Influence of Palladium on Ni-based Catalyst for Hydrogen Production via Thermo-catalytic Methane Decomposition

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This study investigates the effect of introducing palladium (Pd) as a promoter on the catalytic performance of Ni/Al_2O_3 catalysts which were prepared by wet impregnation method at various reaction temperatures. The catalytic activity, thermal stability and deactivation rate of the synthesized catalysts were evaluated at atmospheric pressure on a conventional fixed bed reactor at the temperature ranges of 873−1073 K for 4 h at constant methane flow-rate. The results suggested that the introduction of Pd on Ni/Al_2O_3 can significantly enhance the catalytic activity of the catalysts. A slower deactivation rate was observed for $Ni-Pd/Al_2O_3$ catalyst. This is due to the positive effect of Pd on metallic Ni particles, improving the ability of the catalyst to accumulate carbon, thus enhancing the thermal stability at elevated temperatures.

1. Introduction

Hydrogen is an attractive source of clean fuel because the combustion of hydrogen for energy production produces only water and does not contribute towards any greenhouse gasses (GHGs) emissions. Hydrogen has the highest energy density as compared to other types of conventional fossil fuels such as methane, gasoline, and coal because the amount of energy produced during hydrogen combustion is higher than the other fuels on a mass basis (Ammendola et al., 2007). Steam methane reforming (SMR) is the most popular hydrogen production technology because of its high efficiency, low heating value and low operating cost. The drawback of this technology is the generation of GHGs as a by-product, which is estimated to be 13.7 kg of CO_2 per kg of H_2 produced (Wu et al., 2013). The discovery that methane can be directly decomposed into hydrogen and carbon has garnered the attention for hydrogen production through thermocatalytic decomposition (TCD) of methane, alternatively known as catalytic cracking of methane. This process is feasible because it does not produce CO_2 or CO as by-products and does not contribute towards any GHGs emission to the atmosphere. The production cost for hydrogen by methane TCD can be significantly reduced by marketing the solid carbon for construction material (Wang and Lua, 2013, Ashok et al., 2008, Wenge et al., 2012, Zhang et al., 2013). In this present work, the effect of adding Pd metal over Ni/Al2O3 to the catalytic activity and catalytic lifetime were investigated. The composition of catalysts is 2 wt.% Ni supported on alumina, 2 wt.% Pd supported on alumina and 1 wt.% Ni-1 wt.% Pd supported on which were prepared by wet impregnation method and evaluated at temperature ranges 600-800℃. The morphologies and physicochemical properties of the synthesized catalysts were characterized by various characterization methods in the methodology section.

2. Methods

2.1 Catalyst preparation and characterization

The catalysts were prepared by using the wet impregnation method. The alumina support used was γ-Al_2O_3. The alumina support was pre-calcined in the air in a furnace chamber at 900 ℃ for 12 h with a ramping rate of 5℃/min. The support was then mixed with deionized water to wet the support and aqueous solution of nickel

(II) nitrate hexahydrate and tetraamine palladium (II) chloride monohydrate were titrated dropwise onto the alumina support. This slurry was heated to 80℃ with stirring to facilitate homogeneous mixing until most of the water had evaporated. The impregnated catalysts were dried at 120℃ overnight and calcined at 500℃ for 6 h with a ramping rate of 5℃/min. The catalysts were subjected to various characterization methods such as N_2 isotherms, Scanning Electron Microscopy (SEM), Temperature Programmed Reduction (TPR) and Thermogravimetric Analysis (TGA) to understand their physical properties.

2.2 Experimental set-up

The catalysts were subjected to reduction at 400℃ under a stream of H_2 gas for 4 h prior to reaction study. Catalytic activity and operational lifetime of the synthesized catalysts were evaluated in a conventional fixed bed continuous flow reactor with 500 mg of catalyst, using the single-zone furnace at atmospheric pressure. The detailed experimental work was based on our previous setup (Mei et al., 2016).

3. Results and discussion

3.1 Surface area and pore volume analysis by N_2 isotherms

The specific surface areas and pore volumes which were determined by N_2 physisorption for the calcined catalysts and shown in Table 1, while the absorption isotherms and pore size distributions were indicated in Figure 1. The specific surface area for the commercial γ-Al_2O_3 support is determined to be 208 m^2/g while the pore volume is 0.38 m^3/g. It can be observed that the addition of Ni and Pd onto the alumina support reduced the specific surface areas and pore volumes, as well as shifted the pore size distribution towards smaller pore diameters. The results indicate that the impregnated Ni and Pd particles have blocked some pores of the support. The low pore volume of the Ni-Pd/Al_2O_3 catalyst suggested the strong agglomeration of the impregnated Ni and Pd particles onto the support and by the formation of new phase such as Ni aluminate or Pd aluminate due to the diffusion of Ni^{2+} and Pd^{2+} into the support. From the pore size distribution, it can be observed that the Ni/Al_2O_3 catalyst had a bimodal pore size distribution with one peak around 45 Å and another peak around 60 Å. In comparison, the peak maximums occurred at approximately 50 Å and 70 Å for Pd/Al_2O_3 and Ni-Pd/Al_2O_3, respectively.

Table 1: Specific surface area and pore volumes with calcined catalysts

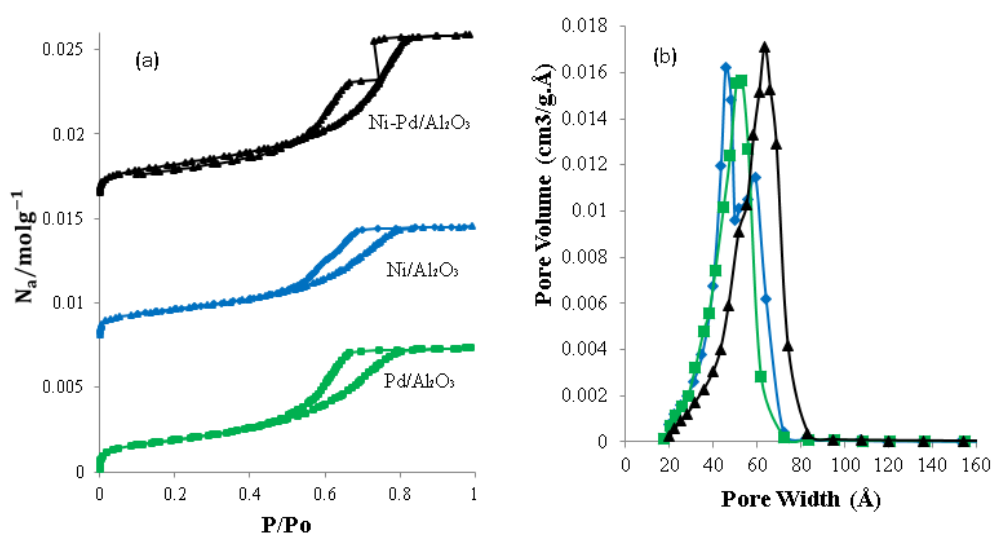| Type of catalysts	Surface Area (m^2/g)	Pore Volume (cm^3/g)
γ-Al_2O_3	208.00	0.38
Ni/Al_2O_3	186.34	0.34
Pd/Al_2O_3	182.89	0.32
Ni-Pd/Al_2O_3	196.73	0.31

Figure 1: (a)Adsorption/desorption isotherms (b) and pore size distribution of calcined catalysts. The symbol represents :(♦) Ni/Al_2O_3; (■) Pd/Al_2O_3 and (▲) Ni-Pd/Al_2O_3.

3.2 SEM images

SEM technique was used to analyze the surface morphology of the prepared catalysts. The catalysts which were prepared by the impregnation method (Figures. 2(a)-2(c)) exhibited morphologies, in which the catalysts appeared to have wrinkled surfaces with the formation of crevices on the catalysts. The metal particles were found to be accumulated near to the channel and active sites of these catalysts. The SEM image of the Ni/Al_2O_3 sample (Figure 2(d)) revealed the formation of two types of Ni particles onto the surface of the alumina support. The first type consisted of spherical grains which were connected to the support by incipient melting. These particles have the size ranging from 200-500 nm and corresponded to the formation of NiO species as suggested by Deraz et al. (Deraz, 2012). The second type of Ni particles formed was smaller in size (50 to 100 nm) and corresponded to the elemental Ni particle. The micrograph of the Pd/Al_2O_3 sample (Figure 2(e)) showed the alumina grains with the Pd particles on the surface, which demonstrated the similar morphology as the Ni/Al_2O_3. The elemental Pd particles tend to agglomerate on the alumina support, resulting in poorer dispersion as compared to the Ni/Al_2O_3 sample. In contrast, the $Ni-Pd/Al_2O_3$ sample exhibited different morphology, in which two types of metal particles have been observed to be formed on the alumina support. The first type is a spherical shaped grain which corresponded to the formation of NiO and PdO species. In addition, needle-like particles which were not seen for Ni/Al_2O_3 and Pd/Al_2O_3 sample were observed on the surface of the alumina support. This results suggested the presence of a strong interaction between NiO and PdO to form new phase within the structure of the catalyst.
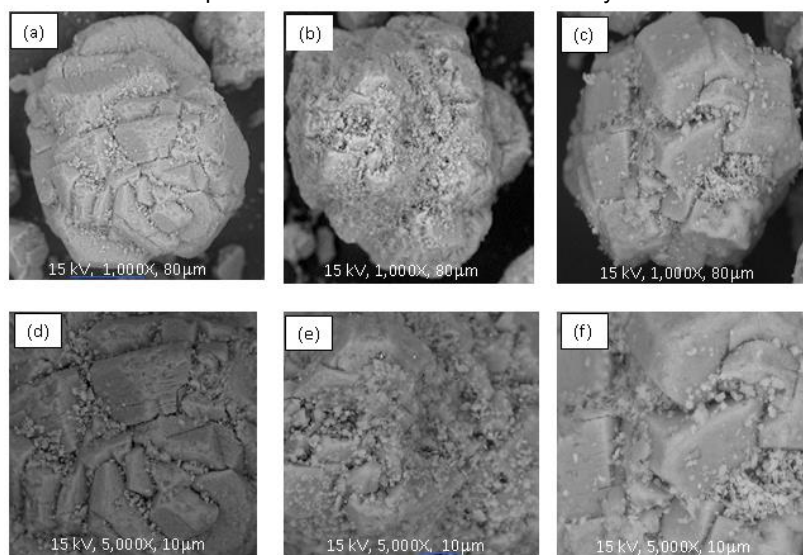

Figure 2: SEM micrographs at 1,000× magnification (80µm scale): (a) Ni/Al_2O_3, (b) Pd/Al_2O_3, (c) $Ni-Pd/Al_2O_3$ and at 5,000× magnification (10µm scale): (d) Ni/Al_2O_3, (e) Pd/Al_2O_3, (f) $Ni-Pd/Al_2O_3$.

3.3 TPR Profile

Temperature programmed reduction (TPR) was used to investigate the reducibility of Ni^{2+} and Pd^{2+} in the alumina supported catalysts. Figure 3 showed the TPR profiles from the three catalysts. The TPR profile for the Ni/Al_2O_3 catalyst (Figure 3(a)) agrees well with literature (Li et al., 2006), showing a reduction peak at 410℃, which corresponded to the reduction of NiO species on Ni/Al_2O_3 sample. In addition, the Ni/Al_2O_3 catalyst was also reduced between the temperatures from 500 to 800℃, with a reduction peak observed at 740℃. The second peak at higher temperature is typical in Ni/alumina catalysts consisting of Ni spinel and corresponded to the reduction of highly dispersed Ni^{2+} species and Ni aluminate which has a stronger interaction with the alumina support (Kim et al., 2004). On the other hand, the TPR trace of the Pd/Al_2O_3 catalyst (Figure 3(b)) demonstrated a main hydrogen consumption peak at 170℃, which may be attributed to the reduction of PdO crystallites and the formation of Pd hydride species (Ferrer et al., 2005). A second hydrogen peak is observed at 380℃ which was also due to the reduction of PdO species. Two hydrogen consumption peaks were observed during the reduction of PdO species which corresponded to the existence of two oxide phases having different interactions with the alumina support on the Pd/Al_2O_3 sample. Smaller PdO particles have a stronger interaction with the alumina support and thus resulting in a higher reduction temperature. The TPR profile of $Ni-Pd/Al_2O_3$ catalyst (Figure 3 (c)) is more complex than that for monometallic

phase. The TPR profile showed three major peaks at 175℃, 500℃ and 780℃. The first peak at 175℃ corresponded to the reduction of PdO or NiO crystallites which have a weak interaction with the alumina support. The second peak suggested that the presence of Pd shifted the peaks of superficial Ni^{2+} and Ni aluminate from 740℃ in the Pd free catalyst to lower temperature at 500℃. The third peak at 780℃ may be due to the reduction of complicated $NiAl_2O_4$ and $PdAl_2O_4$ phase which were formed by the diffusion of Ni^{2+} and Pd^{2+} into the support. The observed shifts of the spectra towards lower temperature suggested that Pd has an activating effect on the reduction of NiO species (Paryjczak and Rynkowski, 1984).
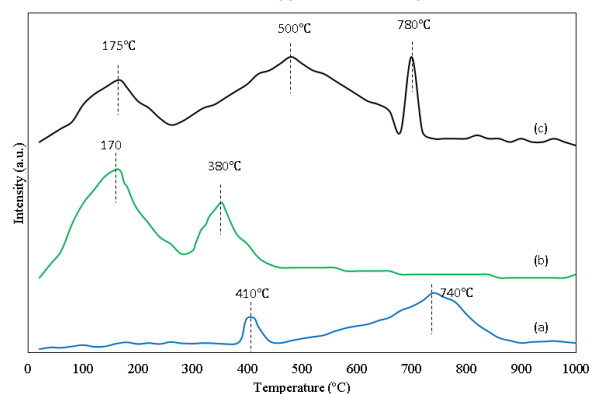

Figure 3: Temperature-programmed reduction (TPR) profiles for catalysts: (a) Ni/Al₂O₃, (b) Pd/Al₂O₃ and (c) Ni-Pd/Al₂O₃.

3.4 Thermal analysis of synthesized catalysts

TGA was performed to study the weight loss, thermal stability and structural decomposition during TCD of methane as depicted in Figure 4. The total weight loss for the catalysts was only around 3 % which occurred in one-step from room temperature to 120℃. This reduction is mainly attributed towards the removal of water adsorbed on the catalyst samples. There was no appreciable reduction in weight when the temperature is further increased. Furthermore, it can be confirmed that the calcination treatment at 500℃ for 6 h should be sufficient for the removal the bulk and structure water from the catalysts as well as decomposition of nickel nitrate into nickel oxide and tetraamine palladium chloride into palladium oxide. All the catalysts demonstrated good thermal behavior at an elevated temperature of 600℃, 700℃ and 800℃, which were the temperatures in which the catalytic activity of these catalysts was evaluated.
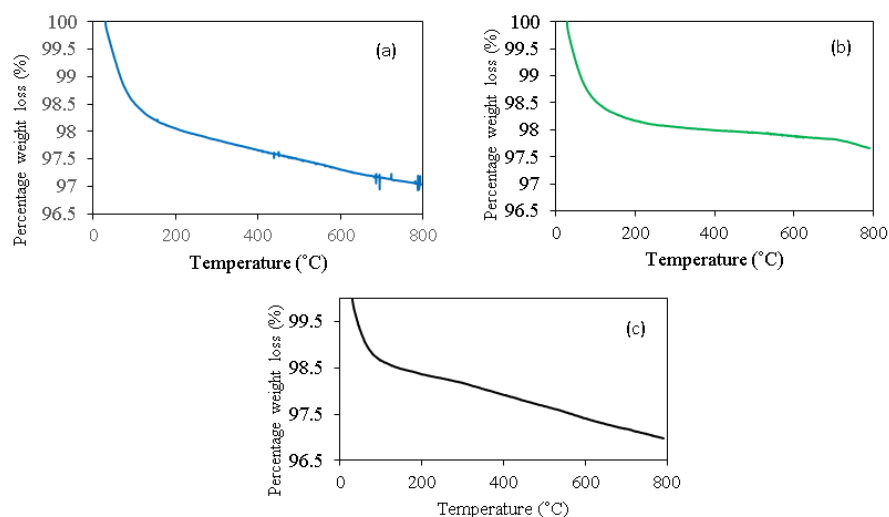

Figure 4: Thermogravimetric analysis (TGA) for catalysts: (a) Ni/Al₂O₃, (b) Pd/Al₂O₃ and (c) Ni-Pd/Al₂O₃.

3.5 Catalytic Activity Evaluation

The effect of introducing Pd as promoter onto Ni-based catalysts was evaluated by comparing the catalytic activity of the bimetallic Ni-Pd/Al₂O₃ catalyst with the catalytic activity of the monometallic Ni/Al₂O₃ and

Pd/Al$_2$O$_3$ as seen in Figure 5. It is also observed that the methane conversion decreased over time which is due to the deposition of carbon produced as a by-product during the methane cracking reaction, resulting in the blockage of active sites and reduction in catalyst surface area (Abbas and Wan Daud, 2010, Sy et al., 2012, Choudhary et al., 2001). The methane conversions obtained for all the synthesized catalysts for the initial 15 min on stream is indicated in Table 2. The experimental results suggest that the catalytic activity of monometallic Pd/Al$_2$O$_3$ is the lowest as compared to the monometallic Ni/Al$_2$O$_3$ and bimetallic Ni-Pd/Al$_2$O$_3$ catalysts for all the tested temperatures. The Ni/Al$_2$O$_3$ catalyst shows promising methane conversion at 800℃ with the conversion rate of 48.12 %. However, the methane conversion rate remains low at only 28.11 % at a lower temperature of 600℃. On the other hand, the bimetallic Ni-Pd/Al$_2$O$_3$ catalyst demonstrates the highest methane conversion and catalytic activity for all the tested temperatures. When Pd is doped onto Ni/Al$_2$O$_3$ catalyst, the percentage of methane conversion to hydrogen has improved significantly: from 48% to 70% at 800℃; from 39% to 59% at 700℃ and from 28% to 45% at 600℃. In addition, the methane conversion for the synthesized catalysts after 240 min on stream are summarized in Table 3. It was observed that the methane conversion values for Ni/Al$_2$O$_3$ and Pd/Al$_2$O$_3$ were low at T=600℃, with the conversion rate of only 5%. However, the methane conversion rate for Ni-Pd/Al$_2$O$_3$ catalyst was higher at 14%. The similar result was observed at the reaction temperature of 700℃ and 800℃. When Pd metal is doped onto Ni/Al$_2$O$_3$ catalyst, the methane conversion rate after 4 h on-stream improved from 9%-15% and 13%-16% at 700℃ and 800℃, respectively. This improvement is attributed towards the presence of Pd on the surface of the catalyst, which enhanced the thermal stability of the catalyst at elevated temperatures by reducing the tendency for sintering of the catalyst.

Table 2: Methane conversion within 15 min on stream

Catalyst	Temperature (℃)		
	600	700	800
Ni/Al$_2$O$_3$	28.11 %	38.93 %	48.12 %
Pd/Al$_2$O$_3$	19.34 %	24.87 %	37.12 %
Ni-Pd/Al$_2$O$_3$	45.31 %	58.77 %	70.33 %

Table 3: Methane conversion within 240 min on stream

Catalyst	Temperature (℃)		
	600	700	800
Ni/Al$_2$O$_3$	5.43 %	9.98 %	13.08 %
Pd/Al$_2$O$_3$	5.18 %	8.54 %	13.02 %
Ni-Pd/Al$_2$O$_3$	14.11 %	14.96 %	16.45 %

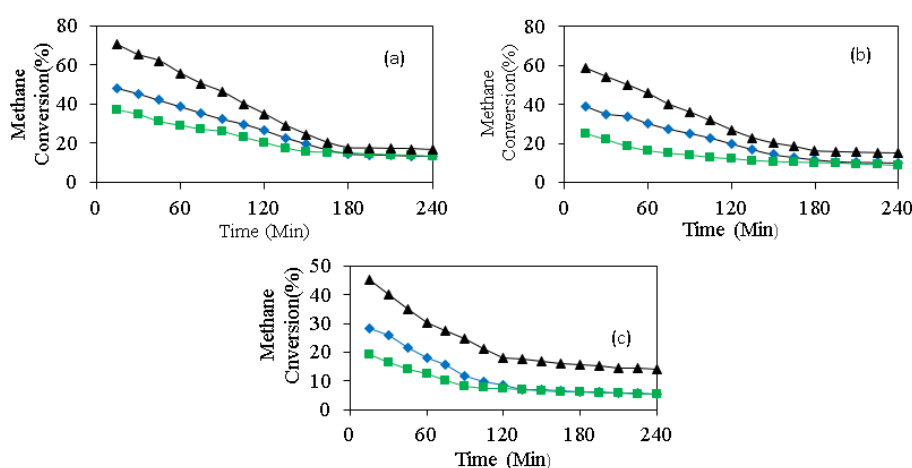*Figure 5: Percentage of methane conversion against time at (a) 800 ℃ (b) 700 ℃ and (c) 600℃. Symbols represent: (♦) Ni/Al$_2$O$_3$; (■) Pd/Al$_2$O$_3$ and (▲) Ni-Pd/Al$_2$O$_3$.*

4. Conclusions

The results of the study indicated that the addition of Pd over Ni/Al_2O_3 catalyst has a positive effect on both the catalytic activity and thermal stability of the catalyst for TCD of methane. The Ni/Al_2O_3 without Pd loading provided promising methane conversion at the beginning of the methane cracking reaction. However, the catalyst deactivated rapidly due to the deposition of carbon on the surface of the catalyst which will block the active site and reduce the effective surface area. The $Ni-Pd/Al_2O_3$ catalyst demonstrated significant improvement in the catalyst activity with higher methane conversion rate as compared to Ni/Al_2O_3 without Pd loading for all the tested temperatures. The $Ni-Pd//Al_2O_3$ catalyst has higher thermal stability and slower deactivation rate. The enhancement of the stability of the $Ni-Pd/Al_2O_3$ catalyst is due to the positive effect of doping Pd onto the catalyst surface. The interaction of Pd particles with metallic Ni particles resulted in the formation of Ni-Pd alloys, which can enhance the ability of the catalyst to accumulate carbon. The improved capability of the catalyst to accumulate carbon is beneficial to prolong the catalytic lifetime of the catalysts by making it less susceptible to sintering and coking. *Further studies on TCD of methane over $Ni-Pd/Al_2O_3$ catalyst may focus on the effect of different Pd and Ni loading as well as methane flow rate on the catalytic activity and catalytic lifetime. This study has shown a marked improvement in producing hydrogen via TCD of methane and can be potentially applied in real industry processes.*

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