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The effect of noble metals on catalytic methanation reaction over supported Mn/Ni oxide based catalysts

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Abstract Carbon dioxide (CO_2) in sour natural gas can be removed using green technology via catalytic methanation reaction by converting CO_2 to methane (CH_4) gas. Using waste to wealth concept, production of CH_4 would increase as well as creating environmental friendly approach for the purification of natural gas. In this research, a series of alumina supported manganese–nickel oxide based catalysts doped with noble metals such as ruthenium and palladium were prepared by wetness impregnation method. The prepared catalysts were run catalytic screening process using in-house built micro reactor coupled with Fourier Transform Infra Red (FTIR) spectroscopy to study the percentage CO_2 conversion and CH_4 formation analyzed by GC. Ru/Mn/Ni(5:35:60)/Al_2O_3 calcined at 1000 °C was found to be the potential catalyst which gave 99.74% of CO_2 conversion and 72.36% of CH_4 formation at 400 °C reaction temperature. XRD diffractogram illustrated that the supported catalyst was in polycrystalline with some amorphous state at 1000 °C calcination temperature with the presence of NiO as active site. According to FESEM micrographs, both fresh and used catalysts displayed spherical shape with small particle sizes in agglomerated and aggregated mixture. Nitrogen Adsorption analysis revealed that both catalysts were in mesoporous structures with BET surface area in the range of 46–60 m^2/g. All the impurities have been removed at 1000 °C calcination temperature as presented by FTIR, TGA–DTA and EDX data.

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1. Introduction

To date, methanation reaction has been widely used as a method of removal carbon dioxide from gas mixtures in hydrogen or ammonia plants, for purification of hydrogen stream in refineries and ethylene plants. Nickel is a well established catalyst decades ago since they are known to be active in hydrogenation, dehydrogenation, hydrotreating and steam reforming reaction and thus have gained great attention (Richardson, 1982 and Azadi et al., 2001). Nickel oxide has

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been widely used due to high activity and low cost (Mok et al., 2010). However, most nickel-based catalysts undergo deactivation due to sintering and carbon deposition during reaction. Thus, nickel based catalysts are needed to be modified in order to produce a catalyst resistant towards deactivation. Combination of nickel catalyst with other transition metal oxides and other promoters has been reported to be active in many reactions such as catalytic oxidation and steam reforming. Addition of manganese oxides are effective in decreasing the coke formation in the dry reforming of methane over Ni/Al_2O_3 (Park et al., 2010 and Ouaguenouni et al., 2009). Although noble metals such as Ru, Rh, Pd and Pt, are known to give high activity and selectivity, but because of limited availability and high cost of them have restricted their applications. In this work, we modified the nickel oxide based catalyst by incorporating manganese and noble metals into the system throughout the impregnation method and applied them in catalytic methanation reaction. Then, the potential catalyst was characterized using different techniques and tested in the flow of CO_2 and H_2.

2. Experimental

2.1. Preparation of catalysts

Impregnation method was used in the production of all catalysts according to the previous work (Wan Abu Bakar et al., 2010). 5 g $Ni(NO_3)_2 \cdot 6H_2O$ purchased from GCE Laboratory Lab was dissolved in little amount of distilled water. Mixed solution was prepared by mixing appropriate amount of $MnCl_2 \cdot 2H_2O$ and noble metal salts ($Pd(NO_3)_2 \cdot xH_2O$ and $RuCl_3 \cdot xH_2O$) according to the desired ratio (40:60, 20:80, 5:35:60, 5:15:80). The solution was stirred continuously for 20 min. Alumina beads with a diameter of 3 mm were immersed in the solution for 20 min as support material in this study. It was then aged in the oven at 80–90 °C for 24 h. It was then followed by calcination in the furnace at preferred calcination temperatures (400, 700 and 1000 °C) for 5 h using a ramp rate of 5 °C/min in order to remove all the metal precursors, impurities and excessive of water .

2.2. Catalytic performance test

All the prepared catalysts underwent catalytic screening test to study their catalytic activity towards CO_2/H_2 methanation reaction using in house built micro reactor coupled with FTIR Nicolet Avatar 370 DTGS as illustrated in Fig. 1. The analysis was carried out using simulated natural gas comprising of continuous flow of CO_2 and H_2 in 1:4 ratio with the flow rate of 50 cm^3/min. The weight hourly space velocity was fixed at 500 mL g^{-1} h^{-1}.The prepared catalyst was put in the mid of the glass tube with diameter 10 mm and length of 360 mm. Glass wool was used at both ends of the Pyrex glass tube and positioned in the micro reactor furnace for catalytic testing. Heating of the reactor was supplied by a programmable controller which was connected via a thermocouple placed in the centre of the furnace. A mass flow controller was used to adjust the feed of gas flow. The catalytic testing was performed from 80 °C up to the maximum reaction temperature studied (400 °C) with the increment of 5 °C/min. The FTIR spectra were recorded in the range of 4000–450 cm^{-1} with 8 scans at

4 cm^{-1} resolution to maximize the signal to noise (S/N) ratio. Methane formation was detected by Hewlett Packard 6890 Series GC System (Ultra 1) with 25.0 m × 200 μm × 0.11 μm nominal columns, with helium (He) gas as the carrier gas with a flow rate of 20 mL/min at 75 kPa, and Flame Ionization Detector (FID).

2.3. Characterization of catalysts

XRD analysis was conducted using a Siemens D5000 Crystalloflex X-ray Diffractometer equipped with Cu target (λ Cu-Ka = 1.54 Å) radiation between 20° to 80° (2θ) running at 40 kV and 40 A. The morphology of catalysts was visualized using a Field Emission Scanning Electron Microscope (FESEM) coupled with EDX analyzer for semi quantitative composition. The Nitrogen Adsorption analysis was obtained throughout Micromeritics ASAP 2010. Functional group present was detected by Fourier Transform Infra-Red (FTIR). Thermal stability of desired catalyst was carried out by TGA–DTA analysis.

3. Results and discussion

3.1. Catalytic performance on CO_2/H_2 methanation reaction

3.1.1. Catalytic activity screening of alumina supported nickel oxide based calcined at 400 °C for 5 h

The supported monometallic oxide catalyst (Ni/Al_2O_3, Mn/Al_2O_3, Ru/Al_2O_3 and Pd/Al_2O_3) calcined at 400 °C showed very low catalytic activity towards CO_2/H_2 methanation reaction. Ni/Al_2O_3 catalyst gave a high CO_2 conversion of 13.30% at maximum reaction temperature studied compared to the other oxides catalysts (Table 1). These catalysts did not able to achieve high conversion at low reaction temperature however they showed the capability to be used in methanation reaction. Thus by incorporating manganese and noble metals into system, they would enhance the catalytic activity.

Referring to Table 1, it can be observed that the addition of Mn slightly increased the catalytic performance compared to the monometallic oxide (Ni/Al_2O_3) catalyst. At 400 °C reaction temperature, $Mn/Ni(20:80)/Al_2O_3$ catalyst gave 17.50% of CO_2 conversion while $Mn/Ni(40:60)/Al_2O_3$ catalyst was able to obtain 15.30% conversion only. It is probably due to the largest amount of dopant blocking the pores structure of the catalyst and thus decreasing the activity. Besides, the catalytic performance of both $Ru/Ni(20:80)/Al_2O_3$ and $Pd/Ni(20:80)/Al_2O_3$ catalysts also increased in a little amount. As can be noticed in Table 1, these bimetallic oxide catalysts have a low percentage of CO_2 conversion (< 18%). Thus, alumina supported manganese–nickel oxide based catalyst was modified by incorporating with noble metal, ruthenium and palladium to study their effect towards the catalytic activity.

Incorporating palladium (Pd) into this catalyst ($Pd/Mn/Ni(5:35:60)/Al_2O_3$) slightly increased the catalytic performance towards CO_2 conversion up to 25.30%. Meanwhile, when ruthenium ($Ru/Mn/Ni(5:35:60)/Al_2O_3$) was added as a co-dopant further reduction of catalytic performance was observed which only gives 14.00% CO_2 conversion. The decreasing performance of this catalyst could be due to the Ru precursor, $RuCl_3 \cdot xH_2O$ used in this research. A small amount of chloride ion present in Ru/Al_2O_3 catalyst could give poisoning effect to