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Selective Methanation of CO in Reformate Gas over Ni/TiO_2 Catalyst

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Selective methanation of CO was performed over Ni/TiO_2. CO in reformate gas was completely removed at 150–300 °C. The CH_4 concentration in the outlet gas could be maintained below 1% in the entire temperature region because Ni/TiO_2 suppressed the CO_2 methanation reaction. It can be considered that the formation of CO by the reverse water-gas-shift reaction is blocked by the application of TiO_2 to the support of Ni catalyst and that it results in the high CO/CO_2 selectivity of Ni/TiO_2.

The technology of removing carbon monoxide (CO) in reformate gas has become increasingly important because of its potential applications for a proton-exchange membrane fuel cell system. The preferential oxidation of CO (PROX) is widely utilized for removal of CO in reformate gas. The PROX process requires an accurate control of air (oxygen) supply and a fine temperature adjustment to keep the possibly lowest hydrogen oxidation as a side reaction. Recently, selective methanation of CO has been proposed as an alternative candidate for CO removal. Methanation does not require any air (oxygen) addition because the reactants (CO and hydrogen) are included in reformate gas. The methanation catalyst must maintain high selectivity for the CO methanation because the methanation of carbon dioxide (CO_2) which is contained in the reformate gas often causes the loss of hydrogen and decreases the energy efficiency.[1] The development of highly selective CO methanation catalyst active over a wide temperature range is important to make a small and simple catalytic fuel processor using the methanation.

It has been generally recognized that Ru, Rh, and Ni metals are active for the methanation of CO[2,3] or selective methanation of CO.[4–13] For example, Takenaka et al. carried out CO methanation over Ru, Pd, Pt, Ni, Fe, and Co catalysts supported on various metal oxides, and Ru and Ni metals were suitable for the selective CO methanation.[4] It has also been known that the properties of support materials are important to keep the high CO methanation and CO/CO_2 selectivity.[4,8,10] Metal-crystal sizes and the amounts of metals affect both the CO methanation activity and CO/CO_2 selectivity.[6,10] Recently our group has compared the CO methanation activitiy and CO/CO_2 selectivity over various Ru catalysts supported on some metal oxides (Al_2O_3, TiO_2, zeolites, and so on).[13] In this work, base-metal (Ni, Co, and Fe) catalysts supported on Al_2O_3 and TiO_2 were investigated for the purpose of cost reduction of selective CO methanation catalysts.

Al_2O_3 (Catalysis Society of Japan, JRC-ALO-6) and TiO_2 (Catalysis Society of Japan, JRC-TIO-4), were used for support materials. Ni, Co, and Fe catalysts were prepared by a conventional impregnation method using aqueous solution of $Ni(NO_3)_2$, $Co(NO_3)_2$, and $Fe(NO_3)_3$, respectively (Wako Chemicals). The obtained samples were dried at 110 °C for 12 h and calcined at 500 °C for 2 h in air. Metal contents in the prepared catalysts were adjusted to 10 wt %. Commercially available methanation catalyst, 0.5 wt % Ru/Al_2O_3 (EA catalyst) supplied by N.E. CHEMCAT Corp., was used as a standard catalyst.

Catalytic activity was measured by using a continuous fixed-bed flow tubular reactor at 150–300 °C and 0.1 MPa. 300 mg of catalysts was pretreated in a reduction gas stream (20% H_2 balanced by He) at 450 °C for 0.5 h. After the reduction, a reaction gas mixture (0.2% CO, 16.1% CO_2, 65.3% H_2, and 18.4% H_2O) assuming the equilibrium composition of the outlet gas of CO shift converter at 180 °C (initial steam carbon ratio $S/C = 3.0$) was fed into the reactor ($50\,cm^3\,min^{-1}$). The GHSV was ca. $10000\,h^{-1}$. Inlet and outlet gases were analyzed using a gas chromatograph equipped with a thermal conductivity detector (Shimadzu GC-8A). Gas concentration was described as a basis of dry gas composition. The target CO and CH_4 concentration in this study is below 0.05% and 1%, respectively.

Figure 1 shows the changes of CO and CH_4 concentrations in the outlet gas over Ni, Co, Fe, and Ru catalysts supported on Al_2O_3 at various reaction temperatures. The CO concentration in the outlet gas over Ru/Al_2O_3 and Ni/Al_2O_3 decreased to below 0.05% at 200–250 °C. However, the CH_4 concentrations in the outlet gas over Ru/Al_2O_3 and Ni/Al_2O_3 exceeded 1.0% at temperatures higher than 250 °C due to the methanation of CO_2. Then, both catalysts showed moderate CO methanation activity and CO/CO_2 selectivity at temperatures from 200 to 250 °C.

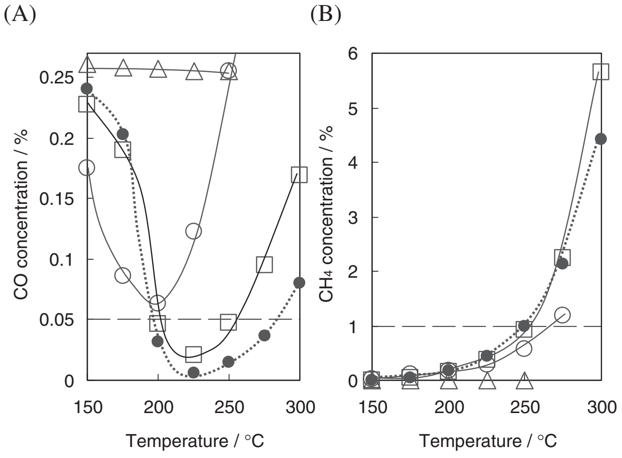

Figure 1. Changes of (A) CO concentration and (B) CH_4 concentration in selective methanation of CO over (□) 10 wt % Ni/Al_2O_3, (○) 10 wt % Co/Al_2O_3, (△) 10 wt % Fe/Al_2O_3, and (●) 0.5 wt % Ru/Al_2O_3.

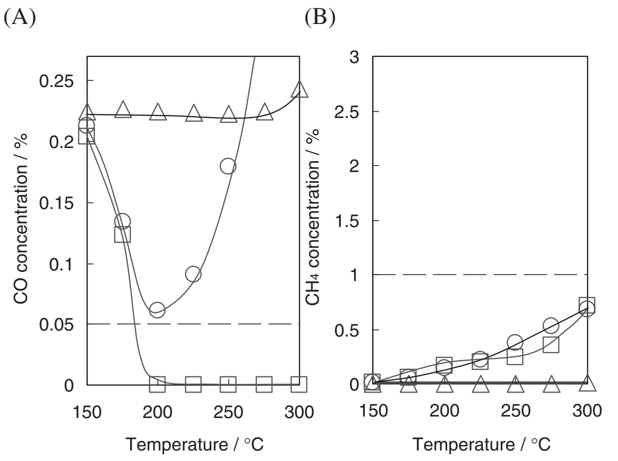

Figure 2. Changes of (A) CO concentration and (B) CH_4 concentration in selective methanation of CO over (□) 10 wt % Ni/TiO_2, (○) 10 wt % Co/TiO_2, and (△) 10 wt % Fe/TiO_2.

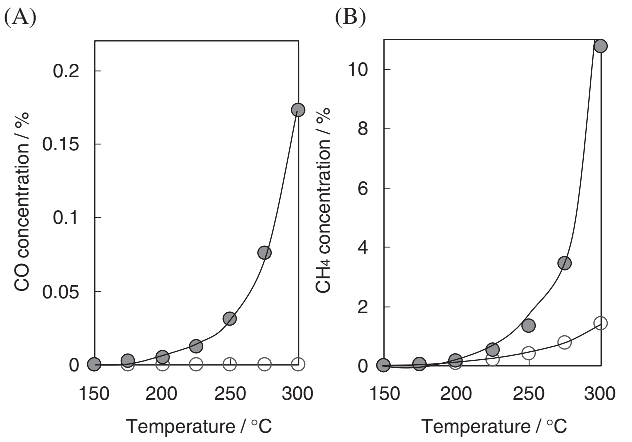

Figure 3. Changes of (A) CO concentration and (B) CH_4 concentration in methanation of CO_2 over (○) 10 wt % Ni/TiO_2 and (●) 10 wt % Ni/Al_2O_3.

Although the CO concentration in the outlet gas over Co/Al_2O_3 was lower than those over Ru/Al_2O_3 and Ni/Al_2O_3 at the temperatures lower than 175 °C, the CO concentration could not be decreased to below 0.05% in the entire temperature region because the reverse water-gas-shift reaction ($CO_2 + H_2 \rightarrow CO + H_2O$) is thought to be enhanced at temperatures higher than 175 °C over Co/Al_2O_3. Fe/Al_2O_3 catalyst showed no activity for selective methanation of CO in reformate gas.

Figure 2 shows the changes of CO and CH_4 concentrations in the outlet gas over Ni, Co, and Fe catalysts supported on TiO_2 at various reaction temperatures. The behaviors of CO and CH_4 concentration over Co and Fe catalysts supported on TiO_2 were similar to those over Co and Fe catalysts supported on Al_2O_3, respectively. On the other hand, the performance of Ni catalyst was drastically affected by the kind of support material. The CO concentration in the outlet gas over Ni/TiO_2 decreased to below 0.05% at 180 °C and was maintained lower than 0.05% even at 300 °C. The CH_4 concentration in the outlet gas over Ni/TiO_2 was below 1.0% in the entire temperature region (150–300 °C). Therefore, both the CO methanation activity and CO/CO_2 selectivity of Ni catalyst were greatly improved. Moreover, we examined the catalytic performances of Ni catalysts supported on some types of TiO_2 and found that any other TiO_2 except for JRC-TIO-4, which is generally known as Degussa P-25, did not show such high activity and selectivity in the selective CO methanation reaction (results are not shown in this paper).

It is suggested that the drastic enhancement of CO/CO_2 selectivity over Ni/TiO_2 is due to the suppression of CO_2 methanation and/or reverse water-gas-shift reaction over the Ni/TiO_2. CO_2 methanation over Ni catalysts was carried out at various temperatures in order to investigate the role of TiO_2 support. After reduction, 20.6% CO_2 balanced by hydrogen was fed into the reactor. Other reaction conditions were the same as those in selective CO methanation activity tests. Figure 3 shows the changes of CO and CH_4 concentrations in the outlet gas over Ni catalysts supported on Al_2O_3 and TiO_2 at various reaction temperatures. With an increase in temperature, the concentrations of both CO and CH_4 over Ni/Al_2O_3 increased rapidly. On the other hand, the amount of CO_2 converted was very small in the case of Ni/TiO_2. In whole temperature region, CO was not detected and the concentration of CH_4 was very low. It is generally recognized that the CO_2 methanation reaction proceeds via formation and subsequent methanation of CO.[14] When the reaction scheme of CO_2 methanation reaction is taken into account, it can be considered that the CO formation due to the reverse water-gas-shift reaction is suppressed by the application of TiO_2 to the support of Ni and that this leads to the high CO/CO_2 selectivity of Ni/TiO_2 and little formation of CO in high temperature regions. At this point in time, the more detailed mechanism for suppressing the CO_2 methanation over Ni catalyst supported on TiO_2 (JRC-TIO-4) is not clear, and this is the subject of our future study.

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