
The Characterization of NiO-CoO/MgO Catalyst for Autothermal Reforming of Methane

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Submitted 9 Mei 2005, reviewed 20 Mei 2005, and accepted 12 Juli 2005

Abstract

The drawback of conventional reforming of methane such as partial oxidation and steam reforming was carbon formation. The research was developed a suitable catalyst for combination of partial and steam reforming of methane and called autothermal reforming to reduce the coke formation. The NiO-CoO/MgO catalysts were prepared by an impregnation method and characterized by Temperature Programmed Reduction (TPR), X-ray Diffraction (XRD) and Thermal Gravimetry Analysis (TGA). The TPR and XRD results reveal that the catalyst characteristic is strongly influenced by the Co/Ni ratio. From TPR and TGA analysis, the sintering phenomena did not occur in the autothermal reforming of methane. The results reveal that Co/Ni ratios have a small effect in the catalytic activity for autothermal reforming. Nevertheless, the catalyst showed an optimum performance in this process when its Co/Ni ratio was 0.75.

Keywords: Autothermal Reforming

Abstrak

Masalah yang terjadi pada proses konvensional reformasi metana seperti oksidasi parsial metana dan reformasi kukus adalah pembentukan karbon. Penelitian yang dilakukan adalah mengembangkan katalis yang sesuai untuk gabungan proses oksidasi parsial dan reformasi kukus atau yang disebut reformasi metana secara autothermal. Katalis NiO-CoO/MgO yang digunakan dibuat dengan metode impregnasi dan dilakukan pengujian dengan TPR, XRD dan TGA untuk mengetahui sifat-sifat dari katalis tersebut. Hasil TPR dan XRD menunjukkan bahwa karakteristik dari katalis sangat dipengaruhi oleh perbandingan Co/Ni. Hasil pengamatan TPR dan TGA menunjukkan bahwa sintering tidak terjadi di dalam proses reformasi metana secara autothermal. Hasil eksperimen juga menunjukkan bahwa perbandingan Co/Ni hanya kecil pengaruhnya pada unjuk kerja katalis. Namun demikian katalis menunjukkan unjuk kerja yang optimum pada perbandingan Co/Ni = 0.75.

Kata Kunci: Reformasi Autothermal

1. Introduction

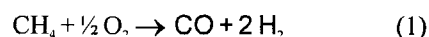
Energy availability is the first condition for high level development in human society. The most important challenge for all scientists is to find new energy sources. Since petroleum reservoirs seem to be insufficient for the next century, natural gas can be exploited in the next future as a primary energy source. Natural gas consists of a gas mixture containing mainly methane, and it is utilized for producing synthesis gas (a mixture of H_2 and CO). Hydrogen is considered as a clean energy source and a large amount of hydrogen will be used as the fuel for fuel cell in the future. In the production of hydrogen from methane, highly active and stable catalyst becomes more critical for an on site H_2 generation system (Dong et al., 2002 and Roh et al., 2002).

At present, steam reforming of methane (SRM) is the commercial process for the production of synthesis gas. However, a large amount of energy is required because SRM is a highly endothermic reaction and in this process excess steam is introduced to prevent carbon formation. As an alternative, catalytic partial oxidation of methane (POM) (equation.2.5) can be considered owing to the mild exothermicity, high conversion, high selectivity and very short residence time compared to the conventional highly endothermic steam reforming process (Drago et al., 1998; Ruckenstein and Hu, 1999 and Utaka et al., 2003). However, POM has also some disadvantages such as the occurrence of dangerous explosion and carbon formation. As another alternative, combination of steam reforming and partial oxidation of methane or autothermal reforming of methane can also be considered.

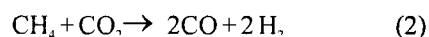
Many researches have been devoted to increase the stability of Ni catalysts, and it has been reported that the catalytic activity and thermal stability could be improved by using CoO or MgO (Choudhary et al., 1998a and Ruckenstein and Hu, 1999). The CoO modifiers contribute to avoiding sintering of catalyst metals, since MgO not only stabilizes the support but also stores and releases oxygen under oxidation and reduction conditions, respectively (Wang and Ruckenstein, 2001). It is well known that CoO-MgO solid solutions have better thermal stability. In the present paper, the autothermal reforming of methane was investigated experimentally using a NiO-CoO/MgO solid solution catalyst. We studied effects of the Co/Ni ratio, and time on stream on the autothermal reforming process.

2. Fundamental

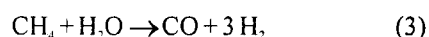
Reforming of methane to syngas can be carried out in four different ways, partial oxidation of methane, steam reforming, dry reforming and combination of partial and steam reforming or autothermal reforming. Of these, partial oxidation uses oxygen directly



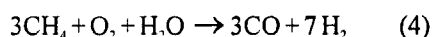
Dry reforming, using carbon dioxide in place of water



while steam reforming



is the conventional process and produces syngas with high H_2 /CO ratios. Autothermal reforming uses oxygen and steam



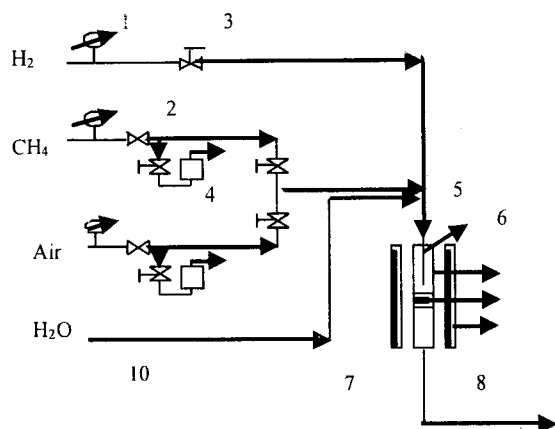
has been proposed as a promising technology. By co-feeding steam and oxygen, one can avoid the explosion danger in POM, lower additional steam cost in SRM, shorten the start-up time and control the H_2 /CO ratio by changing the feeding rate of steam or oxygen per methane (Choudhary et al., 1998a; Takeguchi et al., 2003; Dong et al., 2002; Ayabe et al., 2003 and Roh et al., 2003). Furthermore, methane conversion and hydrogen yield enhancement can be obtained by combining the two reforming reactions (Roh et al., 2003 and Choudhary et al., 1998b).

3. Methodology

The NiO-CoO/MgO catalyst was prepared by the incipient wetness impregnation of the MgO support 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), X-ray Diffraction and Thermal Gravimetry Analysis (TGA).

Catalytic performance tests were carried out using an apparatus consisting of a flow controller system; the reactor unit and the analysis system (see Figure 1). The catalyst was placed in a quartz wool bed system inside a continuous flow micro-reactor (12 mm diameter). In this paper, autothermal reforming of methane is defined as the combination process composed of partial oxidation and steam reforming. 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.



Note:

1. Pressure controller; 2. Safety valve; 3. Valve; 4. Flow meter; 5. Thermocouple; 6. Reactor; 7. Catalyst Bed; 8. Furnace; 9. GC, 10. Syringe pump

Figure 1. Schematic Diagram of The Experimental Set-up Apparatus for Autothermal Reforming of Methane

4. Results and Discussion

The TPR curves for the NiO-CoO-MgO catalysts with various Co/Ni ratios are presented in Figure 2. The TPR is quite similar to that observed for a typical NiO-MgO and CoO-MgO complete solid solution from the previous work by Ruckenstein and Hu (1999), Ulla et al. (2001) and Wang and Ruckenstein (2002). As expected for the solid solution, the degree of reduction was small. TPR patterns of the NiO-CoO/MgO catalysts with various Co/Ni ratios exhibited three distinct peaks. The maximum peak between 350-400 °C was attributed to the reduction of relatively free CoO species. The second peak (peak maximum = 480 °C) can be assigned to the free NiO species (Roh et al., 2003). The other peak, with a peak maximum above 800 °C was attributed to the NiO-CoO/MgO solid solution (Choudhary et al., 1997 and Wang and Ruckenstein, 2002).

The NiO-CoO/MgO solid solution reduction occurred at higher temperatures compared to free NiO and free CoO due to the incorporation of Ni²⁺ and Co²⁺ deep in the MgO matrix forming NiO-CoO-MgO solid solution. In addition, several literatures (Tang et al., 1998; Ruckenstein and Hu, 1999 and Wang and Ruckenstein, 2001) 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 Ni, Co and Mg shared oxygen in the solid solution.

Figure 2 shows the small TPR peaks between 300 - 500 °C for Co/Ni ratios = 0.3, 0.5, 1 and 1.2, indicating the presence of small amounts of either free NiO or CoO. These sites may result in sintering and carbon formation during autothermal reforming of methane. The presence of free NiO or CoO suggests that the formation of NiO-CoO-MgO solid solution was not complete for Co/Ni ratios below and above than 0.75. But at Co/Ni ratio = 0.75 only a single TPR peak (above 800 °C) was observed suggesting that the formation of NiO-CoO-MgO solid solution was complete. The formation of NiO-CoO/MgO solid solution made NiO or CoO more intimate with the support, preventing the formation of free NiO or CoO species suspected to be responsible for sintering and carbon formation during methane reforming. The sintering was very harmful for the supported metal catalysts because the aggregation of metal crystallites decreased the number of active site and also accelerated the carbon deposition since large metal ensembles stimulated the carbon deposition.

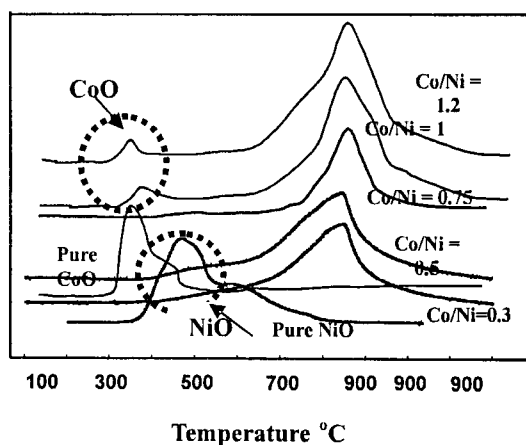


Figure 2. TPR Profiles of NiO-CoO-MgO Solid Solution Catalyst with Various Co/Ni Ratios

The XRD patterns of fresh NiO-CoO/MgO catalyst with Co/Ni ratios and pure MgO are shown in Figure 3. The XRD spectra indicated that all the synthesized NiO-CoO/MgO catalysts exhibited the same pattern of diffraction peaks with the parent MgO catalyst support. There are two possible reasons for this. One is that the

impregnation of nickel and cobalt into MgO has not significantly destructed the original structure of the MgO catalysts or the dispersion of nickel and cobalt oxide is too high to be detected using XRD. The other reason is that nickel oxide and cobalt oxide enter the lattice of the MgO to form a uniform solid solution. The XRD result is in agreement with the TPR analysis. The XRD diffractograms can be assigned to NiO, CoO and NiO-CoO/MgO solid solution. The NiO and CoO crystallites did not appear in the catalyst with Co/Ni ratio of 0.75 which implies that the NiO and CoO species were highly dispersed in the lattice of MgO to form ideal solid solution as similarly reported by Wang and Ruckenstein (2001) and Dong et al. (2002). The generations of NiO and CoO crystallites became competitive with Co/Ni ratio above or below 0.75. The fresh catalyst with Co/Ni = 0.3 and 0.5, NiO peaks were identified at $2\theta = 36.44$ and 44.3° (Roh et al., 2002). Meanwhile, in the fresh catalyst with Co/Ni = 1 and 1.2 the peaks shown are identified as CoO peaks at 30.9° and 58.8° (Wang and Ruckenstein, 2002).

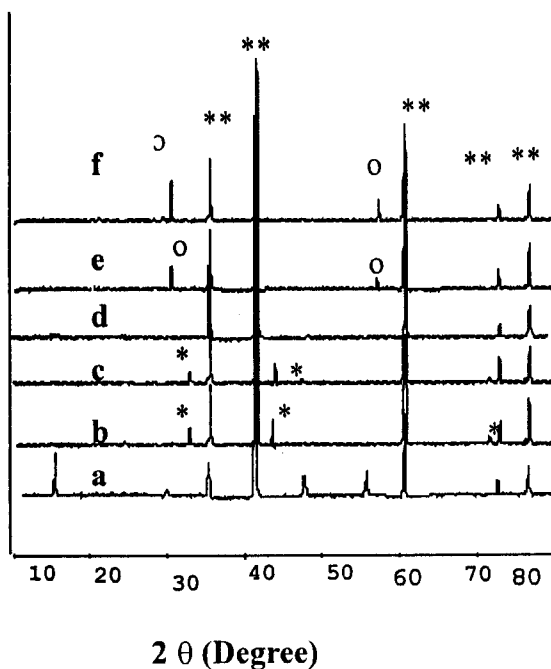


Figure 3. XRD Patterns of the NiO-CoO/MgO catalyst: (a) MgO, (b) Co/Ni = 0.3, (c) Co/Ni = 0.5, (d) Co/Ni = 0.75, (e) Co/Ni = 1, (f) Co/Ni = 1.2. (*) Represents The Diffraction Peaks of NiO, (o) Represents The Diffraction Peaks of CoO, (x) Represents The Diffraction Peak of Metallic Ni, (**) Represents The Diffraction Peak of The NiO-CoO Solid Solution

Figure 4 shows the results of the TGA experiments as a function of Co/Ni ratio after conducting autothermal reforming of methane. For the ATR reaction, the coking resistant performances of the NiO-CoO/MgO catalysts were more pronounced for all Co/Ni ratios. Autothermal reforming of methane is a combination of partial oxidation and steam reforming, therefore by co-feeding H_2O and O_2 , coke formation can be reduced.

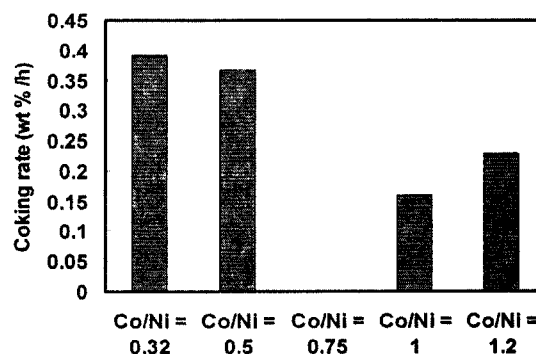


Figure 4. Coke Rate on The NiO-CoO/MgO Catalyst After Conducting Autothermal Reforming of Methane ($T = 850^\circ C$, $CH_4/O_2 = 2.7$, $CH_4/H_2O = 2.7$)

The effects of the Co/Ni ratio of the catalyst are shown in Figure 5. The results (Figure 3) reveal that the Co/Ni ratio has a small effect on the conversion and selectivity. Nevertheless, the catalyst showed an optimum performance in this process when its Co/Ni ratio was 0.75. From TPR and XRD analysis, a complete solid solution of NiO and CoO in MgO was identified in the Co/Ni ratio = 0.75, which is responsible for its superior activity (highest conversion and selectivity). From the TPR and TGA analysis, the sintering phenomena did not occur in the autothermal reforming process. In the autothermal reforming process over the catalyst, the endothermic (steam reforming) and exothermic (partial oxidation) reactions were at least partly coupled by their simultaneous occurrence over the same catalyst. Although the partial oxidation of methane to CO and H_2 was mildly exothermic, a large amount of heat was expected to be produced in a small catalyst volume because of the high conversion at a very low contact time. However, because of the presence of the steam along with O_2 , the heat that was produced in the exothermic reaction was absorbed in the highly endothermic steam reforming reaction, thus setting a buffer like action that can stabilize the catalyst bed temperature.

This is a great practical importance to avoid the hot spot in the reactor. Therefore, this phenomenon can reduce the sintering process and coke formation. Similar observations were also claimed by Choudhary et al. (1998a), Ayabe et al. (2003), Dong et al. (2002) and Supat et al. (2003). In addition, Roh et al. (2003) also has stated that the autothermal reforming, combination of exothermic (POM) and endothermic (SRM) reactions can hinder the carbon formation in the process.

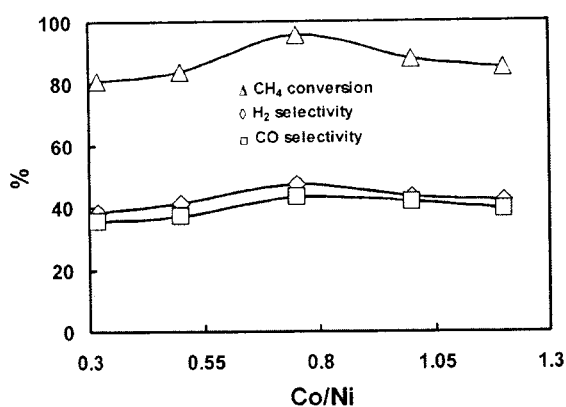


Figure 5. Effect of Co/Ni Ratio of The Catalyst on The CH₄ Conversion, H₂ Selectivity and CO Selectivity in The Autothermal Reforming (GHSV $5.4 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$, $T = 880^\circ \text{C}$, $\text{CH}_4/\text{O}_2 = 2.2$, $\text{CH}_4/\text{H}_2\text{O} = 2.6$)

In order to compare the stability of NiO-CoO/MgO catalyst with commercial catalyst, autothermal reforming of methane was conducted at 880°C and $5.4 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$ GHSV with CH_4/O_2 ratio = 2.2 and $\text{CH}_4/\text{H}_2\text{O}$ ratio = 2.6. Methane conversion, CO and H₂ selectivity with time on stream over both catalysts in autothermal reforming of methane is illustrated in Figure 6. The conversion and selectivity for NiO-CoO/MgO were stable with time on stream. After 12 hours, the methane conversion abruptly dropped to 60 % for the commercial catalyst. It is clear that the commercial catalyst remarkably deactivated with time on stream (Figure 4 (a)) which is most likely due to the carbon formation while NiO-CoO/MgO catalyst maintained its stability. This result indicates that the commercial catalyst was rather more susceptible to carbon formation compared with NiO-CoO/MgO catalyst. Yamazaki et al. (1996) and Roh et al. (2003) reported a similar result that commercial reforming catalyst deactivated due to carbon formation under the condition of low steam/carbon ratio ($\text{H}_2\text{O}/\text{CH}_4 = 1$).

Therefore, it was confirmed that the NiO-CoO/MgO catalyst was more stable than commercial catalyst. The high stability can be explained as follows. As indicated by XRD and TPR, only solid solution NiO-CoO/MgO species were present in the catalyst with $\text{Co/Ni} = 0.75$. Due to inherent difficulty of reducing a solid solution, the size of the metal clusters generated via the reduction of the solid solution was expectedly small. Being small, these clusters did not stimulate coke formation.

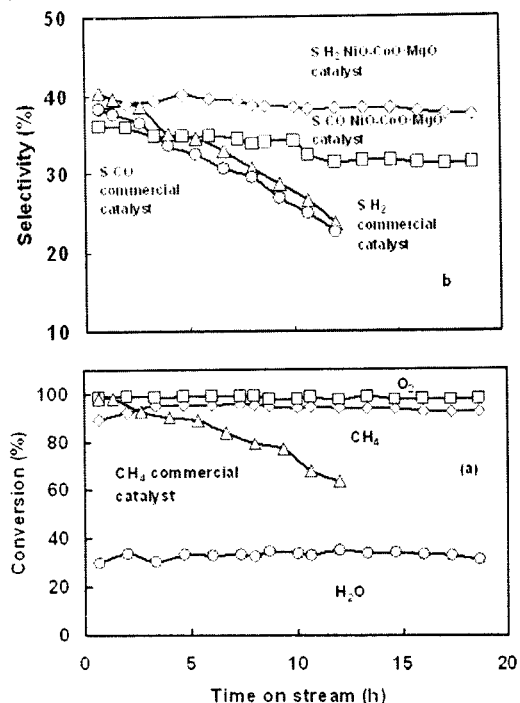


Figure 6. The Effects of Time on Stream on The Conversion (a), Selectivity (b) in The Autothermal Reforming of Methane at 880°C for NiO-CoO/MgO and Commercial Catalyst (Reaction Condition: $\text{CH}_4/\text{O}_2 = 2.2$, $\text{CH}_4/\text{H}_2\text{O} = 2.6$; GHSV = $5.4 \times 10^4 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$)

5. Conclusion

Autothermal reforming of methane has been regarded as an important process for the first step in the catalytic process for production of hydrogen. The NiO-CoO/MgO catalysts demonstrated high activity for this reaction. The formations of complete solid solution of NiO-CoO-MgO catalysts are strongly influenced by the different Co/Ni ratio used. The Co/Ni ratios have a small effect on the conversion and selectivity in the autothermal reforming process. Among the catalyst, NiO-CoO-MgO solid solution catalyst with Co/Ni ratio = 0.75 showed best performance in the autothermal reforming of methane.

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