Degradation Factors of Ni/TiO2 Catalysts for Selective CO Methanation: Effect of Loss of Residual Cl on Catalyst

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Accelerated deterioration tests for selective CO methanation over Ni/TiO2 catalysts were performed to investigate the catalyst degradation factors. The accelerated deterioration test treated the catalyst in the reaction gas flow at the specified temperature (200, 250 or 300 °C) for 24 h. After the accelerated deterioration test, the Ni/TiO2 selectivity in CO methanation was reduced due to the enhancement of an undesirable reverse water-gas shift reaction. Powder X-ray diffraction found no change in the TiO2 structure between the fresh and spent catalysts. In-situ X-ray absorption spectroscopy demonstrated that the Ni species reduced by H2 were present as metallic Ni and remained unchanged in the fresh and spent catalysts. The number of surface Cl species for the spent catalyst was much smaller than that for the fresh catalyst. Therefore, disappearance of surface Cl components during the accelerated deterioration test caused the degradation of Ni/TiO2 catalysts for selective CO methanation.

Keywords
Selective carbon monoxide methanation, Nickel catalyst, Titania, XAS, Durability

1. Introduction

New technologies for the efficient utilization of fossil fuels are important to develop to reduce fossil fuel consumption and ameliorate the harmful effects on the global environment. Polymer electrolyte fuel cell (PEFC) systems are one of these technologies, which offer high power density and high total energy conversion efficiency. The PEFC can be operated at low temperature (ca. 80 °C), leading to easy start up and shut down, which is one of the main advantages, compared to other types of fuel cell such as solid oxide fuel cells. The PEFC produces electric energy via H2 oxidation. In the future, H2 could be produced from water electrolysis, although hydrogen-rich gas is presently obtained from fossil fuels. However, the hydrogen-rich gas contains a significant amount of CO which poisons the Pt catalysts on the anode. Therefore, the CO concentration must be reduced from ca. 10 % to 0.2-2 % by a water-gas shift reaction (WGS reaction, CO + H2O → CO2 + H2)1), and then to <100 ppm by preferential oxidation of CO in the presence of excess H2 (PROX, CO + 1/2 O2 → CO2)2,3). However, the PROX process is associated with oxidation of hydrogen in the presence of oxygen, leading to lower overall energy conversion efficiency for the PEFC.

CO methanation (CO + 3H2 → CH4 + H2O) is another process of CO purification carried out in the presence of excess CO24). In 1970, Rehmat and Randhava suggested a concept of CO methanation for a fuel cell application5). Methanation of CO has the advantages that the reactants are already present for this reaction (CO and H2) in the reformed gas, and that the produced CH4 can be recycled as a heating fuel for the reforming unit. High selectivity is important for the removal of CO by methanation, or simultaneous CO2 methanation (CO2 + 4H2 → CH4 + 2H2O) and reverse water gas shift reaction (RWGS reaction, CO2 + H2 → CO + H2O) will result in significant consumption of produced H2. Additionally, exothermic CO2 methanation carries the risk of runaway of the methanation reactor. Therefore, suitable catalysts must be developed to promote CO methanation at low temperatures and suppress CO2 methanation and RWGS reaction at high temperatures, leading to a wide operating temperature range for selective CO methanation.

A great deal of effort has been made in studies of selective CO methanation in the presence of CO2 and H2O.
over Ru-Ni monometallic and bimetallic catalysts. However, industrial uses require more developed catalysts with high durability (> 40,000 h) and high activity and selectivity for CO methanation. Many developed catalysts offer high activity and selectivity for CO methanation, but lack adequate stability as operating durability is less than 10,000 h. Therefore, new catalysts must be developed with high activity and selectivity for CO methanation as well as high durability.

Previously, we reported that TiO2 supported Ni catalysts (Ni/TiO2), prepared by an impregnation method, exhibited high activity/selectivity in CO methanation for 7000 h. Further examination observed residual Cl component on the Ni/TiO2 catalysts derived from the support material TiO2 (Evonik Degussa, P-25) which was prepared by a Cl method. This Cl component suppressed unfavorable CO2 methanation via the RWGS. This phenomenon has been reported by other groups as well. Many studies have investigated the activity and selectivity of CO methanation over Cl-modified catalysts, but little is known about the cause of catalyst deterioration. Recently, the Cl component on Ni/ZrO2 was suggested to gradually disappear during selective CO methanation, leading to low selectivity, although any change in the structure of Ni and support material (in this case ZrO2) during the reaction were not examined. The present study of the developed Ni/TiO2 catalyst examined the changes in TiO2 structure, Ni structure and the amount of surface Cl components during accelerated deterioration tests for selective CO methanation, to clarify the degradation factors of Ni/TiO2 catalyst for selective CO methanation.

2. Experimental

2.1. Catalyst Preparation

10 wt% Ni/TiO2 (named Ni/TiO2) was obtained from Nikki-Universal Co., Ltd., as prepared by a conventional impregnation method. TiO2 (Evonik Degussa, P-25) was impregnated with an aqueous solution of nickel (II) nitrate hexahydrate (Wako Pure Chem. Ind., Ltd., 98%) at 80°C. The crude material was dried at 120°C overnight, and then calcined at 500°C for 3 h.

2.2. Reaction Test

Catalytic activity tests of selective CO methanation were carried out in a fixed bed flow reactor under atmospheric pressure (MicrotracBEL Corp., BEL-REA). The reaction temperature was measured at the catalyst bed using a K-type thermocouple. The reaction gas mixture, which modeled the gas mixture produced by methane steam reforming (S/C = 2.5) and equilibrated in a WGS reactor at 180°C, consisted of 0.19% CO, 16.1% CO2, 66.1% H2, and 17.7% H2O (dry-base: 0.242% CO, 19.5% CO2, and 80.3% H2). Ni/TiO2 was pelletized and sieved to a size of 850-1180 μm. The catalyst of 300 mg was placed into the reactor and then pretreated as follows: the sample was heated to 400°C in N2 (10°C min⁻¹), reduced in 33% H2/N2 at 400°C for 30 min, and then cooled down to 150°C in a N2 gas stream. After pretreatment, the flow rate of the reaction gas was set at 116 mL (stp) min⁻¹ (contact time: ca. 0.8 kgcat h molCO⁻¹). The reaction temperature was increased in the order: 150, 175, 200, 225, and 250°C with each condition maintained for 2 h. Next, as an accelerated deterioration test, the catalyst was treated in the reaction gas flow at the desired temperature (200, 250 or 300°C) for 24 h. Subsequently, the temperature was cooled down to 150°C and then increased from 150 to 250°C again to examine the activity of the deactivated catalyst. Water vapor was segregated in an ice-water trap from the reaction gas mixture, and the products were analyzed with a non-dispersive infrared spectrometer (NDIR, HORIBA Ltd., VA-3000) to measure the CO, CO2, and CH4 concentrations of the outlet gas mixture. After the Ni/TiO2 catalyst was reduced by 33% H2/N2, it was named Ni/TiO2-R. In addition, the Ni/TiO2 catalyst heated in the reaction gas at T°C (T = 200, 250 and 300) was named Ni/TiO2-T.

2.3. Powder X-ray Diffraction

The crystalline phase of catalysts was determined by powder X-ray diffraction (Rigaku Corp., Ultima IV), equipped with a CuKα radiation source, at a voltage of 40 kV and a current of 40 mA.

2.4. X-ray Absorption Spectroscopy

Ni K-edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were measured using in-situ X-ray absorption spectroscopy (XAS) at the BL14B2 beamline at SPring-8. XAS data were collected in a quick mode every 5 min; that is the Si (1 1 1) monochromator was continuously moved from 14.31 to 11.93° in 196 s. Spectra were collected in transmission mode using ion chambers filled with an Ar/N2 mixture on pressed pellets of fresh catalysts. The powder samples 11 mg were pressed into a thin disk, using a 7 mm die set, and were then placed into an in-situ cell. The catalysts were heated to 450°C for 45 min, and then reduced at 450°C under pure H2 for 30 min. The catalysts were then cooled to the desired temperature (250°C or 320°C) under He atmosphere, before the reaction test using a CO/CO2/N2 gas mixture (30 mL min⁻¹, 0.25% CO, 20% CO2, and 79.8% H2). Spectra were background corrected and normalized using Athena and Artemis. Fourier transform data were analyzed by a curve-fitting method using theoretical phase-shift and amplitude functions derived by the FEFF8 program.

2.5. Analysis for Cl Residual on Catalyst Surface

The amount of Cl residual on the catalysts was analyzed as follows. The catalyst of 0.6-1.0 g was stirred with pure water of 100 mL at 50°C for 30 min. The
solution was then decanted from the suspension and stored in a beaker. This process was repeatedly carried out using the remaining catalyst. The five samples of decanted solution were mixed in a measuring cylinder. Then, the crude solution was diluted to 500 mL total. The Cl concentration of the diluted solution was analyzed by a high performance ion chromatography system, consisting of a pump (Shimadzu Corp., LC-20ADsp), column (Shimadzu, Shim-pack IC-A3), column oven (Shimadzu, CTO-20A), detector (Shimadzu, CDD-10Avp), and degassing unit (Shimadzu, DGU-20A3R). Based on the catalyst amount and the Cl concentration, the amount of Cl residual on the catalysts (gCl gcat. –1) was evaluated.

3. Results and Discussion

3.1. Activity Test

Figure 1(a) shows the changes in CO concentration over TiO2 supported Ni catalysts at various reaction temperatures. CO concentration fell from 2066 to 255 ppmv over Ni/TiO2-R as the reaction temperature increased from 150 to 200 °C. CO concentration was below 50 ppmv at higher temperatures. CO concentration decreased from ca. 2000 to <50 ppmv over Ni/TiO2-200 and Ni/TiO2-250 with increasing reaction temperature from 150 to 200 °C, and then remained stable. The accelerated deterioration test at 200 °C or 250 °C enhanced the apparent activity of Ni/TiO2-R for CO removal at <200 °C. For Ni/TiO2-300, CO concentration also fell right down as the temperature increased to 200 °C and then was steady. However, CO concentration over Ni/TiO2-300 at 175 °C (1224 ppmv) was higher than over Ni/TiO2-200 (1010 ppmv) and Ni/TiO2-250 (974 ppmv). Therefore, Ni/TiO2-300 had lower apparent activity for CO removal than Ni/TiO2-200 and Ni/TiO2-250.

Figure 1(b) shows plots of CH4 concentration against reaction temperature over Ni/TiO2 catalysts. CH4 concentration went up to 0.2 % over Ni/TiO2-R with higher reaction temperature from 150 to 200 °C, and then remained unchanged. CH4 concentration for Ni/TiO2-T was almost the same as that for Ni/TiO2-R in the temperature range between 150 °C and 200 °C. According to our previous study, CH4 is generated via CO methanation29). CH4 concentration over Ni/TiO2-T was higher than that for Ni/TiO2-R at >225 °C. CH4 concentration monotonically increased as T increased at 225 °C and 300 °C. CH4 concentration at high temperature reflects the activity in the RWGS reaction because CO2 methanation proceeds via the RWGS reaction and subsequent CO methanation7),21),27). Figure 1(a) shows that CO was completely methanated at high temperatures, which means that the generation rate of CO via the RWGS reaction was much slower than the consumption rate of CO. In other words, the RWGS reaction is the rate-determining step for CO2 methanation. Therefore, catalytic activity of the Ni/TiO2 catalyst for the RWGS reaction was enhanced by treatment with the reaction gas mixture at high temperature.

Based on the enhancement of catalytic activity for the RWGS reaction, we can explain why the CO concentration for Ni/TiO2-300 was higher than that for Ni/TiO2-200 or Ni/TiO2-250. Ni/TiO2-300 showed the highest activity for the RWGS reaction (Fig. 1(b)), so...
the CO production rate via the RWGS reaction was the highest in the four catalysts. The CO concentration is determined by the difference between CO production, CO consumption, and CO content in the reaction gas. Therefore, a high CO production rate is expected to result in a slower decrease in CO concentration over Ni/TiO2-300.

3.2. Structure of Ni Species during H2 Pretreatment and Reaction

To elucidate the relationship between the structure of the catalysts and their activity, PXRD measurements were carried out for Ni/TiO2 and Ni/TiO2-250, as shown in Fig. 2. TiO2 was mainly present as anatase with minor amounts of rutile in both catalysts. The TiO2 phase did not change after the long-term test at 250 °C. Ni/TiO2 showed a peak at 43.3° which was attributed to NiO, whereas Ni/TiO2-250 had peaks at 44.5° and 51.8° of metallic Ni.

The structure of Ni species on Ni/TiO2 during pretreatment and reaction were investigated using in-situ XAS. Figure 3 shows Ni K-edge XANES spectra for Ni/TiO2 during pretreatment. Ni foil and NiO powder were used as standard reference samples. The spectrum obtained at 50 °C was nearly identical to that of NiO (Fig. 3(a)). The spectrum shape did not change during heat treatment from 50 to 450 °C under N2 (Fig. 3(a)). Just after the N2 gas flow was changed to a H2 gas flow at 450 °C, the XANES spectra gradually changed: the white-line intensity (at 8345 eV) slightly decreased and new peaks at 8330 eV and 8352 eV appeared simultaneously (Fig. 3(b)). These peaks were attributed to the presence of pure fcc-Ni. The XANES spectra remained unchanged during CO and CO2 methanation at 250 °C (Fig. 3(c)) and 320 °C (Fig. 3(d)). Therefore, the Ni species in Ni/TiO2 was metallic Ni and unchanged during the reaction.

After the durability test under CO/CO2/H2 at the desired temperature (250 °C or 320 °C), the sample was cooled down to room temperature. Then, the Ni K-edge radial structure functions (RSFs) of the spent samples were obtained referenced to the Ni foil, as shown in Fig. 4. The RSF exhibited a strong peak attributed to the first-nearest-neighbor Ni-Ni distance of 2.49 Å (1 Å = 10–10 m) for the Ni foil (Table 1). Furthermore, the second-, third-, and fourth-order Ni-Ni distances were observed at 3.54, 4.33 and 4.87 Å, respectively. The RSFs of the spent Ni/TiO2 were similar to that of Ni foil despite the reaction temperature of the durability test. Therefore, the Ni species in the spent catalysts were similar to pure fcc-Ni. The coordination number of nearest-neighbor Ni-Ni for the spent catalysts was estimated based on the shape of the

Fig. 2 PXRD Patterns for Ni/TiO2 and Ni/TiO2-250

Fig. 3 Ni K-edge XANES Spectra for Ni/TiO2 during Heat Treatment and Reaction
3.3. Influence of Residual Cl on Selective CO Methanation

Finally, the effect of residual Cl was examined on selective CO methanation over Ni/TiO₂, Ni/TiO₂-200, and Ni/TiO₂-250. Figure 5 shows the weight ratio of residual Cl to the catalysts. The ratios of Ni/TiO₂ and Ni/TiO₂-R were 1157 ppmw and 1148 ppmw, respectively, indicating that the pretreatment of Ni/TiO₂ by H₂ reduction did not remove any Cl components. After the reaction test, the ratio dropped to 449 ppmw for Ni/TiO₂-200 and 288 ppmw for Ni/TiO₂-250. Therefore, the accelerated deterioration tests decreased the number of surface Cl species on Ni/TiO₂ catalysts.

The undesirable RWGS reaction over Ni/TiO₂ was improved by treating the catalyst with a CO/CO₂/H₂/H₂O mixture (Fig. 1). As described in Section 3.2, the accelerated deterioration tests did not change the TiO₂ structure (Fig. 2) or metallic Ni structure (Fig. 4). In addition, surface Cl species were lost on Ni/TiO₂ after the tests (Fig. 5). Therefore, the improvement of RWGS reaction activity was caused by the loss of the surface Cl species during the reaction, resulting in low selectivity in CO methanation. The larger amount of surface Cl led to higher selectivity in CO methanation in the range of Cl amount from 0 to ca. 1150 ppmw.

RSFs (Table 1). The coordination numbers for the spent catalysts were ca. 10 despite the reaction temperature for the durability test. Therefore, metallic Ni size and structure showed almost no difference between the spent catalysts, and sintering of Ni species was not related to the deactivation of Ni/TiO₂.

| Sample Description | Shell | CN | σ [Å] | ΔE₀ [eV] | R [Å] | R factor |
|--------------------|-------|----|-------|----------|-------|----------|
| Ni foil            | Ni-Ni | First | 12 (fixed) | 0.085 | −1.004 | 2.49 | 0.025 |
|                    |       | Second | 6 (fixed) | 0.102 | 3.580 | 3.54 |
|                    |       | Third  | 24 (fixed) | 0.097 | −1.844 | 4.33 |
|                    |       | Fourth | 12 (fixed) | 0.067 | 6.774 | 4.87 |
| Ni/TiO₂ after a durability test at 250 °C for 8 h | Ni-Ni | First | 10 | 0.084 | −1.931 | 2.49 | 0.015 |
|                    |       | Second | 5.0 | 0.105 | 5.603 | 3.56 |
|                    |       | Third  | 20 | 0.099 | −2.133 | 4.33 |
|                    |       | Fourth | 10 | 0.068 | 7.424 | 4.88 |
| Ni/TiO₂ after a durability test at 320 °C for 3 h | Ni-Ni | First | 9.6 | 0.082 | −1.988 | 2.48 |
|                    |       | Second | 4.8 | 0.104 | 6.639 | 3.57 |
|                    |       | Third  | 19 | 0.098 | −1.656 | 4.33 |
|                    |       | Fourth | 9.6 | 0.066 | 7.462 | 4.88 |

Intrinsic loss factor $S₀² = 0.969$ (nearest-neighbor Ni-Ni from Ni foil data).

Notations: CN, coordination number; σ, Debye-Waller factor; ΔE₀, increase in the threshold energy; R, distance.

Fig. 4 Fourier Transforms of $k^3$ Weighted EXAFS Oscillations Measured at Room Temperature Near the Ni K-edge of (a) Ni/TiO₂ after the Durability Test at 250 °C for 8 h, (b) Ni/TiO₂ after the Durability Test at 320 °C for 3 h and (c) Ni Foil.

Fig. 5 Weight Ratios of Residual Cl to (a) Ni/TiO₂, (b) Ni/TiO₂-R, (c) Ni/TiO₂-200 and (d) Ni/TiO₂-250.
3.4. Deactivation Behaviors under Wet and Dry Conditions

To elucidate the effect of H2O in the reaction gas on CO methanation, the accelerated deterioration test was carried out under wet and dry conditions at 250 °C. Figure 6(a) shows the change in CO concentration with reaction time using Ni/TiO2. CO concentration was <100 ppm and did not change for 24 h under both conditions. Figure 6(b) shows the change in CH4 concentration over Ni/TiO2 during the accelerated deterioration test. CH4 concentration under the dry condition was lower than that under the wet condition, probably because the presence of H2O in the gas stream suppressed undesirable CO2 conversion via the RWGS reaction. CH4 concentration gradually increased with longer reaction time under both conditions, indicating that Ni/TiO2 catalysts were deactivated regardless of the presence of H2O in the gas stream.

4. Conclusions

The degradation factors of Ni/TiO2 catalysts during selective CO methanation were investigated using accelerated deterioration tests. The undesirable RWGS reaction over Ni/TiO2 was boosted by the tests, resulting in poor selectivity in CO methanation. The structures of the fresh and spent Ni/TiO2 catalysts were analyzed by powder X-ray diffraction and in-situ X-ray absorption spectroscopy. TiO2 structure was similar for both of the fresh and spent catalysts. In addition, the Ni species was metallic Ni after Ni/TiO2 was reduced by H2, and was identical for the spent catalysts. The accelerated deterioration tests decreased the number of surface Cl species on Ni/TiO2. Therefore, the improvement of RWGS reaction activity was caused by the loss of the surface Cl species during the reaction, resulting in low selectivity in CO methanation.

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