Research article

Reforming and cracking of CH_4 over Al_2O_3 supported Ni, Ni-Fe and Ni-Co catalysts

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ABSTRACT

Supported Ni, Ni-Fe and Fe catalysts of the same total metal loading and different Ni to Fe ratios were studied for the dry reforming and cracking of methane (CH_4). The supported Ni-Fe catalysts containing Ni and Fe in the ratio of 3:1 (75Ni25Fe/Al_2O_3) was the most active for both reactions and was slightly more active than the supported Ni catalyst. The same Ni to Co ratio of 3:1 was present in the most active Ni-Co catalyst (75Ni25Co/Al_2O_3). Characterization of 75Ni25Fe/Al_2O_3 revealed the formation of Ni_3Fe alloy, whose surface properties were different from the $Ni_{1-x}Co_x$ alloy present in 75Ni25Co/Al_2O_3. The presence of Ni based alloys of specific composition seemed responsible for the enhanced activity of 75Ni25Fe/Al_2O_3 and 75Ni25Co/Al_2O_3 relative to supported Ni catalyst for both the reactions. Furthermore, 75Ni25Co/Al_2O_3 was the most active catalyst for both reactions though deactivation occurred. In contrast, lower deactivation occurred with 75Ni25Fe/Al_2O_3. The turnover frequency during reforming and cracking were closely related for the supported Ni, Ni-Fe and Ni-Co catalysts. The higher activity of the 75Ni25Co/Al_2O_3 for the dry reforming reaction appeared to be due to the higher turnover frequency of this catalyst for the cracking reaction. Thus, the formation of alloys with specific composition, which improved the CH_4 cracking capability, seems to be the key factor for determining the best catalytic performance for the reforming reaction over the promoted Ni catalysts.

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1. Introduction

The reforming of methane (CH_4) with CO_2 had been extensively investigated during the past several years [1–7]. This process is often referred to as Dry Reforming of Methane (DRM), in contrast to the industrially relevant steam reforming of methane. Some of the interesting features leading to the extensive investigations are:

(i) The DRM reaction produces synthesis gas with a H_2/CO ratio more favourable for the production of valuable synthetic liquid fuels and oxygenates [1–4,8].
(ii) The DRM reaction has the lowest operating cost compared to other methane reforming processes [5].
(iii) The DRM reaction allows exploitation of natural gas resources with high CO_2 content, thereby avoiding the expensive and intricate gas separation process [3–5].
(iv) The DRM reaction offers the use of biogas, a renewable resource containing CH_4 (40–70%) and CO_2 (30–60%) produced by anaerobic digestion of biomass [5,6].
(v) The DRM reaction offers the best solution for simultaneous utilization of these two greenhouse gases, CH_4 and CO_2 [2,5,7–9].

Considering the diminishing nature of petroleum oil reserves, efficient upgrading of CH_4 is necessary and CO_2 being a major environmental concern requires its effective utilization.

Therefore, investigations involving the DRM reaction are very important from an industrial and environmental standpoint.

The DRM reaction is catalytic and the commonly investigated catalysts for this reaction are supported noble metals and non-noble metals [2–4,10–12]. The noble metals include Pt, Pd, Ru, Rh and Ir, and these metals are very active and resistant toward deactivation by carbon deposition [1–4]. However, the high cost and limited availability of noble metals restrict their use. Amongst the non-noble metals supported Ni and Ni based catalysts are widely used due to their favourable activity, availability and cost [2,5,7]. The major difficulty associated with supported Ni and Ni based catalysts is carbon deposition, which render these catalysts unstable over long periods of time-on-stream (TOS) [1, 6,11]. To improve the catalytic activity and enhance the stability of supported Ni based catalysts different approaches have been undertaken. These approaches include support modification, addition of promoter and change in preparation method [1,5,12].

The effect of using a promoter is particularly interesting. Previous studies reveal that the catalytic activity and stability for the DRM reaction was improved by introducing a small amount of noble metal

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(Ru, Rh, Pt, or Pd) to supported Ni catalysts [1,3,13,14]. Significantly improved performance was also achieved by adding non-noble metals, such as Co or Fe, to supported Ni catalysts [15–18]. Furthermore, the specific ratio of Ni to Co and Ni to Fe had an effect on the catalytic activity and performance of the DRM reaction [1,7].

Closely associated with the DRM reaction is the cracking of CH_4 (CRM). During DRM the CRM reaction was suggested to be an important step [3,4,19–21]. In the DRM reaction CH_4 dissociates to various CH_x species and the ultimate formation of C_{ads} was substantiated [22–26]. The C_{ads} is subsequently oxidized by CO_2. Furthermore, the dissociation of CH_4 to CH_{3ads} and H_{ads} species was proposed as the rate determining step in DRM [22]. The dissociation of CH_4 was also suggested as the rate determining step in CRM [27]. Therefore, examining the CRM reaction over various catalysts is expected to assist in the understanding and development of catalysts for DRM. In addition to the importance during the DRM reaction the CRM reaction independently possesses significant industrial importance as it produces CO_x free hydrogen [27–29].

In a previous study co-precipitated Ni-Co, Ni-Fe, Ni-Cu, and Ni-Mn catalysts of fixed Ni-M composition were compared for the DRM reaction [2]. Based on initial screening additional studies were carried out only for the Ni-Co catalyst. However, in co-precipitated catalysts the surface concentrations of the metals may be different from the bulk. Furthermore, determining the reasons for the higher activity of the Ni-Co catalyst, compared to other Ni-metal systems, were not pursued. The increase in DRM and CRM activity by alloying Ni with Co was also shown in our previous study using co-impregnated catalysts [7]. However, the most active supported Ni-Co catalyst deactivated during the course of the reaction. Thus, developing cheap, active and stable Ni based alloy catalyst apart from Ni-Co is highly desirable. Another recent study showed that a particular Fe/Ni ratio in a series of bimetallic Fe-Ni/$MgAl_2O_4$ catalysts deactivated to a lesser extent and had a better catalytic activity than Ni alone [1]. Furthermore, Ni-Fe alloy is one of the most promising catalysts for CO_2 methanation [30], where CO_2 is also one of the key reactants in DRM reaction. Therefore, bimetallic Ni-Fe appears to be a potential and economically viable option for the DRM reaction. Our present work attempts to understand the effect of using supported Ni-Fe catalysts for the DRM reaction and comparing the activity and deactivation with supported Ni and the most active supported Ni-Co catalyst.

To achieve the above objective supported Ni, Ni-Fe and Fe catalysts were synthesized, characterized and tested for the two reactions. Alumina (Al_2O_3) was chosen as the support. The total metal loading was constant and the amount of Ni and Fe in the Ni-Fe/Al_2O_3 catalysts was varied similarly to our previous study. The supported Ni, Ni-Fe and Fe catalysts were characterized by H_2-Temperature programmed reduction (H_2-TPR), X-ray diffraction (XRD) and H_2-Temperature programmed desorption (H_2-TPD). The surface areas of the catalysts were also determined. All the catalysts were tested for the DRM under similar operating conditions to enable proper comparison. Furthermore, a moderate temperature was used to test the catalytic activity. The use of moderate temperatures was

intentional since carbon formation was favoured and catalyst stability can be analyzed. Under such conditions the conversions and yields were determined. Additionally, the reactivity results were compared with the best Ni-Co catalyst established in our previous study [7]. Thermogravimetric analysis (TGA) was also carried out to quantify the amount of carbon in some of the spent catalysts. Finally, the CRM reaction was carried over the catalysts and the conversions were compared with those observed for the DRM reaction. Based on the results and comparing with the best Ni-Co catalyst the reason for the increased catalytic activity of the Ni-M (M = Fe or Co) catalysts was proposed. This would enable us to develop robust Ni based catalysts that are active and stable for the DRM reaction at moderate and higher reaction temperatures.

2. Experimental

2.1. Catalyst synthesis

Alumina supported Ni, Fe, and Ni-Fe catalysts were synthesized by the incipient wetness impregnation or co-impregnation method. A total metal loading of 15 wt.% was maintained for each supported catalysts. The Al_2O_3 (SASOL) support was pretreated with known amounts of water following previously published procedures [31]. The required amounts of an aqueous solution of Ni, and Fe precursors (nickel (II) nitrate hexahydrate (Sigma-Aldrich, 99.99%) and iron (III) nitrate nonahydrate (Sigma-Aldrich, 99.99%)) were thoroughly mixed with this pretreated support. The mixture was then dried and calcined at increasing temperatures and finally at 773 K for 6 h. A fresh batch of alumina supported Ni-Co and Co catalysts was synthesized based on the procedure described elsewhere [7]. The calcined catalysts were reduced in a reactor at 823 K for 4 h under flowing H_2 stream prior to DRM and CRM reactions. The sample nomenclature and nominal compositions are given in Table 1.

2.2. Catalyst characterization

2.2.1. Surface area measurement

The surface areas of the catalysts were measured by the BET method using N_2 adsorption data at 77 K. The instrument used for surface area measurement was SMART SORB 92/93 surface area analyzer. A 30% N_2-He gas mixture was used for adsorption. All the samples were degassed at 498 K for 8 h prior to the measurement.

2.2.2. Hydrogen-temperature programmed reduction (H_2-TPR)

The H_2-TPR experiment was performed using an Altamira AMI-200 setup, which was equipped with a thermal conductivity detector (TCD). The reduction was analyzed in the temperature range of 323 to 1223 K using a constant flow (30 ml/min) of 10% H_2-Ar gas mixture. Hydrogen consumption during reduction was measured by the TCD and a H_2-TPR profile was obtained. The H_2 consumption was obtained by integrating the area under the TPR profile and calibration amount used. This

Table 1
Sample nomenclature and characterization information of 15Ni/Al_2O_3, Ni-Fe/Al_2O_3 and 15Fe/Al_2O_3. Supported Ni-Co, 75Ni25Co/Al_2O_3 and 15Co/Al_2O_3 have been included for comparison. Samples were reduced at 823 K for 4 h prior to analysis.

Sample nomenclature	% Metal loading		Surface area[a] (m^2/g)	Metal-oxide reduction[a] (%)	Metal crystallite size (nm)[b]	H_2 desorbed (μmole/g)[b,c]
	Ni Nominal	Co/Fe Nominal				
15Ni/Al_2O_3	15	–	164	75	34	82
75Ni25Fe/Al_2O_3	11.25	3.75	162	73	15	101
50Ni50Fe/Al_2O_3	7.5	7.5	167	55	17	170
25Ni75Fe/Al_2O_3	3.75	11.25	169	40	16	508
15Fe/Al_2O_3	–	15	162	23	40	376
75Ni25Co/Al_2O_3	11.25	3.75	163	80	19	62
15Co/Al_2O_3	–	15	150	78	23	39

[a] Calcined catalysts.
[b] Reduced catalysts.
[c] Desorbed amount from Al_2O_3 has been subtracted.