Carbon Dioxide Reforming of Methane over K, Ce and Mn Promoted Ni/Al_2O_3 Catalysts: Catalyst Characterization and Activity

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Abstract

Reforming of methane with carbon dioxide into syngas over $Ni/\gamma-Al_2O_3$ catalysts modified by potassium, MnO and CeO_2 was studied. The catalysts were prepared by impregnation technique and were characterized by BET surface area, pore volume, X-ray diffraction, scanning electron microscopy, temperature programmed studies (TPR, CO_2-TPD, H_2-TPD) and pulse chemisorption. The performance of these catalysts was evaluated by conducting the reforming reaction in a fixed bed reactor. Results of the investigation suggested that stable Ni/Al_2O_3 catalysts for the carbon dioxide reforming of methane can be prepared by addition of both potassium and CeO_2 (or MnO) as promoters. The results of the various characterization techniques were used to relate the observed catalytic activity and stability to the catalyst property. The stability and lower amounts of coking on promoted catalysts were attributed to partial coverage of the surface of nickel by patches of promoters, strong metal-support interaction (TPR, H_2 pulse chemisorption, H_2-TPD) and to their increased CO_2 adsorption (CO_2-TPD).

Keywords: CO_2-CH_4 reforming; characterization; Ni/Al_2O_3 catalysts; CeO_2; MnO; dispersion

Catalytic activity and coke deposition

The CH_4 and CO_2 conversion obtained using the different catalysts during the isothermal reaction at 700 ^{0}C are given in Table 1. The $13.5Ni/Al_2O_3$ catalyst showed a high initial CH_4 conversion of 81%, but also rapidly deactivated with time on stream. After 6 h time on stream, the CH_4 conversion reduced to 74% and there was a significant amount of coke deposited (3.1 wt.%) on this catalyst. The other catalysts showed an initial conversion value slightly less than that of $13.5Ni/Al_2O_3$; but no appreciable loss in activity with time on stream was observed for these catalysts. The amount of carbon on the used catalysts determined by TGA is also given in Table 1. Thus the most significant effect of addition of K, CeO_2, MnO was the improvement in catalytic stability.

Table 1. Catalytic activity and coke content during CO_2 methane reforming reaction at 700 ^{0}C (CH_4:CO_2:N_2 = 1:1:1; $W/F_{CH4,0}$ = 1.725 kg-cat.h/kg_{methane})

Catalyst	CH_4 conversion (%)	CO_2 conversion (%)	Coke* (wt. %)
$13.5Ni/Al_2O_3$	81.0	81.0	3.1
$13.5Ni-2K/Al_2O_3$	79.9	80.8	0.6
$13.5Ni/10CeO_2-Al_2O_3$	79.7	80.6	0.6
$13.5Ni-2K/10CeO_2-Al_2O_3$	78.5	77.0	trace
$13.5Ni-2K/5MnO-Al_2O_3$	77.0	78.0	<0.1

* determined by TGA

Characterization of support and catalysts
Based on the results of the various characterization techniques the above observed catalytic activity and stability was related to the catalyst property.

BET Surface Area and Pore Volume: The BET surface areas, pore volumes and average particle sizes of the calcined catalysts is summarized in Table 2. It can be seen that the surface area and the pore volume for $13.5Ni/Al_2O_3$ catalyst decreased compared to $\gamma-Al_2O_3$ support. Addition of the other promoters K, CeO_2, MnO further slightly reduced the surface area.

Table 2. Physical properties of calcined catalysts

Support/Catalyst	S_{BET} (m^2/g)	V (cm^3/g)	Dp $(\overset{0}{A})$
Al_2O_3	227.8	0.367	64.5
$13.5Ni/Al_2O_3$	158.6	0.285	73.5
$13.5Ni-2K/Al_2O_3$	150.2	0.310	80.7
$13.5Ni/10CeO_2-Al_2O_3$	130.3	0.294	92.0
$13.5Ni-2K/10CeO_2-Al_2O_3$	127.2	0.289	93.0
$13.5Ni-2K/5MnO-Al_2O_3$	123.8	0.293	96.9

XRD: The reduced $13.5Ni/Al_2O_3$ and $13.5Ni-2K/Al_2O_3$ catalyst showed weak nickel diffraction peaks, whereas the reduced $13.5Ni-2K/10CeO_2-Al_2O_3$ and $13.5Ni-2K/5MnO-Al_2O_3$ catalyst showed strong nickel diffraction peaks. The broad Ni peaks in the former represent the presence of small Ni crystallite indicating good dispersion of Ni crystallites. In case of the latter, the sharp Ni peak at $2\theta = 44.5°$ lies on the small shoulder suggesting the presence of both large and small size nickel particles. This small shoulder could also be attributed to $NiAl_2O_4$. The formation of nickel aluminate is an indication of strong metal-support interaction in the CeO_2 and MnO promoted catalyst.

TPR: The reduction characteristics of the prepared samples were studied over the range 30-900 ^{0}C. The H_2 responses as a function of temperature are given in Fig.1. The support $\gamma-Al_2O_3$ showed no reducibility. The support $10CeO_2-Al_2O_3$ showed a small peak at 255 ^{0}C assigned to the reduction of ceria. The support $5MnO-Al_2O_3$ showed three distinct peaks with Tmax 329, 400 and 456 ^{0}C respectively, which could be ascribed to the different oxidation state of the manganese ion. For the catalysts, peaks in the range 200-480 ^{0}C, could be ascribed to the reduction of relatively free NiO species. The three peaks with Tmax 530-540 ^{0}C, 670-690 ^{0}C, 750-760 ^{0}C respectively is ascribed to complex NiOx species having strong interaction with $\gamma-Al_2O_3$. The first and third peaks appear as shoulders. Comparing the areas under the TPR curves, it can be concluded that all catalysts show similar degree of reduction and the number of the exposed metallic Ni atoms on all catalysts is approximately the same. For the $13.5Ni/Al_2O_3$ catalyst the first peak occurs at 264 ^{0}C. This peak has shifted to a higher temperature for the other catalysts. Metallic Ni sites reduced from both NiO weakly interacting with the support and NiOx strongly interacting with the support are active sites for methane-reforming reactions. Eventhough free NiO sites are prerequisite for high activity, the increase of NiO population in high Ni loading favorably promotes Ni sintering and carbon deposition resulting in relatively low

catalytic activity with time on stream. Therefore, the population of NiOx, compared with those of NiO should be higher for high catalytic activity and stability. In the present case, the fraction of nickel present as free Ni resulting from the low temperature reduction of NiO species is larger on 13.5Ni/Al$_2$O$_3$ catalyst compared to other catalysts. Therefore the initial activity of 13.5Ni/Al$_2$O$_3$ catalyst is slightly higher than the other catalysts. Since the fraction of nickel resulting from the reduction of NiOx strongly interacting with the support is higher on other catalysts compared to 13.5Ni/Al$_2$O$_3$; they show more stability compared to 13.5Ni/Al$_2$O$_3$ catalyst.
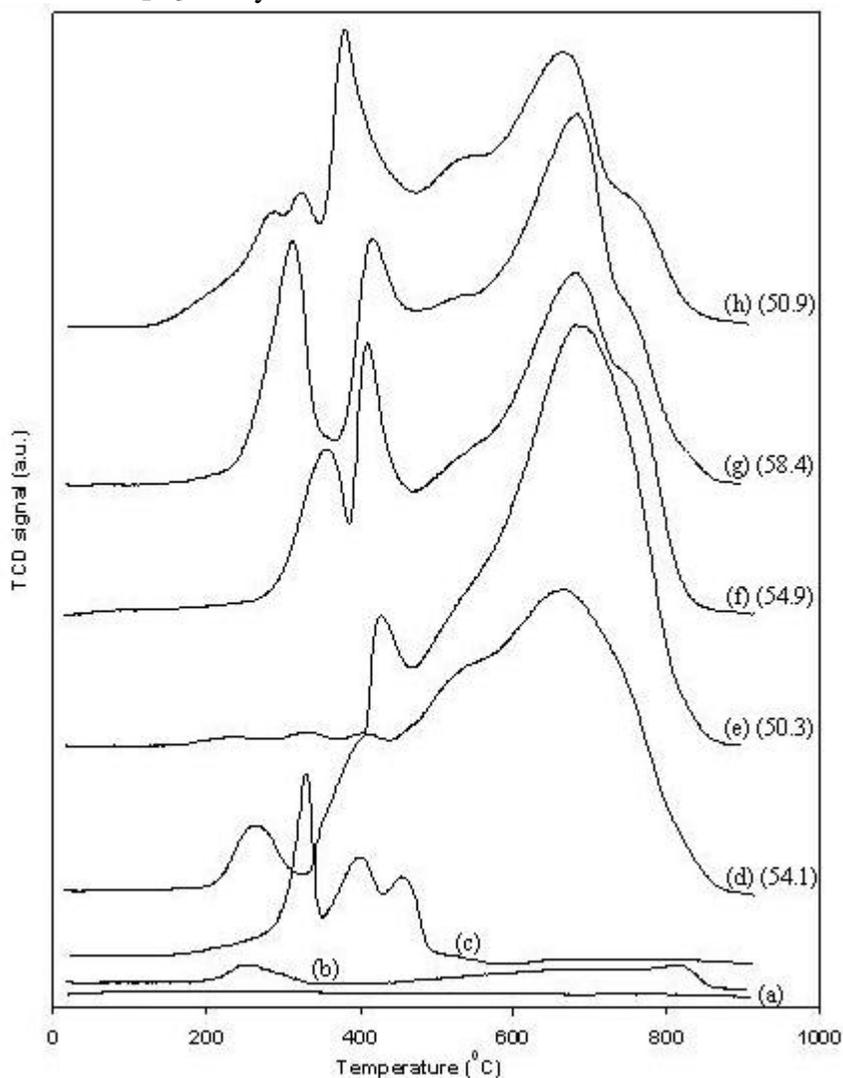

Fig. 1. TPR profiles of various promoted Ni catalysts (a)Al$_2$O$_3$; (b)10CeO$_2$-Al$_2$O$_3$; (c)5MnO-Al$_2$O$_3$; (d)13.5Ni/Al$_2$O$_3$; (e)13.5Ni/10CeO$_2$-Al$_2$O$_3$; (f)13.5Ni-2K/Al$_2$O$_3$; (g)13.5Ni-2K/10CeO$_2$-Al$_2$O$_3$; (h)13.5Ni-2K/5MnO-Al$_2$O$_3$ (Values in brackets represent H$_2$ consumption in mL/g STP)

H$_2$ pulse chemisorption experiments for the reduced catalysts were done at 50°C. The results of H$_2$ chemisorption show that addition of promoter reduces the metal dispersion, while TPR study shows similar H$_2$ consumption for all catalysts. The strong possibility is

that because of the occurrence of the strong metal/support interaction (SMSI) for the promoted catalysts, the surface of nickel is decorated by manganese oxide / cerium oxide species. Thus a large part of the surface Ni atoms is covered by addition of promoters. It is noteworthy that the catalytic activity of the promoted catalysts is almost same as that of $13.5Ni/Al_2O_3$ catalyst, even though the Ni surface area of the former is considerably lower than that of the latter. In terms of turnover frequency, the activity would follow the following order $13.5Ni-2K/5MnO-Al_2O_3 > 13.5Ni-2K/10CeO_2-Al_2O_3 > 13.5Ni-2K/Al_2O_3 > 13.5Ni/10CeO_2-Al_2O_3 > 13.5Ni/Al_2O_3$.

H_2-TPD: The hydrogen responses of the reduced catalysts were obtained in the temperature range 50-750 °C during TPD after adsorption at 60 °C and 400 °C respectively. Comparison of the area under the curve showed that H_2 desorbed for the $13.5Ni/Al_2O_3$ catalyst is higher compared to the promoted catalysts, in agreement with the results of pulse chemisorption. The results of H_2-TPD revealed that the Ni-H bond on promoted catalysts is fewer and weaker than that of $13.5Ni/Al_2O_3$ catalyst because of stronger interaction between Ni and the support for the promoted catalysts which leads to weakening of Ni-H bond. The observed shift in the desorption peaks to higher temperatures and higher amounts of H_2 desorbed after adsorption at 400 °C, implies that hydrogen adsorption on the promoted and unpromoted catalysts is an activated process.

CO_2-TPD of reduced samples was performed in flowing He (30 mL/min) with a heating rate of 10 °C/min after adsorption of CO_2 at room temperature for 1 h. Addition of promoter results in an increased amount of adsorbed CO_2 and a shift of the desorption peak to higher temperatures. The promoted catalysts show a broad distribution of base sites over the entire temperature range of 50-800 °C. Because CO_2 is an acidic gas, adsorption and dissociation of CO_2 could be promoted by a basic catalyst. Thus, the moderate basicity of K, CeO_2, MnO seems responsible for the increased adsorption of CO_2 for promoted catalysts. Increased CO_2 adsorption decreases CO disproportionation and results in the formation of surface carbonate species which remove carbon precursors from the catalyst surface. Therefore the promoted catalysts show better stability compared to $13.5Ni/Al_2O_3$ catalyst.

Reforming of methane with carbon dioxide into syngas over $Ni/\gamma-Al_2O_3$ catalysts modified by potassium, MnO and CeO_2 was studied. Results of the investigation suggested that stable Ni/Al_2O_3 catalysts for the carbon dioxide reforming of methane can be prepared by the addition of both potassium and CeO_2 (or MnO) as promoters without any significant loss in activity. Based on the results of the various characterization techniques employed the observed catalytic activity and stability was related to the catalyst property. The stability and lower amounts of coking on promoted catalysts were attributed to partial coverage of the surface of nickel by patches of promoters and to their increased CO_2 adsorption, resulting in the formation of surface carbonate species which remove carbon precursors from the catalyst surface