High Dependence for Reaction Pressure on Ru/(MgO–CeO$_2$)/Ag–Pd Ammonia Synthesis Membrane Reactor

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Ammonia production characteristics were conducted on Ru/(MgO–CeO$_2$) catalysts loaded on Ag–Pd-hydrogen-permeable membrane, in which the ammonia formation rate on the membrane reactor was more increased than that on conventional flow reaction. This result is responsible for the high reactivity of atomic hydrogen supplied from the Ag–Pd-permeable membrane to retard the hydrogen poisoning generally observed on Ru-based ammonia synthesis catalysts.

It is well known that Ru-based catalysts promoted by alkali metal shows the excellent activity for ammonia synthesis which is higher than traditional doubly promoted Fe–Al$_2$O$_3$–K$_2$O catalysts under mild conditions.[1,2] Consequently, they have been attracted much attention as a second generation ammonia synthesis catalysts and the commercial plant, in fact, started in 1992 using promoted Ru catalysts supported on carbon.[3] However, such Ru-based catalysts essentially have a strong hydrogen poisoning problem on ammonia synthesis due to the high affinity of Ru metal to hydrogen.[4] In our previous work, ammonia production characteristics were studied on Ru/Al$_2$O$_3$ catalysts loaded on the hydrogen-permeable Ag–Pd membrane,[5] on which ammonia was more readily formed than those for conventional flow-type reactors at 423 K because of the high reactivity of atomic hydrogen continuously provided from the Ag–Pd membrane. The ammonia formation mechanism on such membrane reactor is thought to be different from the usual flow reaction system, as the reaction order of hydrogen partial pressure is positive in a region of suitable hydrogen supplying rate.

In this study, Ru/(MgO–CeO$_2$) catalysts were applied for the ammonia synthesis membrane reactor, since they showed high catalytic activity for ammonia synthesis in our recent study.[6] The ammonia production characteristics were performed on the Ru/(MgO–CeO$_2$)/Ag–Pd membrane reactor especially for the high pressure condition.

Plates of Ag–Pd (75 atom %) alloy (reaction area: 9 cm^2, thickness: 100 μm) were used for the hydrogen-permeable membrane. The Ru/(MgO–CeO$_2$) catalysts were individually loaded on each Ag–Pd alloy plate by the following procedures. Mixed hydroxyl gels, Mg(OH)$_2$–Ce(OH)$_{4-x}$, were prepared as support precursors by coprecipitation method from their acetate salt solutions with 50 mol % of Ce(OH)$_{4-x}$ contents. After washing the resultant gels were impregnated with a Ru$_3$(CO)$_{12}$ THF solution. The Ru metal loading amount was 5 wt % with respect to the resulting MgO–CeO$_2$ support. The detail of preparation method is described in elsewhere.[6] The slurry mixing catalyst precursor Ru(CO)$_n$/Mg(OH)$_2$–Ce(OH)$_{4-x}$ and water was spread over one side of the Ag–Pd plate.[7] Then they were heated at 723 K for 2 h in a flow of H$_2$ gas (40 mL min^{-1}) to obtain Ru/(MgO–CeO$_2$)/Ag–Pd membrane. Ammonia formation rates on the membrane reactor were measured at 573–673 K by flowing N$_2$ gas (>99.999% in purity) with a rate of 40 mL min^{-1} on the one side (catalyst side) of plate and N$_2$–H$_2$ mixed gases (>99.999% in purity) with various gas compositions (different hydrogen partial pressure) in the opposite side to control the hydrogen permeation rate. A schematic illustration of the membrane reactor was shown in ref 5. The hydrogen permeation rate was checked on a gas chromatograph. Ammonia formation rate was evaluated from the differences of the pH values of H$_2$SO$_4$ solution trap before and after the reactions.

Figure 1 shows the dependence of the ammonia formation rate on the hydrogen permeation rate over the membrane reactor at reaction pressure of 0.1 MPa in the temperature range of 573–673 K, together with the result of conventional flow reaction as reference. It is noted that the amount of Ru/(MgO–CeO$_2$) catalyst loaded on the membrane was 50 mg and the ammonia formation rate was calculated per 1 g of the Ru/(MgO–CeO$_2$) catalyst. The ammonia formation rates on membrane reactor at every reaction temperature were increased with the increase of hydrogen permeation rate below the each optimum one, suggesting that reaction order of partial pressure for hydrogen is positive. The conventional flow reaction was also carried out by flowing N$_2$–H$_2$ mixed gas (N$_2$: 40 mL min^{-1}, H$_2$: 20 mL min^{-1}) in the both side of Ag–Pd plate at 673 K as the same reaction conditions on the membrane reactor. The ammonia formation rate was 1250 μmol g^{-1} h^{-1} which is lower than that observed on the membrane reactor (1600 μmol g^{-1} h^{-1}). These results are attributed to the fact that the highly reactive atomic hydrogen supplied from the Ag–Pd membrane by spillover reacts with atomic nitrogen dissociated on the catalyst to readily form ammonia and

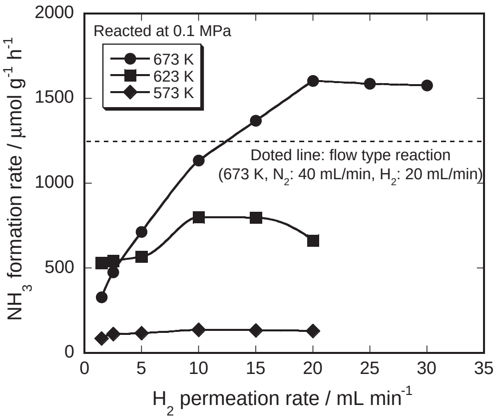

Figure 1. Dependence of hydrogen permeation rate on the ammonia formation on one of the Ru/(MgO–CeO$_2$)/Ag–Pd membrane reactor at 673 K under 0.1 MPa, together with the result observed on the conventional flow reaction.

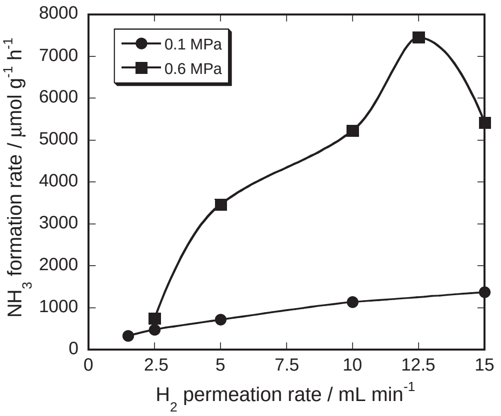

Figure 2. Dependence of reaction pressure of ammonia formation rate on the Ru/(MgO–CeO_2)/Ag–Pd membrane reactor at 673 K with hydrogen permeation rate.

also such unusual activation way of hydrogen reduces the hydrogen poisoning. In addition, CeO_2 used as the support partially in this study can avoid the hydrogen poisoning further than the case using Al_2O_3 as the support.[8] As a reference, the ammonia formation rate (catalyst weight 0.2 g) on the fixed bed quartz tube (i.d. 10 mm) with the N_2–H_2 mixed gas (N_2: 15 mL min^{-1}, H_2: 45 mL min^{-1}) at 673 K was 3660 µmol g^{-1} h^{-1}.[6] The performance of catalyst loaded on the Ag–Pd membrane was degraded in the process of catalyst loading. Energy dispersive X-ray analysis for the Ru/(MgO–CeO_2)/Ag–Pd membrane revealed that Ru component was diffused to the Ag–Pd membrane, while Ag and Pd components were found on the region of catalyst surface. This may be the reason of the deterioration of intrinsic catalyst activity on the membrane reactor. In fact, the ammonia formation rate on the Ru/(MgO–CeO_2) catalyst stripped from the membrane was ≈1300 µmol g^{-1} h^{-1} by the conventional flow reaction. Optimal hydrogen permeation rates at reaction temperatures of 573, 623, and 673 K were 10, 10, and 20 mL min^{-1}, respectively. They have a tendency to increase with elevating reaction temperature because the atomic hydrogen adsorbed on the Ru metal easily desorbed at high reaction temperature, allowing the high hydrogen permeation rate at 673 K.

Figure 2 shows the dependence of reaction pressure of ammonia formation rate on the Ru/(MgO–CeO_2)/Ag–Pd membrane at 673 K with hydrogen permeation rate. The ammonia formation rate reacted at 0.6 MPa was sharply increased compared to that at 0.1 MPa. The maximum ammonia formation rate (7450 µmol g^{-1} h^{-1}) was observed when hydrogen permeation rate was 12.5 mL min^{-1}. Hydrogen conversion for the above condition is about 1.6% and the ammonia concentration is 0.26% which dose not reach to a theoretical equilibrium limitation of 2.3%.[3] When the hydrogen permeation rate exceeded 12.5 mL min^{-1}, the ammonia formation rate rapidly dropped. One of the reasons for this decline is presumably the hydrogen poisoning by excess hydrogen permeation.[5] On the other hand, the ammonia formation rate performed on the conventional flow reaction was 4470 µmol g^{-1} h^{-1} by flowing N_2–H_2 mixed gas (N_2: 40 mL min^{-1}, H_2: 12.5 mL min^{-1}) at 673 K, which is about 60% of the membrane reactor. The dependence of reaction pressure on the membrane reactor is higher than the conventional flow one. This result supports the unusual mechanism for ammonia formation on the membrane reactor mentioned above. Ru-based catalysts generally have a problem of hydrogen poisoning especially at high pressure.[9,10] Hydrogen and nitrogen gases simultaneously adsorb and dissociate on the catalyst in the conventional flow reaction system. However, in the present membrane reactor, already dissociated atomic hydrogen supplied from the Ag–Pd membrane can lower the catalyst loading, avoiding the hydrogen poisoning. To elucidate our proposition, the reaction orders with respect to hydrogen, nitrogen, and ammonia are now determining according to a power-law kinetics.[10] It is additionally worthy to say that the sole catalyst Ru/(MgO–CeO_2) can produce more amount of ammonia even at high pressure compared to the reaction at ambient pressure. The hydrogen poisoning was effectively improved by substituting CeO_2 in a support.[8] Furthermore, strong metal–support interaction on the Ru/(MgO–CeO_2) catalyst was emerged by the unique preparation method of this study where $Ru_3(CO)_{12}$ was loaded on $Mg(OH)_2$–$Ce(OH)_{4-x}$ to resultantly increase the contact area between metal and support.

In conclusion, the Ru/(MgO–CeO_2)/Ag–Pd membrane reactor has the higher catalytic activity than the conventional flow reaction because of the high reactivity of atomic hydrogen supplied from the Ag–Pd-permeable membrane with the moderation of hydrogen poisoning. In addition, the ammonia formation rate on the membrane reactor was significantly increased when the reaction was conducted at 0.6 MPa, supporting the novel ammonia formation mechanism on the present membrane reactor.

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