Catalytic methanation reaction over supported nickel–ruthenium oxide base for purification of simulated natural gas

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Abstract The presence of carbon dioxide and water molecules as impurities in crude natural gas decreases the quality of natural gas. Recently, the catalytic treatment of this toxic and acidic gas has become a promising technique by converting CO\textsubscript{2} to methane gas in the presence of H\textsubscript{2}S gas; thus, enhancing methane production and creating an environmentally friendly approach to the purification of natural gas. A series of catalysts based on nickel oxide were prepared using the wetness impregnation technique and aging, followed by calcination at 400 °C. Pd/Ru/Ni(2 : 8 : 90)/Al\textsubscript{2}O\textsubscript{3} catalyst was revealed as the most potential catalyst, and achieved 43.60% of CO\textsubscript{2} conversion, with 6.82% of methane formation at 200 °C. This catalyst had the highest percentage of 52.95% CO\textsubscript{2} conversion and yielded 39.73% methane at a maximum temperature of 400 °C. In the presence of H\textsubscript{2}S in the gas stream, the conversion dropped to 35.03%, with 3.64% yield of methane at a reaction temperature of 400 °C. However, this catalyst achieved 100% H\textsubscript{2}S desulfurization at 140 °C and remained constant until the reaction temperature of 300 °C. Moreover, the XRD diffractogram showed that the catalyst is highly amorphous in structure, with a BET surface area in the range of 220–270 m\textsuperscript{2} g\textsuperscript{-1}. FESEM analysis indicated a rough surface morphology and non-homogeneous spherical shape, with the smallest particles size in the range 40–115 nm.

1. Introduction

Nickel based catalysts are generally considered reference methanation catalysts and are known to eliminate H\textsubscript{2}S by a desulfurization process. According to Jose et al. [1], nickel oxide exhibits high activity and selectivity for producing methane, due to the ability of NiO to undergo the reduction process owing to the presence of a defect site on the surface of NiO. It had also been reported that NiO has a bimodal pore structure, which entails high activity for CO\textsubscript{2} methanation [2]. This bimodal pore structure will serve as an optimum pore size for the adsorption of both reactants. The strength of adsorption on nickel has ‘intermediate’ binding energies for hydrogen. It also has ‘intermediate’ values of heat of adsorption. Souma et al. [3], showed that the methanation reaction seems to be accelerated by the absorption of H\textsubscript{2} on metallic nickel. Yamasaki et al. [4] found that an amorphous alloy of Ni–25Zr–55Sm catalyzed the methanation reaction, with 90% conversion of CO\textsubscript{2} and 100% selectivity towards CH\textsubscript{4} at 300 °C.

Noble metals such as rhodium, ruthenium, platinum and palladium, exhibit promising CO\textsubscript{2}/H\textsubscript{2} methanation performance, high stability and less sensitivity to coke deposition. Finch and Ripley [5] claimed that the noble metal promoters may enhance the activity of the catalysts to increase the conversion to methane. In addition, noble metal promoted catalysts maintained greater activity for methane conversion than non-promoted catalysts in the presence of sulfur poison. Kusmierz [6] found that ruthenium catalysts are highly selective towards methane, even if supported on Al\textsubscript{2}O\textsubscript{3}. The main products of the reaction were CH\textsubscript{4} and water. Traces of carbon monoxide were present among the product, too, but methanol was completely absent. However, Takeishi and Aika [7] who studied Raney Ru catalysts, found a small amount of methanol was produced on supported Ru catalyst, but the production of methane gas was thousands of times more than the amount of methanol from CO\textsubscript{2} hydrogenation.

Research done by Miyata et al. [8] revealed that the addition of Pd and Pt noble metals drastically improved the behavior...
of Ni/Mg(Al)O catalysts. The addition of noble metals on Ni resulted in a decrease in the reduction temperature of Ni and an increase in the amount of H2 uptake on Ni on the catalyst. Panagiotopolou and Kodarides [9] found that the platinum catalyst is inactive in the temperature range of 200–400 °C, since temperatures higher than 450 °C are required in order to achieve conversion above 20%. Erdohelyi et al. [10] studied the hydrogenation of CO2 on Rh/TiO2. The rate of methane formation was unexpectedly higher in the CO2 + H2 reaction on Rh/TiO2 in the presence of H2S. At higher temperatures of 400 °C, around 75% selectivity for CH4 formation and CO was also formed from the reaction. The selection of support is considered as important, since it may influence both the activity and selectivity of the reaction. It has also been discovered that the addition of alumina may increase methanation activity, despite the presence of low concentrations of H2S [11]. Therefore, Al2O3 is selected as the support for all studied catalysts in this research.

Since the catalytic process through methanation reactions offers the best way to remove CO2 in natural gas, the present study is to develop a catalyst based on nickel oxide by modifying the dopants using noble metals in order to fully remove this CO2 gas at the highest conversion percentage possible at low temperatures. The addition of noble metals was studied, aiming to understand the effect of the presence of noble metals on the Ni catalyst, towards better catalytic performance.

2. Experimental

2.1. Chemicals and reagents

Nickel nitrate hexahydrate, with a chemical formula of Ni(NO3)2·6H2O, produced by GCE Laboratory Chemicals, was used as the base in this research. Meanwhile, ruthenium(III) chloride hydrate (RuCl3·xH2O), palladium(II) nitrate hydrate (Pd(NO3)2·xH2O) and tetraamineplatinum nitrate ((NH3)4Pt(NO3)2), produced by Sigma Aldrich Chemical, rhodium(III) nitrate hydrate (Rh(NO3)3·xH2O) from Fluka Analytical, copper(II) nitrate hydrate (Cu(NO3)2·6H2O) from Riedel-de-Haën and manganese acetate tetrahydrate Mn(CH3COO)2·4H2O from Rinting Scientific, were used as dopants. In addition, aluminium oxide beads (Al2O3) produced by MERCK Eurolab, and photocatalytic ceramic beads (SiO2/TiO2) produced by Titan PE Technology Inc., were used as the support materials for the preparation of catalysts. Polyethylene glycol 2000, with a chemical formula of Hi(OCH2CH2)nOH (Fluka Chemicals), and diethanolamine, with a chemical formula of HN(CH2CH2OH)2 (Merck-Schuchhardt), were used for sol–gel preparation.

2.2. Catalyst preparation

All catalysts were prepared by the aqueous incipient wetness impregnation method. The nickel loading used was 90 wt% 3 g of Ni(NO3)2·6H2O was dissolved in a small amount of distilled water, then mixed together with a solution of noble metal chloride salts or nitrate salts in a beaker, according to the desired ratio. A homogeneous mixture was obtained by magnetic stirring at room temperature for 30 min. For catalysts coated using a noble metal chloride precursor, the metal chloride salt was stirred in doubly distilled water and dispersed. This process was repeated several times until there were no changes occurring in the catalyst solution after AgNO3 was added. This indicated that the chloride ion was completely removed. Al2O3 alumina beads with diameter of 4–5 mm were used as support material in this study. The support was immersed into the catalyst solution for 24 h and the supported catalysts were transferred onto an evaporating dish with glass wool on it. It was then aged inside an oven at 80–90 °C for 24 h to remove water and allow the well homogenized immobilization of the catalysts on the surface of the supported material. It was then followed by calcination in the furnace at 400 °C for 5 h, using a ramp rate of 10 °C/min, to further eliminate all metal precursors and any excess of water or impurities. A similar procedure was repeated for other ratios of the catalyst. Finally, the potential catalysts were studied in detail on various optimization parameters.

2.3. Catalytic activity measurement

The supported catalyst sample was packed into a cylindrical glass tube with diameter of 10 mm and length of 360 mm, and was stored in the furnace of the home-built micro-reactor, as shown in Figure 1. No pretreatment was done prior to beginning the heating experiment. In-situ reactions of methanation and desulfurization were performed from ambient temperature up to 300 °C, with an increment temperature rate of 5 °C/min. Each experiment was repeated twice, and each treatment temperature was maintained for 30 min before the next temperature increment was accomplished. It was found that catalytic activity on the second treatment did not differ significantly. Composition of the reactant gases in comparison with the real composition of sour gases in Malaysian crude natural gas is depicted in Table 1. The mixture of CO2 and H2 gases was introduced into the reactor system in a stoichiometric ratio of 1:4. The product gas coming out from the furnace was collected in a FTIR sample cell and scanned at every 20 °C by a FTIR Shimadzu 8300 Spectrometer. Percentage conversion of CO2 and H2S was obtained by calculating the peak area of their respective stretching bands relative to the peak area of the gas during calibration without a catalyst. Off line GC analysis (Hewlett Packard 6890 Series GC System) was done to determine the yield of CH4 gas, due to the low sensitivity of FTIR spectroscopy towards the stretching band of CH4.

2.4. Catalyst characterization

Characterizations were studied by X-ray Diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM), Nitrogen Adsorption/desorption (NA) and Thermogravimetric analysis (TGA). The XRD patterns of the prepared powder samples were recorded at 2θ between 5° and 75° using a Bruker Advance D8 with Siemens 5000 diffractometer. The Cu Kα radiation operates at 40 kV and 40 mA, with λ = 1.5418 Å.
To assess the surface by FESEM-EDX analysis, the samples were analyzed using Zeiss Supra 35 VP FESEM with the energy of 15.0 kV, coupled with the EDX analyzer and 1500× magnification. Prior to analysis, the sprinkled sample was coated with gold, as a conducting material, by gold sputter, at 10⁻¹⁰ Mbar, using the Bio Rad Polaron Division SEM coating system machine. The catalyst sample was bombarded by an electron gun, with a tungsten filament, under 25 kV resolution. The N₂ adsorption/desorption isotherm of the catalyst analyses was obtained using a Micromeritics ASAP 2010 volumetric adsorption analyzer at −196 °C. Prior to measurement, the calcined catalysts were degassed at 200 °C overnight. The isotherms were used to determine the following parameters: surface area (using Brunauer–Emmett–Teller (BET) equation), total pore volume, total micropore volume, and total mesopore volume. TGA analysis for the samples was carried out by a TGA-SDTA 851 Mettler Toledo simultaneous thermal analyzer, up to 800 °C at 15 °C/min. The sample in the form of fine powder was placed in an alumina covered crucible, an empty crucible being the reference. Nitrogen gas, with a flow rate of 50 μL/min, was used as the atmosphere.

3. Results and discussion

3.1. Catalytic performance of supported NiO based catalyst with ruthenium as a first dopant

Table 2 illustrates the catalytic performance of supported nickel oxide based catalysts, which were calcined at 400 °C for 5 h. According to the results, a Ni/Al₂O₃ catalyst gives only 24.58% conversion of CO₂ at a reaction temperature of 400 °C. Incorporating ruthenium into this catalyst further lowered the catalytic performance towards CO₂ conversion to 7.21%. The decreasing performance of this catalyst could be due to the Ru precursor; RuCl₃.nH₂O used in this study. This is in good agreement with Nurunnabi et al. [12], who found that the small amount of chloride ion in the Ru/Al₂O₃ catalyst could lead to a decrease in the active sites of the Ru catalyst surface. The presence of residual chloride ions forms a partition between the support and the metal, and therefore inhibits both CO and hydrogen chemisorption phenomena on the catalyst surface [12].

However, the addition of palladium into the Ru/Ni(10:90)/Al₂O₃ catalyst to form Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst coincidently enhanced catalytic activity for the conversion of CO₂ of the prepared catalysts. It showed 37.94%, 43.60% and 45.77% of CO₂ conversion at reaction temperatures of 100 °C, 200 °C and 300 °C, respectively, while 52.95% CO₂ conversion was achieved at the maximum studied temperature of 400 °C. This suggests that small amounts of Pd addition can play an important role in the improvement of catalyst activity. This is in accordance with the findings of Baylet et al. [13] who studied the catalytic activity and stability of Pd doped hexaaluminate catalysts for the CH₄ catalytic combustion. They found that the addition of palladium to the alumina support material gives a sufficient absorption for the CO₂ dissociation process, which is due to the increasing of active sites created on the catalyst surface.

When platinum was added into the Ru/Ni catalyst, the Pt/Ru/Ni (2:8:90)/Al₂O₃ catalyst did not perform well, and managed to convert only 34.74% at the maximum reaction temperature, 400 °C, while at 200 °C, the conversion of CO₂ was around 18.03%. Bi et al. [14] reported that the Pt catalyst is generally effective for the Reverse Water–Gas Shift (RWGS) reaction. It can be seen from Table 2 that the result of Ru/Ni doped with Pt was not as good as Ru/Ni doped with Pd. It showed that Pd is better than Pt. Our finding was in agreement with Lapisardi et al. [15] who revealed that the conversion rate of the Pd catalyst was four times higher than that of the Pt catalyst for the production of syngas. As previously reported by Gelin et al. [16], Pd/Al₂O₃ did not exhibit any deactivation with time, on stream, under experimental conditions, but Pt/Al₂O₃ slowly deactivates with time. The decreasing activity of this catalyst is mostly due to the sintering of Pt particles, exaggerated by local hot spots, owing to the highly exothermic CO₂ methanation reaction, which is responsible for the loss of Pt dispersion [17].

The presence of rhodium in the Rh/Ru/Ni (2 : 8 : 90)/Al₂O₃ catalyst was even worse, with poor activity and selectivity in comparison to Ni/Al₂O₃. Only 19.29% CO₂ conversion was observed under similar experimental conditions, even at the highest reaction temperature of 400 °C. These findings might be explained by the fact that the addition of Rh in this catalyst caused poor metal dispersion. This was also reported by Wachs [18], and the reason given was due to the poor interaction between active basic metal oxide and the support material. Thus, the metals are easily migrated and sintered to form large metal particles [19], leading to the agglomeration on the surface of the catalyst, which will reduce the degree of dispersion. Furthermore, when Ru was added into the Mn/Ni/Al₂O₃ catalyst to form the Ru/Mn/Ni (2 : 8 : 90)/Al₂O₃ catalyst, it did not show good performance in its catalytic activity, which only gave 22.1% and 34.86% of CO₂ conversion at reaction temperatures of 200 °C and 400 °C, respectively. Meanwhile, the CO₂ conversion of Ru/Cu/Al₂O₃ catalyst with a ratio of 2:8:90 gave no more than 25.87% of conversion, even at the maximum reaction temperature of 400 °C.

Pd and Ru are a good combination for Ni based catalysts only when the ratio of Ru is higher than that of Pd. It can be observed from Table 2 that only 35.64% of CO₂ conversion was obtained at the reaction temperature of 400 °C for the Ru/Pd/Ni (2 : 8 : 90)/Al₂O₃ catalyst compared to the Pd/Ru/Ni (2 : 8 : 90)/Al₂O₃ catalyst. From the results, it was suggested that the

<table>
<thead>
<tr>
<th>Gas</th>
<th>Flow gas mixture (%)</th>
<th>Composition in crude natural gas (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>47.0</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>19.0</td>
<td>23.5</td>
</tr>
<tr>
<td>H₂S</td>
<td>4.8</td>
<td>5.4</td>
</tr>
<tr>
<td>Others (CO₂, N₂)</td>
<td>24.1</td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>76.2</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Percentage conversion of CO₂ from methanation reaction over various alumina supported nickel oxide based catalysts with ruthenium as a dopant and co-dopant.

<table>
<thead>
<tr>
<th>Alumina supported catalysts</th>
<th>Reaction temperature</th>
<th>% conversion of CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (100%)/Al₂O₃</td>
<td>100 °C</td>
<td>3.65</td>
</tr>
<tr>
<td>Ru/Ni (10 : 90)/Al₂O₃</td>
<td>100 °C</td>
<td>1.42</td>
</tr>
<tr>
<td>Pd/Ru/Ni (2 : 8 : 90)/Al₂O₃</td>
<td>100 °C</td>
<td>37.94</td>
</tr>
<tr>
<td>Pt/Ru/Ni (2 : 8 : 90)/Al₂O₃</td>
<td>100 °C</td>
<td>10.75</td>
</tr>
<tr>
<td>Rh/Ru/Ni (2 : 8 : 90)/Al₂O₃</td>
<td>100 °C</td>
<td>3.23</td>
</tr>
<tr>
<td>Ru/Mn/Ni (2 : 8 : 90)/Al₂O₃</td>
<td>100 °C</td>
<td>7.74</td>
</tr>
<tr>
<td>Ru/Cu/Ni (2 : 8 : 90)/Al₂O₃</td>
<td>100 °C</td>
<td>14.62</td>
</tr>
<tr>
<td>Ru/Pd/Ni (2 : 8 : 90)/Al₂O₃</td>
<td>100 °C</td>
<td>17.30</td>
</tr>
</tbody>
</table>

The presence of rhodium in the Rh/Ru/Ni catalyst was even worse, with poor activity and selectivity in comparison to Ni/Al₂O₃. Only 19.29% CO₂ conversion was observed under similar experimental conditions, even at the highest reaction temperature of 400 °C. These findings might be explained by the fact that the addition of Rh in this catalyst caused poor metal dispersion. This was also reported by Wachs [18], and the reason given was due to the poor interaction between active basic metal oxide and the support material. Thus, the metals are easily migrated and sintered to form large metal particles [19], leading to the agglomeration on the surface of the catalyst, which will reduce the degree of dispersion. Furthermore, when Ru was added into the Mn/Ni/Al₂O₃ catalyst to form the Ru/Mn/Ni catalyst, it did not show good performance in its catalytic activity, which only gave 22.1% and 34.86% of CO₂ conversion at reaction temperatures of 200 °C and 400 °C, respectively. Meanwhile, the CO₂ conversion of Ru/Cu/Al₂O₃ catalyst with a ratio of 2:8:90 gave no more than 25.87% of conversion, even at the maximum reaction temperature of 400 °C.

Pd and Ru are a good combination for Ni based catalysts only when the ratio of Ru is higher than that of Pd. It can be observed from Table 2 that only 35.64% of CO₂ conversion was obtained at the reaction temperature of 400 °C for the Ru/Pd/Ni catalyst compared to the Pd/Ru/Ni catalyst. From the results, it was suggested that the
Pd/Ru/Ni (2 : 8 : 90)/Al₂O₃ catalyst is the potential catalyst for CO₂ conversion. Generally, the conversion rate of CO₂ for all prepared catalysts increased with the increasing of reaction temperature.

Based on the results taken from catalytic activity testing, it was found that Pd/Ru/Ni (2 : 8 : 90)/Al₂O₃ was the potential catalyst for CO₂ conversion. Several optimization parameters were conducted on these catalysts including the amount of Ni loading, the calcination temperature of the supported catalyst, the type of support material, method of preparation, H₂S testing, reproducibility testing and, finally, regeneration testing.

3.1.1. Effect of nickel loading

Figure 2 compares the amount of Ni loading towards the percentage CO₂ conversion by the Pd/Ru/Ni/Al₂O₃ catalyst. The Ni loadings used were 90, 80 and 70 wt%. The catalytic activity of the Pd/Ru/Ni (5:25:70)/Al₂O₃ catalyst is only slightly lower than that observed on the same catalyst with Ni loadings of 90 and 80 wt%. The CO₂ conversions over the Pd/Ru/Ni (5:25:70)/Al₂O₃ catalyst reached their maximum conversions at 400 °C, around 32%, and achieved 45.06% for the Pd/Ru/Ni (5:15:80)/Al₂O₃ catalyst at the same reaction temperature. The lowest activity of the Ni catalyst, with the lowest amount of Ni, was due to partial Ni particles located in the pores, thus, leading to lesser active sites for the reduction process, as mentioned by Perkas et al. [20]. From this observation, it can be concluded that the catalytic activity of Ni loading follows a trend in the order of 90 wt% > 80 wt% > 70 wt%. The selection of metal loading is tremendously important in order to properly balance the activity with selectivity. Then, these catalysts were further analyzed by varying the calcination temperature of the supported catalyst.

3.1.2. Effect of different calcination temperature towards supported catalyst

This parameter was investigated to determine the effect of calcination temperature on alumina supported catalyst towards CO₂ conversion. Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst was coated on alumina and aged in an oven for 24 h before calcined the catalyst at five different temperatures of 300, 400, 500, 700 and 1000 °C. Figure 3 indicates the trend plot of catalytic activity over Pd/Ru/Ni (2:8:90)/Al₂O₃ at various calcination temperatures.

From Figure 3, it can be observed that the highest CO₂ conversion was obtained from the Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst calcined at 400 °C, with 43.60% conversion, followed by the Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst calcined at 500 and 700 °C, which achieved only 24.1% and 10.36% of CO₂ conversion at 200 °C, respectively. This phenomena could be explained by the drastic increase in calcination temperature, which decreases the specific surface area of the solids and, thus, catalytic activity. This is probably due to the deep encapsulation of sintered noble metal particles, which limit its diffusion by reducing the pore size, as stated in the research of Ruckenstein and Hu [21]. As expected, further increase of calcination temperature to 1000 °C induces the decreasing of catalytic activity over this Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst. However, the Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst calcined at 300 °C achieved 35.77% CO₂ conversion at a reaction temperature of 200 °C. It can be concluded in this research that 400 °C was the optimum calcination temperature over the Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst. In other words, the conversion of CO₂ over the alumina supported catalyst in this research, with different calcination temperatures, is in the following increasing order: 400 °C > 300 °C > 500 °C > 700 °C. It was then further optimized by varying the support materials.

3.1.3. Effect of different support materials

As the acid or base properties of the support may influence the catalysts, either electronically or structurally, the potential Pd/Ru/Ni (2:8:90) catalyst calcined at 400 °C was chosen to be supported on various supports, such as alumina beads (Al₂O₃), TiO₂/SiO₂ beads and carbon chips from the palm kernel shell in order to compare the compatibility and suitability of the supports towards the catalyst. The comparison of the support effect towards the catalytic performance of the Pd/Ru/Ni (2:8:90) catalyst is summarized in Figure 4.

It could be seen that catalysts on the Al₂O₃ support gave the highest CO₂ conversion. It still appeared as the most suitable support, as it showed a stable performance on CO₂ conversion. The carbon support from the palm kernel shell was found to convert 25.54% of CO₂ at the reaction temperature of 200 °C. Meanwhile, the TiO₂/SiO₂ support gives a very low conversion of CO₂ (4.8%) at 200 °C, and achieved a maximum CO₂ conversion of 17.87% at the maximum studied reaction temperature of 400 °C. These results implied that the TiO₂/SiO₂ support was not appropriate for CO₂ conversion, as also suggested by Takekaka et al. [22]. They found that TiO₂/SiO₂ supported catalysts are effective for the complete removal of CO through methanation, because they react more strongly with the metal surface compared to CO₂. De Boer et al. [23] reported that less than...
100% metal oxide dispersion on the SiO2 support was obtained, because of lower reactivity and the higher acidic character of this support. Such properties will decrease its reduction ability of CO2 to CH4 during catalytic testing. In other words, the conversion of CO2 over Pd/Ru/Ni (2:8:90), with different support, is in the following increasing order: Pd/Ru/Ni (2:8:90)/Al2O3 > Pd/Ru/Ni (2:8:90)/Carbon > Pd/Ru/Ni (2:8:90)/TiO2. Further, the catalyst was undergoing other optimization parameters, which are calcination temperatures of the alumina support.

3.1.4. Effect of H2S gas on the alumina supported catalysts

The potential catalysts were further tested for the CO2 methanation reaction in the presence of H2S to check the durability of the catalysts. In the presence of a sulfur compound in the gas stream, nickel catalysts for CO2 methanation are easily deactivated. Thus, the toughness of the catalyst towards the H2S attack is an important factor for the practical use of catalysts, as has been suggested by Habazaki et al. [24]. Figure 5 indicates the comparison of catalytic activity over the Pd/Ru/Ni (2:8:90)/Al2O3 catalyst in the presence of H2S gas.

As seen in the above figure, the Pd/Ru/Ni (2:8:90)/Al2O3 catalyst had achieved 100% H2S desulfurization at 100 °C, to sulfur, and remains constant until the reaction temperature of 300 °C. It began to decrease from 100% to 57.31% at temperatures 300–400 °C. The catalyst lost its H2S activity, probably due to the high concentration of S, which forms an external layer on the catalyst surface, preventing the next incoming H2S from passing and continuing its reaction with active sites of the catalyst, as suggested by Hassan [25].

3.1.5. Reproducibility testing towards potential catalyst

The reproducibility catalytic activity of the catalyst was tested using the same catalyst several times until the catalyst was deactivated. Figure 6 shows the trend plot of reproducibility testing over the Pd/Ru/Ni (2:8:90)/Al2O3 catalyst. It can be seen that the conversion of CO2 over the fresh catalyst is 43.60% at the reaction temperature of 200 °C. However, the conversion was slightly decreased to 35.10% after the second testing, using the spent catalyst, and continuously decreased to 26.17% for the third testing over the same spent catalyst at the same reaction temperature. For the fourth testing, CO2 conversion was lower, even though the conversion of the catalyst kept increasing from temperatures of 60–240 °C, and then slowly deactivating until the maximum studied temperature of 400 °C. From the observation in Figure 6, it can be suggested that the Pd/Ru/Ni (2:8:90)/Al2O3 catalyst started to deactivate after the first testing.

3.1.6. Regeneration testing on the potential catalyst

This experiment was demonstrated to determine the optimum operating conditions needed to regenerate the spent catalyst and re-test its activity. The spent catalyst from Section 3.1.5 was used to carry out this experiment. Figure 7 shows the trend of the regenerated catalyst testing of the Pd/Ru/Ni (2:8:90)/Al2O3 catalyst at various temperatures and times. There are two methods of catalyst regeneration process: oxidative regeneration and non-oxidative regeneration as classified by Furimsky and Massoth [27]. In this research, the regeneration process is categorized as oxidative regeneration, because the waste catalyst was exposed to the oxygen. Eq. (1) seems to include the idea of using compressed air in this research:

\[
\text{NiC}_{(p)} + 3\text{O}_{2(g)} \xrightarrow{\Delta} 2\text{NiO}_{(p)} + 2\text{CO}_{2(g)}. \tag{1}
\]
oxidation reaction. This is because the formation of CO and the asthe CO₂ shows the testing results of CO determined via GC, because of the low sensitivity of FTIR.

phylist can be reused without losing its good catalytic activity. NiRu/... from the PdRuYaccato et al. [17] found that when the methanation process was conducted in the presence of H₂S over the Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst. At 200 °C, the methaneproduction decreased from 6.82% to 1.73%, while at 400 °C, the formation of methane dropped around 91% from 39.73% to only 3.64% indicating that the catalyst was possibly poisoned by the presence of H₂S in the gas stream. The active sites of the catalyst were blocked by the sulfur compound. This phenomenon prevents CO₂ and H₂ from being absorbed and converted to CH₄ on the surface of the catalyst.

3.3. Characterization of the potential catalysts

3.3.1. X-ray diffraction analysis (XRD)

Figure 8 shows the diffractograms of XRD analysis for the Pd/Ru/Ni (2:8:90)/Al₂O₃ catalysts, which were calcined at 400, 700 and 1000 °C. The XRD diffractogram for the potential catalyst that was calcined at 400 °C showed a very low degree of crystallinity and a high noise to signal ratio. It can be seen that the slight significant peaks in the diffractogram could all be attributed to the presence of Al₂O₃, as the support for the catalyst which occurred centered at 2θ = 67.000° and 37.000°. Research done by Wang et al. [30] also reveals that no crystalline phases were detected in the Cu–Mn–O/Al₂O₃ catalyst that was calcined at 400 °C by XRD, because the active components of metal oxides are highly dispersed in the alumina support, which is highly amorphous.

However, at a calcination temperature of 700 °C, the intensity of alumina peaks over the Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst was slightly increased and became more profound. This revealed that an intermediate crystallinity was observed in this catalyst. The phase that was dominated by alumina support was revealed as cubic Al₂O₃ at 2θ = 67.114° (I₁₀₀), 45.450° (I₁₀₁), and 37.505° (I₉₅) with d spacing value of 1.393, 1.994 and 2.396 Å (PDF d values for cubic Al₂O₃ (Å) = 1.403, 1.985 and 2.394 Å). From the calculation based on the relative intensity ratio, the overlapping of cubic NiO diffraction peaks with those of the support peaks was assumed to be occurred at 2θ of 45.450° (I₁₀₀) and 37.505° (I₉₅), with d spacing values of 1.994 and 2.396 Å (PDF d values for cubic NiO (Å) = 2.088 and 2.412 Å).

Interestingly, four new peaks were also observed in the XRD pattern. Among the four peaks, one peak was obtained as cubic NiO at 2θ of 62.878° (I₄₄), with d spacing value of 1.463 Å (PDF

### Table 3: The product and by-product of CO₂ methanation reaction over Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst detected via GC.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactant</th>
<th>Reaction temp (°C)</th>
<th>CO₂ conversion (%)</th>
<th>Selectivity (%)</th>
<th>Unreacted CO₂ (%)</th>
</tr>
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<tbody>
<tr>
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<td></td>
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<td>7.33</td>
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<td>31.39</td>
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</table>

Figure 7: Regeneration catalytic testing over Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst for 3 h at various temperatures towards CO₂ conversion from methanation reaction.

The use of compressed air in this research is the most practical approach, since the industrial equipment used for the regeneration temperature is usually limited to 430 °C, as suggested by Trimm [28]. Figure 7 reveals that the carbon was removed from the Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst surface by heating the catalyst at 200 °C for 3 h in the flow of compressed air, since the conversion of CO₂ was comparable to that fresh catalyst, which was 42%. Therefore, the Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst can be reused without losing its good catalytic activity.

3.2. Methane gas formation measurement via gas chromatography

The reactor gas product from the FTIR cell was collected and analyzed for CH₄ formation. The methane formation was determined via GC, because of the low sensitivity of FTIR spectroscopy towards the methane stretching region. Table 3 shows the testing results of CO₂/H₂ methanation over the potential alumina supported catalyst. There are three possible products obtained during the CO₂ methanation reaction, namely, carbon monoxide, water and methane. From Table 3, it can be seen that the percentage of unreacted CO₂ decreases as the CO₂ was converted into CH₄, CO and H₂O, while the CH₄ content increased as the temperature increased. However, the CO₂ methanation in this research could be considered a partial oxidation reaction. This is because the formation of CO and the amount of unreacted CO₂ are higher than the formation of CH₄.

Even at the reaction temperature of 200 °C, the conversion of CO₂ did not yield 100% CH₄, but tended to form CO and H₂O. These results are in good agreement with other researchers. Yaccato et al. [17] found that when the methanation process was tested, the main product observed was CO at low temperature and, when using higher temperature, CH₄ was formed. This is due to the indirect conversion of CO₂ into C₁ hydrocarbons through the formation of intermediate CO, as suggested by Silver et al. [29]. Only 39.73% of methane was formed over this catalyst at the maximum studied temperature.

The methane production lowered when the CO₂ methanation was conducted in the presence of H₂S over the Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst. At 200 °C, the methaneproduction decreased from 6.82% to 1.73%, while at 400 °C, the formation of methane dropped around 91% from 39.73% to only 3.64% indicating that the catalyst was possibly poisoned by the presence of H₂S in the gas stream. The active sites of the catal-
d values for NiO (Å) = 1.477 Å. The other two peaks were obtained at 2θ of 28.198 (I_{100}) and 34.066° (I_{111}), with d spacing values of 3.162 and 2.630 Å (PDF d values for RuO₂ (Å) = 3.182 and 2.690 Å), and were assigned for the tetragonal of RuO₂. As shown by Graph (b) in Figure 8, the pattern showed very small peaks, which were hardly distinguishable from the background noise, possibly indicating that there was only a very small amount of RuO₂ present on the surface, or that the particles dispersed on the support were relatively small. A similar species of the tetragonal RuO₂ phase was also observed by Chen et al. [31] at diffraction peaks of 2θ = 28.000°, and 35.100° over the Ru-L₂O₂/Al₂O₃ catalyst, even calcination at a temperature of 500 °C. It can be suggested that the presence of RuO₂ is not resolved over the catalyst.

The cubic phase of PdO peaks was assumed in the envelope of RuO₂ peaks at 2θ of 34.066° (I_{100}) or d spacing values of 2.630 Å (PDF d value for PdO (Å) = 2.820 Å). Meanwhile, the emergence of a new broad peak at 2θ of 54.177° (I_{400}), with d spacing value of 1.692 (PDF d value for PdO (Å) = 1.630 Å), was also observed for the same compound.

All peaks observed became more intense, sharper and narrower when the catalyst was calcined at 1000 °C (Graph (c) in Figure 8) indicating that the degree of crystallinity over the Pd/Ru/Ni (2.8:90)/Al₂O₃ catalyst increased with increasing calcination temperature. The highest intensity was also due to the cubic phase of Al₂O₃ at 2θ = 66.671° (I_{1100}), 45.648° (I_{1000}) and 37.416° (I_{100}) or d spacing values of 1.402, 1.986 and 2.402 Å (PDF d values for cubic Al₂O₃ (Å) = 1.403, 1.985 and 2.394 Å).

In addition, one of the peak corresponding to the cubic NiO was covered with alumina support at 2θ of 37.16° (I_{400}) or d spacing values of 2.402 Å (PDF d values for cubic NiO(Å) = 2.412 Å). Another two peaks appeared sharply at 2θ of 43.294° (I_{1000}) and 62.902° (I_{100}) or d spacing values of 2.088 and 1.476 Å (PDF d values for cubic NiO (Å) = 2.088 and 1.477 Å). The nickel oxide cubic phase is thermostable and it can prevent the changing phase from occurring, as suggested by Richardson et al. [32].

Furthermore, peaks assigned to the tetragonal of RuO₂ remained similar at 2θ of 27.265° (I_{1100}) and 32.131° (I_{111}) or d spacing values of 3.268 and 2.783 Å (PDF d values for RuO₂ (Å) = 3.182 and 2.690 Å). In the meantime, the broad peaks of the PdO cubic phase have been transformed into high intensity and sharper peaks at 2θ of 31.702° and 56.820° (I_{400}) or d spacing values of 2.820 and 1.619 Å (PDF d values for PdO (Å) = 2.820 and 1.630 Å).

However, all the NiO, RuO₂ and PdO species were not observed in the catalyst that was calcined at 400 °C (Graph (a) in Figure 8). It can be suggested that these species are present with small crystallite size and highly dispersed, so, they could not be detected, due to the insensitivity of the XRD instrument. This was confirmed by EDX analysis, which showed the existence of Ni, Ru, Pd, Al and O elements in the Pd/Ru/Ni (2.8:90)/Al₂O₃ catalyst itself. Therefore, it can be concluded that these species can lead to a higher conversion of CO₂ at a reaction temperature of 200 °C, as shown in Figure 3. The highest CO₂ conversion was obtained for the Pd/Ru/Ni (2.8:90)/Al₂O₃ catalyst calcined at 400 °C (43.60%), followed by the Pd/Ru/Ni (2.8:90)/Al₂O₃ catalyst calcined at 500 °C (24.10%), 700 °C (10.36%) and 1000 °C (3.16%).

The formation of active species, such as the cubic phase of NiO, also leads to higher catalytic activity towards the CO₂ methanation reaction.

3.3.2. Field emission scanning electron microscopy and energy dispersive X-ray

Figure 9 shows the FESEM micrographs of fresh and spent Pd/Ru/Ni (2.8:90)/Al₂O₃ catalysts, calcined at 400 °C for 5 h with magnification of 5000× and 50,000×. The fresh Pd/Ru/Ni (2.8:90)/Al₂O₃ catalyst showed rough surface morphology with an inhomogeneous spherical shape, and comes with small particles sizes. The morphology of the fresh catalyst changed significantly after the hydrogenation of the methanation reaction, which showed the formation of aggregated and agglomerated undefined shapes on the surface of the spent catalyst (Figure 9(b)). This observation was possibly due to the heat generated during the catalytic reaction, which caused the catalyst to agglomerate, thus, decreasing the activity, as shown in Figure 6.

In this research, it was found that the particle size of fresh Pd/Ru/Ni (2.8:90)/Al₂O₃ catalyst is categorized at the nano (<100 nm) level, which varies from 40 to 115 nm. The smaller particle size plays an important role in exhibiting higher catalytic activity. This result is consistent with the results of the XRD analysis, which revealed very broad peaks, denoting the amorphous state observed in the diffractogram calcined at 400 °C, caused by the very small nanocrystallite sizes. The smaller particle size of the catalyst will lead to the higher dispersion of the catalyst and the large surface area of the...
supported nickel oxide based catalyst. One of the most efficient ways to improve the reactivity for CO₂ methanation is to use materials with a large surface area and high dispersion, as explained by Kodama et al. [33].

Furthermore, Table 4 shows the EDX analysis for the fresh and spent Pd/Ru/Ni (2:8:90)/Al₂O₃ catalysts. The elemental analysis performed by EDX confirmed the presence of Ni, Ru, Pd, Al, and O in the potential catalyst.

From EDX analysis, it can be observed that the composition of Ru was higher than the composition of Ni on the fresh and spent Pd/Ru/Ni (2:8:90)/Al₂O₃ catalysts. This phenomenon can be explained, due to the incorporation of Ni into the support after calcination of the respected catalyst at 400 °C. This is in good agreement with the findings observed by Nurunnabi et al. [12], who claimed that Ni may have been adsorbed into the porous support, hence, the lower concentration of Ni on the catalyst surface than can be detected by EDX. The migration of Ni atoms from bulk matrices to the surface of the catalyst making the higher composition of Ni was detected for the spent catalyst.

Moreover, the spent Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst confirms the existence of 3.80% carbon on the surface of the catalyst. The difference of fresh and spent catalyst surfaces was due to the presence of carbon, as shown in FESEM analysis (Figure 9). The formation of agglomerated catalyst particles in the spent Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst was observed. As mentioned by Hu and Lu [34], the catalyst containing nickel is subjected to deactivation by carbon after running the catalytic testing. The low activation energy also can be related to deactivation by coke formation at higher temperature, as explained by Paál et al. [35]. However, the surface state under these conditions is regenerable as confirmed by the regeneration reaction on this catalyst, as discussed in Section 3.1.6.

3.3.3. Nitrogen absorption analysis (NA)

The potential catalyst, Pd/Ru/Ni (2:8:90)/Al₂O₃, in fresh and spent forms, were characterized by nitrogen adsorption analysis. Table 5 summarizes the BET surface area and average pore diameter of the Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst. Meanwhile, Figures 10 and 11 show the N₂ adsorption–desorption isotherms of the fresh and spent Pd/Ru/Ni (2:8:90)/Al₂O₃ catalysts.

From BET surface area analysis of the Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst, it can be seen that the surface area of the fresh catalyst was 266.10 m² g⁻¹; 16.58% higher than its spent catalyst (221.97 m² g⁻¹). According to Wan Abu Bakar et al. [36], the BET surface area is presumed to be reduced when there is no generation of new active sites and no transformation of active species occurred during the catalytic reaction. By referring to the EDX analysis, the existence of carbon may also reduce the surface area by blocking the pores of the spent catalyst. As a result, the conversion of CO₂ over the spent Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst was decreased to 35.10%, compared to the fresh catalyst (43.60%), at the reaction temperature of 200 °C. However, the surface area of the Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst is considered higher. The higher surface area of the catalyst denoted the increased active sites of the catalyst. This result agrees well with the particle size of the Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst obtained from the FESEM micrograph, where the catalyst showed nano particle levels. This smaller particle size is presumed to contribute to the increment in surface area. This may contribute to the increasing of catalytic activity over the Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst, while the average pore diameter of fresh and spent Pd/Ru/Ni (2:8:90)/Al₂O₃ catalysts is around 50 Å. The preferable effect of the pore structure of the support could also enhance the conversion of CO₂, as claimed by Chang et al. [37]. Unfortunately, a nitrogen analysis for the catalyst calcined at 700 and 1000 °C cannot be carried out due to instrument breakdown.

The N₂ adsorption–desorption isotherms of the fresh Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst demonstrated an isotherm Type IV with a hysteresis loop of type H3 for that of mesoporous materials (Figure 10). The type of isotherm and pore distribution of the Pd/Ru/Ni (2:8:90)/Al₂O₃ catalyst is
The existence of the mesoporous structure gives an optimum performance, which has been mentioned previously by Inui [2]. The mesoporous oven for 24 h at 80–90°C serves similar to the spent catalyst (Figure 11). The mesoporous oven for 24 h at 80–90°C, the catalyst was sent for characterization using TGA-DTA. Figure 12 shows the TGA thermogram of the Pd/Ru/Ni (2:8:90)/Al2O3 catalyst.

It showed two significant weight loss curves, which occurred around 60 and 280°C. The total weight loss is 14.66%. Starting from a temperature of 60°C until 280°C, free water molecules and the nitrate compound from the supported catalysts were removed, while 280°C onwards, the nitrate compound and surface hydroxyl molecule were decomposed from the samples. Savva et al. [38], who studied the Ni/Al2O3 catalyst prepared by conventional impregnation and sol–gel methods, found that the physisorbed water was completely removed up to 150 and 200°C. Meanwhile, the decomposition of nitrate was observed at a temperature range of 190°C onwards. Finally, they observed that weight loss at temperatures higher than 360°C should be attributed to the removal of structural water from the alumina.

From this investigation, the calcination temperature of 400°C is insufficient to remove all nitrate compounds that originate from the metal precursor. The presence of nitrate compounds in this catalyst was also observed by FTIR analysis, which detected the stretching mode of the free nitrate group. It can be seen that all impurities were removed from the catalysts at temperature higher than 800°C, meaning that a pure metal oxide had been obtained. Thus, the catalyst calcined at 1000°C should be good for this catalyst. However, the investigation found that calcination temperatures higher than 400°C decreased its catalytic activity.

4. Conclusions

The overall performance from catalytic activity studies did not yield any catalyst that gives 100% conversion of CO2 at lower reaction temperatures. However, Pd/Ru/Ni (2:8:90)/Al2O3 was assigned as the most potential catalyst resulted from catalytic activity measurements of FTIR and GC. This catalyst was prepared using the wetness impregnation technique aged at 85°C, followed by calcination at 400°C for 5 h. The Pd/Ru/Ni (2:8:90)/Al2O3 catalyst shows 43.60% of CO2 conversion with 6.82% of methane formation at 200°C. This catalyst had the highest percentage of 52.95% CO2 conversion, and yielded 39.73% methane at the maximum temperature of 400°C. In the presence of H2S in the gas stream, the conversion dropped to 35.03%, with 3.64% yield of methane. However, this catalyst achieved 100% H2S desulfurization at 140°C and remained constant until a reaction temperature of 300°C.

Acknowledgments

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References


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