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THESIS

PRELIMINARY STUDY OF Pd/CeO_2 DERIVED FROM CERIUM COMPLEXES AS SOLID SUPPORT CATALYSTS FOR HYDROGENATION REACTION IN A MICRO-REACTOR

WORAWAT WATTANATHANA

A Thesis Submitted in Partial Fulfillment of
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This work was studied on the Pd/CeO_2 used as catalyst for hydrogenation reaction in micro-reactor. A simple cerium complex for CeO_2 was prepared from cerium nitrate and triethanolamine in 1-propanol. The feasible structures of cerium complexes as four-coordinate and five-coordinate Ce-TEA complexes were determined by ESI-MS and FTIR. By calcining the Ce-TEA complexes at 600°C for 2 h, the single phase of CeO_2 identified by XRD was obtained. Pd/CeO_2, the hydrogenation catalyst, was prepared by doping palladium nitrate into the cerium complex before calcining at 600°C for 2 h and investigated by XRD and SEM. The Pd-doped CeO2 was preliminarily studied for catalytic hydrogenation of 4-cyanobenzaldehyde in a continuous-flow micro-reactor. Among all Pd/CeO_2 prepared, 10% Pd doped CeO_2 exhibited the greatest performance towards hydrogenation of 4-cyanobenzaldehyde in terms of the amount of hydrogenated products as 4-cyanobenzyl alcohol, 4-hydroxymethylbenzylamine, and 4-hydroxymethyltoluene.

Student's signature	Thesis Advisor's signature	___ / ___ / ___

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Ultimately, I am appreciated my parents, my brothers for their love, understanding, encouragement, and constant inspiration.

Worawat Wattanathana
May, 2012

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LIST OF ABBREVIATIONS

BET = Brunauer-Emmett- Teller
D_{BET} = Average particle size
ESI-MS = Electrospray Ionization Mass Spectrometry
FTIR = Fourier Transform Infrared Spectroscopy
JCPDS = Joint Committee on Powder Diffraction Standard
S_{BET} = Specific surface area
SEM = Scanning Electron Microscopy
SMSI = Strong Metal Support Interaction
TEA = Triethanolamine
TEM = Transmission Electron Microscopy
TGA = Thermal Gravimetric Analysis
XRD = X-Ray Diffraction

PRELIMINARY STUDY OF Pd/CeO_2 DERIVED FROM CERIUM COMPLEXES AS SOLID SUPPORT CATALYSTS FOR HYDROGENATION REACTION IN A MICRO-REACTOR

INTRODUCTION

Cerium (IV) oxide (ceria or CeO_2) has been considered as materials for applications of automotive exhaust catalyst, polishing material, reforming reaction catalyst, and electrochemical device. The success of the material applications depended on the routes of powder synthesis, many synthetic routes were, therefore, proposed in the relevant literatures, such as solid-solid reaction, co-precipitation of hydroxides, and sol-gel method. However, The obtained ceramic powders lack of homogeneity and purity, complicated procedure, or high processing temperature leading to high cost were found from these synthetic routes. Laobuthee *et al.* (2000) successfully prepared various high purity and homogeneous ceramic powders from the metal complexes decomposition method, a very simple, low cost, and straightforward process. Based on the basis of this process, CeO_2 was successfully prepared.

Nowadays, hydrogenation reactions show important roles in pharmaceutical, chemical and petroleum industries. Yoswathananont *et al.* (2005) reported an efficient hydrogenation reaction in a tube reactor. In this flow system, a substrate solution was running through narrow channels formed in the Pd/C packed column with provided various advantages, such as, reducing in mass transfer between phases, no need for separation of products from catalyst, and providing an efficient hydrogenation reaction.

In this work, our group proposed an idea to prepare Pd-doped CeO_2 prepared from mixtures of cerium complex with palladium nitrate salt for using as hydrogenation catalyst in flow system micro-reactor.

OBJECTIVES

1. To develop the metal complex method to prepare ceria and palladium-doped ceria catalysts from cerium (III) nitrate

2. To study catalytic activity of all prepared catalysts

LITERATURE REVIEW

1. Hydrogenation reaction

Hydrogenation is a chemical reaction between molecular hydrogen (H_2) and related compounds and also a type of chemical reduction. This process is commonly used to reduce many organic compounds by adding pairs of hydrogen atoms to unsaturated parts of molecules such as double and triple bonds.

Hydrogenation is widely used in many processes. In petrochemical processes, hydrogenation is used to convert alkenes and aromatics into less toxic and less reactive alkanes and cycloalkanes, respectively. Apart from that, hydrogenation is also used to convert heavy residues from crude oil refinery process into more value diesel. This process is called hydrocracking. In food industry, hydrogenation is applied to convert liquid vegetable oils to solid or semi-solid fats, such as those present in margarine.

Hydrogenation usually takes place in the presence of a catalyst. Non-catalytic hydrogenation occursonly at very high temperatures. Thus, hydrogenation process usually consists of three components, the substrate, the hydrogen molecule (or other hydrogen sources) and any catalyst. The reaction condition varies at different temperatures and pressures depending on activities of the substrate and the catalyst.

There are two types of catalyst used in hydrogenation reaction e.g., homogeneous and heterogeneous catalysts. Homogeneous catalysts, the catalysts with dissolve in media which contains the substrate, are coordination complexes so the activity and selectivity of homogeneous catalysts are adjusted by changing the ligands.Heterogeneous catalysts, the catalysts with different phase from the substrate, are metals such as palladium (Pd), platinum (Pt), and nickel (Ni), which can also modified activity and selectivity by varying supports. Heterogeneous catalysts for hydrogenation are more common industrially because of their ease of separating from reaction.

Nowadays, there have three main choices of hydrogenation equipment:

1. Batch hydrogenation under atmospheric conditions

This is the original form of hydrogenation that solid catalyst is added to a container of dissolved reactant which has been evacuated by using inert gas and sealed with a rubber. Hydrogen gas is then supplied from a H_2-filled balloon which hydrogen uptake can be monitored to measure progress of hydrogenation. The reaction occurs by mixing of three phase components.

2. Batch hydrogenation at elevated temperature and/or pressure

In these cases, catalyst is added to a solution of reactant under an inert atmosphere in a pressure vessel. Heat may also be used, as the pressure compensates for the associated reduction in gas solubility.

3. Flow hydrogenation

This technique involves in continuously flowing a dilute stream of dissolved reactant over a fixed bed catalyst in the presence of hydrogen. This technique allows the application of pressures in a wide range.

2. Supports for heterogeneous catalyst

Catalyst support is the material, usually a high surface area solid, to which a catalyst is fixed. The support may be inert or active in the catalytic reactions. The reaction mostly occurs at the surface catalyst atoms. Accordingly, To improve efficiency of heterogeneous catalyst is to maximize the surface area of a catalyst by distributing it over the support. Typical supports include various kinds of carbon (C), alumina (Al_2O_3), and silica (SiO_2).

Somorjai *et al*. (2008) reported active supported catalysts with strong metal support interaction (SMSI). The metals are iron (Fe), nickel (Ni), rhodium (Rh), platinum (Pt), palladium (Pd) andiridium (Ir) and the supports are titania (TiO_x), tantalia (TaO_x), ceria (CeO_x) andniobia (NbO_x).

3. The structure of ceria

Cerium (IV) Oxide (ceria or CeO_2), a yellow powder, isa fluorite structure (face centered cubic unit cell with space group *Fm3m*) as shown in Figure 1.

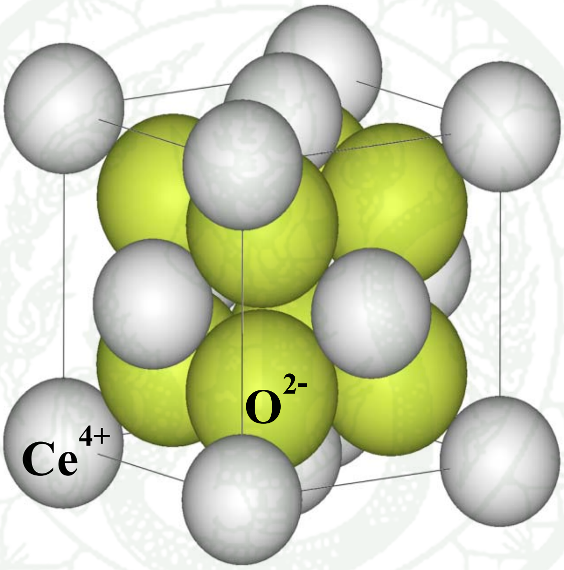


Figure 1 The crystal structure of CeO_2

4. Methods for ceria ceramic powder preparation

4.1 Solid-solid reaction

The solid-solid reaction is the oldest and most typical method to prepare multi component material by direct reaction of corresponding solid compounds at high temperatures, where reacting atoms diffuse through solid phase to react with other atoms.

In the sample preparation procedure, grinding starting materials to provide small particles, cooling and regrinding of samples, and ball-milling treatment facilitate the solid-solid reaction. The good reactants blending and increasing of reactants surface area can enhance the process.

4.2 Precipitation and co-precipitation method

Chemical precipitation is an extensively used method for preparing solid materials from solution. A liquid-phase reaction is used to prepare insoluble compounds that are amorphous or crystalline precipitates. The precipitates are usually composed of fine particles.

In a typical precipitation method, metal cations are directly added to a precipitant to obtain oxide powders or their precursors. The morphology and particle size of powders can be controlled by simply adding the solution to the participant due to the rapid change of solution concentration and the discontinuous nature of precipitate formation. The pH of precipitation may be different for each metal component. The composition at the beginning of the precipitation is different from the composition at the end. To improve this drawback, many scientists attempted to develop a homogeneous precipitation method, where precipitants are generated simultaneously and uniformly the solution using controlled release of the reaction-precipitation ligands by another chemical source in the solution.

In the preparation of mixed oxides, the co-precipitation method is the most commonly used. Mixed metal salts are dissolved in the same solvent. In the ideal solutions, all cations can be simultaneously precipitated in a qualitative way without segregation of any particularconstituents in the solution. However, the homogeneous co-precipitation at an atomic level is very difficult due to the differences in solubility between more than two metal cations.

4.3 Sol-gel method

Sol-gel processes are interesting to prepare many materials in various shapes and forms, and are appropriate for the synthesis and preparation of ultrafine oxide materials at relatively low temperatures.

A sol is stable colloid of small particles suspended in a liquid. The particles can be amorphous or crystalline. Electrostatic repulsion is used for preventing aggregation. The particles in sols interact to form continuous network of connected particles called gel. In case of drying a gel by evaporating the interstitial liquid, the capillary forces cause the gel to shrink and cause the formation of cracks as a result of the differential stresses generated in the drying gel. The obtained dried gel is known as a xerogel. When the wet gel is dried under supercritical conditions, the pore and network structure of the gel is maintained even after drying. The resulting gel in this case is called aerogel. These sol-gel materials are frequently applied to catalysts and catalyst supports because of their high surface area.

The sol can be prepared by hydrolyzing reactive metal compounds, for example alkoxides, $M(OR)_m$, where M is a metal and R is an alkyl group. In the sol-gel method, metal alkoxides are dissolved in an alcohol and addition of water causes hydrolysis of metal alkoxides.

$$M(OR)_m + nH_2O \longrightarrow M(OH)_n + nROH \qquad (1)$$

Consequently, a series of condensation reactions occurs between hydroxide groups and the overall reaction is represented by the following chemical reaction:

$$M(OH)_n \longrightarrow MO_{n/2} + n/2H_2O \tag{2}$$

Based on this method, mixed oxide gels can be produced readily by mixing of their alkoxides solutions prior to hydrolysis.

4.4 The oxide one pot synthesis (OOPS)

Laobuthee *et al.* successfully prepared magnesium aluminate ceramic powders ($MgAl_2O_4$) by oxide one pot synthesis (OOPS). In OOPS process, the reaction of aluminium hydroxide ($Al(OH)_3$), magnesium oxide (MgO) and triethnolamine (TEA, $N(CH_2CH_2OH)_3$) in ethylene glycol (EG, $HOCH_2CH_2OH$) was carried out to prepare the metal complex or the spinel precursor for $MgAl_2O_4$. The chemical reaction of OOPS was shown as follows.

$$2Al(OH)_3 + MgO + 3TEA + xEG \xrightarrow[-H_2O]{200\ ^{o}C} \tag{3}$$

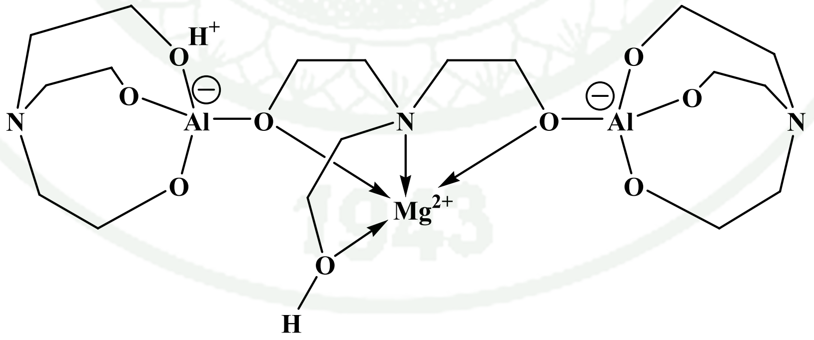


Figure 2 The oxide one pot synthesis of magnesium aluminate precursor formation

Moreover, this method can be adapted to synthesize other ceramic products such as nickel aluminate ($NiAl_2O_4$), cobalt aluminate ($CoAl_2O_4$) and Lathanum ferrate ($LaFeO_3$).

5. Review of some researches

This section mentioned a review of works done by some previous researchers on the preparation, characterization and application of the palladium-doped ceria.

Monteiro *et al.* (1995) studied the effect of the preparation method and amount of CeO_2 on the interaction of$Pd/CeO_2/Al_2O_3$catalysts. The prepared catalysts were characterized by temperature-programmed reduction, hydrogen chemisorption and X-ray photoelectron spectroscopy. The 1,3-butadiene hydrogenation was used as a model reaction. The Pd-Ce interaction affected the reduction behavior of the catalysts. From temperature-programmed reduction (TPR) results, the presence of CeO_2 shiftedthe reduction temperature of PdO to lower values, while palladium similarly facilitated the reduction of the cerium surface species. The hydrogen uptake decreased when increasing the ceria content. XPS results showed that the Pd/A1 ratio decreased with CeO_2 addition being affected by the preparation method and content. The formation of catalytic sites at the interface of Pd-Ce was postulated from turnover frequency (TOF) results of the 1,3 -butadiene hydrogenation. The number of these new sitesincreases with the addition of ceria.

Shen *et al.* (2001) studied the impact of palladium precursors on the catalytic behavior of Pd/CeO_2 catalysts for methanol synthesis through hydrogenation of carbon monoxide. Catalysts prepared from palladium chloride and palladium acetate showed much higher overall catalytic activities than those prepared using palladium nitrate. Palladium precursors caused no change inselectivity of reaction. The palladium precursor, or more specifically its anion, had an effect on the final palladium particles, and therefore affected the interaction between Pd and ceria, which would cause different reaction results such as catalytic deactivation with time-on-stream.

Zhang *et al.* (2008) prepared Pd/C catalysts doped with cerium oxide and iron oxide nanoparticles by thermal decarboxylation using cetylsulfonyl acetate.The hydrogenation of *o*-chloronitrobenzeneto give high yields of 2,2-dichlorohydrazobenzene was a model reaction. It was found that the stability and activity of the Pd/C catalysts were significantly affected by doping with the nanosized metal oxides.

Amoroso *et al.* (2010) synthesized the Pd/CeO_2catalyst for the Suzuki-Miyaura cross-coupling under mild conditions (298 K, in air) in ethanol/water solvent. A variety of aryl bromides and arylboronic acids underwent Suzuki-Miyaura coupling with quantitative GC yields of asymmetric biaryls. Isolated yields and purity of the coupling products were good to excellent. A careful investigation through a series of suitable tests unequivocally showed that the C-C cross-coupling is accomplished via homogeneous mechanism by leached palladium (0). Noticeably, the Pd/CeO_2 system can be recycled at least ten times without loss of activity.

Wang *et al.* (2010) investigated the metal-support interaction in Pd-CeO_2 system. Pd-doped CeO_2 catalyst was prepared by the sol-gel method and was then treated in the H_2-O_2 redox atmosphere at 300, 500 and 800 °C, respectively. The Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD) and temperature-programmed reduction (TPR) results indicate that the redox treatment at 300 °C mainly affect the surface properties of the catalyst, while those at higher temperatures have an influence on the bulk properties. The step-scanning XRD and Raman results prove that Pd species on the surface of the sample mainly exist in the form of bulk Pd and PdO crystallites after the redox treatment at 500 °C, which are encapsulated by CeO_2 particles after the treatment at 800 °C. The CO oxidation activity, dynamic oxygen storage capacity (DOSC) and oxygen storage complete capacity (OSCC) of the catalyst vary with the treating temperature. The 300 °C treated sample presents the highest activity for CO oxidation and oxygen storage capacity. The reduction-ratio dependent activation energy (E_a) is extremely low for the surface reduction of this sample, suggesting the participation of highly active oxygen. The active oxygen are suggested to originate from the enlarged Pd-Ce interface, which depends on the avaibility of surface Pd sites and contact between metal and support.

Wang *et al*. (2011) investigated the interaction between noble metal and CeO_2. Pd-doped CeO_2 catalyst was prepared by sol-gel method, and the catalyst was then treated in static air and a H_2/O_2 alternating flow at 800 °C, respectively. It is found by step-scanning XRD that Pd ions migrate out of the ceria lattice during the redox treatment, while the exudation of Pd is not so obvious after the oxidative treatment. For the CO oxidation activity, the redox treated catalyst is seriously weakened compared with the oxidative-treated one. This difference is ascribed to the encapsulation of Pd crystallites by the CeO_2 support during the redox treatment, which is confirmed by XPS and CO-TPR. Based on the activity and FTIR results, it is proposed that, CO oxidation at low temperatures proceeds mainly via the reaction between the adsorbed CO on Pd sites and the lattice oxygen of surface CeO_2 at the Pd-Ce interface.

MATERIALS AND METHODS

Materials

1. Chemicals

1.1 4-cyanobenzaldehyde (Aldrich)

1.2 Cerium (III) chloride heptahydrate ($CeCl_3{\cdot}7H_2O$, Acros Organics, 99.0% purity)

1.3 Cerium (III) nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$, Acros Organics, 99.5% purity)

1.4 1-Propanol ($CH_3CH_2CH_2OH$, Carlo Erba, 99.5% purity)

1.5 Palladium nitrate hydrate ($Pd(NO_3)_2.xH_2O$, Aldrich)

1.6 Triehanolamine (TEA, $N(CH_2CH_2OH)_3$, Carlo Erba, 98% purity)

2. Instruments

2.1 Electrospray Ionization Mass Spectrometer (ESI-MS, Bruker Esquire mass spectrometer)

2.2 Fourier Transform Infrared Spectrophotometer (FTIR, Perkin Elmer system 2000 FTIR)

2.3 High Temperature Furnace (Nebertermo, maximum temperature 1400 ^{o}C)

2.4 RamanSpectrometer (Renishaw, Type 2000, Ar laser 514 nm)

2.5 Rotary Evaporator

2.6 Scanning Electron Microscope (SEM, XL30 series, Phillips)

2.7 Surface Area Analyzer (BET, Micromeritics ASAP 2020 surface analyzer)

2.8 Thermogravimetric Analyzer (Perkin-Elmer TGA 7)

2.9 Transmission Electron Microscope (TEM, Hitachi H-7650)

Methods

1. Preparation and characterization of cerium complex

1.1 Preparation of cerium complex

The cerium complex of $CeO_2$was prepared as follows:

$$\text{Ce (III) nitrate + triethanolamine} \xrightarrow[\text{1-propanol}]{80\ ^{o}\text{C}} \text{cerium complex} \qquad (4)$$

Firstly, cerium (III) nitrate (10.8558 g) was dissolved in 1-propanpol in a round bottom flask. Triethanolamine (TEA, 3.3 cm^3) used as ligand in order to form complex with cerium was then added into the solution in the molar ratio of TEA to cerium salt as 1:1. The mixture was heated and stirred for 5 h under ambient atmosphere to distill off 1-propanol and water. After that the precipitate occurred and the mixture was evaporated to remove solvent and obtain the powder of cerium complex.

1.2 Characterization of cerium complex

1.2.1 Functional group analysis

The obtained cerium complex was taken functional group analysis by Fourier Transform infrared spectrophotometer (FTIR, Perkin Elmer system 2000 FTIR). The sample powders were finely grinded with KBr and pressed into pellet before measurement. All the peak in the range 4000-400cm^{-1} were recorded with spectral resolution 4 cm^{-1}.

1.2.2 Molecular weight determination

Electrospray ionization mass spectrometer (ESI-MS, Bruker Esquire mass spectrometer) was employed to determine to molecular weights of the cerium complex. The cerium complex was dissolved in methanol used as matrix. The spectra were recorded in positive mode on a micro OTOF instrument. The scanning time for each sample was 2.4 min.

1.2.3 Thermogravimetricanalysis

The decomposition aspect and weight loss of the cerium complex were studied by thermogravimetric analysis which carried out bya TGA analyzer. Samples were topped on the surface of alumina which was loaded in the pan and heated at the heating rate of 5 ^{o}C/min under ambient pressure. The thermogram was recorded at the temperature range 50-1000 ^{o}C.

2. Preparation and characterization of ceria and palladium-doped ceria powders

2.1 Preparation of ceria ceramic powder

Calcination process was used to convert cerium complex to ceria ceramic powder. According to the thermogramof cerium complex was calcined in alumina crucible at 600 ^{o}C for 2 h in air.

2.2 Preparation of palladium-doped ceria powders

Palladium nitrate hydrate [$Pd(NO_3)_2.xH_2O$, 0.1728, 0.2880 and 0.5760 g] was mixed with 25 mmol of prepared cerium complex from cerium(III) nitrate to obtain the precursors of CeO_2 doped with 3%, 5% and 10% by mol of palladium. All the precursors were calcined at 600 ^{o}C for 2 h in air.

2.3 Characterization of the ceramic products

2.3.1 Vibrational spectroscopy

The obtained ceria powder was taken functional group analysis by Fourier Transform infrared spectrophotometer (FTIR, Perkin Elmer system 2000 FTIR) and Raman spectrometer (Renishaw, Type 2000, Ar laser 514 nm). For IR spectroscopy, the sample was finely grinded with KBr and pressed into pellet before measurement. All the peaks in range 4000-400 cm^{-1} were recorded with spectral resolution 4 cm^{-1}. For Raman spectroscopy, the sample was finely grinded and then topped on the slide and flatted the surface before measurement.

2.3.2 Phase identification

All ceramic products were studied by X-ray diffraction technique (XRD) using a Bruker D8-Advance X-ray diffract to meter with CuK$_{\alpha}$ radiation.

Diffraction patterns were recorded over the range of 2θangles from 5 to 90 degrees in step-scanning mode (0.02° steps with a step counting time of 2 s).

2.3.3 Surface area analysis

Specific surface area (S_{BET}) measurement was carried out using Brunauer-Emmett-Teller (BET) analysis by nitrogen absorption isotherm at-196 °C using a Micromeritics ASAP 2020 surface analyzer and a value of 0.162 nm^2 for the cross section of the nitrogen molecule. Samples were degassed at 350 °C under nitrogen vacuum for 20 h before measurement.

$$D_{BET} = 6000 / d_{th} \times S_{BET} \qquad (5)$$

Where D_{BET} is average particle size (nm), S_{BET} is specific surface area (m^2/g), and d_{th} is the theoretical density of the solid solution oxide (7.215 g/cm^3).

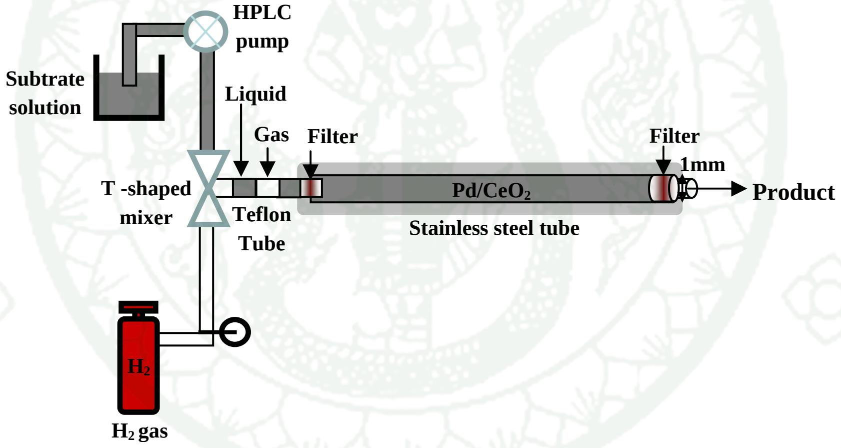
2.3.4 Morphology observation

The particle morphology of calcined products was observed by Scanning Electron Microscope (SEM, XL30 series, Phillips) operating at an acceleration voltage of 15 kV and magnification value in 10000X. Samples were mounted on alumina stubs using carbon tape and then sputter coated with Au to avoid particle charging.

Transmission Electron Microscope(TEM, Hitachi H-7650)at an acceleration voltage of 100 kV was also employed to observe the particle morphology.

3. Catalytic activity testing of ceria and palladium-doped ceria powders

Each of the calcined products was packed in a stainless steel tube (25 cm in length, 1.0 mm and 6.3 mm as inner and outer diameters, respectively) with two filters at both ends to hold the catalyst in the column, was performed in a high pressure flow system operating via a continuous-flow micro-reactor with the residence time of 2 min 50 s (Scheme 1). 4-Cyanobenzaldehyde in methanol as a substrate solution was mixed with hydrogen gas at the T-shaped mixer. The flow rate of the substrate solution controlled by HPLC pump was 0.038 mL/min while the hydrogen gas was set around 2.0 MPa. To observe the gas-liquid flow, a transparent teflon tube was connected between the T-shaped mixer and the tube column. The product solution eluted at the end of the column was characterized by ^{1}H-NMR.



Scheme 1

RESULTS AND DISCUSSION

1. Preparation and characterization of cerium complexes

To prepare the cerium complex, the cerium (III) salts (cerium (III) chloride or cerium (III) nitrate) were firstly dissolved in 1-propanol. Then, triethanolamine was added to the solution to provide the clear solution. After heating for 5 h, the clear solution turned milky and finally the pale yellow precipitate of cerium complex occurred. The solvent was removed by a rotary evaporator to collect the cerium complex. Figure 3 shows the physical appearance of the cerium complex.

Figure 3 Physical appearance of the prepared cerium complex

Figure 4 shows FTIR spectrum of the cerium complex. The broad peak centered at 3402 cm^{-1} was assigned to the O-H stretching due to moisture absorption and/or triethanolamine residue from the reaction. The peaks at 2988 and 2915 cm^{-1} were assigned to asymmetric and symmetric modes of methylene (-CH$_2$-) stretching, respectively. The peak at 1627 cm^{-1} was assigned to O-H bending overtone. The C-H bending bands were shown in the region of 1450-1200 cm^{-1}. The N-O stretching of nitrate group showed absorption bands in region of 1550-1250 cm^{-1}. The Ce-O-C bending resonated at 1082 cm^{-1}. Moreover, the band at 554 cm^{-1} was assigned to Ce-O stretching.

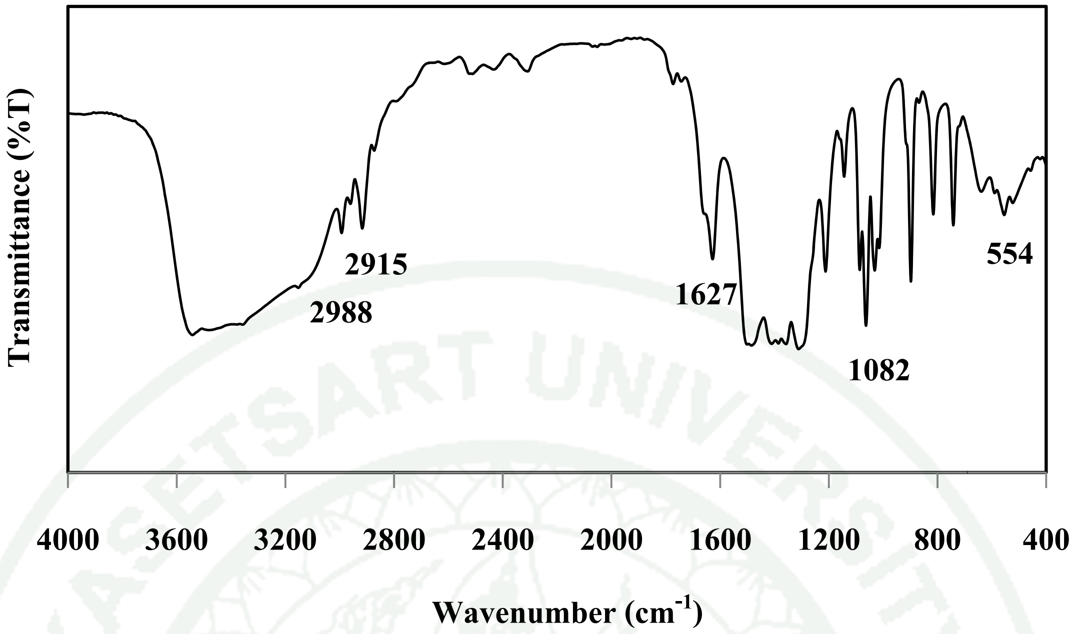


Figure 4 FTIR spectrum of cerium complex

Figure 5 shows ESI-MS spectrum of the cerium complex. There are two intense peaks at m/z = 286 and 349 corresponding to [Ce(TEA)] and [Ce(TEA)NO_3], respectively.

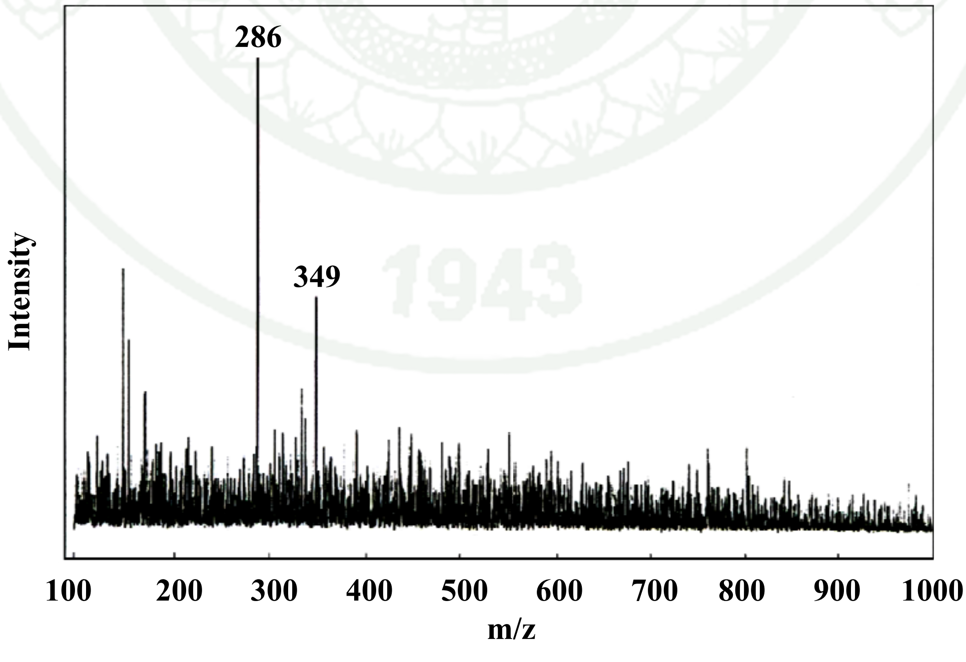
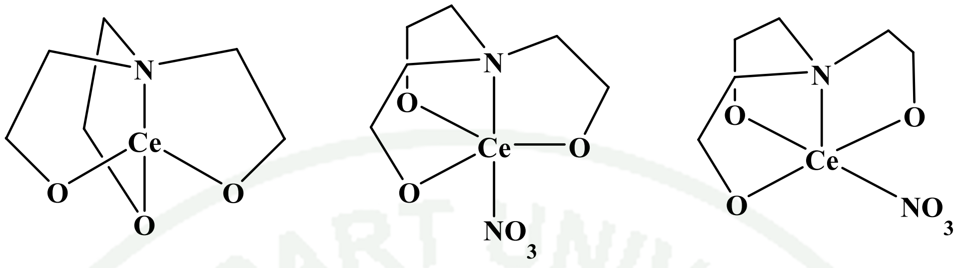


Figure 5 Mass spectrum of cerium complex

Based on the results from FTIR and ESI-MS, three possible structures were proposed as shown in Figures 6.



(a) (b) (c)

Figure 6 The possible structures of cerium complex (a) corresponding to m/z = 286, (b) and (c) corresponding to m/z = 349

Figure 7 shows TGA thermogram of the cerium complex. The decomposition of the cerium complex on heating occurred through weight loss in three steps. The first weight loss around 100-200 °C was attributed to the loss of physisorbed humidity and propan-1-ol. The drastic weight loss at 250 °C was caused by the decomposition of the organic ligand. A slight weight loss observed between 300 and 400 °C was ascribed to the burning of the residual char. The calcination temperature to burn out organic content was selected at 600 °C.

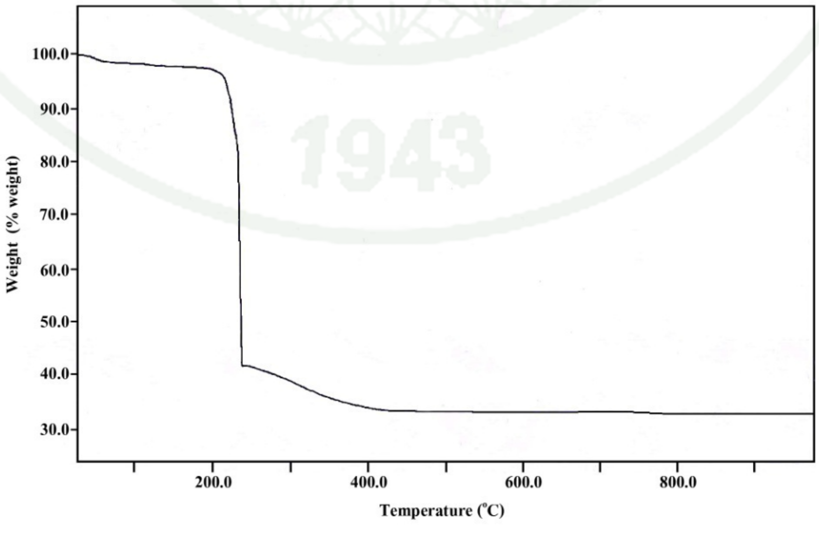


Figure 7 Thermogram of cerium complex

2. Preparation and characterization of ceria and palladium-doped ceramic powders

All cerium complexes were calcined at 600 °C according to thermogram. After completion of calcination, the pale yellow coloredceria ceramic powders were obtained.

To confirm that the organic contents in the cerium complex were completely eliminated, FTIR spectra of the obtained ceria ceramic powders spectra and the corresponding cerium complexes were compared. Both ceria ceramic powders exhibited only the Ce-O stretching absorption bands in the range of 600-400 cm^{-1} as illustrated in Figures 8.

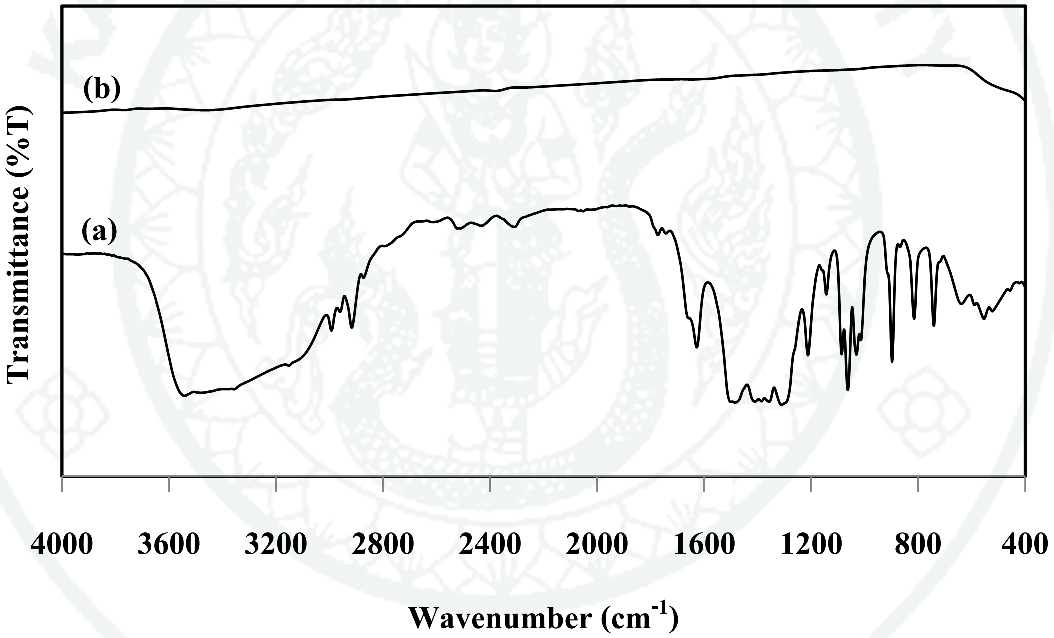


Figure 8 FTIR spectra of (a) cerium complex comparing with (b) ceria ceramic powder

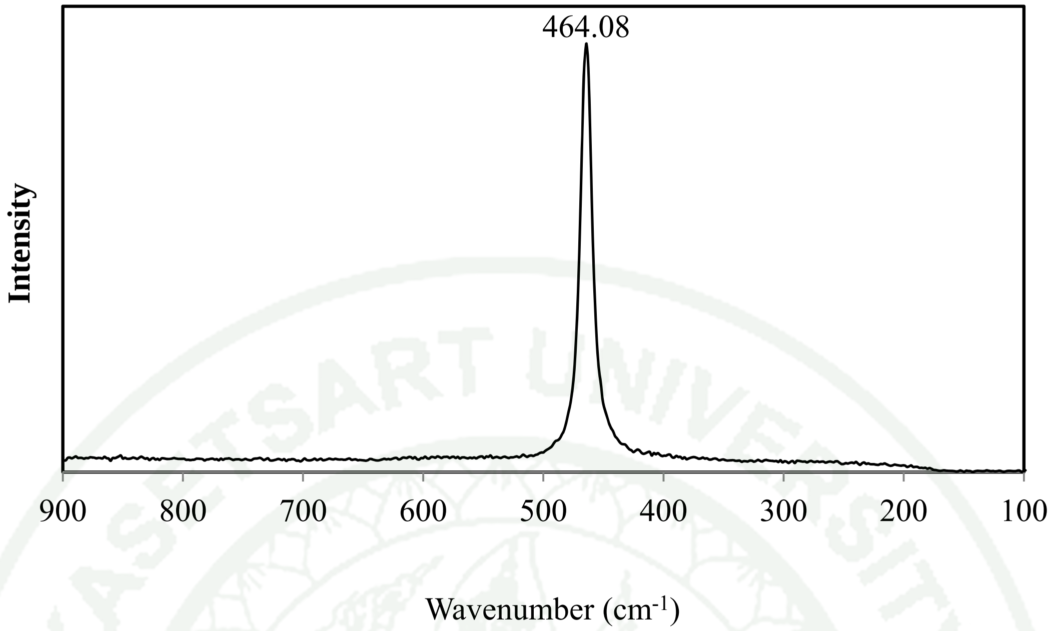


Figure 9 Raman spectrum of ceria ceramic powder

The Raman spectrum shows remarkable absorption peak at 464.08 cm^{-1}according to F_{2g} vibration mode in a fluorite type structure of ceria nanoparticles.

The XRD pattern indicates that ceria ceramic powder was single phase with a cubic structure (space group *Fm3m*). The characteristic peaks corresponding to (111), (200), (220), (311), (222), (400), (331), (420), and (422) planes located at 2θ of 28.535, 33.080, 47.495, 56.348, 59.102, 69.427, 76.710, and 88.447 degree, respectively. All the diffraction peaks were identical to the original substance of pure CeO_2 (JCDPS No. 34-0394).

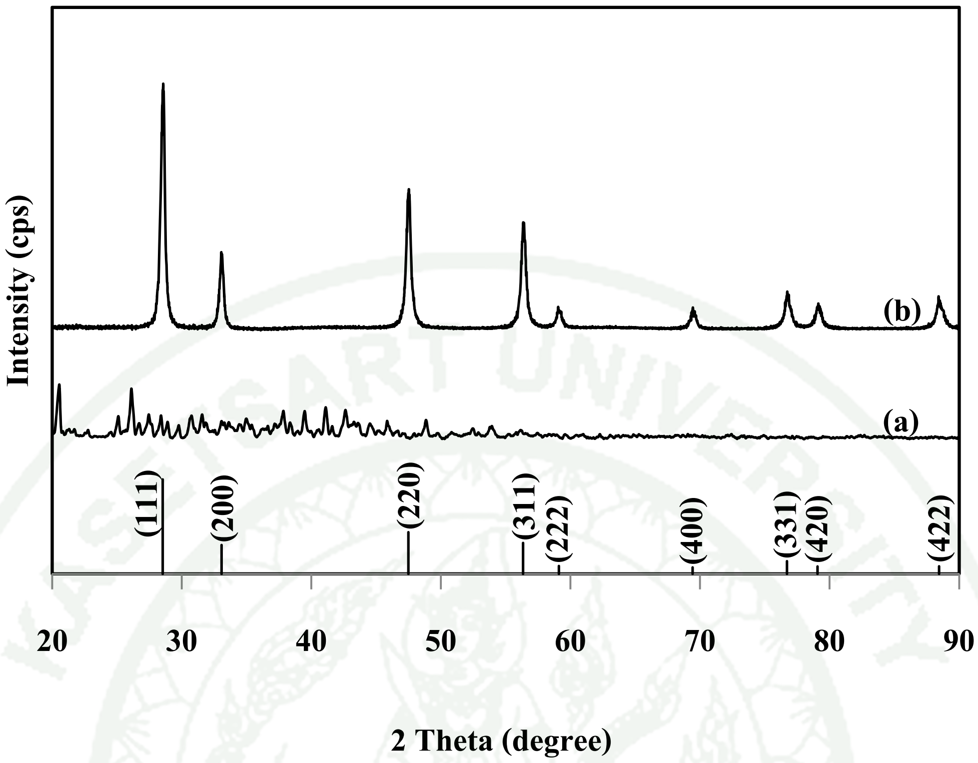


Figure 10 XRD patterns of (a) cerium complex comparing with (b) ceria ceramic powder

For 3% and 5% palladium-doped ceria catalysts, no additional phase was observed in XRD patterns while PdO phase corresponding to JCPDS No. 88-2434 was observed in10% palladium-doped ceria catalyst (Figure 11).

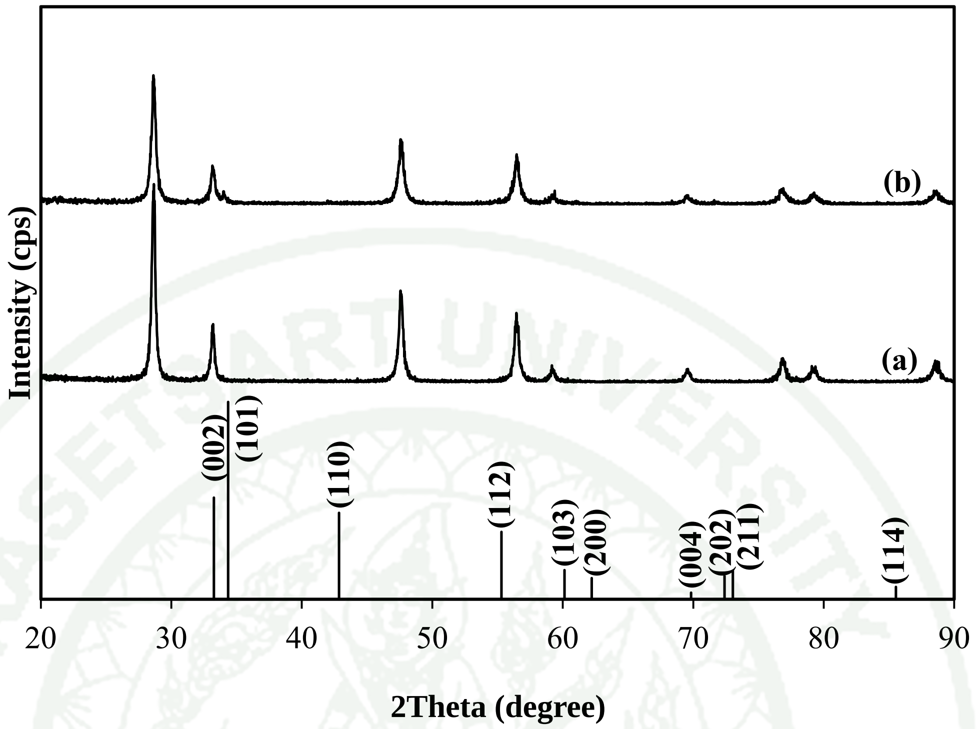
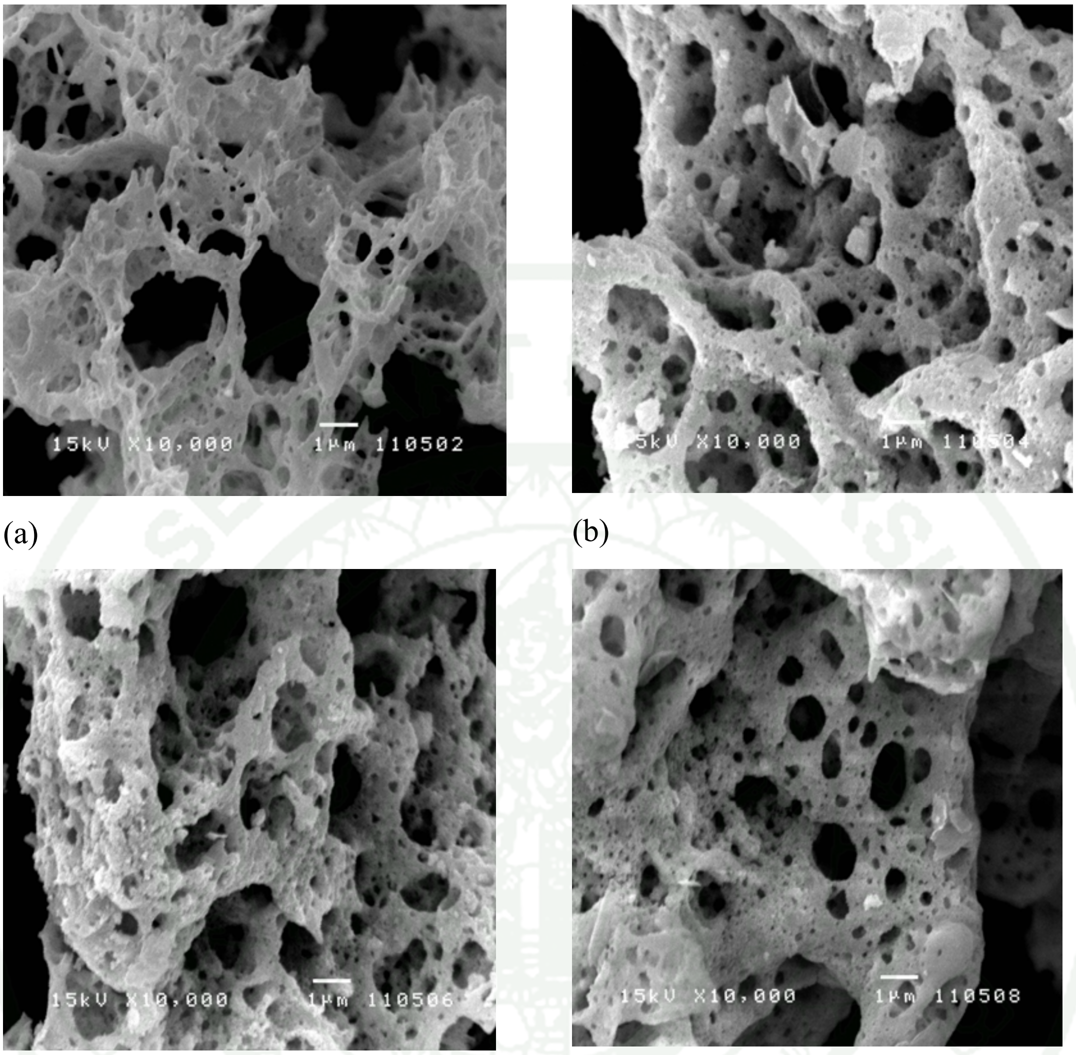


Figure 11 XRD patterns of (a) ceria comparing with (b) 10% palladium-doped ceria

SEM micrograph of all catalysts was shown in Figure 12. The SEM micrographs reveal that all prepared catalysts have a foam-like structure.

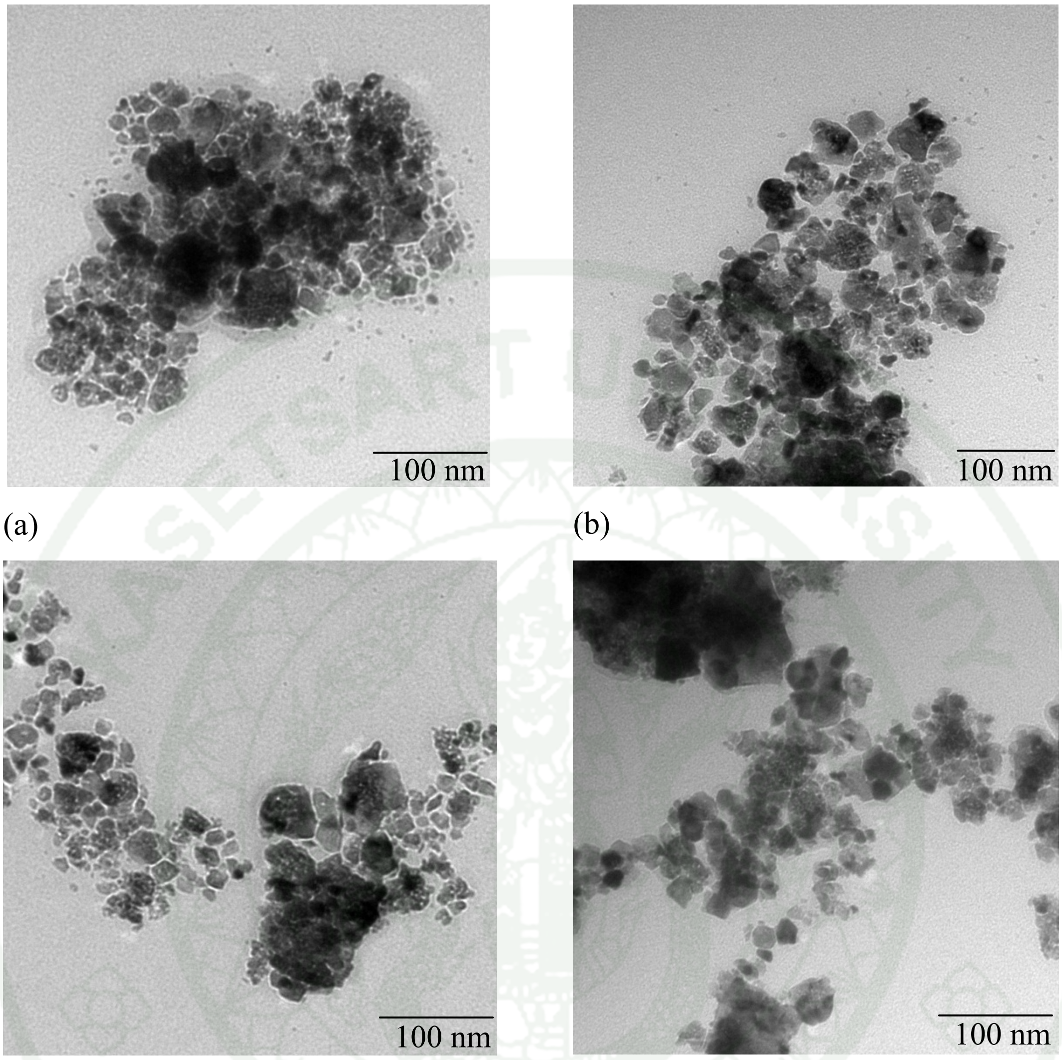


(a) (b)

(c) (d)

Figure 12 SEM micrographs of (a) ceria, (b) 3%, (c) 5%, and (d) 10% palladium-doped ceria

TEM micrograph of ceria and all the palladium-doped ceria was shown in Figure 13. The TEM micrographs show all ceramic products are irregular shape with average diameter 20 nm.



(a) (b)

(c) (d)

Figure 13 TEM micrographs of (a) ceria, (b) 3%, (c) 5%, and (d) 10% palladium-doped ceria

The specific surface area (S_{BET}) of ceria and all the palladium-doped ceria, along with average particle size (D_{BET}) were shown in Table 1.

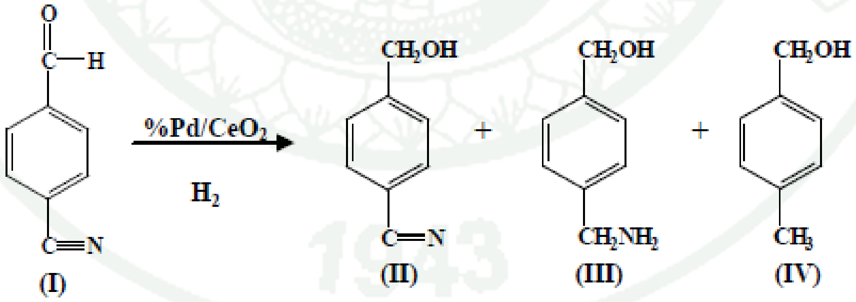
Table 1 S_{BET}, D_{BET} of ceria and all palladium-doped ceria ceramic powders

Ceramic products	Specific Surface Area (S_{BET}, m^2/g)	Average Particle Size (D_{BET}, nm)
Ceria	22.08	38
3% palladium-doped ceria	24.14	34
5% palladium-doped ceria	27.16	30
10% palladium-doped ceria	17.92	46

The results showed specific surface of ceria ceramic powder slightly increased from ceria to 5% palladium-doped ceria because of additional palladium surface. However, the specific surface area of 10% palladium-doped ceria decreased, so the agglomeration of palladium particles occurred.

3. Catalytic activity testing of ceria and palladium-doped ceria powders

Catalytic activity of all calcined products for the following reaction (Scheme 2) was shown in Table 2.



Scheme 2

Table 2 Catalytic activity of ceria and all palladium-doped ceria ceramic powders

Type of catalyst	Pressure of H_2 gas (MPa)	Reaction time (second)	Compound (%)			
			(I)	(II)	(III)	(IV)
0% Pd/CeO_2	2	170	0	0	0	0
3% Pd/CeO_2	2	170	0	3.6	81	15.4
5% Pd/CeO_2	2	170	0	0	88.7	11.3
10% Pd/CeO_2	2	170	0	0	84	16
5% Pd/$NiAl_2O_4$	1.8	120	0	85	15	0
5% Pd/$NiAl_2O_4$	1.8	120	0	72	28	0

Aldehyde and cyanide functional groups consisting in 4-cyanobenzaldehyde (I) were hydrogenated by Pd/CeO_2 to obtain 4-cyanobenzyl alcohol (II), 4-hydroxy methylbenzylamine (III), and 4-hydroxymethyltoluene (IV) (Table 2). No starting material remained in this condition. As comparing the results with that of 5% Pd/$NiAl_2O_4$ and 5% Pd/C studied previously by Ummartyothin *et al.* (2008) and Yoswathananont *et al.* (2005), respectively, the same products (II and III) were obtained but the product (IV) was only obtained in this work. The results indicated that Pd/CeO_2, especially 10%Pd/CeO_2, shows the most efficiency to use as a catalyst for hydrogenation of 4-cyanobenzaldehyde. This result shows the strong metal support interaction between palladium and ceria.

CONCLUSION

The cerium complex decomposition which retains the advantages of purity, homogeneity, low processing temperatures is an inexpensive, straightforward alternative to prepare CeO_2. A pure and homogeneous CeO_2 powder was obtained by calcining the cerium complex at 600°C for 2 h.

The doping palladium on CeO_2 was successfully prepared by calcining the mixture of cerium complex with palladium nitrate at 600°C for 2 h. Among all prepared Pd/CeO_2, 10% Pd/CeO_2 showed the greatest performance towards hydrogenation reaction of 4-cyanobenzaldehyde in terms of the highest 4-hydroxymethyltoluene. In addition, the catalytic efficiency of the prepared Pd/CeO_2 for hydrogenation reaction in the continuous-flow micro-reactor was higher than Pd/C and $Pd/NiAl_2O_4$.

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APPENDIX

Calculation of reactant quantities

1. Preparation of cerium complex

The reaction was also carried out in the scale of 25mmol of cerium (III) nitrateand 25 mmol of TEA.

The weight of cerium (III) nitrate from $Ce(NO_3)_3{\cdot}6H_2O$ (Acros Organics, 99.5% purity, MW = 434.23 g/mol) equaled to 25 mmol of cerium (III) nitrate was calculated as follows:

$$\text{g Ce(NO}_3)_3{\cdot}6\text{H}_2\text{O} = 25\ \text{mmol}\left(\frac{10^{-3}\ \text{mol}}{1\ \text{mmol}}\right)\left(\frac{434.23\ \text{g}}{1\ \text{mol}}\right) = 10.856\ \text{g}$$

The volume of cerium(III) chloride from triethanolamine (TEA, Carlo Erba, 98% purity, MW = 149.19 g/mol, density = 1.124 g/cm^3) equaled to 25mmol of triethanolamine was calculated as follows:

$$\text{cm}^3\ \text{TEA} = 25\ \text{mmol}\left(\frac{10^{-3}\ \text{mol}}{1\ \text{mmol}}\right)\left(\frac{149.19\ \text{g}}{1\ \text{mol}}\right)\left(\frac{1\ \text{cm}^3}{1.124\ \text{g}}\right) = 3.3\ \text{cm}^3$$

2. Preparation of palladium-doped ceria

The amounts of palladium nitrate from $Pd(NO_3)_2{\cdot}xH_2O$ (Aldrich, FW = 230.41 g/mol) mixed with 25mmol of the prepared complex to prepare 3%, 5%, and 10% Pd/CeO_2 were calculated as:

3% Pd/CeO$_2$

$$\text{g Pd(NO}_3)_2\cdot\text{xH}_2\text{O} = 25\times10^{-3}\ \text{mol CeO}_2\left(\frac{3\ \text{mol Pd}}{100\ \text{mol CeO}_2}\right)\left(\frac{230.41\ \text{g}}{1\ \text{mol Pd}}\right) = 0.1728\ \text{g}$$

5% Pd/CeO$_2$

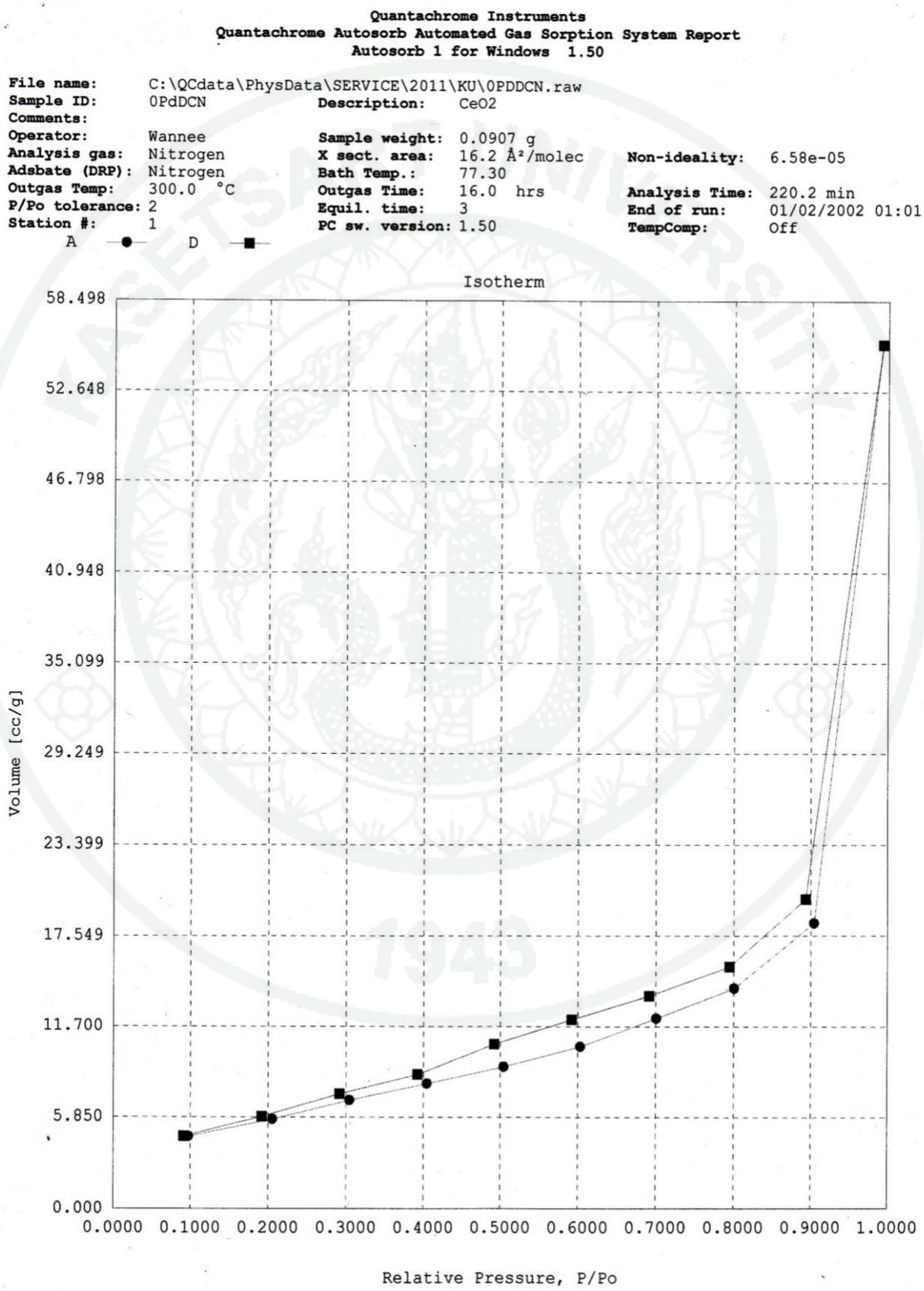
$$\text{g Pd(NO}_3)_2\cdot\text{xH}_2\text{O} = 25\times10^{-3}\ \text{mol CeO}_2\left(\frac{5\ \text{mol Pd}}{100\ \text{mol CeO}_2}\right)\left(\frac{230.41\ \text{g}}{1\ \text{mol Pd}}\right) = 0.2880\ \text{g}$$

10% Pd/CeO$_2$

$$\text{g Pd(NO}_3)_2\cdot\text{xH}_2\text{O} = 25\times10^{-3}\ \text{mol CeO}_2\left(\frac{10\ \text{mol Pd}}{100\ \text{mol CeO}_2}\right)\left(\frac{230.41\ \text{g}}{1\ \text{mol Pd}}\right) = 0.5760\ \text{g}$$

BET data

1. Ceria powder



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P/Po tolerance: 2
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Description: CeO2
Sample weight: 0.0907 g
X sect. area: 16.2 Å²/molec
Bath Temp.: 77.30
Outgas Time: 16.0 hrs
Equil. time: 3
PC sw. version: 1.50

Non-ideality: 6.58e-05
Analysis Time: 220.2 min
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Quantachrome Autosorb Automated Gas Sorption System Report
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Adsbate (DRP):     Nitrogen        Bath Temp.:      77.30
Outgas Temp:       300.0  °C       Outgas Time:     16.0  hrs        Analysis Time:   220.2 min
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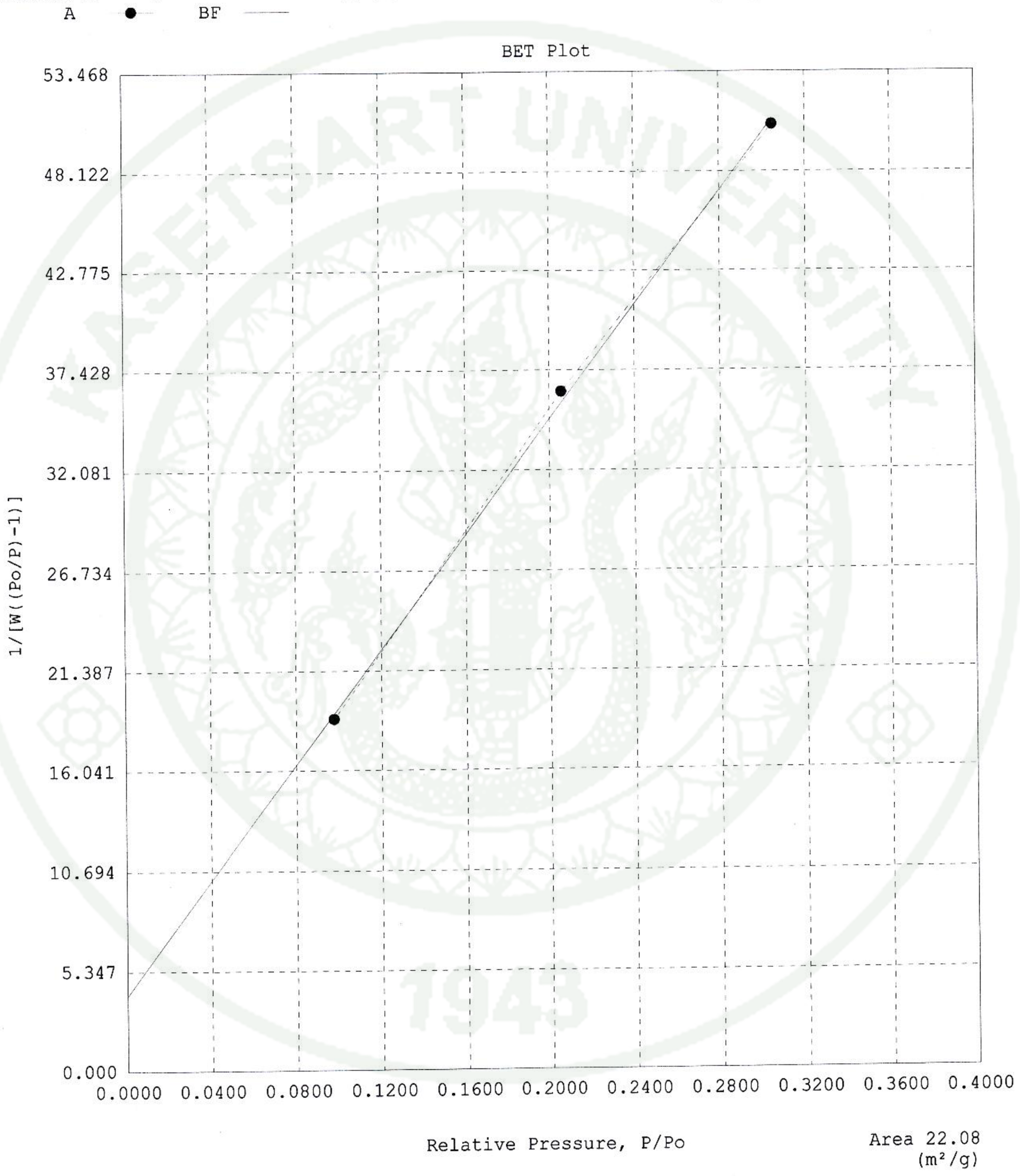

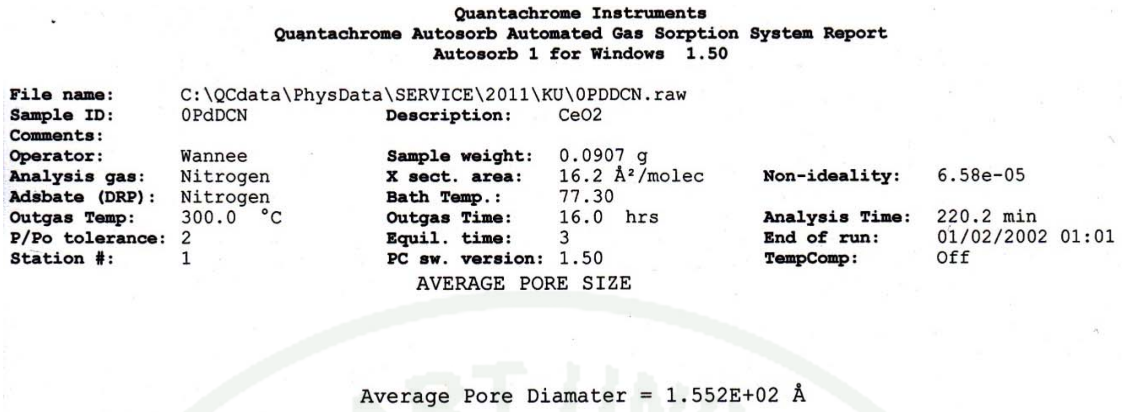

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P/Po tolerance:   2               Equil. time:     3                End of run:     01/02/2002 01:01
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                         Average Pore Diamater = 1.552E+02 Å
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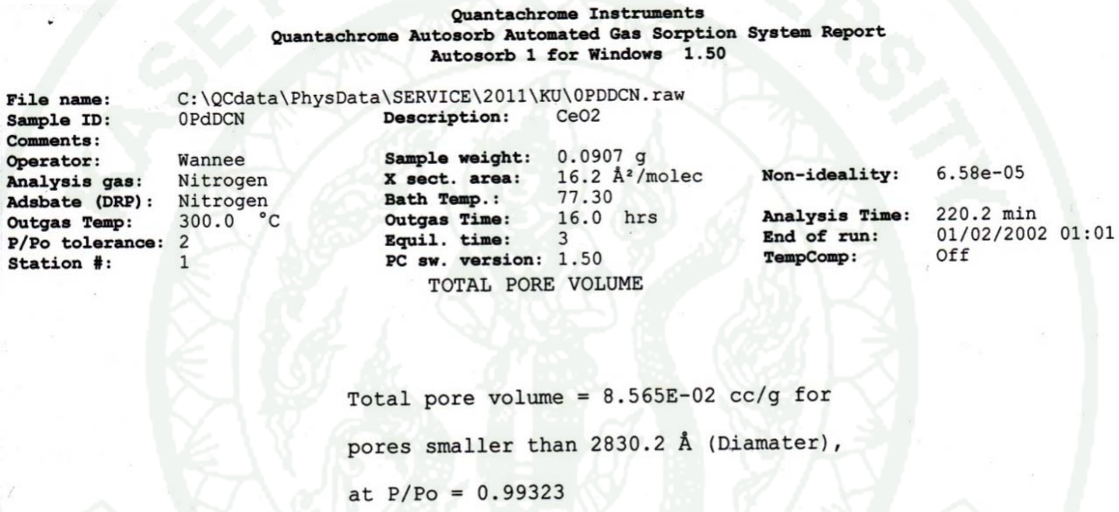

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Adsbate (DRP):    Nitrogen        Bath Temp.:      77.30
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                                    TOTAL PORE VOLUME


                        Total pore volume = 8.565E-02 cc/g for

                        pores smaller than 2830.2 Å (Diamater),

                        at P/Po = 0.99323
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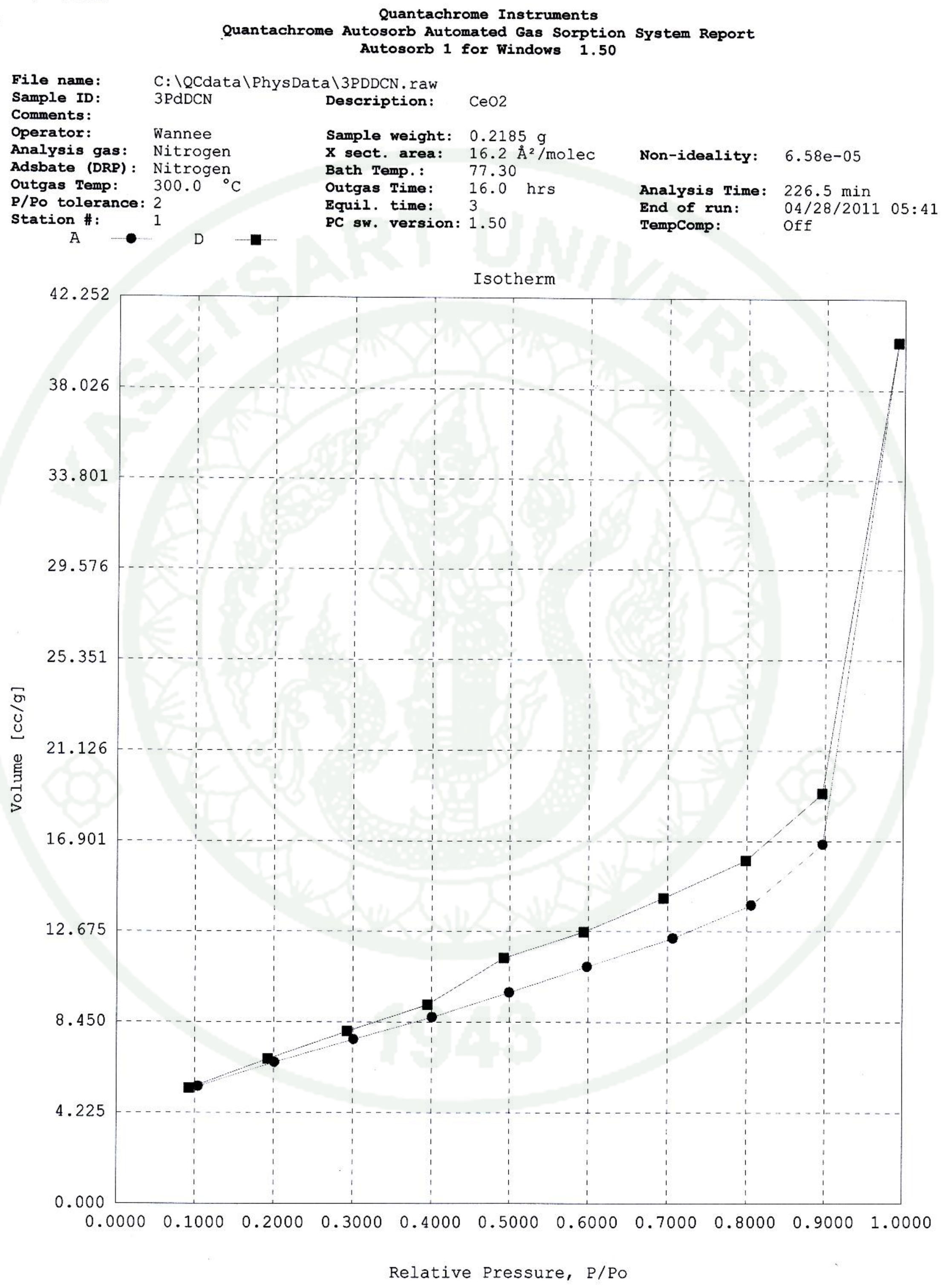
2. 3% palladium-doped ceria powder



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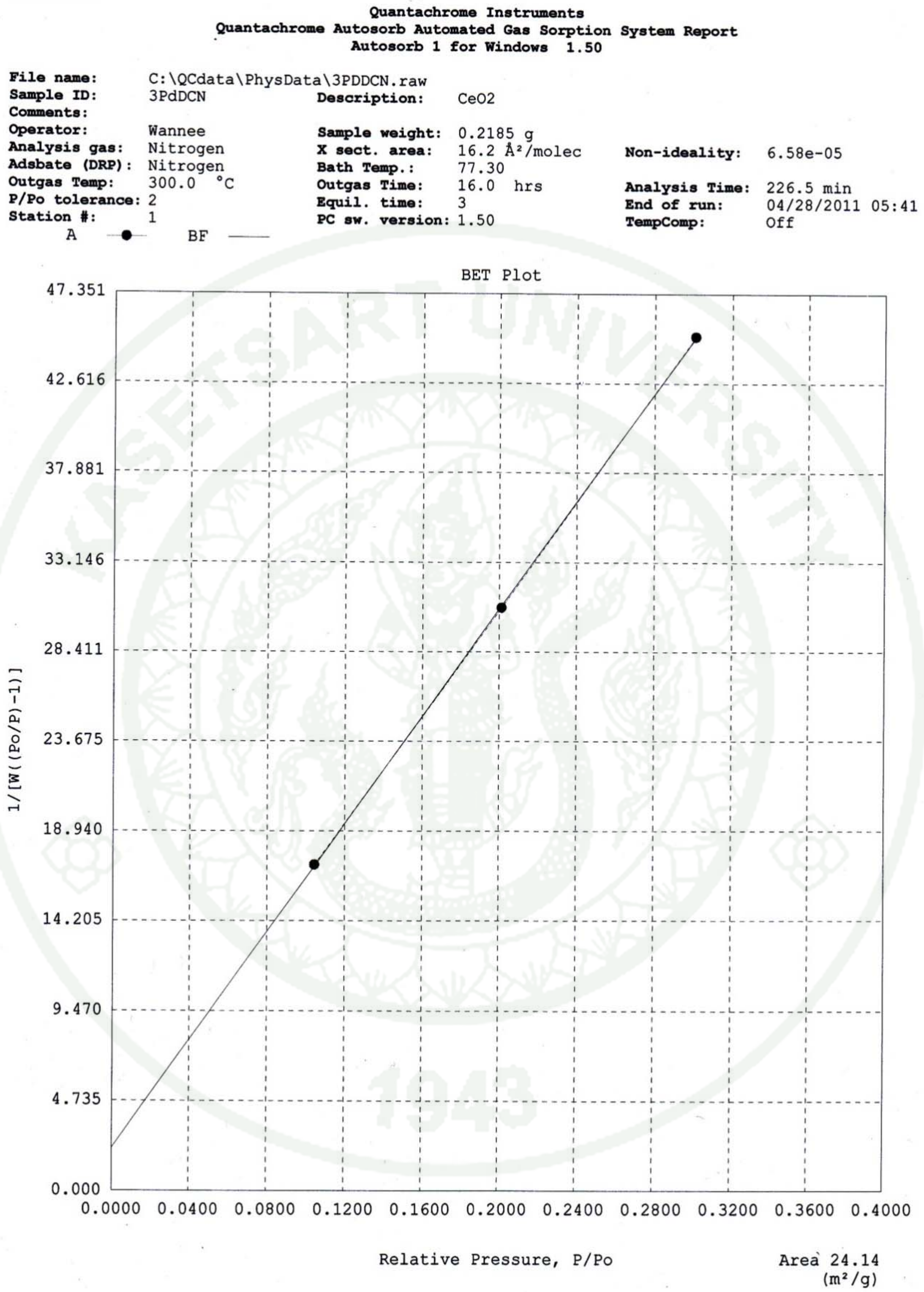

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Adsbate (DRP):    Nitrogen            Bath Temp.:      77.30
Outgas Temp:      300.0  °C           Outgas Time:     16.0  hrs         Analysis Time:   226.5 min
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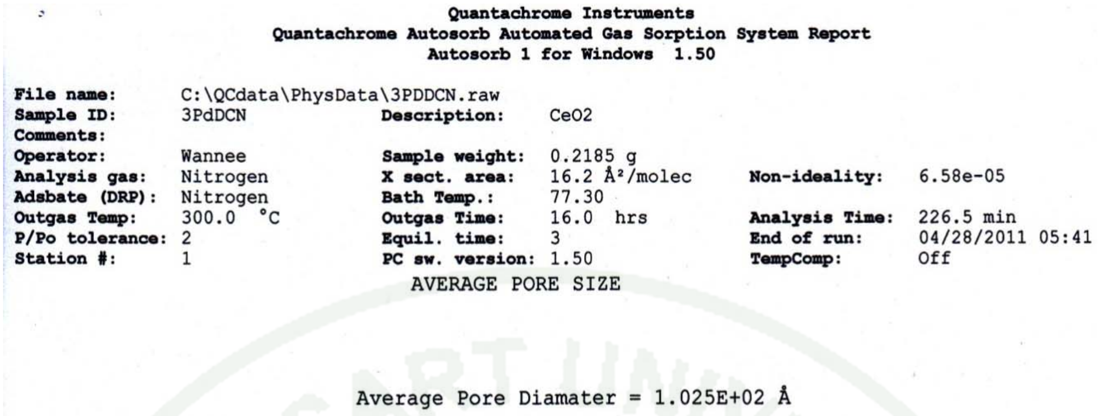

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Outgas Temp:      300.0  °C           Outgas Time:    16.0  hrs         Analysis Time:   226.5 min
P/Po tolerance:   2                   Equil. time:    3                 End of run:      04/28/2011 05:41
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                                         AVERAGE PORE SIZE


                              Average Pore Diamater = 1.025E+02 Å
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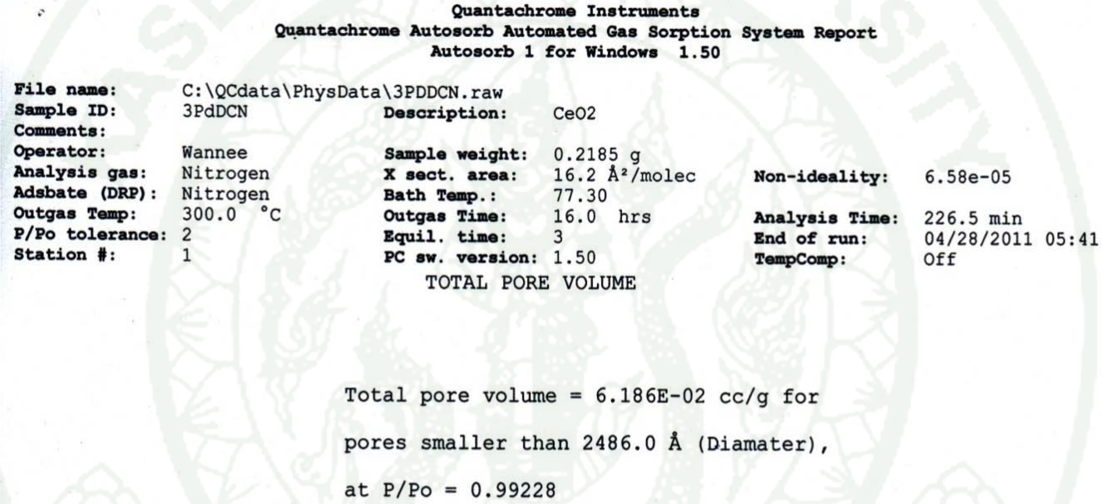

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Adsbate (DRP):    Nitrogen            Bath Temp.:     77.30
Outgas Temp:      300.0  °C           Outgas Time:    16.0  hrs         Analysis Time:   226.5 min
P/Po tolerance:   2                   Equil. time:    3                 End of run:      04/28/2011 05:41
Station #:        1                   PC sw. version: 1.50              TempComp:        Off
                                         TOTAL PORE VOLUME


                             Total pore volume = 6.186E-02 cc/g for

                             pores smaller than 2486.0 Å (Diamater),

                             at P/Po = 0.99228
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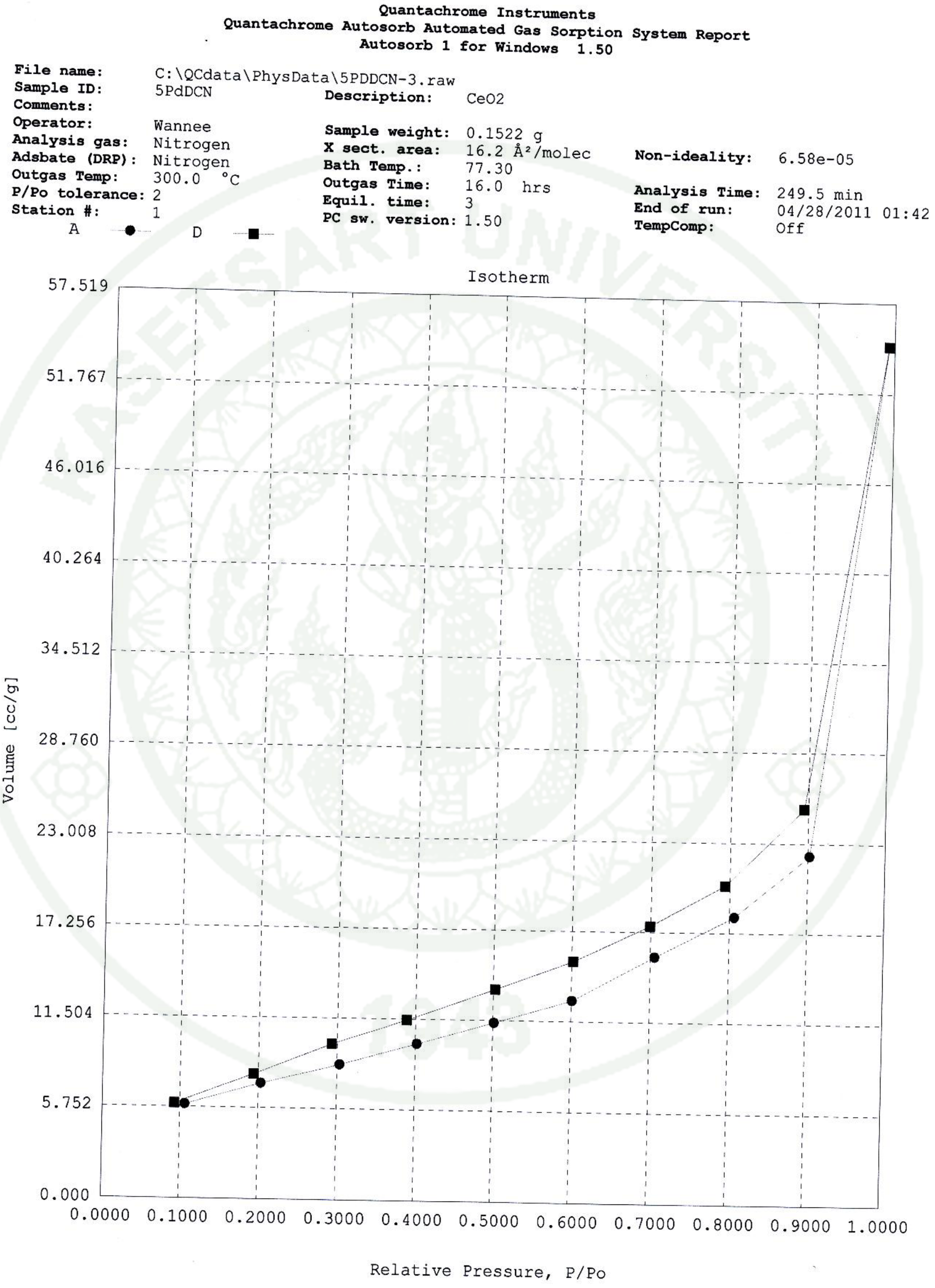
3. 5% palladium-doped ceria powder



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Adsbate (DRP):   Nitrogen        Bath Temp.:      77.30
Outgas Temp:     300.0  °C       Outgas Time:     16.0  hrs
P/Po tolerance:  2               Equil. time:     3                Analysis Time:  249.5 min
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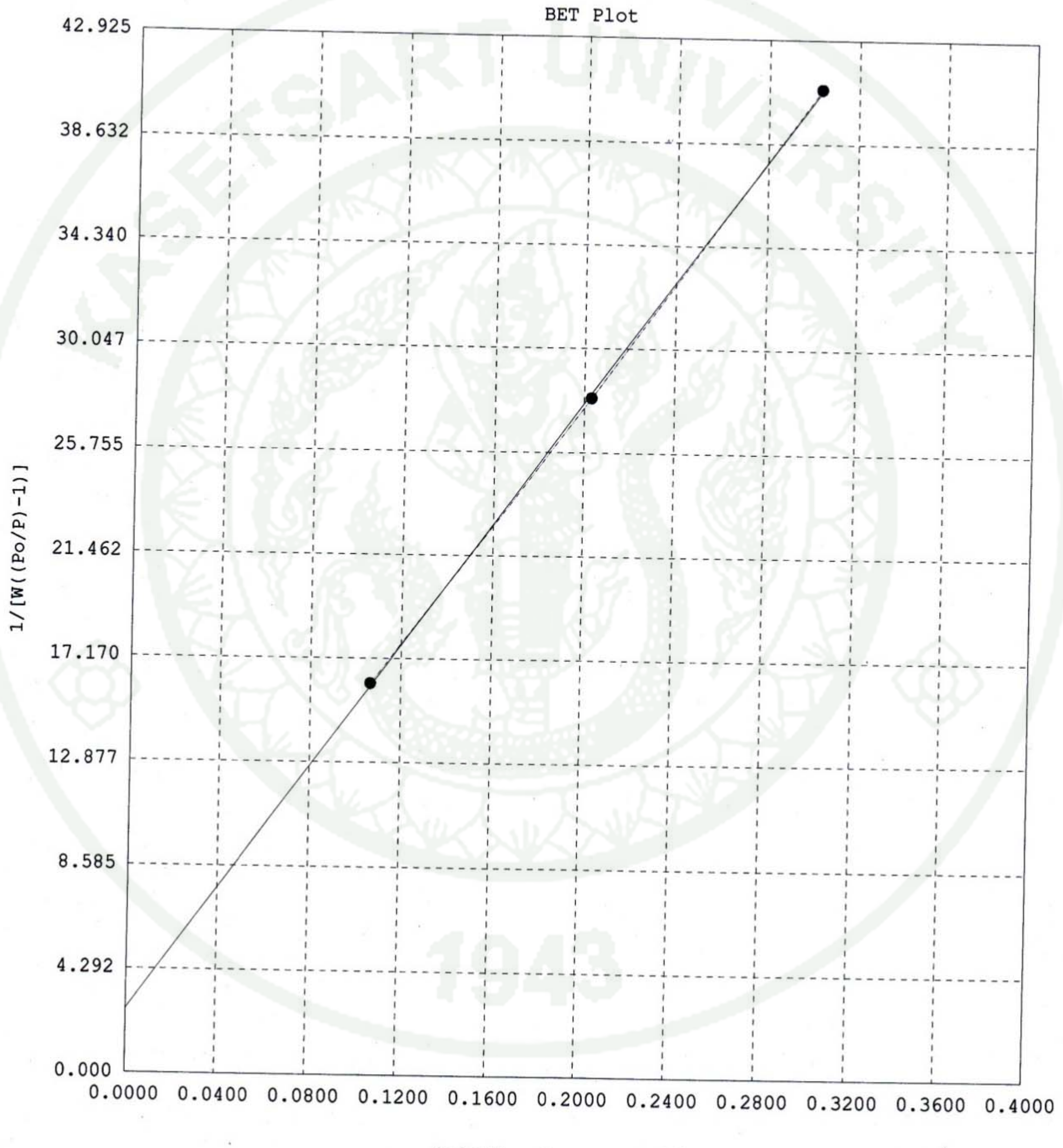
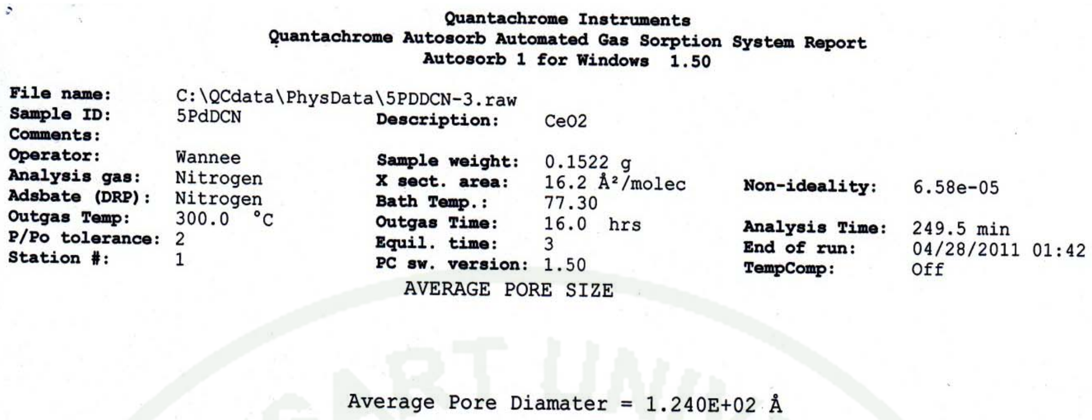


Area 27.16
(m²/g)



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Adsbate (DRP):    Nitrogen         Bath Temp.:      77.30
Outgas Temp:      300.0  °C        Outgas Time:     16.0  hrs         Analysis Time:   249.5 min
P/Po tolerance:   2                Equil. time:     3                 End of run:      04/28/2011 01:42
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                                     AVERAGE PORE SIZE


                          Average Pore Diamater = 1.240E+02 Å
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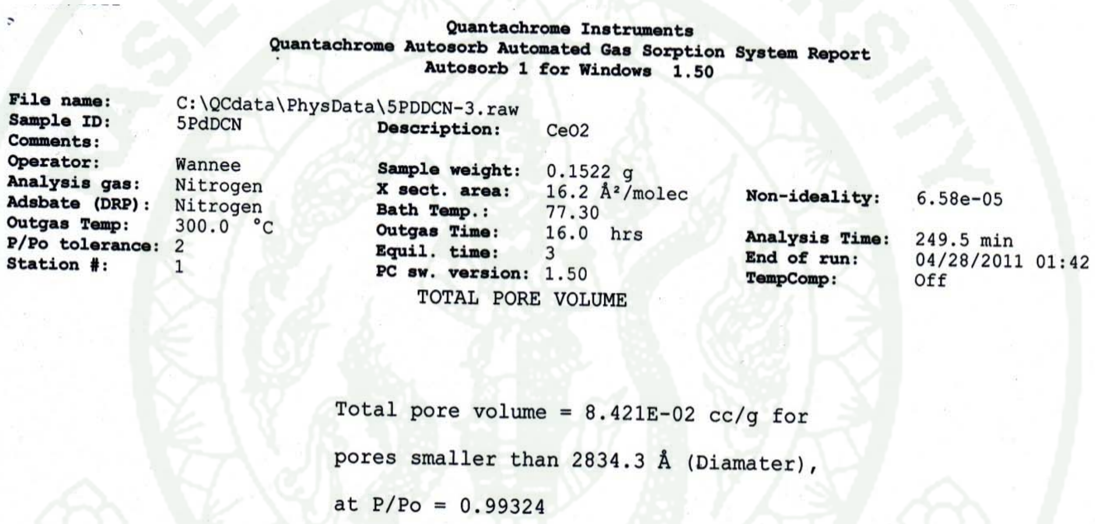

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Analysis gas:     Nitrogen         X sect. area:    16.2 Å²/molec     Non-ideality:    6.58e-05
Adsbate (DRP):    Nitrogen         Bath Temp.:      77.30
Outgas Temp:      300.0  °C        Outgas Time:     16.0  hrs         Analysis Time:   249.5 min
P/Po tolerance:   2                Equil. time:     3                 End of run:      04/28/2011 01:42
Station #:        1                PC sw. version:  1.50              TempComp:        Off
                                      TOTAL PORE VOLUME


                         Total pore volume = 8.421E-02 cc/g for

                         pores smaller than 2834.3 Å (Diamater),

                         at P/Po = 0.99324
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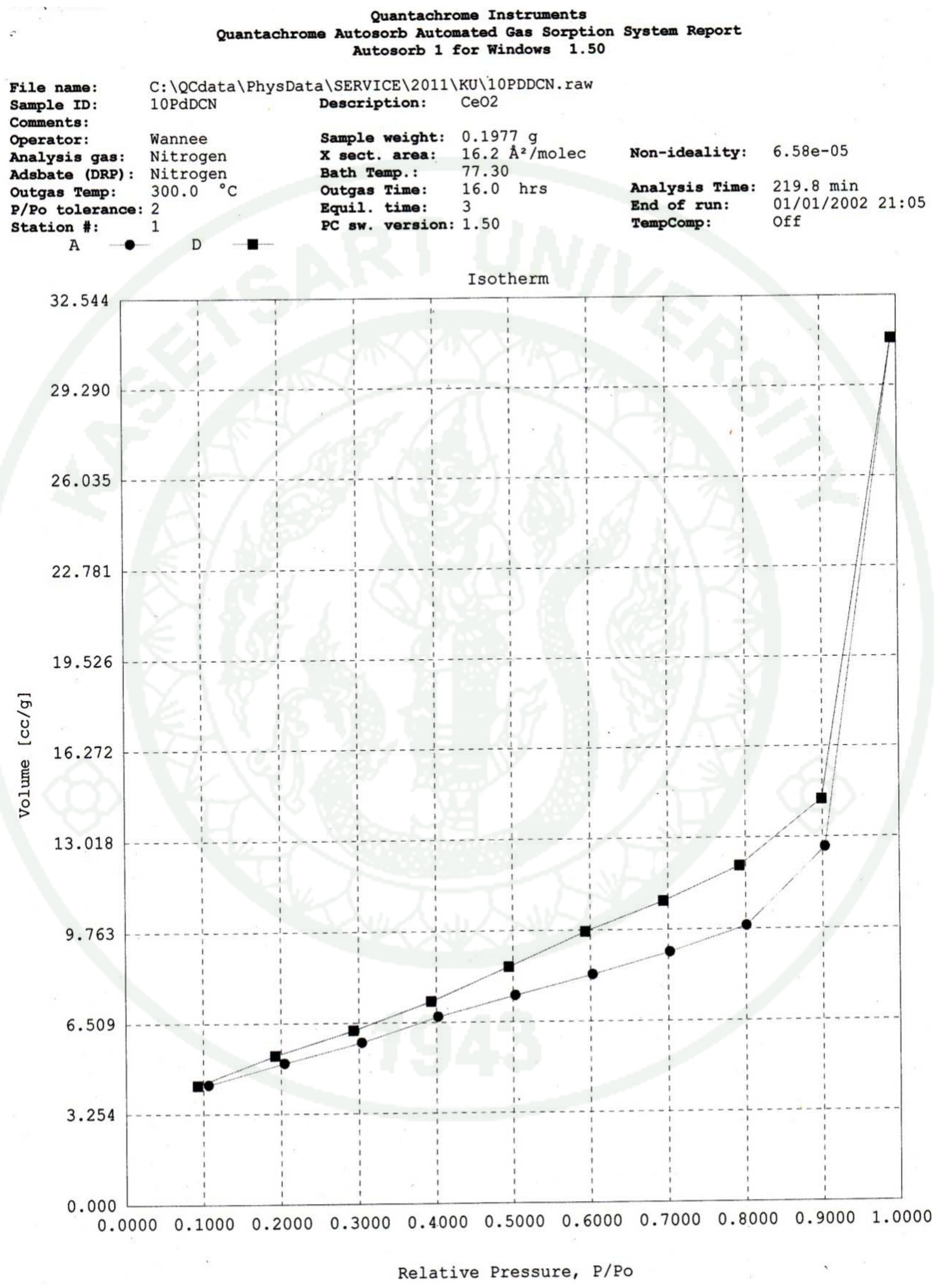
4. 10% palladium-doped ceria powder



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Adsbate (DRP):    Nitrogen           Bath Temp.:       77.30
Outgas Temp:      300.0  °C          Outgas Time:      16.0  hrs        Analysis Time:   219.8 min
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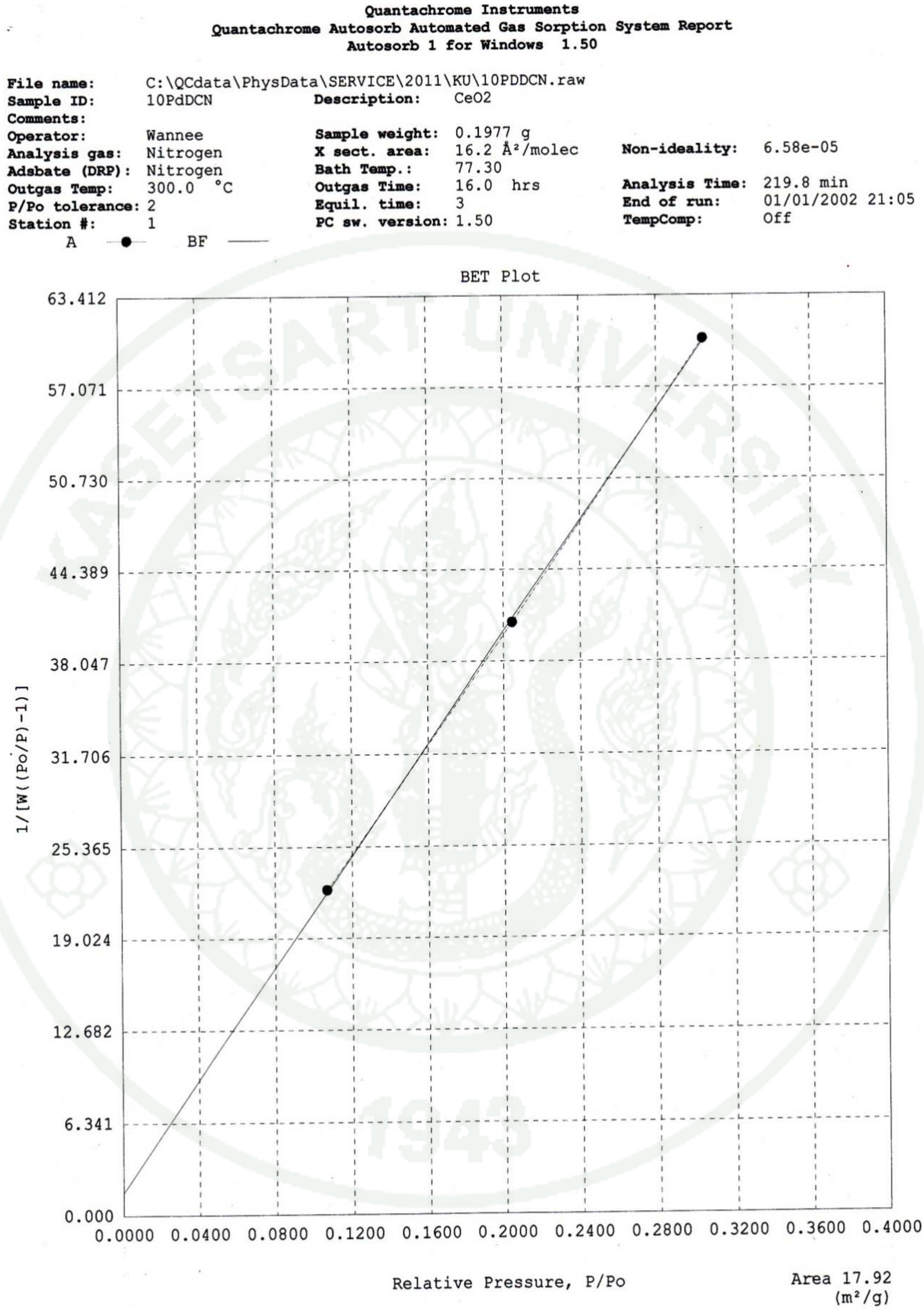

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Comments:
Operator:        Wannee             Sample weight:  0.1977 g
Analysis gas:    Nitrogen           X sect. area:   16.2 Å²/molec      Non-ideality:    6.58e-05
Adsbate (DRP):   Nitrogen           Bath Temp.:     77.30
Outgas Temp:     300.0  °C          Outgas Time:    16.0  hrs          Analysis Time:   219.8 min
P/Po tolerance:  2                  Equil. time:    3                  End of run:      01/01/2002 21:05
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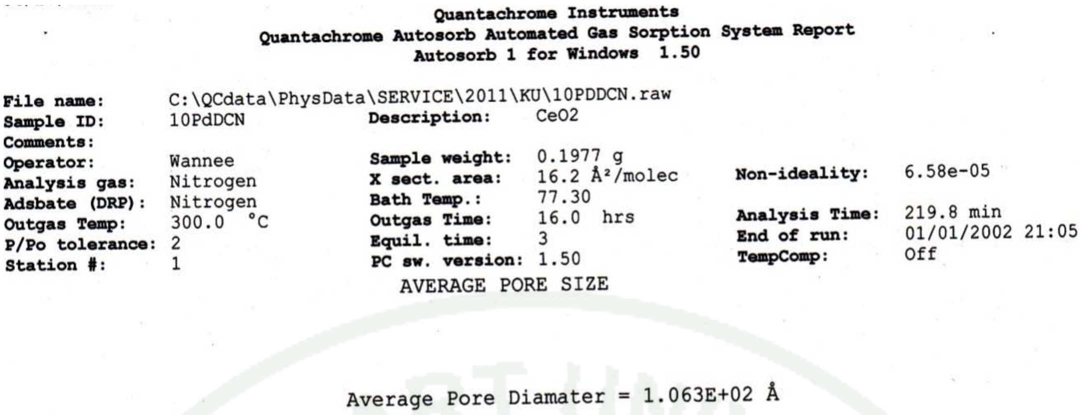

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Comments:
Operator:         Wannee           Sample weight:    0.1977 g
Analysis gas:     Nitrogen         X sect. area:     16.2 Å²/molec     Non-ideality:     6.58e-05
Adsbate (DRP):    Nitrogen         Bath Temp.:       77.30
Outgas Temp:      300.0  °C        Outgas Time:      16.0  hrs         Analysis Time:    219.8 min
P/Po tolerance:   2                Equil. time:      3                 End of run:       01/01/2002 21:05
Station #:        1                PC sw. version:   1.50              TempComp:         Off
                                      AVERAGE PORE SIZE


                          Average Pore Diamater = 1.063E+02 Å
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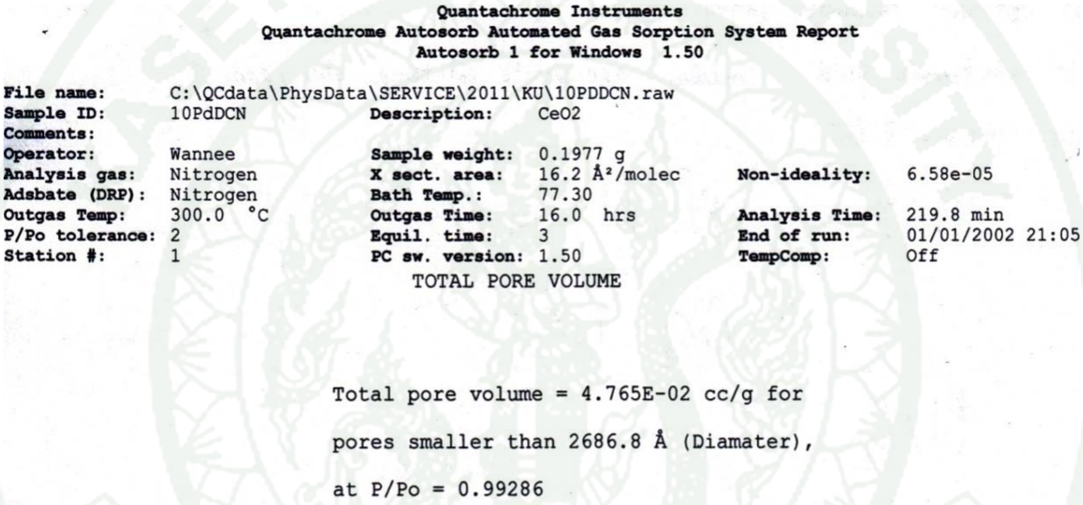

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Sample ID:        10PdDCN          Description:      CeO2
Comments:
Operator:         Wannee           Sample weight:    0.1977 g
Analysis gas:     Nitrogen         X sect. area:     16.2 Å²/molec     Non-ideality:     6.58e-05
Adsbate (DRP):    Nitrogen         Bath Temp.:       77.30
Outgas Temp:      300.0  °C        Outgas Time:      16.0  hrs         Analysis Time:    219.8 min
P/Po tolerance:   2                Equil. time:      3                 End of run:       01/01/2002 21:05
Station #:        1                PC sw. version:   1.50              TempComp:         Off
                                      TOTAL PORE VOLUME


                        Total pore volume = 4.765E-02 cc/g for

                        pores smaller than 2686.8 Å (Diamater),

                        at P/Po = 0.99286
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Preliminary Study of Pd/CeO_2 Derived from Cerium Complexes as Solid Support Catalysts for Hydrogenation Reaction in a Micro-reactor

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Abstract

This work was studied on the Pd/CeO_2 used as catalyst for hydrogenation reaction in micro-reactor. A simple cerium complex for CeO_2 was prepared from cerium nitrate and triethanolamine in 1-propanol. The feasible structures of cerium complexes as four-coordinate and five-coordinate Ce-TEA complexes were determined by MS and FTIR. By calcining the Ce-TEA complexes at 600°C for 2 h, the single phase of CeO_2 identified by XRD was obtained. Pd/CeO_2, the hydrogenation catalyst, was prepared by doping palladium nitrate into the cerium complex before calcining at 600°C for 2 h and investigated by XRD and SEM. The Pd-doped CeO_2 was preliminarily studied for catalytic hydrogenation of 4-cyanobenzaldehyde in a continuous-flow micro-reactor. Among all Pd/CeO_2 prepared, 10% Pd doped CeO_2 exhibited the greatest performance towards hydrogenation of 4-cyanobenzaldehyde in terms of the amount of hydrogenated products as 4-cyanobenzyl alcohol, 4-hydroxymethylbenzylamine, and 4-hydroxymethyltoluene.

Keywords: Ceria; cerium complex; hydrogenation; micro-reactor

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1. Introduction

Cerium(IV) oxide (ceria or CeO_2) has been considered as materials for applications of automotive exhaust catalyst [1], polishing material [2], reforming reaction catalyst [3], and electrochemical device [4]. The success of the material applications depended on the routes of powder synthesis. Many synthetic routes were, therefore, proposed in the relevant literatures, such as solid-solid reaction [5], co-precipitation of hydroxides [6], and sol-gel method [7]. However, many drawbacks such as lack of homogeneity and purity, complicated procedure, and high processing temperature leading to high cost were found from these synthetic routes. Laobuthee *et al.* [8]-[14] successfully prepared various high purity and homogeneous ceramic materials from the metal complex decomposition method, a very simple, low cost, and straightforward process. Based upon the basis of this process, CeO_2 was successfully prepared [14].

Nowadays, hydrogenation reactions show important roles in pharmaceutical, chemical and petroleum industries. Yoswathananont *et al.* reported an efficient hydrogenation reaction in a tube reactor [15]. In this flow system, a substrate solution was running through narrow channels formed in the Pd/C packed column with provided various advantages, such as, reducing in mass transfer between phases, no need for separation of products from catalyst, and providing an efficient hydrogenation reaction.

In this work, our group proposed an idea to prepare Pd-doped CeO_2 from mixtures of cerium complex with palladium nitrate salt for using as hydrogenation catalyst in flow system micro-reactor.

2. Experimental

2.1. Materials

Cerium (III) nitrate hexahydrate [$Ce(NO_3)_3.6H_2O$, 99.5% purity] was supplied from Acros Organics Co. Inc. (USA). Palladium nitrate hydrate [$Pd(NO_3)_2.xH_2O$] and 4-cyanobenzaldehyde were purchased from Aldrich Chemical Co. Inc (USA). Triethanolamine [TEA, $N(CH_2CH_2OH)_3$, 98% purity] and 1-propanol were obtained from Carlo Erba (Barcelona). All chemicals were used without further purification.

2.2. Instrumentals

The cerium complex was characterized by ESI-MS (Bruker Esquire mass spectrometer). Methanol was used as a solvent to prepare a cerium complex solution for mass analysis. The mass range of a complex was set from m/z 100 to 1000.

Fourier Transform infrared spectra were obtained by a Perkin-Elmer 2000-FTIR. Potassium bromide (KBr) as a matrix was mixed with a solid sample (0.3-0.5 wt %) by an agate mortar and pestle to prepare a pellet specimen for identifying the cerium complex functional group.

The decomposition of the cerium complex was studied by thermogravimetric analysis (TGA, a Perkin-Elmer TGA 7). Each sample (10 mg) was heated by heating rate 5°C/min in N_2 (20 psi) from 50-1000°C. The TGA balance flow meter was set at 20 psi N_2, while the purge flow meter was adjusted at 20 psi of synthetic air.

The powder product obtained after calcining a cerium complex was spread on glass microscope slides and then characterized by XRD (X'PertPRO MPD diffractometer) using nickel-filtered CuK_α radiation. Diffraction patterns were recorded over a range of 2θ angles from 5 to 90° and identified using the Joint Committee on Powder Diffraction Standards (JCPDS) file No. 34-0394.

Scanning Electron Microscope (SEM, a JEOL JSM-6510 scanning microscope) operating at an acceleration voltage of 5 kV, a work distance of 10 mm and magnification values in 5,000x was used to identify the microstructure of powder samples. Samples were mounted on stubs using a liquid carbon paste and then sputter coated with Pt to avoid particle charging.

2.3. Procedure

2.3.1. Preparation of CeO_2 from cerium complex

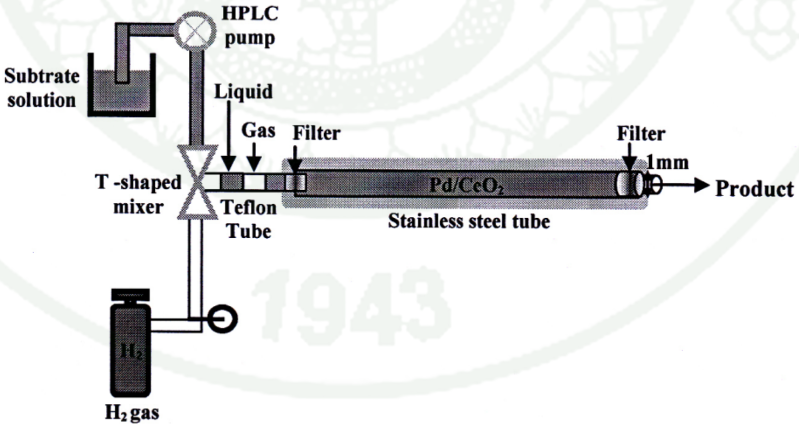
The mixture of cerium nitrate hexahydrate [$Ce(NO_3)_3.6H_2O$ (10.86 g, 25 mmol)], triethanolamine (TEA, 3.4 ml, 25 mmol) and 200 ml of 1-propanol as a solvent, was added into a round bottom flask and then heated for 5 h to complete the reaction. The homogeneous product was characterized by ESI-MS, FTIR, and TGA.

Cerium complex was calcined in the horizontal tube furnace at 600°C for 2 h. The powder product was ground in an alumina mortar and characterized by XRD and SEM.

2.3.2. Study on Pd/CeO_2 as solid support catalysts in hydrogenation reaction

Palladium nitrate hydrate [$Pd(NO_3)_2.xH_2O$, 0.1728, 0.2880 and 0.5760 g] was mixed with the obtained cerium complex to prepare CeO_2 doped 3%, 5% and 10% by mol of palladium. The doped cerium complex was calcined in a furnace at 600°C for 2 h. The powder products were characterized by XRD and SEM.

Each of the Pd/CeO_2 powders was packed in a stainless steel tube (25 cm in length, 1.0 mm and 6.3 mm as inner and outer diameters, respectively) with two filters at both ends to hold the catalyst in the column, was performed in a high pressure flow system operating via a continuous-flow micro-reactor with the residence time of 2 min 50 s (Scheme 1). 4-Cyanobenzaldehyde in methanol as a substrate solution was mixed with hydrogen gas at the T-shaped mixer. The flow rate of the substrate solution controlled by HPLC pump was 0.038 mL/min while the hydrogen gas was set around 2.0 MPa. To observe the gas-liquid flow, a transparent teflon tube was connected between the T-shaped mixer and the tube column. The product solution eluted at the end of the column was characterized by ^1H-NMR.



Scheme 1

3. Results and Discussion

3.1. Cerium complex preparation

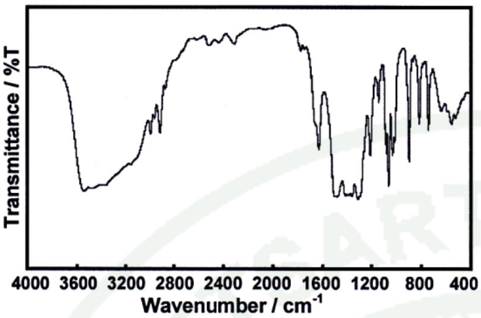


Fig. 1. FTIR Spectrum of Cerium Complex.

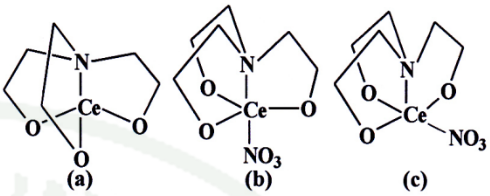


Fig. 2. The Possible Structures of Cerium Complex: (a) Corresponding to m/z = 286, (b) and (c) Corresponding to m/z = 349.

By FTIR, the yellowish powder obtained from the complete reaction of $Ce(NO_3)_3$ and TEA in 5 h was studied. FTIR spectrum (Figure 1) revealed characteristic groups in the cerium complex. The broad peak centered at 3402 cm^{-1} was assigned to the O-H stretching due to moisture absorption and/or triethanolamine residue from the reaction. The peaks at 2988 and 2915 cm^{-1} were assigned to asymmetric and symmetric modes of methylene ($-CH_2-$) stretching, respectively. The peak at 1627 cm^{-1} was assigned to O-H bending overtone. The C-H bending bands were shown in the region of 1450-1200 cm^{-1}. The N-O stretching of nitrate group showed absorption bands in region of 1550-1250 cm^{-1}. The Ce-O-C bending resonated at 1082 cm^{-1}. Moreover, the band at 554 cm^{-1} was assigned to Ce-O stretching.

The possible structures of the product were identified using electrospray ionization (ESI) techniques. The major peaks was appeared at m/z = 286 and 349. The structures of product were proposed in Figure 2.

To obtain CeO_2, TGA was used to clarify the appropriate calcination temperature for the cerium complex. Thermogram (Figure 3) shows three regions of mass loss. The first mass loss involved the decomposition of the organic ligand occurs between 100° and 250°C. In this step, volatiles and char were generated. The obtained char was continuously oxidized by heating from 250° to 500°C as shown in the region of second mass loss. The TGA result indicated that the appropriate temperature for calcination was 600°C. Hence, cerium complex was then calcined at 600°C for 2 h to obtain a yellowish color of CeO_2.

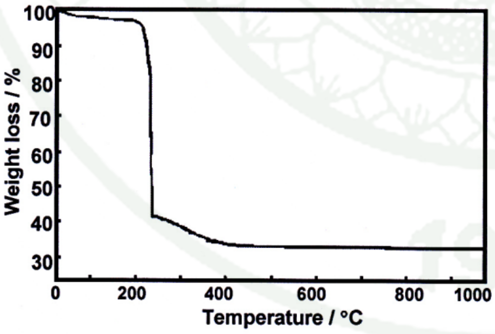


Fig. 3. Thermogram of Cerium Complex.

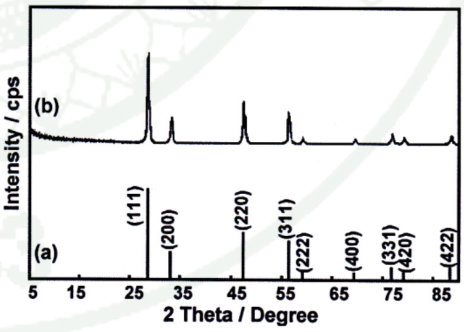


Fig. 4. (a) CeO_2 Reference (JCDPS No 34-0394) and (b) XRD Pattern of Prepared CeO_2.

X-ray powder diffraction pattern (Figure 4) of the calcined product showed nine major peaks of CeO_2 with *hkl* reflections at (111), (200), (220), (311), (222), (400), (331), (420), and (422) which are located at 2θ are 28.555, 33.082, 47.479, 56.335, 59.087, 69.402, 76.700, 79.070, and 88.412, respectively. All peak positions were identified by comparing with JCPDS file No. 34-0394, indicating the phase purity of CeO_2.

3.2. Study on Pd/CeO_2 as solid support catalysts in hydrogenation reaction

The obtained Pd-doped cerium complexes are black-yellow color powders while the cerium complex was a yellow powder. The Pd-doped cerium complexes were calcined with the same condition as an undoped cerium complex (600°C for 2 h) to obtain the brown powder products. To confirm the successfully doping of palladium on CeO_2, XRD and SEM were employed.

By comparing XRD patterns of single phase CeO_2 and Pd-doped CeO_2 (Figure 5), it was found that no difference in CeO_2 matrix phase; however, there are some addition peaks generated in Pd-doped CeO_2 implying the presence of palladium (II) oxide.

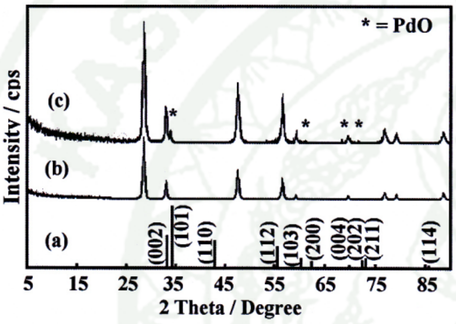


Fig. 5. (a) PdO Reference (JCDPS No 88-2434) and XRD Patterns of (b) prepared CeO_2 and (c) 10% Pd-doped CeO_2.

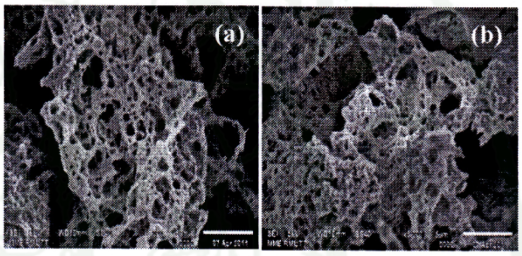
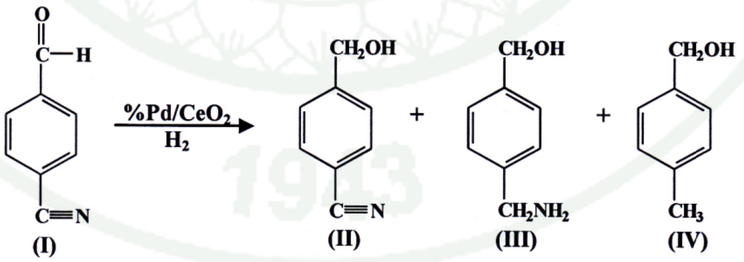


Fig. 6. SEM Micrographs of (a) CeO_2 and (b) 10%Pd/CeO_2.

SEM micrographs of CeO_2 and 10% Pd doped CeO_2 were shown in Figure 6. The CeO_2 and 10% Pd/CeO_2 exhibited the foam-like structures containing various sizes of porosity. In this work, all of the samples; 0%, 3%, 5%, and 10% Pd/CeO_2, were preliminarily applied as catalysts for hydrogenation of 4-cyanobenzaldehyde. The obtained products from hydrogenation were shown in Scheme 2 while the amount of products quantitatively analyzed by ^1H-NMR was presented in Table 1.



Scheme 2

Table 1. Catalytic Activity of Pd/CeO_2 to Hydrogenation Reaction.

% Pd in CeO_2	Compound (%)			
	(I)	(II)	(III)	(IV)
0%	0	0	0	0
3%	0	4	81	15
5%	0	0	89	11
10%	0	0	84	16

Aldehyde and cyano functional groups consisting in 4-cyanobenzaldehyde (I) were hydrogenated by Pd/CeO_2 to obtain 4-cyanobenzyl alcohol (II), 4-hydroxymethylbenzylamine (III), and 4-hydroxymethyltoluene (IV) (Table 1). No starting material remained in this condition. As comparing the results with that of 5% $NiAl_2O_4$ and 5% Pd/C studied previously by Ummartyothin *et al.*[11] and Yoswathananont *et al.* [15], respectively, the same products (II and III) were obtained but the product (IV) was only obtained in this work. The results indicated that Pd/CeO_2, especially 10% Pd/CeO_2, showed the most efficiency to use as a catalyst for hydrogenation of 4-cyanobenzaldehyde.

4. Conclusion

The cerium complex decomposition which retains the advantages of purity, homogeneity, low processing temperatures is an inexpensive, straightforward alternative to prepare CeO_2. A pure and homogeneous CeO_2 powder was obtained by calcining the cerium complex at 600°C for 2 h.

The doping palladium on CeO_2 was successfully prepared by calcining the mixture of cerium complex with palladium nitrate at 600°C for 2 h. Among all prepared Pd/CeO_2, 10% Pd/CeO_2 showed the greatest performance towards hydrogenation reaction of 4-cyanobenzaldehyde in terms of the highest 4-hydroxymethyltoluene. In addition, the catalytic efficiency of the prepared Pd/CeO_2 for hydrogenation reaction in the continuous-flow micro-reactor was higher than Pd/C and Pd/$NiAl_2O_4$.

Acknowledgments

This work was supported by Junior Science Talent Project (JSTP-50-19R), National Science and Technology Development Agency (NSTDA), and the Postgraduate Education and Research Programs in Petroleum and Petrochemical Technology (ADB-MUA). The authors would like to thank Dr. Nungruethai Yoswathananont and Prof. Masaaki Sato from Department of Chemistry, Faculty of Science, Osaka Prefecture University, Osaka, Japan for helping in the study on the hydrogenation by using a continuous-flow micro-reactor.

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