Partial Oxidation of Methane over Ni/θ-Al_2O_3 Catalysts

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(Received March 19, 2001; CL-010241)

Ni/θ-Al_2O_3 exhibits remarkably high catalytic activity and stability in partial oxidation of methane to synthesis gas. It gives more than 98% CH_4 conversion, 98% H_2 selectivity and 100% CO selectivity at 850 °C and the activity was maintained for 100 h.

Catalytic partial oxidation of methane (POM) has received much attention as a promising alternative to steam reforming of methane (SRM) due to mild exothermicity, high conversion, high selectivity, suitable H_2/CO ratio (=2.0), and very short residence time.[1–3]

As a catalyst for the POM reaction, Ni/γ-Al_2O_3 catalyst has been used.[4] However, Ni/γ-Al_2O_3 is usually unstable at high temperature (> 700 °C) because of the thermal deterioration of the γ-Al_2O_3 support as well as phase transformation into α-Al_2O_3. Therefore, it is necessary to modify γ-Al_2O_3 support in order to obtain thermally stable support for the POM reaction like Xiong and co-workers,[5] who modified Ni/γ-Al_2O_3 with alkali metal oxide and rare earth metal oxide. By the way, Liu and co-workers[6] reported that the catalyst surface with coexistence of both Ni^0 sites and NiO_x species was active and selective for the POM reaction. Also, we reported that Ni/Ce–ZrO_2 showed highly stable activity in POM owing to the strong interaction between Ni and Ce–ZrO_2 and mobile oxygen species.[3] Therefore, we aimed to prepare stable Ni/θ-Al_2O_3 catalyst having NiO_x species and strong interaction between Ni and θ-Al_2O_3, which overcomes the demerits of Ni/γ-Al_2O_3 catalyst without further modification. Consequently, we have successfully performed the POM reaction over Ni/θ-Al_2O_3 with high activity as well as high stability.

Supports employed in this study were γ-Al_2O_3 (S_{BET} = 234 m^2/g), θ-Al_2O_3 (S_{BET} = 167 m^2/g), and α-Al_2O_3 (S_{BET} = 1 m^2/g). θ-Al_2O_3 was prepared by calcining γ-Al_2O_3 for 6 h after the temperature reaching 900 °C by careful heating with the heating rate of 1 °C/min. Supported Ni catalysts were prepared by the impregnation of appropriate amounts of $Ni(NO_3)_2 \cdot 6H_2O$ onto supports followed by drying at 100 °C and calcining at 550 °C for 6 h in air. Activity tests were carried out using a conventional fixed-bed microreactor. The detailed procedures for the reaction and TPR were described elsewhere.[3,7] The supported Ni catalysts (3 wt% Ni) mentioned above were tested at 750 °C and space velocity of 55200 $cm^3/h \cdot g_{cat}$, and the change in CH_4 conversion with time on stream are presented in Figure 1. In the case of Ni/α-Al_2O_3 catalyst, the activity decreased gradually with increasing time due to the carbon which was formed during the reaction. Ni/γ-Al_2O_3 showed relatively high initial activity (68% conversion), but the activity decreased slowly but steadily with time due to the phase transformation. However, Ni/θ-Al_2O_3 exhibited the highest activity (77% CH_4 conversion) as well as high stability. The activity was maintained for 100 h during a prolonged test. Thus, it is confirmed that Ni/θ-Al_2O_3 showed higher activity than those of Ni/α-Al_2O_3 and Ni/γ-Al_2O_3 as well as high stability without further modification.

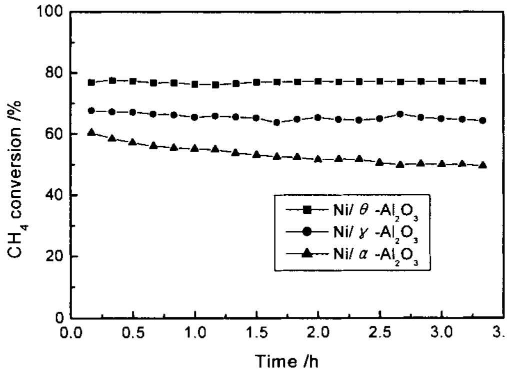

Figure 1. CH_4 conversion with time on stream over 3% Ni/support systems. Reaction conditions: P = 1 atm, T = 750 ℃, CH_4/O_2 = 1.875, GHSV = 55200 $cm^3/h \cdot g_{cat}$.

Table 1 summarizes the Ni content effect on CH_4 conversion, H_2 selectivity, CO selectivity, and H_2/CO ratio over Ni/θ-Al_2O_3. Both CH_4 conversion and selectivity to H_2 and CO increased with the rise of Ni loading up to 12%, and above this level decreased. All the catalysts showed stable activities without any significant decrease during the reaction process. Especially, 12% Ni/θ-Al_2O_3 exhibited the highest CH_4 conversion (90%), H_2 selectivity (93%), and CO selectivity (93%). H_2/CO ratios of the catalysts were 2.0 except 2% and 15% Ni loading. This is due to the fact that 2% Ni/θ-Al_2O_3 has less Ni^0 sites and 15% Ni/θ-Al_2O_3 has relatively large amounts of free Ni sites resulting in Ni sintering, which will be explained later. The activities of 12% Ni/θ-Al_2O_3 with various GHSV and temperature were tested. GHSV effect was not so significant. The conversion was almost unchanged without regard to GHSV.

Table 1. CH_4 conversion, H_2 selectivity, CO selectivity, and H_2/CO ratio over Ni/θ-Al_2O_3 catalyst (Reaction conditions: P = 1 atm, T = 750 ℃, CH_4/O_2 = 1.875, GHSV = 55200 $cm^3/h \cdot g_{cat}$)

Ni content /%	X_{CH4} /%	S_{H2} /%	S_{CO} /%	H_2/CO ratio
2	13	40	65	1.1
3	77	87	86	2.0
6	86	90	89	2.0
9	87	90	90	2.0
12	90	93	93	2.0
15	86	85	89	1.9

But temperature had significant effect on activities. CH_4 conversions were 93–94% at 800 °C showing a little change with GHSV, and 97–98% at 850 °C. The selectivities to H_2 and CO at 850 °C were 98% and 100%, respectively.

Table 2. Comparison of the activities depending on the catalyst

Catalyst	X_{CH4} /%	S_{H2} /%	S_{CO} /%	H_2/CO ratio	ref
Ni/θ-Al_2O_3	90	93	93	2.0	This work
Ni/Ce-ZrO_2	85	98	89	2.1	3
Ni/MgO	78	97	85	2.3	3

Reaction conditions: P = 1 atm, T = 750 ℃, CH_4/O_2 = 1.875, GHSV = 55200 $cm^3/h{\cdot}g_{cat}$.

Table 2 compares the results over 12% Ni/θ-Al_2O_3 with those of Ni/Ce–ZrO_2[3] and Ni/MgO,[3] which have been reported as the best candidates for the POM reaction. The experimental condition for Ni/Ce–ZrO_2 and Ni/MgO is same as that of Ni/θ-Al_2O_3. Ni/θ-Al_2O_3 shows the highest CH_4 conversion, H_2 yield, and CO yield. Also, it gives the most suitable H_2/CO ratio (= 2.0). Thus, this table clearly shows that Ni/θ-Al_2O_3 has higher activity than Ni/Ce–ZrO_2 and Ni/MgO, strongly indicating that Ni/θ-Al_2O_3 is the best catalytic system in the POM reaction.

This fact that Ni supported on θ-Al_2O_3 showed high activity and stability can be explained as follows. Firstly, θ-Al_2O_3 support is stable at high temperature because it has been treated at 900 °C. Secondly, Ni/θ-Al_2O_3 system has both Ni^0 sites and NiO_x species, which are necessary to perform the POM reaction effectively. The existence of NiO_x is confirmed by TPR results (Figure 2). Liu and co-workers[6] explained that the POM reaction over Ni/γ-Al_2O_3 proceeds via a CH_4 pyrolysis, followed by the reduction of NiO_x by surface C atoms, which is reoxidized by adsorbing oxygen from feed gas. Thirdly, The existence of the strong interaction between Ni and θ-Al_2O_3, results in preventing carbon formation and Ni sintering during the reaction. TPR patterns of Ni/θ-Al_2O_3 with various Ni loading illustrate three distinct peaks. One (peak maximum = 480 °C) is attributable to the reduction of relatively free NiO species. The second peak (peak maximum = 640 °C) can be assigned to the complex NiO_x species which have the strong interaction with θ-Al_2O_3. And the third peak, appearing at 800 °C, is attributed to highly dispersed $NiAl_2O_4$ species. Compared with TPR patterns of Ni/θ-Al_2O_3, Ni/γ-Al_2O_3 shows only a strong high temperature peak at 800 °C with a fresh catalyst. According to Liu and co-workers' results,[6] TPR patterns of the reduced catalysts and the fresh catalyst following the POM reaction showed peaks with maxima at 520–560 °C and no peak appeared at 800 °C, indicating that NiO_x species were formed during the reaction. However, Ni/θ-Al_2O_3 shows NiO_x species with the fresh catalyst. This means that Ni was deposited on the thermally stable θ-Al_2O_3 so that NiO_x species are formed rather than $NiAl_2O_4$. Thus, it can be strongly expected that NiO_x species over Ni/θ-Al_2O_3 are more stable and effective in POM than those over Ni/γ-Al_2O_3. The retardation of NiO_x reduction, compared with that over Ni/γ-Al_2O_3, can be interpreted as the strong interaction between NiO_x species and θ-Al_2O_3. According to our previous results,[3,7] the strong interaction between Ni and support results in stable activity without catalyst deactivation in POM or SRM. Ni/θ-Al_2O_3 shows different TPR patterns depending on Ni loading. 2%-Ni loading catalyst shows only reduction peak of $NiAl_2O_4$, over which low CH_4 conversion (12%) and low selectivity to H_2 and CO were measured (Table 1). Therefore, it is clear that NiO_x species are necessary to perform the POM reaction with high activity and selectivity. NiO_x reduction peaks can be seen over the catalysts having more than 3%-Ni loading, which is good consistent with the high activities over these catalysts. 6%-Ni catalyst clearly shows 3 distinct peaks, which are assigned above. For 12% Ni system, 3 peaks can be seen but the first and the third peak appears as a shoulder. However, 15% Ni/θ-Al_2O_3 clearly shows the first peak, suggesting the existence of the relatively large amounts of free NiO sites. These sites may result in Ni sintering and carbon formation. Consequently, the activity of 15% Ni/θ-Al_2O_3 was lower than that of 12%-Ni loading. Based on the above results it can be suggested that Ni/θ-Al_2O_3 is partially oxidized under the POM condition and the partially oxidized sites produce active oxygen species, which may react with the deposited carbon or prevent the carbon formation, and then is reoxidized with oxygen molecules from feed gas.

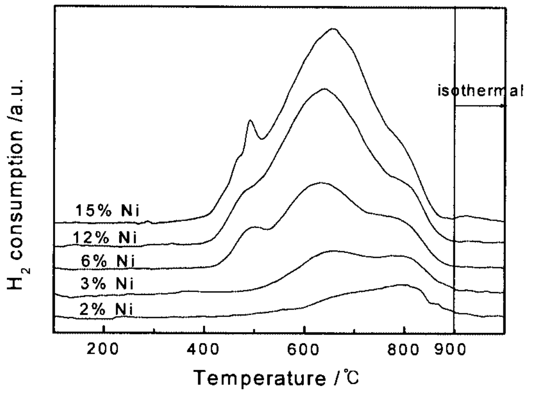

Figure 2. TPR patterns of Ni/θ-Al_2O_3 with various Ni loading.

In summary, Ni/θ-Al_2O_3 catalyst reveals high activity as well as high stability in the POM reaction compared with generally reported catalytic systems such as Ni/MgO and Ni/Ce–ZrO_2. The high catalyst activity and stability are mainly ascribed to the combination of the strong interaction between Ni and θ-Al_2O_3 and the coexistence of Ni^0 and NiO_x species.

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