Ni/TiO₂ Catalysts Supported with Al₂O₃ Over CO₂ Reforming†

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The 5 wt % Ni/TiO₂-Al₂O₃ xerogels catalyst was prepared by the sol-gel synthesis of titanium *n*-butoxide in methanol with nickel and aluminum. X-Ray diffraction, TG/DTA and SEM were used to characterize the function of addition aluminum to Ni/TiO₂ catalyst. The role of aluminum addition promotes the formation of large metallic Ni ensembles increase the dispersion of Ni, suppression of Ni/TiO₂ catalyst deactivation and carbon deposition.

Keywords: CO₂-reforming, Methane, Nickel catalysis, Aluminum, Carbon deposition.

INTRODUCTION

Carbon dioxide reforming is meaningful because it produces a more suitable H_2/CO ratio for the Fisher-Tropsch. However, this reaction has not been established industrial due to the serious catalyst deactivation. It is well known that many transition metal-based are good catalysts for the CO_2 reforming reaction, especially noble and Ni-based catalysts. Although noble metal catalysts show better performance than nickel, but the high cost of noble metals renders their application. Therefore, development of Ni-based catalysts with little or no carbon deposition is of great interesting to industrial application for CO_2 reforming.

Some researchers have stated that the addition of titanium improves the stability of these catalysts, especially inhibiting the carbon deposition. When a titanium-supported nickel was employed in catalytic CO_2 reforming, the catalyst showed a high initial activity but suffered instability based both on the poor reduced surface area and Ti_3O_5 was covering the active sites of Ni catalysts.

Zhang and Reller[1] showed that the larger metal particles stimulated the amorphous carbon deposition because of the ensemble result which was covering the active metal surface. So solid solution formation and decorating Ni crystallites with other oxides *etc*. are proved to be effective in the elimination of large Ni metal ensemble. For instance, the formation of $NiAl_2O_4$ results in the formation of small Ni crystallites which resist to carbon deposition[2,3]. A number of articles reported that mobile oxygen on the surface of catalysts is related to the

carbon elimination[4,5]. As a high temperature reation, it is required that the catalyst has good thermal stability. The formation of $NiAl_2O_4$ solid solution can improve the oxygen storage capacity, the redox property and the thermal resistance.

In this work, we reported on the study of CO_2 reforming over Ni/TiO₂-Al₂O₃ catalyst. It also reported an effect of adding aluminum to Ni/TiO₂ catalysts. The major function of an aluminum additive was to improve development of pore structure and inhibit Ti_3O_5 formation. The best effect in securing stability without sacrificing much activity was obtained when aluminum was used as a modifying additive. In this paper, the role of aluminum oxide as a promoter in Ni/TiO₂-Al₂O₃ is discussed.

EXPERIMENTAL

Preparation of catalyst: 5 wt % Ni/TiO₂-Al₂O₃ was prepared by sol-gel process from analytical-grade (Sinopharm Chemical Reagent Co., Ltd.). The precursors were $Ni(NO_3)_2 \cdot 6H_2O$, $Ti(BuO)_4$ and $Al(NO_3)_3 \cdot 9H_2O$. Methanol has been used as a solvent for precursor solution and hydrolyzate. The molar ratio of Ti/MeOH was at 0.12. Hydrolysis was catalyzed by HNO_3 with an acid/alkoxide ratio of 0.10 and hydrolysis ratio of 5.22. Appropriate amounts of $Al(NO_3)_3 \cdot 9H_2O$ were added into $Ti(BuO)_4$ and $Ni(NO_3)_2 \cdot 6H_2O$ solution in MeOH to make the gel solutions. Hydrolysis of the colloidal suspension was obtained by slowly dropping acid/alkoxide and at the same time stirring to keep the hydrolysis speed slow. A distinct lightly green gel was made where hydrolysis solution has been

dropped into the colloidal suspension after 24 h. The gel was dried in air at 453 K for 10 h then calcined at 973 K for 10 h with a rate of 1 K/min from 298 K.

X-Ray powder diffraction patterns obtained by using Rigaku D/max 2250 diffraction equipment with CuK_α source at 40 kV and100 mA. 2θ angles ranged from 20-80 with a speed of 8 °/min. SEM image was obtained on a Philips XL-30 microscope operated at 15 kV. The thermal behaviour and carbon deposited on the catalysts were obtained by a Perkin Elmer. Pyris Diamond TG/DTA equipment. The temperature was increased to 1023 K from 303 K at a rate of 5 K/min.

Performance measurement of catalyst: Catalytic performance measurement of CO_2 reforming was conducted under atmospheric pressure with a tubular fixed-bed quartz reaction (5.6 mm i.d. 255 mm length). The reaction gases consisted of CO_2, CH_4 and N_2 with the ratio of 1:1:1.8 at a GHSV of 942000 $cm^3 h^{-1} g^{-1}$. The catalyst of 100 mg with the particle size of 60-80 meshes diluted with 0.5 g quartz sand (45-55 Mesh). The catalyst was reduced in-suit at 973 K for 2 h with a feed composition of $H_2/N_2 = 1:2$. The analyses of the tailgas were carried out on a Haixin GC-950 gas chromatograph equipped with a TCD detector.

RESULTS AND DISCUSSION

Activity and stability of catalyst: The characteristic of catalytic was tested at 973 K with a feed gas ratio CH_4/CO_2 of one. Table-1 listed that the Ni/TiO_2-Al_2O_3 catalyst illustrated a high response rate initially and exhibited continuous higher stability during the 10 h. On the contrary, the Ni/TiO_2 catalyst showed low activity and a rapid deactivation comparable to the Ni/TiO_2-Al_2O_3 during the 10 h stream response. The significantly effect of aluminum improved the stability of catalytic. Table-2 showed the time-dependent reaction rate of CH_4 over 5 wt % Ni/TiO_2-Al_2O_3 catalyst with different Al_2O_3 loading. As Al_2O_3 content increased, the activity improved accordingly. It is observed that the reaction rate of the catalyst with 25 wt % Al_2O_3 appears to be higher than that of 35 wt % Al_2O_3 with time on stream. However, at the highest Al_2O_3 loading (75 wt %), it showed the lowest reaction rate on stream. Overall evaluation of the effect of Al_2O_3 addition is that proper content of Al_2O_3 can improve the activity, but excessive Al_2O_3 can easily cause catalyst deactivation. It was 50 wt % Al_2O_3 loading that provides well stability.

TABLE-1
TIME-DEPENDENT REACTION RATE OF CH_4 OVER 5 wt % Ni/TiO_2 AND 5 wt % Ni/TiO_2-Al_2O_3 CATALYSTS

Catalyst	Time (h)				
	0	2	4	6	8
Ni/TiO_2	83.0	56.0	42.0	38.0	32.0
$Ni/TiO_2/Al_2O_3$	125.0	129.0	128.0	129.0	132.0
Raction condition: temperature 973 K, p = 1 atm. GHSV = 9,2000 $cm^3 h^{-1} g^{-1} CH_4/CO_2 = 1$.					

Role of aluminum in Ni/TiO_2: Aluminum addition to Ni/TiO_2-Al_2O_3 over CO_2 reforming was the suppression of catalyst deactivation and carbon deposition. The deactivation of Ni-based catalysts can be described to carbon deposition and nickel sintering. X-Ray powder diffraction patterns of Ni/TiO_2-

TABLE-2
TIME-DEPENDENT REACTION RATE OF CH_4 OVER 5 wt % Ni/TiO_2-Al_2O_3 CATALYST WITH DIFFERENT Al_2O_3

Cat.	Time (h)				
	0	2	4	6	8
$Ni/TiO_2/25$ wt % Al_2O_3	182.0	180.0	179.0	177.0	176.0
$Ni/TiO_2/35$ wt % Al_2O_3	146.0	142.0	143.0	144.0	145.0
$Ni/TiO_2/50$ wt % Al_2O_3	201.0	201.0	201.0	200.0	200.0
$Ni/TiO_2/75$ wt % Al_2O_3	118.0	118.0	118.0	119.0	119.0
Reaction condition: temperature 973 K, P = 1 atm, GHSV = 942000 $cm^3 h^{-1} g^{-1}$, $CH_4/CO_2 = 1$.					

Al_2O_3 catalyst in fresh, reduced and post-reaction are presented in Fig. 1. It showed that no nickel reflection occurred on fresh Ni catalyst reduced at 973 K (Fig. 1). It indicated that the interaction between NiO and Al_2O_3 was strong. There is still no pure NiO observed and nickel is present in the formal of $NiAl_2O_4$. The XRD analyses of the fresh, reduced and post-reaction Ni/TiO_2-Al_2O_3 catalysts are presented will generate more active sites, attributing to its high activity. In this research, it can been seen that the lower catalytic activities of Ni/TiO_2 catalyst is possibly due to the blockage of the active sites. It suggests that the pores of this catalyst be blocked by the Ti_3O_5, which could prevent the contact between the reactants and the active sites. Some researchers have reported the coverage of active sites by Ti_3O_5 was the main cause of Ni/TiO_2 deactivation. The addition of aluminum can inhibit the reduction of TiO_2. It was the main reason that Ni/TiO_2-Al_2O_3 could perform well much longer with a much better action than Ni/TiO_2 catalyst.
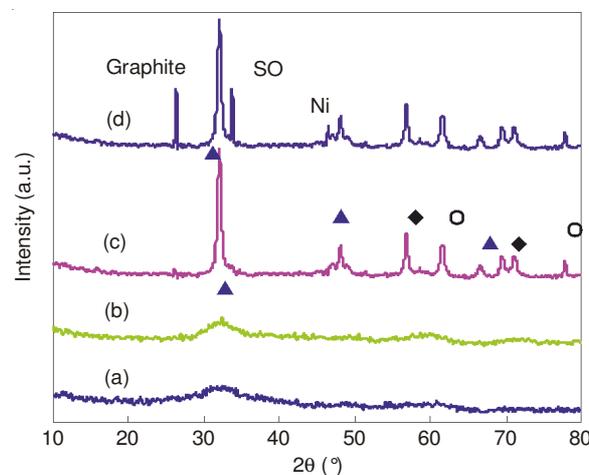
Fig. 1. X-Ray diffraction patterns for 5 wt % Ni/TiO_2-Al_2O_3 catalyst. (a) Calcinaed at 453 K for 10 h, (b) Calcinaed at 773 K for 10 h, (c) Reduced at 973 for 2 h and (d) after 120 h reaction at 973 K. ▲: Anatase; ◆: Rutile; ○: Al_2O_3 or $NiAl_2O_4$. SO: SiO

The sample of Ni/TiO_2-Al_2O_3 catalyst remained X-ray amorphous up to 453 K. It can be seen that a pure anatase phase was obtained at 773 K, it would be desirable to have a single-phase support for establishing a structure-reactivity relationship in catalytic applications. It can be seen that rutile TiO_2 began to form at 973 K. It was reported that, brookite, anatase and rutile can coexist in the temperatures from 673-973 K[6] and TiO_2 transforms to rutile between 903 and 973 K[7]. These results are in agreement with what the XRD presents. Rutiles was more stable and final phase of titania and anatase

transforms into rutile at 973 K. The extension of the coexistence of rutile and anatase may be due to the integration of aluminum. A existence of anatase may also contribute to the higher performance.

It can been seen that no nickel peaks in fresh catalyst due to the interaction between the metal and support Al$_2$O$_3$ in XRD patterns. Phase transformation occurred on Al$_2$O$_3$ supported Ni catalyst during calcination to form nickel aluminate NiAl$_2$O$_4$ which is difficult to reduce to metallic nickel at 973 K. Assist with more porous structure has lower nickel particle size. The metallic Ni in the reduced samples preferentially forms small crystallites and the dispersion of Ni increases by adding Al$_2$O$_3$. The interaction among components can affect the distribution of components and the structure of the catalyst and in addition, thus affect the activity of the catalyst. Several research groups[8] have reported that the migration of Ni from the bulk to the surface of the catalyst may migrate to the surface during the reaction. For the XRD result (Fig. 1) Al$_2$O$_3$ can react with the reduced NiO to form NiAl$_2$O$_4$. This process may promote the migration of Ni. Therefore the activity of the sample with 50 wt % Al$_2$O$_3$ increased more quickly than the samples with different content of Al$_2$O$_3$ (Table-2).

Tang et al.[9] reported that NiAl$_2$O$_4$ can form after calcinations at 973 K which is easier to reduce than NiTiO$_3$. Several researchers have found that higher calcination temperatures increase the metal-support interaction and the formation of nickel aluminum resulting in greater difficulty in reduction[3,10,11]. It will affect the nickel dispersion and carbon deposition. Chen and Ren[3] showed that carbon deposition is markedly suppressed if NiAl$_2$O$_4$ is made. The strong interaction of the Ni-O bond in NiAl$_2$O$_4$ results, in the formation of small Ni crystallites on the catalyst surface, which are relatively stable toward sintering and carbon deposition[1].

It is known that nickel crystallites are the active sites for CO$_2$ reforming. XRD results have shown that NiAl$_2$O$_4$ was the main phase of nickel in fresh catalyst Ni/TiO$_2$-Al$_2$O$_3$. The catalyst showed higher activity and carbon resistance from nickel crystallite. Chen and Ren[3] also showed that NiAl$_2$O$_4$ may be as the active site in CO$_2$ reforming. Hence, it is deduced that the reduced NiAl$_2$O$_4$ may be an active site for this reaction exhibiting different catalytic and stability. It suggested that the calcined NiAl$_2$O$_4$ spinel phase made not active in the reforming reaction but its reduced form could lead to a significant increase in activity and stability. It is deduced that the higher activity of Ni/TiO$_2$-Al$_2$O$_3$ in this research was probably due to the synergetic effect of the reduced NiAl$_2$O$_4$ and surface nickel particles.

To the surface of the catalysts and blocked the accessibility of reacting molecules to active sites. The deactivation of Ni/TiO$_2$-Al$_2$O$_3$ catalysts can also be attributed to the sintering of the active phase. The result drawn from the XRD characterizations in the catalyst indicate that there is no NiO present in fresh catalyst. XRD measurements give insight into the structural changes of Ni particles and deposited carbon after the reaction. It can be seen In Fig. 1, pattern (d), shows the size Ni crystalline.The nickel crystallite phase peak on Ni/TiO$_2$-Al$_2$O$_3$ appeared after 120 h.

Characterization of carbon deposits: TG/DTA profiles of carbon deposits on the Ni/TiO$_2$-Al$_2$O$_3$ catalyst after 10 h

carbon are illustrated in Fig. 2. The TG mode shows a weight drop from the starting point to 542 K, it was the evaporation of moistures, methanol solvent and BuOH generated during hydrolysis and the decomposition of nitrate. The steep weight increase indicates nickel oxidized during 542-738 K. Then the weight gradually decreased until leveling off at 973 K and then shows no further weight loss (Fig. 2). The oxidation of carbonaceous species starts at 807 K, showing a maximum at 834 K, which is in agreement with the formation of filamentous carbon species, this conforms to the result of XRD. There are two types of carbon, deactivating (amorphous carbon) and non-deactivating (graphite) were found[3,12]. The morphology of graphitic carbon is that of carbon filaments. Chen and Ren[3] reported that the filamentous carbon with a hollow inner channel would form on the surface of 10 wt % Ni/6-Al$_2$O$_3$ catalysts. They did not lose their activity in tests for as long as 120 h.
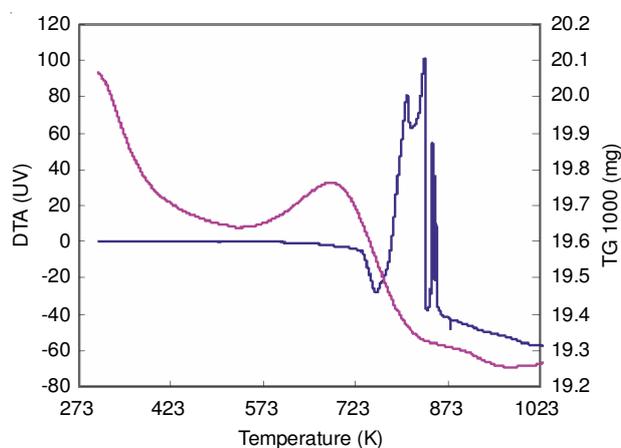
Fig. 2. TG/DTA profiles of 5 wt % Ni/TiO$_2$-Al$_2$O$_3$ catalyst after 10 h reaction. Reaction condition: temperature 974 K, P = 1 atm, CH$_4$/CO$_2$ = 1 GHSV = 942000 cm^3 h^{-1} g^{-1}

Fig. 3 illustrates the SEM micrograph of the Ni/TiO$_2$-Al$_2$O$_3$ catalyst showing the well-surface area and mesoporous.
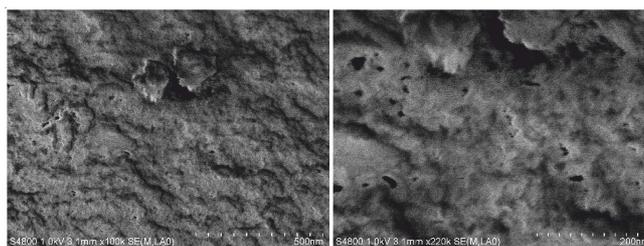
Fig. 3. SEM micrograph of the Ni/TiO$_2$-Al$_2$O$_3$ catalyst illustrating well-surface area and mesoporous

Carbon deposition on Ni/TiO$_2$-Al$_2$O$_3$ catalyst is mainly graphitic as shown in XRD. It can be seen that the peak of graphitic carbon appears in Ni/TiO$_2$-Al$_2$O$_3$ after CO$_2$ reforming for 120 h. The foregoing discussions have shown that graphitic carbon is more active in the CO$_2$ reforming, probably due to its close contact with nickel particles. Therefore, Ni/TiO$_2$-Al$_2$O$_3$ catalyst showed higher stability in this reaction, because of its more active carbon species. This behaviour may be attributed to the formation of NiAl$_2$O$_4$. It was reported that NiAl$_2$O$_4$ solid solution could minimize the Ni particle size to suppress the carbon formation[3]. It is expected that the Al$_2$O$_3$ addition to

Ni/TiO$_2$ can modify the Ni ensembles environment by the Ni-Al alloy formation. Hence, the Al$_2$O$_3$ addition effects the Ni/TiO$_2$ catalyst to suppress the carbon deposition during CO$_2$ reforming. Although the amount of carbon deposition on the Ni/TiO$_2$-Al$_2$O$_3$ catalyst was appeared, the catalyst kept high activity with reaction rate as shown in Table-1. The amount of carbon deposition was not always to the catalyst deactivation. Chen and Ren[3] reported that the carbon deposition on the NiAl$_2$O$_4$ spinel was markedly suppressed during the CO$_2$ reforming. Their results agreed with our results during the reaction time till 120 h in the carbon deposition on the Ni/TiO$_2$-Al$_2$O$_3$ catalyst. Hence, the deactivation of Ni/TiO$_2$-Al$_2$O$_3$ catalyst has been ascribed to Ni sintering. The presence of a nickel phase in the XRD pattern of used catalyst after 120 h reaction indicates that nickel was sintered after 120 h on stream in the CO$_2$ reforming. The results from TG/DTA and XRD support the same conclusion that the Ni/TiO$_2$-Al$_2$O$_3$ catalyst deactivation is mainly due to the Ni sintering rather than to carbon deposition in the CO$_2$ reforming.

Conclusion

The Ni-based catalysts modified by Al$_2$O$_3$ are efficient for the CO$_2$ reforming, despite the fact that a significant amount of carbon is formed during the reaction over Ni/TiO$_2$-Al$_2$O$_3$. This catalyst exhibited high activity and stability as compared with Ni/TiO$_2$. When Al$_2$O$_3$ is added to the support, the formation of NiAl$_2$O$_4$ depressed the carbon deposition over Ni/TiO$_2$-Al$_2$O$_3$. It resulted in the catalyst exhibiting stable activity during the CO$_2$ reforming. On the other hand, the presence of Ni aluminate spine decreases the carbon deposition in the Ni/TiO$_2$-Al$_2$O$_3$ catalysts. The results suggest that the deactivation of Ni/TiO$_2$-Al$_2$O$_3$ catalyst have been ascribed to Ni sintering in the catalysts will be investigated in future.

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