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Partial oxidation of methane over monometallic and bimetallic Ni-, Rh-, Re-based catalysts: Effects of Re addition, co-fed reactants and catalyst support

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ABSTRACT

Partial oxidation reactions of CH_4 over monometallic Ni, Rh, Re and bimetallic Re-Ni catalysts supported by Al_2O_3 were studied at 400–700 °C. Among monometallic catalysts, Rh/Al_2O_3 exhibited the highest catalytic activity. Lower CH_4 conversion and H_2 yield were observed over Ni/Al_2O_3 catalyst, while Re/Al_2O_3 catalyst did not promote the reaction under the studied condition. Addition of Re over Ni to form a bimetallic catalyst considerably promoted the activity of Ni/Al_2O_3 catalyst, particularly at a higher temperature (600 °C). Re-Ni proportion was then optimized; $Re\text{-}Ni/Al_2O_3$ at Re:Ni ratio of 3:7 resulted in a significantly higher CH_4 conversion as well as H_2 and CO yields when compared to noble-metal Rh/Al_2O_3 catalyst. Stability testing of $Re\text{-}Ni/Al_2O_3$, Ni/Al_2O_3 and Rh/Al_2O_3 catalysts was also conducted. After 18-h operation, $Re\text{-}Ni/Al_2O_3$ catalyst still exhibited high stability with slight deactivation in terms of H_2 yield, whereas Ni/Al_2O_3 and Rh/Al_2O_3 catalysts showed higher deactivation rates. Post-reaction temperature programmed oxidation confirmed the better resistance toward carbon deposition of $Re\text{-}Ni/Al_2O_3$ catalyst. The effect of steam and CO_2 addition on the $Re\text{-}Ni/Al_2O_3$ catalyst performance was also investigated. The presence of a suitable H_2O content could increase H_2 and CO yields and reduce the amount of carbon deposition, whereas the presence of CO_2 showed undesirable influence on the reaction by reducing CH_4 conversion and H_2/CO ratio. Lastly, $Re\text{-}Ni/Gd\text{-}CeO_2$ catalyst was prepared and tested to study the effect of catalyst support. The catalyst stability and resistance toward carbon deposition were significantly improved, which could be due to the high oxygen storage capacity of $Gd\text{-}CeO_2$.

1. Introduction

Catalytic partial oxidation of methane (CPOM) for hydrogen and synthesis gas production has attracted much attention, especially in the petroleum and chemical industries [1]. CPOM is an exothermic reaction and requires less energy input and lower capital costs in comparison to steam reforming [2]; CPOM produces 2 mol of hydrogen and ~36 kJ/mole of energy and costs ~30% less than steam reforming [3]. In addition, CPOM provides syngas with a suitable H_2/CO ratio (equal to 2) for the production of synthetic fuels via the Fischer-Tropsch reaction [4].

CPOM has been widely studied using several heterogeneous catalysts with or without noble-metal components. Although group-8 noble metals (e.g., Pt, Rh, Ru, Pd) are highly active for the CPOM reaction, nickel-based catalysts are most widely used and show good activity. Ni/Al_2O_3 catalyst has widely been studied and reported to exhibit good catalytic performance for hydrogen and syngas production [5–8]. However, the major issue of Ni-based catalysts is carbon deposition on the surface of solid catalysts, which reduces the number of active sites and leads to degradation of the catalysts [9]. Therefore, modifications are required to reduce coking as well as to promote catalytic activity and stability. Such modifications include the use of different Ni precursors and synthesis methods as well as the use of appropriate supports or the addition of suitable promoters. For instance, Nichio et al. [10] compared the influences of different precursor compounds on the coking of $Ni/\alpha\text{-}Al_2O_3$ catalysts prepared from $Ni(NO_3)_2$ and Ni-acetylacetonate. Less carbon formation occurred on the catalyst surface prepared from the organic precursor, while higher filamentous and encapsulating carbon were observed on the catalyst prepared from $Ni(NO_3)_2$ precursor. However, significant sintering was observed on the organic precursor. Shiraz et al. [11] synthesized nanocrystalline Ni/Al_2O_3 catalyst for syngas production via the dry reforming of methane. The synthesized catalyst had high surface area and small crystallite size and exhibited high catalytic activity and stability. Garbarino et al. [12]

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studied the effect of adding silica to Ni/Al_2O_3 and found that the addition of silica to alumina supports contributed to more easily reducible Ni catalysts. Ni/Al_2O_3, hexaaluminate-type $BaNi_xAl_{12-x}O_{19-\alpha}$ and perovskite-type $LaAl_{5/6}Ni_{1/6}O_3$ catalysts were investigated for partial oxidation of methane by Utaka et al. [13]. XPS analysis revealed that the hexaaluminate catalysts provided Ni-rich surfaces and highly dispersed Ni species obtained from hexaaluminate crystals, resulting in greatly improved catalytic activity.

The catalytic performance can be improved not only by modifications of precursors, synthesis methods or supports, but also by doping the supported catalysts with other added metals or promoters. Ma et al. [14] studied the effect of rare earths and other basic promoters such as Na, Sr, Ce and La on CPOM to syngas over monolithic $Ni/\gamma\text{-}Al_2O_3$ catalyst. The results indicated that adding a small amount of promoters could improve the reducibility and activity of the catalyst. Ce and La could fully restrain the side reaction and gave 100% H_2 selectivity. Chromium added to Ni/Al_2O_3 catalyst was tested by González et al. [15]. Ni-Cr alloy was formed, resulting in increasing stability in methane partial oxidation. Wang et al. [16] showed the beneficial effect of Ce, La, Ca on the catalytic performance of Ni catalysts; Ce was noted to be the best promoter. Based on the catalyst characterization results, Ce could improve the reducibility of the Ni catalyst and could be made highly dispersed within the catalyst matrix. Apart from the addition of these promoters, Re has been previously reported as good catalyst and/or promoter for hydrocarbon conversion [17–19]. Claridge et al. [17] studied $Re/\gamma\text{-}Al_2O_3$ as catalyst for partial oxidation and dry reforming of methane. They indicated that the catalytic activity of $Re/\gamma\text{-}Al_2O_3$ was strongly dependent on temperature, from which high operating temperature is required. Wang et al. [18] reported the conversion of methane and ethane to oxygenated molecules (formaldehyde and acetaldehyde) over Re_2O_7/SiO_2. They found that rhenium oxide not only increased methane conversion but also increased oxygen transfer to form oxygenated compounds. Enger et al. [19] studied the CPOM over $Ni/\alpha\text{-}Al_2O_3$ modified by Re and claimed that the addition of Re promoted ethane formation at high GHSV. Recently, we found that the addition of Re to Cu/cerium oxide and gadolinium doped ceria significantly improved the activity of Cu catalysts in the water-gas shift reaction [20]. The good properties of Re as catalyst promoter has also been reported for Co/CeO_2 [21] and for Ir/TiO_2 [22].

Therefore, in the present work, the effect of Re promoter doping on $Ni/\gamma\text{-}Al_2O_3$ catalyst for CPOM was studied. Bimetallic Re-Ni supported on $\gamma\text{-}Al_2O_3$ catalyst was tested and compared to 10% Ni and 1% Rh monometallic catalysts. We expect that addition of Re promoter would enhance the catalytic activity of $Ni/\gamma\text{-}Al_2O_3$. In addition, catalytic stability test was carried out along with the investigation of the effects of co-fed reactants (i.e., H_2O and CO_2). Lastly, $Re\text{-}Ni/Gd\text{-}CeO_2$ catalyst was prepared and tested toward the reaction to study the effect of catalyst support. Characterization of the prepared catalysts by BET surface area determination, X-ray diffraction, scanning electron microscopy and energy dispersive X-ray spectroscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, X-ray fluorescence, temperature programmed oxidation and H_2-temperature programmed desorption was performed to establish relationships between the activity and physicochemical properties of the catalysts.

2. Experimental

2.1. Catalyst preparation

The catalysts used in the present work were prepared by the impregnation technique. Commercial $\gamma\text{-}Al_2O_3$ (Sasol, Germany) and $Gd\text{-}CeO_2$ (GDC; Fuel Cell Materials, USA) were crushed and sieved to obtain the particle size of 0.425 mm. To prepare the catalyst precursor, calculated amount of the required metal of nickel (II) nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$, Univar, Australia), ammonium perrhenate (H_4NO_4Re, Sigma-Aldrich, Germany) and rhodium (III) nitrate ($Rh(NO_3)_3$, Sigma-Aldrich, Germany) were dissolved in deionized water. The metal aqueous solutions were then impregnated on $\gamma\text{-}Al_2O_3$ and GDC; this was followed by drying overnight in an oven at 105 °C and calcining at 700 °C in air for 6 h at a heating rate of 10 °C min^{-1}. For bimetallic Re-Ni catalysts, the amount of Re loading was varied in the range of 1, 3 and 5 wt.%; Ni was added to balance the total weigh to 10 wt.%. The catalysts were denoted as X% Re-Y% Ni, where X and Y represent the weight percentages of Ni and Re, respectively.

2.2. Catalyst characterization

Specific surface area and pore size distribution of the catalysts were measured via the nitrogen adsorption-desorption experiments at the liquid N_2 temperature of −196 °C using a volumetric gas adsorption instrument (Belsorpmax, MicrotracBEL, Japan). Prior to each measurement, a fresh sample was degassed at 350 °C for 4 h. The surface area and pore size distribution were determined using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively.

The crystalline phases of the fresh solid catalysts were analyzed by an X-ray diffractometer (Philips X'Pert, Netherlands) with CuK-α radiation at 40 kV and 30 mA at a scanning rate of 0.02° min^{-1} in the range of 10–90°. A scanning electron microscope (JEOL, JSM-6610 LV, Japan) connected with an energy dispersive X-ray spectrometer analyzer was used for observing the morphology and elemental composition of the bimetallic Re-Ni catalysts. To analyze the shape and size of metals in the catalyst structure, transmission electron microscope (JEOL, JEM 2010, Japan) was used. The chemical states of elements in the fresh catalysts were anatomized by X-ray photoelectron spectroscope (AXIS Ultra DLD, UK). High-resolution X-ray photoelectron spectroscopy was also used to determine the information on the chemical composition and oxidation state of the bimetallic Re-Ni catalysts. The weight contents of the loaded metals were determined by X-ray fluorescence analysis.

H_2 chemisorption analysis was performed on Micromeritics Pulse ChemiSorb 2700 (USA). A sample (100 mg) was first placed in a quartz sample cell and purged with He at 400 °C to remove the moisture. Then, the sample was reduced under H_2 flow at 400 °C for 2 h. After the reduction, the sample was purged again with He to remove hydrogen and cooled to 100 °C. The sample was subsequently submitted to temperature programmed desorption (TPD) with He at the heating rate of 10 °C min^{-1} to 800 °C A stoichiometry of H_2 to metal atom of 1:1 was assumed for calculating the metal surface area and metallic dispersion. It should also be noted that, after catalyst testing, the post-reaction temperature programmed oxidation (TPO) was carried out to identify the quantity of carbon deposited on the catalyst surface by feeding 10% O_2 in He into the system while increasing the temperature from room temperature to 1000 °C (with the rate of 10 °C min^{-1}, after purging the post-reaction catalyst bed with helium). The quantity of carbon was calculated by measuring the amounts of CO and CO_2 generated from the test. The calibrations of CO and CO_2 were performed by injecting known amounts of these gases into an injection valve in the bypass line, from which the response factors were known by dividing the number of moles of each component with the respective areas under the peaks. It should also be noted that the spent catalysts after TPO were further tested with thermo gravimetric analyzer-mass spectrometer (PerkinElmer, USA) at 1000 °C to ensure that no carbon formation remained on the surface of the catalysts.

2.3. Apparatus and procedures

CPOM was carried out in a tubular quartz reactor with high-purity methane (CH_4, UHP grade 99.999%), oxygen (O_2, UHP grade 99.995%) and argon (Ar, UHP grade 99.995%). In order to test the catalysts, about 100 mg of each catalyst was filled inside the reactor and then reduced by H_2 at 500 °C for 3 h. According to the temperature