

Effect of traces of chlorine in Ni/TiO₂ catalyst for the CO selective methanation in reformed gas

N. Shimoda¹, D. Shoji¹, K. Tani¹, M. Fujiwara¹, R. Kikuchi², S. Satokawa^{1*}

¹Seikei University, Kichijoji-kitamachi, Musashino-shi, Tokyo, 180-8633 Japan

²The University of Tokyo, Bunkyo-ku, Tokyo, 67890 Japan

*corresponding author: satokawa@st.seikei.ac.jp

Introduction

In the hydrogen supply process to polymer electrolyte fuel cell system, carbon monoxide (CO) was produced as a by-product during the reforming process of hydrocarbon fuels. This produced CO deteriorates the electrode performance significantly, which is serious problem in polymer electrolyte fuel cell. Recently, the CO selective methanation (CO-SMET) process has been considered as a CO removal process in reformed gas instead of the CO preferential oxidation (CO-PROX) process. In our previous works, we have reported that Ru and Ni based catalysts exhibit the superior activity [1], and especially, the titania supported Ni (Ni/TiO₂) catalyst shows the highest activity and high CO/CO₂ reaction selectivity in the CO-SMET among various metal oxides supported Ni catalysts [2]. Djinojic et al. have studied the effect of chloride doping to Ru/Al₂O₃ catalyst and reported the positive effect of chloride doping on the CO/CO₂ selectivity in CO-SMET [3]. Thus, in this study, we have focused on the effect of chlorine content in Ni/TiO₂. The effects of the pretreatment of TiO₂ support and the starting materials of Ni component have been studied to obtain the scientific insights on the difference of reactivity for the CO-SMET over Ni/TiO₂ catalyst.

Materials and Methods

All the Ni/TiO₂ catalysts were prepared by the impregnation method using an aqueous solution of Ni(NO₃)₂·6H₂O and NiCl₂·6H₂O mixture with the appropriate molar ratio. As a support, the commercial TiO₂ (Evonik Degussa, P25) was used in this study. The pretreatments of TiO₂ were carried out as follows: the calcination in air at 500 °C (TiO₂-500) and 800 °C (TiO₂-800) for 2 h; the cyclic water washing at 50 °C for 1 h (TiO₂-water). The ion chromatography (IC, Shimadzu, CDD-6A) analysis of the supernatant liquid after the water washing was conducted to estimate the amount of residual chlorine in the catalysts. The Ni content was adjusted to 10 wt%. The obtained samples were calcined in air at 500 °C for 2 h and then were reduced in 20% H₂/N₂ at 450 °C for 30 min prior to the activity test. The catalytic activity test of CO-SMET was carried out in a fixed bed flow reactor at 150–300 °C under atmospheric pressure. A reaction gas mixture (0.2% CO, 16.1% CO₂, 65.3% H₂, and 18.4% H₂O), assuming the outlet gas of water gas shift converter, was fed into the reactor tube, and the GHSV value was adjusted to ca. 10,000 h⁻¹. The compositions of influent and effluent 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.

Results and Discussion

Firstly, the amount of residual chlorine was measured by IC analysis for the pretreated TiO₂ samples. As a result, it was found that chlorine component in TiO₂ could be removed by more than three cycles water washing to the low concentration level which is lower than the detection limit of IC analysis (1.1 ppm). Additionally, no chlorine component

was detected for the supernatant wash liquid of the calcined at 500 °C and subsequently water washed TiO₂, indicating that the calcination could remove the chlorine component adequately. For the as-obtained TiO₂, total amount of chlorine content was ca. 1300 ppm after the cyclic water washing. Fig. 1 represents the catalytic activity of the Ni/TiO₂ prepared using the TiO₂ supports with various pretreatment for CO-SMET. For the untreated catalyst (□), CO concentration was maintained at low level and the abrupt increase in CH₄ concentration was suppressed even when the reaction temperature increases. In contrast, for the pretreated TiO₂ supported Ni catalysts, CO and CH₄ concentration increased drastically at temperatures above 275 °C due to the progression of reverse water-gas shift reaction, leading to a decrease in CO/CO₂ selectivity. From these results, it is considered the effect of chlorine content on the CO/CO₂ selectivity of Ni/TiO₂ catalyst. As shown in Fig. 2, the effect of molar ratio of the starting Ni salts was investigated using the TiO₂-500 supported Ni catalysts. It is seen that an increase in the NiCl₂ ratio causes the deactivation of Ni/TiO₂ for CO methanation and the inhibition of CO₂ methanation. The amount of chlorine in Ni/TiO₂ catalysts with the low molar ratio is considered several hundred ppm. Therefore, we suppose that traces of chlorine affect the catalytic performance of Ni/TiO₂ effectively from the aspect of the high CO methanation activity and CO/CO₂ selectivity for CO-SMET.

Significance

The commercial TiO₂ contains a certain amount of chlorine component. For the CO-SMET over Ni/TiO₂ catalyst, traces of chlorine have a positive effect on the catalytic performance.

References

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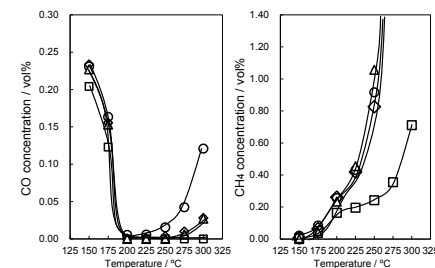


Figure 1. Change of (A) CO concentration and (B) CH₄ concentration for the selective methanation of CO over (□) Ni/TiO₂-800, (○) Ni/TiO₂-500, (△) Ni/TiO₂-water, and (□) Ni/TiO₂.

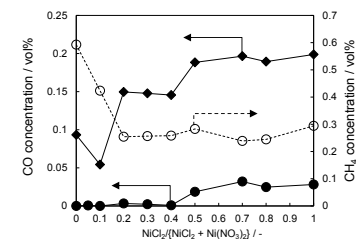


Figure 2. Effect of molar ratio of Ni nitrate to Ni chloride on CO concentration at (●) 200 °C and (◆) 175 °C, and (○) CH₄ concentration at 250 °C for the selective methanation of CO over Ni/TiO₂-500 catalysts.