Ammonia Production Characteristics of Ru/Al$_2$O$_3$ Catalysts Using Hydrogen Permeable Membrane

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Ammonia production characteristics were performed on Ru–Al$_2$O$_3$ catalyst loaded on a Ag–Pd hydrogen permeable membrane in the temperature range from room temperature to 523 K under atmospheric pressure, by which the activation energy observed (33.1 kJ mol^{-1}) was lower than the sole Ru–Al$_2$O$_3$ catalyst (66.8 kJ mol^{-1}). Ammonia was formed over the membrane reactor even at room temperature due to the high reactivity of atomic hydrogen supplied from the membrane.

Hydride forming alloys exhibit various interesting catalytic properties. These alloys easily dissociate molecular hydrogen on their surface, allowing the rapid formation of metal hydrides under mild conditions. The dissociation step of molecular hydrogen plays the significant role for the hydrogenation. Furthermore, hydrogen in the metal hydrides exists in a monoatomic state and is highly reactive, so that useful hydrogenation processes using hydride forming alloys have been investigated.[1–4] On ammonia synthesis, it has been reported that ammonia formation is observed on MmNi$_5$ (Mm = La-rich mischmetal) under 5 MPa of a N$_2$–H$_2$ mixed gas at room temperature owing to the high reactivity of atomic hydrogen provided by MmNi$_5$H$_x$.[5] However, the ammonia formation activity is expected to be more improved by hybridization of hydrogen storage alloys and high performance catalysts for ammonia synthesis.[6,7] In this study, a membrane reactor was constructed by loading with the Ru–Al$_2$O$_3$ catalyst on the outer side of a hydrogen permeable Ag–Pd alloy tube, where atomic hydrogen was continuously supplied through the membrane by introducing H$_2$ gas into the inner side, and its ammonia formation property was characterized.

Tube of Ag–Pd alloy (Ag–25 at.%) with 5 mm in diameter, 100 mm in length and 0.5 mm in thickness was used as the hydrogen permeable membrane. The Ru–Al$_2$O$_3$ catalyst was loaded at the outer side of the tube by the following procedures: Al$_2$O$_3$ was repeatedly several times coated by dipping the alloy tube in a hexane solution of Al(C$_2$H$_5$)$_3$ and decomposing it in air. Ru was subsequently impregnated in a Ru$_3$(CO)$_{12}$–hexane solution via the decarbonylation by heating in H$_2$ at 573 K.[8,9] The amount of Ru–Al$_2$O$_3$ catalyst loaded on the membrane was 7.8 × 10^{-3} g. As a reference for the membrane reactor, the powdered Ru–Al$_2$O$_3$ catalyst was also prepared: after dipping the stainless tube in the hexane solution of Al(C$_2$H$_5$)$_3$ and impregnating Ru metal in the Ru$_3$(CO)$_{12}$–hexane solution, the powder was stripped from the substrate. The Ru metal amount of catalyst powder was about 2 wt% as well as that for the Ru–Al$_2$O$_3$/Ag–Pd. The ammonia product rates were measured in a temperature range from room temperature to 523 K by flowing N$_2$ gas (> 99.999% in purity) with a rate of 10 mL min^{-1} on the outer side (catalyst side) of tube and Ar–H$_2$ mixed gases (both > 99.999% in purity) with various gas compositions

in the inner one to control the hydrogen permeation rate at the individual reaction temperatures. The hydrogen permeation rate was checked on a gas chromatograph. Ammonia product rate was evaluated from the differences between the pH values of H$_2$SO$_4$ solution trap and/or the absorbances of the Nessler's test solutions before and after the reactions.
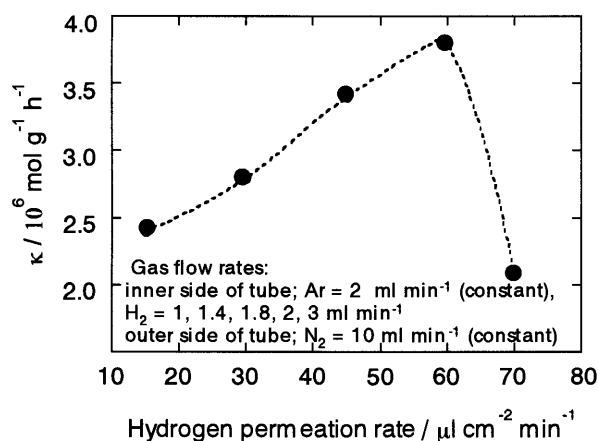

Figure 1. Dependence of hydrogen permeation rate on the ammonia product rate of the Ru-Al$_2$O$_3$/Ag-Pd membrane reactor at 423 K. Y axial index k represents ammonia product rate.

Figure 1 shows the dependence of the ammonia product rate on the hydrogen permeation rate as observed at 423 K under gas flow rates in the inner side of tube: [Ar 2 mL min^{-1} (constant)]–H$_2$ (1, 1.4, 1.8, 2, and 3 mL min^{-1}) for the respective hydrogen permeation rates of 15, 30, 45, 60, and 70 μL cm^{-2} min^{-1}. The activity of ammonia product over the membrane reactor was given by the weight of Ru–Al$_2$O$_3$ per gram. The ammonia product rate was monotonously accelerated with increasing the hydrogen permeation rate up to 60 μL cm^{-2} min^{-1} (overall H$_2$ flow rate through the membrane was 0.9 mL min^{-1}). However, as the hydrogen permeation rate exceeded 60 μL cm^{-2} min^{-1}, the rate sharply dropped. This sharp decline indicates that the mechanism of the ammonia formation over the membrane reactor is changed by the hydrogen permeation rate through the membrane. Since the pressure of generated ammonia is negligible due to its low yield under the moderate conditions (atmospheric pressure <523 K). The order of hydrogen pressure for the rate equation of ammonia synthesis is positive below the hydrogen permeation rate of 60 μL cm^{-2} min^{-1} and inversely negative above that of 60 μL cm^{-2} min^{-1}. One of the reasons for this change is presumably attributed to the hydrogenation processes of nitrogen on the catalyst. The atomic hydrogen is continuously provided from the membrane and

spilled over the surface of Ru–Al$_2$O$_3$ catalyst. Below the hydrogen permeation rate of 60 μL cm^{-2} min^{-1}, the hydrogenation process of dissociated nitrogen with the atomic hydrogen supplied through the Ag–Pd membrane is dominant. Above the hydrogen permeation rate of 60 μL cm^{-2} min^{-1}, the main process is the reaction between nitrogen and hydrogen atoms adsorbed on the catalyst. Since the adsorption energy of hydrogen atom on Ru metal is great to inhibit the nitrogen adsorption, the activation energy of the latter process is expected to be higher than that of the former one. The conventional flow reaction over the sole Ru–Al$_2$O$_3$ catalyst (1 g) was performed using a fixed-bed reactor at 423 K in a N$_2$–H$_2$ mixed gas with a composition of N$_2$:H$_2$ = 0.9:10 and the same space velocity in the case of the membrane reactor. The ammonia product rate over the sole Ru–Al$_2$O$_3$ catalyst was only 0.84 μmol g^{-1} h^{-1}. The product rate for the membrane reactor with the hydrogen permeation rate of 60 μL cm^{-2} min^{-1} (optimal permeation rate) was 3.8 μmol g^{-1} h^{-1}. The activity of ammonia product rate over the membrane reactor was about 4 times higher than that over the sole Ru–Al$_2$O$_3$ catalyst, suggesting that the high reactivity of atomic hydrogen supplied from the membrane spilled over the Ru–Al$_2$O$_3$ catalyst.

Figure 2 shows the Arrhenius plots for the ammonia product rates of the Ru–Al$_2$O$_3$/Ag–Pd membrane reactor and the
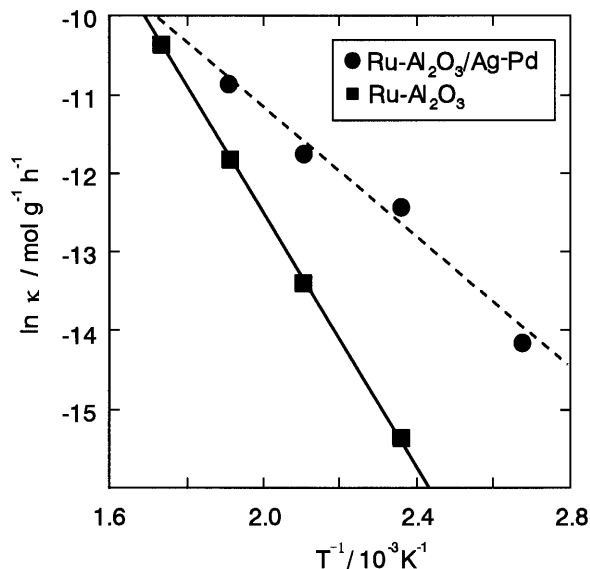
sole Ru–Al$_2$O$_3$ catalyst in the temperature range of 373–573 K. The N$_2$ gas flow rate was 10 mL min^{-1} and hydrogen permeation rates over the membrane for every reaction were fixed to be 60 μL cm^{-2} min^{-1} for the membrane reactor (gas composition in the inner side of the reactor tube: [Ar 2mL min^{-1} (constant)]–H$_2$ 1.4, 1.8, 2.0, and 3.0 mL min^{-1} at the respective reaction temperatures of 373, 423, 473, 523 K). The conventional ammonia formation reaction over the sole Ru–Al$_2$O$_3$ catalyst was carried out in the N$_2$–H$_2$ mixed gas (N$_2$:H$_2$ = 1:3) with a flow rate of 30 mL min^{-1}. The respective activation energies for the Ru–Al$_2$O$_3$/Ag–Pd membrane reactor and the sole Ru–Al$_2$O$_3$ catalyst were 33.1 and 66.8 kJ mol^{-1}, and the latter one fairly coincided with the value reported by Murata and Aika.[7] The activation energy of the Ru–Al$_2$O$_3$/Ag–Pd membrane reactor is apparently lower than that of the sole Ru–Al$_2$O$_3$ catalyst, so that the Ru–Al$_2$O$_3$/Ag–Pd membrane reactor is concluded to maintained the high activity compared with that of the sole Ru–Al$_2$O$_3$ catalyst, particularly, in the low temperature region below 523 K. Furthermore, even at ambient temperature, when the hydrogen permeation rate was controlled to be very low, the ammonia formation over the present membrane reactor was confirmed by the Nessler's reagent test and the pH value change of the H$_2$SO$_4$ solution trap, and the evaluated product rate was 0.47 μmol g^{-1} h^{-1}, whereas no ammonia formation was observed on the sole Ru/Al$_2$O$_3$ catalyst at the same reaction temperature.

Figure 2. Arrhenius plots of the rates of ammonia formation on the Ru-Al$_2$O$_3$/Ag-Pd alloy membrane reactor and the sole Ru-Al$_2$O$_3$ catalyst. The gas flow rates; N$_2$ = 10 ml min^{-1}, hydrogen permeation rate regulated to be 60 μl cm^{-2} min^{-1} over the membrane reactor, N$_2$ + 3H$_2$ = 30 ml min^{-1} for the sole Ru-Al$_2$O$_3$ catalyst.

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