1. Introduction

Partial oxidation of methane/hydrocarbons to produce syngas (H₂ and CO) or hydrogen is an important and useful conversion. Steam reforming of methane/hydrocarbons is a well-known reaction for this process, but the reforming reaction is highly endothermic, requiring huge external input of heat. In contrast, partial oxidation of methane (POM) is a mild exothermic reaction that produces syngas directly, and the H₂/CO ratio of the product is 2 (Eq. (1)), which is suitable for downstream conversion processes such as Fisher-Tropsch synthesis and methanol synthesis.

\[
\text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow 2\text{H}_2 + \text{CO} \quad \Delta H^{\circ} = -206.2 \text{ kJ mol}^{-1}
\]

Two reaction routes have been postulated for POM\(^1\): (a) direct partial oxidation at high temperature (DPO or DCPO: direct catalytic partial oxidation) and (b) indirect oxidation through combustion and steam-reforming or dry-reforming (CRR: combustion and reforming reaction). In fact, DPO is a high space-velocity reaction which occurs at high temperatures of more than 1000 K. The best known catalysts for DPO are expensive Rh catalysts such as Rh\text{-CeO}_2/MgO\(^2\), and Rh/Al\text{O}_3\(^3\). Indirect POM (CRR) has been investigated widely over many metal catalysts such as Pt, Ir, and Ni\(^4\). These studies have required high reaction temperatures (973-1073 K) because of the equilibrium limitation of the endothermic steam reforming of methane. Therefore, reducing the reaction temperature is important to increase the energy efficiency for the exothermal POM reaction, but POM at low reaction temperatures has received little attention. Low temperature POM was achieved at 723-623 K on Ni-based catalysts using a temperature programmed reaction (TPR) with decreasing temperature\(^5\). Generally, TPR with decreasing temperature shows reduced activity because TPR is not a steady state reaction. Noble metals such as Pt, Ir, Ru, and Rh are known to be highly active catalysts for POM\(^6\), but these metals are expensive. Therefore, less expensive transition metal catalysts are desirable for this reaction. Actually, Ni shows high activity, but carbon deposition is difficult to inhibit over Ni catalyst. To inhibit carbon deposition, Ni catalysts have been modified with various basic oxides. In particular, La is widely used for the catalyst support\(^7\)\(^-\)\(^9\); La\text{O}_2 has good properties to suppress carbon deposition on the catalyst\(^10\). Low temperature partial oxidation of methane has also been achieved with La-containing catalyst, but the minimum temperature for POM (= ignition temperature of POM) was not lower than 773 K\(^10\)\(^-\)\(^20\).

The present study investigated low temperature partial oxidation of methane to syngas over Ni catalyst supported on La-containing oxide, which proceeded below 773 K and under steady state conditions (i.e. not a temperature-decreasing reaction). Two methods...
were applied to enhance the catalytic activity for POM at low temperature: application of modified La-containing oxide support; and additional impregnation of a second metal on the Ni/La-oxide catalyst.

2. Experimental

2.1. Preparation of Catalyst

Various Ni catalysts supported on La-containing oxides were prepared. La-containing oxides were prepared using a citric acid method as follows. Precursors La(NO$_3$)$_3$·6H$_2$O and transition metal nitrates were dissolved into distilled water with subsequent addition of an aqueous solution of ethylene glycol and citric acid. After heating at 353 K in a water bath for 18 h, the solvent was evaporated completely. The resultant complex was calcined at 673 K for 2 h and at 1123 K for 10 h. As a control support, $\alpha$-Al$_2$O$_3$ was prepared by calcination of $\gamma$-Al$_2$O$_3$ (JRC-ALO-8) at 1573 K for 3 h using a muffle furnace. Ni-supported catalysts were prepared using an impregnation method with aqueous solution of Ni nitrate on the support. The amount of supported Ni was 6.6 wt%. Prepared catalysts were dried at 393 K for 18 h and calcined at 1073 K for 1 h in air, and then crushed and pressed to obtain 250-355 mm diameter particles. The sequential impregnation of second metal was conducted after preparation of the Ni-supported catalyst.

2.2. Catalytic Activity Tests

The POM reaction was conducted at atmospheric pressure in a fixed-bed reactor consisting of a quartz tube, containing 80 mg of catalyst charged with 350 mg of SiC as diluent to avoid the formation of hot spots. Pre-reduction was performed in a mixed stream of H$_2$ at 10 mL min$^{-1}$ and Ar at 100 mL min$^{-1}$ at 1023 K for 0.5 h. Then the reactant gases (CH$_4$/O$_2$/Ar = 2/1/3, total flow rate 420 mL min$^{-1}$, W/F = 0.233 g h mol$^{-1}$) were introduced into the reactor. A cold trap at the reactor outlet was used to remove water from the effluent gas. The dried gas was analyzed using a FID gas chromatograph with a Porapak Q packed column (for analyzing CH$_4$, CO, CO$_2$) with methanation at 673 K using Ru catalyst, and a TCD gas chromatograph with a molecular sieve 5A packed column (for analyzing H$_2$, O$_2$). Typically, >97% of carbon mass balance was confirmed, and the reproducibility of the activity tests was within 98-103%. The respective conversions of methane and oxygen, selectivity for each product, and hydrogen yield are defined by the following Eq. (2):

$$\text{CH}_4 \text{ conversion (%) } = \frac{\Sigma \text{ Production rate of CO or CO}_2}{\text{Methane feed}} \times 100 \quad (2)$$

$$\text{O}_2 \text{ conversion (%) } = \frac{\text{Consumed O}_2}{\text{Feed O}_2} \times 100 \quad (3)$$

To elucidate the active site for POM, CH$_4$ pulse testing was conducted using a fixed-bed micro reactor connected with a TCD gas chromatograph. The CH$_4$ pulses were injected with a syringe as shown in Fig. 1. For evaluating the activity of reduced Ni (operation 1), the catalyst was preliminarily reduced in a fixed bed reactor under the same conditions as the pre-reduction (step 1). A 30 mg sample of reduced catalyst was charged into the fixed-bed micro reactor connected with a TCD gas chromatograph (step 2). Then, 3 pulses of 0.6 mL H$_2$ were introduced into the micro reactor at 1023 K to reduce the catalyst surface. These procedures (steps 1 and 3) resulted in thorough reduction of the supported Ni. To investigate the reactivity of CH$_4$ over such metallic Ni, 3 pulses of 0.1 mL CH$_4$ were introduced into the catalyst bed at 673 K (step 4). Additionally, the activity of oxidized Ni was also investigated by operation 2. Five pulses of 0.8 mL air were injected to oxidize the surface of the catalyst (step 2), then 3 pulses of 0.1 mL CH$_4$ were introduced at 673 K (step 3). The amount of O$_2$ in these air pulses was excess for the oxidation of all Ni particles in these samples.

2.3. Characterization

Crystalline structures of catalysts were characterized by X-ray diffraction (XRD) using an X-ray diffractometer (RINT-2000; Rigaku Corp.) operating at 40 kV and 20 mA, with CuK$_\alpha$ radiation filtered by nickel. The specific surface area of the support was measured by N$_2$ adsorption using the BET method (AUTOSORB-1; Quantachrome Instruments). Scanning transmission
microscopy (STEM, HF-2210; Hitachi, Ltd.) and energy dispersive X-ray spectroscopy (EDX, Genesis4000; EDAX Inc.) were used to observe the structure of the supported metal. To estimate the amount of carbon deposition, temperature programmed oxidation (TPO) of the catalyst was also conducted after the reaction. The TPO profile was obtained in O2 and N2 flow (O2/N2 1/9, total flow rate of 100 mL min⁻¹) at a heating rate of 10 K min⁻¹. To evaluate the reducibility of the supported Ni, temperature programmed reduction (TPR) was performed using a TG apparatus (Thermo plus EVO; Rigaku Corp.). Before the TPR, the sample was heated at 1073 K for 0.5 h in a muffle furnace. The sample was then heated at 10 K min⁻¹ from room temperature to 1023 K in a flow of 10 % H2 90 % N2 at 100 mL min⁻¹.

3. Results and Discussion

3.1. POM Activity of Ni/La2O3, Ni/α-Al2O3, and Ni/LaAlO3 Catalysts

Nickel catalysts supported on La2O3 and α-Al2O3 are well known as good catalysts for POM10)16). First, Ni catalysts supported on La2O3 and α-Al2O3 were prepared for the basic evaluation of the catalytic activity for POM at various temperatures. Table 1 shows the POM activity of Ni/La2O3 and Ni/α-Al2O3. These catalysts showed high POM activity at high temperature, but no activity below 723 K. At the low temperature of 673 K, Ni/La2O3 and Ni/α-Al2O3 catalysts caused no combustion activity: the initial step in the indirect route reaction.

We attempted to achieve low temperature POM ignition by controlling the nature of the catalyst support. La-containing perovskite oxide is well known to have CO or CH4 oxidation ability22,23). We compared several Ni catalysts supported on La-containing perovskite oxides (LaBO3) such as LaAlO3, LaFeO3, LaCoO3, and LaMnO3, with Ni catalysts supported on La2O3 and α-Al2O3. Among these catalysts, only Ni/LaAlO3 catalyst showed high activity at 673 K with pre-reduction (not shown). In particular, the pre-reduced Ni/LaAlO3 catalyst showed 52.3 % methane conversion and 100 % oxygen conversion even at 673 K as shown in Table 1. TPO analysis observed no carbon deposition on Ni/LaAlO3 catalyst after the POM activity test for 3 h, and the catalyst showed stable activity for a long time. No other Ni catalysts showed any activity at 673 K.

We examined POM activity over Ni/LaAlO3 catalyst in a wide temperature range with or without pre-reduction. Although Ni/LaAlO3 catalyst showed high activity without pre-reduction at 823 K and 773 K, no activity was observed at 723 K and 673 K without pre-reduction. On the other hand, Ni/LaAlO3 catalyst showed high activity with pre-reduction even at 673 K. Therefore, pre-reduction of supported Ni was important for low temperature ignition on Ni/LaAlO3 catalyst.

Next, we considered steady state activity over Ni/LaAlO3 catalyst at 673 K. The equilibrium conversion of methane and product compositions was calculated based on the indirect route (CRR) assumption. Methane conversion over Ni/LaAlO3 catalyst at 673 K was higher than the thermodynamic equilibrium conversion at 673 K, as shown in Table 1. The difference between the experimentally obtained results and calculated results for the equilibrium gas composition for selectivity to CO/CO2 and H2 yield could apparently be explained by the temperature increase of about 150 K in the catalyst bed caused by the combustion heat. The catalyst bed in POM has a temperature distribution21,4,24). The temperature at the introduction part of the catalyst bed is higher than that at the bottom part of the catalyst bed, because CH4 combustion (exothermic) proceeds at the introduction part of the catalyst bed, and steam- and dry-reforming (both endothermic) proceed at the bottom part of the catalyst bed.

| Catalyst        | Temperature [K] | CH4 conversion [%] | O2 conversion [%] | CO selectivity [%] | CO2 selectivity [%] | H2 yield [%] |
|-----------------|-----------------|--------------------|-------------------|-------------------|---------------------|------------|
| Ni/La2O3        | 773             | 40.7               | 100.0             | 50.0              | 49.2                | 22.4       |
| Ni/La2O3        | 723             | 0.0                | 0.0               | -                 | -                   | 0.0        |
| Ni/α-Al2O3      | 723             | 60.0               | 100.0             | 66.2              | 33.8                | 51.6       |
| Ni/α-Al2O3      | 673             | 1.2                | 2.7               | 46.2              | 53.8                | 0.0        |
| Ni/LaAlO3       | 823             | 68.5               | 100.0             | 78.7              | 21.3                | 58.1       |
| Ni/LaAlO3       | 773             | 61.6               | 100.0             | 70.1              | 29.9                | 44.9       |
| Ni/LaAlO3       | 723             | 1.2                | 2.7               | 29.4              | 70.6                | 0.0        |
| Ni/LaAlO3       | 673             | 0.0                | 0.0               | -                 | -                   | 0.0        |
| Ni/LaAlO3       | 723             | 57.3               | 100.0             | 65.1              | 34.9                | 46.6       |
| Ni/LaAlO3       | 673             | 52.3               | 100.0             | 56.9              | 43.1                | 40.1       |
| Ni/LaAlO3       | 623             | 0.0                | 1.3               | -                 | -                   | 0.0        |
| Pd/Ni/LaAlO3    | 673             | 49.9               | 100.0             | 53.1              | 46.9                | 37.1       |
| Pd/Ni/LaAlO3    | 623             | 0.0                | 0.0               | -                 | -                   | 0.0        |
| Equilibrium     | 823             | 50.6               | 100.0             | 47.7              | 52.3                | 38.6       |
|                 | 673             | 30.0               | 100.0             | 0.0               | 100.0               | 10.2       |

a) Catalyst was pre-reduced in a hydrogen flow at 1023 K.
thermodynamic equilibrium of indirect POM is dominated by the steam-/dry-reforming and water gas shift; CH₄ combustion completely proceeds under the CRR assumption. We inferred that the temperature at the bottom of the catalyst bed was about 823 K, and the temperature at the introduction part of the catalyst bed was higher than 823 K.

3.2. Structure of Ni Catalysts

We found that POM ignition at 673 K was observed on only Ni/LaAlO₃ catalyst with pre-reduction, whereas neither Ni/La₂O₃ catalyst nor Ni/α-Al₂O₃ catalyst had POM activity at 673 K. To elucidate the involvement of the catalyst support, we characterized the structures and physical/chemical properties of these catalysts. The BET specific surface area of prepared catalysts was measured using the N₂ adsorption method. Ni/La₂O₃, Ni/α-Al₂O₃, and Ni/LaAlO₃ catalysts had very low surface areas, less than 10 m² g⁻¹, specifically 4.6 m² g⁻¹ for Ni/La₂O₃, 6.0 m² g⁻¹ for Ni/α-Al₂O₃, and 7.3 m² g⁻¹ for Ni/LaAlO₃. Only small differences were detected between these catalysts, so the high activity of Ni/LaAlO₃ catalyst cannot be explained by the BET specific surface area.

XRD measurement was also conducted to elucidate the crystalline structure of these catalysts. Figure 2 shows the XRD spectra of Ni/La₂O₃, Ni/α-Al₂O₃, and Ni/LaAlO₃ catalysts before and after pre-reduction. For all these catalysts, supported Ni was reduced to metallic Ni after pre-reduction at 1023 K. Ni particles on the Ni/LaAlO₃ catalyst without pre-reduction were contained in NiO and LaNiO₃ structures, and the catalyst did not show POM activity at 673 K. Therefore, metallic Ni particles are important in the catalyst activity.

To compare the nature of supported Ni on La₂O₃, α-Al₂O₃, and LaAlO₃ supports, the diameter of the Ni particles was measured using STEM-EDX after pre-reduction at 1023 K. Figure 3 shows the observed size distributions of Ni particles. Ni/La₂O₃ and Ni/α-Al₂O₃ catalysts had smaller Ni particles (mode 17.0 nm, median 19.6 nm for Ni/La₂O₃, and mode 11.0 nm, median 19.2 nm for Ni/α-Al₂O₃) than Ni/LaAlO₃ catalyst (mode 18.0 nm, median 23.3 nm). TPR was also performed on Ni/La₂O₃, Ni/α-Al₂O₃, and Ni/LaAlO₃ catalysts to elucidate the reducibility of Ni particles on these catalyst supports. In this case, weight loss for NiO→Ni was responsible for weight decrease of ca. 1.8 %. To clarify the temperature of reduction start, DTG (differential value of TG by temperature) was obtained from the TG profile of the TPR. Figure 4 shows the TPR profiles and DTG profiles for these catalysts. In the case of Ni/La₂O₃ catalyst, reduced Ni particles were generated by the reduction of NiO or the decomposition of LaNiO₃ phase during pre-reduction at 1023 K (Fig. 2). In the TPR, weight loss was observed at over 400 K. We considered that the weight loss of about 1 wt% in 400-650 K region was derived from the desorption of adsorbed water or decomposition of La hydroxide. We assigned the weight loss of about 1.8 wt% from 650 to 1023 K as metallic Ni formation from NiO or LaNiO₃. DTG of Ni/La₂O₃
showed a peak corresponding to the reduction of Ni at about 760 K, at a higher temperature than for Ni/LaAlO3. These reduced Ni particles on La2O3 strongly interacted with the support. STEM showed that Ni/α-Al2O3 also had smaller Ni particles than Ni/LaAlO3, and the temperature of reduction start of NiO was also about 760 K. Ni particles on α-Al2O3 were highly dispersed and interacted strongly with Al2O3 support, and the phenomenon coincides with previous findings.25) Compared with Ni/La2O3 and Ni/α-Al2O3 catalysts, Ni/LaAlO3 catalyst had the largest Ni particle diameter, and lowest temperature of reduction starting at 680 K (Figs. 3 and 4). The interaction between Ni particles and LaAlO3 support was weaker than for the other two Ni catalysts. These phenomena coincide with previous reports (e.g., ref.33).

To elucidate the relationship between the reducibility of Ni particles and the catalytic activity for POM, we conducted pulse tests using reduced Ni catalysts and oxidized Ni catalysts on various supports. CH4 pulse testing results in operation 1 are summarized in Table 2. Here we assumed that H2 was derived from CH4 decomposition, then CH4 conversion at each pulse could be calculated from the formation of H2. TON (turn over number on the catalyst) was obtained by dividing the amount of converted CH4 by surface Ni (not bulk Ni) on 30 mg catalyst. Surface Ni molar amount on 30 mg catalyst was obtained from the particle size distribution of Ni as shown in Fig. 3.

To elucidate the relationship between the reducibility of Ni particles and the catalytic activity for POM, we conducted pulse tests using reduced Ni catalysts and oxidized Ni catalysts on various supports. CH4 pulse testing results in operation 1 are summarized in Table 2. Here we assumed that H2 was derived from CH4 decomposition, then CH4 conversion at each pulse could be calculated from the formation of H2. TON (turn over number on the catalyst) was obtained by dividing the amount of converted CH4 by surface Ni (not bulk Ni) on 30 mg catalyst. Surface Ni molar amount on 30 mg catalyst was obtained from the particle size distribution of Ni as shown in Fig. 3.

Table 2  CH4 Conversion, Surface Ni Molar Amount, and TON for CH4 Pulse Operation 1 over Ni/La2O3, Ni/α-Al2O3, and Ni/LaAlO3 Catalysts

| Catalyst       | Surface Ni [μmol] | CH4 conversion [%] | TON [-] |
|----------------|------------------|--------------------|--------|
| Ni/La2O3       | 0.618            | 1st pulse 4.2       | 0.28   |
|                |                   | 2nd pulse 4.1       | 0.27   |
|                |                   | 3rd pulse 4.0       | 0.26   |
| Ni/α-Al2O3     | 0.569            | 1st pulse 4.3       | 0.31   |
|                |                   | 2nd pulse 4.2       | 0.30   |
|                |                   | 3rd pulse 4.2       | 0.30   |
| Ni/LaAlO3      | 0.429            | 1st pulse 8.8       | 0.84   |
|                |                   | 2nd pulse 7.6       | 0.73   |
|                |                   | 3rd pulse 7.0       | 0.67   |

a) Surface Ni molar amounts on these catalysts were obtained from the particle distribution in Fig. 3.
patterns on all catalysts as shown in Fig. 5. Therefore, metallic Ni reduced at 1023 K had CH4 activation ability at 673 K. We inferred that reduced Ni was also the active site of steam-/dry-reforming in the bottom part of catalyst bed, because reduced Ni species have C-H dissociation activity. In contrast, no CH4 activation was detected in operation 2 over any of these catalysts. No metallic Ni was detected after step 3 in operation 2 on any of these catalysts. These findings show that oxidized Ni had no CH4 activation ability at 673 K. Ni/LaAlO3 catalyst had apparently higher TON than the other two catalysts as shown in Table 2. Ni particles on La2O3 or α-Al2O3 had strong interactions with the supports as discussed above. The low TONs on Ni/La2O3 and Ni/α-Al2O3 catalysts can be explained by considering the interactions between Ni particles and these supports. On the other hand, NiO on LaAlO3 support was easily reduced because Ni particles on this support weakly interacted with the support as suggested by the findings of TPR and STEM. Therefore, the POM ignition activity at 673 K of pre-reduced Ni/LaAlO3 catalyst was attributable to the CH4 activation ability of reduced Ni.

3.3. Effect of Pd Addition on Ni/LaAlO3 Catalyst

As described in previous sections, application of LaAlO3 as a catalyst support showed higher POM activity at low temperature. However, this catalyst required pre-reduction at 1023 K before POM reaction. Pre-reduction treatment is not favorable for industrial processes because this requires more energy and an extra step. Therefore, we attempted further modification of Ni/LaAlO3 catalyst by second metal impregnation on the catalyst to achieve low temperature POM ignition without the requirement for pre-reduction. We attempted to modify the Ni catalyst with a second metal such as Pd, Pt, Fe, Bi, Co, Mn, Cr, or Ag to promote oxidation activity. These elements are regarded as oxidation catalysts for several hydrocarbons. Pd has been reported as a promoter for POM over Ni catalyst. Our screening tests also confirmed that addition of 0.25 wt% Pd on Ni/LaAlO3 catalyst showed high activity at 673 K without pre-reduction.

The activity of Pd/Ni/LaAlO3 catalyst at 673 K without pre-reduction is shown in Table 1. Ni/LaAlO3 catalyst showed no activity without pre-reduction before POM, whereas Pd/Ni/LaAlO3 catalyst showed high activity at 673 K without pre-reduction. Non pre-reduced Pd/Ni/LaAlO3 catalyst exhibited almost identical activity/selectivity to pre-reduced Ni/LaAlO3 catalyst. Pd/Ni/LaAlO3 catalyst had stable activity for a long time and no carbon deposition on the catalyst. This Pd promotion effect was stable for repeated tests. These findings show that addition of a small amount of Pd had a promotional effect for reduction of Ni on the catalyst to activate POM ignition at the low temperature of 673 K.

3.4. Mechanism of POM Ignition over Pd/Ni/LaAlO3 Catalyst

Addition of Pd on the Ni/LaAlO3 catalyst enabled POM at 673 K without pre-reduction, so we examined the mechanism of ignition of POM over Pd/Ni/LaAlO3 catalyst. Chemical and physical structures of Ni/
LaAlO₃ and Pd/Ni/LaAlO₃ were investigated by BET specific surface area, XRD, and STEM/EDX measurements. Pd modification caused a slight decrease in the BET specific surface area from 7.3 m² g⁻¹ (Ni/LaAlO₃) to 5.8 m² g⁻¹ (Pd/Ni/LaAlO₃), so the difference in catalytic activities between these two catalysts is not explained by the BET specific surface area.

Figure 6 depicts XRD patterns for Ni/LaAlO₃ and Pd/Ni/LaAlO₃ catalysts before and after the reaction at 673 K. The surface nickel state was NiO for fresh Pd/Ni/LaAlO₃ catalyst. This NiO was reduced to metallic Ni after the reaction, despite the oxidative atmosphere. As stated in the previous section, metallic Ni particles are the active sites of POM. The perovskite phase of LaAlO₃ was stable during the reaction, and no additional peak or peak shift caused by distortion of the structure was detected. XRD of Pd/Ni/LaAlO₃ catalyst before and after the 673 K reaction (not pre-reduced before the reaction) detected no Pd peak because the amount of Pd was small. No difference was found in the XRD results for Ni/LaAlO₃ and Pd/Ni/LaAlO₃ catalysts before and after POM.

The surface structure of the Ni/LaAlO₃ and Pd/Ni/LaAlO₃ catalysts was characterized by STEM as shown in Fig. 7. STEM detected particles of about 20-30 nm on the fresh Ni/LaAlO₃ catalyst. EDX measurements were performed to identify these particles, as shown in Fig. 8. EDX measuring spots are labeled in Fig. 7. Small particles with size of about 20 nm were observed for both Ni/LaAlO₃ and Pd/Ni/LaAlO₃ catalysts. Comparison of EDX spot A (on the 20-30 nm particles) with EDX spot B (not on the particle) for Ni/LaAlO₃
NiO particles on LaAlO3 perovskite were reduced to PdO is important for methane combustion. Post-reduction. Using the Pd combustion (initial step in the indirect POM) without atmosphere forms a Pd/PdO mixture phase, and that identified as supported Ni. Furthermore, supported metallic Ni particle, which promoted indirect PO2 reaction heat of methane oxidation over Pd, and was increased from 673 K to about 823 K by the exothermic reaction heat of methane oxidation over Pd, and NiO particles on LaAlO3 perovskite were reduced to metallic Ni particle, which promoted indirect POx.

4. Conclusion

The present study found that Ni/LaAlO3 catalyst had POM activity at 673 K after pre-reduction at 1023 K. In contrast to Ni/La2O3 and Ni/α-Al2O3 catalysts, Ni catalysts supported on LaAlO3 perovskite had high reducibility, showing the weaker interaction between Ni particles and LaAlO3 allowed easy reduction of the Ni particle. The reduced Ni particles on the LaAlO3 promoted methane oxidation and steam-/dry-reforming of methane. Addition of Pd to the Ni/LaAlO3 catalyst promoted the oxidation of methane at the introduction part of the catalyst bed, and the exothermic heat enabled reduction of the supported Ni particles. These characteristics resulted in low temperature (673 K) POM over Pd/Ni/LaAlO3 catalyst.

References

1) Navarro, R. M., Peña, M. A., Fierro, J. L. G., Chem. Rev., 107, 3952 (2007).
2) Tanaka, H., Kaino, R., Okumura, K., Kizuka, T, Tomishige, K., J. Catal., 268, 1 (2009).
3) Hickman, D. A., Schmidt, L. D., Science, 259, 343 (1993).
4) York, A. P. E., Xiao, T., Green, M. L. H., Top. Catal., 22, 345 (2003).
5) Utaka, T., Al-Drees, S. A., Ueda, J., Iwashu, Y., Takeguchi, T., Kikuchi, R., Eguchi, K., Appl. Catal. A: General, 247, 125 (2003).
6) Choudhary, V. R., Rave, V. H., Raiput, A. M., Catal. Lett., 22, 289 (1993).
7) Elmaslides, C., Verykios, X. E., J. Catal., 203, 477 (2001).
8) Pantu, P., Gavalas, G. R., Appl. Catal. A: General, 223, 253 (2002).
9) Nakagawa, K., Ikenaga, N., Kobayashi, T., Suzuki, T., Catal. Today, 64, 31 (2001).
10) Choudhary, V. R., Uphade, B. S., Belhekar, A. A., J. Catal., 163, 312 (1996).
11) Hu, Y. H., Ruckenstein, E., Catal. Lett., 34, 41 (1995).
12) Requies, J., Cabrero, M. A., Barrio, V. L., Güemez, M. B., Cambra, J. F., Arias, P. L., Pérez-Alonso, F. J., Ojeda, M., Peña, M. A., Fierro, J. L. G., Appl. Catal. A: General, 289, 214 (2005).
13) Mo, L., Zheng, X., Jing, Q., Lou, H., Fei, J., Energy & Fuels, 19, 49 (2005).
14) Fleys, M., Simon, Y., Swierczynski, D., Kienemmann, A., Marquaire, P.-M., Energy & Fuels, 20, 2321 (2006).
15) Barbero, J., Peña, M. A., Campos-Martin, J. M., Fierro, J. L. G., Arias, P. L., Catal. Lett., 87, 211 (2003).
16) Gonzalez-Cortes, S. L., Orozco, J., Fontal, B., Catal. A: General, 213, 259 (2001).
17) Tispouriari, V. A., Zhang, Z., Verykios, X. E., J. Catal., 179, 283 (1998).
18) Tispouriari, V. A., Verykios, X. E., J. Catal., 179, 292 (1998).
19) Nakagawa, K., Ikenaga, N., Teng, Y., Kobayashi, T., Suzuki, T., Appl. Catal. A: General, 180, 183 (1999).
20) Zhu, T., Flytzani-Stephanopoulos, M., Appl. Catal. A: General, 208, 403 (2001).
21) Liu, M., Wang, D., J. Mater. Res., 10, 3210 (1995).
22) Peña, M. A., Fierro, J. L. G., Chem. Rev., 101, 1981 (2001).
23) Cimino, S., Lisi, L., Rossi, S. D., Faticanti, M., Porta, P., Appl. Catal. B: Environmental, 208, 403 (2001).
24) Sato, K., Adachi, K., Nagaoa, K., Nishiguchi, H., Takita, Y., Catal. Commun., 10, 1478 (2009).
25) Burch, R., Louder, P. K., Appl. Catal. B: Environmental, 5, 149 (1994).
26) Lyubovskiy, M., Pfefferle, L., Appl. Catal. A: General, 173, 107 (1998).
27) Pecchi, G., Reyes, P., Concha, I., Fierro, J. L. G., J. Catal., 179, 309 (1998).
28) Carstens, J. N., Su, S. C., Bell, A. T., J. Catal., 176, 136 (1998).
29) McCarty, J. G., Gusman, M., Lowe, D. M., Hildenbrand, D. L., Lau, K. N., Catal. Today, 47, 5 (1999).
30) Trumble, K. P., Rühle, M., Acta Metal. Mater., 39, 1915 (1991).
31) Wang, J., Dong, L., Hu, Y., Zheng, G., Hu, Z., Chen, Y., J. Solid State Chem., 157, 274 (2001).
32) Li, B., Kado, S., Mukainakano, Y., Miyazawa, T., Miyao, T., Naito, S., Okumura, K., Kunimori, K., Tomishige, K., J. Catal., 245, 144 (2007).
33) Parizotto, N. V., Zanchet, D., Rocha, K. O., Marques, C. M. P., Bueno, J. M. C., Appl. Catal. A: General, 366, 122 (2009).
34) Chu, Y., Li, S., Lin, J., Gu, J., Yang, Y., Appl. Catal. A: General, 134, 67 (1996).
35) Berger-Karlin, C., Radnik, J., Kondratenko, E. V., J. Catal., 280, 116 (2011).
36) Choudhary, V. R., Prabhaker, B., Rajput, A. M., J. Catal., 157, 752 (1995).

J. Jpn. Petrol. Inst., Vol. 56, No. 3, 2013
要 旨

Ni/LaAlO₃触媒上でのメタン部分酸化における低温活性発現

向井 大輝, 江田 登志成, 田中 啓介, 菊地 英一, 関根 奈
早稲田大学先進理工学部応用化学科, 169-8555 東京都新宿区大久保3-4-1

メタンの接触部分酸化を低温で駆動するためのニッケル触媒を検討し, 担体としてパロプスカイト型酸化物を用いた。LaAlO₃パロプスカイト型酸化物にNiを担持した触媒は, 水素還元後にメタンの部分酸化を673 Kというこれまでに例を見ない低い温度で活性を示した。LaAlO₃パロプスカイト上に担持したニッケルは他の担体と比べ相互作用が弱く, より還元を受けやすいことが分かった。反応はメタンの燃烧とそれに伴う水蒸気凝縮などにより進行し, 還元されたニッケルはこれら両方の活性点であった。パラジウムをさらに逐次浸没した触媒は, 無還元でも反応が進行した。この際のニッケルとLaAlO₃パロ

パロプスカイトの相互作用, パラジウムの役割について各種キャラクタリゼーションにより詳細な検討を行った結果, パラジウム

がメタン酸化を促進し, 還元されやすいLaAlO₃上のニッケルが活性点となり接触部分酸化が進行していることが分かった。

..........................................................