

AUTOTHERMAL REFORMING OF METHANE TO HYDROGEN IN A PALLADIUM MEMBRANE REACTOR : CHARACTERIZATION OF BIMETALLIC Pt-NiO/ δ -Al₂O₃ CATALYST

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ABSTRACT

A bimetallic Pt_{0.2}-Ni₂₅/ δ -Al₂O₃ (wt/wt %) was prepared by incipient wetness technique. The catalyst was characterized by X-ray diffraction (XRD) and Temperature-programmed reduction (TPR) analysis. The catalyst characterization results showed that doping of Pt catalyses the complete reduction of Ni²⁺ to Ni⁰ and a bimetallic surface interaction was formed. The NiAl₂O₃ spinel phases were observed and reduced at lower temperatures.

Keywords: Bimetallic, Pt, Ni, Al₂O₃, Spinel.

1 INTRODUCTION

As autothermal reforming (ATR) is a combination of exothermic partial oxidation and endothermic steam reforming, the common active catalysts used are the same as those for these two processes, namely the VIII-B group metals, especially Ni, Pt, Pd, Rh, Ru and Ir. Nakagawa and co-workers (1999) reported that reduced Ni/Al₂O₃ is an active catalyst and is commonly used in synthesis gas production, where Ni has been regarded as the active component. Meanwhile, δ -Al₂O₃ support has a relatively high surface area and thermal stability at high temperature. In addition, Choudhary and co-workers (1995) reported that oxidized Ni/Al₂O₃ catalyst can be activated at temperatures lower than 750°C by adding small amount of noble metals to the NiO/Al₂O₃ catalyst because of synergistic effect of Pt and Ni bimetallic catalyst. Moreover, Choi and co-workers (1998) and Wang and Ruckenstein (2001) demonstrated that the addition of metal additives into nickel-based catalysts could be a relatively effective method to increase their resistance to coking or lower carbon deposition, due to much smaller amount of carbon can be dissolved in Pt particles, and on Pt, hydrogen was spilled over to support oxide and thus reacted with coke to form hydrocarbon (Takeguchi et al., 2003).

Ma and Trimm (1996) demonstrated that the activity of nickel catalyst could be increased with the addition of noble metal (e.g. 0.2wt%Pt). Nickel-platinum bimetallic catalysts showed higher activity, selectivity and stability during ATR than separate nickel and platinum catalyst blended in the same bed. It was hypothesized that nickel catalyzes SR, while platinum catalyzes POX and, when they are added to the same support, the heat transfer between the two sites is enhanced on a microscale, thus allowing advanced heat management and thermally efficient hydrogen production. Dias and Assaf (2004) found that Pt strongly promoted conversion of methane with concentrations of H₂ and CO in the product stream are much higher than in the unpromoted catalyst. Furthermore, the effect of Pt addition to Ni-catalyst favours the reduction of this metal, meaning that, an increase in reduction would cause an expansion of the metal surface area of the catalyst. With the increase in the surface area of the active phase, an increased in catalyzed conversion of

methane is expected. This increase of metal surface area is probably due to the fact that the noble metal is reduced at lower temperature than nickel and, once in the reduced phase, Pt metal adsorbs hydrogen dissociatively and, through hydrogen spillover, catalyzes nickel reduction. In this study, δ -alumina supported Pt-Ni catalyst (or bifunctional catalyst) was chosen for the autothermal reforming of methane to hydrogen in a palladium membrane reactor.

Lastly, the rationale in using nickel- and alumina based catalyst is discussed. The use of Ni-based catalysts is common in chemical industries - due to their low cost and active catalyst as those Pt, Pd, Rh, Ru and Ir. However, the main disadvantage of Ni catalyst is their rapid deactivation due to carbon formation and carbon deposition, but this problem was solved by using excess steam and temperature in the range $\sim 600^\circ\text{C}$ in which under these conditions the carbon formation is not favored thermodynamically. In addition, high dispersion of Ni metal over the catalyst or the use of some additives can overcome this problem. As a result, nickel catalyst has emerged as the most practical catalyst to be used. The advantage of this essentially "free" of coke operation was helped by the long-term stability and its fast turnover rates. In general, the performance and the deactivation of nickel catalyst can be influenced by catalyst compositions (e.g. Ni particle size, %Ni loading) and calcination temperature, T_c (e.g. high catalytic at high T_c). The acidity of support also has a strong effect on the reducibility of NiO to Ni. Lower acidity supports are preferred because they promote easy and high degree of reduction, in turn, this maximises methane reforming activity (Al-Ubaid and Wolf, 1987). A very important note: It has been known that nickel aluminates (or spinels) could be formed during calcination step of alumina supported-Ni catalyst. So, in nickel-based catalyst synthesis, it is aimed to secure the formation of 'free-nickel' (NiO). Under low Ni loading, nickel can be in the form of surface spinel (NiO- Al_2O_3 sites) which affects the catalyst reduction temperature. These nickel aluminates (or spinels), once reduced, form 'fixed-nickel' (NiAl_2O_4) which is non-catalytically active. The ability to reduce and liberate this 'fixed-nickel' from these spinel structures is very critical (Rynkowski et al., 1993). Interestingly, Chen and Ren (1994) reported that this NiAl_2O_4 spinel formed could markedly reduce the carbon deposition because the reduction of nickel aluminate would result in the formation of small nickel particles (NiO_x) which are very resistant to sintering and carbon formation (Bhattacharyya and Chang, 1994). Al-Ubaid and Wolf (1987) also demonstrated that at high nickel loading ($\sim 30\text{wt}\%$), a saturated support surface was observed and spinels were easier to be reduced, thus resulting a very high catalytic activity which was assigned to the predominant free-reduced nickel. An effective nickel loading in $\delta\text{-Al}_2\text{O}_3$ is closely related to the ease of spinel reduction. Highly dispersed Ni metal on high surface area of $\delta\text{-Al}_2\text{O}_3$ with strong interaction, could be related to the expansion of active metal surface area with high catalyst stability. The formation of bimetallic or solid-solution catalyst by adding additives e.g. Pt, can also increase the active metal surface area and catalyst activity which was attributed to Pt metal segregation and exposure on the catalyst surface (Dias and Assaf, 2004), while bifunctional catalyst could minimise the heat transfer limitation (Ma and Trimm, 1996).

2 EXPERIMENTAL

2.1 PREPARATION OF BIMETALLIC CATALYST

The Pt-NiO/ Al_2O_3 catalyst was prepared by incipient wetness technique using aqueous solutions of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$. Two types of alumina are usually used as supports: α and γ alumina. The α -alumina has a low surface area and as a result provide a less active catalyst. However, $\delta\text{-Al}_2\text{O}_3$ which has a fairly high surface area and is more stable under high temperature was therefore employed for this study. The $\delta\text{-Al}_2\text{O}_3$ support material was prepared by thermally treating $\gamma\text{-Al}_2\text{O}_3$ at 1000°C in a furnace for 5 h. The support was then impregnated with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to form a slurry. In order to ensure complete penetration of the solution into the pores of the support, the slurry was stirred with gentle heating at 30°C for 3 h. The catalyst was then dried overnight in an oven at 120°C . The same procedure was repeated using the $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution. The resulting Pt- and Ni- based catalyst were calcined in a muffle furnace at 850°C in a stream of air for 3 h and then grounded and screened between 100 and 200 meshes.

2.2 CHARACTERIZATION OF CATALYST

XRD profiles were recorded on a Bruker XRD-D8 Advance diffractometer by using Cu K_{α} radiation. Patterns were recorded between 10° to 80° (2θ scale). TPR was performed in ThermoFinnigan TPDRO 1100 instrument in a quartz tube reactor, and the amount of H_2 consumed was measured with a TCD detector. A weigh amount (45 mg) of the sample was placed in the reactor. The sample was first pretreated in a flow of 20 ml/min N_2 from $100^{\circ}C$ to $550^{\circ}C$ at a heating rate of $10^{\circ}C/min$. The pretreatment was hold for 60 min after the maximum pretreated-temperature was reached. The reduction step was carried out using 5% H_2 -95% N_2 gas mixture with a flow of 30 ml/min and heating rate of $10^{\circ}C/min$. The analysis was run from $200^{\circ}C$ to $1000^{\circ}C$ and the holding time was set to 1 hr.

3 RESULTS AND DISCUSSION

3.1 TPR ANALYSIS

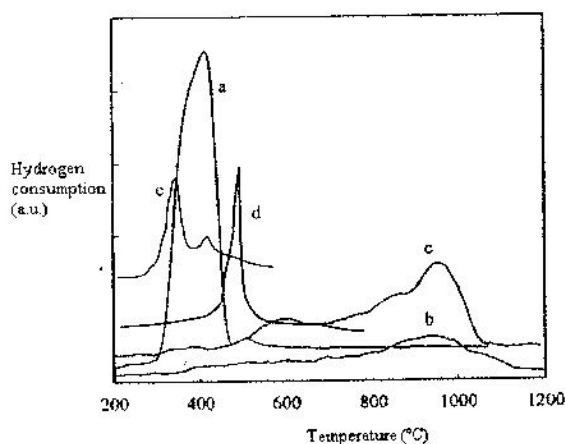


FIGURE 1. TPR profiles for (a) NiO, (b) NiO/ Al_2O_3 , (c) Pt-NiO/ δ - Al_2O_3 and unsupported (d) Pt-NiO and (e) Pt, flowrate of 5% H_2 = 30 ml/min, heating rate = $10^{\circ}C/min$.

Figure 1 showed different reduction patterns of NiO, NiO/ Al_2O_3 and Pt-NiO/ δ - Al_2O_3 as compared to unsupported Pt-NiO and Pt reductions. The reduction peaks of NiO/ Al_2O_3 and Pt-NiO/ δ - Al_2O_3 (appeared around $950^{\circ}C$) demonstrated that, NiO with Al_2O_3 could be transformed into $NiAl_2O_4$ spinel structures and NiO crystallites (Scheffer et al., 1989; Ran et al., 2003), and also a probable formation of bimetallic PtNi species after reduction (Jablonski et al., 1999), which favor the reduction at high temperature (above $600^{\circ}C$). Only NiO could be reduced around $450^{\circ}C$, while Pt-NiO/ γ - Al_2O_3 and NiO/ Al_2O_3 were reduced around $950^{\circ}C$, meaning that, the NiO species on the alumina support was transformed into different nickel species since there could be different nickel species formed in an alumina supported catalysts depend on the temperature range in which the species were reduced. No diffraction peak of NiO species in Pt-NiO/ γ - Al_2O_3 catalyst, suggesting that Ni is well dispersed on the catalyst surface. The spinels formed can be reduced at lower temperature ($850^{\circ}C$) since the nickel aluminate (spinel) is reducible up to $1000^{\circ}C$. This suggests that Pt is beneficial to lower (i) catalyst reduction temperature due to synergistic effect of Pt and Ni bimetallic catalyst (Choudhary and co-workers 1995) and (ii) the activation energy of bimetallic Pt-NiO (80.8 kJmol^{-1}) as compared with monometallic Pt (86.45 kJmol^{-1}) and NiO ($103.73 \text{ kJmol}^{-1}$) (Gyamfi and Adesina, 1999).

3.2 XRD ANALYSIS

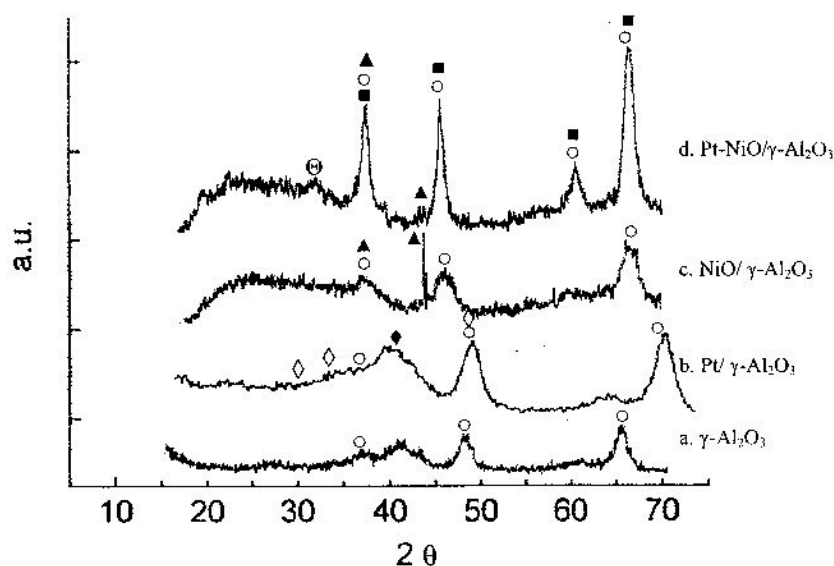


FIGURE 2. XRD profiles for (a) γ - Al_2O_3 (b) Pt/γ - Al_2O_3 (c) NiO/γ - Al_2O_3 (d) $\text{Pt-NiO}/\gamma$ - Al_2O_3 ; (■) NiAl_2O_4 (▲) NiO (○) γ - Al_2O_3 (◆) Pt (◇) PtO (⊙) δ - Al_2O_3 .

Figure 2 shows the X-ray patterns for unreduced samples. The decreasing intensities of the line at $2\theta = 35 - 45^\circ$ corresponds to NiO . In $\text{Pt-NiO}/\delta$ - Al_2O_3 catalyst, an increase in the intensities of broad lines at $2\theta = 36 - 37^\circ$, $44.5 - 45.5^\circ$, $59 - 61^\circ$ and $65 - 65.5^\circ$ is also observed, suggesting the appearance of NiAl_2O_4 as previously also observed by Chen and Ren (1994). The diffraction peaks of NiO phases did not appear in $\text{Pt-Ni}/\delta$ - Al_2O_3 which implies very small NiO crystalline or a strong interaction between Pt-Ni and support. The appearance of γ - Al_2O_3 and unreformed δ - Al_2O_3 are observed which may be these remnants contributed to somewhat unusually high surface area (Molina and Poncelet, 1998). No diffraction peaks from Pt oxide species (Pt agglomeration) are present in $\text{Pt-NiO}/\delta$ - Al_2O_3 sample suggesting that Pt is well dispersed on the catalyst surface. This confirms that the addition of a small amount of noble metal (Pt) to $\text{Ni}/\text{Al}_2\text{O}_3$ does not destroy the original bulk structure of the catalyst (Chen et al., 1997; Cho et al., 1998). However, for Pt/γ - Al_2O_3 sample, an agglomeration of Pt is observed at $2\theta = 42^\circ$ that can be associated with a thermal decomposition of the surface complex $[\text{PtO}_x\text{Cl}_y]_x$, formed from the Pt precursor (Damyanova and Bueno, 2002). As result of this decomposition, Pt atoms rapidly migrate on the alumina surface, and via nucleation, metallic crystallites are formed (Lietz et al., 1983). As conclusions, the high calcination temperature ($\sim 850^\circ\text{C}$) give higher amount of nickel compounds like NiAl_2O_4 , coming from strong metal-support interactions. Despite the high temperatures required for the reduction ($\sim 850^\circ\text{C}$), the formation of surface spinel, NiAl_2O_4 , produces a good effect on the suppression of carbon deposition (Becerra et al., 2001).

4 CONCLUSION

The following are the conclusions that can be drawn from this characterization: (i) NiO or NiAl_2O_4 species having strong interaction with support are favorable in resulting high stability and activity (ii) a small amount of Pt addition to $\text{NiO}/\text{Al}_2\text{O}_3$ causes not only a bimetallic surface interaction and spinels reduction at lower temperature, but also complete the Ni reduction, meaning that, an expansion of the metal surface area of the catalyst. With this increase of active phase surface area, so an increase in catalyzed conversion of methane is expected.

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REFERENCES

- Al-Ubaid, A. and Wolf, E. (1988). "Steam reforming of methane on reduced non-stoichiometric nickel aluminate catalysts." *Applied Catalysis*, **40**, 73 – 81.
- Bhattacharyya, A and Chang, V. W. (1994). "CO₂ reforming of methane to syngas I: Evaluation of hydrotalcite clay-derived catalyst." *Stud. Surf. Sci. Catalysis*, **88**, 616 – 625.
- Becerra, A., Dimitrijewits, M., Arciprete, C. and Luna, C. (2001). "Stable Ni/Al₂O₃ catalysts for methane dry reforming." *Granular Matter*, **3**, 79 – 81.
- Chen, Y. and Ren, J. (1994). "Catalytic performance and catalyst structure of Ni-based catalysts for CO₂ reforming of methane." *Catalyst Letter*, **29**, 39 – 42.
- Chen, Y. G., Tomishige, K., Yokoyama, K. and Fujimoto, K. (1997). "Promoting effect of Pt, Pd and Rh noble metals to the Ni_{0.03}Mg_{0.97}O solid solution catalysts for the reforming of CH₄ with CO₂." *Applied Catalysis A: General*, **165**, 335 – 347.
- Choi, J. S., Moon, K. I., Kim, Y. G., Lee, J. S., Kim, C. H. and Trimm, D. L. (1998). "Stable carbon dioxide reforming of methane over modified Ni/Al₂O₃ catalysts." *Catalysis Letters*, **52**, 43 – 47.
- Choudhary, V. R., Prabhakar, B. and Rajput, A. M. (1995). "Beneficial effects of noble metal addition to Ni/Al₂O₃ catalyst for oxidative methane-to-syngas conversion." *Journal of Catalysis*, **157**, 752 – 752.
- Damyanova, S. and Bueno, J. M. C. (2002). "Promoter effect of cerium on Pt/Al₂O₃ catalyst for CO₂ reforming of CH₄." *Applied Catalysis A: General*, **234**, 271 – 279.
- Dias, J. A. C. and Assaf, J. M. (2004). "Autothermal reforming of methane over Ni/ γ -Al₂O₃ catalysts: the enhancement effect of small quantities of noble metals." *Journal of Power Sources*, **130**, 106 – 110.
- Gyamfi, O. K. and Adesina, A. A. (1999). "Kinetic studies of CH₄ oxidation over Pt-NiO/ δ -Al₂O₃ in a fluidised bed reactor." *Applied Catalysis A: General*, **180**, 113 – 122.
- Jablonski, E L., Castro, A. A., Scelza, O. A. and de Miguel, S. R. (1999). "Effect of Ga addition to Pt/Al₂O₃ on the activity, selectivity and deactivation in the propane dehydrogenation." *Applied Catalysis A: General*, **183**, 189 – 198.
- Lietz, G., Lieske, H., Spindler, H., Hanke, W. and Volter, J. (1983). "Reactions of platinum in O₂- and H₂ treated Pt/ γ -Al₂O₃ catalysts." *Journal of Catalysis*, **81**, 17 – 25.
- Ma, L. and Trimm, D. L. (1996). "Alternative catalyst bed configurations for the autothermic conversion of methane to hydrogen." *Applied Catalysis A: General*, **138**, 265 – 273.
- Molina, R. and Poncelet, G. (1998). " α -Alumina-supported nickel catalysts prepared from nickel acetylacetonate: A TPR study." *Journal of Catalysis*, **173**, 257 – 267.
- Nakagawa, K., Ikenaga, N., Teng, Y., Kobayashi, T. and Suzuki, T. (1999). "Partial oxidation of methane to synthesis gas over iridium-nickel bimetallic catalysts." *Applied Catalysts A: General*, **180**, 183 – 193.
- Ran, R., Xiong, G., Sheng, S., Yang, W., Stroh, N. and Brunner, H. (2003). "Catalytic partial oxidation of n-heptane for hydrogen production." *Catalysis Letters*, Vol. **88**, Nos. 1 – 2.
- Rynkowski, J., Paryjczal, T. and Lenik, M. (1993). "On the nature of oxidic nickel phases in NiO/ γ -Al₂O₃ catalyst." *Applied Catalysis A*, **106**, 73 – 85.

Scheffer, B., Molhoek, P. and Moulijn, J. A. (1989). "Temperature -programmed reduction of NiO-WO₃/Al₂O₃ hydrosulphurization catalysts." *Applied Catalysis*, 1989, **46**, 11 – 18.

Takeguchi, T., Furukawa, S-N., Inoue, M. and Eguchi, K. (2003). "Autothermal reforming of methane over Ni catalysts supported over CaO-CeO₂-ZrO₂ solid solution" *Applied Catalysis A: General*, **240**, 223 – 233.

Wang, H. Y. and Ruckenstein, E. (2001). "CO₂ Reforming of CH₄ over Co/MgO solid solution catalysts – Effect of calcination temperatures and Co loading." *Applied Catalysis A: General*, **209**, 207 ~ 215.