THE CHARACTERIZATION OF Ni-BASED CATALYSTS FOR AUTOTHERMAL REFORMING PROCESS

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ABSTRACT

A simple technique approach was used to characterize the structural and chemical properties of CoO-NiO catalysts supported on 8-Al2O3, HZSM-5 and MgO-Al2O3. The morphology of the catalysts was studied by X-Ray diffraction to determine the phase composition and the particle size of the catalysts. Temperature-programmed reduction (TPR) reveals the formation of NiO and Co3O4 in dependence on temperature in case of catalysts supported on 8-Al2O3 and MgO-Al2O3 at higher metal loading. The catalysts supported on HZSM-5 also show appearance of NiO, CoO and Co3O4, which could lead to deactivation of the catalysts via formation of coke on the catalyst surface. The formation of NiO-CoO-MgO solid solution supported on MgO-Al2O3 exhibited stronger interaction between metal and support thus can make the catalysts more resistant to sintering and enhance the structure durability of catalyst in high temperature methane reforming process.

Keywords: Alumina, CoO-NiO, Characterizations, HZSM-5, MgO-Al2O3, Solid Solution, Temperature-Programmed Reduction, X-Ray Diffraction.

1 INTRODUCTION

Synthesis gas composed of CO and H2 are used for methanol production and Fischer-Tropsch synthesis. Hydrogen is used for ammonia synthesis as well as in various processes in oil refineries, chemical industries and fuel cell. Syngas is produced by steam reforming of natural gas (Hegarty et al., 1998). In future, a large amount of hydrogen will be used as a fuel for fuel cells. Therefore, syngas production from natural gas by several routes such as CO2 reforming (Nichio et al., 2000), partial oxidation (Lago et al., 1997; Wang and Ruckenstein, 2001) and autothermal reforming (Ma and Trimm, 1997; Takeguchi et al., 2003) has been investigated.

Many studies have focused on Ni/Al2O3-based catalysts (Nichio et al., 2000; Takeguchi et al., 2003) for reforming of methane, sometimes with modifiers to improve the catalytic stability. Nickel catalysts have high activity and selectivity in the reforming of hydrocarbon to syngas (i.e. CO and H2) and also have low cost (Tsang et al., 1995). Hence, these catalysts are commonly used in the syngas production processes. These catalysts are, however, also known for whisker type carbon deposition on them in the hydrocarbon reforming process, creating technical problems (Tsang et al., 1995). The coke deposition on nickel is much faster than that on noble metals (Tsang et al., 1995). Choudhary and co-worker (1997) found the NiO/Yb2O3, NiO/ZrO2 and NiO/ThO2 catalysts showed high activity and selectivity but carbon deposition on them is very fast. The addition of the cobalt to the catalysts dramatically reduced the rate of carbon
deposition on these catalysts in the oxidation conversion of methane to syngas and also the reaction over the catalysts starts (i.e., the catalyst is activated) at lower temperature.

Various kinds of supports, such as Al2O3 (Liu et al., 2002), MgO (Ma and Trimm, 1996) and zeolite (Choudhary et al., 1997), were used for Ni and Co catalysts. Among them, MgO-supported Co showed a high activity and stability for partial oxidation of methane at high temperatures (Wang and Ruckenstein, 2001). However, Al2O3 is a very suitable support for a high temperature reaction due to its large surface area and thermal stability. The combination of MgO as a modifier with alumina may give some advantages such as reduced sintering and enhances the dispersion of active metals. Autothermal is a combination of multi processes that gives much interest to many researchers, whereby the partial oxidation and adiabatic steam reforming (main reaction) are combined in a single reactor. Partial oxidation of methane: \( \text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \), proceeds via the following combustion-reforming reaction steps: \( \text{CH}_4 + \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O} \); \( \text{CH}_4 + \text{H}_2 \text{O} \rightarrow 3\text{H}_2 + \text{CO} \); \( \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO}_2 \); and water gas shift reaction (side reaction): \( \text{CO} + \text{H}_2 \text{O} \rightarrow \text{H}_2 + \text{CO}_2 \). In this study, CoO-NiO/Al2O3, CoO-NiO/ZSM-5 and CoO-NiO/MgO-Al2O3 catalysts were prepared by co-impregnation method involving a calcination step, and materials were characterized by X-ray diffraction, temperature-programmed reduction with hydrogen and nitrogen adsorption. The results of characterization were used to investigate the structural and chemical properties of Co-Ni-supported catalysts.

2 EXPERIMENTAL

2.1 PREPARATION OF CATALYSTS

Support materials employed in this study were ZSM-5 (Zeolyst International), MgO-Al2O3, and γ-Al2O3, which was prepared by calcining γ-Al2O3 (Merck) at 800 °C for 8 h (Ma and Trimm, 1996; Wang and Ruckenstein, 2001). The MgO-Al2O3 support was prepared by impregnating γ-Al2O3 with Mg(NO3)2·6H2O (Merck). After impregnation, the sample was dried overnight at 110 °C and subsequently calcined at 800 °C for 8 h. The catalysts were prepared by co-impregnating the supports (γ-Al2O3, ZSM-5 and MgO-Al2O3) with mixed aqueous solutions of Co(NO3)2·6H2O and Ni(NO3)2·6H2O. The required amount of nickel nitrate and cobalt nitrate were weighed and dissolved in distilled water, subsequently the selected support was added. After gentle stirring for 3 hours, the slurry was heated to 50–70 °C until dry, followed by overnight drying at 110 °C. The catalysts were then calcined at 800 °C for 8 hours. Except for CoO-NiO/ZSM-5 catalysts, the sample was calcined at 550 °C for 4 h. All the catalysts were then crushed and sieved to 100 meshes.

2.2 CHARACTERIZATION OF CATALYSTS

Structural characterization of catalysts was performed by powder X-ray diffraction (XRD) technique on a Bruker XRD D8 Advance diffractometer using Cu Kα radiation. Patterns were recorded from 2° to 80° (2θ) for CoO-NiO/ZSM-5 catalyst and 10° to 80° for CoO-NiO/γ-Al2O3 and CoO-NiO/MgO-Al2O3 catalysts.

Temperature-programmed reduction (TPR) experiments were performed on Thermo Finnigan TPDRO 1100 instrument. The sample of catalyst was first pretreated in a flow of \( \text{N}_2 \) from 100 to 750 °C, with a temperature gradient of 25 °C/min and flow of 20 ml/min, excluding CoO-NiO/ZSM-5 catalysts; the sample was pretreated at 100 to 500 °C with a temperature gradient and flow of \( \text{N}_2 \) same as above. The pretreatment was held for 60 minutes after the temperature reached 750 °C. The reduction gas used was 5% \( \text{H}_2 \) in \( \text{N}_2 \). The experiments were run in the range of 100–900 °C with approximately 45 mg of sample, a temperature gradient of 10 °C/min and flow of 25 ml/min (NTP) for CoO-NiO/ZSM-5 and CoO-NiO/MgO-Al2O3 catalyst only. For CoO-NiO/γ-Al2O3 catalyst, the running conditions are 35 ml/min of flow and 20 °C/min of a temperature gradient. Same as pretreatment process, the run was held for 10 minutes after the experiment temperature was reached at 900 °C excluding CoO-NiO/γ-Al2O3, the sample was held for 60 minutes.
3 RESULTS AND DISCUSSION

3.1 TPR PROFILE

3.1.1 CoO-NiO/α-Al₂O₃ Catalyst

![Graph showing TPR profiles](image)

**FIGURE 1**: TPR Profile obtained over (a) 5 wt% CoO-NiO/α-Al₂O₃, (b) 10 wt% CoO-NiO/α-Al₂O₃, (c) 15 wt% CoO-NiO/α-Al₂O₃, (d) 20 wt% CoO-NiO/α-Al₂O₃, and (e) 24 wt% CoO-NiO/α-Al₂O₃.

Temperature-programmed reduction (TPR) experiments were carried out in order to measure the reducibility of Co and Ni species on the Co-Ni-supported catalysts. TPR profiles of CoO-NiO/α-Al₂O₃ with various weights loading are shown in Figure 1. Several reduction peaks were observed in the TPR profiles. Since Ni²⁺ and Co²⁺ are reduced to Ni⁰ and Co⁰, respectively, without going through intermediate oxides, the hydrogen consumption peaks appearing in different temperature regions are assigned to the reduction of different species (Dong et al., 2002). Generally, low temperature peaks are attributed to the reduction of free NiO and CoO₂, while the higher temperature peaks are attributed to the reduction of CoO-NiO in intimate contact with the oxide support.

It is seen that the reduction of CoO-NiO/α-Al₂O₃ catalysts occurred in the temperature range between 850-900°C. The 20 wt% CoO-NiO/α-Al₂O₃ catalyst shown that existing free NiO and for 24 wt% CoO-NiO/α-Al₂O₃ existed both NiO and CoO₂ that confirmed by XRD. The reduction peak for CoO₂ occurred at 350°C and NiO at 480°C. The temperature region for both NiO and CoO₂ is similar to that found by Coudurier et al. (1997) and Dong et al. (2002). Based on the above analysis, the reduction peak appearing in the low temperature region (350°C and 480°C) for the catalysts corresponds to free CoO₂ and NiO with small interaction with support, respectively. While the reduction peak at high temperature region (~900°C) can be attributed to fixed Co and Ni which has stronger interaction with support, as well as to the reduction of highly dispersed Co and Ni in CoO-NiO/α-Al₂O₃.

From the results in Figure 1, it shows that the optimum weight loading among the catalysts is 15 wt% because of the absence of free CoO₂ and NiO in the catalyst. In autothermal reforming process, the free NiO or CoO₂ is one of the precursors to coke problem (Dong et al., 2002). Wang and Ruckenstein (2001) has reported that higher reduction temperature occurred from strong interaction between active metal and support can prevent sintering thus coke formation can be minimize. This explain that the reduction peak at higher temperature region (900°C) for the CoO-NiO/α-Al₂O₃ catalysts is better than NiO/α-Al₂O₃ alone that has reduction peak at 450-540°C (Quincecoes et al., 2002).

One of the major problems encountered in the autothermal reforming of methane to yield syngas over nickel- and cobalt-based catalysts is rapid deactivation.
caused by carbon deposition or sintering with high temperature and high pressure reaction conditions. δ-Al₂O₃ is a very suitable support for a high temperature reaction due to its large surface area and thermal stability, but the Ni/Al₂O₃ and Co/Al₂O₃ catalysts have been shown to be very susceptible to carbon deposition in many reports (Xu et al., 2001). However, there could be several kinds of Ni and Co active phases formed on the surface of δ-Al₂O₃, such as microcrystalline nickel oxide and cobalt oxide, NiAl₂O₄ and CoAl₂O₄ spinel, which have been studied by various techniques, such as TPR and XRD (Huang and Schwarz, 1988). The microcrystalline nickel oxide has been reported as the 'free state' of the Ni active phase because of its mobility, which leads to migration aggregation and growth of particles at high temperature so that the dispersion of the active phase rapidly decreases, which is one of the main reasons why the supported Ni-based catalysts is easily deactivated.

The spinel NiAl₂O₄ and CoAl₂O₄ is usually considered to be the “fixed of bound state” of the Ni and Co active phase due to its strong interaction with the support (Huang and Schwarz, 1988). Although reduction is difficult, at least above 850°C for NiAl₂O₄ and above 900°C for CoAl₂O₄, it exhibits very high resistant to sintered at high temperature thus also resistant to coking. It has also been reported that the structure of NiAl₂O₄ and CoAl₂O₄ spinel can effectively inhibit carbon deposition. In this case, the nickel or cobalt ions tend to be highly dispersed and can be “fixed” into the alumina lattice, in tetrahedral or octahedral sites in the support. Although no free Ni species were detected by XRD with lower Ni loading, confirmed that complete NiAl₂O₄ and CoAl₂O₄ spinels are formed with Al₂O₃ support when the catalysts were calcined at higher temperature.

3.1.2 CoO-NiO/ZSM-5 Catalyst

![Image of TPR Profile](image)

**FIGURE 2: TPR Profile obtained over**
(a) 5 wt% CoO-NiO/ZSM-5
(b) 10 wt% CoO-NiO/ZSM-5
(c) 15 wt% CoO-NiO/ZSM-5
(d) 20 wt% CoO-NiO/ZSM-5
(e) 24 wt% CoO-NiO/ZSM-5

Metal ions such as Co²⁺ and Ni²⁺ are reduced with H₂ to lower valence states with simultaneous production of protons. The H₂-TPR profiles of Co-Ni/ZSM-5 with various weights loading are shown in Figure 2. A detailed hydrogen and CO (in order to distinguish between ions and oxides) TPR analysis of Co-zeolite is given by Sachtle and co-workers and the peaks will be assigned accordingly. For all curves, peak of CoₓOᵧ can be found at around 380°C, is similar to that found by Pieterse et al. (2002) and NiO peak can be found at 480-570°C. Peaks around 750°C and higher were assigned to Co⁵⁺ and Ni⁷⁺ ions associated to charge compensating (exchange) sites. Strikingly, pore volume impregnation of cobalt or nickel precursor results, like ion-exchanged cobalt/nickel, in highly stabilized Co²⁺/Ni²⁺ cations. Nevertheless, at comparable loading (Figure 2) the pore volume impregnation method gives some CoₓOᵧ and NiO as well.
At higher loading of catalysts shows broader peak of free NiO, mean that more species of free NiO in the catalysts. The presence of NiO and CoO in the Co-Ni/HZSM-5 catalysts can cause deactivation of catalyst via formation of coke, as explain in the topic above. So, perhaps all the catalysts supported ZSM-5 may not suitable for ATR reaction.

3.1.3 CoO-NiO/MgO-Al₂O₃ Catalyst

TPR profiles of CoO-NiO/MgO-Al₂O₃ with various weights loading are shown in Figure 3. Low temperature peaks shown only at 30 wt% are attributed to the reduction of free NiO and CoO particles, while the higher temperature peaks are attributed to the reduction of Co and Ni in the intimate contact with the MgO-Al₂O₃ support. It seen that the reduction of CoO-NiO/MgO-Al₂O₃ catalysts occurred in the temperature above 900°C. From the results in Figure 3, it shows that the optimum weight loading among the catalysts is 24 wt% because of the absence of free NiO and CoO in the catalyst, which causes to coking problems.

The reduction temperature increased with the addition of MgO as a modifier for alumina. MgO exhibited a change in the metal-support interaction with increasing of weight loading of metal in the alumina support. The increasing of reduction temperature due to a presence of (Co,Mg)O and NiO-MgO solid solution on the catalysts (Wang and Ruckenstein, 2001). The both solid solution species are detected in the XRD as shown in Figure 4. The addition of MgO as a modifier in the alumina catalyst also can make the catalysts more resistant to sintering and enhance the structure durability of catalyst in the high temperature methane reforming process (Xu et al., 2001).

![Figure 3: TPR Profile obtained over (a) 5 wt% CoO-NiO/MgO-Al₂O₃, (b) 10 wt% CoO-NiO/MgO-Al₂O₃, (c) 15 wt% CoO-NiO/MgO-Al₂O₃, (d) 20 wt% CoO-NiO/MgO-Al₂O₃, (e) 24 wt% CoO-NiO/MgO-Al₂O₃.]

3.2 XRD PATTERN FOR Co-Ni/MgO-Al₂O₃ CATALYST

Figure 4 show the XRD patterns of catalysts Co-Ni/MgAl₂O₃ at various metal loading. All the XRD patterns of 5–30 wt% of CoO-NiO revealed the presence of MgAl₂O₄, NiAl₂O₄ and CoAl₂O₄ (32.1°, 37.0°, 44.9°, 59.4° and 65.3°) spinels overlapping each other at the same 2θ. The overlapping is due to likely some distance between atoms of the species and they have the same cubic structure. The formation of spinels was expected because of the high calcinations temperature (800°C), which causes diffusion of NiO and CoO into Al₂O₃ to form NiAl₂O₄ and CoAl₂O₄, respectively (Mako, et al., 1999). The presence of (Co,Mg)O solid solution at 2θ of 43.0°, 62.3°, 74.7° and 78.6° and MgNiO₂ solid solution at 2θ of 43.0°, 74.7° and 78.6° reveal that the presence of MgO in the catalyst can enhance the structure of Ni and Co in the catalyst with existing of solid solution, which
has been proved that the species with structure of solid solution can prevent the catalyst from sintering and reduce coke formation (Wang and Runkenstein, 2001). Free NiO and Co$_3$O$_4$ species were not appeared in any circumstances in XRD, but both species were detected in TPR analysis for 30 wt% of CoO-NiO catalyst. The species were not detected in XRD because of lower amount of both NiO and Co$_3$O$_4$ exist in the catalyst.

\[ \text{MgO} \]
\[ \text{NiAl}_2\text{O}_4, \text{MgAl}_2\text{O}_4 \]
\[ \Theta \text{CoAl}_2\text{O}_4 \]
\[ \Delta \text{(Co,Mg)}\text{O} \]
\[ \ast \text{MgNO}_2 \]

**FIGURE 4:** XRD patterns obtained over (a) 5 wt% Co-Ni/MgO-Al$_2$O$_3$ (b) 10 wt% Co-Ni/MgO-Al$_2$O$_3$ (c) 15 wt% Co-Ni/MgO-Al$_2$O$_3$ (d) 20 wt% Co-Ni/MgO-Al$_2$O$_3$ (e) 24 wt% Co-Ni/MgO-Al$_2$O$_3$ (f) 30 wt% Co-Ni/MgO-Al$_2$O$_3$

4 CONCLUSION

The effects of strong interaction between metal and support play a very important role in the formation of the active phase of nickel and cobalt and are mainly responsible for the performance of nickel- and cobalt-based catalysts in the high temperature reaction of autothermal reforming process. The 'free state' NiO and Co$_3$O$_4$, often formed as the major phase over CoO-NiO-Al$_2$O$_3$, CoO-NiO/ZSM-5 and CoO-NiO/MgO-Al$_2$O$_3$ at lower calcination temperature or higher metal loading and considered to be responsible for catalyst deactivation.

\[ \text{Co}_3\text{O}_4 \] as the support has a strong tendency to interact with Ni and Co, and other metal oxides such as MgO to form a composite support and can easily form a new Ni species such as NiAl$_2$O$_4$ and CoAl$_2$O$_4$ when prepared by impregnation method at high calcined temperature. These Ni and Co species give strong interaction between support with presence MgO in the catalyst, which maybe can prevent sintering at high reaction temperature, thus coke formation can be minimize.

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