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Production of hydrogen from methane over lanthanum supported bimetallic catalysts

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ABSTRACT

Hydrogen production as a clean source of energy has drawn the attention of many researchers in recent decades. Hydrogen, an environment-friendly source of energy, enjoys many applications such as fuel cells, spaceships and production of lighter petroleum fractions from heavy ones. Catalytic decomposition of methane has recently attracted researchers for the production of CO_x-free hydrogen. In this work, catalytic decomposition of methane was investigated for the production of hydrogen over bimetallic Ni and Co based catalysts supported on La₂O₃. Bimetallic catalysts having 12.5wt% each of Ni and Co were prepared by the co-precipitation technique. The activity tests were performed in a fixed bed micro-activity reactor. The effect of different calcination temperatures was studied. The 12.5NCL catalyst calcined at 500 °C provided the highest hydrogen yield at 700 °C reaction temperature and a volume hourly space velocity of 5000 L.h⁻¹.kg_{cat}⁻¹. The catalysts were characterized by BET, TGA, XRD, TPR and TEM before and after reaction.

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Introduction

Conventional fuels are recognized as major sources of CO₂ emission leading to global warming; so hydrogen has been taken as an evolving alternative to these conventional fuels. The market demand for hydrogen fuel is progressively increasing because it is a clean energy source [1–3]. It is an accepted fact that in the near future, fossil fuels, more specifically methane, will remain the major source for the production of hydrogen. Currently, the production of hydrogen is mainly based on hydrocarbon reforming using metal based catalysts [4–8]. The main problem associated with the reforming technique is the emission of CO₂ which needs to be captured and stored to assure clean hydrogen production.

Taking this point into account, catalytic decomposition of methane (CDM) could be chosen as an alternative route to reforming for the production of hydrogen. Moreover, from economic view point, the production of solid carbon as a high value co-product makes CDM more attractive as well [9].

Different metal based catalysts, both mono- and bimetallic, have been studied in the recent years [10–17]. Catalysts based on transition metals i.e., Ni, Fe and Co supported over different oxides e.g. MgO, Al₂O₃, SiO₂ have been employed in CDM [18,19]. Bimetallic catalysts based on group VIII metals supported on MgO were investigated for CDM. It was found that complete segregation of Fe₂O₃ and Co₂O₃ resulted in better catalytic performance and stability of 25%Fe–25%Co/MgO catalyst [20]. Awadallah et al. [21] studied the effect of adding group VI metals to Co/MgO catalyst for hydrogen

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production via CDM. They showed that addition of group VI metals enhanced the surface properties and resulted in a strong interaction between group VI metals and CoO_x/MgO crystals. Moreover, formation of CoMO_4 and CoWO_4 species led to good dispersion and stabilization of Co particles which, in turn, increased the catalytic stability for CDM. The cited literature has discussed combinations of Ni, Co and Fe but no specific article containing Ni and Co based bimetallic catalysts as well as role of La_2O_3 support for CDM reaction, to our knowledge, has been published yet [11–21].

In this work, the role of co-precipitated bimetallic catalysts based on 12.5wt% Ni and 12.5wt% Co supported over La_2O_3 will be studied for CDM reaction. Furthermore, the effect of different calcination temperatures will be investigated to find the better calcination temperature in terms of catalytic performance. Effect of reaction temperature and volume hourly space velocity (VHSV) will also be investigated. Catalyst characterization techniques, such as, BET, XRD, TGA, TPR and TEM will also be employed.

Experimental

Catalyst preparation

Ni and Co based bimetallic catalyst, containing 12.5 wt% each of Ni and Co, supported on La_2O_3 was prepared by the co-precipitation method. Typically, stoichiometric amounts of the precursors of the active metals ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and support ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) were dissolved in distilled water under constant stirring at 60 °C. 10% NH_3 solution was added drop-wise under constant stirring to obtain a pH of 9–10. The resulted precipitates were filtered, washed with deionized water and acetone, dried over night at 120 °C and finally calcined at different temperatures i.e., 500, 700 and 900 °C for 3 h. For convenience, the catalyst calcined at different temperatures were designated as 12.5NCL-500, 12.5NCL-700 and 12.5NCL-900 where 12.5NCL presents catalyst containing 12.5wt% each of Ni and Co supported over La_2O_3 while 500, 700 and 900 present the respective calcination temperatures. H_2 Yield and carbon yield are calculated using following equations:

$$\text{H}_2 \text{ Yield (\%)} = \frac{\text{H}_{2(\text{out})}}{2 \times \text{CH}_{4(\text{in})}} \times 100 \quad (1)$$

$$\text{Carbon Yield (\%)} = \frac{\text{Weight of deposited carbon on the catalyst}}{\text{weight of metal content (Ni + Co) in the catalyst}} \times 100 \quad (2)$$

Catalyst testing

The prepared catalysts were tested in a micro-activity fixed bed tubular reactor (10 mm ID) coupled with K-type thermocouple using 0.3 g of the catalyst at different reaction temperatures and space velocities. Prior to CDM reaction, each catalyst was first reduced under H_2 flow (40 mL/min) at 500 °C for 100 min which was then flushed with N_2 for 20 min. Then, the reactor was allowed to set at the desired reaction

temperature in the presence of N_2 gas. The products of the reactor were analyzed by using an online GC (Varian Star 3400 cx; Ar as carrier) equipped with a thermal conductivity detector and a gas sampling valve.

Catalyst characterization

The specific surface area of the catalysts was determined from N_2 adsorption-desorption data at -196 °C by using a Micromeritics Tristar II 3020 surface area and porosity analyzer. For each analysis, 0.3 g of catalyst was degassed at 300 °C for 3 h to rid the catalyst surface from moisture content and other adsorbed gases.

The TPR measurements were completed on a chemisorption apparatus (Micromeritics Auto Chem II apparatus) using 70 mg for each sample. The samples were pretreated with high purity Argon (Ar) flowing at 150 °C for 30 min, followed by cooling to room temperature and then heating in a furnace up to 800 °C using a constant heating rate of 10 °C/min using a H_2/Ar mixture (volume ratio, 1:9) flowing at a rate of 40 mL/min. The signal of H_2 consumption was monitored by a thermal conductivity detector (TCD).

Powdered X-ray diffraction (XRD) analysis of the fresh and used catalyst was carried out using a Rigaku (Miniflex) diffractometer with a $\text{Cu K}\alpha$ radiation operated at 40 kV and 40 mA. The scanning step and range of 2θ for analysis were 0.02° and 20 – 75° respectively.

The quantitative analysis of coke deposition on the surface of the spent catalysts was carried out by thermo-gravimetric analysis (TGA) in an air atmosphere using EXSTAR SII TG/DTA 7300 (Thermo-gravimetric/Differential) analyzer. 10–15 mg of the used catalyst were heated from room temperature to 800 °C at a heating rate 20 °C/min.

TEM measurements of the spent catalysts were performed on a JEOL JEM-2100F transmission electron microscope operated at 200 kV accelerating voltage to analyze the morphology of the deposited carbon. Prior to TEM analysis the samples were first dispersed ultrasonically in ethanol at room temperature. A drop of the suspension was then put on a lacey carbon-coated Cu grid to take images.

Results and discussion

X-ray diffraction

Fig. 1 shows the diffractograms of 12.5NCL catalysts at different calcination temperatures. The peaks at 29.6, 30 (for 500 °C calcination), 48.8 (for 900 °C calcination) and 58.8° can be assigned to the support i.e., La_2O_3 [JCPDS: 00-05-0602]. Moreover, the peak, in case of 500 and 900 °C calcination temperature, at 43.3° may be ascribed to NiO [JCPDS: 00-044-1159] and diffraction peak at 44.8° (for 500 °C calcination) can be attributed to Co_3O_4 [JCPDS: 00-042-1467]. From the profiles, the existence of species such as LaNiO_3 , LaCoO_3 and their overlapping diffractograms can also be observed. The diffraction peaks at 23.2, 33, 40.8 and 47.5° may be assigned to overlapping of $\text{LaNiO}_3/\text{LaCoO}_3$ [JCPDS: 00-088-0633/JCPDS: 00-25-1060] while the peak at 53.5° can be attributed solely to

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