CHARACTERIZATION OF BIMETALLIC Pt-NiO/δ-Al₂O₃ CATALYST FOR AUTOTHERMAL REFORMING OF METHANE

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ABSTRACT

A bimetallic Pt₀₂-Ni₁₂/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 nobel metal (e.g. 0.2 wt%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 the 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 in 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 ~600°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 one of 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 rate. In general, the performance and the deactivation of nickel catalysts can be influenced by catalyst compositions (e.g. Ni particle size, Ni loading) and calcination temperature, T, (e.g. high catalytic activity at high T). 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-Al₂O₃) which affects the catalyst reduction temperature. These nickel aluminates (or spinels), once reduced, form 'fixed-nickel' (Ni₃Al₂O₄) which is non-catalytically active. The ability to reduce and liberate this 'fixed-nickel' from these spinel structure is very critical (Rynkowski et al., 1993). Interestingly, Chen and Ren (1994) reported that this Ni₃Al₂O₄ spinel formed could markedly reduce the carbon deposition because the reduction of nickel aluminates would result in the formation of small nickel particles (NiO) 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 (~30wt%), 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 δ-Al₂O₃ is closely related to the ease of spinel reduction. Highly dispersed Ni metal on high surface area of δ-Al₂O₃ with strong interaction, could be related to the expansion of active metal surface area with high catalytic 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/Al₂O₃ catalyst was prepared by incipient wetness technique using aqueous solutions of Ni(NO₃)₂·6H₂O and H₂PtCl₆·6H₂O. 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, δ-Al₂O₃ which has a fairly high surface area and is more stable under high temperature was therefore employed for this study. The δ-Al₂O₃ support material was prepared by thermally treating γ-Al₂O₃ at 1000°C in a furnace for 5 h. The support was then impregnated with Ni(NO₃)₂·6H₂O 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 H₂PtCl₆·6H₂O 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 Kα 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 H₂ 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 N₂ from 100°C to 550°C at a heating rate of 10°C/min. The pretreatment was hold for 60 min after the maximum pretreated-temperature was reached. The reduction step was carried out using 5%H₂-95%N₂ gas mixture with a flow of 30 ml/min and heating rate of 10°C/min. The analysis was run from 200°C to 1000°C and the holding time was set to 1 hr.

3. RESULTS AND DISCUSSION

3.1 TPR analysis

Figure 1 showed different reduction patterns of NiO, NiO/Al₂O₃, and Pt-NiO/δ-Al₂O₃ as compared to unsupported Pt-NiO and Pt reductions. The reduction peaks of NiO/Al₂O₃ and Pt-NiO/δ-Al₂O₃ (appeared around 950°C) demonstrated that, NiO with Al₂O₃ could be transformed into NiAl₂O₄ 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°C). Only NiO could be reduced around 450°C, while Pt-NiO/γ-Al₂O₃ and
NiO/Al₂O₃ were reduced around 950°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-Al₂O₃ catalyst, suggesting that Ni is well dispersed on the catalyst surface. The spinels formed can be reduced at lower temperature (850°C) since the nickel aluminate (spinels) is reducible up to 1000°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 monometallies Pt (86.45 kJmol⁻¹) and NiO (103.73 kJmol⁻¹) (Gyamfi and Adesina, 1999)

![Figure 1. TPR profiles for (a) NiO, (b) NiO/Al₂O₃, (c) Pt-NiO/δ-Al₂O₃ and unsupported (d) Pt-NiO and (e) Pt, flowrate of 5%H₂ = 30 ml/min, heating rate = 10 °C/min.](image)

3.2 XRD analysis

![Figure 2. XRD profiles for (a) γ-Al₂O₃ (b) Pt/γ-Al₂O₃ (c) NiO/γ-Al₂O₃ (d) Pt-NiO/γ-Al₂O₃: (•) NiAl₂O₄ (▲) NiO (○) γ-Al₂O₃ (●) Pt (○) PtO (Θ) δ-Al₂O₃.](image)

Figure 2 shows the X-ray patterns for unreduced samples. The decreasing intensities of the line at 2θ = 35 - 45° corresponds to NiO. In Pt-NiO/δ-Al₂O₃ catalyst, an increase in the intensities of broad lines at 2θ = 36 - 37°, 44.5 - 45.5°, 59 - 61° and 65 - 65.5° is
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also observed, suggesting the appearance of NiAl$_2$O$_4$ as previously also observed by Chen and Ren (1994). The diffraction peaks of NiO phases did not appear in Pt-Ni/δ-Al$_2$O$_3$ which implies very small NiO crystalline or a strong interaction between Pt-Ni and support. The appearance of γ-Al$_2$O$_3$ and unrefomed δ-Al$_2$O$_3$ 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 Pt-NiO/δ-Al$_2$O$_3$ 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 Ni/Al$_2$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$_2$O$_3$ sample, an agglomeration of Pt is observed at 2θ = 42° that can be associated with a thermal decomposition of the surface complex [PtO$_2$Cl$_2$], 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 (~850°C) give higher amount of nickel compounds like NiAl$_2$O$_4$, coming from strong metal-support interactions. Despite the high temperatures required for the reduction (~850°C), the formation of surface spinel, NiAl$_2$O$_4$, 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$_2$O$_4$ species having strong interaction with support are favorable in resulting high stability and activity (ii) a small amount of Pt addition to NiO/Al$_2$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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