# Hydrogen production from dry-reforming of biogas over $Pt/Mg_{1-x}Ni_xO$ catalysts

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***Abstract:***
*Dry reforming of biogas carried out over $Pt/Mg_{1-x}Ni_xO$ catalysts, where x= 0, 0.03, 0.07, and 0.15 with 1 wt% Pt for each, prepared by the co-precipitation method from aqueous solution of $Ni(NO_3)_2.6H_2O$ and $Mg(NO_3)_2.6H_2O$ using $K_2CO_3$, then the platinum(II)acetylacetonate impregnated on MgO–NiO. The synthesized catalysts analyzed by XRD, FT-IR, XRF, XPS, BET and TEM. at 700°C, the catalysts reduced by $H_2$ prior to each reaction. The order of conversions of $CO_2$ and $CH_4$ at 900°C of the reduced catalysts after being on the stream for 200 h was as follows: $Pt/Mg_{0.85}Ni_{0.15}O$ > $Pt/Mg_{0.93}Ni_{0.07}O$ > $Pt/Mg_{0.97}Ni_{0.03}O$ > Pt/MgO with a $CH_4$:$CO_2$ mole ratio of 2:1 that displayed the best resistance to deactivation by carbon formation and formed high selectivity of $H_2$ and CO. The dry reforming reaction was also carried out with the presence of low concentrations of oxygen (1.25%) flow and showed an enhancement in the conversion of $CH_4$.*

***Keywords:*** *Synthesis gas; $H_2$ production; Dry-Reforming of biogas; MgO-NiO catalyst*

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## 1. Introduction

Palm oil biomass is the most abundant and bio-renewable resource in Malaysia and Indonesia with great potential for sustainable production of chemicals and fuels. Effluents from palm oil mills also known as palm oil mill effluent (POME) is always regarded as a highly polluting wastewater. Anaerobic digestion is widely adopted in the oil palm industry as a primary treatment for POME. At many palm-oil mills this process is already in place to meet water quality standards for industrial effluent. The biogas, however, is flared off. Biogas contains two greenhouse gases (GHG) *i.e.* about 60-70% methane ($CH_4$) and 30-40% carbon dioxide ($CO_2$) and also trace amount of hydrogen sulphide, ($H_2S$). (Chin et al., 2013; Poh et al., 2009). Dry reforming of methane (DRM) has received great attention due to its environmental benefits from utilizing these two greenhouse gases and producing highly valuable synthesis gas (syngas, $H_2$ and CO) as a feedstock.

## 2. Material and methods

$Pt/Mg_{1-x}Ni_xO$ catalysts, where x= 0, 0.03, 0.07, and 0.15 with 1 wt% Pt for each, were prepared by the co-precipitation method from aqueous solution of Ni $(NO_3)_2.6H_2O$ and Mg $(NO_3)_2.6H_2O$ using $K_2CO_3$, after being filtered and washed with hot water, the precipitate was dried at 120°C for 12 h, and then pre-calcined in air at 500℃ for 5 h. following that, they were pressed into disks at 600 kg/m$^2$, and calcinated in air at 1150℃ for 20 h. $Pt/Ni_xMg_{1-x}O$ and Pt/MgO, catalysts were prepared by impregnating support with a dichloromethane solution of $Pt(C_5H_7O_2)_2.H_2O$. The catalysts were dried at 120℃ after impregnation in air for 12 h. The synthesized catalysts were analyzed by XRD, BET surface area and TEM. Crystalline structures of the samples were investigated using X-ray diffraction (XRD) with a Shimadzu XRD-6000 diffractometer. The surface area, pore volume and pore size diameter of the samples were determined using $N_2$ adsorption–desorption technique with a Thermo Finnigan Sorptomatic Instrument, model 1900. The coke formation of the used catalysts was examined by temperature programmed oxidation (TPO) using a Thermo Finnigan TPD/R/O 1100 Instrument.

The catalytic evaluation for dry reforming of biogas was performed in a continuous flow system using a fixed bed stainless steel micro-reactor. The reactor was connected to a mass flow gas controller and an online gas chromatograph (GC) (Agilent 6890N; G 1540N). Prior to reaction, approximately 0.02 g catalyst was reduced by flowing 5% $H_2$/Ar (30 ml/min) from 100 to 700°C and holding for 3 h. The reforming reaction was performed by flowing a gas mixture consisting of $CH_4$:$CO_2$ = 2:1 and 1:1 at a rate of 30 ml/min from 700 to 900°C , then holding for 200 h.

The surface analysis was performed using an X-ray Photoelectron Spectroscopy (XPS) model Kratos Ultra Axis that operated at ultra high vaccum of $10^{-11}$ Torr. A monochromatic Al Kα sources is used as a photon to irradiated the sample surface. The carbon charging correction of the spectrum was corrected using the adventitious carbon binding energy value at 284.6 eV.

**3. Results and Discussion**

The XRD patterns of the catalysts are shown in (Fig. 1). Reflections of MgO were detected in NiO-MgO supported by Platinum catalysts in their wide-angle XRD patterns The smart diffraction peaks at around 2θ = 39.7, 42.9, 62.5,75 and 79° are due to the cubic form of catalyst. Whereas the diffraction lines at about 2θ = 37, 43.1, 62.3, 74.8 and 78.7° are ascribed to the cubic phase of magnesia The XRD patterns of the catalysts showed the crystal system for the catalysts are in cubic phase and was confirmed by TEM image (Fig. 2).

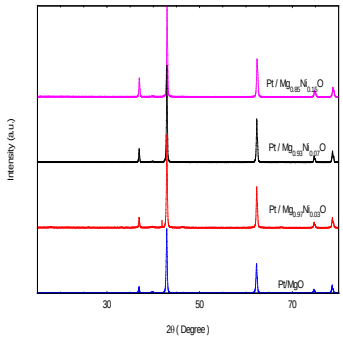


**Fig. 1** XRD pattern of the catalyst

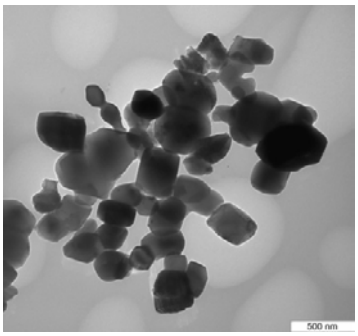


**Fig. 2** TEM image for $Pt/Mg_{0.85}Ni_{0.15}O$.

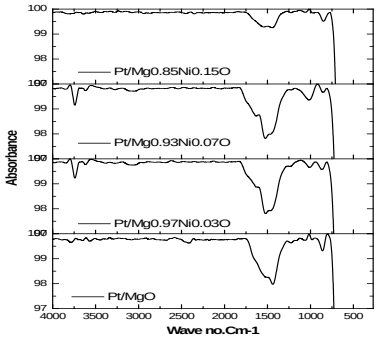


**Fig. 3** FTIR of catalyst.

FTIR measurement shows (Fig.3) that the bonds for Pt-O, Ni-O, and MgO exists in the far IR region and all the peaks in the spectra are attributed to acetylacetonate. Surface study of the catalyst at a few nanometer layer of its uppermost using XPS indicate that there are a photoelectron signal from C1s, O1s, Mg2p, Ni2p and Pt4f, as illustrated in Fig. 4(a-e). A deconvolution of a C1s narrow scan indicated that there are three type of carbon species which is C-C (or C-H), C-O and C=O. The O1s photoelectron signal shows that it is contribute by five type of oxygen species which is contributed by $O^{2-}$ (from the bulk), MgO, NiO, PtO and hydroxyl ($OH^-$) component. This is also a significant splitting of this O1s spectrum, whereby NiO exhibit as the highest intensity of photoelectron signal at the lower binding energy region compared to the others. However, the $O^{2-}$, NiO, PtO and $OH^-$ are detected under a similar photoelectron envelope. However, the contribution of $OH^-$ component is considered very low at the binding energy of 533.0 eV. On the other hand, the narrow scan of Mg2p, Ni2p and Pt4f revealed that the oxide species of these metal are a mixture of MgO and $Mg(OH)_2$, NiO and $Ni(OH)_2$ and PtO respectively. The existence of two component of hydroxyl species by Ni and Mg indicate that, these metal is easily to react with water vapour compound ($H_2O$).

BET specific surface area ($S_{BET}$) value and pore properties of catalyst supports and freshly prepared catalysts are shown in Table 1. After impregnation, the $S_{BET}$ value and pore volume decreased in all

three of the catalysts. This phenomenon might be caused by pore blocking during the impregnation process. The $S_{BET}$, pore volume, and average Pt-loading of freshly prepared catalysts are also prese nted in Table 1.

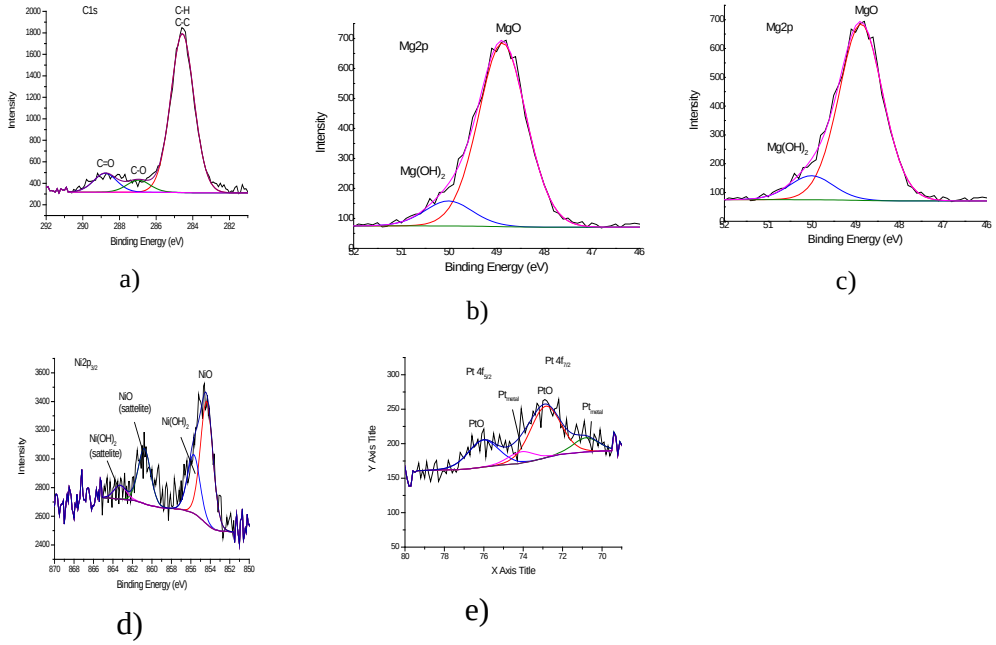


**Fig. 4** XPS of the $Pt/Mg_{0.85}Ni_{0.15}O$ catalyst.

**Table 1** The main textural properties of fresh catalysts

| Sample name | Specific [a] Surface Area $m^2/g$ | Pore Volume $Cm^3/g$ | Pore volume to $S_{BET}$ ratio $10^{-9}m$ | Pore radius $^oA$ | Pt [b] Loading Wt % | Average [c] Crystal size nm |
|---|---|---|---|---|---|---|
| Pt / MgO | 8.46 | 0.41 | 48.4 | 18.26 | 0.95 | 38.7 |
| Pt $Mg_{0.97}Ni_{0.03}O$ | 9.64 | 0.17 | 17.6 | 18.25 | 0.98 | 44.7 |
| Pt $Mg_{0.93}Ni_{0.07}O$ | 3.82 | 0.06 | 15.7 | 18.26 | 0.94 | 42.4 |
| Pt $Mg_{0.85}Ni_{0.15}O$ | 3.77 | 0.04 | 10.6 | 18.24 | 0.93 | 40.4 |

[a.] Specific surface area calculated by BET method, [b.] Determined by the XRF method, [c.] Determined by the Debye-Scherrer equation of the Mg (200) plane of XRD.

The largest pore volume was found in Pt / MgO, while Pt / $Mg_{0.97}Ni_{0.03}O$ had the largest $S_{BET}$ value. There was no obvious connection between the $S_{BET}$ value and pore volume of catalysts, but the pore volume/$S_{BET}$ ratio increased in the order Pt / MgO > Pt / $Mg_{0.97}Ni_{0.03}O$ > Pt / $Mg_{0.93}Ni_{0.07}O$ > Pt / M $g_{0.85}Ni_{0.15}O$ which was in accordance with the Pt-dispersion order, and Bappy Saha[30] also proved th at a high pore volume/$S_{BET}$ ratio contributes to high catalytic performance. The XRF results in Tabl e 1 show that the Pt-loading was slightly lower than the set value of 10%.This might be caused by weight loss during the pre-calcination of the supports, resulting in a higher Ni content in the catalyst

The dry reforming reaction's activity was indicated by the conversion of $CH_4$ and $CO_2$, and the selectivity was expressed in terms of the $H_2$/CO ratio.Fig. 5 shows the most active catalyst in the dry reforming of biogas. The reaction was carried out for 200 h at 900$^o$C and revealed that the catalyst gave > 95% conversion for both $CO_2$ and $CH_4$. The order of conversions of $CO_2$ and $CH_4$ are as follows: $Pt/Mg_{0.85}Ni_{0.15}O$ > $Pt/Mg_{0.93}Ni_{0.07}O$ > $Pt/Mg_{0.97}Ni_{0.03}O$ > Pt/MgO with a $CH_4$:$CO_2$ mole ratio of 2:1. $Pt/Mg_{0.85}Ni_{0.15}O$ displayed the best resistance to deactivation by carbon formation and formed high selectivity of $H_2$ and CO. Both pore of supporter and doping metal played a vital role in the conversion process as indicated by BET results. Dry reforming of biogas reaction was also carried out with the presence of low concentration of oxygen flow (1.25%) and Fig. 6 showed

an enhancement in the conversion of $CH_4$.This oxygen reacted with $CH_4$ to produce CO and $H_2O$ Eq.(1), and finally the steam reacts with deposited carbon to gives syngas Eq.(2).

$$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O \quad (1)$$

$$C(s) + H_2O \rightarrow CO + H_2 \quad (2)$$

Results should be clear and concise. Quantitative results should be expressed using SI units. Tables and Fig.s should be referred to in the text.

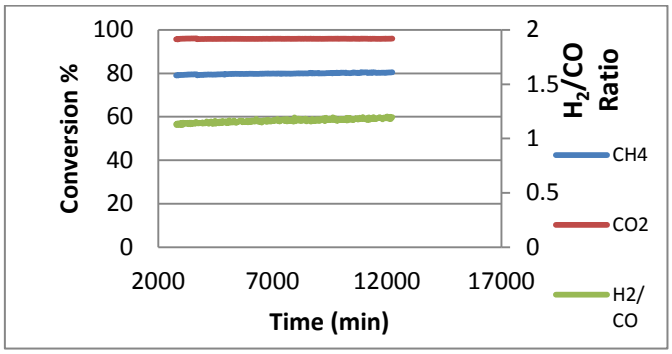


**Fig. 5** Stability tests of $CH_4$, $CO_2$ Conversion and $H_2$/CO ratio over $Pt/Mg_{0.85}Ni_{0.15}O$ catalyst.

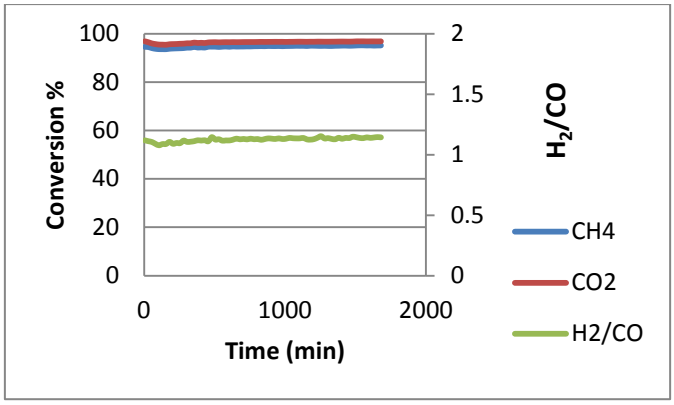


**Fig. 6** The effect of oxygen on dry reforming of methane.

## 4. Conclusion

Incorporation of NiO onto MgO exhibited a notable conversion when a compared to MgO alone, while addition of Pt to MgO-NiO as promoter has augmented conversion of $CO_2$ up to 99%.$CH_4$ to $CO_2$ gases at 2:1 ratio had produced highest conversion as compared to that obtained by 1:1 ratio. Hence, as result of this process, the carbon deposition is reduced and consequently the life time of the catalyst has improved.

## 5. References

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