

## THE CHARACTERIZATION OF Ni-BASED CATALYSTS FOR AUTOHERMAL 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  $\delta$ -Al<sub>2</sub>O<sub>3</sub>, HZSM-5 and MgO-Al<sub>2</sub>O<sub>3</sub>. 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 Co<sub>3</sub>O<sub>4</sub> in dependence on temperature in case of catalysts supported on  $\delta$ -Al<sub>2</sub>O<sub>3</sub> and MgO-Al<sub>2</sub>O<sub>3</sub> at higher metal loading. The catalysts supported on HZSM-5 also show appearance of NiO, CoO and Co<sub>3</sub>O<sub>4</sub>, 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-Al<sub>2</sub>O<sub>3</sub> 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-Al<sub>2</sub>O<sub>3</sub>, Solid Solution, Temperature-Programmed Reduction, X-Ray Diffraction.

### 1 INTRODUCTION

Synthesis gas composed of CO and H<sub>2</sub> 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 CO<sub>2</sub> 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/Al<sub>2</sub>O<sub>3</sub>-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 H<sub>2</sub>) 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/Yb<sub>2</sub>O<sub>3</sub>, NiO/ZrO<sub>2</sub> and NiO/ThO<sub>2</sub> 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  $\text{Al}_2\text{O}_3$  (Liu et al., 2002),  $\text{MgO}$  (Ma and Trimm, 1996) and zeolite (Choudhary et al., 1997), were used for Ni and Co catalysts. Among them,  $\text{MgO}$ -supported Co showed a high activity and stability for partial oxidation of methane at high temperature (Wang and Ruckenstein, 2001). However,  $\text{Al}_2\text{O}_3$  is a very suitable support for a high temperature reaction due to its large surface area and thermal stability. The combination of  $\text{MgO}$  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 flowing combustion-reforming reaction steps:  $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ ;  $\text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}$ ;  $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO}$ ; and water gas shift reaction (side reaction):  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$ . In this study,  $\text{CoO-NiO/Al}_2\text{O}_3$ ,  $\text{CoO-NiO/ZSM-5}$  and  $\text{CoO-NiO/MgO-Al}_2\text{O}_3$  catalysts were prepared by co-impregnation method involving a calcination step, and the 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),  $\text{MgO-Al}_2\text{O}_3$  and  $\delta\text{-Al}_2\text{O}_3$ , which was prepared by calcining  $\gamma\text{-Al}_2\text{O}_3$  (Merck) at  $800^\circ\text{C}$  for 8 h (Ma and Trimm, 1996; Wang and Ruckenstein, 2001). The  $\text{MgO-Al}_2\text{O}_3$  support was prepared by impregnating  $\delta\text{-Al}_2\text{O}_3$  with  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Merck). After impregnation, sample was dried overnight at  $110^\circ\text{C}$  and subsequently calcined at  $800^\circ\text{C}$  for 8 h. The catalysts were prepared by co-impregnating the supports ( $\delta\text{-Al}_2\text{O}_3$ , ZSM-5 and  $\text{MgO-Al}_2\text{O}_3$ ) with mixed aqueous solutions of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . 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  $50-70^\circ\text{C}$  until dry, followed by overnight drying at  $110^\circ\text{C}$ . The catalysts were then calcined at  $800^\circ\text{C}$  for 8 hours. Except for  $\text{CoO-NiO/ZSM-5}$  catalysts, the sample was calcined at  $550^\circ\text{C}$  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  $\text{Cu K}_\alpha$  radiation. Patterns were recorded from  $2^\circ$  to  $80^\circ$  ( $2\theta$ ) for  $\text{CoO-NiO/ZSM-5}$  catalyst and  $10^\circ$  to  $80^\circ$  for  $\text{CoO-NiO}/\delta\text{-Al}_2\text{O}_3$  and  $\text{CoO-NiO/MgO-Al}_2\text{O}_3$  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  $750^\circ\text{C}$ , with a temperature gradient of  $25^\circ\text{C}/\text{min}$  and flow of  $20\text{ ml}/\text{min}$ , excluding  $\text{CoO-NiO/ZSM-5}$  catalysts; the sample was pretreated at  $100$  to  $500^\circ\text{C}$  with a temperature gradient and flow of  $\text{N}_2$  same as above. The pretreatment was held for 60 minutes after the temperature reached at  $750^\circ\text{C}$ . The reduction gas used was  $5\%$   $\text{H}_2$  in  $\text{N}_2$ . The experiments were run in the range of  $100-900^\circ\text{C}$  with approximately  $45\text{ mg}$  sample, a temperature gradient of  $10^\circ\text{C}/\text{min}$  and flow of  $25\text{ ml}/\text{min}$  (NTP) for  $\text{CoO-NiO/ZSM-5}$  and  $\text{CoO-NiO/MgO-Al}_2\text{O}_3$  catalyst only. For  $\text{CoO-NiO}/\delta\text{-Al}_2\text{O}_3$  catalyst, the running conditions are  $35\text{ ml}/\text{min}$  of flow and  $20^\circ\text{C}/\text{min}$  of a temperature gradient. Same as pretreatment process, the run was held for 10 minutes after the experiment temperature was reached at  $900^\circ\text{C}$  excluding  $\text{CoO-NiO}/\delta\text{-Al}_2\text{O}_3$ , the sample was held for 60 minutes.

### 3 RESULTS AND DISCUSSION

#### 3.1 TPR PROFILE

##### 3.1.1 CoO-NiO/ $\delta$ -Al<sub>2</sub>O<sub>3</sub> Catalyst

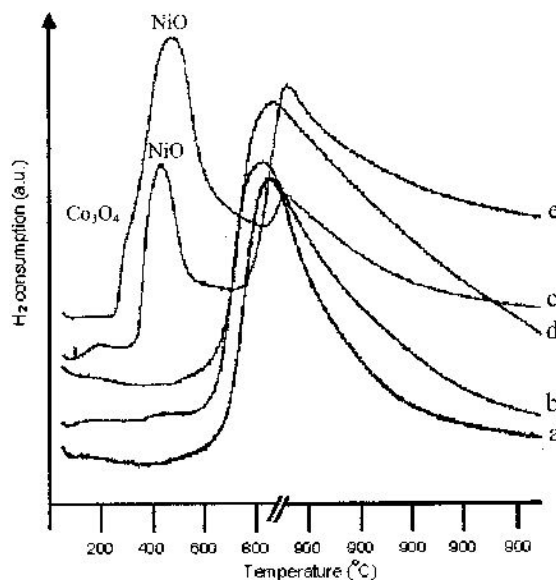


FIGURE 1: TPR Profile obtained over (a) 5 wt% CoO-NiO/Al<sub>2</sub>O<sub>3</sub> (b) 10 wt% CoO-NiO/Al<sub>2</sub>O<sub>3</sub> (c) 15 wt% CoO-NiO/Al<sub>2</sub>O<sub>3</sub> (d) 20 wt% CoO-NiO/Al<sub>2</sub>O<sub>3</sub> (e) 24 wt% CoO-NiO/Al<sub>2</sub>O<sub>3</sub>

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/Al<sub>2</sub>O<sub>3</sub> with various weights loading are shown in Figure 1. Several reduction peaks were observed in the TPR profiles. Since Ni<sup>2+</sup> and Co<sup>2+</sup> are reduced to Ni<sup>0</sup> and Co<sup>0</sup>, 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 Co<sub>3</sub>O<sub>4</sub> particles, 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/Al<sub>2</sub>O<sub>3</sub> catalysts occurred in the temperature range between 850-900°C. The 20 wt% CoO-NiO/Al<sub>2</sub>O<sub>3</sub> catalyst shown that existing free NiO and for 24 wt% CoO-NiO/Al<sub>2</sub>O<sub>3</sub> existed both NiO and Co<sub>3</sub>O<sub>4</sub>, that confirmed by XRD. The reduction peak for Co<sub>3</sub>O<sub>4</sub> occurred at 350°C and NiO at 480°C. The temperature region for both NiO and Co<sub>3</sub>O<sub>4</sub> is similar to that found by Coudhary 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 Co<sub>3</sub>O<sub>4</sub> and NiO with small interaction with support, respectively. While the reduction peak at high temperature region (~900°C) can be attribute 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-Al<sub>2</sub>O<sub>3</sub>.

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 Co<sub>3</sub>O<sub>4</sub> and NiO in the catalyst. In autothermal reforming process, the free NiO or Co<sub>3</sub>O<sub>4</sub> is one of the precursors to coking 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/Al<sub>2</sub>O<sub>3</sub> catalysts is better than Ni/Al<sub>2</sub>O<sub>3</sub> alone that has reduction peak at 450-540°C (Quincoces et al., 2002).

One of the major problems encountered in the autothermal reforming process 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.  $\delta$ - $\text{Al}_2\text{O}_3$  is a very suitable support for a high temperature reaction due to its large surface area and thermal stability, but the  $\text{Ni}/\text{Al}_2\text{O}_3$  and  $\text{Co}/\text{Al}_2\text{O}_3$  catalysts has 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  $\delta$ - $\text{Al}_2\text{O}_3$ , such as microcrystalline nickel oxide and cobalt oxide,  $\text{NiAl}_2\text{O}_4$  and  $\text{CoAl}_2\text{O}_4$  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 reason why the supported Ni-based catalysts is easily deactivated.

The spinel  $\text{NiAl}_2\text{O}_4$  and  $\text{CoAl}_2\text{O}_4$  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  $850^\circ\text{C}$  for  $\text{NiAl}_2\text{O}_4$  and above  $900^\circ\text{C}$  for  $\text{CoAl}_2\text{O}_4$ , it exhibits very high resistant to sintered at high temperature thus also resistant to coking. It has also been reported that the structure of  $\text{NiAl}_2\text{O}_4$  and  $\text{CoAl}_2\text{O}_4$  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 and/or octahedral sites in the support. Although no free Ni species were detected by XRD with lower Ni loading, confirmed that complete  $\text{NiAl}_2\text{O}_4$  and  $\text{CoAl}_2\text{O}_4$  spinels are formed with  $\text{Al}_2\text{O}_3$  support when the catalysts were calcined at higher temperature.

### 3.1.2 CoO-NiO/ZSM-5 Catalyst

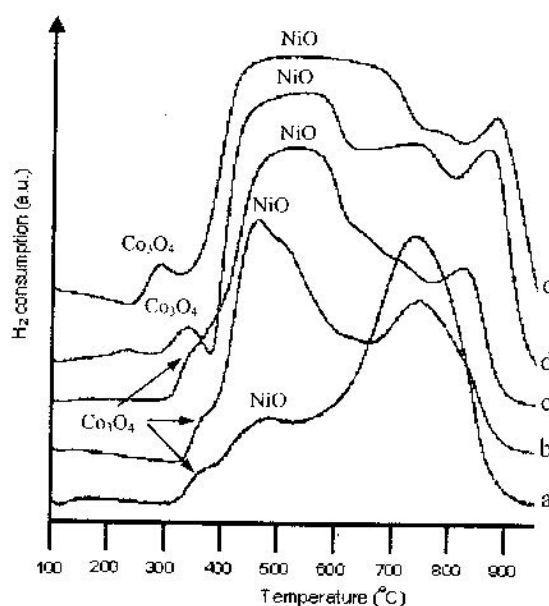


FIGURE 2: TPR Profile obtained over (a) 5 wt% CoO-NiO/ZSM-5 (b) 10 wt% CoO-NiO/ ZSM-5 (c) 15 wt% CoO-NiO/ZSM-5 (d) 20 wt% CoO-NiO/ZSM-5 (e) 24 wt% CoO-NiO/ZSM-5

Metal ions such as  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  are reduced with  $\text{H}_2$  to lower valence states with simultaneous production of protons. The  $\text{H}_2$ -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 Sachtler and co-workers and the peaks will be assigned accordingly. For all curves, peak of  $\text{Co}_3\text{O}_4$  can be found at around  $380^\circ\text{C}$ , is similar to that found by Pieterse et al. (2002) and NiO peak can be found at  $480$ – $570^\circ\text{C}$ . Peaks around  $750^\circ\text{C}$  and higher were assigned to  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  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  $\text{Co}^{2+}/\text{Ni}^{2+}$  cations. Nevertheless, at comparable loading (Figure 2) the pore volume impregnation method gives some  $\text{Co}_3\text{O}_4$  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 Co<sub>3</sub>O<sub>4</sub> 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-Al<sub>2</sub>O<sub>3</sub> Catalyst

TPR profiles of CoO-NiO/MgO-Al<sub>2</sub>O<sub>3</sub> 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 Co<sub>3</sub>O<sub>4</sub> particles, while the higher temperature peaks are attributed to the reduction of Co and Ni in the intimate contact with the MgO-Al<sub>2</sub>O<sub>3</sub> support. It seen that the reduction of CoO-NiO/MgO-Al<sub>2</sub>O<sub>3</sub> 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 Co<sub>3</sub>O<sub>4</sub> 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 catalysts in the high temperature methane reforming process (Xu et al., 2001).

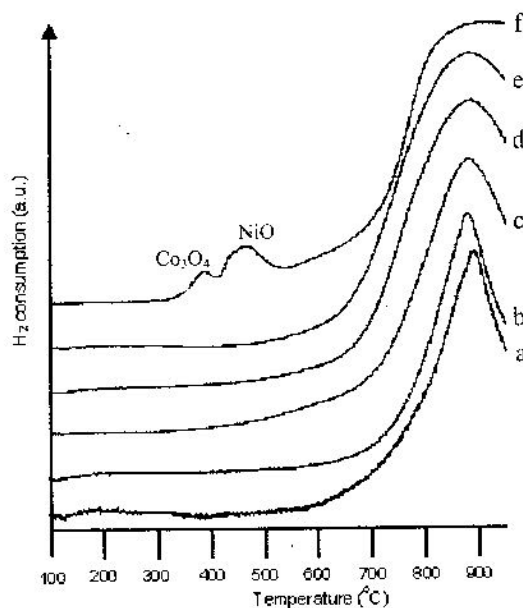


FIGURE 3: TPR Profile obtained over (a) 5 wt% CoO-NiO/MgO-Al<sub>2</sub>O<sub>3</sub> (b) 10 wt% CoO-NiO/MgO-Al<sub>2</sub>O<sub>3</sub> (c) 15 wt% CoO-NiO/MgO-Al<sub>2</sub>O<sub>3</sub> (d) 20 wt% CoO-NiO/MgO-Al<sub>2</sub>O<sub>3</sub> (e) 24 wt% CoO-NiO/MgO-Al<sub>2</sub>O<sub>3</sub>

### 3.2 XRD PATTERN FOR Co-Ni/MgO-Al<sub>2</sub>O<sub>3</sub> CATALYST

Figure 4 show the XRD patterns of catalysts Co-Ni/MgAl<sub>2</sub>O<sub>4</sub> at various metal loading. All the XRD patterns of 5–30 wt% of CoO-NiO revealed the presence of MgAl<sub>2</sub>O<sub>4</sub>, NiAl<sub>2</sub>O<sub>4</sub> and CoAl<sub>2</sub>O<sub>4</sub> (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 same 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 Al<sub>2</sub>O<sub>3</sub> to form NiAl<sub>2</sub>O<sub>4</sub> and CoAl<sub>2</sub>O<sub>4</sub>, respectively (Makoa et al., 1999). The presence of (Co,Mg)O solid solution at 2θ of 43.0°, 62.3°, 74.7° and 78.6° and MgNiO<sub>2</sub> 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 Ruckenstein, 2001). Free NiO and  $\text{Co}_3\text{O}_4$  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  $\text{Co}_3\text{O}_4$  exist in the catalyst.

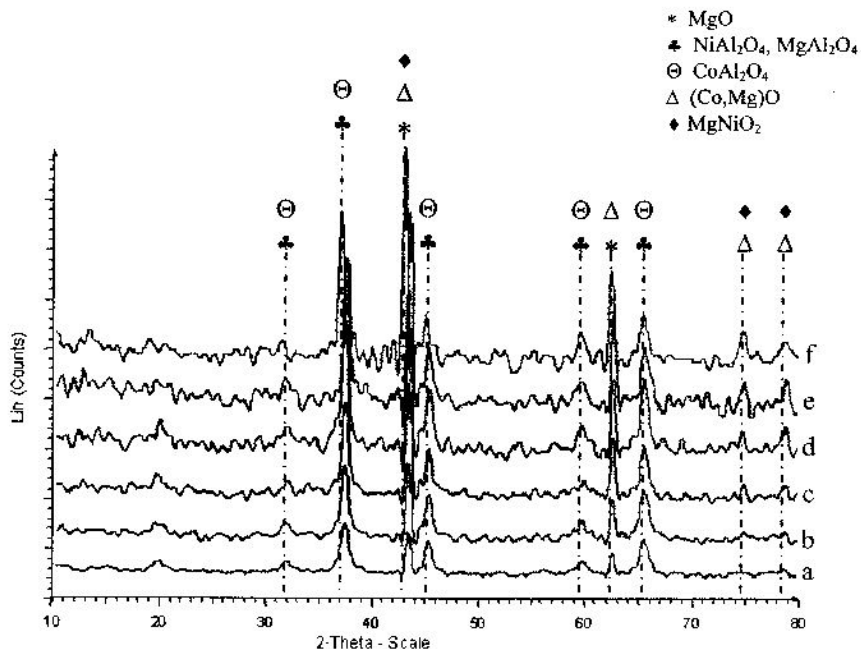


FIGURE 4: XRD patterns obtained over (a) 5 wt% Co-Ni/MgO-Al<sub>2</sub>O<sub>3</sub> (b) 10 wt% Co-Ni/MgO-Al<sub>2</sub>O<sub>3</sub> (c) 15 wt% Co-Ni/MgO-Al<sub>2</sub>O<sub>3</sub> (d) 20 wt% Co-Ni/MgO-Al<sub>2</sub>O<sub>3</sub> (e) 24 wt% Co-Ni/MgO-Al<sub>2</sub>O<sub>3</sub> (f) 30 wt% Co-Ni/MgO-Al<sub>2</sub>O<sub>3</sub>

#### 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  $\text{Co}_2\text{O}_3$ , often formed as the major phase over CoO-NiO/ $\text{Al}_2\text{O}_3$ , CoO-NiO/ZSM-5 and CoO-NiO/MgO- $\text{Al}_2\text{O}_3$  at lower calcination temperature or higher metal loading and considered to be responsible for catalyst deactivation.

$\delta$ - $\text{Al}_2\text{O}_3$  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  $\text{NiAl}_2\text{O}_4$  and  $\text{CoAl}_2\text{O}_4$ , 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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