CATALYSTS FOR SYNTHESIS/DECOMPOSITION OF AMMONIA AS A HYDROGEN CARRIER

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Development of a carbon-free hydrogen storage and transportation system (Fig. 1) using ammonia has been motivated by the desire to achieve a carbon-free society and the facts that (1) ammonia has a high hydrogen content (17.6 wt%) and energy density (12.8 GJ m^{-3}); (2) ammonia is easily liquefied at room temperature; and (3) carbon dioxide is not released when hydrogen is produced by ammonia decomposition. To establish such a system using ammonia, development of highly efficient catalysts and processes for ammonia synthesis and decomposition are needed.

Ammonia is commonly produced by the Haber-Bosch process, which accounts for more than 1% of global energy consumption. In this process, 60% of the energy is recovered as the enthalpy of ammonia. However, the remaining 40% is lost to the production of hydrogen from natural gas, ammonia synthesis, and gas separation. Ammonia is produced at high temperatures (>450 °C) and pressures (>20 MPa) over an iron-based catalyst. A catalyst that yields ammonia with high efficiency under milder reaction conditions than are required by iron-based catalysts would reduce energy consumption in the process. Our group has found that Ru/Pr_2O_3 without any dopant catalyzes the highest observed ammonia synthesis rate among oxide-supported Ru catalysts under mild reaction conditions (400 °C, 1.0 MPa) [1]. STEM analysis revealed that the Ru was loaded as a low-crystalline nano-layer. The unique structure of Ru in this catalyst as well as the strong electronic character of Pr_2O_3 were found to synergistically accelerate cleavage of the N≡N bond, which is the rate-determining step.

Hydrogen produced from ammonia is used in fuel cells, engines, and turbines. However, its adoption as a hydrogen source, especially for household and transportable devices, has been limited by lack of an efficient process for producing hydrogen and nitrogen by ammonia decomposition. To overcome this limitation, it is necessary to develop a process that can be initiated rapidly, produces hydrogen at a high rate, and does not need external heat. We have found that hydrogen can be produced by supplying ammonia and oxygen at room temperature to a pre-treated $Ru/\gamma\text{-}Al_2O_3$ catalyst without external heating [2]: the heat generated by ammonia adsorption onto this catalyst warms it from room temperature to the catalytic ammonia auto-ignition temperature. Subsequent oxidative decomposition of ammonia produces hydrogen (NH_3 (g) + $0.25O_2$ (g) → H_2 (g) + $0.5N_2$ (g) + $0.5H_2O$ (g) $\Delta H = -75$ kJ mol^{-1}). Differential calorimetric measurements combined with volumetric gas-adsorption analysis revealed that a large amount of heat was evolved by chemisorption of ammonia onto RuO_2 and $\gamma\text{-}Al_2O_3$ and by physisorption of multiple ammonia molecules.

We believe that these catalysts and processes will facilitate the development of effective methods for synthesizing and decomposing ammonia. Such methods can be expected to contribute to the development of efficient, carbon-free energy production and thus to global solutions for energy and climate crises.

REFERENCES

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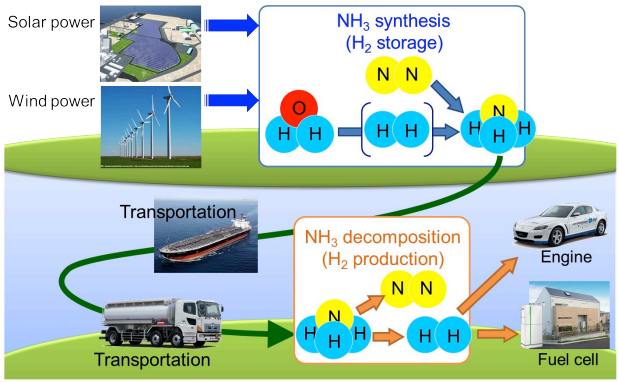

Fig. 1. Carbon-free hydrogen storage and transportation system using ammonia as a hydrogen carrier.