

Partial Oxidation of Methane over Nickel Catalysts Supported on Various Aluminas

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Abstract—Partial oxidation of methane (POM) was systematically investigated in a fixed bed reactor over 12 wt% Ni catalysts supported on α -Al₂O₃, γ -Al₂O₃ and θ -Al₂O₃ which were prepared at different conditions. Results indicate that the catalytic activity toward POM strongly depends on the BET surface area of the support. All the Ni/ θ -Al₂O₃ catalysts showed high activity toward POM due to the less formation of inactive NiAl₂O₄ species, the existence of NiO_x species and stable θ -Al₂O₃ phase. Although Ni/ γ -Al₂O₃ showed the highest activity toward POM, long-time stability cannot be expected as a result of the deterioration of the support at higher temperature, which is revealed from BET results. From the reaction and characterization results, it is inferred that the optimal conditions for the preparation of θ -Al₂O₃ are 1,173 K and 12 h.

Key words: Partial Oxidation of Methane, Ni Catalyst, θ -Al₂O₃, α -Al₂O₃, γ -Al₂O₃

INTRODUCTION

Although the reserve of conventional petroleum, which is the main raw material for basic chemicals, is limited, new deposits of natural gas, one of the abundant resources, are being continuously discovered at a significant rate around the globe. In addition, new sources of natural gas such as coal-bed methane, natural hydrates, and biomass emissions are now being tapped [Zhu et al., 2001]. So, the effective chemical utilization of natural gas to produce basic chemicals is one of the desirable goals in the current chemical industry. Although the direct conversion of methane to valuable chemicals such as methanol is the most effective route, there is still no practical or efficient catalyst or process that can be commercialized presently. The most competitive process for the conversion of methane is an indirect route in which methane is first converted to syngas and then syngas is used as feedstock to synthesize chemicals via Fischer-Tropsch or other processes. The syngas and/or hydrogen production via natural gas route, such as steam reforming of methane (SRM), methane reforming with carbon dioxide, and POM, has been investigated intensively [Ashcroft et al., 1991; Hickman and Schmidt, 1993; Jung et al., 1999; Nam et al., 2000; Chang et al., 1998; Dong et al., 2001]. In comparison with SRM, which is a highly endothermic process, the catalytic POM is more attractive since the reaction is mildly exothermic and highly efficient and can produce syngas with an H₂/CO ratio of 2, which is well suitable for methanol synthesis and Fischer-Tropsch reaction [Peña et al., 1996].

There has been a wide range of studies on POM over supported metal catalysts, such as Rh, Ir, and Ni [Wang and Ruckenstein, 1999a; Nakagawa et al., 1998; Choudhary et al., 1993; Tsang et al., 1995; Diskin et al., 1998; Tang et al., 1998]. It has been reported that supported precious metals have much higher activity and stability for POM than nickel-based catalysts. However, because of the high

cost and very limited reserves of precious metals, supported Ni catalysts are more attractive and practical for the commercialization of the POM process.

Various supports such as Al₂O₃, SiO₂, MgO, ZrO₂, CeO₂ and La₂O₃ have been used for POM in nickel-based catalysts [Hu and Ruckenstein, 1996, 1999b; Au et al., 1996; Roh et al., 2001; Lu et al., 1998a]. The support plays an important role in catalytic performance due partially to the strong interaction between Ni and support. The main problem with the supported Ni catalysts is the deactivation caused by carbon deposition and sintering of the catalyst at high temperatures. Carbon deposition mainly comes from methane decomposition and CO disproportion. Besides the mechanistic studies for understanding the process in a more detailed way, the recent focus has been on the development of a highly active and stable nickel-based catalyst for POM.

As a catalyst for POM, Ni/ γ -Al₂O₃ has been studied [Lu et al., 1998b]. However, Ni/ γ -Al₂O₃ is usually unstable at high temperatures (>973 K) because of the thermal deterioration of the support and phase transformation. The addition of alkali metal oxide and rare earth metal oxide was used to modify the catalyst both for a high activity and stability [Miao et al., 1997].

In our previous studies [Roh et al., 2001a, b; Dong et al., 2002], we have successfully developed catalysts for POM, SRM and Oxy-SRM. By heat treatment of γ -Al₂O₃ and impregnation of Ni salt, a Ni/ θ -Al₂O₃ catalyst with high activity and high stability was obtained [Roh et al., 2001c]. This motivated us to further probe the reason why this catalyst showed high activity and stability in POM. In comparison, Ni catalysts supported on α -Al₂O₃, γ -Al₂O₃ and θ -Al₂O₃ prepared under different conditions were systematically investigated. To obtain enough samples for the surface and bulk analysis of the used samples, a larger reactor was used in this study.

EXPERIMENTAL

1. Catalysts

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Table 1. Summary of the pretreatment conditions and BET results of Al₂O₃ supports

Sample name	Pretreatment conditions		BET surface area (m ² /g)
	Temperature (K)	Pretreatment time (h)	
γ -Al ₂ O ₃	-	-	234
θ -Al ₂ O ₃ (A)	1173	6	149
θ -Al ₂ O ₃ (B)	1173	12	108
θ -Al ₂ O ₃ (C)	1173	24	101
θ -Al ₂ O ₃ (D)	1223	12	100
α -Al ₂ O ₃ (E)	1373	12	6

Support materials used in this study were α -Al₂O₃ (99.5%, Strem Chemicals), γ -Al₂O₃ (CONDEA Chemie GmbH) and θ -Al₂O₃ which was prepared by heat treatment of γ -Al₂O₃ at different conditions as shown in Table 1. Among the pretreatment conditions, 1,173 K for 6 h, which was used in our previous study, was selected as a standard condition. The temperature was carefully increased at a 1 K/min rate. Supported Ni catalysts (12 Ni wt%) were prepared by impregnating a Ni(NO₃)₂·6H₂O solution and calcining at 823 K for 6 h.

2. Catalyst Characterization

The reduced and used samples were passivated by diluted oxygen of 0.5% O₂ in N₂ for 30 min at room temperature before unloading. The used samples were taken out under atmospheric conditions and stored in a dry room with inert gas of Ar for test.

The XRD patterns were recorded on a Rigaku 2155D6 diffractometer using a copper target at 40 kV×50 mA and scanning speed of 2° (2 θ) per minute. Ni particle sizes were estimated from line broadening analysis using Scherrers equation. The surface analysis of the catalysts was performed at room temperature on a VG ESCALAB 210 spectrometer with an Al K α radiation generated at 300 watts. The analysis was operated at pass energy of 20 eV and a step size of 0.1 eV. Binding energies were adjusted relative to adventous carbon at 284.6 eV. The specific surface areas of the samples, which were evacuated at 473 K, were measured by the BET nitrogen adsorption method in volumetric equipment Micromeritics ASAP-2400.

3. Reaction Procedure

The catalytic POM was carried out in a fixed-bed reactor system which consisted of reactant feed parts, a reactor, and an on-line GC. The reactants (CH₄ and O₂) and diluent (N₂), which were controlled by mass flow controllers, were mixed before the reactor. The reactor (Incolloy 800H) with an inner diameter of 18 mm was heated in an electric furnace. The bed temperature was monitored by a K-type thermocouple placed in catalyst bed with a thermowell. Typically, 2 grams of catalyst with a particle size of 16-20 mesh was loaded for the POM test. In a higher space velocity test, 50 mg catalyst was loaded and tested in a quartz reactor. Before reaction, catalyst was reduced at 973 K for 3 h with 5% H₂ in N₂. The ratio of feed gases was fixed at CH₄/O₂=1.95 and N₂/(CH₄+O₂)=1. A cold trap at the outlet of the reactor was used to condense any water from the product gas stream. The products were analyzed by an on-line GC equipped with a TC detector and a Carbosphere packed column (Alltech).

RESULTS AND DISCUSSION

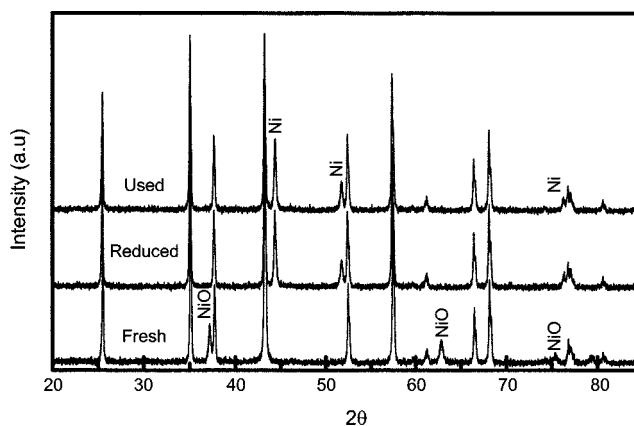
1. Catalyst Characterization

1-1. Characteristics of the Supports

From the BET results of the supports shown in Table 1, we can see that the BET surface area of γ -Al₂O₃ decreased greatly when it was calcined at 1,173 K for 6 h, which was caused by the phase transformation from γ -Al₂O₃ to θ -Al₂O₃. A further sharp decrease of the BET surface area was observed for the support calcined at 1,173 K from 6 to 12 h [θ -Al₂O₃(B)]. However, when the calcination time was 24 h [θ -Al₂O₃(C)], the BET surface area was maintained almost the same as that of θ -Al₂O₃(B). When γ -Al₂O₃ was calcined at 1,223 K for 12 h [θ -Al₂O₃(D)], very similar BET surface area was obtained to that calcined at 1,173 K for 12 or 24 h. However, for γ -Al₂O₃ calcined at 1,373 K for 12 h (α -Al₂O₃(E)), the BET surface area decreased to a very low value, which is similar to that of α -Al₂O₃. XRD results (not shown) indicate that θ -Al₂O₃(A), θ -Al₂O₃(B), θ -Al₂O₃(C) and θ -Al₂O₃(D) showed broad diffractions of θ -Al₂O₃ while only very sharp peaks assigned to α -Al₂O₃ were observed for the sample calcined at 1,373 K for 12 h [α -Al₂O₃(E)]. So, there exists a strong influence of heat treatment on the structure of Al₂O₃ phases.

1-2. XRD Analysis

Fig. 1 shows the XRD patterns of the Ni/ α -Al₂O₃ samples that were treated under different conditions. From Fig. 1 we can see that the Ni species and α -Al₂O₃ phases were clearly observed for all the samples. The XRD patterns of Ni/ θ -Al₂O₃(A) samples are given in Fig. 2. The XRD lines of NiO and Ni over Ni/ θ -Al₂O₃(A) were broad, which is ascribed to smaller particle size of the Ni species on the support. Fig. 3 shows the XRD patterns of the used Ni/ θ -Al₂O₃ samples. It is clear that Ni/ α -Al₂O₃(E) shows the characteristic lines of α -Al₂O₃ which means that γ -Al₂O₃ was transformed to α -Al₂O₃ under the pretreatment conditions. For other samples, broad lines of θ -Al₂O₃ were observed. Although the XRD pattern of NiAl₂O₄ spinel phase is very similar to that of alumina, they can be distinguished from each other by the peak intensities of the main diffractions. Even though NiAl₂O₄ spinel phase was not detected for all the samples in this work, the formation of NiAl₂O₄ was confirmed by TPR results [Roh, 2001d] that the reduction peak at peak maximum of about 1,073 K, which can be assigned to the reduction of NiAl₂O₄, only appeared as a small shoulder peak. It is inferred that the content of

**Fig. 1. XRD patterns of the Ni/ α -Al₂O₃ catalyst.**

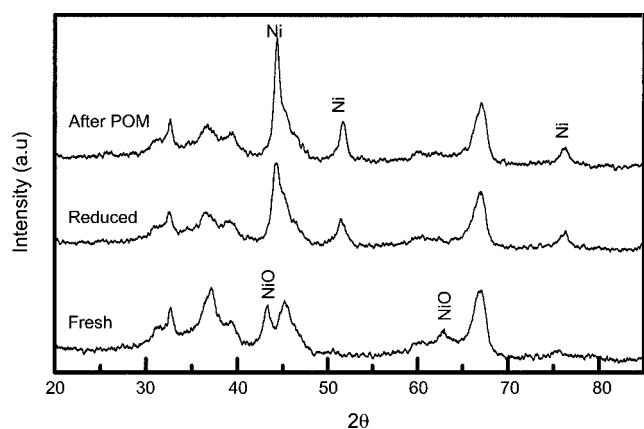


Fig. 2. XRD patterns of the Ni/θ-Al₂O₃(A) catalyst.

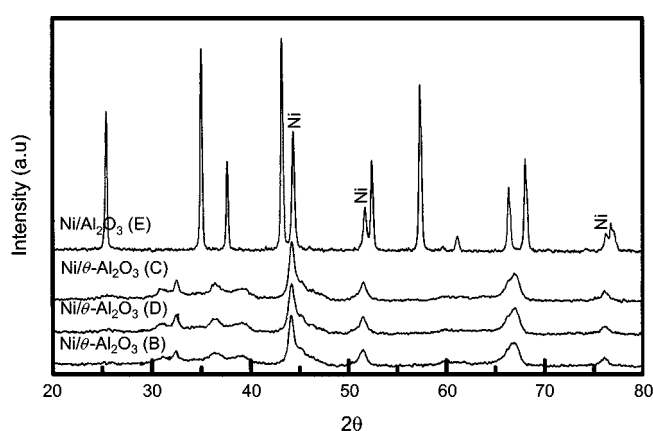


Fig. 3. XRD patterns of the used Ni/θ-Al₂O₃ catalysts.

spinel phase was too low to be detected by XRD. The NiO phase was not detected for samples reduced and used in POM for 24 h although the samples were passivated with diluted oxygen at room temperature before unloading. This means that the bulk phase of the Ni was not oxidized under the passivation conditions. The interaction between oxygen and Ni surfaces has been studied intensively, and the oxidation of metallic Ni at room temperature brings about the formation of a two-dimensional oxide with a thickness of 2 to 3 NiO layers [Looij and Geus, 1997]. This low NiO content cannot be detected by XRD. No observable phase transformation occurred for the samples used in POM by comparing the XRD patterns of the fresh, reduced and used samples. So, the θ-Al₂O₃ is sta-

Table 2. Summary of the particle sizes of Ni obtained from XRD

Sample	Particle size (Å)	
	Reduced	Used
Ni/α-Al ₂ O ₃	665.6	585.1
Ni/γ-Al ₂ O ₃	78.1	124.7
Ni/θ-Al ₂ O ₃ (A)	90.1	134.8
Ni/θ-Al ₂ O ₃ (B)		157.9
Ni/θ-Al ₂ O ₃ (C)		153.9
Ni/θ-Al ₂ O ₃ (D)		154.6
Ni/α-Al ₂ O ₃ (E)		449.6

bilized by heat treatment. To study the sintering of Ni, the particle size was determined based on the line broadening by Scherrer's equation. As the diffraction peak corresponding to NiO overlaps with that of Al₂O₃, only the particle size of Ni was estimated as shown in Table 2. The particle sizes of Ni for Ni/θ-Al₂O₃ were much smaller than that of Ni/α-Al₂O₃. Therefore, Ni has bigger particle size when it is dispersed over low surface area support. This was confirmed from the results for Ni/α-Al₂O₃(E) in which α-Al₂O₃(E) has a BET

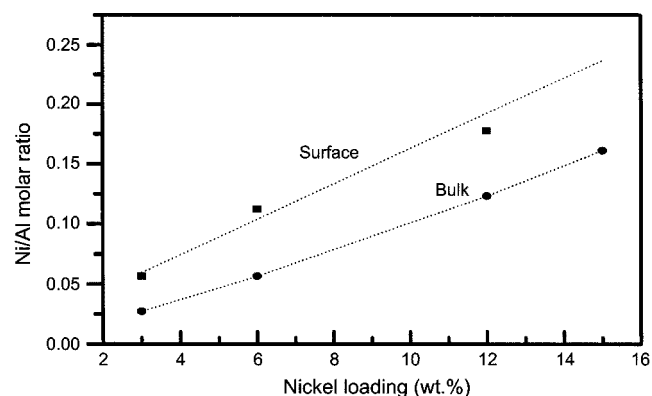


Fig. 4. The variation of the surface Ni/Al molar ratio detected by XPS as a function of Ni loading for the fresh Ni/θ-Al₂O₃(A) catalyst.

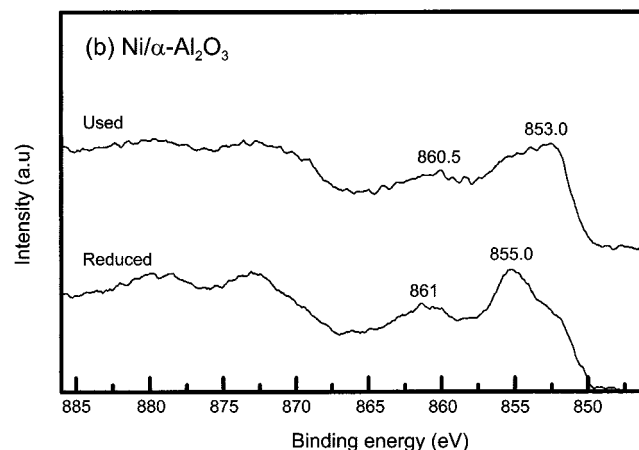
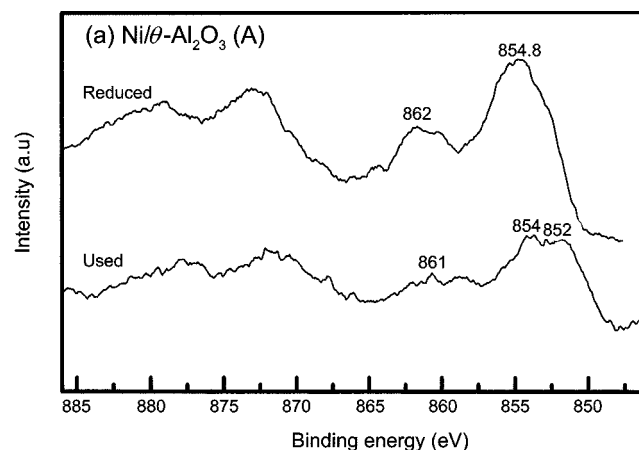


Fig. 5. XPS spectra of (a) Ni/θ-Al₂O₃(A) and (b) Ni/α-Al₂O₃ catalysts in Ni 2p region.

surface area similar to that of α - Al_2O_3 .

1-3. XPS Analysis

To investigate the dispersion of Ni over the support, $\text{Ni}/\theta\text{-Al}_2\text{O}_3$ (A) catalysts with different Ni loadings were prepared and analyzed by XPS as illustrated in Fig. 4. The surface Ni/Al molar ratio versus Ni loading curve displayed a remarkable linearity in the Ni loading ranged from 3 wt% to 15 wt%. This indicates that Ni was dispersed very well over the support and there was no obvious particle size variation with the increase of Ni loading.

To obtain information on the surface state of the catalysts, XPS was carried out for the reduced and used samples. The XPS spectra of the samples in Ni 2p region are depicted in Fig. 5. It has been well established that there is a shake-up satellite peak for Ni 2p_{3/2} of NiO at about 862 eV and no peak for metallic Ni although the Ni 2p_{3/2} binding energies of NiO and Ni are very close (~853 and ~852 eV). It is clear that both Ni and NiO were present on the surface of all the tested samples although they were passivated by diluted oxygen. This confirms the fact that the oxidation of dispersed Ni is very limited at room temperature. The deconvolution of the XPS peak at about 853 eV for separating Ni and NiO is very difficult to carry out when both NiO and metallic Ni are present in the same sample. So, we used the ratio of $I_{\sim 862\text{ eV}}/(I_{\sim 862\text{ eV}}+I_{\sim 853\text{ eV}})$ as a measure of the NiO proportion in the surface of the sample, which was proposed by Takeguchi et al. [Takeguchi et al., 2001]. The results are given in Table 3. It is clear that the proportion of Ni in the used samples was higher than that of the reduced samples. This can be explained on the basis that the oxidation of Ni was impaired by the deposited carbonaceous materials on the used samples.

1-4. BET Surface Area

Table 4 shows the BET surface areas for the fresh, reduced and used catalysts. There was no difference between the BET surface areas of the fresh, reduced and used $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$ samples within the test error. However, the BET surface area of the used $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ decreased sharply in comparison with that of the reduced $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$, resulting from the deterioration of $\gamma\text{-Al}_2\text{O}_3$ at high temperatures. The BET surface areas of the fresh $\text{Ni}/\theta\text{-Al}_2\text{O}_3$ (B), $\text{Ni}/\theta\text{-Al}_2\text{O}_3$ (C),

Table 3. The ratios of NiO to total Ni species over the catalysts obtained from XPS

Samples	$\text{Ni}/\alpha\text{-Al}_2\text{O}_3$		$\text{Ni}/\alpha\text{-Al}_2\text{O}_3$ (A)	
	R*	U	R	U
$I_{\sim 862}/(I_{\sim 862}+I_{\sim 853})$	0.298	0.227	0.294	0.238

*R: reduced samples; U: used samples

Table 4. Summary of the BET surface area of the catalysts

	BET surface area (m^2/g)		
	Fresh	Reduced	Used
$\text{Ni}/\alpha\text{-Al}_2\text{O}_3$	3	3	3
$\text{Ni}/\gamma\text{-Al}_2\text{O}_3$	191	160	141
$\text{Ni}/\theta\text{-Al}_2\text{O}_3$ (A)	145	101	96
$\text{Ni}/\theta\text{-Al}_2\text{O}_3$ (B)	96	-	88
$\text{Ni}/\theta\text{-Al}_2\text{O}_3$ (C)	85	-	78
$\text{Ni}/\theta\text{-Al}_2\text{O}_3$ (D)	90	-	83
$\text{Ni}/\alpha\text{-Al}_2\text{O}_3$ (E)	7	-	5

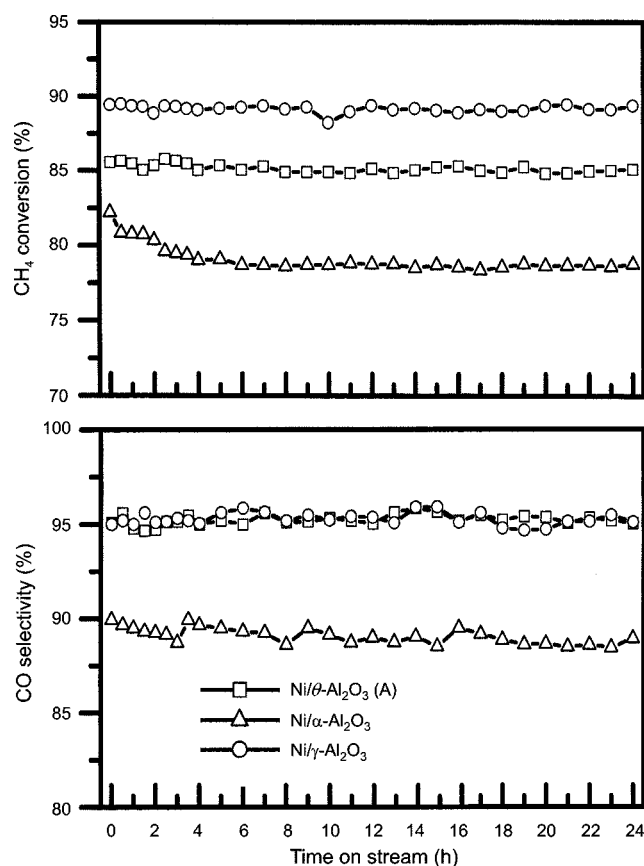


Fig. 6. Methane conversion and CO selectivity as a function of time on stream over $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$, $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Ni}/\theta\text{-Al}_2\text{O}_3$ (A) catalysts (Reaction conditions: $P=1\text{ atm}$, $T=1,018\text{ K}$ for $\text{Ni}/\theta\text{-Al}_2\text{O}_3$ (A) and $1,033\text{ K}$ for $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$ and $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$, $\text{CH}_4/\text{O}_2=1.95$, $\text{N}_2/(\text{CH}_4+\text{O}_2)=1$, $\text{GHSV}=27,600\text{ ml g}_{\text{cat}}^{-1}\text{ h}^{-1}$).

$\text{Ni}/\theta\text{-Al}_2\text{O}_3$ (D) are comparable with those of the corresponding used samples. In the case of $\text{Ni}/\theta\text{-Al}_2\text{O}_3$ (A), the BET surface area of the used sample was slightly decreased compared with that of the reduced sample. Moreover, all the used $\text{Ni}/\theta\text{-Al}_2\text{O}_3$ samples showed similar BET surface area, which suggests that the $\text{Ni}/\theta\text{-Al}_2\text{O}_3$ catalysts were obviously not sintered after POM for 24 h.

2. Catalytic Performance

Fig. 6 presents the results of POM at atmospheric pressure and total GHSV of $27,600\text{ ml g}_{\text{cat}}^{-1}\text{ h}^{-1}$. The reaction temperature of POM over $\text{Ni}/\theta\text{-Al}_2\text{O}_3$ (A) was $1,018\text{ K}$, and $1,033\text{ K}$ for $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$ and $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$. There was no obvious deactivation based on CH_4 conversion for $\text{Ni}/\theta\text{-Al}_2\text{O}_3$ (A) during 24 h of time on stream (TOS). However, CH_4 conversion for $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$ decreased gradually within the initial TOS of 4 h, and then became stable during the following TOS of 20 h. At the same time, CH_4 conversion for $\text{Ni}/\theta\text{-Al}_2\text{O}_3$ (A) was much higher than that of $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$ although the $\text{Ni}/\theta\text{-Al}_2\text{O}_3$ (A) catalyst was tested at a temperature of 15 K lower than that of $\text{Ni}/\theta\text{-Al}_2\text{O}_3$ catalyst. In the case of $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$, the highest CH_4 conversion was maintained for 24 h. The average stable selectivities of CO for $\text{Ni}/\theta\text{-Al}_2\text{O}_3$ (A), $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$ catalysts were 95.2%, 95.3 and 89.1%, respectively.

The performance of $\text{Ni}/\theta\text{-Al}_2\text{O}_3$ catalysts, whose supports were pretreated at different conditions, is given in Fig. 7. It is clear that all the catalysts showed stable CH_4 conversions during 24 h of TOS.

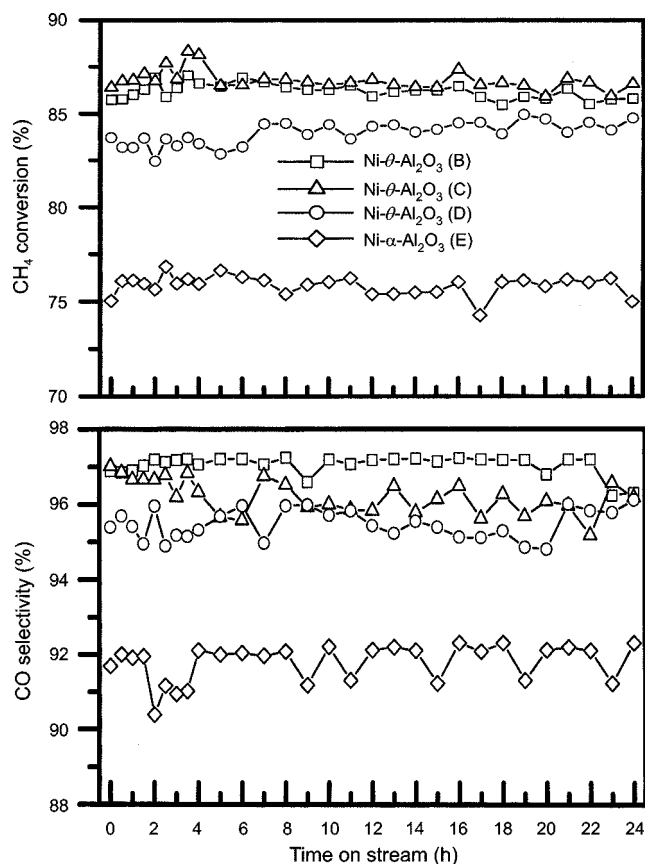


Fig. 7. Methane conversion and CO selectivity as a function of time on stream over Ni/ θ -Al₂O₃ catalysts (Reaction conditions: P=1 atm, T=1,018 K, CH₄/O₂=1.95, N₂/(CH₄+O₂)=1, GHSV=27,600 ml g_{cat}⁻¹ h⁻¹).

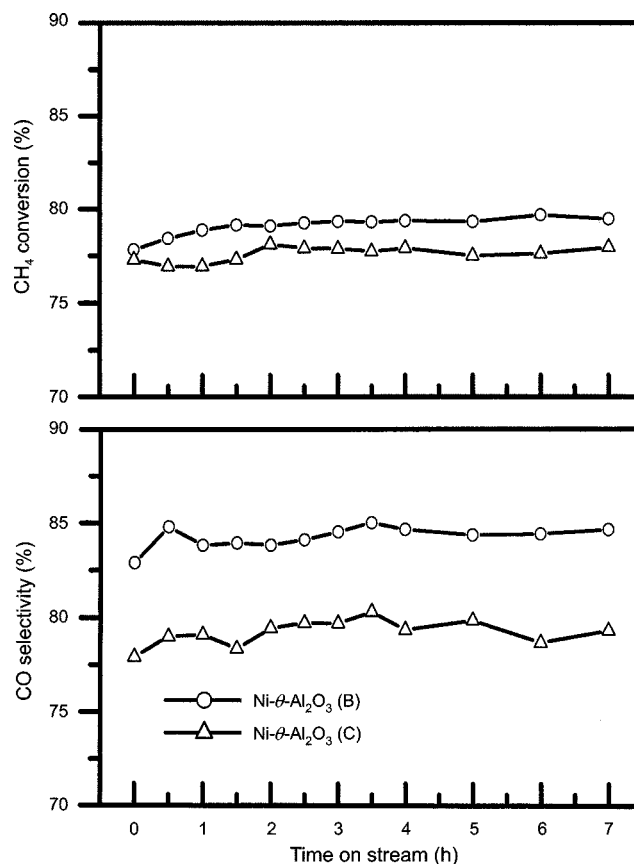


Fig. 8. Methane conversion and CO selectivity as a function of time on stream over Ni/ θ -Al₂O₃ catalysts (Reaction conditions: P=1 atm, T=1,018 K, CH₄/O₂=1.95, N₂/(CH₄+O₂)=1, GHSV=276,000 ml g_{cat}⁻¹ h⁻¹).

Among them, Ni/ α -Al₂O₃(E) showed the lowest CH₄ conversion of about 75%, which is similar to that over Ni/ α -Al₂O₃. However, both Ni/ θ -Al₂O₃(B) and Ni/ θ -Al₂O₃(C) showed higher CH₄ conversion of about 86%, which is almost the same as that over Ni/ θ -Al₂O₃(A). When compared with Ni/ θ -Al₂O₃(B) and Ni/ θ -Al₂O₃(C), Ni/ θ -Al₂O₃(D) showed slightly lower CH₄ conversion of about 84% although three catalysts showed similar stability during the test for 24 h. Related to the CO selectivity, only Ni/ α -Al₂O₃(E) showed slightly lower value (92%) than the others, which gave about 95% CO selectivity.

To further evaluate the performance of the catalysts, Ni/ θ -Al₂O₃(B) and Ni/ θ -Al₂O₃(C) were tested at higher space velocity and the results are shown in Fig. 8. In comparison with Fig. 7, it is clear that the CH₄ conversion over the two catalysts was lower obviously at higher space velocity. Moreover, Ni/ θ -Al₂O₃(B) catalyst showed slightly higher CH₄ conversion and CO selectivity than Ni/ θ -Al₂O₃(C) catalyst did.

3. Discussion

In combining the results shown in Fig. 6 to Fig. 8 and Table 1, we can see that the activity of the catalysts strongly depends on the phase and surface area of the supports, which are determined by calcination conditions. As POM must be carried out at high temperatures, thermal stability of the support for POM catalyst is required. However, as the temperature for calcining the support is too

high, the supported catalyst showed low activity. Therefore, the calcination conditions for preparing the support must be optimized to obtain a catalyst with both high activity and stability. The present results support the above idea.

Ni/ α -Al₂O₃(E) and Ni/ α -Al₂O₃ showed lower CH₄ conversion and CO selectivity as a result of low surface area of the supports. Over Ni/ α -Al₂O₃(E) and Ni/ α -Al₂O₃, as revealed from XRD in which sharp diffraction peaks were observed for Ni or NiO, larger NiO or Ni particles were formed as a result of the very low surface area of the supports. This is consistent with the TPR results. The fresh Ni/ α -Al₂O₃ showed almost the same TPR pattern as free NiO [Roh, 2001d], which suggests that the interaction between NiO and α -Al₂O₃ is very weak. So, the two factors, e.g. bigger particle size of NiO and weak interaction between NiO and α -Al₂O₃, are responsible for the lower activity of Ni/ α -Al₂O₃ and Ni/ α -Al₂O₃(E).

In the case of Ni/ γ -Al₂O₃, the highest CH₄ conversion was observed for POM. This may be related partly to the smallest particle size of Ni among all the samples as a result of the highest surface area of the γ -Al₂O₃ support. Moreover, TPR results [Roh, 2001d] indicate that two high temperature peaks, which can be assigned to the reduction of NiO_x species and highly dispersed NiAl₂O₄ species, appeared for the fresh Ni/ γ -Al₂O₃. This suggests that there exists strong interaction between NiO and γ -Al₂O₃. But, from the BET results, a great loss of surface area occurred when the sample was

applied to POM for TOS of 24 h, which is mainly caused by the deterioration of the thermally unstable $\gamma\text{-Al}_2\text{O}_3$. So, as expected, a long-term stability for Ni/ $\gamma\text{-Al}_2\text{O}_3$ cannot be expected from the above fact.

In our previous study, Ni/ $\theta\text{-Al}_2\text{O}_3$ (A) was developed and applied to POM in a quartz reactor and the catalytic activity was maintained for 100 h. First, as broad diffractions were observed in XRD, the Ni dispersed over $\theta\text{-Al}_2\text{O}_3$ (A) with an appropriate high surface area has a smaller particle size. The TPR results of 12 wt% Ni/ $\theta\text{-Al}_2\text{O}_3$ (A) showed that the main reduction peak can be ascribed to the reduction of NiO_x species having strong interaction with support [Roh et al., 2001c]. The high activity of Ni/ $\theta\text{-Al}_2\text{O}_3$ (A) was ascribed mainly to the existence of NiO_x species other than NiAl_2O_4 over the fresh catalyst. Although the Ni particle size of Ni/ $\theta\text{-Al}_2\text{O}_3$ (A) was increased after being used in POM for 24 h in comparison with that of the reduced sample, there was only about 5% loss of BET surface area after POM, which suggests that the sintering of the catalyst is not obvious. Therefore, the high activity and stability of Ni/ $\theta\text{-Al}_2\text{O}_3$ (A) catalyst can be ascribed to the smaller particle size of Ni, the existence of NiO_x species, stable $\theta\text{-Al}_2\text{O}_3$ phase and strong interaction between NiO and $\theta\text{-Al}_2\text{O}_3$.

$\theta\text{-Al}_2\text{O}_3$ (B), $\theta\text{-Al}_2\text{O}_3$ (C) and $\theta\text{-Al}_2\text{O}_3$ (D) supports showed very similar BET surface area. Moreover, Ni/ $\theta\text{-Al}_2\text{O}_3$ (B) and Ni/ $\theta\text{-Al}_2\text{O}_3$ (C) showed very similar CH_4 conversion and CO selectivity, which are slightly higher than those of Ni/ $\theta\text{-Al}_2\text{O}_3$ (D) at a relatively lower space velocity while Ni/ $\theta\text{-Al}_2\text{O}_3$ (B) showed a slightly higher CH_4 conversion and CO selectivity at a relatively higher space velocity. This may be caused by some structural differences between the supports calcined at 1,223 K and 1,173 K. According to the above results and discussion, it can be suggested that 1,173 K is an optimal temperature to prepare $\theta\text{-Al}_2\text{O}_3$. There was a sharp decrease of surface area when $\gamma\text{-Al}_2\text{O}_3$ was heat treated at 1,173 K from 6 h to 12 h, while there was no further obvious decrease when the calcining time was extended to 24 h. At the same time, the used Ni/ $\theta\text{-Al}_2\text{O}_3$ (A), Ni/ $\theta\text{-Al}_2\text{O}_3$ (B), Ni/ $\theta\text{-Al}_2\text{O}_3$ (C) samples under the same operating conditions had almost the same BET surface area. Moreover, among the three samples, Ni/ $\theta\text{-Al}_2\text{O}_3$ (B) showed a slightly higher activity toward POM at a relatively higher space velocity while very similar stability was obtained for the above-mentioned three catalysts. Thus, one can infer that the optimal conditions for the preparation of $\theta\text{-Al}_2\text{O}_3$ are 1,173 K and 12 h. Furthermore, a long-term stability of Ni/ $\theta\text{-Al}_2\text{O}_3$ (B) toward POM can be reasonably expected.

CONCLUSIONS

Conclusions drawn from this investigation are summarized as follows:

1. All the Ni/ $\theta\text{-Al}_2\text{O}_3$ catalysts showed high activity toward POM ascribed to the elimination of inactive NiAl_2O_4 species, the existence of NiO_x species and stable $\theta\text{-Al}_2\text{O}_3$ phase.
2. The optimal conditions for the preparation of $\theta\text{-Al}_2\text{O}_3$ support are 1,173 K and 12 h. From the present results, a long-term stability of Ni/ $\theta\text{-Al}_2\text{O}_3$ (B) for POM can be reasonably expected.
3. The oxidation of the dispersed Ni under atmospheric conditions is very limited. Moreover, the proportion of Ni in the used samples is higher than that in the reduced samples ascribed to the

deposited carbonaceous materials, which impair the oxidation of Ni.

4. The surface Ni/Al molar ratio versus Ni loading curve displays a remarkable linearity in the Ni loading ranged from 3 to 15 wt%, which indicates that Ni is dispersed very well over the support and there is no obvious particle size variation with the increase of Ni loading.

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