

CHARACTERIZATION OF CoNi-Sn CATALYST FOR AUTOTHERMAL REFORMING OF METHANE

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ABSTRACT

Autothermal reforming (ATR) is a combination of steam reforming and partial oxidation process. It is one of the methods in producing hydrogen from natural gas. CoNiSn with different catalyst supports e.g MgO and Al₂O₃ has been chosen to be used on this autothermal reforming of methane (ATR). The objective of this paper is to study the bulk structure of the catalyst using Temperature Programmed Reduction (TPR) and X-ray Diffraction (XRD). From the TPR and XRD, the addition of tin into MgO-supported catalyst will become the anti coking agent, as it will react with carbide, since it is deposited at the outer layer of the matrix CoO-NiO-MgO solid solution phase.

Keywords: Tin, Nickel-Tin Catalyst, Autothermal Reforming Of Methane.

1 INTRODUCTION

Extensive research is being conducted worldwide to develop hydrogen fuel cells for environmentally benign generation of energy, since these devices operate at high efficiencies and water is the only by-product formed during the operation. It could be a challenge to develop a hydrogen production system, with high conversion and of course at a low price. Hydrogen is usually produced from solid, liquid and fuels such as coal, methanol and hydrocarbons. The well-known process which can produce the maximum quantity of hydrogen is steam reforming. The other route is partial oxidation, CO₂ reforming and mixed (CO₂ + O₂) reforming (Nichio et al, 2000). The other method to produce hydrogen from natural gas is autothermal reforming process (ATR). This process is a combination of partial oxidation (1) and steam reforming (2). The advantage of ATR is less steam is required since the heat from partial oxidation process is used to activate the steam reforming process.



Nickel based catalyst has been reported to be the most suitable catalyst for steam reforming (Ming et al., 2002) and for partial oxidation (Choudhary and Mamman, 2000). This family of catalyst have been investigated for several years and now are of large use in the industry because they offer an appreciable catalyst activity, a good stability and of course low price (Freni et al., 2000). Many researchers reported that cobalt based catalyst give good activity and selectivity for catalytic conversion of methane to produce hydrogen (Choudhary et al., 1998, Wang and Ruckenstein, 2001). According to Liu et al. (2002), the problem with the supported nickel catalysts is easily deactivation due to coking, a consequence of nickel sintering and carbon deposition. In order to inhibit the problem,

Nickel catalyst required the addition of small amount of certain compounds and tin or stanum is one of the chemical compounds that have been introduced as the additional compound to nickel catalyst. Tin is recognized, as a stability promoter against coke formation in many processes, like paraffin dehydrogenation, naphtha aromatization and dehydrogenation of propane (Nichio *et al.*, 2000).

Bimetallic Pt-Sn supported on alumina, widely used as catalysts in platforming and dehydrogenation processes, have been studied by Barias *et al.* (2001), and found that the addition of Sn into the catalyst system, showed the significant effect by increasing the selectivity and the stability of the catalyst. Nichio *et al.*, 2000, Huber *et al.*, 2003, Shabaker *et al.*, 2004 and Onda *et al.*, 2003, worked with Ni-Sn catalyst and they also found that the combination of catalyst enhances the catalyst stability by the strong interaction between the support, Ni and Sn itself. Thus this paper will investigate the effect of addition of tin into CoNiSn catalyst with different supports in terms of the bulk structure and their reduction temperature.

2 METHODOLOGY

2.1 CATALYST PREPARATION

All samples were prepared by impregnation process. A MgO ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) support material from Merck and Al_2O_3 also from Merck were dissolved in distilled water, stirred and dried in a process which took place at 110°C for 12 h. The support then calcined in air for 800°C for 8 h. The unpromoted catalyst, CoNi/MgO and CoNi/ Al_2O_3 were prepared by impregnating the support with Ni ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and Co ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), both from Merck, using a distilled water as a solvent, dried 110°C for 12 h, followed by calcinations process at 800°C for 8h. The Sn promoted catalyst were prepared by impregnating the support (MgO and Al_2O_3) with Sn, using $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and distilled water as a solvent, dried for 12 h at 110°C and calcined at 550°C for 4.5 h. Then the catalyst containing Sn were impregnated with active metal, Co and Ni, using the same procedure as the unpromoted catalyst. The catalyst labeled with A is referred as MgO-supported catalyst and B is referring to Al_2O_3 -supported catalyst. A1 and B1 are referred as unpromoted Sn catalyst while A2, A3, A4 and B2, B3 and B4 are referring to the increasing Sn content from 2.5 wt%, 6wt% and 12wt%, respectively.

2.2 CATALYST CHARACTERIZATION

The reduction behavior of the catalyst was examined by temperature-programmed reduction (TPR) using Thermo Finnigan 1100 system. Samples approximately 0.025 g were previously heated under nitrogen flow (20 ml/min) and then analyzed with a reducing gas (5% H_2/N_2 , 35 ml/min), in the temperature range $25\text{--}900^\circ\text{C}$, with the heating rate at 20 ml/min. The bulk structure of the catalyst was identified by powder X-ray diffraction technique on a Bruker XRD D8 Advance from 10° to 80° with step size 0.05° . The X-ray source is Cu K α at 40kV and 40mA.

3 RESULTS AND DISCUSSION

3.1 TPR PROFILE FOR CoNiSn/MgO

The study of temperature-programmed reduction was carried out in order to determine the reducibility of Co, Ni and Sn species on the CoNiSn-supported catalyst. Figure 1 shows the TPR profile of CoNiSn supported with MgO catalyst. TPR test for Sn/MgO has been done for comparison. The Sn/MgO catalyst shows a reduction profile with a maximum peak at about 870°C . For unpromoted (CoNi/MgO) catalyst, the reduction peak appeared at 900°C . The profile is similar to the one obtained by Choudhary and Manman, 2000 which formed the solid solution phase. It is shown that catalyst A2 and A3 give the lower reduction temperature (800°C , 860°C respectively), compared to A1 (900°C). The difference of the reduction temperature profile may be assigned to a modification in the interaction between nickel oxide and the support as consequence of a close relation between the corresponding nickel and tin oxides (Nichio *et al.*, 2000) and probably because of the existence of another tin compounds. The TPR profile for A2, A3 and A4

show a large reduction peak, which extends over a wide temperature range (from 550 °C to 900 °C) and with a maximum centered at 800 °C is corresponding to tin reduction, as agreed by Armendariz et al., 2001. The peak is more intense for the higher tin content (CatA4).

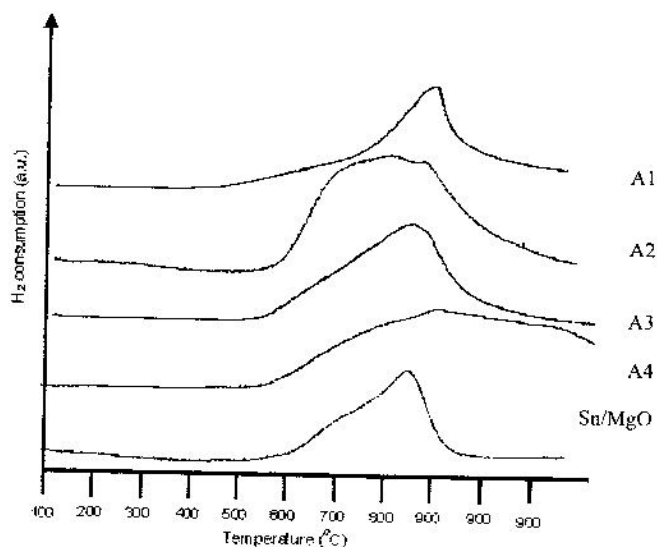


Figure 1. TPR profile for CoNiSn/MgO

The observation from the TPR profile for the catalyst showed no peak for NiO and CoO, both at 480 °C and 350 °C. As admitted by Jones and McNicol, 1986, the peak for tin oxide appeared at around 650 °C. Thus, the free tin does not exist for this type of catalyst. Onda et al., 2000 were using NiSn intermetallic compounds (IMC) in acetylene dehydrogenation. They found that the peak obtained from NiSn IMC is different from the free Ni and tin, which would indicate that the clusters of free nickel and tin do not exist on the surface of the catalyst. From this TPR profile, the addition of tin into the catalyst would give the different profile of reduction temperature while compared to the unpromoted catalyst. Bigger amount of tin will increase the reduction temperature. This is probably corresponding to the interaction between tin, Ni, Co and support itself.

3.2 TPR PROFILE FOR CoNiSn/Al₂O₃

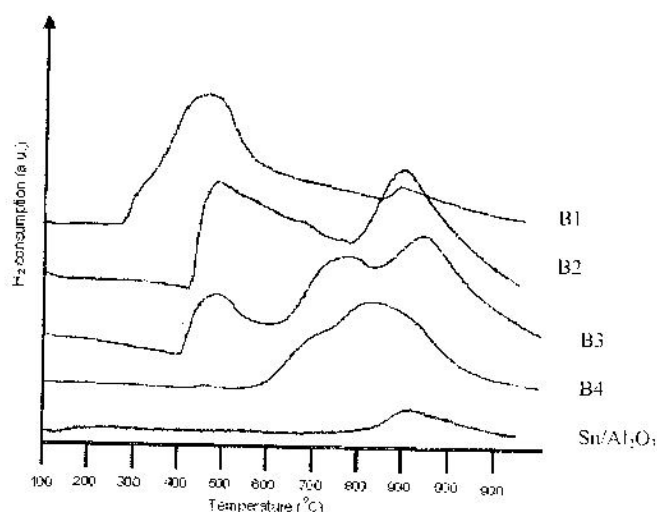


Figure 2. TPR profile for CoNiSn/Al₂O₃

Figure 2 shows the TPR profile for CoNi/Al₂O₃ with and without the addition of tin. TPR profile for tin alumina is also included as comparison. The reduction peak for tin alumina

appeared at 900 °C. For catalyst B1, there were two reduction peaks detected at 460 °C and 900 °C. It is seen that for catalyst B2 and B3, the reduction profile showed approximately the same pattern. Peaks for B2 and B3 appeared at 480 °C, 720 °C and 900 °C and 480 °C, 700 °C and 900 °C respectively. For catB4, one small peak appeared at 750 °C and the other peak is detected at 820 °C. From the above temperature profile, the reduction peak appearing at around 400 °C for the catalyst is corresponding to the presence of small amount of free NiO, as determined by Choudhary et al., 1997. It is found that there is no detection of free CoO for all catalyst. This finding corresponds to the absence of CoO reduction peak at 380 °C. The reduction peak around 400 – 500 °C is also probably due to the formation of Ni_xSn_y compounds. This statement has been given by Onda et al (2000), whom working with NiSn catalyst found out that tin oxides in air-oxidized Ni₃Sn would be reduced at almost the same temperature as NiO.

The observed peak detected at around 700 °C to 720 °C for Cat B2 and B3 is corresponding to the existence of free SnO₂. The peak for SnO₂ would appear at around 650 °C (Jones and McNicol, 1986). This is in agreement with the statement by Armendariz et al (2001), that the position of reduction peaks can be expected to shift to a higher temperature as the amount of Sn increased. For these catalysts, the amount of tin is being increased from 2.5 wt% to 12 wt%, and as the result, the reduction peak for SnO₂ is also increased.

3.3 XRD DIFFRACTOGRAM FOR CoNiSn/MgO

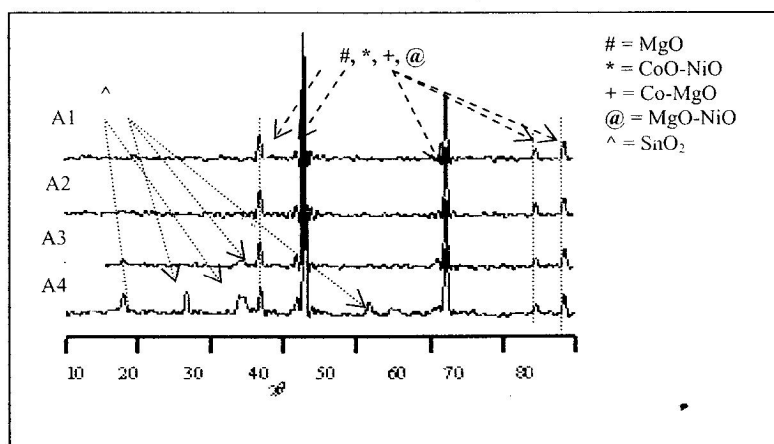


Figure 3. XRD diffractogram of CoNiSn/MgO

Figure 3 represents an XRD diffractogram of CoNiSn/MgO catalyst. From the XRD pattern, A1, A2 and A3 show almost the similar diffractogram. Some overlapping peak is detected at 37°, 44°, 52°, 74° and 78°. Those peaks correspond to the formation of CoOx compounds, NiOx compounds and compounds of Mg-NiO and CoO. The similar properties of those types of compounds and the formation of solid solution might be the reason for this behavior. For A4, SnO₂ peaks clearly appeared at 26°, 34° and 52°, which means that free SnO₂ exists in A4. It has been agreed by Onda et al., 2003, that the peak around 30° and 43° becomes clear with the increasing number of Sn content. However, the free SnO₂ cannot be detected via TPR. Perhaps the reduction for SnO₂ is occurred almost at the same temperature as any other compounds in the catalyst system, and this shows a very broad reduction peak starting from 600 to 900 °C in TPR in figure 1.

From this XRD also, it is clearly shown that SnO₂ is not deposited in the matrix of CoO-NiO-MgO, but perhaps at the outer layer of it. So the addition of tin might not modify the solid solution of CoNi/MgO. The importance of this behavior is SnO₂ may react with carbide and leave the active site of Co and Ni and prevent them from contacting with carbide. This is the reason why tin is known as anti-coking agent.

For A2, there is no detection of any Sn compound. The failure is probably due to untraced amount of Sn content in the catalyst system, or the Sn is washed away during the preparation of catalyst. The other possibility is the formation of any other Sn compound with Ni, Co and support itself that cannot be detected by XRD.

3.4 XRD DIFFRACTOGRAM FOR CoNiSn/Al₂O₃

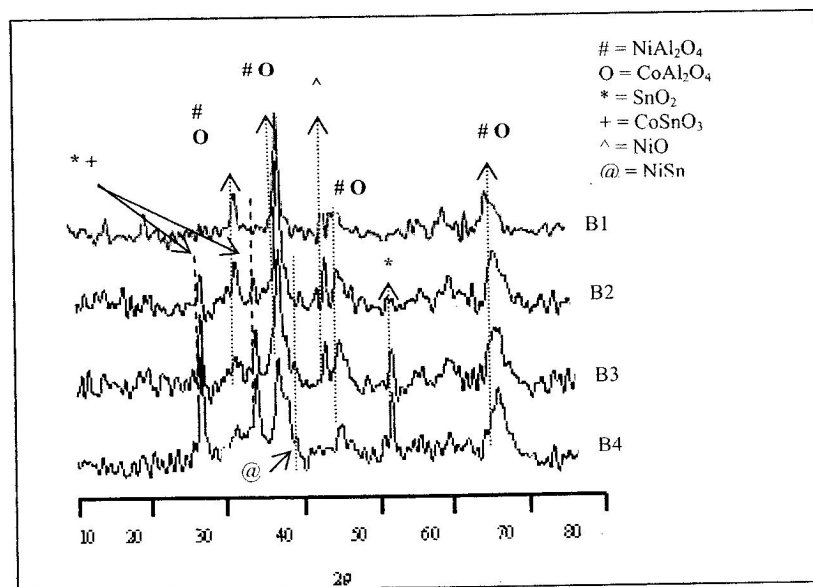


Figure 4. XRD diffractogram of CoNiSn/Alumina

Figure 4 represents the XRD diffractogram for CoNiSn catalyst supported with alumina. The diffractogram showed that all the catalyst was formed in NiAl₂O₄ spinel at 37°, 45° and 56° and approximately similar to the one obtained by Hardiman (Hardiman et al., 2004). For catalyst B4, B3 and B2, there were a formation of free SnO₂, CoSnO₃ and Ni₃Sn. Free tin oxide was formed at 27°, 34° and 52°. Peak for CoSnO₃ appeared at approximately at the same 2θ of tin oxide. Peak appeared at around 38° is suggested to assigned as NiSn compound. As found by Huber et al., (2003), the importance of the formation of NiSn is it will give the beneficial effect on the selectivity for production of hydrogen.

The formation of free tin oxide for those catalysts is perhaps due to the excess deposition of tin (Oliveira et al., 2001). Free NiO is also detected from this diffractogram for B1, B2 and B3 at 43° as been revealed by the TPR.

4 CONCLUSIONS

The addition of tin into CoNi/MgO catalyst might not modify their solid solution phase. Free tin oxides deposited at the outer layer of Co-Ni-MgO matrix will act as anti coking agent by the reaction with carbide and reduce the sintering problem. The bulk structure of CoNiSn/Alumina consists of NiAl₂O₄, CoAl₂O₄, SnO₂, NiO, CoSnO₃ and Ni₃Sn as obtained by XRD. Perhaps by the formation of Co-Sn and Ni-Sn compounds, this will decrease the coking problem in the nickel-based catalyst for ATR of methane.

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