0.467	0.226	0.177	0.078	0.052	0.000	26
SiO_2 (LP)	0.448	0.391	0.097	0.004	0.024	0.000	11
SiO_2 (LP)-Ga-1.0%	0.595	0.241	0.101	0.040	0.021	0.000	14
SiO_2 (SP)	0.472	0.190	0.168	0.096	0.074	0.000	26
SiO_2 (SP)-Ga-1.0%	0.612	0.211	0.094	0.053	0.030	0.000	15

E refers to ethylene monomer and O refers to 1-octene comonomer.

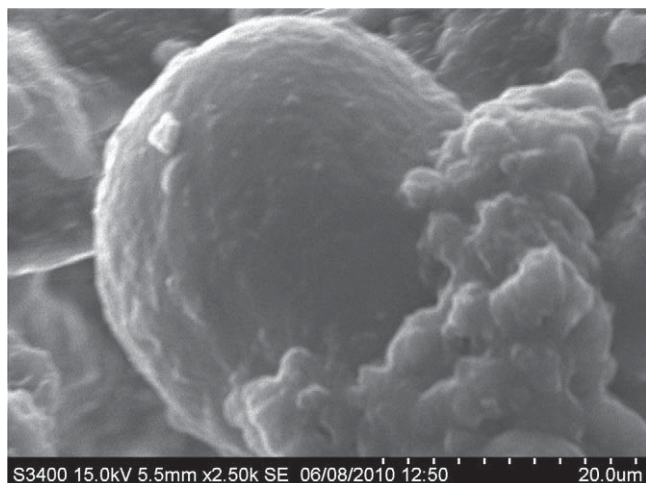


Fig. 5. A typical SEM micrograph of copolymer using Ga-modified silica support.

4. Conclusion

Copolymerization of Ga-modified silica-supported zirconocene/MMAO catalyst via *in situ* impregnation on different pore sizes of supports was investigated. It revealed that the small-pored silica support exhibited higher polymerization activity than the large-pored silica due to lower content of MMAO present in small pore. However, MMAO remains in external surface, and therefore activity increased. In the part of Ga-modification, it was found that Ga loading improves catalytic activity without any significant change in the polymer microstructure.

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Effect of Ga- and BCl₃-modified silica-supported [t-BuNSiMe₂(2,7-t-Bu₂Flu)]TiMe₂/MAO catalyst on ethylene/1-hexene copolymerization

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ABSTRACT

In this present study, the copolymerization of ethylene and 1-hexene was conducted over the [t-BuNSiMe₂(2,7-t-Bu₂Flu)]TiMe₂ (CGC)/MAO catalyst immobilized on different supports. The effects of Ga and the Lewis acid BCl₃ modification of the silica support on the copolymerization behavior were investigated based on catalytic activity and polymer properties. It was found that the silica support modified with BCl₃ exhibited the highest activity. However, both Ga and BCl₃ modifiers are capable of enhancing the catalytic activity, probably attributed to stronger interaction between the MAO and support together with the acidic sites exerted by the modification which could assist MAO to activate the catalyst during polymerization. Besides, a role of BCl₃ as a spacer to keep apart the catalyst on the silica surface was proposed as another probable reason for activity increased. This led to the more homogeneous-like behavior with less effect of support and also caused the higher comonomer incorporation content. Moreover, the results revealed that narrow polymer molecular weight distribution can be achieved by the supported CGC catalyst, especially for acidic modified supports. On the other hand, there was no noticeable effect with regards to the melting temperature and copolymer microstructure of the Ga and BCl₃ modification. Therefore, based on the study it may be regarded that the efficient supported CGC catalyst can be accomplished through the acidic modification namely Ga and BCl₃.

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1. Introduction

Based on the volume of material consumed annually worldwide consumption, polyolefins, especially linear low-density polyethylene (LLDPE), are the largest volume polymers in the plastics industry. This is because they exhibit many useful properties, such as low density, high strength, and resistance to chemical attack, as well as being cost-effective. Therefore, much effort in both academic and

industrial research has been directed towards the development of highly active olefin polymerization catalysts for the synthesis of desired copolymers [1–3]. Single site catalysts, namely metallocene catalyst, have been reported to be potentially useful for the copolymerization of ethylene and α -olefins, such as 1-butene, 1-hexene and 1-octene, to produce LLDPE with short chain branching. Comparable to conventional Ziegler–Natta systems, metallocene catalysts display a high activity and allow rational catalyst design to construct a relationship between catalyst structure and resulting polymer microstructure [4]. They also offer superior product properties in terms of a narrow molecular

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weight distribution (MWD) and a uniform short chain branching distribution [5].

Even if there are many advantages of homogeneous metallocene catalysts, such as high activity and stereoregularity, there are also some crucial problems for the commercial applications, including the difficulties in controlling the polymer morphology, instabilities for slurry or gas phase processes and the requirement of a large amount of expensive methylaluminoxane (MAO) [6]. To overcome these drawbacks, it is desirable to heterogenize the soluble catalysts on supports such as silica, alumina and titania for their possible industrial applications [7]. It has been reported that silica has been the attractive and the most widely used support for metallocene catalysts [8–10]. Nonetheless, the properties of silica itself probably bring about some dissatisfaction based on activities and quality of polymer produced. Thus, some additives or modifiers are required for modification in order to achieve the better performance [11–13]. Most researchers reviewed that treating the silica surface with hydrophobic functional groups such as aryl, alkyl, and silane can improve the catalytic behavior [14–19]. Some researchers accentuated that the surface acidity properties of solid supports may play the determinant role in the activation of the metallocene catalyst, contributing to the polymerization activity increase [20,21]. The most frequently used pathway to modify the acidic surface property is the incorporation of acidic metal atoms in their frameworks [22–24]. Recently, it has been reported that the exploitation of acidic Ga metal is a promising alternative way to enhance the performance of metallocene catalysts during the ethylene polymerization [25,26].

In previous studies, a unique catalyst type called constrained geometry catalyst (CGC) using half sandwich titanocenes has been found and categorized as one of the metallocene group. This complex provides high catalytic activity and high insertion of α -olefins into copolymers. According to our previous research, we investigated the influence of the *t*-butyl and cyclododecyl substitution of ansa-fluorenylamidodimethyltitanium derivatives on ethylene/1-hexene copolymerization in the homogenous system. We revealed that the 2,7 *t*-butyl group led the [t-BuNSiMe₂(2,7-*t*-Bu₂Flu)]TiMe₂ to achieve the highest activity [27].

The main objective of this present study was to investigate how the Ga and the Lewis acid BCl₃ modification of the silica support would impact on the ethylene/1-hexene copolymerization in terms of catalytic activity and polymer properties. The CGC complex of [t-BuNSiMe₂(2,7-*t*-Bu₂Flu)]TiMe₂ was used to be further developed for the heterogeneous system and to generate the more efficient supported CGC catalyst in the near future.

2. Experimental

2.1. Materials

All operations were performed under an argon atmosphere using Schlenk techniques and glove box. All solvents were dried over dehydrated CaCl₂ and distilled over sodium/benzophenone before use. MAO was donated from

Tosoh-Finechem Co. Ltd. Ethylene gas (99.96% pure) was donated by the National Petrochemical Co. Ltd., Thailand. 1-Hexene was purchased from Aldrich Chemical Company and purified by distilling over sodium/benzophenone under argon atmosphere before use. Silica gel (SP9-602 from Grace Davison) was calcined at 673 K for 6 h. Ga(NO₃)₃ and BCl₃ were purchased from Aldrich Chemical Company. [t-BuNSiMe₂(2,7-*t*-Bu₂Flu)]TiMe₂ (CGC complex) was synthesized according to procedures reported previously [28]. The chemical structure of catalyst is shown in Scheme 1.

2.2. Preparation of Ga-modified silica support

The gallium modification on the silica support was prepared by the incipient-wetness impregnation method according to the procedure described previously [26]. Ga(NO₃)₃ was used as a Ga source. Gallium was impregnated onto silica gel with 0.2 wt.% of Ga. The support was dried in oven at 383 K for 12 h and calcined in air at 773 K for 2 h. The resulting mixture was referred to SiO₂-Ga.

2.3. Preparation of BCl₃-modified silica support

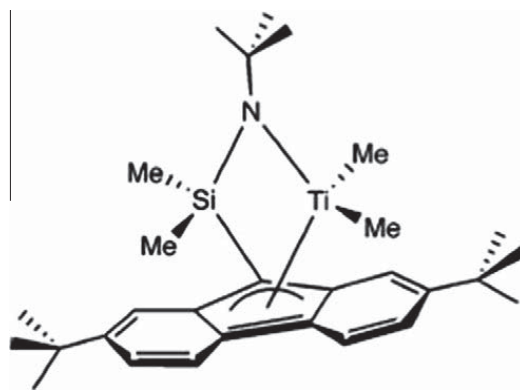
Silica surface was treated with BCl₃ that 14.25 g of silica was added with 150 ml of hexane as diluent, and then 7 ml of BCl₃ were added. The mixture was stirred for 30 min in an oil bath at 313 K, until temperature was raised up to 343 K, followed by drying under vacuum. The resulting mixture was referred to SiO₂-BCl₃.

2.4. Preparation of supported MAO

One gram of calcined silica or modified silica was reacted with the desired amount of MAO in 20 ml of toluene at room temperature for 30 min. The solid part was separated and washed 3 times with 20 ml of toluene, followed by drying in vacuum at room temperature to obtain the catalyst precursor.

2.5. Polymerization procedure

The ethylene/1-hexene copolymerization reaction was performed in a 100 ml semi-batch stainless steel autoclave reactor equipped with magnetic stirrer. At first the desired



Scheme 1. Chemical structure of [t-BuNSiMe₂(2,7-*t*-Bu₂Flu)]TiMe₂ (CGC complex).

amount of the support/MAO was introduced into the reactor. After that the catalyst was put into the reactor to make the amount of catalyst at 10 μmol , and then toluene was injected to adjust the total volume to 30 ml. Then, the reactor was immersed in liquid nitrogen, followed by addition of the 1-hexene into the frozen reactor. The reactor was heated up to the polymerization temperature at 343 K. Lastly, the reaction was terminated by adding acidic methanol. After filtration, the resulting polymers were washed with methanol and dried at room temperature.

2.6. Supports and supported MAO characterization

2.6.1. N_2 physisorption

BET surface area, average pore diameter and pore size distribution of silica and modified silica were determined by Brunauer–Emmett–Teller (BET) method via nitrogen adsorption. The instrument was an AUTOSORB 1-MP, Quantachrome Instruments. Samples were determined using N_2 adsorption at 77 K and handled to the analysis tubes under nitrogen atmosphere and the surface area measurements were carried out inertly. The temperature of evacuated degassing was 423 K.

2.6.2. X-ray diffraction (XRD)

SIEMENS D-5000 X-ray diffractometer with Cu $\text{K}\alpha$ ($\lambda = 1.54439 \text{ \AA}$) was conducted to determine the bulk crystalline phases of samples. The spectra were scanned at a rate of $2.4^\circ \text{ min}^{-1}$ in the range of $2\theta = 20\text{--}80^\circ$.

2.6.3. Temperature programmed desorption of ammonia (NH_3 -TPD)

Acidity of the supports was determined by temperature programmed desorption of ammonia using a Micromeritics Chemisorp 2750 system. The samples were activated at 773 K for 1 h in a flow of helium. Subsequently, the samples were loaded with ammonia and thermal desorption was carried out in a dried He stream at a heating rate of 10 K/min.

2.6.4. Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX)

Scanning electron microscope (SEM), JEOL model JSM-6510 LV, was employed to investigate the morphology of silica, modified silica and catalyst precursor. EDX was performed using Link Isis series 300 program to observe catalyst precursor elemental distribution.

2.6.5. Thermogravimetric analysis (TGA)

TGA was performed to determine the interaction force of the supported MAO. It was conducted using TGA Instruments TG 209F1 analyzer. The samples of 10 mg and a temperature ramping from 303 to 923 K at 5 K/min were used in operation. The carrier gas was N_2 UHP.

2.7. Polymer characterization

2.7.1. Gel permeation chromatography (GPC)

The average molecular weight and molecular weight distribution of obtained polymer in this study were determined

by GPC Waters 150 CV at 413 K with 1,2,4-trichlorobenzene as the solvent and the feed flow rate is 1.0 ml/min.

2.7.2. Differential scanning calorimetry (DSC)

The melting temperature (T_m) of polymer was measured by means of DSC, using DSC 204 F1 Phoenix[®] operating at a heating rate of 10 K/min from 303 K to 473 K. The heating cycle was run twice. In the first scan, the samples were heated, and then cooled to room temperature. In the second, the samples were reheated at the same rate, but only the results of the second scan were reported because the first scan was influenced by the mechanical and thermal history of samples.

2.7.3. ^{13}C Carbon nuclear magnetic resonance spectroscopy (^{13}C NMR)

The ^{13}C NMR spectra were recorded at 383 K using JEOL JNM-A500 operating at 125 MHz. Copolymer solutions were prepared using 1,2,4-trichlorobenzene as solvent and benzene- d_6 for internal lock.

3. Results and discussion

3.1. Characteristics of catalyst support

In this study, three kinds of supports composing of unmodified silica (SiO_2), Ga-modified silica ($\text{SiO}_2\text{--Ga}$), and BCl_3 -modified silica ($\text{SiO}_2\text{--BCl}_3$) were used for supporting the $[\text{t-BuNSiMe}_2(2,7\text{-t-Bu}_2\text{Flu})]\text{TiMe}_2$ (the CGC complex)/MAO catalyst. After modification with Ga and Lewis acid BCl_3 , the silica and modified silica supports were characterized by means of N_2 physisorption, NH_3 -TPD and SEM/EDX. The specific properties of supports determined by N_2 physisorption are shown in Table 1. As seen, the BET surface area, pore volume and pore diameter of all supports were in the same range, indicating that the acidic modification on silica surface did not have significant effect on these structural parameters.

The XRD patterns (not shown) for all supports were similar exhibited only a broad peak between 20° and 30° , as seen typically for the conventional amorphous silica. No XRD peaks of Ga or BCl_3 were observed after impregnation due to its homogeneous distribution or at least that the aggregates formed do not have a significant size to be detected by XRD [25].

Temperature-programmed desorption of ammonia was used to estimate the number and the strength of acid sites on modified silica supports based on the fact that the acidic properties of supports may influence the type of interaction with the metallocene complex and its activation process,

Table 1
Specific properties of various supports obtained from N_2 physisorption.

Support	BET surface area (m^2/g)	Pore volume (mL/g)	Pore diameter ($\text{\AA}$)
SiO_2	309	1.53	198
$\text{SiO}_2\text{--Ga}$	300	1.50	199
$\text{SiO}_2\text{--BCl}_3$	299	1.47	197

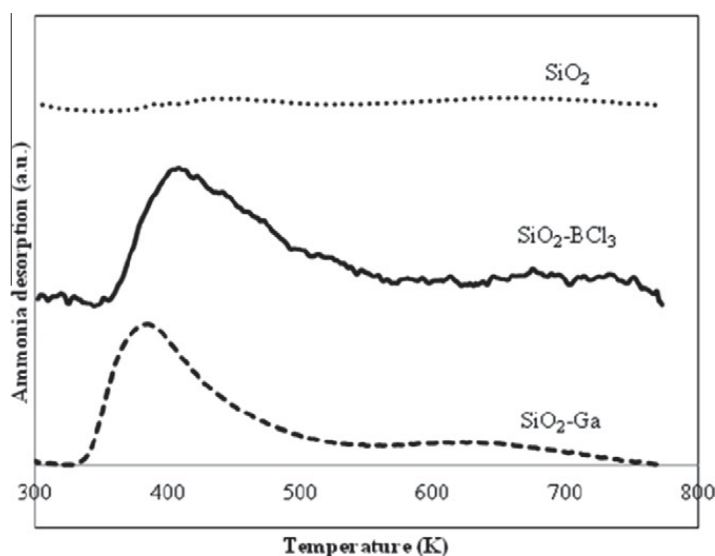


Fig. 1. NH_3 -TPD profiles of SiO_2 , SiO_2 -Ga and SiO_2 - BCl_3 supports.

consequently resulting in overall productivity [22]. The typical NH_3 -TPD profiles for silica support before and after treatment with Ga and BCl_3 can be represented in Fig. 1. The SiO_2 support exhibited no peak, indicating no acidic sites before treatment; on the other hand, both of SiO_2 -Ga and SiO_2 - BCl_3 supports showed two broad peaks at the temperature ranged around 350–550 K and 570–750 K. According to Kosslick et al. [23], these peaks can be ascribed to the NH_3 desorbed from acid sites with low and medium to high strengths. The total acidity concentration of SiO_2 -Ga and SiO_2 - BCl_3 determined by NH_3 temperature program desorption experiments was 283 and 325 $\mu\text{mol NH}_3/\text{g}$, respectively. Therefore, it is clearly shown that the acidity of silica support can be improved with the modification of Ga and BCl_3 .

The morphologies and elemental distributions of the supports before and after MAO impregnation were investigated by using SEM and EDX, respectively. The SEM images of different supports prior to MAO impregnation are shown in Fig. 2. The similar spherical shape was mainly observed, indicating no change of support morphology with the acidic modification.

After impregnation with MAO, the $[\text{Al}]_{\text{MAO}}$ content on the silica surface was measured using EDX. Table 2 represents the $[\text{Al}]_{\text{MAO}}$ content on various silica supports. It can be seen that the $[\text{Al}]_{\text{MAO}}$ concentration of each support slightly varied probably due to the adsorption ability. Results revealed that the SiO_2 -Ga supported MAO achieved the highest amount of $[\text{Al}]_{\text{MAO}}$, suggesting that the adsorption ability of MAO on silica support can be enhanced with

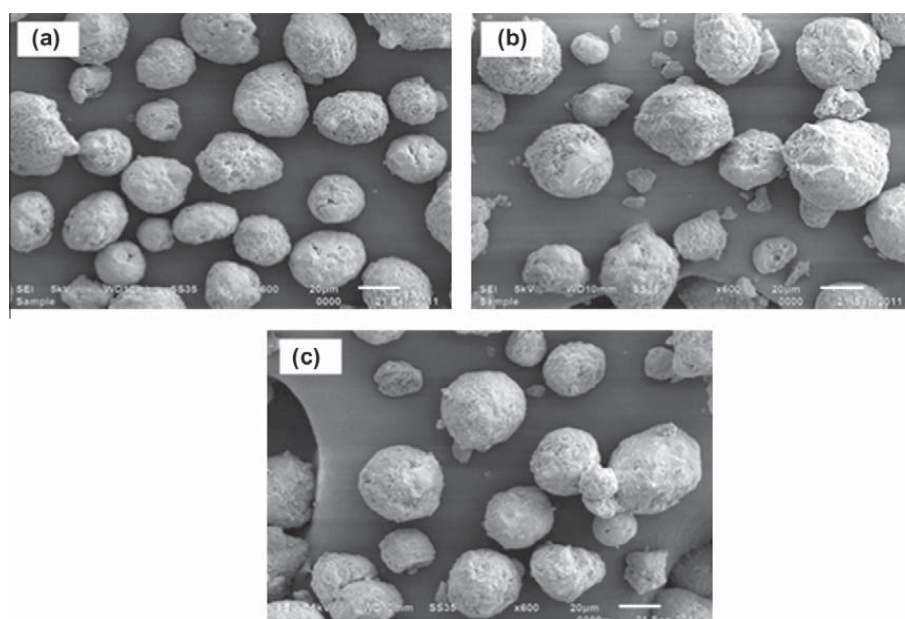


Fig. 2. SEM micrographs of different supports before MAO impregnation: (a) SiO_2 , (b) SiO_2 -Ga and (c) SiO_2 - BCl_3 .

Table 2

[Al]_{MAO} content of the supported MAO from EDX analysis.

Catalyst precursor	[Al] _{MAO} (wt.%)
SiO ₂ /MAO	13.6
SiO ₂ -Ga/MAO	14.5
SiO ₂ -BCl ₃ /MAO	13.4

the introduction of Ga. However, the modification of silica with BCl₃ caused only a slight decrease of immobilized MAO cocatalyst on silica. In addition to the content of [Al]_{MAO}, it should consider the distribution of this element through the support. Therefore, EDX mapping of all elements was used for this purpose and represented in Fig. 3. It can be observed that the distribution for all elements, especially for [Al]_{MAO} was well dispersed all over the catalyst granule without any changes in morphology. Then, the different supports with and without acidic modification having MAO impregnation were employed for ethylene and 1-hexene copolymerization.

3.2. Catalytic activity

Copolymerization of ethylene and 1-hexene via various SiO₂-supported MAO with the CGC catalyst was performed so as to determine the catalytic activities influenced by different acidic modification of support. The polymerization activities of homogeneous system and a variety of supports are summarized in Table 3. Regarding to Table 3, the catalytic activities were in the order of SiO₂-BCl₃ > homogeneous > SiO₂-Ga > SiO₂. It can be apparently seen that the supported system (except SiO₂-BCl₃) exhibited lower activities compared to the homogeneous one, particularly for the unmodified silica. This can be explained taking into

account that in the supported catalyst preparation, different adsorption might take place, contributing to some inactive species for polymerization [29]. Another possible reason for this observation is the depression of the polymerization rate as a result of mass transfer limitation in heterogeneous system. Nonetheless, considering only the supported system, the modification of silica support, like Ga and BCl₃, was able to increase the polymerization activities. Generally, increased activities can be owing to the increased amount of [Al]_{MAO} presented on the support and the interaction between support and MAO [30,31]. However, in this work the former factor can be neglected by using the same ratio of [Al]_{MAO}/[Ti]_{cat} = 400 and adjusting the required amount of the supported MAO in each experiment. Thus, the latter factor should be considered as the probable cause for this increased activity. Based on this study, MAO was dispersed over the silica supports by impregnation prior to polymerization. The degree of interaction between the [Al]_{MAO} and the support can be investigated by the TGA measurement. According to Severn et al. [32], the connection of the support and the cocatalyst occurred via the O_{support}-Al_{cocatalyst} linkage. The TGA can provide the beneficial information on the degree of the interaction for MAO bound to silica in terms of weight loss and removal temperature [26,30,31]. In fact, too strong interaction leads to more difficult for [Al]_{MAO} bound to the support to react with the metallocene catalyst during activation step and thus low polymerization activity. On the contrary, the leaching of MAO can be occurred due to weak interaction between support and MAO. Therefore, the optimum degree of interaction should be required in order to achieve the high activity. Fig. 4 represents TGA profiles of various supports. It was observed that the weight loss of [Al]_{MAO} presented on the supports was in

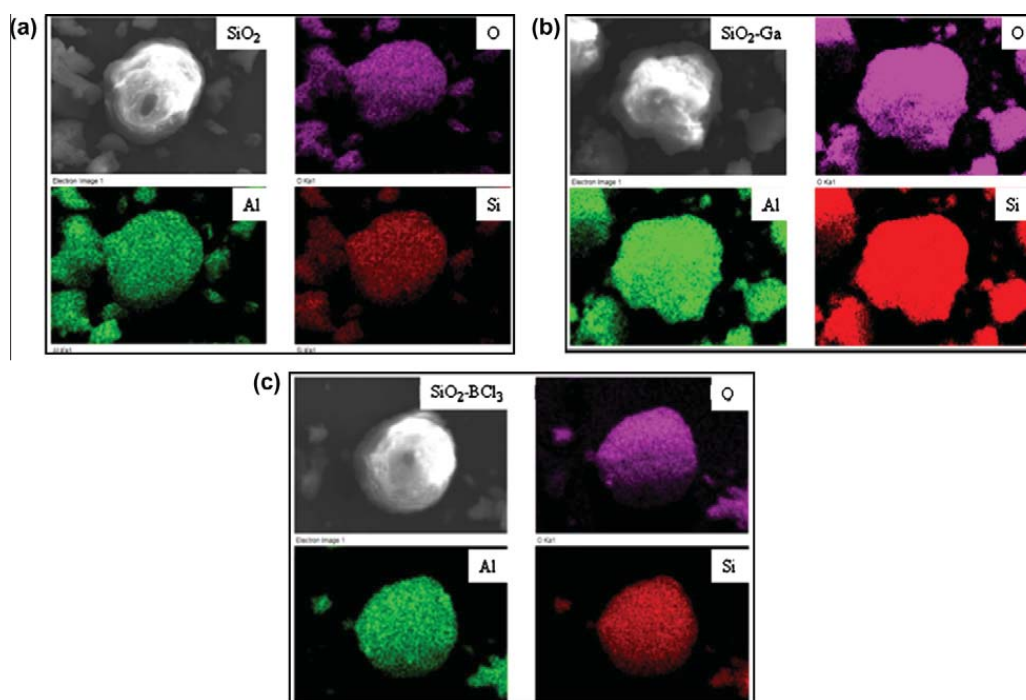


Fig. 3. EDX mapping of (a) SiO₂ supported MAO (b) SiO₂-Ga supported MAO (c) SiO₂-BCl₃ supported MAO.

Table 3
Summary of ethylene/1-hexene copolymerization catalytic activities.

System	Time (s)	Weight (g)	Activity ^a (kg polymer/mol Ti.h)
Homogeneous	85.8	1.04	4377
SiO ₂	99.2	0.97	3519
SiO ₂ -Ga	92.4	1.00	3901
SiO ₂ -BCl ₃	78	0.96	4454

^a Polymerization condition: [Ti] = 10 μ mol, MAO as cocatalyst, [Al]/[Ti] = 400, liquid volume (toluene) = 30 mL, temperature = 343 K, ethylene pressure = 349 kPa (50 psi).

the order of SiO₂-BCl₃ (25.2%) < SiO₂-Ga (25.6%) < SiO₂ (26.2%). This indicated the strongest interaction of the SiO₂-BCl₃ supported MAO, demonstrating the highest activity compared to other supports. Thus, for this supported CGC system, it should be mentioned that the stronger interaction between cocatalyst and support is favorable in order to prevent the leaching of the cocatalyst.

Besides the interaction, one should concern on the acidic property of the silica support after modification with Ga and BCl₃. As a matter of fact, the literature reviewed that the surface acidity properties of supports have the important role in the activation of metallocene catalyst and accordingly on the activity enhancement. Moreover, Campos et al. [25] constructed a correlation between polymerization activity and support acidity and revealed that the activities increased with an increase of acidic sites. In this work, the incorporation of Ga and BCl₃ generated the acid sites in the silica supports (as confirmed by NH₃-TPD) and these sites are able to assist MAO that performed as a main activating agent to activate the CGC catalyst during the polymerization. As a consequence, this should be an explanation for an obvious rise of polymerization activities in modified supports compared to the conventional silica support. Furthermore, a higher degree of activity increase for BCl₃-modified silica system can be mainly attributed to the higher acidity than the Ga-modified one.

With regard to the result in Table 3, it is worth nothing that the catalytic activity obtained from BCl₃-modified

support was the highest and can be comparable to the homogeneous one, suggesting the homogeneous-like behavior of this system. It was presumably on account of the role of BCl₃ as a spacer group on the surface of silica. Investigation of a spacer such as TiO₂, silane and zirconia in copolymerization of ethylene and α -olefins was studied as well [15–17]. In order to gain a better understanding, a conceptual model for BCl₃ effect is illustrated in Scheme 2. As seen, after immobilization MAO or active sites can be anchored on the modified silica through the BCl molecule, which acted as a spacer and hence less steric hindrance between them. Consequently, a monomer during polymerization can insert more easily into this structure, and thus enhancing activity.

3.3. Characteristics of polymer

The various obtained copolymers were further characterized by means of GPC, DSC and ¹³C NMR. Table 4 is constructed to summarize the properties yielded from homogeneous and various supported systems. The GPC was performed to measure *M_w* and MWD of polymers. It should be mentioned that all polymers exhibited rather low molecular weights. However, these results were in the same range (20–40 kg/mol) with other metallocene or CGC catalysts under similar conditions [6,16,33–35]. This is probably due to the nature of metallocene catalyst that is usually relatively sensitive to chain transfer reaction despite no apparent chain termination reagent. Nevertheless, in order to improve or control the molecular weight, this constrained geometry catalyst system should be further investigated in living polymerization. Comparing to the homogeneous system, it was apparently observed that the molecular weight for other heterogeneous systems increased drastically (more than 3 times). This should be because of an obstruction of bimolecular reaction between two catalytic sites by immobilization of MAO on the support surface. Therefore, a β -hydrogen transfer might be lessened, and then enables longer growth of the polymer chain, leading to higher molecular weight of polymers

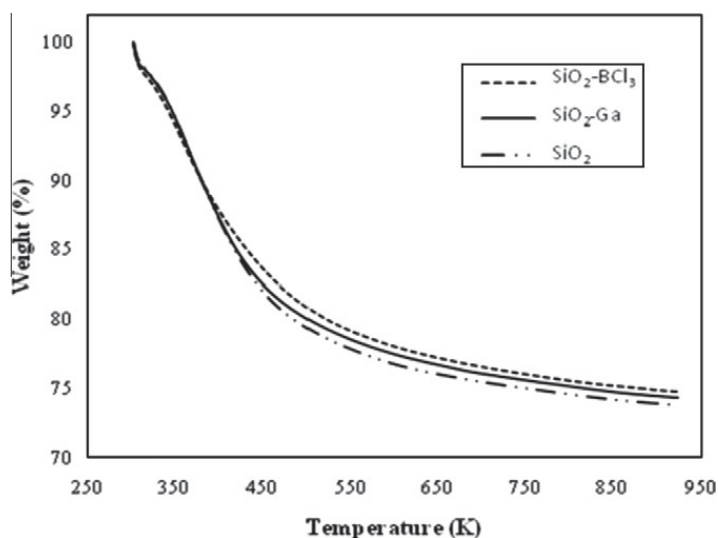
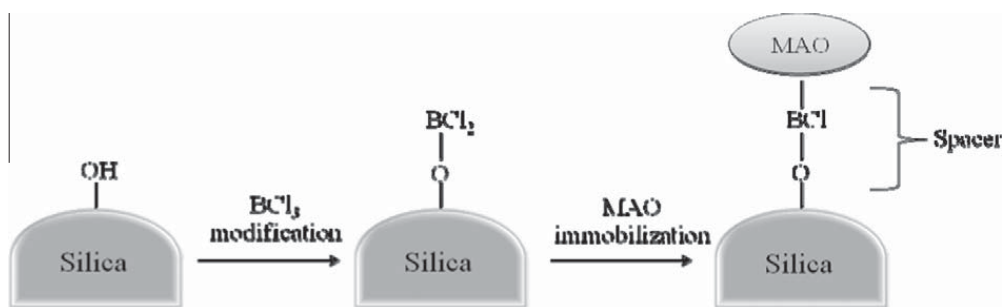


Fig. 4. TGA profiles of supported MAO on various supports.



Scheme 2. Conceptual model for BCl_3 effect as a spacer.

Table 4

Properties of the resulted copolymers from homogeneous and supported system.

System	Melting point ^a (T_m) (K)	Molecular weight ^b (M_w) (kg/mol)	MWD ^b (M_w/M_n)	Insertion% ^c
Homogeneous	378	9	3.26	13.6
SiO_2	391	35	2.81	9.3
$\text{SiO}_2\text{-Ga}$	390	28	2.61	11.3
$\text{SiO}_2\text{-BCl}_3$	382	27	2.40	15.0

^a Determined by DSC.

^b Determined by GPC.

^c 1-hexene insertion in copolymer determined by ^{13}C NMR.

[32]. Fig. 5 shows the GPC curves for all polymers, indicating the unimodal molecular weight distribution. In addition, it was found that the molecular weight distribution of the copolymer resulted from the heterogeneous system became narrower, especially after modification with Ga and BCl_3 . This indicated that the more uniform catalytic sites can be achieved through the acidic modification.

Considering only the supported systems, a slight reduction in molecular weight was observed for the modified support. The cause of this is based on the fact that a rise of 1-hexene insertion compared to unmodified support promotes chain transfer reactions, consequently contributing to lower molecular weight copolymers [29]. The melting temperature (T_m) of copolymers evaluated by DSC is also shown in Table 4. It revealed that T_m was in the range between 378 and 391 K. However, T_m tended to slightly decrease with Ga and BCl_3 modification generally attributed to the increased degree of 1-hexene insertion.

The quantitative analysis of triad distribution for all copolymers was conducted on the basis assignment of the ^{13}C NMR spectra of ethylene/1-hexene copolymer [36]. The triad distributions and 1-hexene contents, which were calculated according to the Randall method [36] are presented in Table 5. Ethylene incorporation in all systems gave copolymers with similar triad distribution regardless of acidic modification. Only random copolymers can be produced with this system. On the other hand, it is shown that the unmodified silica support presented a noticeable

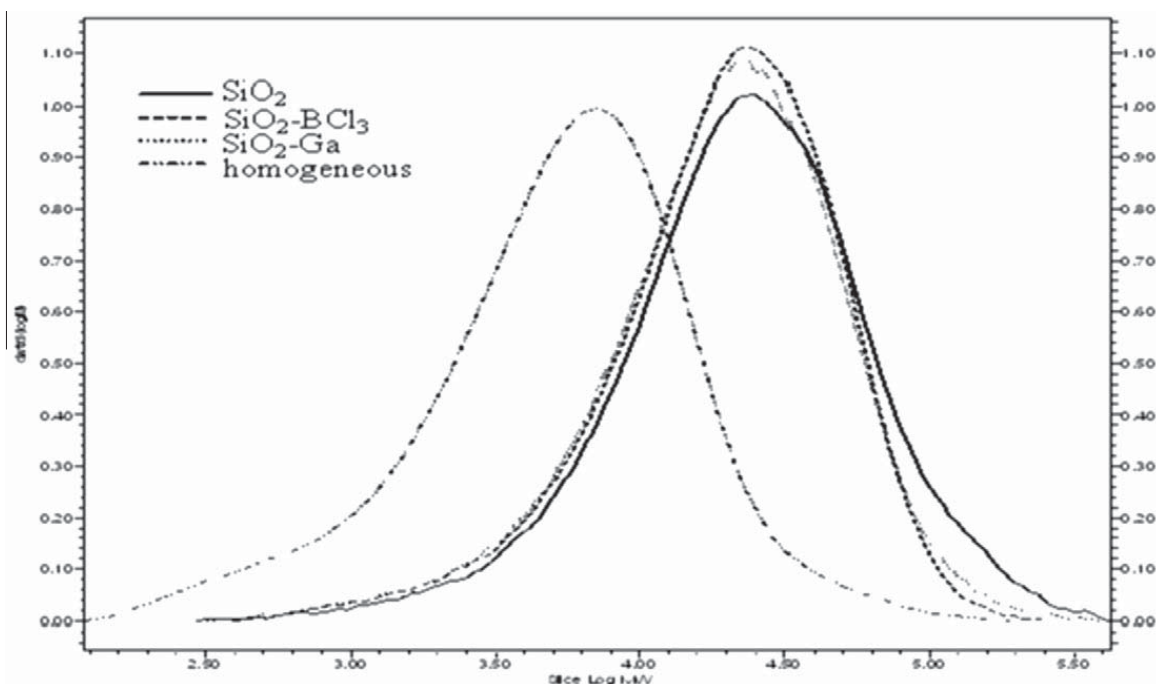


Fig. 5. GPC curves of copolymers obtained from various supports.

Table 5Triad distribution of copolymers obtain from ^{13}C NMR.

System	[HHH]	[EHH]	[EHE]	[EEE]	[HEH]	[HEE]	[H] (%)
Homogeneous	0.000	0.000	0.129	0.630	0.000	0.241	12.9
SiO_2	0.000	0.000	0.090	0.738	0.000	0.172	9.0
$\text{SiO}_2\text{-Ga}$	0.000	0.000	0.094	0.761	0.000	0.145	9.4
$\text{SiO}_2\text{-BCl}_3$	0.000	0.000	0.138	0.646	0.031	0.186	13.8

decrease of 1-hexene insertion compared to the homogeneous one. The lower comonomer incorporation can be by reason of a steric effect inserted by silica surface, preventing one of the CGC catalyst faces, therefore reducing the accessibility of the comonomer onto the active sites [29]. This steric effect is able to be relieved with the silica modification like BCl_3 which can act as a spacer group to keep apart active sites from the silica surface, thus being apt to enhance the 1-hexene extent.

4. Conclusion

The activities of ethylene/1-hexene copolymerization with silica-supported CGC/MAO catalyst can be improved with the Ga and BCl_3 acidic modification on the silica support. Increased activity was due to the stronger interaction between support and cocatalyst coupled with a formation of acidic sites derived from the modification. Additionally, BCl_3 is able to be a spacer on the silica support leading to the highest activity and the highest 1-hexene incorporation. The supported catalytic system resulted in polymers with significantly higher molecular weight (almost 4 times) and narrower molecular weight distribution, especially after acidic modification. However, the Ga and BCl_3 modifications seem not to greatly influence on the melting temperature and the microstructure of copolymers.

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Observation on inhibition of Ti^{3+} reduction by fumed silica addition in Ziegler-Natta catalyst with *in situ* ESR

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ABSTRACT

This study focused on elucidation of effect of fumed silica added in the commercial Ziegler-Natta catalysts by physical solid–solid stirring. The added fumed silica seemed to cover around the catalyst revealed by SEM-EDX and apparently resulted in decreased activity of ethylene polymerization, but increased molecular weight of polyethylene as measured by GPC. Based on the *in situ* ESR measurement, it can be concluded that fumed silica can inhibit the reduction of Ti^{3+} by triethylaluminum (TEA). It is suggested that the delay reduction of Ti^{3+} may be beneficial for propylene polymerization.

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1. Introduction

More than fifty years, many researchers have enormously considered on the Ziegler-Natta catalysts both in academic and industrial viewpoints. Polyethylene has been used widely in many applications such as high strength fabricated structure. Each application has to be produced with particular catalysts and conditions. Silica is known as a support material that provides an advantage on the polymer morphology, but it causes to lose in the catalytic activity [1–5] due to silanol groups (*i.e.* SiOH) on the silica surface [3–7]. In order to remove the OH group on the surface, silica has usually been calcined at different temperatures between 110 and 820 °C [1–9]. Although the silanol groups of the silica have been exerted with high calcination temperature, the experimental evidences showed that the high calcination temperature still cannot get rid of all the OH groups [4,6,8,10,11]. Another method is to functionalize it with some substance such as alkyl silyl, alkyl silyl halide or alkyl aluminum to change the silanol groups into the other forms [1–4,6,7,10,12]. Although the activity has lost, the catalyst produced from mixed supports with silica (*i.e.* magnesium-silica bisupport) tends to affect not only on morphology, but also on the properties of the polymer such as rheological properties afforded by functional groups on the silica surface [1,2].

As in the industrial field of production of high density polyethylene, the commercial Ziegler-Natta catalyst produced from the adduct method with anhydrous magnesium chloride support gives an excellent catalytic activity in the acceptable variation of polymer properties of specific grades for end-use applications. Synthesis of a new catalyst such as bi-supported catalyst may lead to a huge investment due to the need of many manufacturing units. To utilize the advantage and benefit of the commercial catalyst, fumed silica has been considered to be the solid substance interacted at the commercial catalyst surface to control the polymer properties. Fumed silica was able to provide extreme amounts of contact surface bound to another material due to its high surface area.

In this study, fumed silica was used as a hypothetical catalytic controllable material to change the catalytic properties of the commercial Ziegler-Natta catalyst. The effect of fumed silica, which was added physically by solid-solid stirring, on the properties of polyethylene obtained was also investigated. Moreover, to elucidate the role of fumed silica on the reduction of Ti^{4+} , the *in situ* electron spin resonance (ESR) was performed successfully. More details are further discussed.

2. Experimental

2.1. Materials

Purified argon gas (99.999%), commercial polymerization grade ethylene gas and hydrogen gas were purchased from Thai

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Industrial Gas Co., Ltd. The commercial catalyst was a Ziegler-Natta titanium-magnesium based catalyst for ethylene polymerization. Fumed silica purchased from Sigma was non-porous type with surface area of $390 \pm 40 \text{ m}^2/\text{g}$ and its primary particle size was 7 nm as reported by Cabot Corporation. Hexane, triethylaluminum (TEA) and fumed silica were operated under an argon atmosphere via a glove box, glove bags and Schlenk techniques.

2.2. Silica calcination

In order to keep the original OH group on surface, fumed silica was calcined at 150°C for intend to only remove physical adsorbed water from the surface. The calcination was performed under argon atmosphere.

2.3. Polymerization

The ethylene polymerization was carried out with 2 l autoclave reactor connected with the lines available for argon, hydrogen and ethylene gases and also the hexane feed line. The reactor and all connected feed lines were cleared humid and oxygen by evacuation, and then followed by purging with the argon many times. First, 1 l of hexane was filled and heated to 80°C . The desired amount of catalyst was stirred with 0, 10, 20, and 60 wt% with fumed silica in hexane solvent for 15 min. Then, TEA of 1 mmol was injected into the reactor subsequently by the stirred catalyst with 0.003 mmolTi. In the condition with the presence of hydrogen, the reactor was pressurized with 1 bar of argon followed by pressurizing with hydrogen gas to 3.5 bars and finally pressurizing with ethylene gas to 8 bars. In addition, the partial pressure of the gases is 1, 2.5 and 4.5 bars. The catalysts were named as ZN00S, ZN10S, ZN20S, and ZN60S for stirring with 0, 10, 20, and 60% of fumed silica, respectively.

2.4. Characterization

The catalysts were characterized with different techniques to investigate the reasonable model. Electron spin resonance (ESR) was performed to measure changes of Ti oxidation state after activation by TEA. The molecular weights (Mw) and molecular weight distribution (MWD) of polymer were measured by gel permeation chromatography (GPC). Details are as follows;

2.4.1. In situ ESR

The extent of Ti^{3+} content of the catalyst stirred with various amounts of fumed silica was observed by the *in situ* ESR technique. The ESR equipment used is JEOL model JES-RE2X filled with argon atmosphere. DPPH standard was used for g-factor calibration. First, the catalyst was stirred with fumed silica in hexane for 15 min in glove box. After activation by TEA, the sample was measured by ESR starting at room temperature (25°C). In order to evaluate the extent of Ti^{3+} at the polymerization temperature (80°C), the catalyst sample was heated to 80°C and held for 90 min for ESR measurement. The ESR spectrum was collected every 15 min from the beginning until 90 min.

2.4.2. GPC

A high temperature GPC (Waters 150-C) equipped with a viscometric detector was used to determine the molecular weight and molecular weight distribution of the polymers. 1, 2, 4-trichlorobenzene was used as a solvent and the temperature was performed at 140°C .

2.4.3. SEM-EDX

The external surface of the catalysts and their morphologies were obviously revealed by scanning electron microscopy

Table 1

Activities of catalyst and molecular weight of polymer.

Sample	Activity (kgPE/molTi/h)	Mn (kg/mol)	Mw (kg/mol)	MWD
ZN00S	25,043	24	122	5.1
ZN10S	21,335	28	175	6.2
ZN20S	16,120	29	170	5.9
ZN60S	13,230	31	155	5.0

technique with a JEOL model S-3400 and the elemental distributions were also observed by energy dispersive X-ray spectroscopy by EDAX device. The polymer samples for SEM analysis were coated with platinum particles by ion sputtering device to provide electrical contact to the specimen. The samples were performed with overflowing of argon gas to reduce oxygen and moisture toward the catalysts.

3. Results and discussion

Activities of the catalysts stirred with various amounts of fumed silica along with Mw, MWD obtained from GPC are shown in Table 1. The results show that when the amount of fumed silica increased the activities decreased. The molecular weight of polymer tended to increased with fumed silica addition, whereas only slight change in MWD was observed.

In addition, the GPC profiles are also shown in Fig. 1 indicating that they shift to a higher molecular weight position with fumed silica addition along with slightly broader MWD up to ZN20S.

It is well known that the change in activities of ZN catalysts must be related to the Ti oxidation state during polymerization. Based on the results as mentioned above, the addition of fumed silica apparently decreased the catalytic activity during polymerization. Thus, the addition of fumed silica may alter the Ti oxidation state during polymerization. In order to elucidate the effect of fumed silica, the *in situ* ESR measurement was performed. ESR is one of the most powerful techniques used to measure the oxidation of Ti^{3+} , especially upon the *in situ* condition [13]. In this measurement, the catalyst samples having different amounts of fumed silica added were activated by TEA based on polymerization condition. Then, the extent of the Ti^{3+} extent during reduction by TEA for each sample was observed. The ESR results for ZN00S, ZN20S, and ZN60S samples are shown in Fig. 2. For all samples, there are three peaks located at g values equal to 1.985, 1.97, and 1.94 in each spectrum. The different g values refers to the various types of Ti^{3+} coordination. For instance, the g values of 1.97 and 1.985 are assigned to the tetrahedral coordination of Ti^{3+} [14–16] and the g value of 1.94 refers to the six-coordinated Ti^{3+} dissolved in MgCl_2 [14] or to isolated octahedral coordinated Ti^{3+} [15]. It is evident that peak areas between the g values of 1.985 and

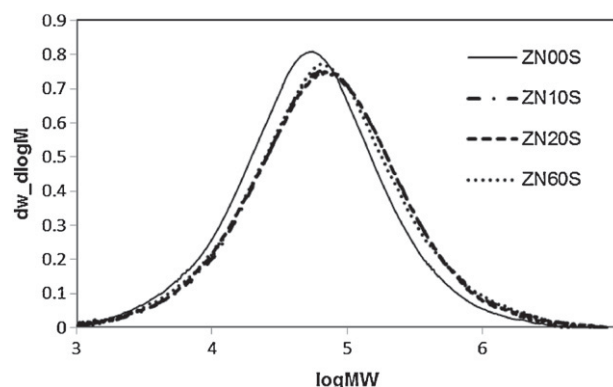


Fig. 1. The GPC profiles of polymers obtained from different catalysts.

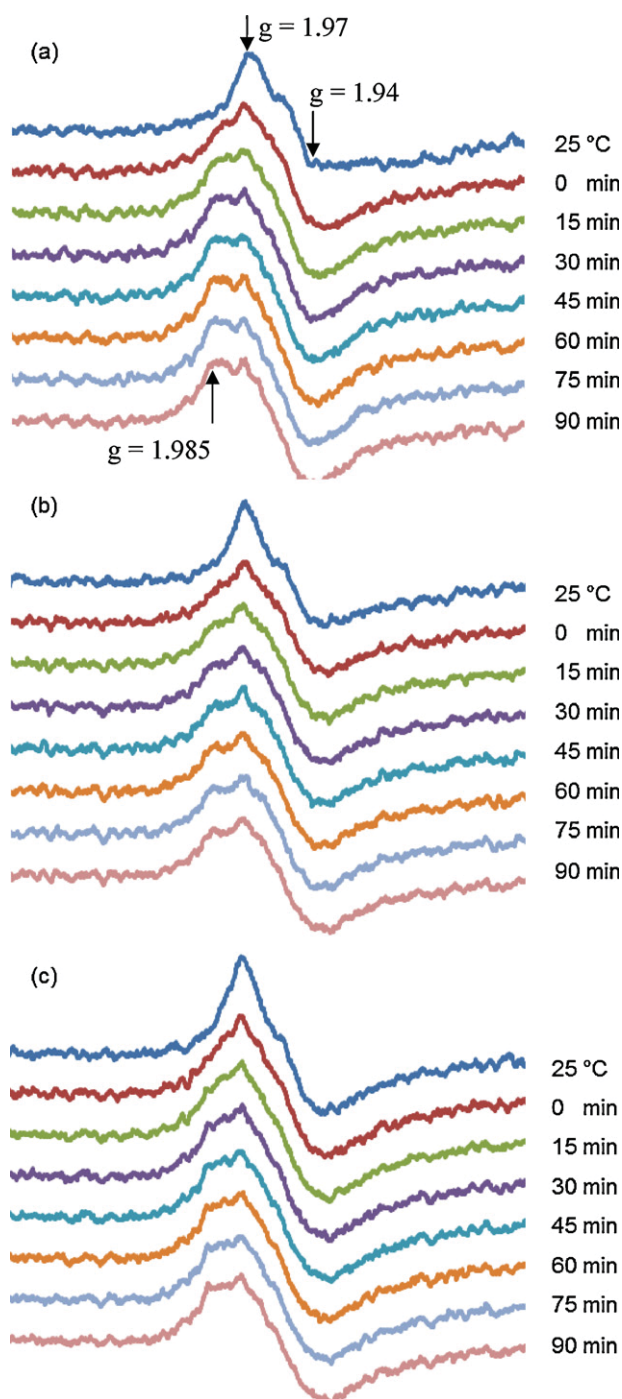


Fig. 2. The ESR spectra of the catalyst; (a) ZN00S, (b) ZN20S and (c) ZN60S.

1.97 are altered by different amounts of fumed silica added. On the other hand, intensity of the peaks at g values of 1.985, 1.94 increased with addition of fumed silica.

From the ESR spectra, it revealed that the catalyst stirred with fumed silica contributed to the inhibition of change in Ti^{3+} extent. The spectra were taken double integration in order to measure the amounts of Ti^{3+} absorbance upon each interval time. The integrated areas are plotted in terms of relative area related to the beginning of 80 °C as shown in Fig. 3.

As seen in Fig. 3, the relative areas for catalyst having fumed silica up to 20% apparently resulted in the less change of Ti^{3+} amounts. This indicates that fumed silica may act as a buffer which inhibits the reducing power of TEA to reduce Ti^{4+} to Ti^{3+} , and Ti^{3+} to

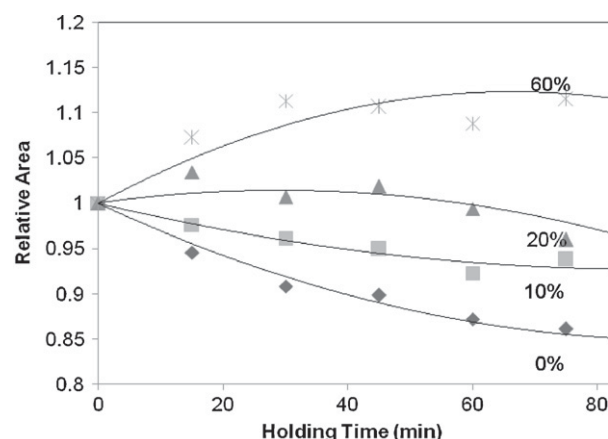


Fig. 3. The relative amount of Ti^{3+} at 80 °C.

Ti^{2+} . Thus, the amounts of Ti^{3+} decreased with time. For such the phenomenon, the slope of 0% of fumed silica added exhibits the highest rate of decreased Ti^{3+} upon time, while the addition of 10% and 20% of fumed silica lowers the rate of decreased Ti^{3+} upon time. It should be noted that with 60% of fumed silica added, Ti^{3+} increased due to the reduction of Ti^{4+} to Ti^{3+} (not Ti^{3+} to Ti^{2+} as mentioned before). It is suggested that fumed silica can be adsorbed on the catalyst particles and inhibit the reduction of Ti^{3+} by TEA. As the result, the activity of ethylene polymerization decreased with silica addition as seen in Fig. 4 due to Ti^{3+} is less active than Ti^{2+} for ethylene polymerization [17]. It should be mentioned that the catalysts with silica showed much lower rate

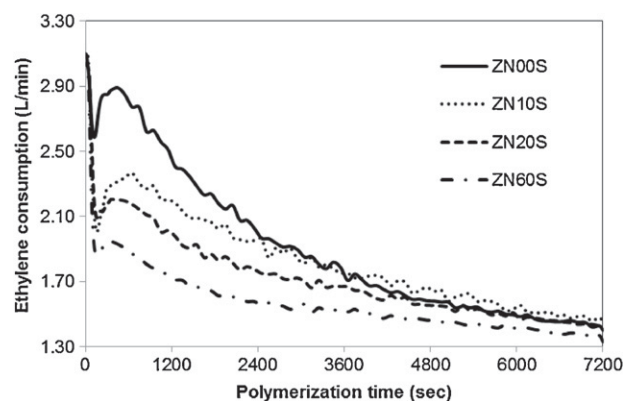


Fig. 4. Ethylene consumption profiles of the catalyst stirred with various amounts of fumed silica.

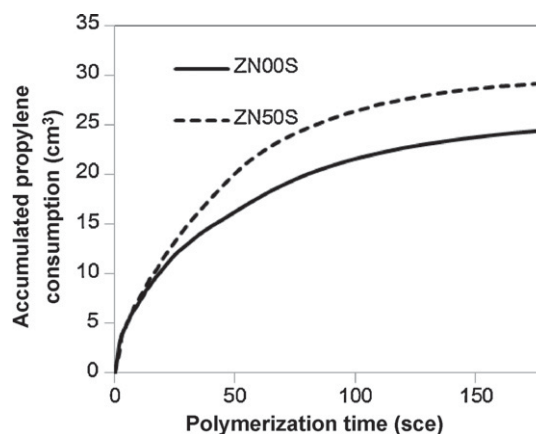


Fig. 5. Effect of fumed silica added on propylene polymerization.

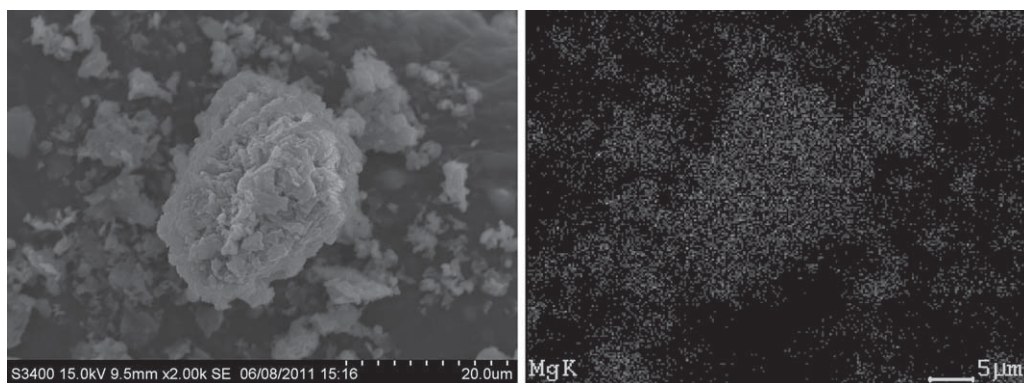


Fig. 6. SEM/EDX of the original commercial catalyst.

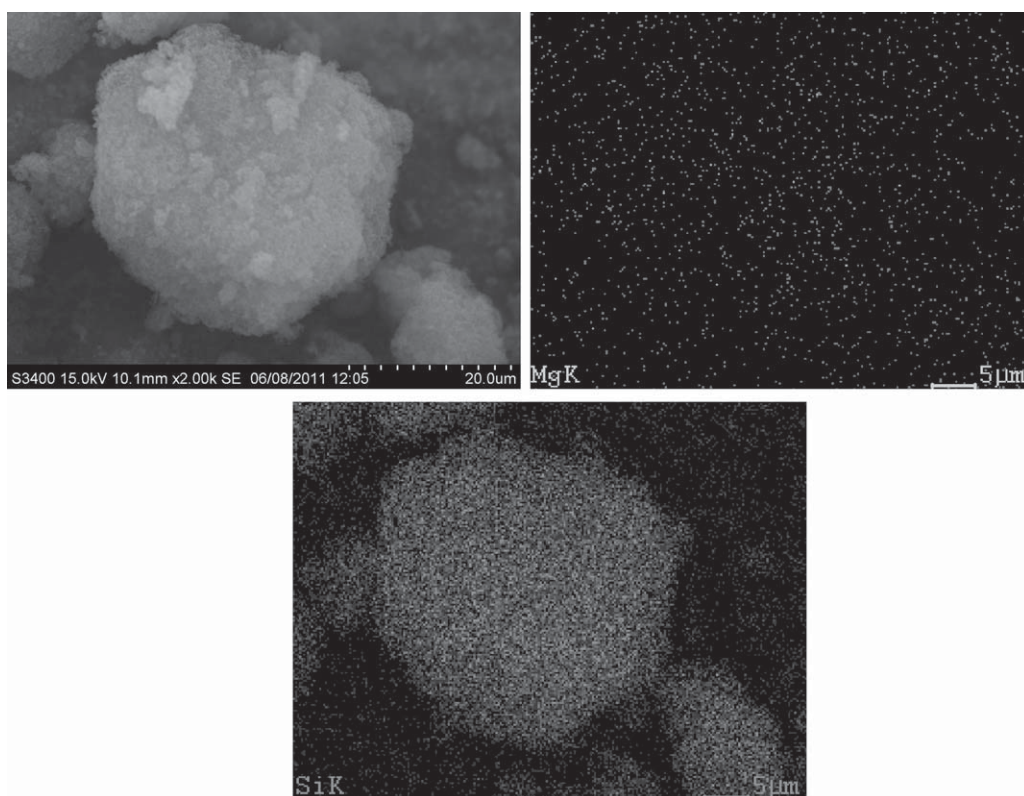


Fig. 7. SEM/EDX of the commercial catalyst stirred with fumed silica.

than the original catalyst in the first hour of reaction, but the rates in the second hour are almost the same for all the catalysts. This phenomenon may reflect the different stability of active centers from Ti^{2+} and Ti^{3+} species as also seen from the ESR results. The slower interaction between catalyst and cocatalyst also contributed to the decrease in polymer chain termination reactions by cocatalyst [18] which results in higher molecular weight polymer.

The other way to trace the increased amounts of Ti^{3+} is to perform propylene polymerization. It is well known that propylene polymerization is only active with Ti^{3+} [19,20]. Thus, propylene polymerization was also performed using ZN00S and ZN50S samples as shown in Fig. 5. It can be observed that activity of propylene polymerization increased (ca. 19%) with fumed silica added indicating more amounts of Ti^{3+} present.

The elemental distributions on the catalyst surface were performed by SEM/EDX. The results revealed that the catalyst was covered by fumed silica which made most of magnesium

element disappeared from the catalyst surface as shown in Figs. 6 and 7.

4. Conclusions

The main objective of this research is to use fumed silica for improvement of the commercial Ziegler-Natta catalyst. It was found that the fumed silica added to the catalyst by physical stirring affected on the catalyst covered around by fumed silica resulted in decreased activity for ethylene polymerization, but increased molecular weight and only slightly increased MWD. The significant finding is to elucidate the effect of fumed silica using the *in situ* ESR measurement. It is evident that fumed silica can inhibit the reduction of Ti^{3+} to Ti^{2+} resulting in decreased ethylene polymerization activity. In contrast, the activity of propylene polymerization remarkably increased.

Acknowledgments

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Effect of nanocrystallite size of titanium dioxide on the catalytic activity of cobalt catalyst

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Abstract—We studied the effect of crystallite size of nanocrystalline TiO_2 derived from the sol-gel method on the properties of Co/ TiO_2 catalysts. First, nanocrystalline TiO_2 supports having different crystallite sizes were prepared via the sol-gel method by varying the water:alkoxide ratios from 4 to 165. Then, they were used as support for the cobalt catalyst. After calcination, the crystallite size of Co_3O_4 was dependent on the size of TiO_2 support. CO hydrogenation under methanation was performed to determine the activity and selectivity of Co/ TiO_2 catalysts. It revealed that the catalyst with smaller size of TiO_2 crystallite exhibited higher catalytic activity due to higher Co dispersion without significant change in product selectivity. In addition, the Ru modification on the TiO_2 support was also investigated. The Ru modification resulted in increased activity regardless of the size of TiO_2 crystallite.

Key words: Nanocrystalline TiO_2 , Sol-gel, Cobalt Catalyst, Methanation, CO Hydrogenation

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Fischer-Tropsch (FT) synthesis has been successfully used for future alternative resources instead of coal or crude oil. There are many active metals, such as Ru, Fe, Co, and Pd that can be used for hydrogenation of carbon monoxide (CO) to petroleum wax. For example, cobalt and iron are used for hydrocarbon synthesis. Even though the cobalt catalysts are more expensive, they are more resistant to deactivation than iron metals [1]. Supported cobalt catalysts have been extensively investigated with many inorganic supports for years, such as SiO_2 [2], Al_2O_3 [3], TiO_2 [4]. They have been the most popular FT catalysts for years due to their high catalytic activity and selectivity [5,6]. CO and H_2 (syngas) have been converted to paraffinic or long chain hydrocarbon through hydrogenation reaction. In fact, the interaction between cobalt oxide species and supports plays an important role in dispersion of cobalt oxide species [7]. The addition of small amount of noble metals apparently improves the catalytic properties [7-9]. For instance, the promotion with Ru in the supported cobalt catalysts also enhances the turnover rate and Co site density during reaction, as reported by Iglesia et al. [10].

Due to the significant developments in nanoscience and nanotechnology over recent years, many inorganic nanomaterials have been captivating the research in heterogeneous catalysis area. These inorganic nanomaterials can be potentially used as catalysts in some specified reactions, as supports for the catalytic phase, and also as nanofillers in composite materials. This can be attributed to their unique properties, great thermal and mechanical stability. In the present work, nanocrystalline TiO_2 having different crystallite sizes was prepared via the sol-gel method and used as the support for Co catalysts. In fact, the crystallite size of TiO_2 can be controlled by varying the water : alkoxide ratios during sol-gel synthesis. Thus, the effect

of crystallite size of the TiO_2 support on the properties of Co catalysts can be elucidated. The characteristics of different supports and catalysts were determined by means of several techniques, such as XRD, SEM/EDX, TEM, TPR, CO chemisorption, and XPS. The activity and product selectivity of catalysts were measured via CO hydrogenation under methanation condition to minimize the catalyst deactivation.

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1. Preparation of Nanocrystalline TiO_2

TiO_2 was prepared by the sol-gel method [11,12]. First, the titania precursor [titanium (IV) isopropoxide] was dissolved in ethanol and then mixed with the solution of water:alkoxide, having molar ratios between 4 to 165 in order to obtain different crystallite sizes of TiO_2 . The mixture was added dropwise to the aqueous solution with ultrasonic stirring at room temperature for 2 h. The obtained amorphous precipitates were centrifuged and redispersed in ethanol five times prior to filtration. After that, the sample was dried and calcined at 450 °C in air flow for 2 h.

2. Preparation of Ru-modified Nanocrystalline TiO_2

The Ru-modified TiO_2 support was prepared by the incipient wetness impregnation having 0.03 wt% of Ru. The desired amount of ruthenium (III) nitrosyl nitrate [$\text{Ru}(\text{NO}(\text{NO}_3)_3)$] was dissolved in deionized water, and then was dropped slowly to the TiO_2 support. The modified support was dried at 110 °C for 12 h and calcined in air at 500 °C for 4 h.

3. Preparation of Cobalt Catalyst

A 20 wt% of Co metal was impregnated onto the TiO_2 supports according to sections 1 and 2 using cobalt nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] as the precursor. The sample was dried at 110 °C for 12 h and calcined in air at 500 °C for 4 h to convert all cobalt nitrate precursors into Co oxide species [13].

The nomenclature used for the catalyst samples in this study is

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as follows:

- Co/TiO₂_xx nm
- Co/TiO₂_xx nm_Ru

Co/TiO₂_xx nm refers to Co/TiO₂ catalyst with TiO₂ having the crystallite size of xx nm.

Co/TiO₂_xx nm_Ru refers to the Co/TiO₂ catalyst with TiO₂ having the crystallite size of xx nm with Ru modification on TiO₂ as mentioned in section 2.

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CO hydrogenation (H₂/CO=10/1) under methanation condition was performed to determine the overall activity of the samples. Hydrogenation of CO was carried out at 220 °C and 1 atm. A flow rate of H₂/CO/Ar=20/2/8 cm³/min in a fixed-bed flow reactor was used. A relatively high H₂/CO ratio was used to minimize deactivation due to carbon deposition during reaction. Typically, 10 mg of a sample was reduced in flowing H₂ (30 cm³/min) at 350 °C for 10 h prior to the reaction. Reactor effluent samples were taken at 30-min intervals and analyzed by GC. Thermal conductivity detector (TCD) with molecular sieve 5A was used to detect the CO. A flame ionization detector (FID) with a VZ-10 column was used to detect the light hydrocarbons, such as C₁-C₄ hydrocarbons. In all cases, steady-state was reached within 5 h.

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5-1. N₂ Physisorption

The surface area was determined by physisorption of nitrogen (N₂) using a Micromeritics Pulse Chemisorb 2700 system. It was calculated based on nitrogen uptake at liquid-nitrogen temperature (77 K) using the Brunauer-Emmett-Teller (BET) equation by the single point method.

5-2. X-ray Diffraction

XRD was performed to determine the bulk crystalline phases of the sample. It was conducted using a SIEMENS D-5000 X-ray diffractometer with Cu K_α (λ=1.54439 Å). The spectra were scanned at a rate of 2.4°/min in the range 2θ=20-80°.

5-3. Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy

SEM and EDX were used to determine the catalyst morphologies and elemental distribution throughout the sample granules, respectively. SEM involved a JEOLmodel JSM-5800LV. EDX was performed using Link Isis series 300 program.

5-4. Transmission Electron Microscopy

TEM was used to determine the dispersion of cobalt oxide species using JEOL-TEM 200CX transmission electron spectroscopy operated at 100 kV with 50 k magnification. The sample was dispersed in ethanol to obtain the uniform dispersion of sample prior to the measurement.

5-5. Temperature-programmed Reduction

TPR was used to determine the reduction behaviors of the samples. It was carried out using 50 mg of a sample and a temperature ramp from 35 to 800 °C at 5 °C/min. The carrier gas was 10% H₂ in Ar. A cold trap was placed before the detector to remove water produced during the reaction.

5-6. X-ray Photoelectron Spectroscopy

XPS was used to examine the binding energy and the surface composition of the catalysts by using an AMICUS spectrometer with X-ray source of Mg K_α radiation operated at voltage of 20 kV, current of 10 mA using the AMICUS "VISION2" software.

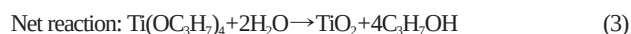
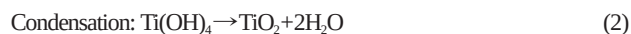
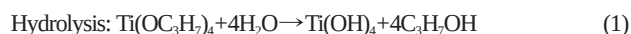
5-7. CO Chemisorption

The active sites and the relative percentages dispersion of cobalt catalyst were determined by CO-pulse chemisorption technique using Micromeritics ChemiSorb 2750 (pulse chemisorption system) and ASAP 2101C V3.00 software. 20 mg of a sample was used and reduced in H₂ flow rate at 50 ml/min with heating from room temperature to 350 °C at rate 10 °C/min and held at this temperature for 3 h after being cooled to room temperature in He flow. Gas volumetric chemisorption at 100 °C was performed. Desorbed CO was measured with a thermal conductivity detector. Pulsing was continued until no further carbon monoxide adsorption was observed.

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First, the crystallite size of the sol-gel derived TiO₂ was varied by changing the water:alkoxide molar ratios (3 values from 4, 40, and 165) during the synthesis. In this sol-gel process, the reaction between the alkoxide precursor and the desired amount of water occurred in an anhydrous alcohol medium. The hydrolysis and condensation reactions can be summarized as follows [14]:



As seen from the net reaction (3), the nucleation rate of TiO₂ increases with increasing the water:alkoxide ratios. As a result, the crystallite size and nanoparticle size should decrease with increasing the water:alkoxide ratios [15]. After calcination, the obtained TiO₂ supports were characterized using XRD and N₂ physisorption. All samples exhibited similar XRD patterns (not shown) at 26° (major), 37°, 48°, 55°, 56°, 62°, 69°, 71°, and 75° assigned to TiO₂ in the anatase phase. The crystallite sizes of TiO₂ were calculated based on the XRD line broadening using the Scherrer equation [16]. The crystallite sizes of TiO₂ were in the range of 11, 13 and 16 nm corresponding to the water:alkoxide ratios of 165, 40 and 4, respectively. It appeared that increased water:alkoxide molar ratio apparently resulted in decreased crystallite size of TiO₂ [14,15]. The BET surface areas of samples were found to be 71, 63 and 48 m²/g for TiO₂_11 nm, TiO₂_13 nm, and TiO₂_16 nm, respectively, which is usual for anatase TiO₂ obtained from the sol-gel method. After Ru modification of the TiO₂ supports, it showed only a slight decrease in surface area. No XRD peaks of Ru were detected due to its highly dispersed form.

After impregnation of Co onto the different TiO₂ supports as mentioned above, the catalysts were calcined and characterized using various techniques. The XRD patterns for the calcined catalyst samples without Ru modification are shown in Fig. 1. Besides the appearance of XRD patterns of the anatase TiO₂ as mentioned above, all calcined samples exhibited XRD peaks at 31° (weak), 36° (strong), 46° (weak), and 65° (weak), which were assigned to the presence of Co₃O₄. Contrarily to Co/TiO₂_16 nm, XRD patterns of Co/TiO₂_11 nm and Co/TiO₂_13 nm both present a huge background. Such a background may originate from a larger water content that would be linked to the higher water:alkoxide ratio used for these catalysts or more probably from the poor crystallinity of TiO₂. However, no

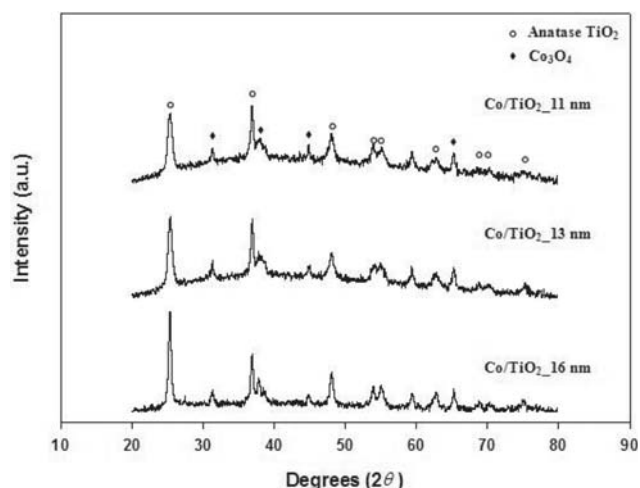


Fig. 1. XRD patterns of Co catalysts with different TiO₂ crystallite sizes and Ru modification.

other forms of Co oxide species can be detected by XRD measurement. The XRD patterns for the calcined catalyst samples with Ru modification (not shown) were similar to those without Ru modification. The surface areas of the catalysts with and without Ru modification are shown in Table 1. They slightly decreased with Ru modification. It should be noted that high surface area could result in better distribution of Co, but somehow does not guarantee good dispersion as shown in our previous work [17]. The crystallite sizes of Co₃O₄ are also shown in Table 1. It indicated that the Ru modification can result in decreased crystallite size of Co₃O₄ on TiO₂ supports. To determine the Co dispersion and active sites, CO chemisorption was performed as also listed in Table 1. Apparently, the Co dispersion increased with Ru modification on the support. This phenomenon was in agreement with our previous work [6] when Ru was co-impregnated with cobalt onto the alumina support.

The morphologies and elemental distribution of the catalyst samples were determined by using SEM and EDX, respectively. The SEM micrographs for all catalyst samples are illustrated in Fig. 2. It can be seen that the larger crystallite sizes of TiO₂ support can result in more agglomeration of catalyst particles. The EDX mapping for all samples (not shown) also revealed good distribution of cobalt on the support granules. To determine the dispersion of cobalt oxide species on the different TiO₂ supports, a more powerful technique such as TEM was applied for all samples. The TEM micro-

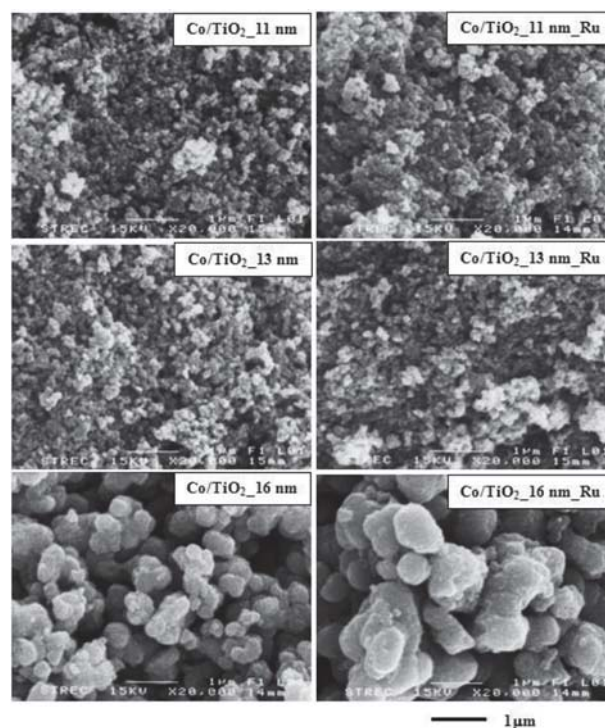


Fig. 2. SEM micrographs of Co catalysts with different TiO₂ crystallite sizes and Ru modification.

graphs of all catalysts are shown in Fig. 3. The dark spots represent cobalt oxide species dispersed on the different TiO₂ supports. Based on TEM micrographs, the catalyst present on smaller size of TiO₂ crystallite exhibits better dispersion (seen as smaller patches) than the larger one. It is suggested that the dispersion of cobalt oxide species could be altered by size of the support, as mentioned in our previous work [18]. The Ru modification on TiO₂ supports shows a similar appearance to those without Ru modification. In addition, with the presence of the highly dispersed form of cobalt oxide species as seen for the smaller size of TiO₂ crystallite, the interaction of the cobalt oxides and support should be considered. Therefore, temperature-programmed reduction (TPR) on the calcined catalyst samples was performed to gain a better understanding according to such a reduction behavior.

The TPR profiles for all catalyst samples are shown in Fig. 4. The reduction of cobalt oxides to cobalt metal (Co⁰) was observed

Table 1. Characteristic of catalyst samples

Samples	Surface area (m ² /g)	Crystallite size of Co ₃ O ₄ (nm)	CO chemisorption	
			CO chemisorption (μmole CO/g cat)	Co ⁰ dispersion (%)
Co/TiO ₂ _11 nm	52	11	23.1	3.5
Co/TiO ₂ _11 nm_Ru	47	8.7	31.1	4.6
Co/TiO ₂ _13 nm	40	14.9	21.4	3.3
Co/TiO ₂ _13 nm_Ru	36	13.9	24.3	3.6
Co/TiO ₂ _16 nm	11	19.5	6.7	1.0
Co/TiO ₂ _16 nm_Ru	10	15.8	11.7	1.8

Calculated based on XRD line broadening using Scherrer Equation

Calculated based on fraction of Co⁰ detected from CO chemisorption per Co⁰ loading × 100

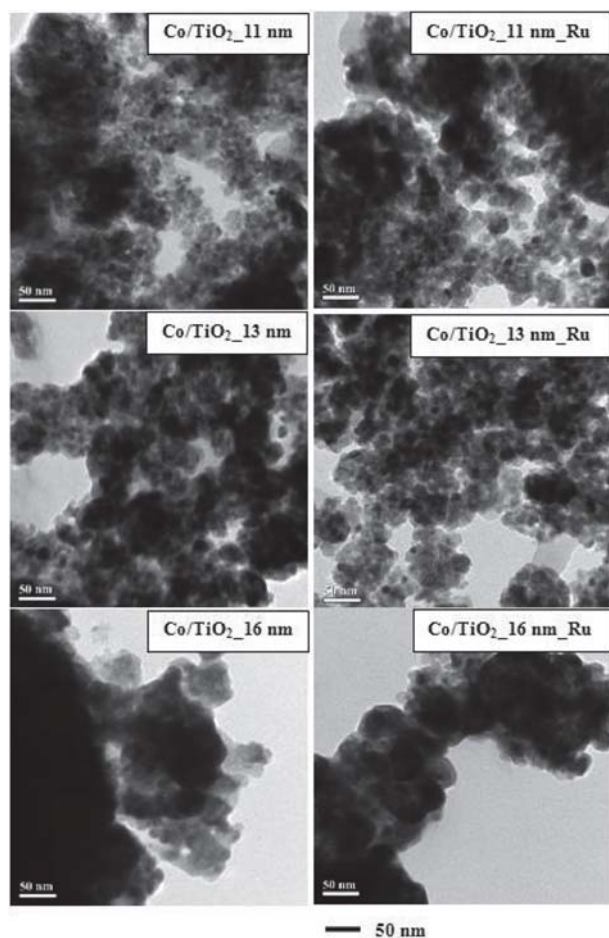


Fig. 3. TEM micrographs of Co catalysts with different crystallite sizes of TiO₂ supports and Ru modification.

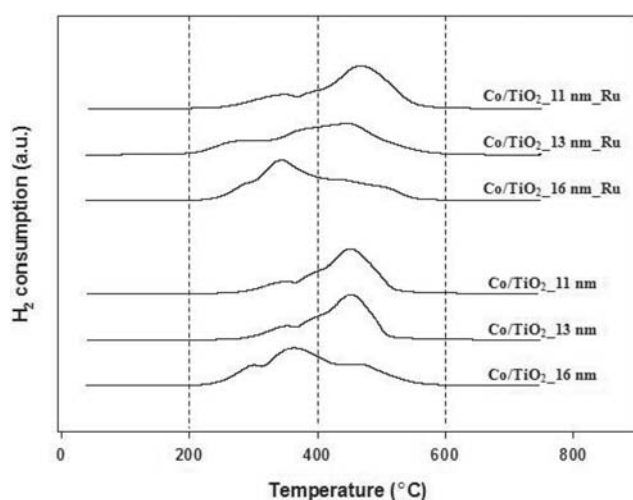


Fig. 4. TPR profiles of Co catalysts with different crystallite sizes of TiO₂ supports and Ru modification.

for all catalyst samples that occurred in a shoulder and one major peak. The lower reduction temperature shoulder peak of the unmodified catalysts was located at the 300 °C (for Co/TiO₂_16 nm) and 350 °C (for Co/TiO₂_11 and _13 nm). The broad peak was related to a two-step reduction of Co₃O₄ to CoO, and then to Co metal [5,

13,18]. The Co/TiO₂_16 nm sample exhibits broader TPR peaks compared to the others. This may be due to the presence of more various Co O species. With Ru modification, there is also one shoulder and one major peak for the catalysts with Ru modification located at 260 and between 350 and 460 °C. It appears that the broad peak is shifted to lower temperature with Ru modification. However, this phenomenon is not clearly seen for the Co/TiO₂_11 nm sample, suggesting that the Ru modification has less pronounced effect on the smaller crystallites. This indicates that Ru modification facilitates the reduction of Co catalysts. In some particular cases, the peak of the decomposition of the cobalt nitrates, as a cobalt precursor can be observed between 200 and 300 °C, especially on silica and alumina supports [6]. Prolonged calcination or reduction and recalcination resulted in complete decomposition of any cobalt nitrates present [6]. In addition, it has been often found that, due to interactions between Co₃O₄ and support materials, such as silica or alumina, the highest temperature peak represented the incomplete reduction of Co O-support. The TPR of supported Co₃O₄ can also manifest a separation of the two reduction steps [6,18-20]. A lower temperature shoulder between 200 and 350 °C peaks was observed due to some possible decomposition of residual Co nitrate. The reduction of Co₃O₄ to CoO and Co⁰ occurred between 300 and 550 °C and can be assigned to the reduction of metal oxides on the support [6, 18-20]. The strong interaction between Co metal and support depends on the size of cobalt oxide species and nature of supports [6]. This suggested that the Ru may possibly help in the reduction of Co oxides and the support to make small crystallite size, which would decrease the Co⁰ crystallite size. These results were in accordance with those reported by Hosseini et al. [21]. It was suggested that the use of Ru modified-TiO₂_11 nm and 13 nm supports can result in higher reduction temperature of Co oxides with larger amount of reducible cobalt oxide species.

XPS analysis was used to examine the binding energy and surface concentrations of species on the catalysts. The catalyst samples were analyzed in the Co 2p, Ti 2p, O 1s, Ru 3d with regards to the binding energy regions (not shown). The peaks of Ru 3d would be detected around 280 eV [22,23], but there was no observation of the Ru 3d due to very small amount of Ru loading. The binding energy values corresponding to Co 2p and Ti 2p were not affected by the small amount of Ru modification with the values of ca. 780 eV and 459.1 eV, respectively. These results are in accordance with those reported by Infantes-Molina et al. [22] and Reinikainen et al. [23].

Reaction Study

The reaction study was carried out via CO hydrogenation under methanation condition in order to minimize the catalyst deactivation due to carbon deposition. The conversion, reaction rate and product selectivity for all samples are shown in Table 2. The CO conversion ranged between 32 and 91% upon different crystallite sizes of TiO₂ supports. Based on the reaction rates, it is obvious that the activities of catalysts decreased with increasing the size of TiO₂ crystallite from 11 to 16 nm due to the decrease of Co dispersion. In addition, Ru modification apparently resulted in increased activity for all different crystallite sizes of TiO₂ supports. However, the Ru modification had more pronounced effect on the larger crystallite size support where the conversion increased about two times. This can be attributed to the promotion of cobalt dispersion by Ru because it can facilitate the reduction of cobalt oxide species [6]. It

Table 1. Effect of Ru modification

Samples	Conversion (%)	SS rate ($\times 10^2$ gCH ₂ /g cat·h)	Product selectivity (%)	
			C ₁	C ₂ -C ₄
Co/TiO ₂ _11 nm	77	28.9	97	3
Co/TiO ₂ _11 nm_Ru	91	34.1	97	3
Co/TiO ₂ _13 nm	49	18.4	94	6
Co/TiO ₂ _13 nm_Ru	89	33.4	99	1
Co/TiO ₂ _16 nm	32	12.0	94	6
Co/TiO ₂ _16 nm_Ru	77	28.9	99	1

is worth noting that Ru can be added into the Co catalyst as a promoter by coimpregnation with the cobalt precursor, such as cobalt nitrate. As a promoter for Co/Al₂O₃ catalysts [6], Ru increased both overall activity and reducibility. It was suggested that the Ru promoter not only facilitates the reduction of cobalt oxide at lower temperature, but also decreases the formation of Co strongly interacting with the alumina (Co-O-Al₂O₃) and nonreducible Co aluminate by minimizing the impact of water vapor on this formation. However, for Ru promotion in Co/TiO₂ catalysts [24], it revealed that Ru promotion can only facilitate the reduction of cobalt oxide species, but has no effect on water vapor produced during reaction. Based on this study, it can be observed that the effects of Ru modification of TiO₂ supports are similar with those of Ru promotion as mentioned earlier. It is worth noting that with Ru modification, the effect of size of TiO₂ crystallite on Co/TiO₂ catalysts is less pronounced.

Considering the product selectivity, in all cases methane was present as a majority product, which is typical for CO hydrogenation under methanation. Without Ru modification, the catalysts having larger crystallite size of TiO₂ tended to give greater amounts of longer chain hydrocarbons (C₂-C₄). However, the C₁-C₄ decreased with the Ru promotion. It is known that CO hydrogenation is a kind of polymerization reaction where insertion of the -CH₂- (methylene group) occurs through the active centers [25], rate of propagation, and rate of termination. Obviously, a termination of chain growth occurs and is recognized as the chain growth probability. Based on product selectivity as found here, it can be concluded that the Ru modification in TiO₂ supports slightly inhibited the chain growth probability. As a matter of fact, it resulted in the observation of higher methane selectivity with Ru modification.

CONCLUSIONS

Based on this study, the effect of different crystallite sizes of TiO₂ supports on the catalytic properties of Co/TiO₂ catalysts can be elucidated. The smaller crystallite size of TiO₂ support exhibited higher catalytic activity due to higher Co dispersion. The crystallite sizes of cobalt oxide species were replicated by those of the TiO₂ support. It also revealed that the Ru modification on the support apparently increased the activity of catalysts as seen when Ru was used as a promoter by coimpregnation with the cobalt precursor. However, with the Ru modification, the effect of size of TiO₂ crystallite on Co/TiO₂ catalyst was less pronounced. The Ru promotion can result in slightly decreased C₂-C₄ hydrocarbons during methanation.

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Integrated methane decomposition and solid oxide fuel cell for efficient electrical power generation and carbon capture

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ABSTRACT

This work proposes the application of methane decomposition (MD) as a fuel processor to replace methane steam reforming (MSR) for hydrogen production for a methane-fuelled solid oxide fuel cell (SOFC) system. In this work, comparison between the MD-SOFC and the MSR-SOFC was performed in terms of SOFC performances and economic analysis to demonstrate a benefit of using MD as a fuel processor. Energy analysis of SOFC system was evaluated based on thermally self-sufficient condition where no external energy is required for the system. Although the MD-SOFC system offers lower electrical efficiency than that of the MSR-SOFC as solid carbon is generated without being further combusted to generate energy; however, the MD-SOFC stack can be operated at higher power density due to high purity of hydrogen supplied to the fuel cell, resulting in smaller size of the system when compared to the MSR-SOFC. Moreover, the MD-SOFC system is less complicated than that of the MSR-SOFC as the CCS facility is not necessary to be included to reduce CO₂ emission. Economic analysis demonstrated that the SOFC system with MD is more competitive than the conventional system with MSR when considering the valuable by-products of solid carbon even with the low-valued carbon black. It is suggested that the success of this proposed SOFC system with MD relies on the technology development on cogeneration of hydrogen and valuable carbon products.

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Keywords: Solid oxide fuel cell; Hydrogen production; Methane decomposition; Energy self-sufficient operation

1. Introduction

Over the past decades, the continuous growth of world economy has caused a number of problems such as shortage of energy resources, environmental problems and climate changes. Based on traditional technologies, combustion of fossil fuels has emitted a large amount of greenhouse gases to environment (Simbeck, 2004; Suelves et al., 2005; Naser and Timothy, 2007; Edwards et al., 2008; Ahmed et al., 2009). Therefore, many researchers have focused on the development of alternative energy with high-efficiency as well as environmental friendly power generation technologies (Karl and Gunter, 1995; Dicks, 1996; Coutelieris et al., 2003; Edwards et al., 2008).

Solid oxide fuel cell (SOFC) is one of promising technologies that directly transforms chemical energy of a fuel into electrical energy with high efficiency and reduced environmental burden (Karl and Gunter, 1995; Poirer and Sapundzhiev, 1997; Martin and Ralph, 2003; Ahmad Hajimolana et al., 2012; Laguna-Bercero, 2012). A variety of fuels (e.g., alcohol, natural gas, coal and petroleum based substance) can be used in SOFC systems due to their high operating temperature range (873–1273 K) (Stambouli and Traversa, 2002; Assabumrungrat et al., 2005; Hernandez-Pacheco et al., 2005; Hussain et al., 2006; Naser and Timothy, 2007; Douvartzides et al., 2003; Sangtongkitcharoen et al., 2008; Piroonlerkgul et al., 2008, 2009a,b,c; Arpornwichanop et al., 2010; Patcharavorachot et al.,

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Nomenclature

$A_{\text{single cell}}$	active area of SOFC single cell (m^2)
A_{total}	total active area of SOFC (m^2)
C_{cell}	capital cost of SOFC single cell (\$)
$C_{\text{compressor}}$	capital cost of compressor (\$)
C_{stack}	capital cost of SOFC stack (\$)
$D_{m(\text{eff})}$	effective diffusion coefficient of electrode m ($\text{cm}^2 \text{s}^{-1}$)
E	theoretical open-circuit voltage of the cell (V)
E^0	theoretical open-circuit voltage of the cell at standard pressure (V)
E_{act}	activation energy (kJ mol^{-1})
F	Faraday constant (9.6495×10^4) (C mol^{-1})
G	Gibb's free energy (kJ mol^{-1})
ΔH°	heat of reaction (kJ mol^{-1})
HP	power consumption in compressor (HP)
i	current density (A cm^{-2})
$i_{o,m}$	exchange current density of electrode m (A cm^{-2})
K_j	equilibrium constant of reactions j (various units)
l_m	thickness of electrode m (μm)
L	thickness of electrolyte (μm)
n_i	mole of component i (mol)
N_{cell}	number of SOFC single cell
N_{stack}	number of SOFC stack
P	pressure (Pa)
p_i	partial pressure of component i (Pa)
p_i^I	inlet pressure of component i (Pa)
Q_{net}	difference between heat demand and heat generation in SOFC system (kW)
Q_{stack}	thermal energy supplied from fuel cell stack (kW)
R	gas constant ($8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$)
T	temperature (K)
U_f	fuel utilization
V	cell voltage (V)
$W_{\text{sep,min}}$	minimum electricity work consumed in CO_2 (kW)
z	number of electron participating in the electrochemical reaction

Greek letters

α	charge transfer coefficient (dimensionless)
ξ	electrode tortuosity (dimensionless)
δ_{O_2}	coefficient used in concentration overpotential (dimensionless)
η_{loss}	total loss (V)
η_{act}	activation loss (V)
η_{conc}	concentration loss (V)
η_{ohm}	ohmic loss (V)
γ	pre-exponential factor for electrode exchange

Subscripts

a	anode
c	cathode
ref	reference condition
MD	methane decomposition
MSR	methane steam reforming
WGS	water-gas shift reaction
RWGS	reverse water-gas shift reaction

CCS	carbon capture storage
SOFC	solid oxide fuel cell
TER	thermal to electrical ratio

2010). Typically, an SOFC system consists of 2 main parts; (1) a fuel processor for hydrogen generation and (2) a SOFC unit, which generates electricity from hydrogen and recovers useful heat from spent fuel for utilization in the system.

Methane is considered as a suitable and convenient fuel for the SOFC system due to its availability, highest hydrogen to carbon ratio in hydrocarbon substances and low cost (Ermakova et al., 2000; Vivanpatarakij et al., 2007; Serrano et al., 2010). There are several reaction routes for generating hydrogen from methane such as methane steam reforming (MSR), partial oxidation, dry reforming, autothermal reforming, and methane decomposition (MD) (Edwards and Maitra, 1995; Laosiripojana et al., 2005; Suelves et al., 2005; Bonura et al., 2006; Vivanpatarakij et al., 2007; Li et al., 2008; Wang et al., 2009). Nowadays, the MSR (Eq. (1)) is probably the most well-established technology and widely used as the fuel processor in the conventional SOFC system. Although, it offers the highest hydrogen production but the MSR demands the highest energy and has impurities such as carbon oxide or steam, in the reformed gas.



A number of researches have been focused on improving efficiency and performances of the methane-fuelled SOFC systems. Due to the impurities in the reformed gas from the conventional SOFC system, membrane reactor technology (a combination of membrane and steam reforming reactor) (Damen et al., 2006a,b; Powell and Qiao, 2006) is the promising pre-carbon capture technology in power generation. Palladium type has been widely applied as a selective hydrogen, installing in the fuel processor, to purify hydrogen and to increase methane conversion (Basile et al., 2003; Gallucci et al., 2004; Fernandes and Soares, 2006; Patel and Sunol, 2007). Vivanpatarakij et al. (2009) presented an upgraded SOFC system with the application of various operation modes in membrane reactor such as the combination of compressor and vacuum pump. However, this system is difficult to apply in real system due to high cost of membrane material. Another technique that is developed to purify hydrogen before feeding to the SOFC is the use of $\text{CaO}-\text{CO}_2$ acceptor after the fuel processor; however, this technique has a disadvantage of which CO_2 is produced afterburner (Iordanidis et al., 2006; Vivanpatarakij et al., 2009; Piroonlerkgul et al., 2010). Consequently, the conventional SOFC system needs to be equipped with a carbon capture and storage (CCS) after the afterburner. The CCS, as shown in Fig. 1, is composed of three main steps; CO_2 separation, CO_2 compression to the liquid form for transport purpose, and CO_2 sequestration (or storage) (Abu-khader, 2006; Damen et al., 2006a,b; House et al., 2009). However, this system is still under developed and is not applied extensively in large scale production due to high capital cost with complex system and high energy demand (Meyer, 2009; Piroonlerkgul et al., 2008, 2009a,b,c; Farhad et al., 2010).

MD (Eq. (2)) is therefore an interesting alternative reaction for hydrogen production as it requires lower energy consumption than the conventional MSR. Moreover, the gas product

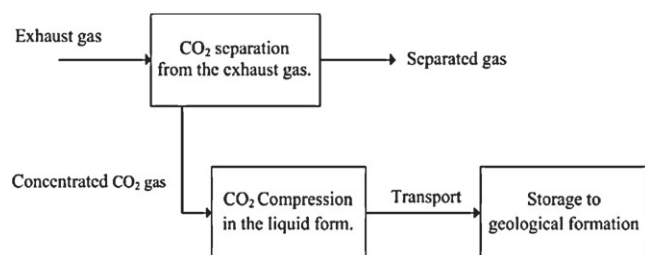


Fig. 1 – Carbon capture and storage facility (CCS).

contains CO_x -free due to the absence of oxidant substances (i.e., steam or oxygen).



It should be noted that although the hydrogen generated from MD is less than that from MSR, the pure hydrogen generated by MD offers potential benefits on improved performance of the SOFC when compared with that achieved in the conventional MSR-SOFC (Baron et al., 2004; Damen et al., 2006a,b; Suwanwarangkul et al., 2006; Piroonlerkgul et al., 2009a,b,c; Yusuke et al., 2009). With the consideration of their by-products, MD produces a separated phase by-product, solid carbon, in different valuable forms. So that no carbon oxides is supplied to SOFC, resulting in a long operation life time of the SOFC stack (Takenaka et al., 2001; Coutelieres et al., 2003; Villacampa et al., 2003; Sangtongkitcharoen et al., 2005). Furthermore, such solid carbon can be used as a commodity product in various fields e.g., sorbent material, membrane, catalyst, electrical devices, and fuel cell or sequestered (or stored) for future use (Muradov, 2001; Meyer, 2009; Muradov et al., 2010). As a consequence, the CCS facility required in the MSR-SOFC is not necessary when MD is applied, resulting in lower cost and energy consumption (Bonura et al., 2006; Abbas and Wan Daud, 2009; Ahmed et al., 2009; Yusuke et al., 2009).

This study is aimed to evaluate and compare performances between the two fuel processors, MD and MSR with and without CCS facility. Our SOFC system operations are performed under an energy self-sufficient condition ($Q_{\text{net}} = 0$), where no external heat is required to supply to the reactor (Sangtongkitcharoen et al., 2005; Palazzi et al., 2007; Piroonlerkgul et al., 2008, 2009a,b,c; Vivanpatarakij et al., 2009). Furthermore, the economic analysis is carried out to determine the appropriate fuel processor for the SOFC at the optimal operating condition (operating voltage and fuel utilization) for the same net electrical power of 1 MW.

2. Process description of SOFC systems

Figs. 2 and 3 show schematic diagrams of the SOFC systems with MSR with/without CCS, and the SOFC system with MD, respectively. The major components in the system include feed pre-heaters, a fuel processor, an SOFC stack, and an afterburner. For the conventional SOFC system with MSR (Fig. 2), steam is generated in a pre-heater and mixed with the heated methane. Then the gas mixture is fed into the fuel processor where the steam methane reforming and water-gas shift reaction take place to generate H_2 -rich gas. After that the reformed gas and air are introduced into the SOFC stack. The exhaust gases are then combusted in the afterburner to generate heat for utilizing in the system. In case of the MSR-SOFC system with the addition of CCS, the CCS is placed after the

afterburner for CO_2 capture. For our proposed SOFC system with MD (Fig. 3), the operation is less complicated as there is no steam input to the reactor and no additional CCS. It should be noted that because solid carbon is also generated as a by-product of the MD, there is a concern of carried-over carbon in hydrogen gas because it could damage the SOFCs.

3. SOFC system modeling

3.1. Fuel processor

For the MSR process, hydrogen production from methane can be obtained via methane steam reforming reaction (Eq. (1)) and water-gas shift reaction (WGS) (Eq. (3)). These reactions usually take place in series, resulting in an overall reaction as shown in Eq. (4).



Several works have reported a suitable amount of steam to provide long activity and reduce carbon formation, basis industrial methane steam reforming reaction is usually run under a steam to carbon molar ratio of 1.4 or higher (Dicks, 1996). With the equilibrium consideration of the side reaction (WGS), the steam to carbon molar ratio is suggested to be 2 or higher (Renner and Marschner, 1985; Palsson et al., 2000; Sangtongkitcharoen et al., 2005; Vivanpatarakij et al., 2009; Arpornwichean et al., 2010). However, it is noted that using high excess of water in the system has some disadvantages; (1) excess steam dilutes the hydrogen concentration in the reformed gas, (2) higher thermal energy is required in the SOFC system, and (3) power density and performance of the SOFC can be lower as reported by Piroonlerkgul et al. (2009a,b,c) and Dokmaingam et al. (2010). In this work, we selected the steam to carbon ratio of 2.5 as the carbon activity at this value tends to approach zero (Renner and Marschner, 1985; Palsson et al., 2000; Sangtongkitcharoen et al., 2005; Zhang et al., 2005). For the MD system, methane is directly decomposed to pure hydrogen and carbon follows Eq. (2) without any side reactions.

To simplify the calculations for the fuel processors, thermodynamic chemical equilibrium is assumed to identify the product compositions under the isothermal operation. The equilibrium constant of the related reactions (K_j) is shown in Eqs. (5)–(7):

Conventional MSR;

$$K_{\text{MSR}} = \frac{p_{\text{H}_2}^3 p_{\text{CO}}}{p_{\text{CH}_4} p_{\text{H}_2\text{O}}} \quad (5)$$

$$K_{\text{WGS}} = \frac{p_{\text{H}_2} p_{\text{CO}_2}}{p_{\text{H}_2\text{O}} p_{\text{CO}}} \quad (6)$$

MD;

$$K_{\text{MD}} = \frac{p_{\text{H}_2}^2}{p_{\text{CH}_4}} \quad (7)$$

3.2. SOFC stack model

The modeling of SOFC stack in this work is based on our previous work (Piroonlerkgul et al., 2009a,b,c). The SOFC

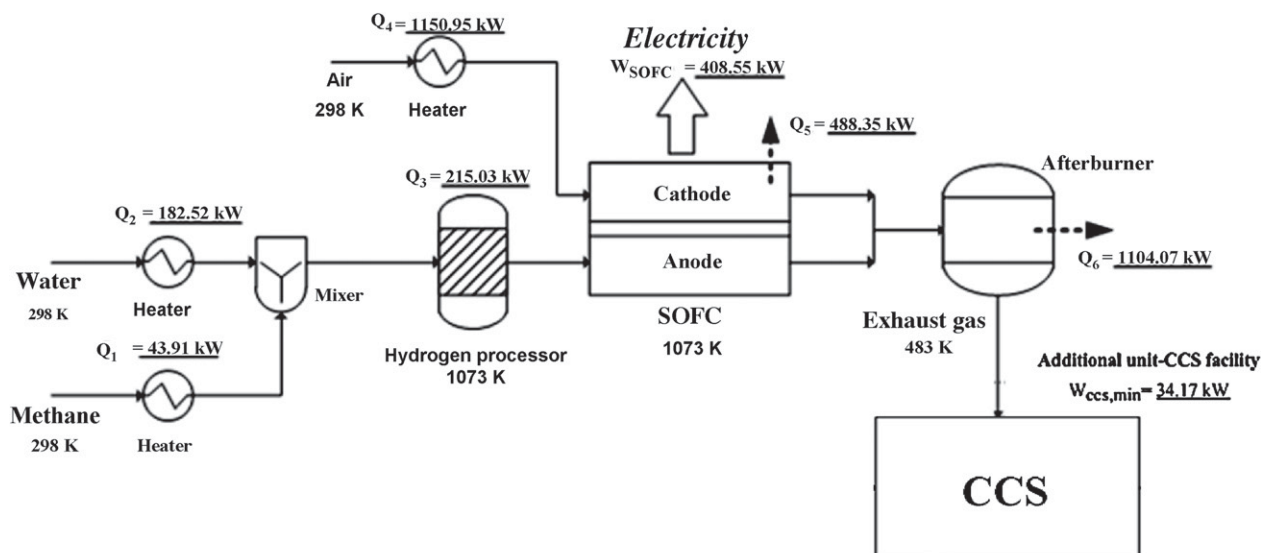


Fig. 2 – The conventional SOFC system configurations with MSR as hydrogen processor with/without CCS facility.

anode, electrolyte, and cathode are made of Ni-YSZ, YSZ, and LSM-YSZ, respectively. It is assumed that only H₂ contributes to the electrochemical reaction and the anode gas in the stack is at its chemical equilibrium compositions due to high operating temperature of SOFC and fast reaction rates. It was reported that the electro-oxidation of H₂ is much faster than that of CO (Khaleel et al., 2004), and the reaction rate of WGS is fast at high temperatures (Blom et al., 1994; Swaan et al., 1994; Bradford and Vannice, 1996).

Open circuit voltage or theoretical voltage (E) can be calculated from the Nernst equation, where the value depends upon the reversible potential (E^0), temperature, and gas compositions. Such open circuit voltage can be obtained by:

$$E = E^0 + \frac{RT}{2F} \ln \left(\frac{p_{H_2} p_{O_2}^{1/2}}{p_{H_2O}} \right) \quad (8)$$

Actual cell potential (V) as expressed in Eq. (9) is always less than the open-circuit voltage (E) due to overpotentials. Three major overpotentials are involved in the system, ohmic

overpotential (η_{ohm}), activation overpotential (η_{act}), and concentration overpotential (η_{conc}).

$$V = E - \sum \eta_{loss} = E - \eta_{act} - \eta_{ohm} - \eta_{conc} \quad (9)$$

The ohmic overpotential (η_{ohm}) involves the resistance to flow of electrons through the electrodes and the interconnectors and to flow of ions through the electrolyte. Due to the high electronic conductivity of the electrodes and the interconnectors compared to the ionic conductivity of the electrolyte, only the ohmic overpotential of the electrolyte (Eq. (10)) is considered (Ferguson et al., 1996).

$$\eta_{ohm} = 2.99 \times 10^{-11} i L \exp \left(\frac{10,300}{T} \right) \quad (10)$$

The activation overpotential (η_{act}) is controlled by the kinetics of electrochemical reaction at the electrode surface. High temperature operation in SOFC promotes fast reaction rate, leading to a reduction of this loss. In this work, the Butler-Volmer equation is performed to compute the activation.

$$i = i_0 \left[\exp \left(\frac{\alpha z F \eta_{act}}{RT} \right) - \exp \left(\frac{(\alpha - 1) z F \eta_{act}}{RT} \right) \right] \quad (11)$$

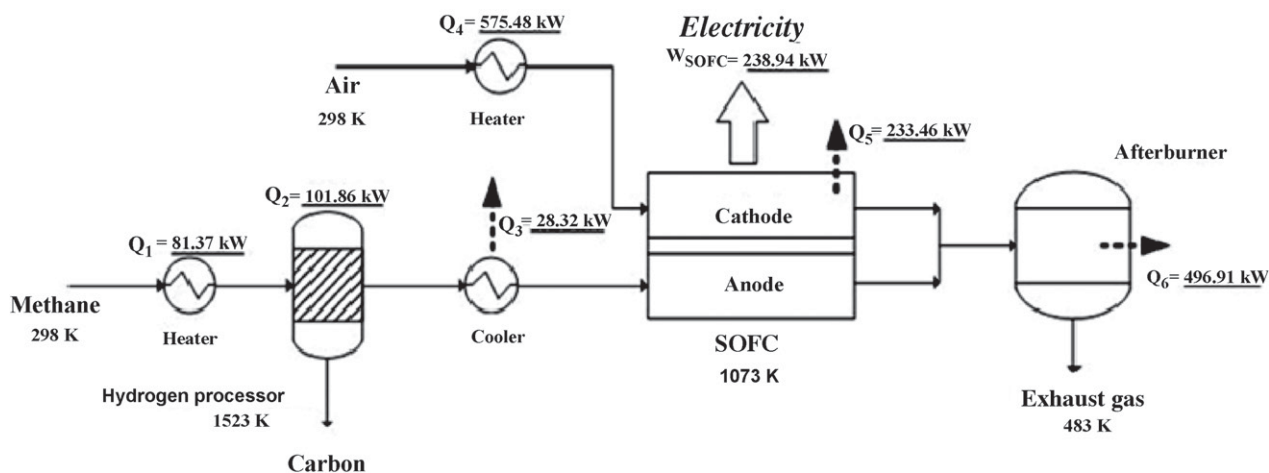


Fig. 3 – The proposed SOFC system configuration with MD as hydrogen processor.

Table 1 – Summary of model parameters.

Parameters	Values
Hydrogen processor	
P	1 atm
T _{MD}	1523 K
T _{MSR}	1073 K
SOFC stack (Piroonlerkgul et al., 2009a,b,c)	
n	0.48
ξ	5.4
γ _a	1.344 × 10 ¹⁰ A m ⁻²
γ _c	2.051 × 10 ⁹ A m ⁻²
E _{act,a}	1 × 10 ⁵ J mol ⁻¹
E _{act,c}	1.2 × 10 ⁵ J mol ⁻¹
l _a	750 μm
l _c	50 μm
L	50 μm
P	1 atm
T _{SOFC}	1073 K

In case of SOFC, α and z are set to be 0.5 and 2 according to Chan et al. (2001). Consequently, the activation potential at each electrode is simplified as:

$$\eta_{act,j} = \frac{RT}{F} \sinh^{-1} \left(\frac{i}{2i_{0,j}} \right), \quad j = a, c \quad (12)$$

The exchange current density (i_0) in each electrode is related to partial pressure and operating temperature. The expression for the anode and cathode electrodes can be computed from the following equations (Fleig, 2003):

$$i_{0,a} = \gamma_a \left(\frac{p_{H_2}}{P_{ref}} \right) \left(\frac{p_{H_2O}}{P_{ref}} \right) \exp \left(-\frac{E_{act,a}}{RT} \right) \quad (13)$$

$$i_{0,c} = \gamma_c \left(\frac{p_{O_2}}{P_{ref}} \right)^{0.25} \exp \left(-\frac{E_{act,c}}{RT} \right) \quad (14)$$

The concentration overpotential (η_{conc}) is a loss occurring from a slow mass transfer. While the electrochemical reaction takes place over the stack, the reactant gases diffuse to the pore of catalyst, resulting in the difference in concentration of gas between the bulk and the reaction site. Therefore, this loss can be computed by the relation between gas diffusion coefficients and operating temperature as shown in Eqs. (15) and (16) (Chan et al., 2001):

$$\eta_{conc,a} = \frac{RT}{2F} \ln \left[\frac{(1 + (RT/2F)(l_a/D_{a(eff)}p_{H_2O}^I)i)}{(1 - (RT/2F)(l_a/D_{a(eff)}p_{H_2}^I)i)} \right] \quad (15)$$

$$\eta_{conc,c} = \frac{RT}{4F} \ln \left[\frac{p_{O_2}^I}{(P_c - \delta_{O_2}) - ((P_c - \delta_{O_2}) - p_{O_2}^I) \exp \left[(RT/4F)(\delta_{O_2}l_c/D_{c(eff)}P_c)i \right]} \right] \quad (16)$$

The parameters of the SOFC stack performance are summarized in Table 1.

3.3. Heat exchanger

Heat requirement for each unit can be determined using conventional energy balance by calculating changes in enthalpy of the inlet and outlet streams. It is assumed that the heat exchangers in the SOFC system are operated under adiabatic condition (no heat loss).

3.4. Afterburner

The anode and cathode exhaust gases are fed to the afterburner unit, where the residual fuels are completely combusted, to generate heat for supplying to all energy-demanding units in the SOFC system. It is assumed that the heat can be extracted from the combusted gas without heat loss and the final exhaust gas emits to the environment at 483 K which is enough to supply heat for steam generation and air preheating.

3.5. CCS facility

For the SOFC system with MSR, an additional CCS facility is installed after the afterburner in order to prevent CO₂ emission to the environment (Simbeck, 2004; Abu-khader, 2006; Damen et al., 2006a,b). The operation of CCS employs the power generation of the SOFC to utilize in its steps. The energy requirement is calculated as follows:

- CO₂ separation from the exhaust gas
The work required for CO₂ separation from the exhaust gas equals the change in Gibbs free energy before and after separation.

$$W_{sep,min} = -dG = \Delta G_{sep} = \sum_i \left(\frac{\partial G_i}{\partial n_i} \right) \quad (17)$$

The calculations follow the procedure suggested by House et al. (2009). The ideal gas was assumed as the separation takes place near atmospheric and N₂ and CO₂ do not chemically interact. It is further assumed that the separation process takes place under isothermal and isobaric, and therefore, the calculated values represent the minimum required work.

- CO₂ compression and transportation
After CO₂ is separated out of the exhaust gas, it is compressed to liquid phase and transported to a geological reservoir (Abu-khader, 2006). Minimum work required in this stage is obtained by the reversible isothermal compression condition; a typical value is about 13 kJ mol⁻¹ CO₂ (House et al., 2009).
- CO₂ storage into the geological reservoir
Liquid CO₂ is compressed to emplace at depth, displacing denser ground water upward. Pressure of this step is around the hydrostatic pressure of ground water at the well head. This step is assumed to overcome the physical barriers which are gravity and surface tension. Minimum work is about the power from the change of pressure and concerned

on the injection lifetime due to an increasing of reservoir pressure (Damen et al., 2006a,b). A typical value of the minimum work over the life time of injection is approximately 2 kJ mol⁻¹ CO₂ (House et al., 2009).

3.6. Operation at thermally self-sufficient condition

The SOFC systems in this study are focused on an operation at the thermally self-sufficient condition. At this condition, the value of Q_{net} is equal to zero, indicating that the total generated thermal energy from the SOFC system is performed

to supply the overall heat-demanding units without external heat input. From the system configuration in Figs. 2 and 3, there are main units which play an important role in releasing thermal energy namely; SOFCs (Q_5) and afterburner (Q_6). But the MD requires a further cooler due to its high temperature in hydrogen processor. Therefore, this proposed system with MD consists of three generated thermal energy units, Q_3 , Q_5 , and Q_6 . In term of thermal energy demand, this value consists of the energy consumption in heaters and fuel processors. The Q_{net} in the thermally self-sufficient operation is calculated by:

SOFC system with MSR;

$$Q_{\text{net}} = (Q_1 + Q_2 + Q_3 + Q_4) - (Q_5 + Q_6) \quad (18)$$

SOFC system with MD;

$$Q_{\text{net}} = (Q_1 + Q_2 + Q_4) - (Q_3 + Q_5 + Q_6) \quad (19)$$

Note that the calculations of Q_i are based on enthalpy changes of the input and output streams of the units.

The thermally self-sufficient condition can be achieved by tuning of fuel utilization (U_f) at various operating voltages. The fuel utilization (Zhang et al., 2005) and electrical efficiency (Piroonlerkgul et al., 2009a,b,c) in the SOFC system are estimated from Eqs. (20) and (21), and overall electrical efficiency is calculated by Eq. (22):

Fuel utilization (%)

$$= \frac{H_{2,\text{equivalent}} \text{ consumption in SOFC stack}}{H_{2,\text{equivalent}} \text{ fed to the SOFC system}} \times 100 \quad (20)$$

Stack cell electrical efficiency (%)

$$= \frac{\text{Net electrical power generated}}{(\text{LHV of fuel} \times \text{fuel feed rate})_{\text{at anode side}}} \times 100 \quad (21)$$

Overall electrical efficiency (%)

$$= \frac{\text{Net electrical power generated}}{\text{LHV of methane} \times \text{methane feed rate}} \times 100 \quad (22)$$

4. Results and discussion

4.1. Thermodynamics of reactions in fuel processors

Thermodynamic chemical equilibrium between two main reactions of methane steam reforming (MSR) and methane decomposition (MD) is firstly investigated in term of product distribution basis on 1 mol of pure methane feed. The steam to carbon molar ratio input of MSR is fixed to higher basis requirement at the value of 2.5 as mentioned earlier. The system is operated under the atmospheric pressure to minimize cost of operation and to obtain higher yield follow the Le Chaterlier's principle at different temperatures, ranging from 273 K to 2000 K.

Product distribution depicted in Fig. 4 shows the endothermic nature of both MD and MSR reactions as the amount of CH_4 was increasingly consumed to produce hydrogen fuel when the operating temperature is raised. It is noted that H_2 can be generated higher in the MSR process due to the

presence of water reagent and higher stoichiometric coefficient in the reactions (Eqs. (2) and (4)) (Dokmaingam et al., 2010; Halabi et al., 2010). At temperature higher than 1100 K, the endothermic reverse water gas shift reaction (RWGS) (reverse of Eq. (3)), in turn, plays an important role in the MSR process, resulting in the declination of H_2 production. Although, the MSR provides higher methane conversion and hydrogen yield but other unwanted-by-products are also produced from this process especially CO_x , which significantly reduces the purity of hydrogen fuel and affects the performance and stability of SOFC stack.

The MD, on the other hand, produces H_2 without any side reactions and hence large amount of purified H_2 can be obtained at high temperature (Poirer and Sapundzhiev, 1997; Muradov, 2001; Liu et al., 2010). The results reveal that almost 100% of hydrogen and carbon production from the MD process can be achieved at temperature over 1373 K. It is noted that the presence of small amount of CH_4 in gas stream from the fuel processor, resulting from unconverted feed, does not affect the electrochemical reaction in the SOFC, in turn, it provides the internal reforming with H_2O to produce H_2 again in SOFC stack (Piroonlerkgul et al., 2008). The reduction of H_2O in the anode chamber promotes the diffusion of H_2 to generate the electrical power as reported by Patcharavorachot et al. (2010). Further, small amount of H_2O at anode side can enhance forward electrochemical reaction so that stack cell efficiency of the MD-SOFC becomes higher than that of the MSR-SOFC as will be discussed later.

Although, the MSR process shows a better performance in producing much larger amount of H_2 over the MD process but to apply the fuel processor with SOFC, the performance of the entire process, MSR-SOFC and MD-SOFC, is needed to be considered. In this study, the performance of the fuel processor with SOFC is determined in terms of maximum power density, electrical efficiency, and the effect of hydrogen purity (which is considered as the overpotential). Finally, economic analysis is taken into account in order to determine a suitable fuel processor for operating with SOFC.

4.2. Comparison of methane-fuelled SOFC systems performance with different fuel processors

For both MD-SOFC and MSR-SOFC, the systems are operated under the thermally self-sufficient condition ($Q_{\text{net}} = 0$) at fuel cell temperature of 1073 K, which is previously reported as a suitable SOFC operating temperature (Vivanpatarakij et al., 2007; Piroonlerkgul et al., 2009a,b,c). To find the optimal condition at thermally self-sufficient condition, the total heat consumption is calculated via a trial-and-error method by tuning the fuel utilization (U_f) at a fixed operating voltage of SOFC stack to where the total heat consumption is equal to the total heat generation from the system. It is noted that the fuel utilization (U_f) can be defined as the equivalent of hydrogen consumption in the SOFC stack divided by overall the equivalent of hydrogen fed to the SOFC. As shown in Fig. 5 (MSR-SOFC) and Fig. 6 (MD-SOFC), Q_{net} can be either positive or negative value. A positive value of Q_{net} means external heat source is required to supply for the thermal energy consumption unit and the negative value indicates that there is some heat release from the overall process. The Q_{net} can be zero when the optimal fuel utilization is elected at varying operating voltage. In addition, the value of produced thermal to electrical ratio (TER), which is defined as the portion of fuel needed to utilize as a thermal energy to obtain an equal

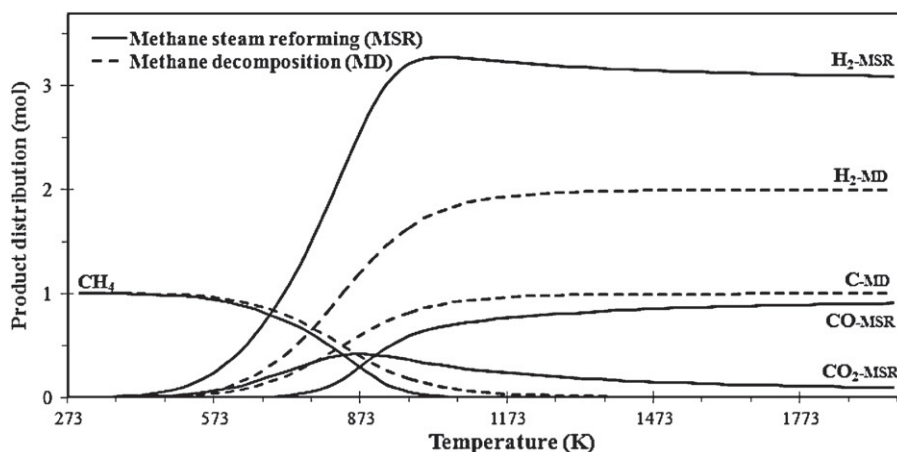


Fig. 4 – Product distribution of methane decomposition (dash line) and of conventional methane steam reforming ($\text{H}_2\text{O}:\text{CH}_4 = 2.5$) (solid line) at atmospheric pressure and varying temperature (basis on 1 mol of pure methane for both processes).

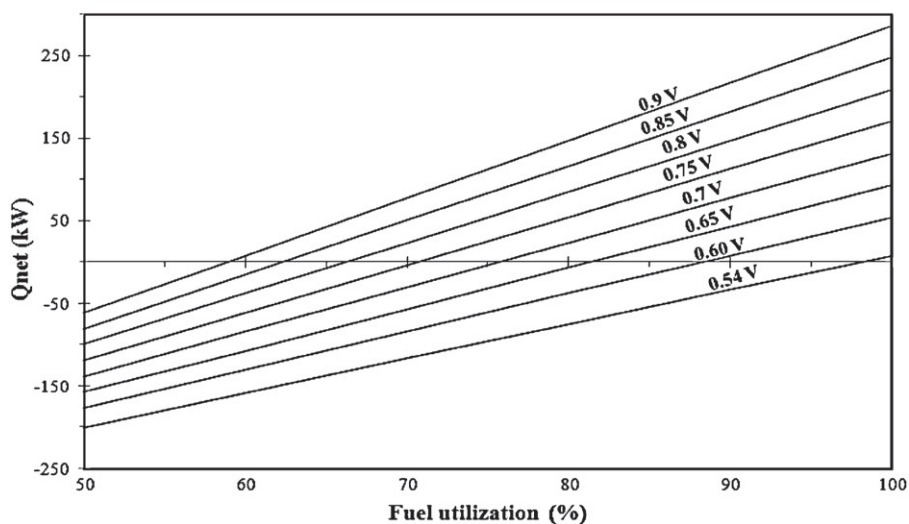


Fig. 5 – Q_{net} at different fuel utilization and operating voltage at 1073 K in conventional SOFC system with MSR, basis on 1 mol of pure methane ($\text{H}_2\text{O}:\text{CH}_4 = 2.5$).

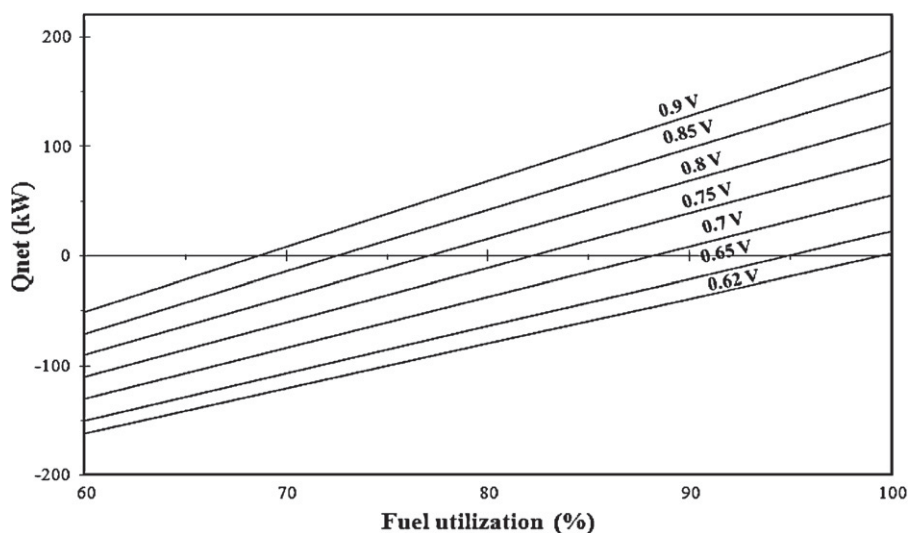


Fig. 6 – Q_{net} at different fuel utilization and operating voltage at 1073 K in proposed SOFC system with MD, basis on 1 mol of pure methane.

electricity production (Farhad et al., 2010), is found to be 3.90 for the MSR-SOFC, and 2.66 for the MD-SOFC system at the thermally self-sufficient point ($Q_{\text{net}}=0$). The higher value of TER observed in the MSR-SOFC system is because the MSR is more endothermic than the MD.

The relationship between the operating voltage and power density at the energy self-sufficient operation is shown in Fig. 7. The optimum operating voltage which offers the maximum power density for the MSR-SOFC system is at 0.60 V and for the MD-SOFC is at 0.65 V. Moreover, higher power density is observed in the case of the MD-SOFC since the MD produces purer H_2 than the MSR-SOFC as will be evidenced later in Fig. 8 showing operating voltage and polarization at various fuel utilizations. The larger the fuel utilization, the more depletion of fuel at the anode is, leading to an increase in polarization. Moreover, because the impurity in hydrogen fuel in case of the MSR is higher than that of the MD, the polarizations in SOFC system in case of the MSR are therefore higher than that of the MD at similar fuel utilization. This result is in good agreement with those reported by Eguchi et al. (2002) and Baron et al. (2004), of which polarizations in SOFC system, such as activation and concentration polarization, are occurred due to CO impurity in hydrogen fuel, leading to lower SOFC performance.

Based on similar 1 MW of net electricity production, the stack cell efficiency of the MSR-SOFC was found to be 45.9%, lower than that of the MD-SOFC of which is 53.5% (Table 3). However, overall electrical efficiency of the MSR-SOFC system, either with or without the CCS, is much higher than that of the MD-SOFC. This is because the flue gas in the MSR-SOFC is combusted and generates thermal energy whereas the by-product, solid carbon, is not further combusted; hence the energy in case of the MD-SOFC is stored in the system. In case of the MSR-SOFC with CCS, the additional CCS has no effect from either external energy or electrical input due to the operation under energy self-sufficient condition, therefore only the electrical power produced from the SOFC has an effect. Slightly higher feed rate of methane is required to produce a surplus of electricity for CCS. The CCS needs the electrical power from the SOFC system to separate out CO_2 ca. 19.2 kW, to compress, transport, and storage approximately 15 kW. Consequently, the addition of CCS reduces the net electrical efficiency ca. 3.9%.

Fig. 9 depicts the influence of feed processor to generating thermal energy from SOFC stack per area and area of the stack under the thermally self-sufficient operation at 1 MW of net electrical power production. For lower operating voltage, the difference between the theoretical voltage and the actual one is larger hence the thermal energy supplied from fuel cell stack ($Q_{\text{stack}}/\text{area}$) is larger and, in turn, the area of the cell stack becomes smaller to obtain thermally self-sufficient operation. It is noted that the trend of $Q_{\text{stack}}/\text{area}$ as a function of operating voltage is similar to that of the power density (Fig. 7). This phenomenon proves that not only MD gives the highest performance (power density and electrical efficiency) but it also has lower SOFC stack area compared to the MSR-SOFC and the MSR-SOFC-CCS.

4.3. Economic analysis

After comparing the optimal operating conditions between two main fuel processors, it is necessary to further consider the benefit in term of economic in order to apply in large-scale industrial operation. In this paper, economic analysis is based on 1 MW of electrical power generation. Three parameters are

Table 2 – Costing models and economic parameters used in the economic analysis.

Costing model	
SOFC (Piroonlerkgul et al., 2009a,b,c)	
Cell cost (US\$)	$C_{\text{cell}} = A_{\text{single cell}} \times 0.1442^a$
Number of cells	$N_{\text{cell}} = A_{\text{total}}/A_{\text{single cell}}$
Number of stacks	$N_{\text{stack}} = N_{\text{cell}}/100$
Fuel cell stacks cost (US\$)	$C_{\text{stack}} = 2.7 \times [(C_{\text{cell}} \times N_{\text{cell}}) + (2 \times N_{\text{stack}} \times A_{\text{single cell}} \times 0.46425)]$
Capture capital cost (US\$/tonne)	42.33 (Herzog, 1999)
Economic parameters	
Fuel feed cost (US\$/1000 ft ³)	9.36 (IEA Natural Gas, 2010)
Carbon selling cost (US\$/lb)	0.5 (http://www.icispricing.com)
Project life time (year)	5

^a A single cell area is fixed at 200 cm².

used to justify the economic benefits: capital cost, cost of raw materials, and return profit from by-products. Table 2 summarizes the costing model and economic parameters used in our analysis. For the capital cost, only the SOFC stack and the CCS facility are considered due to their high costs. The difference in costs of the other units such as heat exchangers, reactor and afterburner for the MSR-SOFC and the MD-SOFC are assumed to be small and therefore not considered in the economic analysis.

Economical profiles under thermally self-sufficient operation are summarized in Table 3. At the optimal condition, the MD-SOFC system can reduce the SOFC stack size 1.89% comparing to the conventional MSR-SOFC, whereas the stack size in case of the MSR-SOFC-CCS is larger than that of the MSR-SOFC 9.13% as it has to produce higher electrical power for CCS facility. In addition, the MD-SOFC can improve the power density 1.93% comparing to the conventional MSR-SOFC. This is why the SOFC stack area of the MD-SOFC is smaller than that of the MSR-SOFC (approximately 4.8 m²). As a consequence, using the MD-SOFC can save the total capital cost approximately \$19,000.

Considering the reactants used and products obtained from different fuel processors. At the similar net electrical power production, the fuel feed cost of the MD-SOFC system is higher than that of the MSR-SOFC or the MSR-SOFC-CCS. This result is because the MD-SOFC requires higher number of methane to produce the same amount of H_2 for the SOFC. It is noted that although the fuel feed cost of the MSR-SOFC-CCS is more expensive than that of the MSR-SOFC system due to the need of more electrical power but it is still a lot lower than the case of MD-SOFC system. With a consideration only of the fuel feed cost, the MD-SOFC might not be a good alternative fuel processor supplying to the SOFC system. However, it is worthy to note that the MD system can remarkably return some precious benefit as the valuable by-product, solid carbon, can be obtained. Many types of solid carbon can be formed depend upon the decomposition conditions such as graphite, carbon black, activated carbon, carbon nanotube, or carbon filaments, of which each has different selling prices (<http://www.timesnano.com/price.asp>; <http://www.helixmaterial.com/Ordering.html>). In this study, we chose to examine the return profit for the cheapest solid carbon, carbon black, along 5 years operation. The evaluation results in Table 3 show that the return profit is around 11 million dollars leads to the net cost saving ca. 9 million dollars.

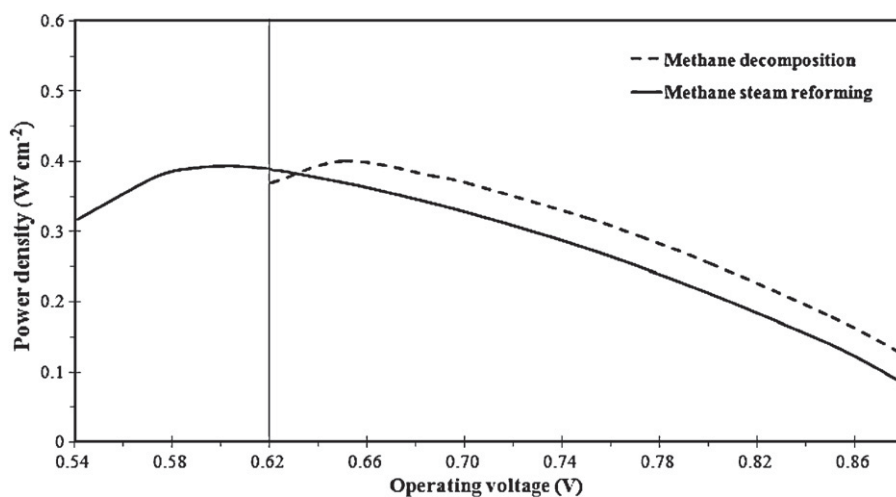


Fig. 7 – Power density at various operating voltages under the energy self-sufficient operation ($Q_{\text{net}} = 0$) in SOFC system.

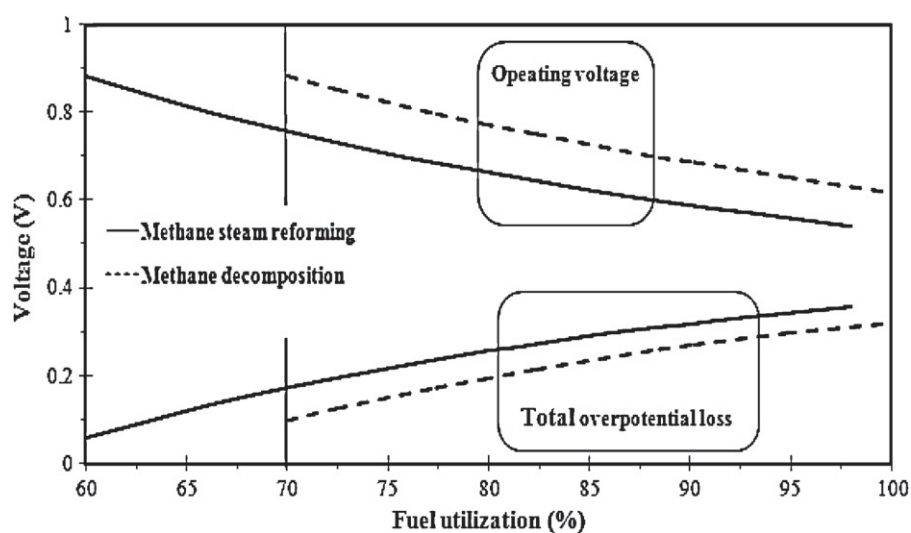


Fig. 8 – Operating voltage and polarization at various fuel utilizations under the energy self-sufficient operation ($Q_{\text{net}} = 0$) in SOFC system.

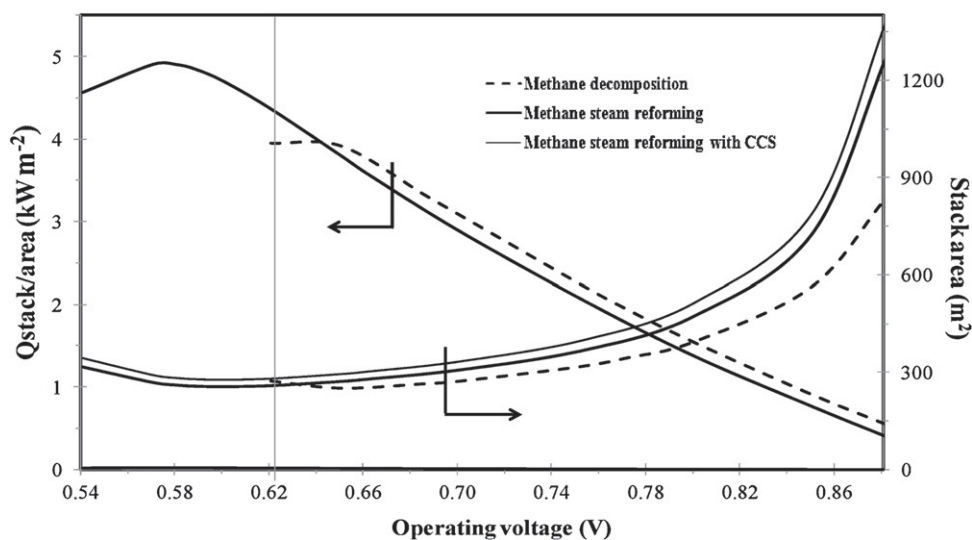


Fig. 9 – $Q_{\text{stack}}/\text{area}$ and stack area for different SOFC systems at the energy self-sufficient operation ($Q_{\text{net}} = 0$).

Table 3 – The technical and economical comparison of two main hydrogen processors.

	Steam methane reforming		Methane decomposition
	Conventional unit	With CCS technology	
Net electricity produced (MW)	1	1	1
Methane feed rate (mol/s)	2.45	2.67	4.19
Operating voltage (V)	0.60	0.60	0.65
% Fuel utilization	88.2	88.2	94.9
Power density (W/cm ²)	0.39	0.39	0.40
Improvement of power density (%)	–	–	1.93
Electricity produced in SOFC (MW)	1	1.09	1
Stack cell efficiency (%)	45.9	42.0	53.5
Overall electrical efficiency (%)	45.9	42.0	26.8
SOFC active area (m ²)	254	278	250
Improvement in SOFC area (%)	–	–9.12	1.89
Capital cost of SOFC (US\$)	997,578	1,088,642	978,719
Capital cost of CCS (US\$)	–	810,246	–
Fuel feed cost (US\$)	3,124,930	3,410,188	5,343,206
Carbon by-product selling cost (US\$)	–	–	11,606,897
Saving capital cost (US\$)	–	–901,309	18,858
Saving of raw material (US\$)	–	–285,259	–2,218,276
Return profit from by product (US\$)	–	–	11,606,897
Net cost saving (US\$)	–	–1,186,568	9,407,480

5. Conclusion

Performances of two fuel processors, conventional methane steam reforming (MSR) and methane decomposition (MD), were investigated in the methane-fuelled SOFC system under thermally self-sufficient condition ($Q_{\text{net}} = 0$). At this condition, the system is operated with no external energy requirement. The results demonstrated that high performances and high electrical efficiency can be obtained when the system was operated at the self-sufficient condition. The MD-SOFC performs more advantages over the MSR-SOFC as high purity of H₂ feed is obtained, giving a lower polarization and thus higher in power density and cell stack efficiency. As a result, lower cell stack area can be used in the case of MD-SOFC. Moreover, the MD yields valuable by-products, solid carbon, rather than undesired-by-products such as CO_x as observed in the MSR. In addition, when CCS is applied to MSR-SOFC, of course the system become more complex with an increase in the capital cost and operating cost of surplus electricity for CCS unit. As a consequence, the MD is more environmental friendly and can gain the return profit from such by-product. Economic analysis reveals that the MD-SOFC has the gratifying result with larger net saving cost (ca. 9 million dollars for 1 MW with 5 years of project life). As such, applying the MD processor with SOFC system is proved to be an attractive method for power generation.

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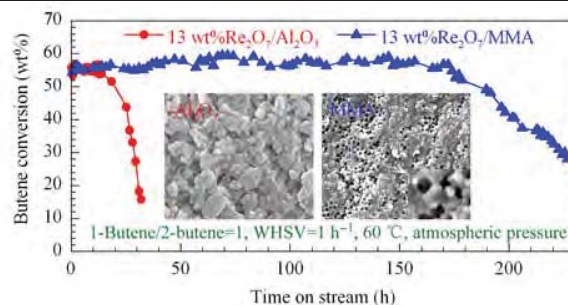
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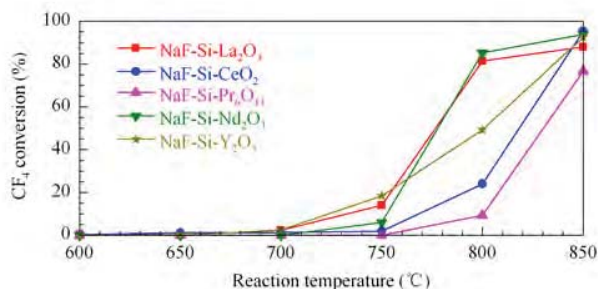
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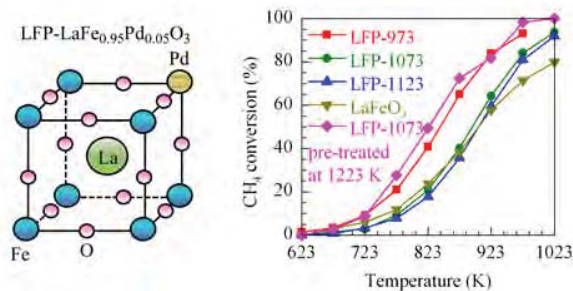


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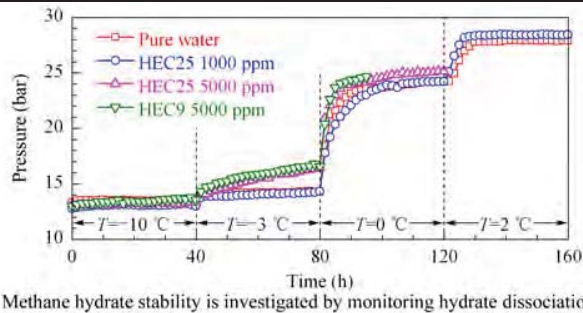
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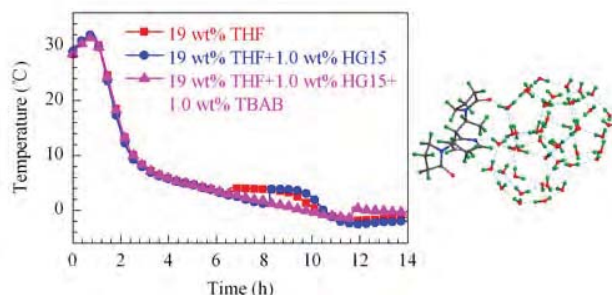


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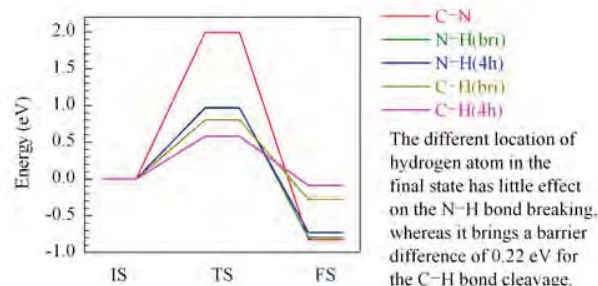
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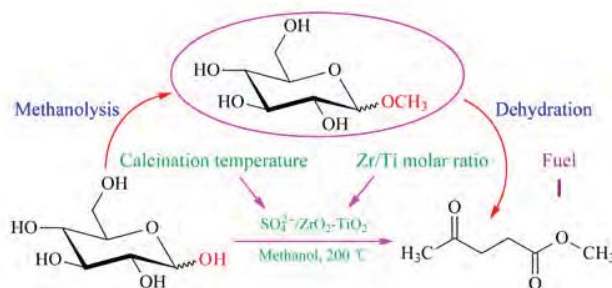
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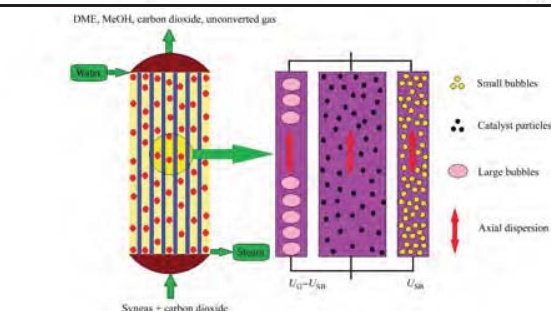
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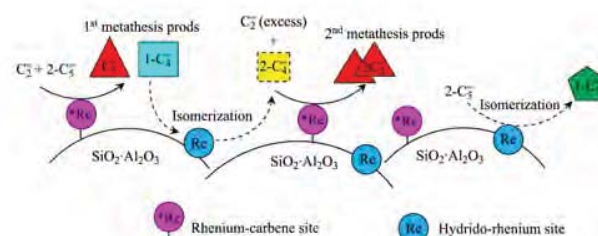
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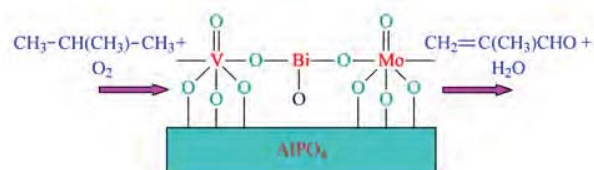
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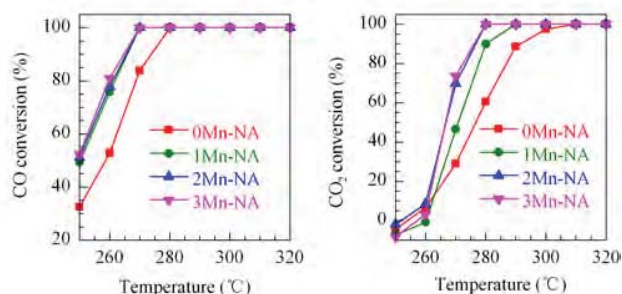
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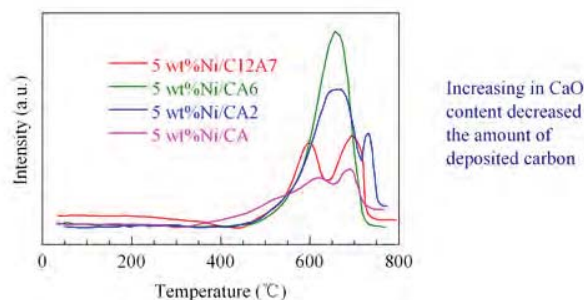
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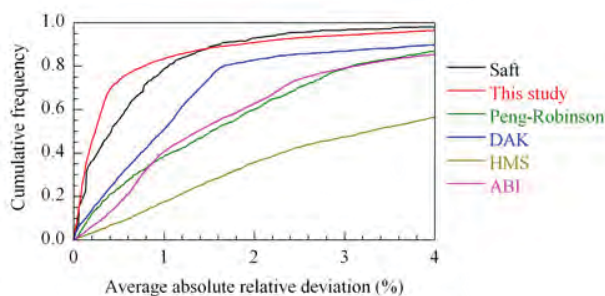
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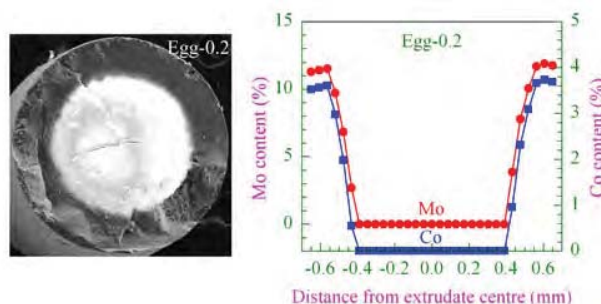


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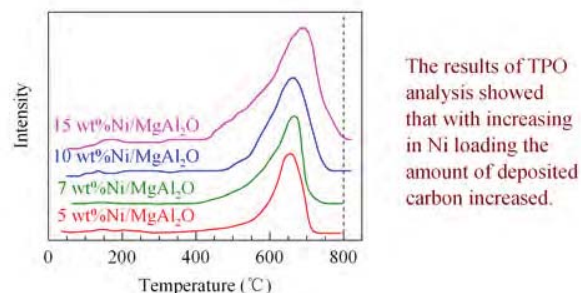
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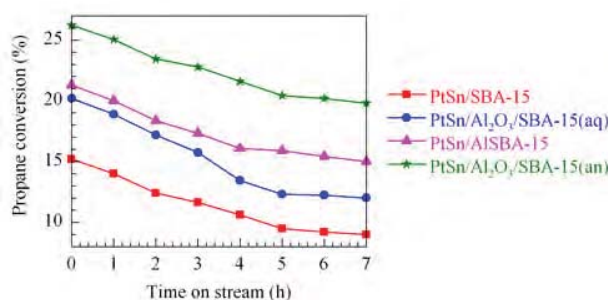
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Role of support nature (γ - Al_2O_3 and SiO_2 - Al_2O_3) on the performances of rhenium oxide catalysts in the metathesis of ethylene and 2-pentene

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Siraprapha Dokjampa², Piyasan Praserttham¹, Joongjai Panpranot^{1*}

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Abstract

The metathesis of ethylene and 2-pentene was studied as an alternative route for propylene production over $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ and $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts. Both NH_3 temperature-programmed desorption (NH_3 -TPD) and H_2 temperature-programmed reduction (H_2 -TPR) results showed that $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$ exhibited stronger acidity and weaker metal-support interaction than $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$. At 35–60 °C, isomerization free metathesis was observed only over $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$, suggesting that the formation of metal-carbene metathesis active sites required only weak acidity. Our results suggest that on the $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$, hydrido-rhenium species ($[\text{Re}]\text{-H}$) were formed in addition to the metathesis active sites, resulting in the isomerization of the initial 1-butene product into 2-butenes. A subsequent secondary metathesis reaction between these 2-butenes and the excess ethylene could explain the enhanced yields of propylene observed. The results demonstrate the potential for high yield of propylene from alternative feedstocks.

Key words

metathesis; isomerization; propylene production; 2-pentene; rhenium

1. Introduction

The growth in propylene production is driven by the industry demand for polypropylene, which is used in everyday products such as packaging and clothing. The majority of propylene worldwide is supplied as a by-product of steam crackers and fluid catalytic cracking units. Because the future propylene demand is expected to grow faster than the supply, the on-purpose technologies for propylene production such as propane dehydrogenation, metathesis, and methanol-to-olefins conversion have received much attention recently [1]. Among them, the cross-metathesis of ethylene and 2-butenes has already been commercialized as an economical means to produce propylene [2–3].

For industrial applications, heterogeneous catalysts are typically preferred due to the ease of catalyst recovery and separation. The most widely studied heterogeneous catalysts for olefin metathesis are based on WO_3/SiO_2 , $\text{MoO}_3/\text{Al}_2\text{O}_3$, and $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ [1,4–8]. The rhenium-based catalysts are of particular interest because they show high activity and selectivity for olefin metathesis at low reaction temperatures

(25–100 °C) [3,9,10] and high tolerance of catalyst poisons such as alkoxycarbonyl and alkoxy groups [9]. Transition $\gamma\text{-Al}_2\text{O}_3$ is the commonly used support because of its suitable textural and acid-base properties for dispersion of the ReO_4 active species. Other inorganic supports that have shown to produce high activity of supported Re_2O_7 catalysts include silica-alumina [11,12], alumina-boria [13,14], phosphated alumina [15], and borated silica-alumina [11]. A certain acidity level appears to be necessary for the formation of the metathesis active sites [14,16–20]. Recently, it has been reported that Re_2O_7 supported on mesostructured aluminas exhibited superior catalytic performances in several metathesis reactions comparing to the conventional $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ [21–25].

Although the process of the metathesis of ethylene and 2-butenes has been established, it presents some drawbacks such as the increasing price and demand of butenes as an industrial feedstock [9,26]. A recent study from our group showed that high propylene yield (88%) can be obtained via an unconventional metathesis of ethylene and 2-pentene over $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts under mild conditions [27]. The main products from this reaction are propylene and 1-butene. 1-butene

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is also an important petrochemical feedstock for organic syntheses, and also used as a monomer and comonomer for oligo/polymeric and co-oligo/polymeric products [28].

In the present work, detailed characterization of the $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts before and after metathesis of ethylene and 2-pentene is reported. For comparison purposes, $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ was also prepared and studied under similar reaction conditions (35 and 60 °C). The catalysts were characterized by N_2 physisorption, inductively coupled plasma optical emission spectrometer (ICP-OES), scanning electron spectroscopy (SEM), X-ray diffraction (XRD), temperature-programmed desorption of NH_3 (NH_3 -TPD), H_2 temperature-programmed reduction (H_2 -TPR), and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by an incipient wetness impregnation method using an aqueous solution of ammonium perhenate (NH_4ReO_4 , 99.999%, Aldrich) as the rhenium precursor with the desired amount of 8 wt% Re metal loading. When the quantity of the solution of desired Re-metal is greater than pore volume of the supports, the impregnation was repeated several times with drying (6 h, 110 °C) between each cycle to eliminate excess solvent. The number of times of impregnation varied depending on the support pore volume. The $\text{SiO}_2\text{-Al}_2\text{O}_3$ (99.9% grade135, Aldrich) and both types of $\gamma\text{-Al}_2\text{O}_3$ (chromatography grade of Fluka and KNH-3 grade of Sumitomo) were obtained commercially and employed as the catalyst supports. After impregnation, the catalysts were dried overnight at 110 °C in air and then calcined at 550 °C for 8 h under oxygen flow with a heating rate of 10 °C/min. Hereafter, $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3\text{-(A)}$, and $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3\text{-(B)}$ are referred to the Re_2O_7 catalysts supported on $\text{SiO}_2\text{-Al}_2\text{O}_3$, chromatographic grade $\gamma\text{-Al}_2\text{O}_3$, and KNH-3 $\gamma\text{-Al}_2\text{O}_3$, respectively.

2.2. Catalyst characterization

The specific surface area, pore volume, average pore diameter and pore size distribution of the supports and catalysts were measured by N_2 -physisorption performed on a Micromeritics model ASAP 2000. The alumina composition of supports and Re mass percentages for each catalyst were measured by ICP-OES on a Perkin Elmer Optima 2100DV. The sample preparation was performed by digestion of each catalyst with a mixture of hydrofluoric and nitric acids at 60 °C. SEM images were recorded on a JEOL JSM 5500LV scanning electron microscope. The XRD patterns of the supports and catalysts were measured in a range of 2θ value between 20° and 80° at a rate of 0.02°/s using a SIEMENS D5000 X-ray diffractometer and $\text{Cu } K_\alpha$ radiation with a Ni filter. The PCPDFWIN database was used to identify the crystalline phases. The H_2 -TPR measurements were carried out in a quartz U-tube reactor. Prior to these measurements, all the

catalyst samples were pretreated with a N_2 flow (25 mL/min, 2 h, 200 °C). The TPR profiles were obtained by passing carrier gas (10% H_2 in argon) through the catalyst samples (25 mL/min, ramping from 30 to 500 °C at 10 °C/min). The NH_3 -TPD measurements were also carried out in a quartz U-tube reactor. Firstly, the catalyst samples were pretreated in a helium flow (25 mL/min) at 200 °C for 2 h prior to measurement. Subsequently they were cooled to 25 °C before 30% NH_3 in He passed over the samples (25 mL/min, 1 h) to ensure thorough adsorption on the acid sites. After ammonia adsorption on catalyst surface was complete, excess ammonia was eradicated by a helium flow (25 mL/min, 1 h, 25 °C). Finally, samples were heated (linearly rise of 10 °C/min) and the TPR and TPD profiles were recorded by a TCD detector and analyzed with a Micromeritics Chemisorb 2750 automated system (ChemiSoft TPx software). The XPS measurement was carried out using an AMICUS photoelectron spectrometer equipped with an $\text{Mg } K_\alpha$ X-ray as a primary excitation and KRATOS VISION2 software. XPS elemental spectra were acquired with 0.1 eV energy step at a pass energy of 75 eV. All the binding energies were referenced to the C 1s peak at 285 eV of the surface adventitious carbon.

2.3. Metathesis of ethylene and 2-pentene

Gas-phase metathesis reactions between ethylene and 2-pentene were carried out in a fixed-bed tabular flow reactor (stainless steel $\text{ID}_{\text{tube}} = 0.7$ cm) at atmospheric pressure. The gas hourly space velocity (GHSV) was 2000 h^{-1} , using a feed gas ratio (ethylene/2-pentene) of 3. In each experiment, the catalyst sample was placed in the middle of the reactor. A temperature sensor-type K thermocouple was mounted into the reactor at the middle. Firstly, the catalyst was pretreated under a nitrogen flow (500 °C, 1 h) and then cooled to the desired operating temperature under the same gas. An on-line gas chromatograph (Agilent GC 7820A), equipped with a capillary GS-Gaspro113–4362 column (60 m × 0.32 mm), monitored both reactant and product levels every 30 min, starting 35 min after commencement of each reaction. GC signals were recorded using an EZChrom Elite integrated peak program integrator.

3. Results and discussion

3.1. Characterization results

The N_2 physisorption results of the supports and the supported Re_2O_7 are shown in Table 1. Both of the $\gamma\text{-Al}_2\text{O}_3$ samples comprised 100 wt% alumina powder whereas the $\text{SiO}_2\text{-Al}_2\text{O}_3$ contained only 13 wt% of alumina. After impregnation of rhenium, the BET surface area and pore volume decreased proportionately, indicating that some of the metal had become lodged inside the pores of the alumina supports. The pore size distribution plots (Figure 1) showed that the impregnation, drying, and calcination processes did not significantly alter the pore size distribution or the average pore diameter of the supports.

Table 1. Characteristics of the supports and supported Re_2O_7 catalysts

Catalyst	Al_2O_3 (wt%)	S_{BET}^a ($\text{m}^2 \cdot \text{g}^{-1}$)	V_{pore}^b ($\text{cm}^3 \cdot \text{g}^{-1}$)	d_{pore}^c (nm)	Total (weak/strong) acidity ^d ($10^3 \mu\text{mol}_{\text{NH}_3} \cdot \text{g}^{-1}$)
$\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3\text{-(A)}$	100	131 (145)	0.21 (0.25)	4.68 (5.09)	4.942/0.133
$\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3\text{-(B)}$	100	191 (247)	0.47 (0.59)	7.68 (6.92)	7.794/0.243
$\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$	13	396 (548)	0.60 (0.79)	5.89 (5.57)	7.428/6.910

The numbers in parenthesis indicate the surface area, pore volume, and average pore diameter of the bare supports; ^a Surface area was determined by the BET method; ^b Pore volume was determined by the BJH desorption method; ^c Average pore size was determined by BJH desorption method; ^d Total surface acidity of the catalysts was probed by the NH_3 -TPD

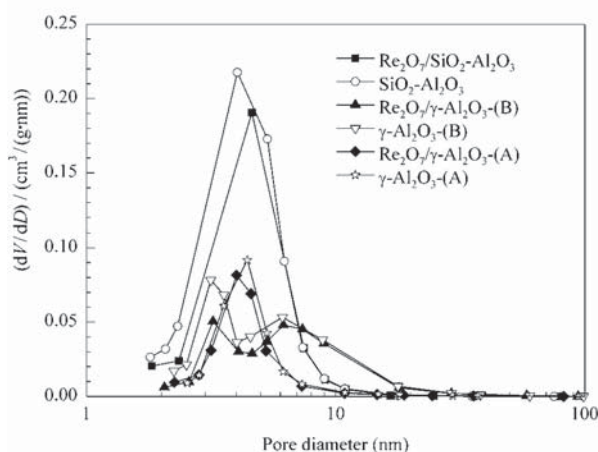
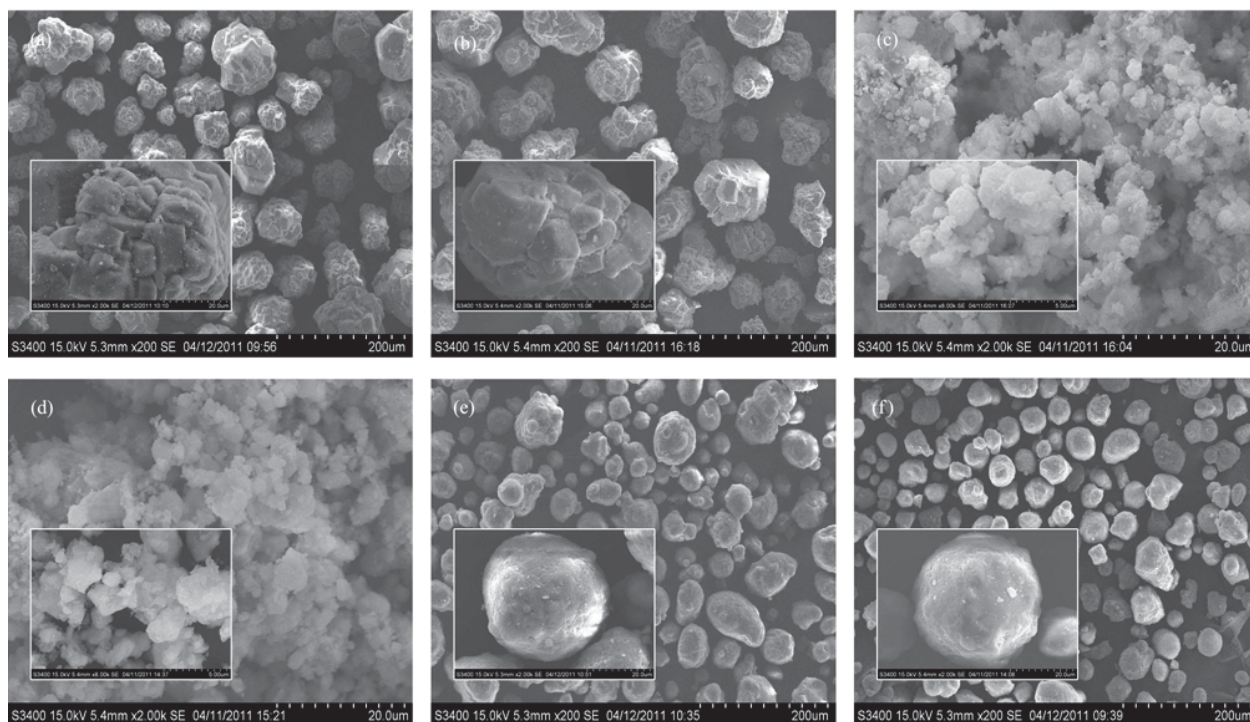
**Figure 1.** Pore size distribution of the supports and supported Re_2O_7 catalysts

Figure 2 shows the SEM images of the supports and the supported rhenium catalysts in the calcined state.

$\gamma\text{-Al}_2\text{O}_3\text{-(B)}$ (Figure 2c), which displayed a higher BET surface area and higher pore volume than $\gamma\text{-Al}_2\text{O}_3\text{-(A)}$ (Figure 2a) (as obtained by Table 1), was predominantly made up of smaller and rather fluffy particles, while the $\gamma\text{-Al}_2\text{O}_3\text{-(A)}$ was composed of denser, plate-like agglomerates. SEM micrographs (Figure 2e) reveal the morphology of $\text{SiO}_2\text{-Al}_2\text{O}_3$ support was rather spherical with rough surfaces. These morphologies remained apparent after impregnation and calcination of the supported Re_2O_7 catalysts. XRD patterns (Figure 3) show the exhibiting peaks of alumina supports $\gamma\text{-Al}_2\text{O}_3\text{-(A)}$ and $\gamma\text{-Al}_2\text{O}_3\text{-(B)}$, characteristic of γ -alumina phase at $2\theta = 32^\circ, 37^\circ, 46^\circ, 61^\circ$ and 67° , according to the PCPDFWIN database. For the silica-alumina support, a broad peak was seen at $2\theta = 20^\circ\text{--}25^\circ$, indicating a typical amorphous solid. No peaks assignable to the crystalline phase of Re_2O_7 were observed for any of the catalysts. According to previous studies [3,21,29,30] involving relatively high rhenium loadings, most of the metal remaining adhered to the surface exists in the form of ReO_4^- , simply because crystalline Re_2O_7 is volatile above calcination temperature of 300°C .

**Figure 2.** SEM images of (a) $\gamma\text{-Al}_2\text{O}_3\text{-(A)}$, (b) $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3\text{-(A)}$, (c) $\gamma\text{-Al}_2\text{O}_3\text{-(B)}$, (d) $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3\text{-(B)}$, (e) $\text{SiO}_2\text{-Al}_2\text{O}_3$ and (f) $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts

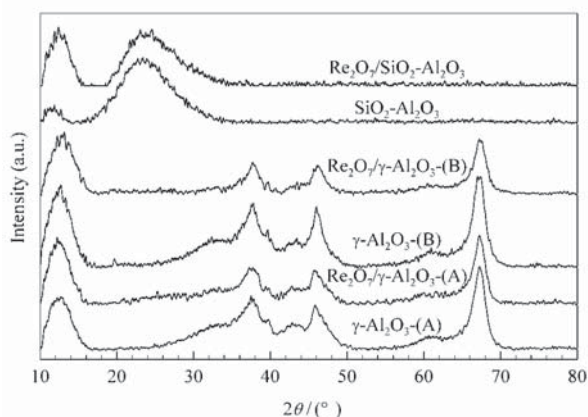


Figure 3. XRD patterns of the supports and supported Re_2O_7 catalysts

Although alkene metathesis is not commonly regarded as an acid-catalyzed reaction, acidity often affects the performance of this reaction [3,14,17,31,32]. The surface acidity of the Re_2O_7 catalysts was determined by NH_3 -TPD and the results are shown in Figure 4. As expected, the $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$ (Figure 4) exhibited not only greater acidity overall but also possessed a significantly higher proportion of stronger acidic sites than the $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$. The desorption peak at around 50–200 °C corresponded to the weak acid sites of alumina [33]. It is typical that silica-alumina supported metathesis catalysts are more acidic than alumina supported catalysts [3,34–36]. The amounts of total surface acidity in terms of mol NH_3 per gram of catalysts are given in Table 1.

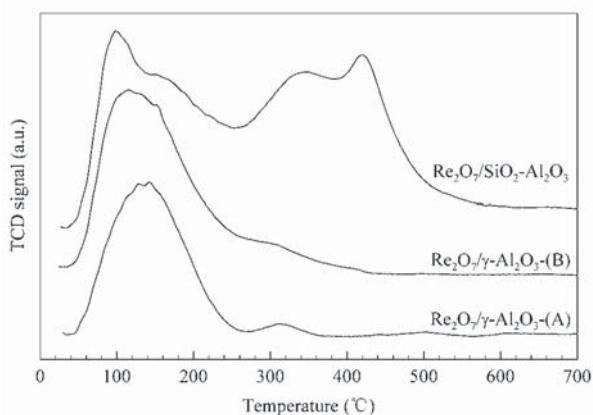


Figure 4. NH_3 -TPD profiles of different catalysts

The reducibility of rhenium oxide catalysts is another important parameter affecting their performance. Partial reduction of rhenium oxides, which affords metal species in a stable lower oxidation state, is a necessary step to generate the metal-carbene metathesis active sites [13,17,37,38]. An over-reduction of rhenium oxide usually results in the formation of inactive rhenium species and rapid catalyst deactivation, especially at high temperature [3,35,39,40]. Figure 5 shows the H_2 -TPR results of various $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ and the $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts. Typically, the reduction of the

Re_2O_7 supported catalysts from +7 oxidation state to zero (Re metal) is very fast and often appears as a single sharp reduction peak [30,38]. In the present study, the reduction temperatures for $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$ and $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ were determined to be ca. 280 °C and 340 °C, respectively. It is suggested that the rhenium oxide on the silica-alumina was easier to reduce while bounded to silica-alumina than to the pure $\gamma\text{-Al}_2\text{O}_3$ support. Moreover, the TPR profiles of the $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts showed a very sharp main reduction peak with a shoulder at higher temperature, inferring the presence of a different rhenium oxide species. Typically, a strong metal-support interaction can diminish sintering of the Re-active sites and sublimation during calcination and/or pre-treatment. The metal-support interaction seemed to be weaker on the $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$ than on the $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$. The actual amounts of Re metal loading, as determined by the ICP-OES, were ca. 8.3 and 5.8 wt%, respectively (see Table 2) for the calcined $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ and the $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$. The lower amount of the actual Re metal loading on the $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$ also corresponded to the weaker metal-support interaction. However, there was no significant decrease in the amount of rhenium after the reaction.

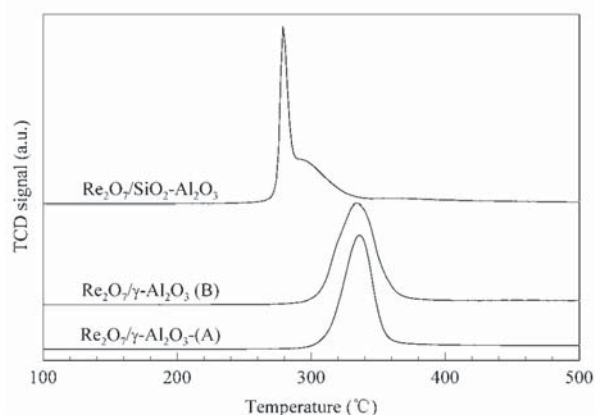


Figure 5. H_2 -TPR profiles of different catalysts

Table 2. Actual amount of Re metal (wt%) from the ICP-OES results

Catalyst samples	Actual amount of Re metal (wt%)		
	Before reaction ^a	After reaction ^b	
		$T = 35\text{ °C}$	$T = 60\text{ °C}$
$\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3\text{-(A)}$	8.23	8.34	8.17
$\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3\text{-(B)}$	8.40	8.57	8.38
$\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$	5.83	5.69	5.78

^a After calcination and N_2 -pretreatment; ^b After metathesis reaction at the conditions of $p = 0.1\text{ MPa}$, mole ratio of ethylene/2-pentene = 3/1, GHSV = 2000 h^{-1} , and time on stream = 455 min

The deconvoluted XPS spectra of Re 4f of all the catalysts after calcination and N_2 pretreatment are shown in Figure 6. The component of rhenium species on the catalyst surface is summarized in Table 3. It was found that rhenium oxide existed in the oxidation state of +7 for both $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3\text{-(A)}$ and $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3\text{-(B)}$ [41–43]. For

the $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$, 85% of rhenium component was assigned to rhenium oxide existed in the oxidation state between +6 and +7 with only 15% in the oxidation state of +7. The two

different Re oxidation states observed on the $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$ were in good agreement with the H_2 -TPR results showing additional peak shoulder.

Table 3. The fraction of different Re oxidation states of fresh catalysts

Catalyst	Fraction of Re (+7) (%)		Fraction of Re (+7 > x > +6) (%)	
	Re $4f_{5/2}$ (48.8–49.2 eV)	Re $4f_{7/2}$ (46.4–46.8 eV)	Re $4f_{5/2}$ (47.4–47.8 eV)	Re $4f_{7/2}$ (45.0–45.4 eV)
$\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3\text{-(A)}$	6	94	—	—
$\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3\text{-(B)}$	6	94	—	—
$\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$	15	—	12	73

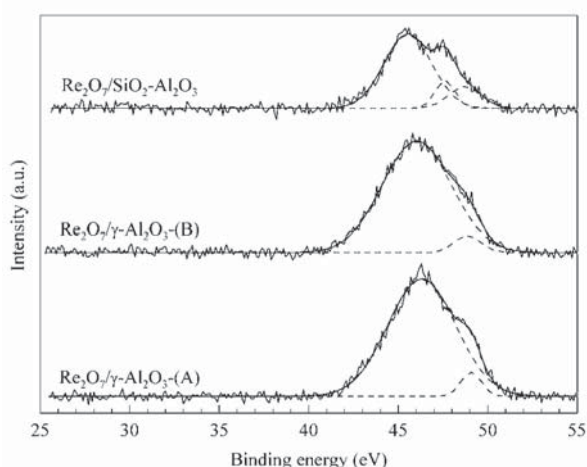


Figure 6. XPS spectra of different catalysts

3.2. Catalyst performances in the metathesis of ethylene and 2-pentene

Figure 7 shows the yields of the dominant products (propylene and 1-butene) from the metathesis of ethylene and 2-pentene over the $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$ and the $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3\text{-(A)}$ catalysts during the 455 min time-on-

stream. It was found that under identical operating conditions, $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$ gave a much higher total yield of propylene than the $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3\text{-(A)}$. Furthermore, $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$ generated relatively little 1-butene (~ 10 wt%), whereas $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3\text{-(A)}$ produced about 55 wt% of this product. Based on the desired complete conversion of 2-pentene, the stoichiometric yields for propylene and 1-butene were 43 wt% and 57 wt%, respectively. In fact, the propylene yield obtained over the $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst far exceeded the theoretical stoichiometric value. This additional propylene is likely to be formed via a secondary metathesis of excess ethylene and 2-butene, itself arising from the isomerization of 1-butene. The double-bond isomerization side reaction became more pronounced at 60°C . However, at this higher temperature the $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$ exhibited more rapid deactivation than $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3\text{-(A)}$. It is assumed that the isomerization side reaction did not occur over $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3\text{-(A)}$ even when the temperature was increased to 60°C , since the propylene yield remained close to its stoichiometric values (ca. 50 mol% or around 43 wt% based on 100% 2-pentene conversion). Although most of the products obtained from the $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3\text{-(A)}$ catalyst were directly derived from the primary metathesis between ethylene and 2-pentene, small amounts of by-products such as 2-butene and 3-hexene were produced via a self metathesis of 2-pentene as illustrated in Figure 8.

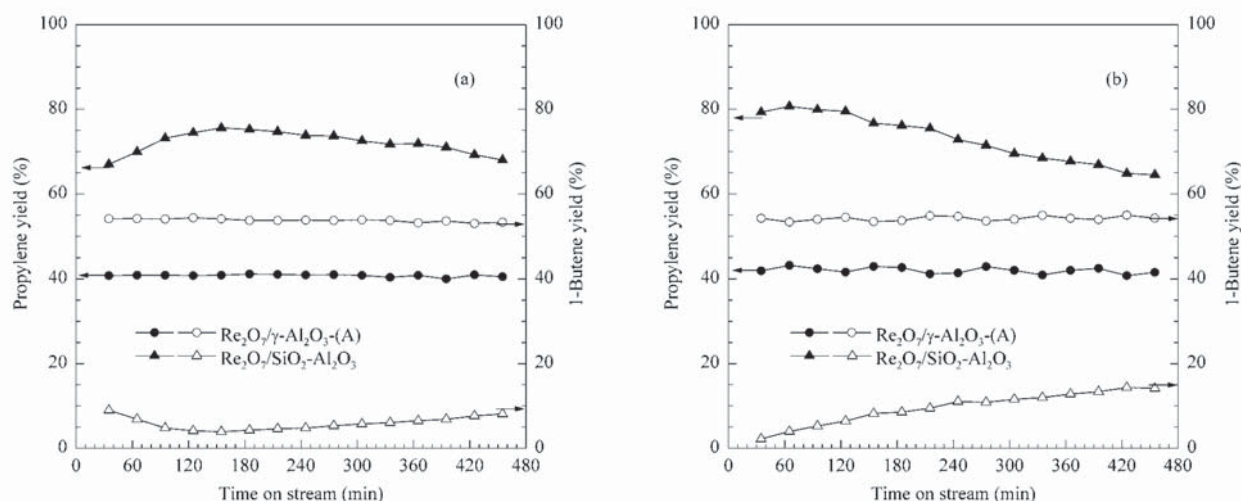


Figure 7. The comparison in the yields of the primary metathesis products (propylene and 1-butene) at reaction temperature of (a) 35°C and (b) 60°C (Reaction conditions: $p = 0.1$ MPa, mole ratio of ethylene/2-pentene = 3/1, GHSV = 2000 h^{-1})

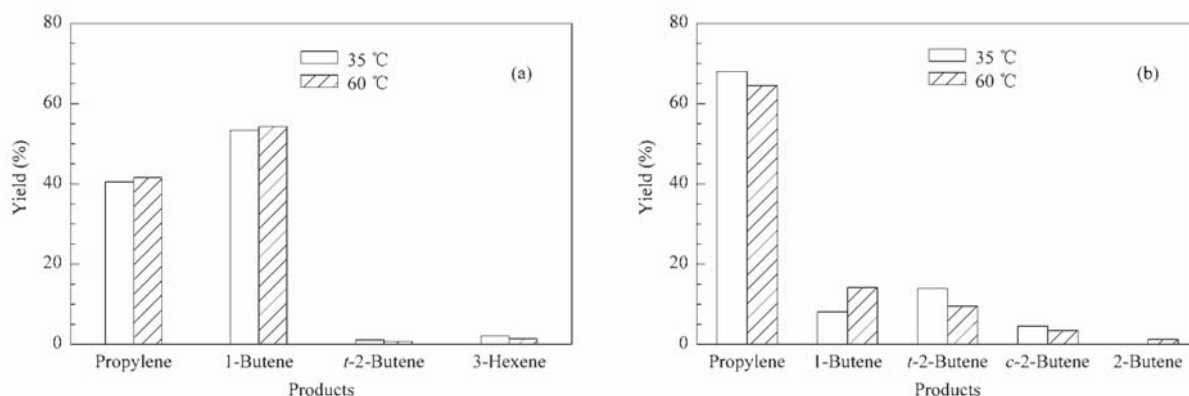


Figure 8. Comparison in total product distribution between $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3\text{-(A)}$ (a) and $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$ (b) catalysts (Reaction conditions: time on stream 455 min, 0.1 MPa, mole ratio of ethylene/2-pentene = 3/1, GHSV = 2000 h^{-1})

3.3. Possible reaction schemes

To better elucidate the reaction mechanisms, two types of $\gamma\text{-Al}_2\text{O}_3$ -supported Re_2O_7 catalysts were studied under similar reaction conditions. The $\gamma\text{-Al}_2\text{O}_3\text{-(A)}$ possessed lower BET surface area and lower pore volume than the $\gamma\text{-Al}_2\text{O}_3\text{-(B)}$. However, there were no significant differences in terms of 2-pentene conversion and product selectivities between the two types of $\gamma\text{-Al}_2\text{O}_3$ -supported Re_2O_7 catalysts (see Table 4). From the $\text{NH}_3\text{-TPD}$ results, both the $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3\text{-(A)}$ and the $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3\text{-(B)}$ contained only weak acid sites in similar abundance. Therefore, it seems that the weak acidic sites of the $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ catalysts promoted the metathesis reaction but were unable to catalyze the isomerization of 1-butene. Noticeably, even at room temperature, isomerization of 1-butene (primary metathesis product) occurred instantaneously over the $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$. The existence of more abundant Brønsted acid sites on silica-

alumina is likely to be responsible for its isomerization activity [12]. This greater acidity and the easier reducibility of the $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts could promote the formation of hydrido-rhenium complexes. Such $[\text{Re}]\text{-H}$ species, generated from protonation of rhenium centers by Brønsted species (silica-alumina), have been claimed to act as isomerization sites [12,29,44]. In order to confirm the role of metal in the isomerization mechanism, bare silica-alumina support was tested. The negative results obtained with 1-butene at 35–60 °C confirmed the lack of isomerization activity of the catalyst supports. Figure 9 illustrates a possible scheme for the origins of various reactions in the metathesis of ethylene and 2-pentene over the $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ and the $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts. It is also well known that metal-carbene active species were generated through the interaction between the partial reduction of rhenium metal and the alkene reactant on an acidic support [3,16,19].

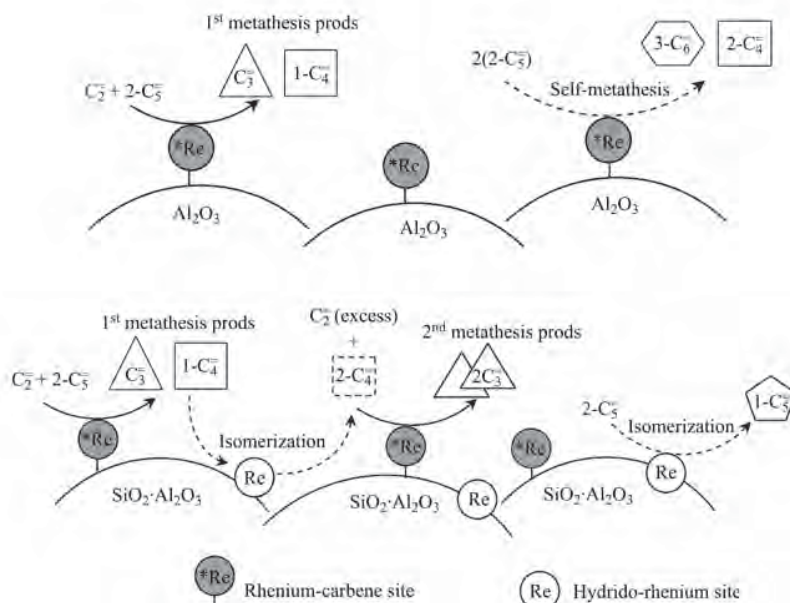


Figure 9. Possible origins of various reactions in the metathesis system of ethylene and 2-pentene over the $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ and the $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts

Table 4. Catalytic performances of Re₂O₇ supported on SiO₂-Al₂O₃ and two types of γ -Al₂O₃ supports

	Selectivity (%) ^a				
	C ₃ ⁼	1-C ₄ ⁼	2-C ₄ ⁼	1-C ₅ ⁼	3-C ₆ ⁼
$T_{\text{Rxn}} = 35\text{ }^{\circ}\text{C}$					
Re ₂ O ₇ /γ-Al ₂ O ₃ -(A)	42.2	55.9	0.8	—	1.2
Re ₂ O ₇ /γ-Al ₂ O ₃ -(B)	42.2	55.6	0.7	—	1.4
Re ₂ O ₇ /SiO ₂ -Al ₂ O ₃	71.9	8.6	19.5	—	—
$T_{\text{Rxn}} = 60\text{ }^{\circ}\text{C}$					
Re ₂ O ₇ /γ-Al ₂ O ₃ -(A)	42.4	55.4	0.8	—	1.4
Re ₂ O ₇ /γ-Al ₂ O ₃ -(B)	43.9	54.2	0.8	—	1.2
Re ₂ O ₇ /SiO ₂ -Al ₂ O ₃	69.4	15.3	14.0	1.3	—

Reaction conditions: $P = 0.1\text{ MPa}$, mole ratio of ethylene/2-pentene = 3/1, GHSV = 2000 h⁻¹, time on stream = 455 min; ^a Selectivity (%) on the basis of 100% 2-pentene conversion

4. Conclusions

The nature of the support material in rhenium-based metathesis catalysts appears to significantly affect their catalytic performances in the unconventional metathesis of ethylene and 2-pentene for propylene production. Under the reaction conditions used (35–60 °C), Re₂O₇/SiO₂-Al₂O₃ exhibited much higher double-bond isomerization activity than Re₂O₇/γ-Al₂O₃. However, unlike the conventional metathesis of ethylene and 2-butenes, isomerization here was considered as a useful reaction for the transformation of 1-butene (primary product) to 2-butenes which could instantly react with excess ethylene to form additional propylene. Metathesis reaction over Re₂O₇/γ-Al₂O₃ occurred without isomerization side reactions. It is proposed that both the presence of weak acidic sites and the stabilization of Re-active species on the support were important factors in the formation of the necessary active metal-carbene complexes.

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Effect of $\text{SiO}_2\text{--Al}_2\text{O}_3$ Composition on the Catalytic Performance of the $\text{Re}_2\text{O}_7/\text{SiO}_2\text{--Al}_2\text{O}_3$ Catalysts in the Metathesis of Ethylene and 2-Pentene for Propylene Production

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Abstract The production of propylene via a gas-phase metathesis of ethylene and 2-pentene has been studied over the $\text{Re}_2\text{O}_7/\text{SiO}_2\text{--}x\text{Al}_2\text{O}_3$ catalysts containing various $\text{SiO}_2\text{--Al}_2\text{O}_3$ compositions (13, 25, 50, 75, and 100 wt% Al_2O_3). Using ethylene and 2-pentene as the reactants, isomerization of the initial 1-butene product into 2-butenes and a subsequent secondary metathesis reaction between 2-butenes and excess ethylene enhanced the propylene formation so that propylene yield higher than its stoichiometric amount (>50 %) could be obtained. While the pure Al_2O_3 supported Re_2O_7 catalyst possessed only the first type of isolated monomeric ReO_4^- tetrahedra structure with a stronger Re–O–support bond, the second type with a weaker Re–O–support bond was observed on the $\text{SiO}_2\text{--Al}_2\text{O}_3$ supported ones. The double-bond isomerization and the metathesis activities were optimized to produce the highest propylene yield over the $\text{Re}_2\text{O}_7/\text{SiO}_2\text{--Al}_2\text{O}_3$ catalyst containing 50 wt% Al_2O_3 .

Keywords Metathesis · Isomerization ·
Propylene production · 2-pentene · Silica–alumina

1 Introduction

Olefin metathesis is one of industrial important reactions in olefin conversion that opens up many new routes to produce important petrochemical products. Current commercial technology for producing propylene via metathesis reaction is based on the conversion of ethylene and 2-butene over heterogeneous catalyst systems [1–4]. However, this route has some drawbacks although high propylene yield can be obtained. It needs C_4 streams that are free of isobutene and butadiene [5] and both cost and demand of butene industrial feedstock have increased continuously [4, 6, 7]. In our recent work, a cross-metathesis of ethylene and 2-pentene over $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts has been studied as an interesting route to produce propylene from cheaper raw materials [8, 9]. The products from this route are not only high valuable propylene but also 1-butene that are increasing in both demand and cost nowadays [6, 7].

The $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts have been employed in large scale metathesis of ethylene and 2-butene into propylene [10]. Their catalytic activities can be further improved by the use of mixed metal oxides supports such as $\text{SiO}_2\text{--Al}_2\text{O}_3$ [2, 11–13], phosphated alumina (AIPO) [14] and $\text{Al}_2\text{O}_3\text{--B}_2\text{O}_3$ [15]. In addition, recently mesoporous materials have been studied as supports for Re_2O_7 catalysts in the metathesis reactions [16–22]. The improved catalytic activity of the mesoporous alumina supported Re_2O_7 than those supported on conventional alumina was directly correlated to their large pore size and higher specific surface area [16]. However, the synthesis of these mesostructured oxides was more complicated and may not be suitable for industrial application [23].

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Among the various mixed oxides used to stabilize the Re species in the favorable oxidation state for the formation of the rhenium carbene active complex, the $\text{SiO}_2\text{--Al}_2\text{O}_3$ receives considerable attention and has shown significant improvement in the metathesis reaction. According to the literature [2, 24, 25], low rhenium-loading $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts exhibited poor or negligible activity for the alkene metathesis. However, 2 wt% Re_2O_7 over $\text{SiO}_2\text{--Al}_2\text{O}_3$ was found to be more active than the 18 wt% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts [26, 27]. In epoxidation of alkenes, the stability of rhenium-based catalysts also depended on the alumina content of mixed silica–alumina supports in which ReO_4^- supported on higher alumina content or pure alumina supports showed no metal lost [28]. According to Moulijn and Mol [12], the Si–O–Re bonds are very weak comparing to the Al–O–Re bonds.

Acidity of the catalysts plays an important role in alkene metathesis reactions [1, 2, 13, 26, 27, 29, 30]. In general, silica–alumina is more acidic than alumina [31] and it contains both strong Lewis and Brönsted acidic sites [13, 30]. Xiaoding et al. [13, 27] showed the distinct correlation between the Brönsted acidity which was directly proportional to the silica–alumina compositions and the metathesis activity for the Re-based catalyst. A model for the generation of metallocarbenes including the function of partial reduced rhenium species and neighboring Brönsted acid sites has been proposed [27, 32]. The presence of Al in the $\text{SiO}_2\text{--Al}_2\text{O}_3$ supports was found to affect the performance of $\text{MoO}_3/\text{SiO}_2\text{--Al}_2\text{O}_3$ catalysts in various works [33–39]. Debecker et al. [33] suggested that the acidity created by the presence of alumina in silica was beneficial for the better dispersion of active Mo species.

A number of previous studies of Re-based catalysts [27, 28, 30, 40–43] have shown that double-bond isomerization activity of silica–alumina was much higher than that of alumina. The isomerization activity of $\text{Re}_2\text{O}_7/\text{SiO}_2\text{--Al}_2\text{O}_3$ catalyst was even more higher than the corresponding sole $\text{SiO}_2\text{--Al}_2\text{O}_3$ support [40]. Nevertheless, in our previous studies [8, 9], double-bond isomerization of 1-butene was found to be useful for producing additional propylene formation in the unconventional metathesis of ethylene and 2-pentene. The present work was aimed to further investigate the influence of $\text{SiO}_2\text{--Al}_2\text{O}_3$ composition on the catalytic performances of $\text{Re}_2\text{O}_7/\text{SiO}_2\text{--Al}_2\text{O}_3$ in the metathesis of ethylene and 2-pentene for propylene production. The catalysts were also characterized by inductively coupled plasma optical emission spectroscopy (ICP-OES), N_2 -physisorption (BET and BJH methods), X-ray diffraction (XRD), temperature program desorption of NH_3 (NH_3 -TPD), X-ray photoelectron spectroscopy (XPS), UV–Visible, and FT-Raman spectroscopy.

2 Experimental

2.1 Catalyst Preparation

2.1.1 Synthesis of $\text{SiO}_2\text{--Al}_2\text{O}_3$ Supports

The $\text{SiO}_2\text{--}x\text{Al}_2\text{O}_3$ supports containing various amount of alumina ($x = 13, 25, 50, 75$, and 100 wt%) were prepared by a co-precipitation method according to that of Okada et al. [44]. Aluminium nitrate nonahydrate [ANN; $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] and tetraethylorthosilicate [TEOS; $\text{Si}(\text{OC}_2\text{H}_5)_4$] solution were coprecipitated and adjusted to 1.2 mol l^{-1} for all the sample preparation. The distilled water and ethanol was first mixed, then ANN was added and the resulting solution was stirred for 15 min. The amount of H_2O in the solution was adjusted to give $\text{H}_2\text{O}/\text{TEOS} = 18/1$, this ratio indicating a large excess of H_2O for hydrolysis of TEOS. An ethanol solution containing a desired amount of TEOS was then added and stirred for 3 h, 25 wt% of ammonia solution was added rapidly to the solution with vigorous stirring. The precipitates were immediately dried over a hot plate at 60°C for 3 h and subsequently dried overnight at 110°C in an oven. After drying, they were calcined under oxygen flowing at 300°C for 4 h with a heating rate of $3^\circ\text{C}/\text{min}$ to obtain the xerogels. These xerogels were then calcined at 550°C for 4 h under oxygen flowing with a heating rate of $10^\circ\text{C min}^{-1}$ before used as the $\text{SiO}_2\text{--Al}_2\text{O}_3$ supports for preparation of supported rhenium oxide catalysts. The synthesized $\text{SiO}_2\text{--Al}_2\text{O}_3$ supports were denoted as SixAl where x indicated wt% of Al_2O_3 in the silica–alumina supports.

2.1.2 Preparation of Supported Rhenium Oxide Catalysts

The catalysts were prepared by incipient wetness impregnation with aqueous solution of ammonium perrhenate (99.999 %, Aldrich). When quantity of the solution of the desired Re-metal loading (8 wt% Re-metal) was greater than pore volume of the supports, the impregnation was performed several times with drying at 110°C in between to eliminate the solvent for 6 h. After impregnation, these catalysts were dried overnight at 110°C and then calcined at 550°C for 8 h under oxygen flow with a heating rate of $10^\circ\text{C min}^{-1}$. The catalyst nomenclature Re/SixAl is referred to the Re_2O_7 supported on the $\text{SiO}_2\text{--}x\text{Al}_2\text{O}_3$ containing x wt% of Al_2O_3 .

2.2 Catalyst Characterization

The weight percentage of actual Re metal for each catalyst after calcination was measured by ICP-OES on a Perkin Elmer Optima 2100DV. The samples were digested with hydrofluoric and nitric acid at 60°C . The specific surface

area, pore volume, average pore diameter and pore sizes distribution of the supports and the supported rhenium catalysts were measured by the N₂-physisorption with using a Micromeritics model ASAP 2000 automated system. The measurements were performed with a degassing at 350 °C (Ramp rate = 10 °C min⁻¹) for 4 h prior to N₂ physisorptions at -196 °C. The specific surface area was calculated based on the Brunauer-Emmett-Teller (BET) isotherms and the pore volume and pore size distribution were calculated based on the Barrett-Joyner-Halenda (BJH) desorption branch analysis. The XRD patterns of the supports and the catalysts were measured in a range of 2θ value between 20° and 80° at a rate of 0.02° s⁻¹ using a SIEMENS D5000 X-ray diffractometer and Cu K_α radiation with a Ni filter. The PCPDFWIN database was used as reference to identify the crystalline phases. The NH₃-TPD measurements were carried out in a quartz U-tube reactor using a Micromeritic Chemisorb 2750 automated system. The catalyst samples were firstly pretreated in a He flow (25 ml min⁻¹) at 200 °C for 2 h prior to measurement. Subsequently they were cooled to room temperature around 25 °C then a 30 %NH₃/He mixed gas was flowed (25 ml min⁻¹) over the samples for 1 h to throughout adsorb on the acid sites. After ammonia adsorption on catalyst surface was completed, the excess ammonia was eradicated by the He flowing (25 ml min⁻¹) at the room temperature for 1 h. Then, the samples were heated linearly with a rate of 10 °C min⁻¹. The TPD profiles were detected by TCD detector and analyzed with a ChemiSoft TPx software. XPS was carried out using an AMICUS photoelectron spectrometer equipped with an Mg K_α X-ray as a primary excitation and KRATOS VISION2 software. XPS elemental spectra were acquired with 0.1 eV energy step at a pass energy of 75 eV. All the binding energies were referenced to the C 1 s peak at 285 eV. Diffuse reflectance UV-Vis spectra were collected on Lambda 650 UV-Vis spectrometer equipped with a diffuse reflectance attachment and an integrating sphere. The samples were studied in the form of powder carried out in sample holder. The spectra were recorded under air-exposed conditions in the range 200–900 nm and the scan speed was 1 nm min⁻¹.

2.3 Catalytic Tests

The catalytic performances were tested in the gas-phase metathesis reaction between ethylene and 2-pentene, which was carried out in a stainless steel (ID_{tube} = 0.7 cm) fixed-bed tabular flow reactor under atmospheric pressure. The gas-phase of 2-pentene was prepared by dilution a small

amount liquid 2-pentene (≥99 % mixture of isomers, Aldrich) in low pressure N₂ gas (4 vol.% of 2-pentene in 12 bar N₂ balance). The reactants were pre-mixed with high purity ethylene (99.999 %), and high purity N₂ to have the composition of 6.75 vol.% 2-pentene, 2.25 vol.% ethylene in N₂ balance before passing through the reactor. The feed flow rates were adjusted to 70–77.5 cm³ min⁻¹ depending on the bed volume of each catalyst. In a typical run, 1 g of the catalyst sample was placed in the middle of the reactor. The reaction temperature, gas hourly space velocity (GHSV), and mole of feed ratio (ethylene/2-pentene) were kept at 35 ± 2 °C, 3,000 h⁻¹ and 3, respectively. Start up with pretreatment the catalyst sample at 500 °C under N₂ flow for 1 h and then cooled down to the reaction temperature. The analysis of reaction products was started after an initial reaction for 35 min. Both reactants and products of reaction were followed and analyzed every half an hour using an on-line gas chromatograph (Agilent GC 7820A) equipped with a capillary GS-Gaspro113-4362 column (60 m × 0.32 mm). The GC signals were collected using an EZChrom Elite integrated peak program integrator.

3 Results and Discussion

3.1 Catalytic Performances of the Re/SixAl Catalysts

The catalytic performances of the SiO₂-*x*Al₂O₃ supported rhenium oxide catalysts were evaluated in the gas-phase metathesis reaction of ethylene and 2-pentene at 35 °C, GHSV 3,000 h⁻¹, and ethylene/2-pentene mole ratio = 3. The conversion of 2-pentene, the yield of propylene, 1-butene, and 2-butene as a function of time-on-stream are shown in Fig. 1a–d, respectively. The conversion of 2-pentene in average at 485 min time-on-stream was ranging between 97 and 84 %. However, lower 2-pentene conversion was obtained over the Re/Si13Al and Re/Si25Al whereas those supported on the SiO₂-*x*Al₂O₃ containing higher amounts of Al₂O₃ Re/Si50Al, Re/Si75Al, and Re/100Al exhibited higher 2-pentene conversion at ca. 95–97 %. As shown in Eq. (1), the theoretical stoichiometric value of reactants in the metathesis reaction of ethylene and 2-pentene is equimolar.



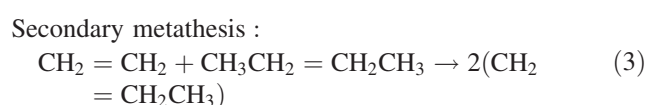
The conversion of limited 2-pentene reactant and the yield of products were calculated using the following equations:

$$\text{Conversion of 2-pentene (\%)} = 100 \times \frac{\text{amount of 2-pentene in feed} - \text{amount of 2-pentene remained in products}}{\text{amount of 2-pentene in feed}}$$

$$\text{Yield of component i (\%)} = \text{conversion of 2-pentene} \times \frac{\text{amount of component i in products}}{\text{amount of total products}}$$

In the present work, the propylene yields for all the Re/Si $_x$ Al catalysts far exceeded the stoichiometric values (propylene selectivity of 50 mol% or ~ 43 wt%). Only the Re/100Al exhibited propylene yield equal to the stoichiometric value. The highest propylene yield ca. 70 % was achieved over the Re/Si50Al with good stability during the 488 min time-on-stream. Thermodynamically, excess ethylene would shift the reaction (1) from left to right, producing more propylene and 1-butene products. However, as shown in Fig. 1, the yield of 1-butene product was not increased in the same trend as that of propylene for the catalysts exhibiting propylene yield higher than its

stoichiometric amount (i.e., for Re/Si50Al and Re/Si75Al). It has been suggested that the isomerization of 1-butene product from the metathesis of ethylene and 2-pentene to 2-butenes (Eq. 2) can further react with excess ethylene in the feed, resulting in additional propylene formation (Eq. 3) [8, 9].



The yield of 1-butene was found to be varied from 55 % for the Re/100Al, 30 % for the Re/Si75Al, and <20 % for the other catalysts (Re/Si13Al, Re/Si25Al, and Re/Si50Al). The lowest yield of 1-butene was obtained over the

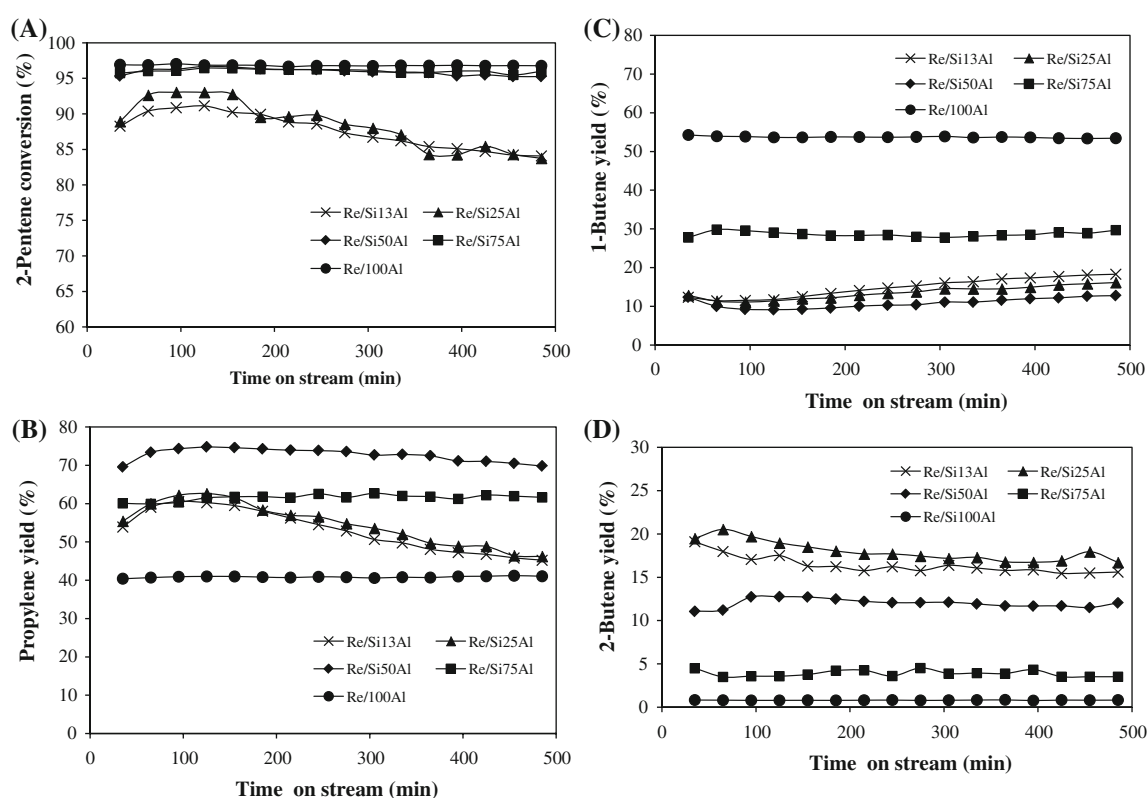


Fig. 1 Effect of silica–alumina composition (SiO $_2$ – x Al $_2$ O $_3$, x = 13, 25, 50, 75 and 100 wt% Al $_2$ O $_3$) of Re $_2$ O $_7$ /SiO $_2$ – x Al $_2$ O $_3$ catalysts on the **a** 2-pentene conversion, **b** propylene yield, **c** 1-butene yield,

d 2-butene yield. (Pressure: 0.1 MPa; E/2P mole ratio: 3; GHSV: 3,000 h $^{-1}$; Temperature: 35 °C)

Re/Si50Al, suggesting that 1-butene was isomerized to 2-butene and further reacted with excess ethylene to form additional propylene product. This view point can also be considered in terms of the yield of 2-butene, higher yields of 2-butene were produced over the Re₂O₇ catalysts supported on the relatively high silica content supports (Re/Si13Al and Re/Si25Al) whereas moderately high and lower 2-butene yields were obtained over Re/Si50Al and Re/75–100Al catalysts, respectively. Both the isomerization and the cross-metathesis activity strongly depended on the Si/Al composition of the SiO₂–xAl₂O₃ supports. Unlike the conventional metathesis of ethylene and 2-butenes that double-bond isomerization was a competing side reaction; it was considered as a useful reaction for the transformation of 1-butene primary product to 2-butenes which could further react with excess ethylene to form additional propylene in the metathesis of ethylene and 2-pentene [8, 9]. The results in this study, however, suggest an optimum composition of the SiO₂–Al₂O₃ supports for the Re₂O₇ catalysts to exhibit high activities for both double-bond isomerization and cross-metathesis reactions so that higher propylene yield (than its stoichiometric amount) was attained with high stability. Besides propylene and 1-butene primary metathesis products, the other by-products including *cis*- and *trans*-2-butene, 1-pentene, 3-hexene, and C₅+ oligomers can also be produced by various side reactions [8]. However, under the reaction conditions used in the present study, the only C₅+ hydrocarbon found in the products was 3-hexene, which was produced in very small amount (<3 % yield) by self-metathesis of 2-pentene. A relationship between the catalyst physicochemical properties and their catalytic performances was further investigated by catalyst characterization using several techniques.

3.2 Catalyst Characterization

The BET surface area, pore volume, and average pore diameter of the supports and the supported rhenium oxide catalysts are shown in Table 1. It was found that all the SiO₂–xAl₂O₃ supports had larger BET surface area and pore volume than that of the pure Al₂O₃ which is in good agreement with those of Okada et al. [44]. However, considering the changes in BET surface area, pore volume, and pore diameter of the supports after impregnation of rhenium metal and calcination, the Re/Si50Al exhibited the least change in their textural properties. Such results suggest that most of the rhenium was highly dispersed on the surface of the SiO₂–xAl₂O₃ support. As revealed by ICP-OES results, the actual Re-metal loadings varied from 4.6 to 8.1 wt%, depending on the supports used. Higher amount of Re-metal (7.8–8.1 wt%) remained on the Al₂O₃ rich supports (≥50 wt% Al₂O₃). Because some of the Re₂O₇ can be volatilized during high temperature calcination step especially the inactive rhenium centers of the type ≡Si–O–ReO₃ [40], the use of SiO₂–xAl₂O₃ supports with relatively higher silica content (i.e., Si13Al and Si25Al) resulted in lower amount of rhenium metal on the catalyst samples. It is quite well known that Re₂O₇/SiO₂ catalyst has no activity in olefin metathesis due to poor interaction between silica and rhenium oxide that tends to form inactive rhenium clusters [45].

Although one can notice the differences in the actual Re metal loadings on the various Re₂O₇/SiO₂–xAl₂O₃ catalysts, they seemed to make little influence on the catalytic performances. The amount of 2-pentene converted per gram Re metal was calculated and was found to be even higher on the catalysts with lower Re contents (Re/Si13Al and Re/Si25Al). However, it is quite well known that the number of rhenium active sites were only small fraction of

Table 1 The physicochemical property of the bare silica-alumina supports and the supported rhenium oxide catalysts

Sample	Al ₂ O ₃ content ^a (wt%)	Surface area ^b (m ² g ^{−1})	Pore volume ^c (cm ³ g ^{−1})	Average pore diameter ^c (nm)	Re-metal loading ^d (wt%)	Total acidity ^e (10 ³ μmol NH ₃ g ^{−1})
Re/Si13Al	13	224 (291)	1.10 (1.07)	13.7 (17.2)	4.7	7.487
Re/Si25Al	25	210 (277)	0.71 (0.58)	8.7 (9.7)	4.6	7.333
Re/Si50Al	50	308 (316)	0.83 (0.79)	8.3 (8.7)	7.5	14.554
Re/Si75Al	75	389 (431)	0.86 (0.77)	6.1 (6.0)	7.8	14.967
Re/100Al	100	213 (233)	0.40 (0.33)	5.1 (4.9)	8.2	7.698

The numbers in parenthesis indicated the values of the bare supports

^a Based on the calculated amounts that were used for synthesis of various SiO₂–Al₂O₃ supports

^b Based on the Brunauer–Emmett–Teller (BET) method

^c Based on the Barret–Joyner–Halenda (BJH) desorption method

^d Actual re-metal loading for each catalyst after calcination was measured by ICP-OES

^e Total surface acidity of the catalysts was probed by the NH₃-TPD

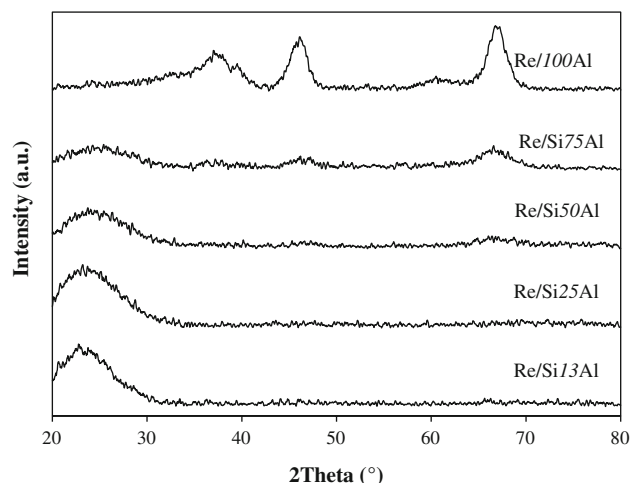


Fig. 2 The X-ray diffraction (XRD) patterns of the different $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-}x\text{Al}_2\text{O}_3$ catalysts ($x = 13, 25, 50, 75$ and 100 wt% Al_2O_3)

the Re atoms presented on supported rhenium oxide catalysts. The rhenium active centers have been quantitatively determined by various techniques including poisoning experiments using NO [4], kinetic studies [46], and chemical counting method [47]. These studies showed the percentage of active Re centers of approximately 1 % of the total actual amount Re loading.

The XRD patterns of the $\text{Re}/\text{Si}_x\text{Al}$ catalysts are shown in Fig. 2. A broad peak around $20\text{--}30^\circ$ represents a typical character of amorphous solid of these samples. The XRD characteristic peaks of the γ -phase alumina appeared at $2\theta = 32, 37, 46, 61$ and 67° for the samples containing ≥ 50 wt% of Al_2O_3 . The intensity of the γ -phase alumina increased with increasing amount of Al_2O_3 in the samples. The peaks corresponding to the crystalline Re_2O_7 were not detected for all the supported Re_2O_7 catalysts. According to the literature [2, 16, 42, 48], most of the rhenium species formed on the surface is isolated ReO_4^- form and the crystalline Re_2O_7 can be volatilized during high temperature calcination at above 300°C .

Although alkene metathesis reaction does not regard as an acid-catalyzed reaction, surface acidity of the catalysts strongly influences the formation of metathesis active sites [2, 26, 27, 29, 33, 49]. Acidity of the catalysts was probed by the NH_3 -TPD measurements and the results are shown in Fig. 3. The total amounts of acidity was found to be directly related to the specific surface area of the catalysts, in which they were increased with increasing alumina content from 13 to 75 wt% and then markedly declined for the 100 wt% Al_2O_3 support (Table 1). It is generally accepted that silica–alumina supported metathesis catalysts are more acidic than alumina supported catalysts [2, 11–13]. From the NH_3 -TPD profiles (Fig. 3), the desorption peaks in the temperature range below and above 300°C were assigned to the weak and the strong acid sites, respectively

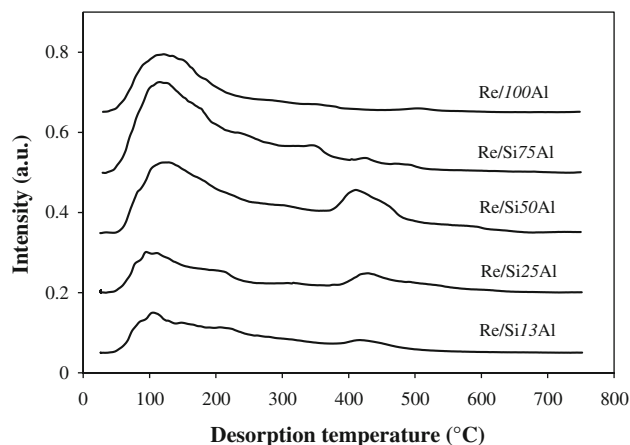


Fig. 3 Temperature programmed desorption of ammonium (NH_3 -TPD) spectra of the $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-}x\text{Al}_2\text{O}_3$ catalysts ($x = 13, 25, 50, 75$ and 100 wt% Al_2O_3)

[8, 9]. In Fig. 4, it was found that the amount of strong acid sites was maximized for the $\text{Re}/\text{Si}50\text{Al}$. The $\text{Re}/100\text{Al}_2\text{O}_3$ shows only the weak acidity characteristic. The acid strength thus strongly influenced both the isomerization and metathesis activity over the supported Re_2O_7 catalyst. Since the major products of the metathesis of ethylene and 2-pentene obtained over the $\text{Re}/100\text{Al}_2\text{O}_3$ catalyst were in accordance with their stoichiometric amounts, it is suggested that the weak acidity of the $\text{Re}/100\text{Al}_2\text{O}_3$ was not strong enough for isomerization reaction of the 1-butene product so that the secondary metathesis reaction did not occur.

The oxidation states of rhenium in the various $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-}\text{Al}_2\text{O}_3$ catalysts were determined by XPS and the results are shown in Fig. 5. According to the literatures [50–52], the XPS spectra revealed that most of rhenium oxidation state of the fresh catalysts lied in oxidation state

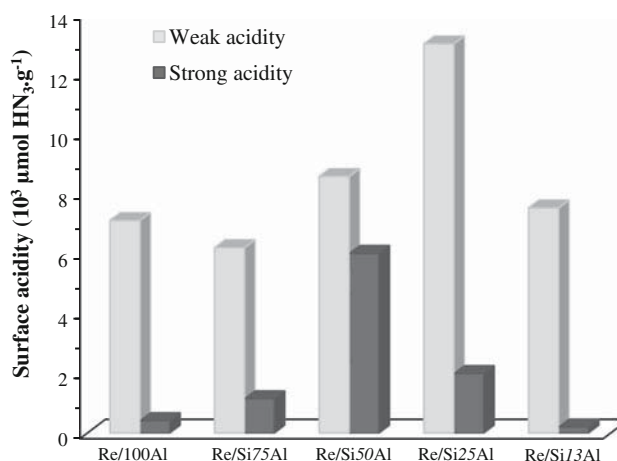


Fig. 4 The amount of surface acidity of the different $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-}x\text{Al}_2\text{O}_3$ catalysts in terms of $\mu\text{mol NH}_3$ per gram of catalysts by classification into weak and strong acidity

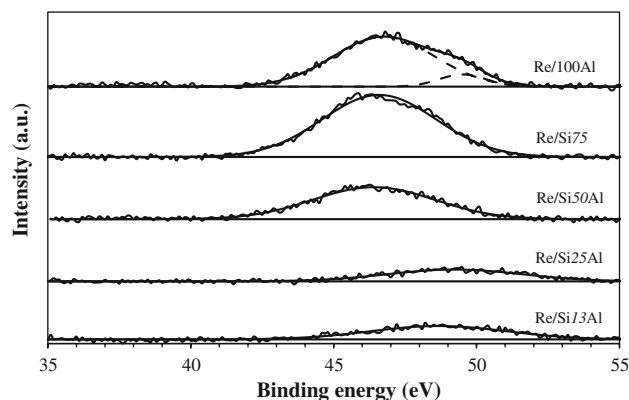


Fig. 5 XPS spectra of the fresh Re₂O₇/SiO₂–*x*Al₂O₃ catalysts (*x* = 13, 25, 50, 75 and 100 wt% Al₂O₃)

+(7), however a fraction of rhenium oxidation state +(6–7) was also detected for the Re₂O₇/SiO₂–50Al₂O₃, Re₂O₇/SiO₂–75Al₂O₃ and Re₂O₇/100Al₂O₃ catalysts. Based on the XPS results, the catalysts in this study can be categorized into three different characters; the first one is the group of low metal–support interaction Re₂O₇/SiO₂–13Al₂O₃ and Re₂O₇/SiO₂–25Al₂O₃ catalysts possessing only the rhenium oxidation state +(7). The second one is the group of stronger metal–support interaction Re₂O₇/SiO₂–50Al₂O₃ and Re₂O₇/SiO₂–75Al₂O₃ catalysts that showed lower binding energy of the rhenium oxidation state +(6–7). Both of the rhenium species (Re⁷⁺ and Re^{6–7+}) were detected on the surface of the Re₂O₇/100Al₂O₃ catalysts, the third type possessing metal–support interaction strength in between the first two groups. The different characteristics observed may be related to the dispersion degree of rhenium oxide on the surface. Well-dispersion species were found on the SiO₂–50Al₂O₃ and the SiO₂–75Al₂O₃. Iwasawa and Yuan [52] also found that the binding energy of rhenium species shifted towards lower binding energy for the catalysts possessing stronger metal–support interaction.

The structure of transition metal species was investigated by diffuse reflectance UV–Visible spectroscopy. The diffuse reflectance UV–Visible spectra of the various supported Re₂O₇ catalysts are shown in Fig. 6. Two intense absorption bands centered at ca. 210 and 240 nm were assigned to the undistorted tetrahedral ReO₄[–] ion [53]. The presence of isolated tetrahedral species of rhenium active species was found on the Re₂O₇/SiO₂–*x*Al₂O₃ composing of higher alumina content (*x* ≥ 50 wt% Al₂O₃). Hence, it would be an evidence for the highly dispersion of rhenium over these suitable support compositions. The isolated tetrahedral structure of rhenium is necessary for the formation of metal–carbene metathesis active sites and better catalyst performance. The Re/100Al₂O₃ shows additional absorption bands centered at ca. 300 and 330 nm which

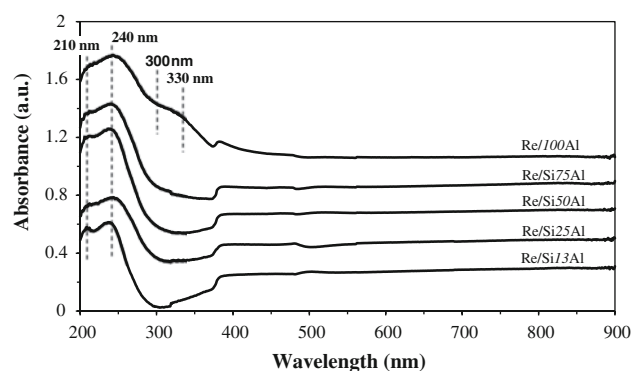


Fig. 6 Diffuse reflectance UV–Visible spectra of the different Re₂O₇/SiO₂–*x*Al₂O₃ catalysts (*x* = 13, 25, 50, 75 and 100 wt% Al₂O₃)

were attributed to the existence of rhenium in a distorted octahedral species [13, 53].

The surface structures of ReO_x species on the various supported Re₂O₇ catalysts were characterized by Raman spectroscopy and the results are shown in Fig. 7. Consistent to the XRD results, the Raman shifts corresponding to the crystalline Re₂O₇ (at 800, 450, and below 200 cm^{–1}) [54, 55] were not detected for all the catalyst samples and only isolated ReO₄[–] species existed. The monomeric tetrahedral ReO₄[–] ions were observed at ~990–975 cm^{–1} [*ν*_s(Re=O), the most intense band], ~900–930 cm^{–1} [*ν*_{as}(Re=O), weak band], and ~340 cm^{–1} [*δ*_{s, as}(O–Re–O), intense band] [48, 54–57]. For all the SiO₂–*x*Al₂O₃ supported Re₂O₇ catalysts, two separated peaks of the terminal Re=O bond were observed at 970 and 990 cm^{–1}, indicating the existence of two different surface rhenium oxide species. The position of the higher frequency peaks tended to shift to lower frequency when the alumina composition in the SiO₂–*x*Al₂O₃ supports increased and eventually merged into a single peak at 976 cm^{–1} for the case of Re/100Al catalyst. The shift of Raman to lower frequency was interpreted as a result of the stronger of the bridging Re–O–support bond strength [58, 59]. The Re/100Al₂O₃

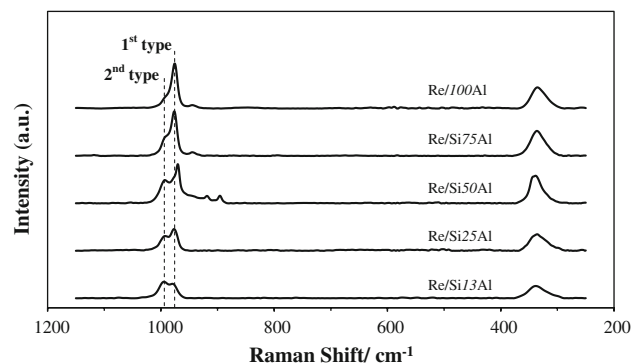


Fig. 7 Raman spectra of the different Re₂O₇/SiO₂–*x*Al₂O₃ catalysts (*x* = 13, 25, 50, 75 and 100 wt% Al₂O₃)

catalyst showed metathesis activity with negligible isomerization activity. It is likely that the catalyst had only one type of surface rhenium species with rather strong Re–O-support bond (shown as a single Raman shift at 976 cm^{-1}). Contrarily, all the Re/SixAl catalysts exhibited double-bond isomerization activity in addition to the metathesis reaction. The second type of surface rhenium species with a weaker Re–O-support bond (additional peak at 990 cm^{-1}) could be attributed to the hydrido–rhenium species ([Re]–H) which was claimed to act as isomerization sites [30, 42, 60]. The Raman spectroscopy results strongly support the UV–Vis results that isolated monomeric ReO_4^- tetrahedra is the rhenium metathesis active structure. It is noted that the hydrolyzed ReO_4^- or the ReO_4^- ion in aqueous solution also resemble in the form of isolated monomeric ReO_4^- tetrahedral species [54, 57, 61–64]. A shift in all Raman bands to lower range of frequency is often observed particularly in the measurements that performed under ambient conditions [54]. It appears that an increase in alumina component in the SiO_2 – $x\text{Al}_2\text{O}_3$ supports could stabilize the surface rhenium species as the first type of isolated monomeric ReO_4^- tetrahedra metathesis active structure whereas the proportion of the second type decreased. The intensity of Raman bands also increased with increasing amount of surface rhenium oxides as determined by the ICP-OES results. The Re/Si50Al catalyst that exhibited the highest propylene yield and good catalyst stability had the highest proportion of isolated monomeric ReO_4^- tetrahedral with relatively strong bond strength.

4 Conclusions

The role of silica–alumina composition in the unconventional metathesis of ethylene and 2-pentene has been investigated over the $\text{Re}_2\text{O}_7/\text{SiO}_2$ – Al_2O_3 catalysts at 35°C , GHSV $3,000\text{ h}^{-1}$, and ethylene/2-pentene mole ratio 3. The SiO_2 – Al_2O_3 composition has strong influence on the acidity, the metal–support interaction, and the dispersion of Re-active species. Higher amount of Re metal remained on the catalysts was observed in the Al_2O_3 rich $\text{Re}_2\text{O}_7/\text{SiO}_2$ – $x\text{Al}_2\text{O}_3$ catalysts ($x \geq 50\text{ wt\% Al}_2\text{O}_3$), corresponding to the stronger metal–support interaction. These characters also suggest a well dispersion of Re-active species as a monolayer of the isolated ReO_4^- species. The second type of the isolated monomeric ReO_4^- tetrahedral structure with a weaker Re–O-support bond appeared in all the catalysts except the one supported on pure alumina. The optimum amount of alumina in the SiO_2 – Al_2O_3 was determined to be $50\text{ wt\% Al}_2\text{O}_3$ in which the highest propylene yield was obtained. The isomerization of the initial 1-butene product into 2-butenes and a subsequent secondary metathesis

reaction between these 2-butenes and excess ethylene enhanced the propylene yield over the $\text{Re}_2\text{O}_7/\text{SiO}_2$ – Al_2O_3 catalysts.

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REVISED II

Formation of CoAl_2O_4 nanoparticles via low temperature solid-state reaction of fine gibbsite and cobalt precursor

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Abstract

Nanocrystalline cobalt aluminate (CoAl_2O_4) was synthesized by the solid-state reaction method with **cobalt chloride hexahydrate** ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) as the source of Co and gibbsite ($\text{Al}(\text{OH})_3$) as the source of Al, respectively. The effects of particle size of the starting fine gibbsite (0.6 and 13 μm) and calcination temperatures (450, 550, and 650°C) on the properties of CoAl_2O_4 were investigated by means of X-ray diffraction (XRD), thermogravimetry analysis and differential thermal analysis (TG/DTA), X-ray photoelectron spectroscopy (XPS), UV-visible absorption spectroscopy (UV-Vis), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Increasing of calcination temperature promoted the insertion amounts of Co^{2+} in alumina matrix in CoAl_2O_4 structure, which resulted in the brighter blue particles and increasing of UV spectra band. The lowest temperature for the formation of nanocrystalline CoAl_2O_4 particles was 550°C for the solid-state reaction of cobalt chloride and 0.6 μm fine gibbsite.

Keywords: cobalt aluminate, cobalt precursor, gibbsite, solid-state reaction

Conflict of Interests:

I, Joongjai Panpranot, the corresponding author of the manuscript, confirm that I do not have a direct financial relation with the commercial identity mentioned in the paper submitted that might lead to a conflict of interest for any of the authors.

1. Introduction

Cobalt aluminate is a binary oxide consisting of cobalt and aluminium oxides. It is a thermally and chemically stable pigment of intense blue color and is usually synthesized at high temperature by solid-state reaction between two oxide components [1-2]. In the past decades, it has received attention due to its applications as inorganic ceramic blue pigment which is widely used for coloration of plastics, paint, fiber, paper, rubber, phosphor, glass, cement, glazes, ceramic bodies and porcelain enamels [3,4,5]. Moreover, its uniqueness optical properties leads to its extensive use as color filter for automotive lamps or pigment layer on luminescent materials in optical devices [6,7,8]. The coloring performance of cobalt pigments strongly depends on their thermal stability, chemical reactivity, and coordination of Co^{2+} ions [9]. Other applications of cobalt aluminate is an important material for heterogeneous catalysis such as selective catalytic reduction of NO_x with hydrocarbons [10] and carbon dioxide reforming of methane [11].

Cobalt aluminate can be synthesized by various routes such as polymerized complex [3], molten salt [4], polyol [8], low temperature combustion [9], co-precipitation [7,12], sol-gel [13,14,15], citrate-gel [16], metal-organic chemical vapor deposition (MOCVD) [17], EDTA chelating precursor [18], glycine chelated precursor [19], hydrothermal [20], polymer aerosol pyrolysis [21] and reverse micelle processes [22]. Nonetheless, the selection of **preparation method** is usually based upon the desired properties of the final materials [3]. The solid-state reaction of a mechanical mixture between gibbsite and cobalt precursor is interested due to three main advantages approach. They (i) are simple, cheaper and convenient; (ii) involve less solvent and reduce contamination; and (iii) give high yields of products [23]. The solid-state reactions involve four steps in a typical proceeding: diffusion, reaction, nucleation, and growth. Any chemical interaction between solids proceeds exclusively on the contact area between the particles [24].

In the present work, cobalt aluminate was synthesized by the solid-state reaction method with **cobalt chloride hexahydrate** ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) as the source of Co and gibbsite ($\text{Al}(\text{OH})_3$) as the source of Al, respectively. The effects of particle size of gibbsite and calcination temperature on the formation of cobalt aluminate and their properties were investigated by means of X-ray diffraction (XRD), thermogravimetry analysis and differential thermal analysis (TG/DTA), X-ray photoelectron spectroscopy (XPS), UV-visible absorption spectroscopy (UV-Vis), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

2. Experimental

2.1 Preparation of CoAl_2O_4

Fine gibbsite ($\text{Al}(\text{OH})_3$, Merck) and cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, Fluka) were used as starting materials. The starting fine gibbsite has an average particle size of 13 μm and is denoted as FG-13 μm . After milling of 100 g of fine gibbsite in an attrition mill for 24 h, the particle size of the fine gibbsite was reduced to 0.6 μm and is denoted as FG-0.6 μm [25]. The solid-state reaction between fine gibbsite and cobalt chloride took place at 450, 550, and 650°C with a Co:Al molar ratio 1:6. Firstly, a certain amount of fine gibbsite and cobalt chloride hexahydrate were mixed in an agate mortar. Secondly, the mixed materials were dried in oven at 110°C overnight. Finally, the mixtures were calcined in a tube furnace in an air flow (95 ml/min) by heating to a desired temperature (450, 550, and 650°C) at a rate of 10°C/min and held at that temperature for 5 h. Then, the mixed materials were cooled down to room temperature in N_2 (75 ml/min).

2.2 Characterization

Particle size distribution was measured using a laser diffraction-based size analyzer (Malvern Mastersizer, reflective index 1.57). All the samples were done on deionized water as dispersant. Dispersion and deagglomeration of particles were ensured by ultrasonic treatment before measurement. XRD was performed to determine the bulk phase of particles by SIEMENS D 5000 X-ray diffractometer connected with a computer with Diffract ZT version 3.3 programs for fully control of the XRD analyzer. The experiments were carried out by using $\text{Cu K}\alpha$ radiation with Ni filter in the 2θ range of 10-80 degrees resolution 0.04°. The crystallite size was estimated from line broadening according to the Scherrer's equation and α -alumina ($\alpha\text{-Al}_2\text{O}_3$) as an external standard. The decomposition of cobalt chloride and fine gibbsite and CoAl_2O_4 formation was studied by TG/DTA using an SDT Analyzer Model Q600 from TA Instruments, USA from room temperature to 1000°C at a heating rate of 10°C/min in air. The chemical state of Co and surface elemental composition were determined by XPS analysis using an AMICUS spectrometer equipped with a $\text{MgK}\alpha$ X-ray radiation. For a typical analysis, the source was operated at voltage of 15 kV and current of 12 mA. The pressure in the analysis chamber was less than 10^{-5} Pa. The AMICUS system is computer controlled using the AMICUS "VISION 2" software. The optical properties of CoAl_2O_4 particles were studied by UV-Vis

analysis using a Perkin Elmer Lambda 650 spectrophotometer. The diffuse absorption spectra were recorded in the wavelength range 200–900 nm with the step size for the scan was 1 nm. BaSO₄ was used as a blank for the measurement. The particles morphology was obtained using a JEOL JSM-35CF SEM operating at 20 kV and JEOL JEM 2010 TEM operating at 200 kV.

3. Results and Discussion

The median particle sizes (d_{50}) of **fine gibbsite** used as starting materials for producing CoAl₂O₄ in this study were determined by a laser diffraction-based size analyzer to be 0.6 and 13 μ m. **Figure 1** shows the XRD patterns of **fine gibbsite samples** with different particle sizes. The intensities of the XRD peaks decreased and the peaks became wider as the average particle size of gibbsite decreased from 13 μ m (FG-13) to 0.6 μ m (FG-0.6). The XRD patterns of samples obtained from the solid-state reaction of cobalt chloride with FG-13 (Figure 2(A)), and FG-0.6 (Figure 2(B)) at various calcination temperatures are shown in **Figure 2**. The XRD peaks at 2θ degrees = 31.3°, 36.8°, 44.9°, 59.3°, and 65.3° were observed and could be assigned to either CoAl₂O₄ or Co₃O₄ because their peak positions are almost identical [26]. CoAl₂O₄ and Co₃O₄ have the same spinel cubic (Fd3m) crystallographic structure with slightly difference in the lattice constant ($a = 8.111$ for CoAl₂O₄ and $a = 8.0885$ for Co₃O₄). Therefore they have a similar peak pattern and the positions of peak are nearly same. The transition alumina phase was also found at $2\theta = 68^\circ$ in some samples. However, the relatively low intensity and broad XRD patterns suggest that crystallinity of the samples was not very good and/or the average crystallite size may be very small. The peak detected at $2\theta = 13^\circ$ corresponded to an impurity peak. **Figure 3** shows the SEM images of CoAl₂O₄ nanoparticles synthesized via the solid-state reaction between cobalt chloride and FG-13 and FG-0.6 at 650°C. Agglomeration of fine particles forming large irregular particle was observed. However, there is inappreciable change in morphology after calcination at different temperatures.

Figure 4(a) shows the TG/DTA curve of the cobalt chloride which included three endothermic peaks and one exothermic peak. The first and the second endothermic peaks with maxima at 100 and 175°C were accompanied by weight losses of 1.79 and 12.92%, respectively. These peaks corresponded to the loss of water. The exothermic peak at 708°C, which was accompanied by a 48.44% loss in weight,

corresponded to the loss of chloride and the subsequent formation of Co_3O_4 . Finally, the last endothermic peak at 920°C , which was accompanied by a 50.49% loss in weight, corresponded to a small oxygen loss and the conversion of Co_3O_4 into CoO [27]. **Figure 4(b) and 4(c)** illustrate the TG/DTA curves of a mechanical mixture of cobalt chloride and FG-13 and FG-0.6, respectively. The dehydration of a mechanical mixture between cobalt chloride with FG-13 (Figure 4(b)); includes a series of endothermic peaks. The first, second, and third of endothermic peaks were corresponding to the loss of water in the sample. The endothermic peak at around 300°C was the formation of boehmite. In addition, the endothermic peak at around 500°C indicated the formation of cobalt aluminate. It is interesting that the exothermic peak at around 708°C corresponding to **chloride elimination** disappeared and the formation of CoAl_2O_4 occurred at much lower temperature. It is suggested that in the presence of gibbsite, cobalt chloride was decomposed easier probably due to the hydrolysis reaction by water dehydrated from gibbsite. Moreover, a decrease of gibbsite particle size from $13\ \mu\text{m}$ to $0.6\ \mu\text{m}$, the series of endothermic peaks decreased and the endothermic peaks at around 230 and 500°C disappeared (comparing to Figure 3(b) and 3(c)). Such results suggest that the dehydration of a mechanical mixture between gibbsite and cobalt chloride was accelerated when the particle size of gibbsite was decreased. As a consequence, **cobalt aluminate** was formed at lower calcination temperature. The images of synthesized CoAl_2O_4 nanoparticles are shown in **Figure 5**. Bright blue color was clearly observed for the FG-13 and FG-0.6 calcined at 650°C and FG-0.6 calcined at 550°C , indicating the formation of CoAl_2O_4 structure.

The XPS analyses were carried out to examine **surface species** on the samples. The samples were analyzed in the Co 2p, Al 2s, and O 1s binding energy regions. The binding energy, the atomic concentration, and the FWHM of Co $2p_{3/2}$ and Al 2s are given in **Table 1**. According to the literature [20, 28], cobalt in an oxide state (Co $2p_{3/2}$ in Co_3O_4) exhibited lower binding energy ($780.0\ \text{eV}$) than that in CoAl_2O_4 ($781.9\ \text{eV}$). The XPS results confirm that the samples prepared by solid-state reaction between cobalt chloride and FG-13 calcined at 650°C and FG-0.6 calcined at 550°C were CoAl_2O_4 which were in good agreement with the blue color observed in Figure 5. Moreover, the relative amount of Co^{2+} ions in tetrahedral sites was found to increase with increasing calcination temperature. Decreasing the particles size of fine gibbsite probably increased the rate of diffusion step during a solid-state reaction [24], thus the CoAl_2O_4 was formed at lower calcination temperature for FG-0.6 than FG-13. **The average crystallite sizes of synthesized CoAl_2O_4 were**

calculated from the full width at half maximum of the XRD peak at $2\theta = 36.8^\circ$ using the Scherrer's equation and are reported in **Table 1** (d_{XRD}). The TEM images of synthesized CoAl_2O_4 are shown in **Figure 6**. The TEM results clearly show that the synthesized CoAl_2O_4 consisted of very fine particles with average size below 10 nm which are in good agreement with the average crystallite size calculated from the Scherrer's equation.

UV-Vis spectroscopy was carried out in order to study the correlation between cation distribution and the optical properties of synthesized CoAl_2O_4 nanoparticles. **Figure 7** shows the absorption spectra of the CoAl_2O_4 particles obtained from the solid-state reaction of cobalt chloride and FG-13 and FG-0.6 at various calcination temperatures. The UV-Vis results were consistent to the XPS analyses. The Co^{2+} in a tetrahedral ligand field is responsible for its blue color. It has been reported that the coloration of CoAl_2O_4 was strongly dependent on the temperature of the heat treatment and on the stoichiometry of Co and Al in the $\text{Co}_{3-x}\text{Al}_x\text{O}_4$ sample with the brightest blue coloration was obtained for $S = 2.25$ [16]. The intense absorption peak at around 600 nm for both of the prepared CoAl_2O_4 particles are the characteristic of Co^{2+} ions in the tetrahedral sites in crystalline materials [9]. From the UV-Vis spectra of the prepared CoAl_2O_4 particles in Figure 7, a triple band were observed at around 540–630 nm, attributing to the spin-allowed [$^4\text{A}_2(\text{F}) \rightarrow ^4\text{T}_1(\text{P})$] transition. This triple band can be attributed to a Jahn–Teller distortion of the tetrahedral structure [29]. It was found that the intensity of this triple band decreased with decreasing particles size of the starting fine gibbsite for a given calcination temperature (i.e., at 650°C). According to the XPS results, the atomic concentration of Co/Al increased with decreasing particles size of the starting fine gibbsite. It has been also reported that the intensity of this triple band decreased as the S value was increased, and might be probably due to the formation of white Al_2O_3 from excess Al in the samples, lowering the intensity of color although the S values were larger than 2.25 and remained blue [16]. The results in this study also suggest that reduction of particle size of the starting material could have an influence on the band shift. However, further detailed study is necessary to confirm whether the blue shift is because of the reduction of particle size [27-30].

4. Conclusions

Nanocrystalline CoAl_2O_4 particles were successfully synthesized at low temperature by solid-state reaction using calcination of the mechanical mixture between fine gibbsite and cobalt chloride. The particle sizes of the starting fine gibbsite were 0.6 and 13 μm and the calcination temperature was varied in the range of 450-650°C. The XRD and XPS results revealed that the crystallization of CoAl_2O_4 from the mixture between cobalt chloride and FG-13 and FG-0.6 occurred at 650°C and 550°C, respectively. The reduction of the starting particle size of fine gibbsite resulted in the lower crystallization temperature of CoAl_2O_4 formation due to the increasing of contact area between reacting particles. However, increasing of calcination temperature promoted the insertion amounts of Co^{2+} in alumina matrix in CoAl_2O_4 structure, which resulted in the brighter blue particles and increasing of UV spectra band.

Acknowledgement

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Table 1 The crystallite size and XPS results of the CoAl_2O_4 particles obtained via solid-state reaction of fine gibbsite and cobalt chloride.

Samples	d_{XRD} (nm)	Co(II) $2p_{3/2}$		Al 2s		Atomic Conc%	
		B.E. (eV)	FWHM	B.E. (eV)	FWHM	Al/O	Co/Al
FG-13-650°C	6	781.9	2.819	119.1	2.828	0.50	0.032
FG-0.6-550°C	6	781.5	3.223	118.6	2.772	0.50	0.050
FG-0.6-650°C	6	782.1	3.385	119.2	2.678	0.48	0.053
^a Co_3O_4		780.0 ± 0.7					
^a CoAl_2O_4		781.9 ± 0.5					

^a ref [20, 27]

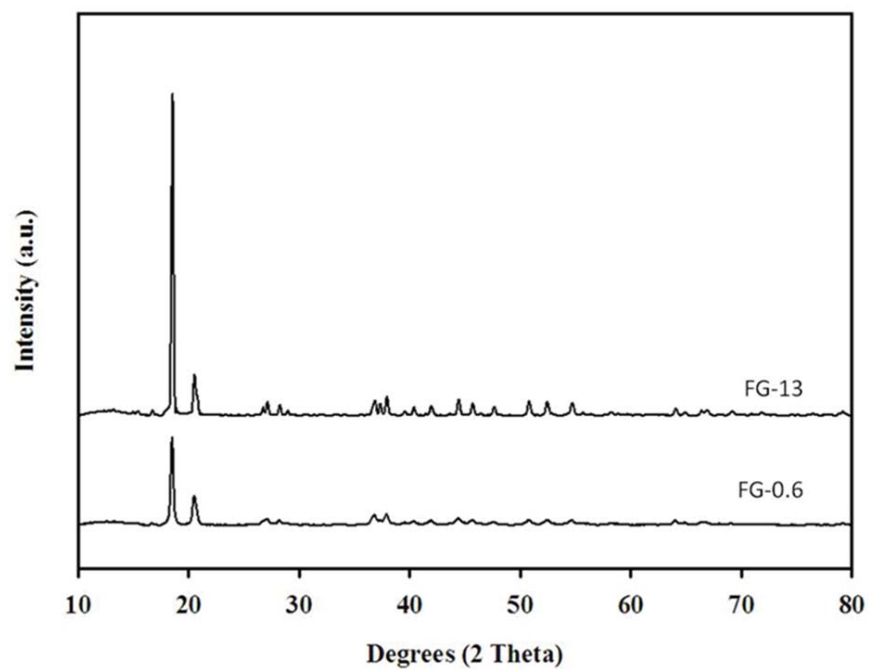


Figure 1 The XRD patterns of fine gibbsite (13 μm and 0.6 μm).

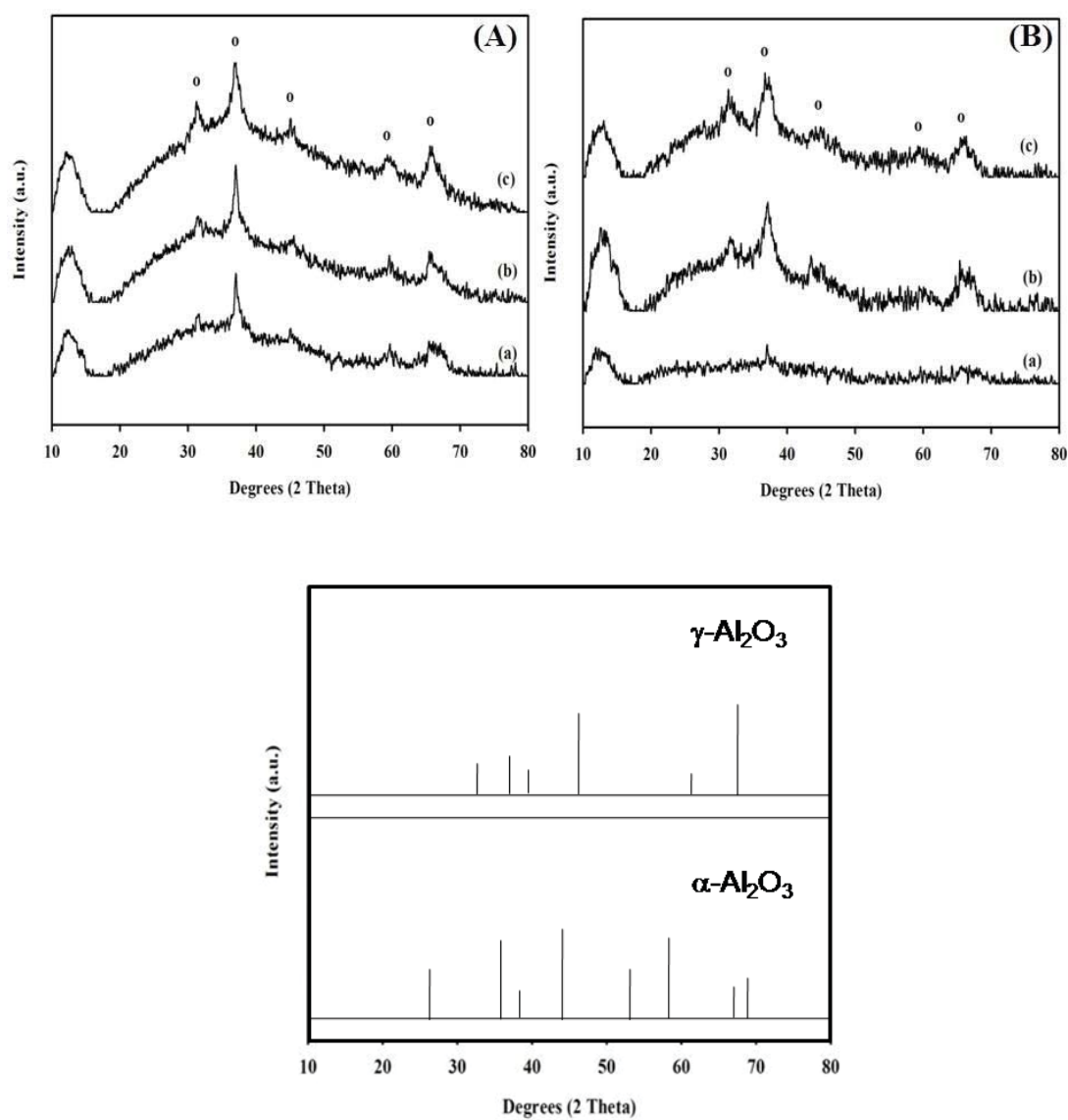


Figure 2 The XRD patterns of the CoAl₂O₄ nanoparticles synthesized via the solid-state reaction between cobalt chloride and FG-13 (A) and FG-0.6 (B), after calcination at various temperatures: 450°C (a), 550°C (b), 650°C (c); o = CoAl₂O₄.

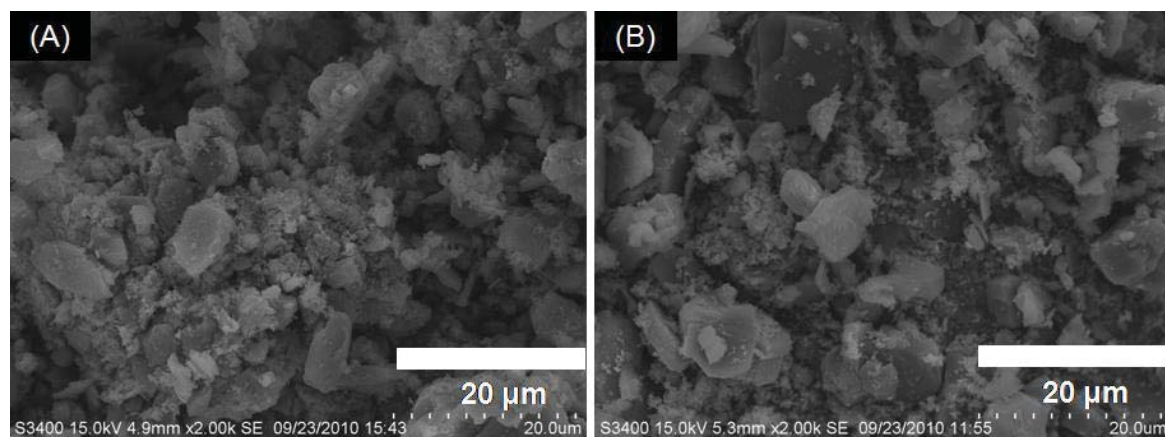


Figure 3 SEM images of the CoAl_2O_4 nanoparticles synthesized via the solid-state reaction between cobalt chloride and FG-13 (A), FG-0.6 (B) at 650°C .

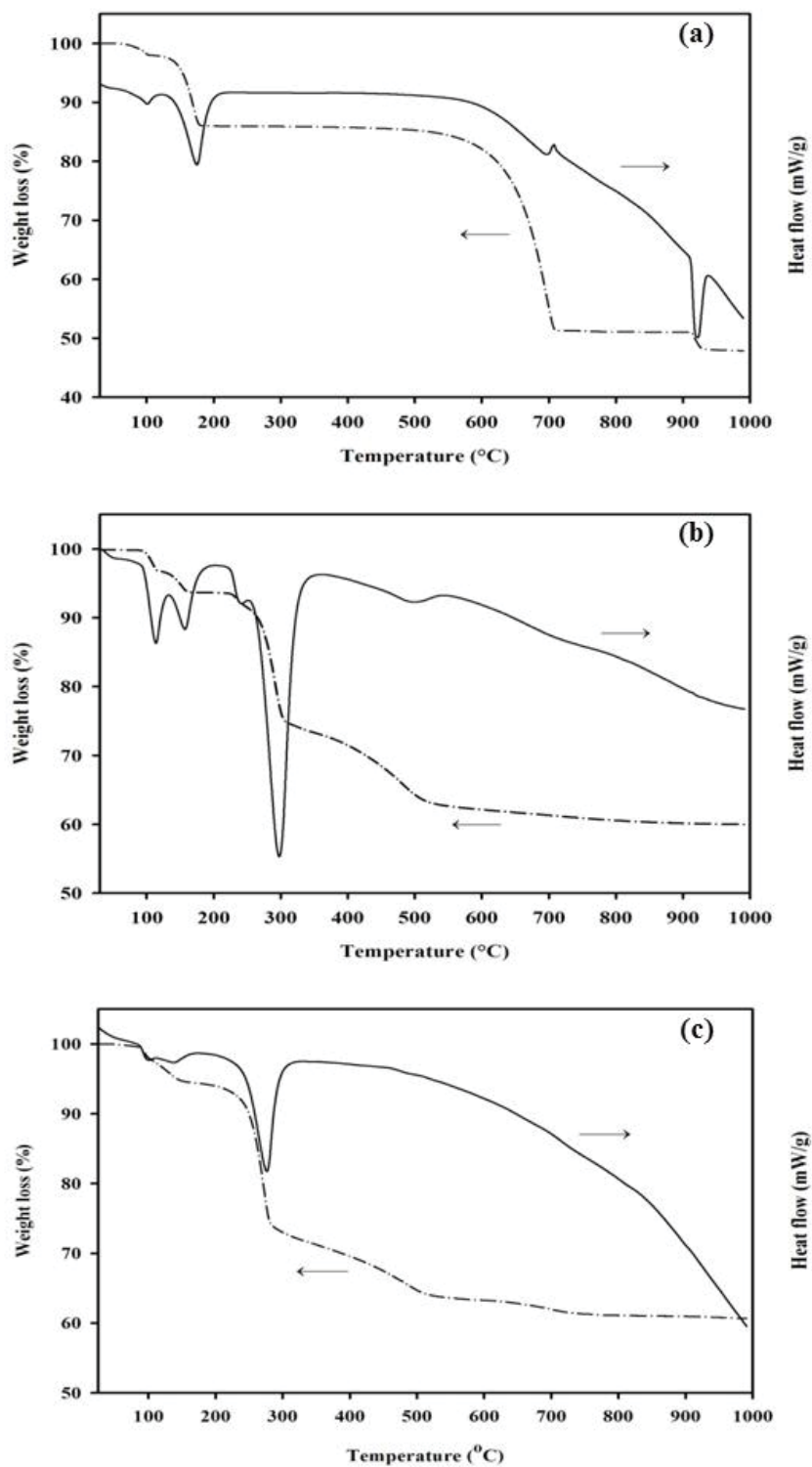


Figure 4 The TG/DTA curves of samples: bulk cobalt chloride (a), a mechanical mixture of cobalt chloride and FG-13 (b), and a mixture of cobalt chloride and FG-0.6 (c).



Figure 5 The images of the CoAl_2O_4 nanoparticles synthesized via the solid-state reaction between cobalt chloride and FG-13 (left-hand side) and FG-0.6 (right-hand side) after calcination at various temperatures: 450°C (a), 550 °C (b), and 650°C (c).

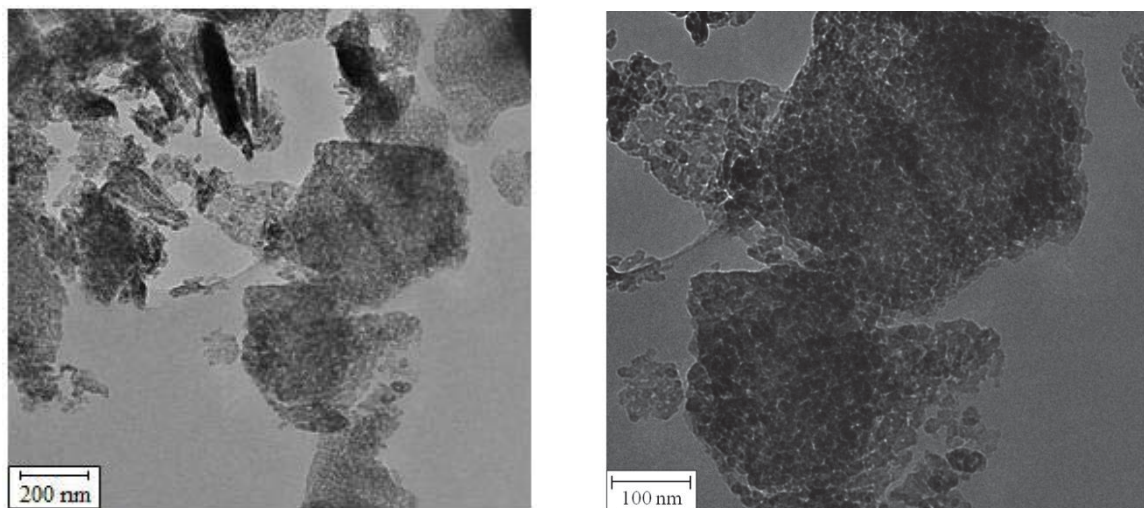


Figure 6 TEM images of the synthesized CoAl_2O_4 nanoparticles (FG-0.6 calcined at 650°C)

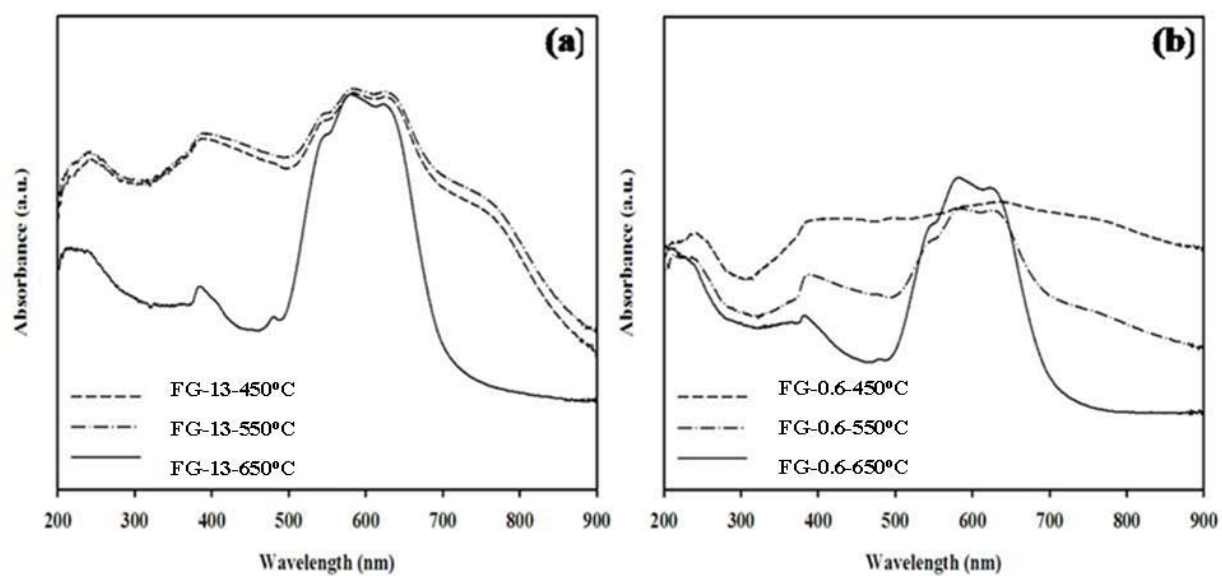


Figure 7 Absorption spectra in the wavelength range 200–900 nm of the CoAl_2O_4 nanoparticles synthesized via the solid-state reaction between cobalt chloride and FG-13 (a) calcined at various temperatures and (b) the solid-state reaction of cobalt chloride and FG-0.6 calcined at various temperatures.

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เมษายน 2554

เรื่อง ขอม้วนผันการส่งเอกสารประกอบคำขอรับสิทธิบัตร ครั้งที่ 1

1101000535

เรียน ผู้อำนวยการสำนักสิทธิบัตร

ด้วยสถาบันทรัพย์สินทางปัญญาแห่งจุฬาลงกรณ์มหาวิทยาลัยได้รับมอบหมายจากจุฬาลงกรณ์มหาวิทยาลัย สำนักงานคณะกรรมการการอุดมศึกษา และสำนักงานกองทุนสนับสนุนการวิจัย ให้ดำเนินการยื่นคำขอรับสิทธิบัตร เรื่อง “กรรมวิธีการเตรียมตัวเร่งปฏิกิริยาทั้งสแตบับตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยออกไซด์ของโลหะทรานสิชันหมู่ IIB เพื่อนำไปใช้เป็นตัวเร่งปฏิกิริยาในปฏิกิริยาเอสเตอร์ริฟิเคชัน” โดยมีข้าพเจ้านายมงคล แก้วมหา ตัวแทนสิทธิบัตร เลขที่ 1453 เป็นผู้ดำเนินการ ซึ่งขณะนี้อยู่ระหว่างดำเนินการให้ผู้ที่เกี่ยวข้องลงนามในสัญญาโอนสิทธิในการขอรับสิทธิบัตร และหนังสือมอบอำนาจ ซึ่งจำเป็นที่จะต้องใช้เวลาหนึ่งในการดำเนินการ แต่เนื่องจากการประดิษฐ์นี้ ทางผู้ประดิษฐ์มีความประสงค์ที่จะเผยแพร่ผลงานวิจัย ซึ่งหากมีการนำไปเผยแพร่ผลงานก่อนที่จะได้มีการยื่นคำขอรับสิทธิบัตร ข้าพเจ้าเกรงว่าจะมีผลต่อการพิจารณารับจดทะเบียนของคำขอรับสิทธิบัตรฉบับนี้ได้

ด้วยเหตุผลดังกล่าวข้างต้น ข้าพเจ้าจึงเรียนมาเพื่อโปรดพิจารณาอนุมัติขอม้วนผันการยื่นเอกสารประกอบคำขอรับสิทธิบัตรพร้อมกับคำขอรับสิทธิบัตรด้วย จักขอบพระคุณยิ่ง

ขอแสดงความนับถือ

มงคล แก้วมหา

(นายมงคล แก้วมหา)

ผู้รับมอบอำนาจ

ตัวแทนสิทธิบัตร เลขที่ 1453

สำเนา

แบบ สป/สผ/อสป/001-ก

หน้า 1 ของจำนวน 3 หน้า



คำขอรับสิทธิบัตร/อนุสิทธิบัตร

- ☒ การประดิษฐ์
☐ การออกแบบผลิตภัณฑ์
☐ อนุสิทธิบัตร

ข้าพเจ้าผู้ลงลายมือชื่อในคำขอรับสิทธิบัตร/อนุสิทธิบัตรนี้
ขอรับสิทธิบัตร/อนุสิทธิบัตร ตามพระราชบัญญัติสิทธิบัตร พ.ศ. 2522
แก้ไขเพิ่มเติมโดยพระราชบัญญัติสิทธิบัตร (ฉบับที่ 2) พ.ศ. 2535 และ
พระราชบัญญัติสิทธิบัตร (ฉบับที่ 3) พ.ศ. 2542

สำหรับเจ้าหน้าที่

วันรับคำขอ 12/01/2561 เลขที่คำขอ
วันยื่นคำขอ 1101000535

สัญลักษณ์จำแนกการประดิษฐ์ระหว่างประเทศ

ใช้กับแบบผลิตภัณฑ์
ประเภทผลิตภัณฑ์

วันประกาศโฆษณา

เลขที่ประกาศโฆษณา

วันออกสิทธิบัตร/อนุสิทธิบัตร

เลขที่สิทธิบัตร/อนุสิทธิบัตร

ลายมือชื่อเจ้าหน้าที่

1. ชื่อที่แสดงถึงการประดิษฐ์/การออกแบบผลิตภัณฑ์

กรรมวิธีการเตรียมตัวเร่งปฏิกิริยาทั้งสเดนบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยออกไซด์ของโลหะทรานสิชันหมู่ IIIB
เพื่อนำไปใช้เป็นตัวเร่งปฏิกิริยาในปฏิกิริยาเอสเทอร์รีฟิเคชัน

2. คำขอรับสิทธิบัตรการออกแบบผลิตภัณฑ์นี้เป็นคำขอสำหรับแบบผลิตภัณฑ์อย่างเดียวกันและเป็นคำขอลำดับที่

ในจำนวน คำขอ ที่ยื่นในคราวเดียวกัน

3. ผู้ขอรับสิทธิบัตร/อนุสิทธิบัตร และที่อยู่ (เลขที่ ถนน ประเทศ)
คูที่หน้า 3

3.1 สัญชาติ

3.2 โทรศัพท์

3.3 โทรสาร

3.4 อีเมลล์

4. สิทธิในการขอรับสิทธิบัตร/อนุสิทธิบัตร

☐ ผู้ประดิษฐ์/ผู้ออกแบบ ☒ ผู้รับโอน ☐ ผู้ขอรับสิทธิโดยเหตุอื่น

5. ตัวแทน(ถ้ามี)/ที่อยู่ (เลขที่ ถนน จังหวัด รหัสไปรษณีย์)

นายมงคล แก้วมหา

สถาบันทรัพยากรพลังงานทางปัญญาแห่งจุฬาลงกรณ์มหาวิทยาลัย

อาคารจักรีสาขามูร์ ชั้น 12 ยูนิต 13 ถนนพญาไท แขวงปทุมวัน เขตปทุมวัน
กรุงเทพฯ 10330

5.1 ตัวแทนเลขที่ 1453

5.2 โทรศัพท์ 0-2160-5340-2

5.3 โทรสาร 0-2160-5343

5.4 อีเมลล์

6. ผู้ประดิษฐ์/ผู้ออกแบบผลิตภัณฑ์ และที่อยู่ (เลขที่ ถนน ประเทศ)

ศาสตราจารย์ ดร.ปิยะสาร ประเสริฐธรรม และ นางสาวเพียงพิศ วงศ์ฉัตรนิล

อยู่ที่ ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย ถนนพญาไท เขตปทุมวัน กรุงเทพฯ 10330

7. คำขอรับสิทธิบัตร/อนุสิทธิบัตรนี้แยกจากหรือเกี่ยวข้องกับคำขอเดิม

ผู้ขอรับสิทธิบัตร/อนุสิทธิบัตร ขอให้ถือว่าได้ยื่นคำขอรับสิทธิบัตร/อนุสิทธิบัตรนี้ ในวันเดียวกับคำขอรับสิทธิบัตร

เลขที่ วันยื่น เพราะคำขอรับสิทธิบัตร/อนุสิทธิบัตรนี้แยกจากหรือเกี่ยวข้องกับคำขอเดิมเพราะ

☐ คำขอเดิมมีการประดิษฐ์หลายอย่าง ☐ ถูกคัดค้านเนื่องจากผู้ขอไม่มีสิทธิ ☐ ขอเปลี่ยนแปลงประเภทของสิทธิ

หมายเหตุ: ในกรณีที่ไม้อาจระบุรายละเอียดได้ครบถ้วน ให้จัดทำเป็นเอกสารแนบท้ายแบบพิมพ์นี้โดยระบุหมายเลขกำกับข้อและหัวข้อที่แสดงรายละเอียด
เพิ่มเติมดังกล่าวด้วย

8.การยื่นคำขออนุญาตนำเข้า				
วันยื่นคำขอ	เลขที่คำขอ	ประเทศ	สัญลักษณ์จำแนกการ ประดิษฐ์ระหว่างประเทศ	สถานะคำขอ
8.1				
8.2				
8.3				
8.4 ☐ ผู้ขอรับสิทธิบัตร/อนุสิทธิบัตรขอสิทธิให้ถือว่าได้ยื่นคำขอนี้ในวันที่ได้ยื่นคำขอรับสิทธิบัตร/อนุสิทธิบัตรในต่างประเทศเป็นครั้งแรกโดย ☐ ได้ยื่นเอกสารหลักฐานพร้อมคำขอนี้ ☐ ขอขึ้นเอกสารหลักฐานหลังจากวันยื่นคำขอนี้				
9.การแสดงผลการประดิษฐ์ หรือการออกแบบผลิตภัณฑ์ ผู้ขอรับสิทธิบัตร/อนุสิทธิบัตรได้แสดงผลการประดิษฐ์ที่หน่วยงานของรัฐเป็นผู้จัด วันแสดง 27 มีนาคม 2551 วันเปิดงานแสดง 27 มีนาคม 2551 ผู้จัด สำนักงานกองทุนสนับสนุนการวิจัย				
10.การประดิษฐ์เกี่ยวกับจุลชีพ				
10.1 เลขทะเบียนฝากเก็บ		10.2 วันที่ฝากเก็บ		10.3 สถาบันฝากเก็บ/ประเทศ
11.ผู้ขอรับสิทธิบัตร/อนุสิทธิบัตร ขอขึ้นเอกสารภาษาต่างประเทศก่อนในวันยื่นคำขอนี้ และจะจัดยื่นคำขอรับสิทธิบัตร/อนุสิทธิบัตรนี้ที่จัดทำ เป็นภาษาไทยภายใน 90 วัน นับจากวันยื่นคำขอนี้ โดยขอขึ้นเป็นภาษา ☐ อังกฤษ ☐ ฝรั่งเศส ☐ เยอรมัน ☐ ญี่ปุ่น ☐ อื่นๆ				
12.ผู้ขอรับสิทธิบัตร/อนุสิทธิบัตร ขอให้อธิบดีประกาศโฆษณาคำขอรับสิทธิบัตร หรือรับจดทะเบียน และประกาศโฆษณาอนุสิทธิบัตรนี้ หลังจากวันที่ เดือน พ.ศ. ☐ ผู้ขอรับสิทธิบัตร/อนุสิทธิบัตรขอให้ใช้รูปเขียนหมายเลข ในการประกาศโฆษณา				
13.คำขอรับสิทธิบัตร/อนุสิทธิบัตรนี้ประกอบด้วย ก. แบบพิมพ์คำขอ 3 หน้า ข. รายละเอียดการประดิษฐ์ หรือคำพรรณนาแบบผลิตภัณฑ์ 7 หน้า ค. ข้อดีสิทธิ 3 หน้า ง. รูปเขียน รูป หน้า จ. ภาพแสดงแบบผลิตภัณฑ์ ☐ รูปเขียน รูป หน้า ☐ ภาพถ่าย รูป หน้า ฉ. บทสรุปการประดิษฐ์ 1 หน้า			14.เอกสารประกอบคำขอ ☐ เอกสารแสดงสิทธิในการขอรับสิทธิบัตร/อนุสิทธิบัตร ☐ หนังสือรับรองการแสดงผลการประดิษฐ์/การออกแบบ ผลิตภัณฑ์ ☐ หนังสือมอบอำนาจ ☐ เอกสารรายละเอียดเกี่ยวกับจุลชีพ ☐ เอกสารการขอนับวันยื่นคำขอในต่างประเทศเป็นวันยื่น คำขอในประเทศไทย ☐ เอกสารขอเปลี่ยนแปลงประเภทของสิทธิ ☐ เอกสารอื่น ๆ	
15. ข้าพเจ้าขอรับรองว่า ☒ การประดิษฐ์นี้ไม่เคยยื่นขอรับสิทธิบัตร/ อนุสิทธิบัตรมาก่อน ☐ การประดิษฐ์นี้ได้พัฒนาปรับปรุงมาจาก.....				
16.ลายมือชื่อ (☐ ผู้ขอรับสิทธิบัตร / อนุสิทธิบัตร: ☒ ตัวแทน) นายมงคล แก้วมหา มงคล แก้วมหา				

หมายเหตุ. บุคคลใดยื่นขอรับสิทธิบัตรการประดิษฐ์หรือการออกแบบผลิตภัณฑ์ หรืออนุสิทธิบัตร โดยการแสดงข้อความอันเป็นเท็จแก่พนักงานเจ้าหน้าที่ เพื่อให้
ได้ไปซึ่งสิทธิบัตรหรืออนุสิทธิบัตร ต้องระวางโทษจำคุกไม่เกินหกเดือน หรือปรับไม่เกินห้าพันบาท หรือทั้งจำทั้งปรับ

3. ผู้ขอรับสิทธิบัตร/อนุสิทธิบัตร และที่อยู่ (เลขที่ ถนน ประเทศ)

จุฬาลงกรณ์มหาวิทยาลัย

อยู่ที่ เลขที่ 254 ถนนพญาไท แขวงวังใหม่ เขตปทุมวัน กรุงเทพฯ 10330

3.1 สัญชาติ ไทย 3.2 โทรศัพท์ 0-2160-5340-2 3.3 โทรสาร 0-2160-5343

สำนักงานคณะกรรมการการอุดมศึกษา

อยู่ที่ เลขที่ 328 ถนนศรีอยุธยา เขตราชเทวี กรุงเทพฯ 10400

3.1 สัญชาติ ไทย 3.2 โทรศัพท์ 0-2610-5200 3.3 โทรสาร 0-2354-5524

สำนักงานกองทุนสนับสนุนการวิจัย

อยู่ที่ ชั้น 14 อาคาร เอส เอ็ม ทาวเวอร์ เลขที่ 979/17-21 ถนนพหลโยธิน แขวงสามเสนใน เขตพญาไท กรุงเทพฯ 10400

3.1 สัญชาติ ไทย 3.2 โทรศัพท์ 0-2278-8200 3.3 โทรสาร 0-2298-0476

รายละเอียดการประดิษฐ์

ชื่อที่แสดงถึงการประดิษฐ์

- กรรมวิธีการเตรียมตัวเร่งปฏิกิริยาทั้งสเดนบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยออกไซด์ของโลหะทรานสิชันหมู่ IIIB เพื่อนำไปใช้เป็นตัวเร่งปฏิกิริยาในปฏิกิริยา
- 5 เอสเทอร์รีฟเคชัน

ลักษณะและความมุ่งหมายของการประดิษฐ์

- การประดิษฐ์นี้เกี่ยวข้องกับกรรมวิธีการเตรียมตัวเร่งปฏิกิริยาเพื่อใช้ในปฏิกิริยาเอสเทอร์รีฟเคชัน โดยใช้เซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยออกไซด์ของโลหะทรานสิชันหมู่ IIIB เป็นตัวรองรับของตัวเร่งปฏิกิริยาทั้งสเดน ซึ่งมีขั้นตอนการเตรียมดังนี้
- 10 - การปรับปรุงตัวรองรับเซอร์โคเนียมไดออกไซด์ ซึ่งทำโดยวิธีการใดวิธีการหนึ่งดังต่อไปนี้คือ
- (1) โดยการเติมสารละลายของสารประกอบของโลหะทรานสิชันหมู่ IIIB ในขั้นตอนการเตรียมตัวรองรับเซอร์โคเนียมไดออกไซด์ หรือ
- (2) โดยการเติมสารละลายของสารประกอบของโลหะทรานสิชันหมู่ IIIB ลงบน
- 15 เซอร์โคเนียมไดออกไซด์
- การเตรียมตัวเร่งปฏิกิริยาทั้งสเดนบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยออกไซด์ของโลหะทรานสิชันหมู่ IIIB ทำโดยการเติมสารละลายของสารประกอบโลหะทั้งสเดนบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยออกไซด์ของโลหะทรานสิชันหมู่ IIIB จากนั้นตั้งทิ้งไว้ที่อุณหภูมิห้อง แล้วนำไปอบให้แห้ง หลังจากนั้นนำตะกอนที่แห้งสนิทไปผ่านขั้นตอนการ
- 20 เผาที่อุณหภูมิสูง
- ความมุ่งหมายของการประดิษฐ์นี้ เพื่อพัฒนาตัวเร่งปฏิกิริยาที่นำมาใช้ในปฏิกิริยาเอสเทอร์รีฟเคชันที่ให้ประสิทธิภาพสูงกว่าหรือดีกว่าตัวเร่งปฏิกิริยาที่ใช้อยู่ในปัจจุบัน

สาขาวิทยาการที่เกี่ยวข้องกับการประดิษฐ์

วิศวกรรมเคมีในส่วนที่เกี่ยวข้องกับกรรมวิธีการเตรียมตัวเร่งปฏิกิริยา

- 25 ภูมิหลังของศิลปะหรือวิทยาการที่เกี่ยวข้อง

ปัจจุบัน ตัวเร่งปฏิกิริยาในเชิงการค้าที่ใช้ในปฏิกิริยาเอสเทอร์รีฟเคชัน คือ ทั้งสเดนบนตัวรองรับเซอร์โคเนียมไดออกไซด์ ซึ่งมีประสิทธิภาพต่ำ ทั้งนี้ จากการตรวจสอบเอกสารสิทธิบัตรพบว่า ยังไม่มีสิทธิบัตรใดที่อ้างถึงการปรับปรุงตัวรองรับเซอร์โคเนียมไดออกไซด์ด้วยโลหะ

ทรานสิชันหมู่ IIIB แต่อย่างใด การปรับปรุงตัวรองรับด้วยโลหะทรานสิชันหมู่ IIIB ทำให้ตัวเร่งปฏิกิริยาตามการประดิษฐ์นี้มีความไวสูงกว่าตัวเร่งปฏิกิริยาที่ใช้ในปัจจุบัน

การเปิดเผยการประดิษฐ์โดยสมบูรณ์

การประดิษฐ์นี้เกี่ยวข้องกับกรรมวิธีการเตรียมตัวเร่งปฏิกิริยาเพื่อใช้ในปฏิกิริยาเอสเทอร์

- 5 ริฟิเคชัน โดยใช้เซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยออกไซด์ของโลหะทรานสิชันหมู่ IIIB เป็นตัวรองรับของตัวเร่งปฏิกิริยาทั้งสเดน ซึ่งมีขั้นตอนการเตรียมดังนี้

- การปรับปรุงตัวรองรับเซอร์โคเนียมไดออกไซด์ ซึ่งทำโดยวิธีการใดวิธีการหนึ่งดังต่อไปนี้คือ

- (1) โดยการเติมสารละลายของสารประกอบของโลหะทรานสิชันหมู่ IIIB ในขั้นตอน
10 การเตรียมตัวรองรับเซอร์โคเนียมไดออกไซด์ หลังจากการทำให้เกิดเป็นตะกอนแล้วจะทำการล้างตะกอนโดยการหมุนเหวี่ยง และนำตะกอนไปอบให้แห้ง ในบางกรณีอาจจะนำตะกอนที่แห้งแล้วไปเผาที่อุณหภูมิสูงเพื่อให้เกิดเป็นเซอร์โคเนียมไดออกไซด์ที่มีออกไซด์ของโลหะทรานสิชันหมู่ IIIB ปนอยู่ หรือ

- (2) โดยการเติมสารละลายของสารประกอบของโลหะทรานสิชันหมู่ IIIB ลงบน
15 เซอร์โคเนียมไดออกไซด์ จากนั้นอบให้แห้ง แล้วนำไปเผาที่อุณหภูมิสูง

- การเตรียมตัวเร่งปฏิกิริยาทั้งสเดนบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยออกไซด์ของโลหะทรานสิชันหมู่ IIIB ทำโดยการเติมสารละลายของสารประกอบโลหะทั้งสเดนบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยออกไซด์ของโลหะทรานสิชันหมู่ IIIB จากนั้น
20 ตั้งทิ้งไว้ที่อุณหภูมิห้อง เป็นเวลา 1-10 ชั่วโมง แต่ที่เหมาะสมคือ 5 ชั่วโมง แล้วนำไปอบให้แห้ง หลังจากนั้นนำตะกอนที่แห้งสนิทไปผ่านขั้นตอนการเผาที่อุณหภูมิสูง

โลหะทรานสิชันหมู่ IIIB ตามการประดิษฐ์นี้ ได้แก่ โลหะสแกนเดียม โลหะอิตเทรียม โลหะแลนทานัม และ โลหะแอกทีเนียม แต่ที่ควรใช้ ได้แก่ โลหะอิตเทรียม และ โลหะแลนทานัม

- สารประกอบของโลหะเซอร์โคเนียมตามการประดิษฐ์นี้ ได้แก่ เซอร์โคเนียมไนเตรด เซอร์โคเนียมคลอไรด์ เซอร์โคเนียมแอกไซด์ เซอร์โคเนียมโพรพอกไซด์ เซอร์โคเนียมไอโซโพรพอก
25 ไซด์ และ เซอร์โคเนียมออกซาลิไดด์ แต่ที่ควรใช้ คือ เซอร์โคเนียมออกซาลิไดด์

สารประกอบของโลหะแลนทานัมตามการประดิษฐ์นี้ ได้แก่ แลนทานัมคลอไรด์ แลนทานัมไนเตรด แลนทานัมแอกไซด์ และ แลนทานัมอะซิโตนอะซิโตน แต่ที่ควรใช้ คือ แลนทานัมไนเตรด

สารประกอบของโลหะอิตเรียมตามการประดิษฐ์นี้ ได้แก่ อิตเรียมคลอไรด์ อิตเรียมไนเตรต อิตเรียมแอซิเตด อิตเรียมอะซิไคอะซิโดเนด และ อิตเรียมอะซิเตรด แต่ที่ควรใช้ คือ อิตเรียมไนเตรด

- 5 สารประกอบของโลหะทั้งสเดนตามการประดิษฐ์นี้ ได้แก่ แอมโมเนียมเมทาทั้งสเดน แอมโมเนียมพาราทั้งสเดน ทั้งสเดนเฮกซะคลอไรด์ ทั้งสเดนเฮกซะคาร์บอนิล และ ทั้งสเดนเพนตะออกไซด์ แต่ที่ควรใช้ คือ ทั้งสเดนเฮกซะคลอไรด์

- 10 ในขั้นตอนการล้างโดยวิธีหมุนเหวี่ยง จำนวนครั้งที่เหมาะสมในการล้างอยู่ในช่วง 3-10 ครั้ง แต่ที่เหมาะสมที่สุดคือ 5 ครั้ง สำหรับความเร็วรอบที่เหมาะสมสำหรับการหมุนเหวี่ยงอยู่ในช่วง 1,000-5,000 รอบต่อนาที แต่ที่เหมาะสมที่สุดคือ 3,000 รอบต่อนาที และสำหรับเวลาที่เหมาะสมในการหมุนเหวี่ยงเพื่อเหวี่ยงแยกตะกอนอยู่ในช่วง 10-30 นาที แต่ที่เหมาะสมที่สุดคือ 15 นาที

ในขั้นตอนการเผาที่อุณหภูมิสูง ช่วงอุณหภูมิที่เหมาะสมอยู่ในช่วง 300-800 องศาเซลเซียส แต่ที่เหมาะสมที่สุดคือ 500 องศาเซลเซียส ส่วนช่วงเวลาที่เหมาะสมอยู่ในช่วง 2-6 ชั่วโมง แต่ที่เหมาะสมที่สุดคือ 3 ชั่วโมง

- 15 ในขั้นตอนการอบให้แห้ง ช่วงอุณหภูมิที่เหมาะสมอยู่ในช่วง 100-200 องศาเซลเซียส แต่ที่เหมาะสมที่สุดคือ 110 องศาเซลเซียส ส่วนช่วงเวลาที่เหมาะสมอยู่ในช่วง 6-30 ชั่วโมง แต่ที่เหมาะสมที่สุดคือ 20 ชั่วโมง

สำหรับตัวอย่างการเตรียมตัวเร่งปฏิกิริยาทั้งสเดนบนตัวรองรับเซอร์โคเนียมไดออกไซด์ และการทดสอบในปฏิกิริยาเอสเทอร์ริฟิเคชัน แสดงในตัวอย่างข้างล่างนี้ แต่ตัวอย่างเหล่านี้มิได้มีวัตถุประสงค์ที่จะจำกัดขอบเขตของการประดิษฐ์นี้แต่อย่างใด

20 ตัวอย่างที่ 1

- การเตรียมเซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยแลนทานัม ร้อยละ 0.1 โดยโมล ทำโดยเติมสารประกอบแลนทานัมไนเตรด จำนวน 2.8 กรัม ลงในสารเซอร์โคเนียมออกไซด์ (ร้อยละ 80 โดยน้ำหนักในสารละลายบิวทานอล) จำนวน 25 กรัม ละลายในสารละลาย 1.4-บิวเทนไดออล (ร้อยละ 90 โดยน้ำหนัก) จำนวน 100 มิลลิลิตร กวนให้สารละลายเป็นเนื้อเดียวกัน นำไปใส่ในเครื่องปฏิกรณ์ความดันสูง โดยเติมสารละลาย 1.4-บิวเทนไดออล จำนวน 30 มิลลิลิตร ในช่องว่างเครื่องปฏิกรณ์เพื่อทำปฏิกิริยาภายใต้ความดันของสารละลาย 1.4-บิวเทนไดออล ให้ความร้อนที่อุณหภูมิ 300 องศาเซลเซียส เป็นเวลา 2 ชั่วโมง เมื่ออุณหภูมิลดลงเท่ากับอุณหภูมิห้อง นำตะกอนที่ได้มาล้างโดยวิธีหมุนเหวี่ยงด้วยเมทานอล ล้างจำนวน 5 ครั้ง หมุนเหวี่ยงด้วยความเร็ว
- 25

รอบ 3,000 รอบต่อนาที เป็นเวลา 15 นาที นำตะกอนไปอบที่อุณหภูมิ 110 องศาเซลเซียส เป็นเวลา 12 ชั่วโมง จะได้ตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ถูกปรับปรุงด้วยออกไซด์ของโลหะแลนทานัม ร้อยละ 0.1

- การเตรียมตัวเร่งปฏิกิริยาทั้งสแตนร้อยละ 15 โดยนำหนักบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ถูกปรับปรุงด้วยออกไซด์ของโลหะแลนทานัม ร้อยละ 0.1 โดยการละลายสารทั้งสแตนเฮกซะคลอไรด์จำนวน 0.76 กรัม ด้วยน้ำบริสุทธิ์ และค่อยๆ หยดสารละลายทั้งสแตนเฮกซะคลอไรด์บนผงเซอร์โคเนียมไดออกไซด์ที่ถูกปรับปรุงจำนวน 2 กรัม ตั้งไว้ที่อุณหภูมิห้อง เป็นเวลา 6 ชั่วโมง หลังจากนั้นนำไปอบที่อุณหภูมิ 110 องศาเซลเซียส เป็นเวลา 12 ชั่วโมง ขั้นตอนสุดท้ายนำไปเผาภายใต้บรรยากาศของอากาศด้วยอัตราการไหล 100 ลูกบาศก์เซนติเมตรต่อนาที อุณหภูมิ 500 องศาเซลเซียสด้วยอัตรา 10 องศาเซลเซียสต่อนาที เป็นเวลา 3 ชั่วโมง จะได้ตัวเร่งปฏิกิริยาทั้งสแตนบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ถูกปรับปรุงด้วยออกไซด์ของโลหะแลนทานัม ร้อยละ 0.1

- การนำตัวเร่งปฏิกิริยาทั้งสแตนบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ถูกปรับปรุงมาทดสอบด้วยปฏิกิริยาเอสเทอร์รีฟิเคชัน ระหว่างกรดอะซิติกและเมทานอลเกินพอในอัตราส่วน 1 ต่อ 3 โดยโมล โดยซึ่งกรดอะซิติก 20 กรัม ลงในขวดสามคอขนาด 250 ลูกบาศก์เซนติเมตร เติมตัวเร่งปฏิกิริยาทั้งสแตนเซอร์โคเนียมไดออกไซด์ที่ถูกปรับปรุง 0.4 กรัม ให้ความร้อนคงที่ที่ 60 องศาเซลเซียสพร้อมกวนอย่างต่อเนื่อง เมื่อได้อุณหภูมิที่ต้องการเติมเมทานอลจำนวน 32.5 กรัม ทำปฏิกิริยาอย่างต่อเนื่องเป็นเวลา 6 ชั่วโมง ผลที่ได้แสดงดังตารางที่ 1

ตัวอย่างที่ 2

- การเตรียมเซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยแลนทานัม ร้อยละ 0.2 โดยโมล ทำเหมือนตัวอย่างที่ 1 แต่ทำการเติมสารประกอบแลนทานัมไนเตรต จำนวน 5.6 กรัม ลงในสารเซอร์โคเนียมออกไซด์ จะ ได้ตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ถูกปรับปรุงด้วยออกไซด์ของโลหะแลนทานัม ร้อยละ 0.2

- การเตรียมตัวเร่งปฏิกิริยาทั้งสแตนร้อยละ 15 โดยนำหนักบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ถูกปรับปรุงด้วยออกไซด์ของโลหะแลนทานัม ร้อยละ 0.2 และการทดสอบตัวเร่งปฏิกิริยาทำเหมือนตัวอย่างที่ 1 ผลการทดสอบที่ได้แสดงดังตารางที่ 1

ตัวอย่างที่ 3

- การเตรียมเซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยแลนทานัม ร้อยละ 0.3 โดยโมล ทำเหมือนตัวอย่างที่ 1 แต่ทำการเติมสารประกอบแลนทานัมไนเตรต จำนวน 8.5 กรัม ลงในสารเซอร์โคเนียมออกไซด์ จะ ได้ตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ถูกปรับปรุงด้วยออกไซด์ของโลหะแลนทานัม ร้อยละ 0.3

การเตรียมตัวเร่งปฏิกิริยาทั้งสแตนร้อยละ 15 โดยน้ำหนักบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ถูกปรับปรุงด้วยออกไซด์ของโลหะแลนทานัม ร้อยละ 0.3 และการทดสอบตัวเร่งปฏิกิริยาทำเหมือนตัวอย่างที่ 1 ผลการทดสอบที่ได้แสดงดังตารางที่ 1

ตัวอย่างที่ 4

- 5 การเตรียมเซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยอิตเทรียม ร้อยละ 0.1 โดยโมล ทำเหมือนตัวอย่างที่ 1 แต่ทำการเติมสารประกอบอิตเทรียมไนเตรต จำนวน 2.5 กรัม ลงในสารเซอร์โคเนียมออกไซด์บิวทอกไซด์ ก่อนละลายด้วยสารละลาย 1,4-บิวเทนไดออล จะได้ตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ถูกปรับปรุงด้วยออกไซด์ของโลหะอิตเทรียม ร้อยละ 0.1

- 10 การเตรียมตัวเร่งปฏิกิริยาทั้งสแตนร้อยละ 15 โดยน้ำหนักบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ถูกปรับปรุงด้วยออกไซด์ของโลหะอิตเทรียม ร้อยละ 0.1 และการทดสอบตัวเร่งปฏิกิริยาทำเหมือนตัวอย่างที่ 1 ผลการทดสอบที่ได้แสดงดังตารางที่ 1

ตัวอย่างที่ 5

- 15 การเตรียมเซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยอิตเทรียม ร้อยละ 0.2 โดยโมล ทำเหมือนตัวอย่างที่ 4 แต่ทำการเติมสารประกอบอิตเทรียมไนเตรต จำนวน 4.9 กรัม ลงในสารเซอร์โคเนียมออกไซด์บิวทอกไซด์ จะได้ตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ถูกปรับปรุงด้วยออกไซด์ของโลหะอิตเทรียมร้อยละ 0.2

การเตรียมตัวเร่งปฏิกิริยาทั้งสแตนร้อยละ 15 โดยน้ำหนักบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ถูกปรับปรุงด้วยออกไซด์ของโลหะอิตเทรียมร้อยละ 0.2 และการทดสอบตัวเร่งปฏิกิริยาทำเหมือนตัวอย่างที่ 1 ผลการทดสอบที่ได้แสดงดังตารางที่ 1

- 20 ตัวอย่างที่ 6

การเตรียมเซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยอิตเทรียม ร้อยละ 0.3 โดยโมล ทำเหมือนตัวอย่างที่ 4 แต่ทำการเติมสารประกอบอิตเทรียมไนเตรต จำนวน 5.9 กรัม ลงในสารเซอร์โคเนียมออกไซด์บิวทอกไซด์ จะได้ตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ถูกปรับปรุงด้วยออกไซด์ของโลหะอิตเทรียมร้อยละ 0.3

- 25 การเตรียมตัวเร่งปฏิกิริยาทั้งสแตนร้อยละ 15 โดยน้ำหนักบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ถูกปรับปรุงด้วยออกไซด์ของโลหะอิตเทรียมร้อยละ 0.3 และการทดสอบตัวเร่งปฏิกิริยาทำเหมือนตัวอย่างที่ 1 ผลการทดสอบที่ได้แสดงดังตารางที่ 1

ตัวอย่างเปรียบเทียบที่ 1

การเตรียมตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ไม่ได้ปรับปรุง ทำเหมือนตัวอย่างที่ 1 ยกเว้นการเติมสารประกอบแลนทานัมไนเตรด จะได้เซอร์โคเนียมไดออกไซด์ลักษณะผงละเอียดสีขาว

- 5 การเตรียมตัวเร่งปฏิกิริยาทั้งสแตนร้อยละ 15 โดยนำนักบนตัวรองรับเซอร์โคเนียมไดออกไซด์ และการทดสอบตัวเร่งปฏิกิริยาทำเหมือนตัวอย่างที่ 1 ผลการทดสอบที่ได้แสดงดังตารางที่ 1

ตารางที่ 1

ประเภท	ตัวเร่งปฏิกิริยา	ปริมาณ H^+ ($\mu\text{mol/g catalyst}$) ¹	ร้อยละการเกิดปฏิกิริยา ที่เวลา 6 ชั่วโมง
ตัวอย่างที่ 1	ร้อยละ 15 โดยน้ำหนักทั้งสแตนบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยออกไซด์ของแลนทานัม ร้อยละ 0.1	373	73
ตัวอย่างที่ 2	ร้อยละ 15 โดยน้ำหนักทั้งสแตนบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยออกไซด์ของแลนทานัม ร้อยละ 0.2	418	75
ตัวอย่างที่ 3	ร้อยละ 15 โดยน้ำหนักทั้งสแตนบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยออกไซด์ของแลนทานัม ร้อยละ 0.3	358	69
ตัวอย่างที่ 4	ร้อยละ 15 โดยน้ำหนักทั้งสแตนบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยออกไซด์ของอิตเทรียม ร้อยละ 0.1	251	67

ประเภท	ตัวเร่งปฏิกิริยา	ปริมาณ H^+ ($\mu\text{mol/g catalyst}$) ¹	ร้อยละการเกิดปฏิกิริยา ที่เวลา 6 ชั่วโมง
ตัวอย่างที่ 5	ร้อยละ 15 โดยน้ำหนัก ทั้งสแตนบนตัวรองรับ เซอร์โคเนียมไดออกไซด์ ที่ปรับปรุงด้วยออกไซด์ของ อิทเทรียม ร้อยละ 0.2	298	69
ตัวอย่างที่ 6	ร้อยละ 15 โดยน้ำหนัก ทั้งสแตนบนตัวรองรับ เซอร์โคเนียมไดออกไซด์ ที่ปรับปรุงด้วยออกไซด์ของ อิทเทรียม ร้อยละ 0.3	368	71
ตัวอย่าง เปรียบเทียบ ที่ 1	ร้อยละ 15 โดยน้ำหนัก ทั้งสแตนบนตัวรองรับ เซอร์โคเนียมไดออกไซด์ ที่ไม่ได้ปรับปรุง	112	55

¹ ทดสอบปริมาณ H^+ ด้วยการไตเตรตโดยใช้เทคนิคการแลกเปลี่ยนไอออนกรด-เบส

ดังแสดงในตารางที่ 1 ปฏิกิริยาเอสเทอร์ริฟิเคชันระหว่างกรดอะซิติกกับเมทานอล โดยตัวเร่งปฏิกิริยาที่ประดษฐ์ขึ้นดังตัวอย่างที่ 1 ถึง ตัวอย่างที่ 6 มีความเป็นกรดและให้ผลการทดสอบที่ดีกว่าใช้ตัวเร่งปฏิกิริยาทั้งสแตนบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ไม่ได้รับการปรับปรุง

5 ดังตัวอย่างเปรียบเทียบที่ 1

วิธีการในการประดษฐ์ที่ดีที่สุด

เหมือนกับที่ได้กล่าวมาแล้วในหัวข้อการเปิดเผยการประดษฐ์โดยสมบูรณ์

ข้อถือสิทธิ

1. กรรมวิธีการเตรียมตัวเร่งปฏิกิริยาทั้งสแตนบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยออกไซด์ของโลหะทรานซิชันหมู่ IIIB เพื่อนำไปใช้เป็นตัวเร่งปฏิกิริยาในปฏิกิริยาเอสเทอร์ฟิเคชัน ซึ่งมีขั้นตอนการเตรียมดังนี้
- 5 - การปรับปรุงตัวรองรับเซอร์โคเนียมไดออกไซด์ ซึ่งทำโดยวิธีการใดวิธีการหนึ่งดังต่อไปนี้คือ
 - (1) โดยการเติมสารละลายของสารประกอบของโลหะทรานซิชันหมู่ IIIB ในขั้นตอนการเตรียมตัวรองรับเซอร์โคเนียมไดออกไซด์ หลังจากการทำให้เกิดเป็นตะกอนแล้วจะทำการล้างตะกอนโดยการหมุนเหวี่ยง และนำตะกอนไปอบให้แห้ง
 - 10 (2) โดยการเติมสารละลายของสารประกอบของโลหะทรานซิชันหมู่ IIIB ลงบนเซอร์โคเนียมไดออกไซด์ จากนั้นอบให้แห้ง แล้วนำไปเผา
 - การเตรียมตัวเร่งปฏิกิริยาทั้งสแตนบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยออกไซด์ของโลหะทรานซิชันหมู่ IIIB ทำโดยการเติมสารละลายของสารประกอบโลหะทั้งสแตนบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยออกไซด์ของโลหะทรานซิชันหมู่ IIIB จากนั้นตั้งทิ้งไว้ที่อุณหภูมิห้อง แล้วนำไปอบให้แห้ง หลังจากนั้นนำตะกอนที่แห้งไปผ่านขั้นตอนการเผา
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2. กรรมวิธีตามข้อถือสิทธิ 1 ที่ซึ่งโลหะทรานซิชันหมู่ IIIB ตามที่กล่าวแล้ว ได้แก่ โลหะสแกนเดียม โลหะอิตเทรียม โลหะแลนทานัม และ โลหะแอกทีเนียม
3. กรรมวิธีตามข้อถือสิทธิ 1 ที่ซึ่งโลหะทรานซิชันหมู่ IIIB ตามที่กล่าวแล้ว ได้แก่ โลหะแลนทานัม และ โลหะอิตเทรียม
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4. กรรมวิธีตามข้อถือสิทธิ 2 หรือ 3 ที่ซึ่งสารประกอบของโลหะแลนทานัมตามที่กล่าวแล้วเลือกจากกลุ่มที่ประกอบด้วย แลนทานัมคลอไรด์ แลนทานัมไนเตรด แลนทานัมแอกซิเดต และ แลนทานัมอะซิโตนอะซิโตน
5. กรรมวิธีตามข้อถือสิทธิ 2 หรือ 3 ที่ซึ่งสารประกอบของโลหะแลนทานัมตามที่กล่าวแล้วเลือกจาก แลนทานัมไนเตรด
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6. กรรมวิธีตามข้อถือสิทธิ 2 หรือ 3 ที่ซึ่งสารประกอบของโลหะอิตเทรียมตามที่กล่าวแล้วเลือกจากกลุ่มที่ประกอบด้วย อิตเทรียมคลอไรด์ อิตเทรียมไนเตรด อิตเทรียมแอกซิเดต และ อิตเทรียมอะซิโตนอะซิโตน
7. กรรมวิธีตามข้อถือสิทธิ 2 หรือ 3 ที่ซึ่งสารประกอบของโลหะอิตเทรียมตามที่กล่าวแล้วเลือกจาก อิตเทรียมไนเตรด
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8. กรรมวิธีตามข้อถ้อยสิทธิ 1 ที่ซึ่งสารประกอบของโลหะเซอร์โคเนียมตามที่กล่าวแล้วเลือกจากกลุ่มที่ประกอบด้วย เซอร์โคเนียมไนเตรด เซอร์โคเนียมคลอไรด์ เซอร์โคเนียมแอซิเตด เซอร์โคเนียมโพรพอกไซด์ เซอร์โคเนียมไอโซโพรพอกไซด์ และ เซอร์โคเนียมนอมัลบิวทอกไซด์
9. กรรมวิธีตามข้อถ้อยสิทธิ 1 ที่ซึ่งสารประกอบของโลหะเซอร์โคเนียมตามที่กล่าวแล้วเลือกจาก
5 เซอร์โคเนียมนอมัลบิวทอกไซด์
10. กรรมวิธีตามข้อถ้อยสิทธิ 1 ที่ซึ่งสารประกอบของโลหะทั้งสแตนตามที่กล่าวแล้วเลือกจากกลุ่มที่ประกอบด้วย แอมโมเนียมเมทาทั้งสแตน แอมโมเนียมพาราทั้งสแตน ทั้งสแตนเฮกซะคลอไรด์ ทั้งสแตนเฮกซะคาร์บอนิล และ ทั้งสแตนเพนตะออกไซด์
11. กรรมวิธีตามข้อถ้อยสิทธิ 1 ที่ซึ่งสารประกอบของโลหะทั้งสแตนตามที่กล่าวแล้วเลือกจาก
10 ทั้งสแตนเฮกซะคลอไรด์
12. กรรมวิธีตามข้อถ้อยสิทธิ 1 ที่ซึ่งจำนวนครั้งในการล้างตะกอนโดยวิธีหมุนเหวี่ยง คือ 3-10 ครั้ง
13. กรรมวิธีตามข้อถ้อยสิทธิ 1 ที่ซึ่งจำนวนครั้งในการล้างตะกอนโดยวิธีหมุนเหวี่ยง คือ 5 ครั้ง
14. กรรมวิธีตามข้อถ้อยสิทธิ 1 ที่ซึ่งความเร็วรอบสำหรับการหมุนเหวี่ยงอยู่ในช่วง 1,000-5,000 รอบต่อนาที
15. 15. กรรมวิธีตามข้อถ้อยสิทธิ 1 ที่ซึ่งความเร็วรอบสำหรับการหมุนเหวี่ยง คือ 3,000 รอบต่อนาที
16. กรรมวิธีตามข้อถ้อยสิทธิ 1 ที่ซึ่งระยะเวลาในการหมุนเหวี่ยงอยู่ในช่วง 10-30 นาที
17. กรรมวิธีตามข้อถ้อยสิทธิ 1 ที่ซึ่งระยะเวลาในการหมุนเหวี่ยง คือ 15 นาที
18. กรรมวิธีตามข้อถ้อยสิทธิ 1 ที่ซึ่งอุณหภูมิที่ใช้ในการเผาตะกอน คือ 300-800 องศาเซลเซียส
19. กรรมวิธีตามข้อถ้อยสิทธิ 1 ที่ซึ่งอุณหภูมิที่ใช้ในการเผาตะกอน คือ 500 องศาเซลเซียส
20. 20. กรรมวิธีตามข้อถ้อยสิทธิ 1 ที่ซึ่งระยะเวลาที่ใช้ในการเผาตะกอน คือ 2-6 ชั่วโมง
21. กรรมวิธีตามข้อถ้อยสิทธิ 1 ที่ซึ่งระยะเวลาที่ใช้ในการเผาตะกอน คือ 3 ชั่วโมง
22. กรรมวิธีตามข้อถ้อยสิทธิ 1 ที่ซึ่งอุณหภูมิที่ใช้ในการอบตะกอนให้แห้ง คือ 100-200 องศาเซลเซียส
23. กรรมวิธีตามข้อถ้อยสิทธิ 1 ที่ซึ่งอุณหภูมิที่ใช้ในการอบตะกอนให้แห้ง คือ 110 องศาเซลเซียส
25. 24. กรรมวิธีตามข้อถ้อยสิทธิ 1 ที่ซึ่งระยะเวลาที่ใช้ในการอบตะกอนให้แห้ง คือ 6-30 ชั่วโมง
25. กรรมวิธีตามข้อถ้อยสิทธิ 1 ที่ซึ่งระยะเวลาที่ใช้ในการอบตะกอนให้แห้ง คือ 20 ชั่วโมง
26. กรรมวิธีตามข้อถ้อยสิทธิ 1 ที่ซึ่งระยะเวลาที่ใช้ในการตั้งทิ้งไว้ที่อุณหภูมิห้อง คือ 1-10 ชั่วโมง
27. กรรมวิธีตามข้อถ้อยสิทธิ 1 ที่ซึ่งระยะเวลาที่ใช้ในการตั้งทิ้งไว้ที่อุณหภูมิห้อง คือ 5 ชั่วโมง
28. กรรมวิธีตามข้อถ้อยสิทธิ 1 ที่ซึ่งขั้นตอนการปรับปรุงตัวรองรับเซอร์โคเนียมไดออกไซด์โดยวิธี
30 ที่ 1 ยังประกอบด้วย ขั้นตอนการเผาตะกอนที่แห้ง
29. กรรมวิธีตามข้อถ้อยสิทธิ 28 ที่ซึ่งอุณหภูมิที่ใช้ในการเผาตะกอน คือ 300-800 องศาเซลเซียส
30. กรรมวิธีตามข้อถ้อยสิทธิ 28 ที่ซึ่งอุณหภูมิที่ใช้ในการเผาตะกอน คือ 500 องศาเซลเซียส

31. กรรมวิธีตามข้ออธิสัทธิ 28 ที่ซึ่งระยะเวลาที่ใช้ในการเผาคะกอน คือ 2-6 ชั่วโมง
32. กรรมวิธีตามข้ออธิสัทธิ 28 ที่ซึ่งระยะเวลาที่ใช้ในการเผาคะกอน คือ 3 ชั่วโมง

บทสรุปการประดิษฐ์

การประดิษฐ์นี้เกี่ยวข้องกับกรรมวิธีการเตรียมตัวเร่งปฏิกิริยาเพื่อใช้ในปฏิกิริยาเอสเทอร์ริฟิเคชัน โดยใช้เซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยออกไซด์ของโลหะทรานสิชันหมู่ IIIB เป็นตัวรองรับของตัวเร่งปฏิกิริยาทั้งสเดน ซึ่งมีขั้นตอนการเตรียมดังนี้

- 5 - การปรับปรุงตัวรองรับเซอร์โคเนียมไดออกไซด์ ซึ่งทำโดยวิธีการใดวิธีการหนึ่งดังต่อไปนี้คือ

(1) โดยการเติมสารละลายของสารประกอบของโลหะทรานสิชันหมู่ IIIB ในขั้นตอนการเตรียมตัวรองรับเซอร์โคเนียมไดออกไซด์ หรือ

- 10 (2) โดยการเติมสารละลายของสารประกอบของโลหะทรานสิชันหมู่ IIIB ลงบนเซอร์โคเนียมไดออกไซด์

- การเตรียมตัวเร่งปฏิกิริยาทั้งสเดนบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยออกไซด์ของโลหะทรานสิชันหมู่ IIIB ทำโดยการเติมสารละลายของสารประกอบโลหะทั้งสเดนบนตัวรองรับเซอร์โคเนียมไดออกไซด์ที่ปรับปรุงด้วยออกไซด์ของโลหะทรานสิชันหมู่ IIIB จากนั้นตั้งทิ้งไว้ที่อุณหภูมิห้อง แล้วนำไปอบให้แห้ง หลังจากนั้นนำตะกอนที่แห้งสนิทไปผ่านขั้นตอนการ

- 15 เผาที่อุณหภูมิสูง