# Effect of Support on the Suppression of Hot Spot Formation in the Partial Oxidation of Methane

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(Received April 15, 2009; CL-090368; E-mail: shishido@moleng.kyoto-u.ac.jp)

Ni-based catalysts supported on perovskite oxides and α-$Al_2O_3$ were prepared to investigate catalytic performance and catalyst bed temperature profile in the partial oxidation of methane. Ni/$LaAlO_3$ showed high activity and remarkably suppressed hot spot formation in the catalyst bed even at high space velocity. The effect of support is discussed on the basis of the state of Ni.

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The partial oxidation of $CH_4$ (POX) (eq 1) has been intensively studied for the purpose of promoting its use in industry for the production of synthesis gas,[1–3] since this process produces synthesis gas with a $H_2$/CO ratio of 2.

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \quad \Delta H_{298} = -36\,\mathrm{kJ\,mol^{-1}} \quad (1)$$

Moreover, this process has an advantage over conventional steam reforming to synthesis gas (SRM), as SRM is a highly endothermic reaction. Ni/$Al_2O_3$, a typical catalyst for steam reforming, has been studied for POX above 973 K.[1] This process over Ni catalyst involves first the oxidation of a portion of the $CH_4$ to $H_2O$ and $CO_2$, followed by the reforming of $CH_4$ with $H_2O$ and $CO_2$:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \Delta H_{298} = -801\,\mathrm{kJ\,mol^{-1}} \quad (2)$$

$$CH_4 + H_2O \rightarrow CO + 2H_2 \quad \Delta H_{298} = +206\,\mathrm{kJ\,mol^{-1}} \quad (3)$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \Delta H_{298} = +247\,\mathrm{kJ\,mol^{-1}} \quad (4)$$

The partial oxidation of $CH_4$ leads to hot spot formation at the catalyst bed inlet, which is a common problem in the reforming of hydrocarbons using oxygen since the combustion (eq 2) is a highly exothermic reaction. Although noble metal catalysts such as Rh and Pt have been reported to be effective for the suppression of hot spot formation,[4,5] the use of nickel is desirable because of the high cost and limited availability of noble metals. However, Ni catalysts tend to form hot spots at the catalyst bed inlet in the presence of oxygen.[6,7] Recently, Tomishige et al. have been developing Ni catalysts modified with a small amount of noble metal such as Pt and Pd for oxidative reforming of methane with high resistance to hot spot formation.[8,9] In their system, high reducibility of noble metals was combined with high reforming activity of Ni. Here we briefly demonstrated effective suppression of hot spot formation of noble-metal-free Ni/$LaAlO_3$. In particular, the effect of the support on catalytic performance and the temperature profile of the catalyst bed in POX were investigated.

Perovskite ($SrTiO_3$, $BaTiO_3$, $CaTiO_3$, and $LaAlO_3$) oxides were prepared by the citrate method and finally calcined at 1123 K in dry air. α-$Al_2O_3$ was purchased from Kanto Chemical Co. Ni catalysts were prepared by impregnation using aqueous Ni nitrate solution and finally calcined at 1123 K in air for 5 h. The molar ratio of Ni/support was fixed at 0.2/1.0. The catalytic activity was measured using a fixed-bed flow reactor. The catalyst of 12.5 mg was set, and the thermocouple by which the reaction temperature was controlled was placed at the bottom of the catalyst bed. The products were analyzed by on-line TCD and FID gas chromatographs. The temperature profile of the catalyst bed was measured using infrared thermograph equipment (TH31; NEC Avio Infrared Technologies Co., Ltd.). The radial temperature gradient was rather flat in the horizontal cross section, indicating that the gas flow is close to a plug flow condition. Therefore, we discuss only the temperature profile along the vertical cross section.

XRD patterns of Ni/perovskite catalysts after calcination showed strong diffraction lines of perovskite oxides and weak diffraction lines of NiO. After reduction at 1173 K, apparently only NiO was reduced to Ni metal in all the catalysts. Figure 1 shows the effect of GHSV (Gas hourly space velocity) on the $CH_4$ conversion in POX at 1073 K and the highest catalyst bed temperature ($T_{max}$). $CH_4$ conversion over all the catalysts increased with increasing GHSV. Ni/$LaAlO_3$ showed the highest

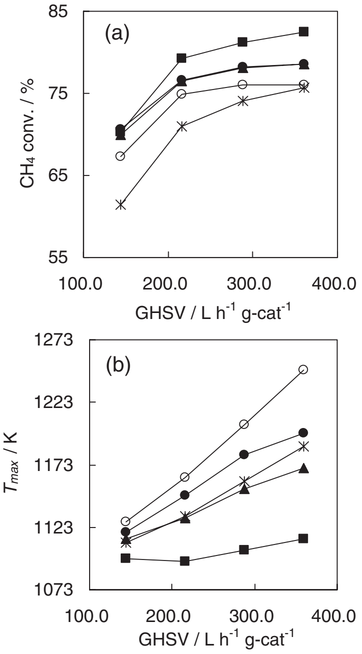

**Figure 1.** Effect of GHSV on $CH_4$ conv. (a) and $T_{max}$ (b) in POX. (●) Ni/$SrTiO_3$, (▲) Ni/$BaTiO_3$, (○) Ni/$CaTiO_3$, (■) Ni/$LaAlO_3$, (×) Ni/α-$Al_2O_3$. Reduction temp = 1173 K, Reaction temp = 1073 K, $CH_4/O_2$ = 2/1.

activity at 360 L h$^{-1}$ g$^{-1}$. Ni/$SrTiO_3$ showed slightly lower activity than Ni/$LaAlO_3$.

The order of $CH_4$ conversion at 360 L h$^{-1}$ g$^{-1}$ was Ni/$LaAlO_3$ > Ni/$SrTiO_3$ = Ni/$BaTiO_3$ > Ni/$CaTiO_3$ = $\alpha$-$Al_2O_3$. The highest catalyst bed temperature was higher than the reaction temperature (1073 K) over all catalysts and increased with increasing GHSV. Although the difference in $CH_4$ conversion between Ni/$LaAlO_3$ and Ni/$SrTiO_3$ was small, the highest catalyst bed temperature of Ni/$SrTiO_3$ (ca. 1200 K) was much higher than Ni/$LaAlO_3$ (ca. 1100 K). This result clearly indicates that Ni/$LaAlO_3$ is active for POX and more effective in the suppression of hot spot formation than other Ni/perovskite and Ni/$\alpha$-$Al_2O_3$ catalysts.

In the case of Ni/$SrTiO_3$, the temperature reached a maximum about 1200 K at 360 L h$^{-1}$ g$^{-1}$, and the temperature gradient became smaller at lower GHSV conditions. Moreover, the local temperature decreased to the reaction temperature (1073 K) after reaching the maximum, and the position showing the maximum temperature gradually moved to the catalyst bed inlet with decreasing GHSV. This behavior can be explained by separation of the reaction zone for combustion (eq 2) and reforming (eqs 3 and 4) of $CH_4$; When oxygen is present (near the catalyst bed inlet), the Ni species is oxidized. Oxidized Ni is active only for methane combustion, and oxygen is consumed near the catalyst bed inlet, resulting in remarkably increase of the catalyst bed temperature. On the other hand, in the absence of oxygen (from the center to the bottom of the catalyst bed), the Ni species is maintained in a metallic state and is active for methane reforming, which decreased the catalyst bed temperature remarkably. Thus, the separation of the reaction zones causes the large temperature gradient in the catalyst bed, and at low GHSV, the overlap between the two reaction zones may increase. In the case of Ni/$LaAlO_3$, the highest catalyst bed temperature was ca. 100–160 K lower than other Ni/perovskite and Ni/$\alpha$-$Al_2O_3$ catalysts, indicating that the overlap between the two reaction zones is larger than those of other Ni/perovskite and Ni/$\alpha$-$Al_2O_3$ catalysts. These results suggest that the state of Ni over $LaAlO_3$ is different from those over other perovskite oxides and $\alpha$-$Al_2O_3$. In other words, it seems that Ni over $LaAlO_3$ has a high resistance to oxidation and suppressed hot spot formation even at high GHSV conditions. In order to evaluate the resistance to oxidation of Ni species, TPR (temperature-programmed reduction) profiles of Ni catalysts were measured after POX.

Figure 2 shows the TPR profiles of the supported Ni catalysts after the reaction. The $H_2$ consumptions of $LaAlO_3$ and $SrTiO_3$ supports ($H_2$/support) were 0.016 and 0.023, suggesting that these values were negligible. The reduction of Ni species on $SrTiO_3$ and $BaTiO_3$ proceeded in the temperature range of 500–1000 K. The ratio of hydrogen consumption based on Ni content was 0.67 and 0.63, respectively. This $H_2$ consumption is assigned to the reduction of NiO, which formed during POX. In the case of Ni/$\alpha$-$Al_2O_3$, the consumption of $H_2$ was observed in the temperature range of 500–700 K, and the ratio of hydrogen consumption based on Ni content was 0.39. The reduction of Ni species on $LaAlO_3$ proceeded in the temperature range of 500–1000 K. The ratio of hydrogen consumption based on Ni content was 0.11. This value is much smaller than those of $SrTiO_3$ and $BaTiO_3$, indicating that a large amount of Ni metal remained on $LaAlO_3$ even under the reaction conditions and that Ni over $LaAlO_3$ has a high resistance to oxidation. As a result, the overlap between the combustion (exothermic) and the reforming (endothermic) reaction zones increased. This overlap gave flatter catalyst bed temperature and suppressed hot spot formation. This also suggests that Ni/$LaAlO_3$ can make effective use of exothermic heat for the reforming reaction.

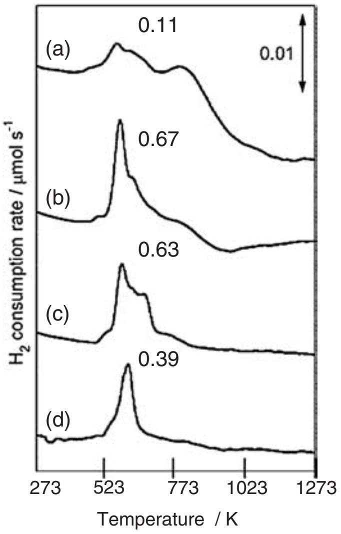

**Figure 2.** Temperature-programmed reduction profiles of supported Ni catalysts after POX. Ramping rate: 10 K min$^{-1}$, 5 vol % $H_2$/Ar. Numbers show the values of $H_2$/Ni ratio ($Ni^{2+} + H_2 \rightarrow 2H^+ + Ni^0$). (a) Ni/$LaAlO_3$, (b) Ni/$SrTiO_3$, (c) Ni/$BaTiO_3$, and (d) Ni/$\alpha$-$Al_2O_3$.

In summary, noble-metal-free Ni/$LaAlO_3$ showed high activity and remarkably suppressed catalyst bed hot spot formation in POX even at high GHSV. High suppression of hot spot formation is due to the high resistance of Ni metal on $LaAlO_3$ to oxidation. We will discuss the cause of the high resistance of Ni metal on $LaAlO_3$ in the future.

We thank Prof. Keiichi Tomishige and Dr. Sigeru Kado of Tsukuba University for infrared thermograph measurements. The work was partially supported by the Grant-in-Aid for Scientific Research for Young Researchers (B) (No. 17760615) under the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan.

### References

1 A. T. Ashcroft, A. K. Cheetham, J. S. Foord, M. L. H. Green, C. P. Grey, A. Murrell, P. D. F. Vernon, *Nature* **1990**, *344*, 319.
2 D. A. Hickman, L. D. Schmidt, *Science* **1993**, *259*, 343; *J. Catal.* **1992**, *138*, 267.
3 V. R. Choudhary, A. M. Rajput, V. H. Rane, *J. Phys. Chem.* **1992**, *96*, 8686.
4 K. Tomishige, S. Kanazawa, K. Suzuki, M. Asadullah, M. Sato, K. Ikushima, K. Kunimori, *Appl. Catal. A* **2002**, *233*, 35.
5 B. Li, K. Maruyama, M. Nurunnabi, K. Kunimori, K. Tomishige, *Appl. Catal. A* **2004**, *275*, 157.
6 D. Dissanayake, M. P. Rosynek, K. C. C. Kharas, J. H. Lunsford, *J. Catal.* **1991**, *132*, 117.
7 B. Li, R. Watanabe, K. Maruyama, M. Nurunnabi, K. Kunimori, K. Tomishige, *Appl. Catal. A* **2005**, *290*, 36.
8 K. Tomishige, S. Kanazawa, S. Ito, K. Kunimori, *Appl. Catal., A* **2003**, *244*, 71.
9 B. Li, S. Kado, Y. Mukainakano, T. Miyazawa, T. Miyao, S. Naito, K. Okumura, K. Kunimori, K. Tomishige, *J. Catal.* **2007**, *245*, 144.