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AUTOTHERMAL REFORMING OF METHANE TO HYDROGEN PRODUCTION OVER Ni/Al_2O_3, Co/Al_2O_3 AND NiO-CoO/MgO

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Abstract

Autothermal reforming of methane to hydrogen gas was examined over Co/Al_2O_3, Ni/Al_2O_3 and NiO-CoO/MgO catalyst. Among the catalyst examined, NiO-CoO/MgO catalyst with 24 % metal loading exhibits not only the highest catalytic activity and selectivity but also remarkable stability. In addition the catalysts were characterized by nitrogen adsorption (NA), TPR, and XRD. The catalyst characteristics is strongly influenced by interaction between support and metal exist. The excellent performance of NiO-CoO/MgO resulted from the formation of an ideal solid solution between NiO, CoO and MgO.

Keyword: *Autothermal reforming of methane, hydrogen production*

Introduction

Increasing concern about world dependence on petroleum oil has generated interest in the use of natural gas. However, the majority of these reserves are located in remote regions which lead to high transportation costs. Therefore, the conversion of methane (the main component of natural gas) to important chemicals remains a challenging task. In general, there are two processes for converting methane to more useful chemical: the direct and indirect conversion. The attempts regarding the direct conversion of methane have focused on the oxygenation to methanol and formaldehyde and also on the oxidative coupling of methane to ethane and ethylene. However, so far the direct processes have not been utilized at industrial scale because of very low yields of the target product. The indirect route for methane conversion is through the synthesis gas (CO and H_2), which is then further converted to either methanol or hydrocarbons. Hydrogen is considered as a clean energy source and in the future, a large amount of hydrogen will be used as a fuel for fuel cell. The principle commercial technology for hydrogen production is steam reforming of methane (SRM) (equation (1)):

$$CH_4 + H_2O \longleftrightarrow CO + 3H_2 \qquad \Delta H = 49.2 \text{ kcal/mole} \qquad (1)$$

However, because of its high endothermicity, this process is characterized by high investment cost and energy consumption. Therefore, in recent years many researchers attempted to produce the synthesis gas via the catalytic partial oxidation of methane (POM) (Utake *et al.*, 2003, Dong *et al.*, 2001 and Roh *et al.*, 2002) or combination of steam reforming and partial oxidation of methane (autothermal reforming of methane). Noble metal catalysts such as Ir, Pt, Pd, and Rh have excellent activity for partial oxidation of methane, but they are costly. Therefore, different kinds of base metal catalysts like Co, Fe, and Ni have been used. Transition metals such as iron, cobalt and nickel are known to be very active catalysts for carbon deposition (Tang *et al.*, 1998). In the production of hydrogen from methane, highly active and stable catalyst becomes more significant for an on site H_2 generation system or a compact fuel system. Coke formation over the catalyst frequently takes place, resulting in catalyst deactivation or reactor plugging (Tang *et al.*, 1998). In practice, Ni-based catalysts are believed to be more promising than noble metal-based catalysts. Choudhary *et al.* (1998a) and Ruckenstein and Hu (1999) reported that the Ni-MgO catalyst showed high activity and selectivity in the process with very low carbon deposition rates. In another study, NiO supported on MgO precoated low surface area macroporous silica-alumina catalyst showed high activity and selectivity in the oxidative conversion of methane and in the oxy-steam and/or CO_2 reforming of methane to synthesis gas (Choudhary *et al.*, 1997). Addition of cobalt to nickel-containing Yb_2O_3, ZrO_2, and ThO_2 catalysts caused a drastic reduction in the filamental carbon formation on the surface of the catalysts, but the selectivity for both CO and H_2 in the oxidative conversion of methane decreased slightly. Therefore, the development of coking-resistant non-noble metal catalysts has potential significance to commercial utilization of partial oxidation of methane and

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autothermal reforming of methane. Due to the same structure and similar lattice parameters, CoO, NiO and MgO can form an ideal solid solution. It is, therefore, interesting to investigate the performance of the combined Co-Ni-MgO catalyst in the autothermal reforming of methane to synthesis gas. The goal of this work is to compare the performance of the Cu/Al_2O_3, Co/Al_2O_3, Ni/Al_2O_3 and NiO-CoO/MgO catalysts on the autothermal reforming of methane.

Experimental

The Co/Al_2O_3, Ni/Al_2O_3 and NiO-CoO/MgO catalysts were prepared by the incipient wetness impregnation of the Al_2O_3 and MgO supports using an aqueous solution of nickel nitrate and cobalt nitrate. The paste thus obtained was dried at 120 °C and calcined at 800 °C in air for 4 h. The catalysts were characterized by temperature programmed reduction with hydrogen (H_2-TPR), nitrogen adsorption and thermal gravity analysis (TGA). The catalytic scheme was displayed in Figure 1. The catalyst (75-150 mesh) was placed in a quarts wool bed system inside a continuous flow micro-reactor (12 mm diameter and 300 mm length). A water pump was used for the evaporator heated at 200 °C to control the steam to carbon ratio in the reaction gas mixture. Prior the autothermal reforming, the catalyst was heated with nitrogen at 500 °C for 1 hour.

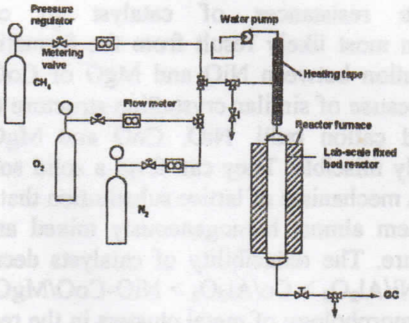

Figure 1. Schematic diagram of the experimental set-up apparatus for autothermal reforming of methane

Result and Discussion

Characterization

Table 1 summarizes BET surface areas of Ni/Al_2O_3, Co/Al_2O_3, NiO-CoO/MgO, pure Al_2O_3 and pure MgO catalysts. Generally, the BET surface area of the catalyst decreases with the impregnation metal loaded in the support. The decrease in the BET surface area must be due to the extinction of surface vacancies. The result is in agreement with previous works conducted by Choudhary *et al.* (1998b), Wang and Ruckenstein (2001) and Maunula *et al.* (2000). Their works affirmed that the loading of metal onto the metal oxide support using impregnation method provokes the reduction in catalysts surface area. The NiO-CoO/MgO catalyst gave the smallest BET surface area compared with the other catalyst. In addition, de Lucas et al. (2001) reported that the reduction of surface area of the metal loaded in the support indicated a strong interaction between the surfaces of the support with the metal species which enabled a good dispersion of metal on the surface.

Table 1. BET surface areas of the catalysts

Catalyst	BET, surface area m^2/g
Ni/Al_2O_3	138.00
Co/Al_2O_3	128.00
NiO-CoO/MgO	27.14
Pure Al_2O_3	167.00
MgO	38.17

In Figure 1, the CH_4 conversion achieved over the Ni/Al_2O_3, Co/Al_2O_3 and NiO-CoO/MgO catalyst with different BET surface area are shown. The results unambiguously present evidence that there was no direct connection between surface area and catalyst activity. The results are totally consistent with the works done by Wang and Ruckenstein (2001) and Roh *et al.* (2003). Thus the nitrogen adsorption analysis was not specifically conducted over Ni/Al_2O_3, Co/Al_2O_3 and NiO-CoO/MgO catalysts.

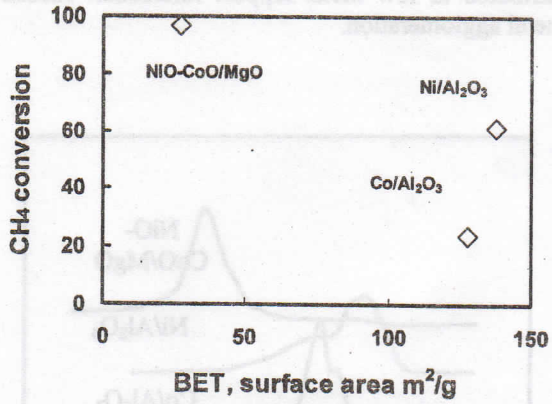

Figure 1. Correlation between CH_4 conversion and BET surface area

The TPR profiles for Co/Al_2O_3, Ni/Al_2O_3 and NiO-CoO/MgO catalysts are illustrated in Figure 3. There were two major peaks for Co/Al_2O_3 located at 350 °C and between 400 – 700 °C. One (peak maximum = 350 °C is attributable to the reduction of relatively free CoO species. These sites may cause in Co sintering and coke formation during reaction. The second peak (peak maximum = 600 °C) can be assigned to the complex CoO species which has a strong interaction with Al_2O_3. A large peak is observed in the TPR profiles of Ni/ Al_2O_3 at 480 °C. The peak can be assigned to free NiO species. These sites may result in Ni sintering and carbon formation during autothermal reforming of methane. On the contrary, NiO-CoO/MgO shows one peak at 800-900 °C assigned to the reduction of solid solution NiO-CoO/MgO. According to previous works (Wang and Ruckenstein, 2001, Choudhary *et al.* 1998b and Roh *et al.* 2003) the reduction of solid-solution NiO/MgO and CoO/MgO could be done at 800-900 °C. The high temperature TPR peaks for the catalysts indicate the formation of NiO-CoO-MgO solid solution in this catalyst. The NiO or CoO reduction occurs at higher temperatures because of the incorporation of Ni^{2+} and Co^{2+} deep in the MgO matrix forming NiO-CoO-MgO solid solution. In addition, several literatures (Dong *et al.*, 2001; Wang and Ruckenstein, 2001; Ruckenstein and Hu, 1999 and Tang *et al.*, 1998) also stated that NiO, CoO and MgO are miscible because of similar crystal line structures. They can form ideal solid solution through a mechanism of lattice substitution that leads to a system almost homogeneously mixed at high temperature. Due to the strong interaction between NiO, CoO and MgO, a temperature higher than 800 °C was required to reduce the solid solution because of the irreducibility of MgO and because both Ni, Co and Mg share the oxygen in the solid solution. The increase of reduction temperature has been reported due to the strong metal-support interaction (Chen et al. 1995). Accordingly, the decrease of reduction temperature in the TPR profiles of Ni/Al_2O_3 and Co/Al_2O_3 compare to NiO-CoO/MgO was attributed to low metal-support interaction caused by metal agglomeration.

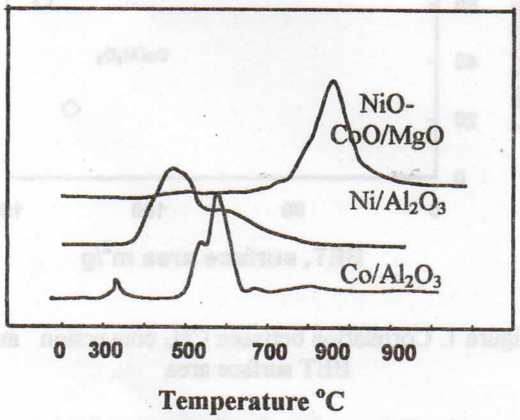

Figure 3. TPR profiles of Co/Al_2O_3, Ni/Al_2O_3 and NiO-CoO-MgO catalyst

Table 2. Coke formation on the Ni/Al_2O_3 and Co/Al_2O_3 NiO-CoO/MgO catalyst after conducting autothermal reforming of methane (T = 880 °C, reaction time = 4 h)

Catalyst	Percentage of coking (wt %)	Coking rate (wt %/h)
Ni/Al_2O_3	12.912	3.228
Co/Al_2O_3	10.336	2.584
NiO-CoO/MgO	2.584	0.646

The rate and amount of coking on the catalyst surface during the autothermal reforming of methane for 4 h at 880 °C measured by TGA are listed in Table 2 and Figure 4. The carbon deposition easily takes place on the surface of Ni/Al_2O_3. As shown in Figure 4, the amount of carbon deposition on NiO-CoO/MgO is much less than Ni/Al_2O_3 and Co/Al_2O_3. Owing to carbon deposition, the Ni/Al_2O_3 and Co/Al_2O_3 catalysts become partially shattered whereas NiO-CoO/MgO still shows good mechanical strength after reaction 4 h. These have shown excellent resistance of NiO-CoO/MgO to carbon deposition even under high steam to carbon ratio (>3). As suggested by Ruckenstein and Hu (1999) and Wang and Ruckenstein (2002), who studied the performance of Ni/MgO and Co/MgO in methane reforming with CO_2 and O_2 to synthesis gas, the excellence resistances of catalyst to carbon deposition most likely result from the formation of solid solution between NiO and MgO or CoO and MgO. Because of similar crystalline structure (NaCl type) and cation radii, NiO, CoO and MgO are completely miscible. They can form a solid solution through a mechanism of lattice substitution that leads to a system almost homogeneously mixed at high temperature. The reducibility of catalysts decreases in order $Ni/Al_2O_3 > Co/Al_2O_3 >$ NiO-CoO/MgO. The size and morphology of metal clusters in the reduced catalysts is strongly affected by its reducibility (Wang and Ruckenstein, 2001). Due to the low reducibility, the metal crystallites formed during the reduction of the solid solution were small and hence little carbon deposition occurred. Besides the solid solution, CoO and NiO were identified in the catalysts with Ni/Al_2O_3 and Co/Al_2O_3 compounds which can be more easily reduced than solid solution. The relatively large metal particles formed during the reduction of the more reducible Co and Ni species, stimulated carbon deposition. In addition, due to the relatively weak interactions between these cluster and substrate, enhanced sintering could occur easily. The sintering and the coke formation are responsible for the deactivation of catalysts. The result indicated that the formation of a complete solid solution plays an important role regarding the reduction behavior and the catalytic performance.

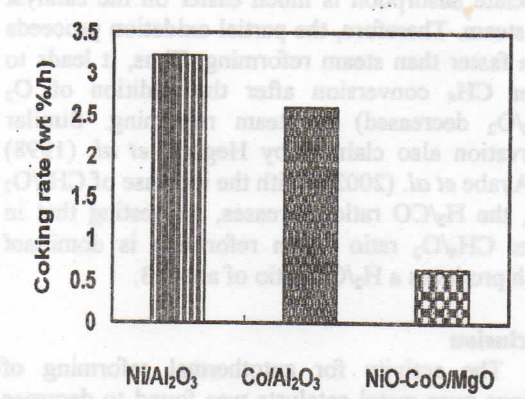

Figure 4. Coke formation on the Ni/Al_2O_3 and Co/Al_2O_3 NiO-CoO/MgO catalyst after conducting autothermal reforming of methane

Catalytic reaction

The catalytic activities of the Ni/Al_2O_3, Co/Al_2O_3 and NiO-CoO/MgO catalysts with $CH_4/O_2 = 2.2$, $CH_4/H_2O = 2.6$, GHSV = 5.4 x 10^4 $cm^3g^{-1}h^{-1}$ and reaction temperature 880 °C are displayed in Figure 5. It is clear that NiO-CoO/MgO showed the best activity and selectivity in the autothermal reforming of methane to synthesis gas. In the ATR reaction, NiO-CoO/MgO showed 96.7 % CH_4 conversion. On the contrary, Ni/Al_2O_3 and Co/Al_2O_3 showed CH_4 conversion of 61.35 % and 58.50 %, respectively. Due to the phase transformation into $NiAl_2O_4$ or $CoAl_2O_4$, Ni/Al_2O_3 and Co/Al_2O_3 showed small activity in autothermal reforming of methane. Thus, it was confirmed that NiO-CoO/MgO showed higher activity than of Ni/Al_2O_3 and Co/Al_2O_3 as well as high stability.

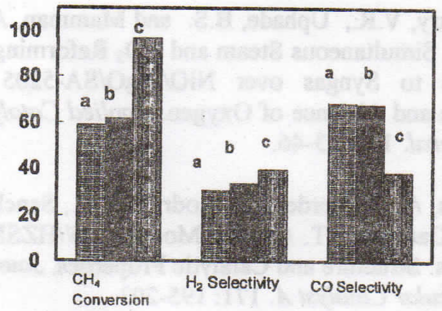

Figure 5. Catalytic activity Co/Al_2O_3 (a), Ni/Al_2O_3 (b), and NiO-CoO-MgO (c) catalyst

The catalytic activity of NiO-CoO/MgO for methane autothermal reforming reaction was tested as a function of temperature, as shown in Figure 6. In this study, a mixture of methane-oxygen-water was supplied to catalysts in the autothermal reforming reaction. The results show that, with the increase in temperature the conversion of methane and selectivities for CO and H_2 increased. With a decrease in temperature, the conversion of methane abruptly dropped at 400 °C to 33. 4%. A high temperature is necessary for the activation of methane, since methane molecules are the most inactive hydrocarbon. Thus, lowering of the reaction temperature results in the extinction of the rich-fuel combustion reaction. The O_2 conversion is above 98 % for all temperature in the range experiment. Moreover, the steam conversion is below 54 % for all temperatures. The composition profiles (Figure 6) confirms that methane combustion occurred to a greater extent at lower temperatures, which explains the high selectivity for CO_2 above 56 %. However, with the increasing temperature, the selectivity of CO and H_2 increased, due to the reforming of methane with steam. The observed low CO selectivity (Figure 6b) indicates the occurrence of the water gas shift reaction (equation 2) simultaneously with steam reforming (1).

$$CO + 2\,H_2O \Longleftrightarrow H_2 + CO_2 \qquad \Delta H = 9.8 \text{ kcal/mole} \qquad (2)$$

The H_2/CO ratio obtained on the autothermal reforming is presented in Figure 6 (c). The results shown that the H_2/CO ratio decreased as temperature increased. This result indicates that the occurrence of water gas shift reaction decreased by increasing the temperature.

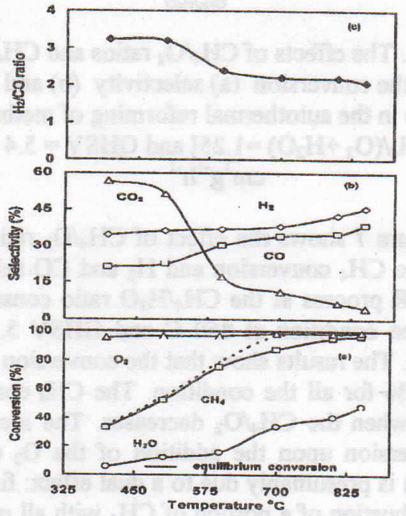

Figure 6. The effects of temperature on the conversion (a), selectivity (b) and H_2/CO ratio (c) in the ATR (reaction condition: $CH_4/O_2 = 2.7$, $CH_4/H_2O = 2.7$; GHSV = 5.4 x 10^4 $cm^3.g^{-1}.h^{-1}$).

The similar trend reported over $Ni/AlPO_4$ (Choudhary *et al.*, 1998b), Ni/Ce-ZrO_2/θ-Al_2O_3 (Roh *et al.*, 2003) and Pt/ZrO_2/Al_2O_3 (Souza and Schmal 2003). The investigation conducted by Souza and Schmal (2003) over platinum catalysts reported that at low temperatures, the H_2/CO ratio is most influenced by the partial oxidation and the water gas shift reaction.

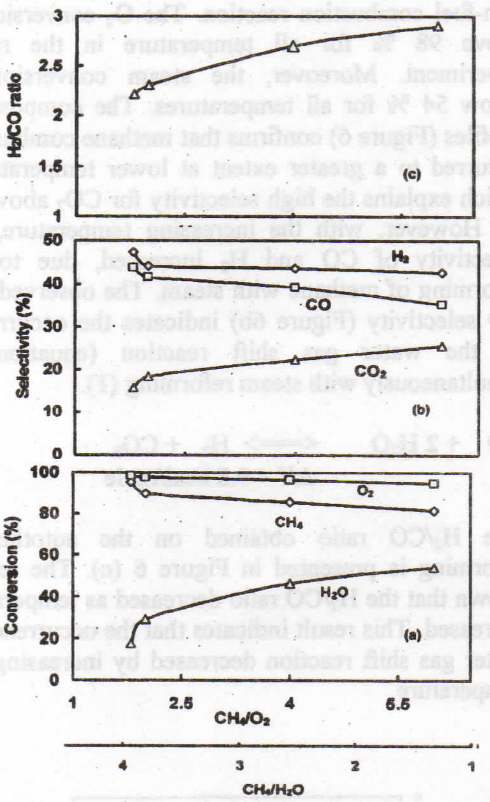

Figure 7. The effects of CH_4/O_2 ratios and CH_4/H_2O ratios on the conversion (a) selectivity (b) and H_2/CO ratio (c) in the autothermal reforming of methane at 850 $[CH_4/(O_2 + H_2O) = 1.25]$ and GHSV = 5.4×10^4 $cm^3 g^{-1} h^{-1}$

Figure 7 shows the effect of CH_4/O_2 ratio in the feed on the CH_4 conversion and H_2 and CO selectivity in the ATR process at the CH_4/H_2O ratio constant and the reaction condition at 850 C and GHSV 5.4×10^4 $cm^3.g^{-1}.h^{-1}$. The results show that the conversion of O_2 is above 98 % for all the condition. The CH_4 conversion increases when the CH_4/O_2 decreases. The increase in CH_4 conversion upon the addition of the O_2 (CH_4/O_2 decreased) is presumably due to a dual effect: firstly the rapid combustion of a portion of CH_4 with all of the O_2 present and secondly, the increased rate of the endothermic reforming reactions as a result of a temperature rise within the bed due to the exothermic combustion reaction. Based on the result indicate that the reaction rate of partial oxidation is much faster than steam reforming process. In comparison to the work reported by Dong *et al.* (2002) which investigated the autothermal reforming of methane over Ni/Ce-ZrO_2 catalyst, this study affirmed that CH_4 dissociate adsorption occurs on metal active surface, while both steam and O_2 competitively adsorb on metal active and support in the autothermal reaction. Meanwhile, O_2 dissociate adsorption is much easier on the catalyst than steam. Therefore, the partial oxidation proceeds much faster than steam reforming. Thus, it leads to higher CH_4 conversion after the addition of O_2 (CH_4/O_2 decreased) to steam reforming. Similar observation also claimed by Hegarty *et al.* (1998) and Ayabe *et al.* (2002). With the increase of CH_4/O_2 ratio, the H_2/CO ratio increases, suggesting that in higher CH_4/O_2 ratio steam reforming is dominant which produces a H_2/CO ratio of about 3.

Conclusion

The activity for autothermal reforming of methane over metal catalysts was found to decrease in the order NiO-CoO/MgO > Ni/Al_2O_3 > Co/Al_2O_3. NiO-CoO/MgO shows excellent resistance to carbon deposition and thus has a rather high stability. Due to the formation of a solid solution between NiO, CoO and MgO in NiO-CoO/MgO catalyst, it shows a beneficial effect on preventing formation of carbon.

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