

Catalytic Hydrogenation of Carbon Dioxide by Platinum Doped Nickel Oxide Catalysts

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Abstract: The abundant amount of carbon dioxide gas from unwarranted activities into the atmosphere creating environmental pollution which leads to green house gas effect as well as global warming. However, carbon dioxide can be utilized for the production of methane in a hydrogenation reaction. The hydrogenation of carbon dioxide requires the presence of catalysts in order to overcome the large kinetic barrier. In this study, platinum doped nickel oxide has been synthesized by the powder mixing method. The catalytic activity of the prepared catalysts was monitored using a fixed-bed reactor which is connected to Fourier transform infrared (FTIR) instrument for the hydrogenation reaction. The catalytic activity study showed that the Pt: Ni of atomic ratio 0.1:1 and calcined at 600°C for 3 hours was capable of converting 89% carbon dioxide at reaction temperature of 400°C. The percentage of methane formation was also 89% at reaction temperature of 400°C. The x-ray diffraction (XRD) analysis indicated the presence of nickel oxide cubic (NiO cubic) phase as the active phase for the particular reaction. The scanning electron microscope (SEM) analysis revealed that the catalyst particle size was in the range of 89-190 nm of slightly definite cubical shape.

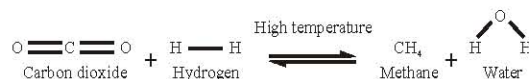
Key words: Hydrogenation of carbon dioxide • Methanation • Platinum doped nickel oxide catalyst

INTRODUCTION

According to Synthesis Report, an assessment of the Intergovernmental Panel on Climate Change, carbon dioxide (CO₂) is the most important anthropogenic greenhouse gases (GHG). Its annual emissions have grown between 1970 and 2004 by about 80%, from 21 to 38 gigatonnes (Gt) and represented 77% of total anthropogenic GHG emissions in 2004 [1]. The rate of growth of CO₂-eq emissions was much higher during the recent 10-year period of 1995-2004 (0.92 GtCO₂-eq per year) than during the previous period of 1970-1994 (0.43 GtCO₂-eq per year) [1]. The increasing emission of CO₂ leads to environmental predicament such as global warming. The increasing emission of CO₂ is parallel with the economic growth. Since the world economic growth is impossible to decrease, therefore CO₂ must be recycled and the methods for CO₂ recycling must be developed. A common CO₂ utilization method is by the production of organic chemicals such as urea, alkylene carbonates (solvent), β-oxy-naphthoic acid (raw materials of dyes), etc [2]. However, this utilization method is only

capable to reduce the CO₂ concentration in a small amount. Therefore, in order to deal with the increasing atmospheric CO₂ concentration, other methods which are capable of utilizing a huge amount of CO₂ are necessary.

The Sabatier reaction, which is hydrogenation of carbon dioxide, is a sustainable method to recycle CO₂. The methanation process produces methane and water from hydrogen and carbon dioxide, as illustrated by the following chemical equation;



Sabatier process is a reversible and exothermic reaction ($\Delta H = -167$ kJ/mol) which occurs spontaneously in the presence of certain appropriate transition metal catalysts such as nickel or ruthenium catalysts at relatively low temperature [3]. This process is a potential solution against the excess carbon dioxide emission to our environment, which reduces the greenhouse effect and prevents global warming. Although carbon dioxide

methanation is thermodynamically favourable ($\Delta G_{298K}^0 < 0$); this reaction is difficult to occur without the presence of appropriate catalyst due to the existence of relatively large kinetic barriers, in which; it involves an eight-electron reduction [4]. Therefore, the presence of catalysts such as nickel or ruthenium is crucial for Sabatier process to proceed. In this project, platinum doped nickel oxide based catalysts were synthesized and the catalytic behaviour of the synthesized catalysts in the hydrogenation of carbon dioxide was investigated. The catalysts were characterized by X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

Over the years, there are many research works done on the catalytic hydrogenation reaction of carbon dioxide for methane production. Guan Du *et. al* (2007) in a study of the methanation of carbon dioxide on Ni-incorporated MCM-41 catalysts reported that the selectivity to methane tends to increase as the reaction temperature increases. It was concluded that the selectivity to methane was enhanced with a higher Ni loading catalyst [4]. A study conducted by Michiaki Yamasaki *et. al* (1999) on CO₂ methanation catalysts prepared from amorphous Ni-Zr-Sm and Ni-Zr-misch metal alloy precursors, revealed that an increase of nickel content in the catalyst tends to lead to a gradual increase in the catalytic activity, towards the production of methane from hydrogenation of carbon dioxide [5]. Hisanori Ando *et. al* (1994) showed that the methanation process of carbon dioxide over LaNi₄X-type intermetallic compounds as catalyst precursor, the presence of metallic nickel in the intermetallic structure was essential for high catalytic activity in the conversion of carbon dioxide into methane [6]. The performance of nickel-containing catalysts in facilitating carbon dioxide methanation process was further supported by another study on co-methanation of carbon monoxide and carbon dioxide on supported nickel and cobalt catalysts conducted by Hiroki Habazaki *et. al* (1998). It concluded that nickel-containing catalysts have shown higher activity than the cobalt-containing catalyst. In particular, the Ni-30Zr-10Sm catalyst showed remarkably high activity for the simultaneous methanation of carbon monoxide and carbon dioxide [7]. Mori *et. al* (1996) conducted a study on the mechanochemical activation of catalysts for carbon dioxide methanation and discovered that mechanical milling of the catalysts increased the production rate of methane and considerably decreased the activation energy of the methanation reaction. The activation energy of 39 kJ mol⁻¹ and 41 kJ mol⁻¹ was obtained respectively

for Ni-Fe-MgO and Ru-MgO catalysts, under the milling system, which was almost half compared to that under the mixing system without mechanical milling activation [8].

MATERIALS AND METHODS

A series of platinum doped nickel oxide based catalysts of atomic ratio Pt:Ni (0.1:1) were synthesized using powder mixing method. 10g of nickel (II) nitrate hexahydrate was weighed and dissolved in 25ml of distilled water in a round-bottom flask and stirred for 30 minutes using magnetic stirrer. The resulting green solution was aged in the oven at 70°C for 24 hours. The dried gel obtained was ground using pestle and mortar. 0.2018g platinum powder weighed and added to the ground nickel oxide powder. The powder mixture was milled using roll mill for 2 hours and calcined later at 400, 500, 600 and 700°C for 3 hours in the furnace in order to obtain the black oxidized catalyst sample powder.

Characterization of Fresh Catalysts: The techniques include XRD and SEM. XRD used to identify the active phases. XRD analyses were performed using a Kratos/Shimadzu X-ray Diffractometer (Model: XRD-6000), equipped with Cu K α X-ray source ($\lambda=1.5406\text{\AA}$) which was operated at 30kV and 25mA. The diffraction patterns were recorded in the 10° to 80° 2 θ ranges at a scanning rate of 2°/min. The obtained diffraction patterns were processed and analyzed by using Shimadzu XRD-6000 V4.1 software. As for SEM analysis, the catalyst powders were ground and then adhered onto the surface of the sample holder by using carbon double-sided tape. The samples were then sputter-coated with platinum by using a JEOL JFC-1600 AUTO FINE COATER prior to the SEM analysis. The coated samples were analyzed by SEM using a JEOL JSM-6460LA scanning electron microscope with the energy of 6-15 kV. For each sample, image with 40000x magnification was taken. Particles sizes of the samples were also estimated.

Catalytic Activity Studies: The catalytic activities of Pt/NiO catalyst with atomic ratio Pt:Ni (0.1:1) were studied. The catalytic testing was carried out by using a fixed bed reactor. The three gases: CO₂, H₂ and the compressed air from the gas cylinders were mixed homogeneously in the gas mixing compartment at which the flow rate of the

gases were controlled by the mass flow controller. Prior to the catalytic testing, the gas mixture was flowed through the reactor system without passing onto the packed catalyst and the composition was analyzed by the online FTIR instrument. The FTIR spectra were recorded in the range of $4000\text{--}450\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} . Once the desired gas flow rates were achieved (CO_2 : 10 mL min^{-1} , H_2 : 40 mL min^{-1}), catalytic testing was carried out by flowing the gas mixture onto the catalyst at room temperature and the gas mixture composition was analyzed by the FTIR instrument. The temperature of the reactor furnace was increased (5°C min^{-1}) and the scanning procedure was repeated. The reaction product from the catalyst that showed the highest CO_2 conversion gas was analyzed using gas chromatography (GC) to calculate the percentage of methane (CH_4) yield. 5 mL of the product gas at particular temperature (100 , 200 , 300 , 350 and 400°C) was injected into the gas chromatographic column. The temperature for the oven and detector were 40 and 200°C respectively.

RESULTS AND DISCUSSION

XRD Analysis: Phase identifications were made by comparing the 2θ values and the d values of the studied catalysts with those of the reference materials from JCPDS Powder Diffraction Files (PDF) 2000. XRD diffractograms of the prepared Pt/NiO catalysts are shown in Figure 1.

NiO cubic phases were detected in the catalyst calcined at 400°C (Figure 1). There is a possibility that the two small peaks at 2θ value approximately 39.75° (d value 2.265). However, due to the absence of two other peaks at d value of 1.96160 and 1.38730 , this possibility is ruled out. The intensity of the peaks increased very slightly when the calcination temperature was increased from 400 to 700°C . No change in terms of peaks detected, all calcined catalyst possessed NiO cubic phase. This could be due to the short duration of calcinations which was 3 hours.

SEM Analysis: SEM analysis provides morphological studies on the catalysts in which useful information including the particle shape and size of the catalyst can be obtained. Figure 2 shows the SEM micrographs for Pt/NiO catalysts with atomic ratio Pt:Ni ($0.1:1$). The particle size for catalyst calcined at 400°C was in the range of $66\text{--}122\text{ nm}$ and shape was of indefinite shape (Figure 2a). Similarly, the particle shapes for 500°C calcined catalyst

were of indefinite shape (Figure 2 b) with increasing particle size of $74\text{--}143\text{ nm}$. It should also be noted that particles agglomeration was observed in the catalyst calcined at 500°C . Slightly definite cubical-like shape particles with particle size in the range of $89\text{--}190\text{ nm}$ were observed for the catalyst calcined at 600°C . The particles for catalyst calcined at 700°C were in more distinguishable cubical-like shape with size in the range of $118\text{--}201\text{ nm}$ (Figure 2d).

Catalytic Activity Studies: Catalytic testing for the synthesized Pt/NiO catalysts of atomic ratio Pt:Ni ($0.1:1$) in the hydrogenation reaction of carbon dioxide was performed by using a fixed-bed microreactor. The activity of the tested catalysts was discussed in terms of the percentage of carbon dioxide (CO_2) conversion with respect to the reaction temperature. For the catalyst with best catalytic activity, the study was continued with the calculation for the percentage of methane (CH_4) yield with respect to the reaction temperature. Only the percentages of CH_4 yield at several particular temperatures were being calculated. The catalytic activity results of the Pt/NiO catalyst with atomic ratio Pt:Ni ($0.1:1$) of different calcination temperatures, in terms of the percentage of CO_2 conversion at various reaction temperatures are illustrated in Figure 3.

For all synthesized Pt/NiO catalysts of atomic ratio Pt:Ni ($0.1:1$), the catalytic activity in term of the percentage of CO_2 conversion showed progressive increment with the increasing reaction temperature. Initially at room temperature, only a low percentage of CO_2 conversion was observed. For the catalyst calcined at 400°C , 13.39% of CO_2 conversion was observed at reaction temperature of 400°C . The percentage of CO_2 conversion had increased to 28.62% when the 500°C calcined catalyst was used. Catalyst calcined at 600°C showed a remarkable catalytic activity when it was enable to carry out 89.05% CO_2 conversion. However, the catalytic activity deteriorated when the 700°C calcined catalyst was used. The activity was similar to the 400°C calcined catalyst when only 13.39% of CO_2 conversion was monitored.

It would seemed to suggest that the Pt/NiO catalyst with atomic Pt:Ni ($0.1:1$), calcined at 600°C for 3 hours had shown the best catalytic activity in the hydrogenation reaction of carbon dioxide. For this catalyst, an 89.05% of CO_2 conversion was observed at reaction temperature of 400°C , which was the highest conversion percentage among all the tested catalysts. The catalytic study was

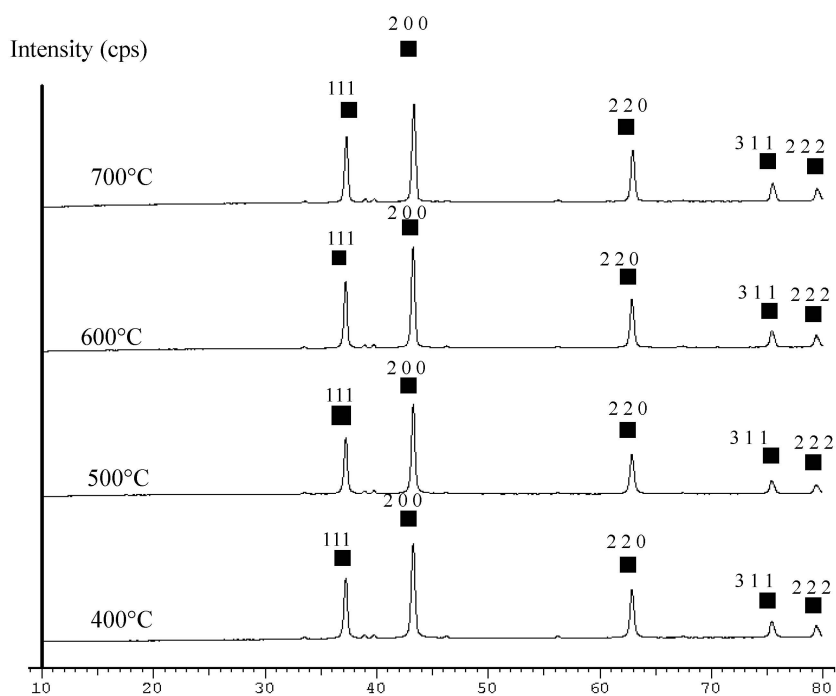


Fig. 1: The XRD diffractogram of Pt/NiO catalysts of atomic ratio Pt:Ni (0.1:1) of increasing calcination temperatures from 400, 500, 600 and 700 °C for 3 hours of calcination

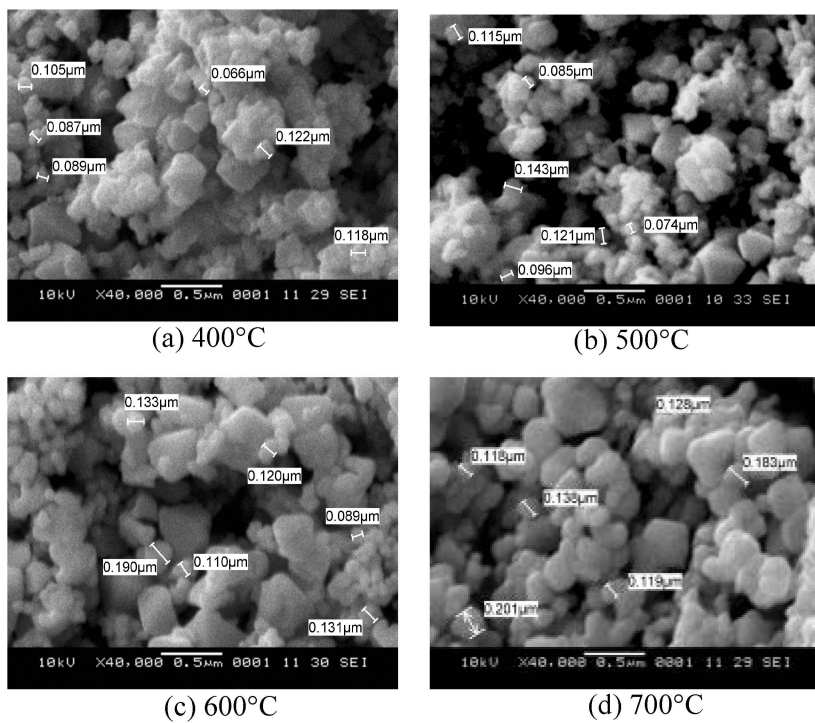


Fig. 2: SEM micrographs the synthesized Pt/NiO catalysts with atomic ratio Pt:Ni (0.1:1) of increasing calcination temperatures

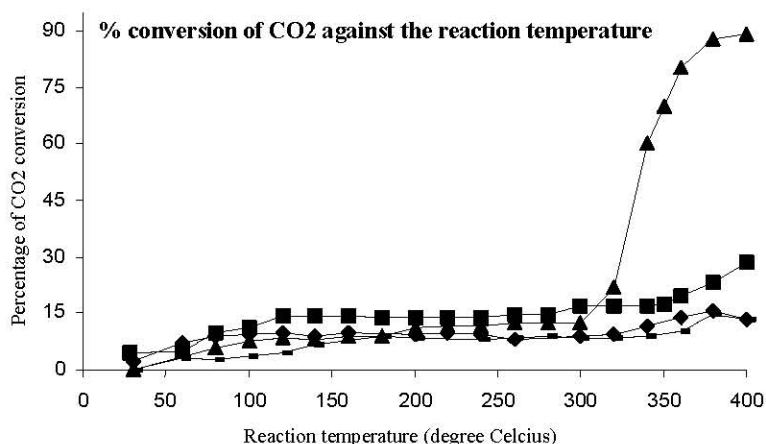


Fig. 3: The percentage of CO₂ conversion by Pt/NiO catalysts of atomic ratio Pt:Ni (0.1:1) of increasing calcination temperatures with 3 hours calcinations; ◆ : 400 °C calcined catalyst, ■ : 500 °C calcined catalyst, ▲ : 600 °C calcined catalyst, — : 700 °C calcined catalyst.

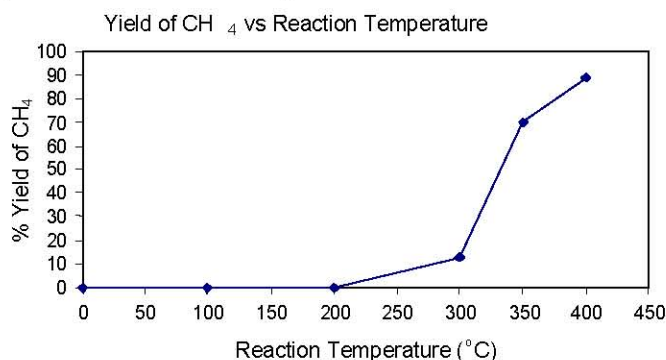


Fig. 4: The percentage of CH₄ yield by Pt/NiO catalyst with atomic ratio Pt:Ni (0.1:1), calcined at 600°C for 3 hours at various reaction temperatures.

further preceded with the calculation for the percentage of methane (CH₄) yielded by this catalyst with respect to the reaction temperature. Figure 4 illustrates the percentage of CH₄ yielded by the catalyst at various reaction temperatures.

The calculated percentage of CH₄ yielded for the catalyst had demonstrated an increasing trend with the reaction temperature. At 100°C, only 0.016% CH₄ yield was observed. This had increased very steadily to 89.05% when the reaction temperature reached 400°C.

CONCLUSIONS

It was observed that the particle size for the calcined Pt/NiO catalysts with atomic ratio of Pt:Ni (0.1:1) had increased as the calcination temperature increased. Upon increasing calcination temperature, the indefinite shaped particles observed in the catalysts calcined at 400°C and 500°C were found to have transformed into slightly

definite cubical-like particle and finally into defined cubic particles. This seemed to be in good agreement with the XRD analysis results.

ACKNOWLEDGEMENT

This research was supported by the Fundamental Research Grant Scheme (FRGS) by the Ministry of Higher Education (No: 9003-00105). The authors would also like to express gratitude to the Catalysis Group UTM, Skudai under Prof Dr Wan Azelee Wan Abu Bakar for their assistance in carrying out catalytic activity studies.

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