

Deactivation of Ru/Al₂O₃ Catalyst for Preferential CO Oxidation in the Presence of Low-concentration NH₃ by Nitrosyl Species

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(Received March 29, 2006; CL-060379; E-mail: wakita.h@jp.panasonic.com)

The behavior of a Ru/Al₂O₃ catalyst for the preferential CO oxidation in the presence of low-concentration NH₃ (21–75 ppm) was investigated. In contrast to the results in the absence of NH₃, the catalyst was rapidly deactivated at higher [O₂]/[CO] ratios in the presence of NH₃. NH₃ was oxidized to nitrosyl species, which was strongly adsorbed on Ru and suppressed the activation of both oxygen and CO. At low [O₂]/[CO] ratios, the catalyst exhibited a stable activity even in the presence of NH₃, and the deactivated catalyst was rapidly regenerated.

Stationary polymer electrolyte fuel cell (PEFC) cogeneration systems using natural gas have recently attracted much attention.¹ The fuel processor of the each system normally comprises not only a steam reformer but also a shift converter and a preferential CO oxidation (PROX) unit, since the CO concentration in the reformed fuel gas must be less than 10 ppm. Though the stoichiometric [O₂]/[CO] ratio is 0.5 for the CO oxidation, it is necessary to supply excess O₂ to achieve high CO conversion for the PROX in H₂-rich gas.² Thus, the PROX is usually conducted at the [O₂]/[CO] ratio of 1.5–2.5, though excess O₂ consumes H₂.

When the autothermal reforming or the steam reforming of fuel containing N₂ is carried out over Ru catalysts, NH₃ is formed from N₂ and H₂ to deteriorate the polymer electrolyte membrane; therefore, NH₃ absorbers have been proposed.³ When natural gas containing 1 vol % of N₂ is reformed with steam, the thermodynamic equilibrium concentration of NH₃ at 650 °C is 10–40 ppm. However, the influence of NH₃ on the catalytic activity for the PROX has not been reported to the best of our knowledge despite the practical importance. Here, we will show the influence of NH₃ on Ru/Al₂O₃ catalysts, which have been widely applied.^{2,4} Unexpectedly, the catalyst was rapidly deactivated at higher [O₂]/[CO] ratios in the presence of NH₃ in contrast to the results in the absence of NH₃.

A 2.0 wt % Ru/ θ -Al₂O₃ catalyst was supported on cordierite honeycombs (20-mm diameter; 10-mm thickness; 400 cell/inch²) as described in detail elsewhere.⁵ The Ru loading was 1.6 g/L. In a fixed bed reactor, a gas mixture composed of 51.5 vol % H₂, 0.3 vol % CO, 13.0 vol % CO₂, 0.4–0.6 vol % O₂, and 28.8 vol % H₂O balanced with He was fed at GHSV = 9300 h⁻¹ and 150 °C (the top of the catalyst bed) in the presence/absence of 21–75 ppm NH₃. For the H₂ oxidation, a gas mixture of 93.6 vol % H₂ and 0.5 vol % O₂ balanced with He was fed in the presence/absence of NH₃. NH₃ was trapped by a boric acid solution and was analyzed by liquid chromatography. For in situ IR measurements, 3.8 wt % Ru/Al₂O₃ catalyst powders were prepared. In a DRIFT apparatus, reaction tests were conducted at 150 °C in the presence/absence of 31 ppm

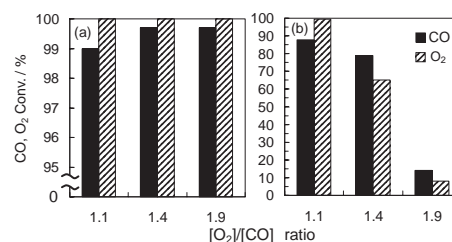


Figure 1. Dependence of [O₂]/[CO] ratios on the catalytic activity (a) in the absence of NH₃ and (b) in the presence of 21 ppm NH₃ at 200 min after the start of the poisoning. Black bar, CO conv.; Hatched bar, O₂ conv.

NH₃ in a gas mixture of 75.5 vol % H₂, 0.5 vol % CO, 19.0 vol % CO₂, 0.7 vol % O₂, and 1.6 vol % H₂O balanced with N₂ for the PROX or 90.9 vol % H₂, 0.7 vol % O₂, and 2.6 vol % N₂ balanced with He for the H₂ oxidation.

Figure 1 shows the effect of the [O₂]/[CO] ratios on the conversions of CO and O₂ for the RROX in the presence/absence of 21 ppm NH₃. In the absence of NH₃, the catalyst exhibited a stable high activity over 200 min and the CO conversion increased with an increase in the [O₂]/[CO] ratios. To the contrary, both conversions at 200 min after the start of NH₃ supply decreased with an increase in the [O₂]/[CO] ratios. Figure 2 shows the changes in the catalytic activity in the presence of NH₃. The CO and O₂ conversions at the high [O₂]/[CO] ratio of 1.9 decreased simultaneously. After NH₃ was stopped, both conversions were slowly restored. At the [O₂]/[CO] ratio of 1.4, the

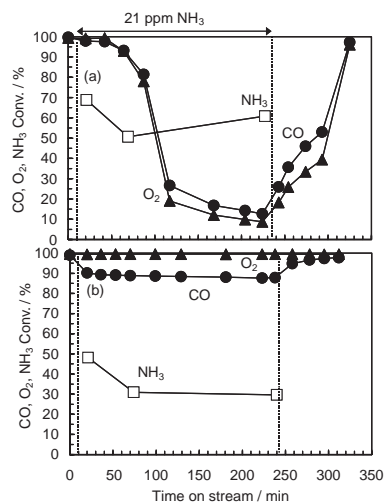


Figure 2. Changes in the catalytic activity in the presence/absence of 21 ppm NH₃: (a) [O₂]/[CO] = 1.9, (b) [O₂]/[CO] = 1.1; (●) CO conv., (▲) O₂ conv., (□) NH₃ conv.

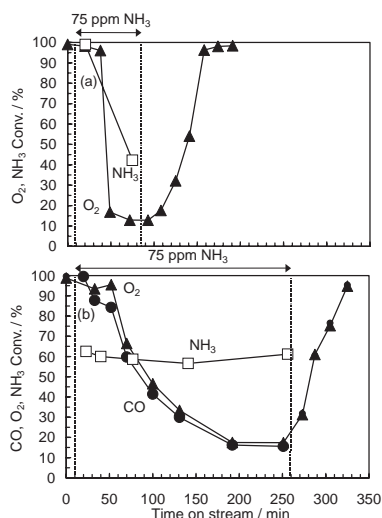


Figure 3. Changes in the catalytic activity in the presence/absence of 75 ppm NH₃: (a) H₂ oxidation and (b) PROX; (●) CO conv., (▲) O₂ conv., (□) NH₃ conv.

catalyst was deactivated more slowly. On the contrary, at the low [O₂]/[CO] ratio of 1.1, the CO and O₂ conversions were held constant at ≈90 and 100% for 240 min, respectively. After NH₃ was stopped, the CO conversion was more rapidly restored than that at the higher [O₂]/[CO] ratios, which indicates that the deactivation was suppressed at lower [O₂]/[CO] ratios and the deactivated catalyst was rapidly regenerated under the reduction atmosphere. Though the amount of NH₃ supplied for ≈30 min was equal to that of the active sites estimated by the amount of CO adsorbed, the CO conversion was still high at this moment, which is consistent with the facts that only part of NH₃ was consumed as shown in Figure 2.

Figure 3 shows the comparison between the H₂ oxidation without CO under excess H₂ condition and the PROX ([O₂]/[CO] = 1.4) at the same O₂ concentration in the presence of 75 ppm NH₃. For the H₂ oxidation without CO, the O₂ conversion has been over 95% for 30 min, and just negligible amount of NH₃ was detected; then the O₂ conversion rapidly decreased with a decrease in the NH₃ conversion. However, for the PROX, the coexistent CO suppressed the deactivation and the NH₃ conversion was held constant. It indicates that CO adsorbed on Ru hindered the adsorption of NH₃.

In the IR apparatus, the PROX at the [O₂]/[CO] ratio of 1.4 was conducted in the presence/absence of 31 ppm NH₃. Figure 4a shows the spectrum over the region of C–O stretching vibrations before the poisoning. A broad peak composed of a few bands was observed at 1850–2100 cm⁻¹, and those bands were attributed to the linearly adsorbed monocarbonyl species on Ru sites with the different oxidation states.^{6,7} During the poisoning, the intensity of a new band, at 1830 cm⁻¹ attributed to linearly adsorbed nitrosyl species on Ru,⁸ increased with time on stream (Figures 4b and 4c). The assignment was also confirmed by the red shift of the band for the ¹⁵NH₃ poisoning. In addition, the intensity of the band, at ≈2020 cm⁻¹ assigned to the monocarbonyl species on Ru⁰, decreased. At the same time, the shoulder band at 2060 cm⁻¹ became clear and a new band appeared at 2176 cm⁻¹. They were tentatively assigned to Ruⁿ⁺–(CO)₂ dicarbonyls and Ru^{m+}(CO)₃ tricarbonyls, respectively.^{6,7} It is suggested that the nitrosyl species enhanced the formation of

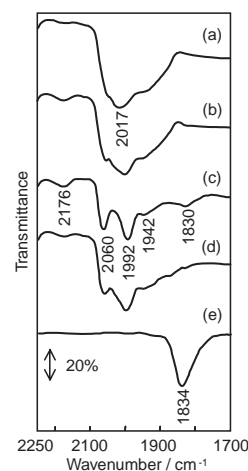


Figure 4. In situ IR spectra: (a) before the poisoning for the PROX, (b) 60-min poisoning with 31 ppm NH₃, (c) 330-min poisoning, (d) at 90 min after the stop of NH₃, and (e) 180-min poisoning for the H₂ oxidation.

the multicarbonyl species and stabilized the oxidized Ru sites to deactivate the catalyst. After NH₃ was stopped at 330 min, the intensities of both nitrosyl and tricarbonyl bands decreased coincidentally with an increase in the intensity of monocarbonyl band at ≈2020 cm⁻¹ (Figure 4d). We concluded that the nitrosyl species suppressed the activation of both oxygen and CO.

The IR spectra for the H₂ oxidation without CO under excess H₂ condition were also taken at the same NH₃ and O₂ concentrations. The intensity of nitrosyl band at 180 min for the H₂ oxidation (Figure 4e) was larger than that at 330 min for the PROX (Figure 4c), which indicates that the catalyst for the PROX was slowly deactivated by the presence of CO. It is consistent with the results shown in Figure 3. For the H₂ oxidation without CO, NH₃ was stopped at 180 min; however, the nitrosyl band has hardly changed for next 60 min, which suggests that the seriously poisoned active sites were regenerated very slowly. Next, the air supply was stopped for 10 min, which largely diminished the band. As a result, the coexistent O₂ suppressed the decomposition of nitrosyl species. We also conducted the PROX in the presence of NO, which rapidly deactivated the catalyst and concluded that the rate of deactivation was determined by the oxidation of NH₃ and the increase in the O₂ concentration promoted the oxidation of NH₃.

We now concluded that the Ru catalyst was rapidly deactivated at higher [O₂]/[CO] ratios by the presence of NH₃, which was oxidized to the nitrosyl species. Under the reduction atmosphere, the deactivated catalyst was rapidly regenerated. On the same score, the catalyst exhibited a high activity for a longer time at lower [O₂]/[CO] ratios.

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