Title

Design of core-shell structured metal catalysts for synthesis of carbon-free ammonia fuel

Speaker

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Abstract

Ammonia has attracted great attenuations as a H_2 (energy) carrier for utilizing renewable energy and a carbon-free fuel because CO_2 is not emitted when ammonia is decomposed to produce H_2 or combusted in power station. Ammonia is commonly produced by the Haber-Bosch process. In this process, ammonia is produced at high temperatures (>450 ºC) and pressures (>20 MPa) over an iron-based catalyst and the use of fossil fuels emits large amount of CO_2. A catalyst that yields ammonia with high efficiency under mild reaction conditions (<400 ºC, <10 MPa) would reduce energy consumption in the green ammonia fuel synthesis process.

Ru-based catalysts shows higher activity than iron-based catalyst under mild reaction conditions. However, active Ru catalyst loaded on oxide support, which is easily prepared and stable in air and thus suitable for practical application, is yet to be developed. We reported that composite-rare-earth oxides such as $La_{0.5}Ce_{0.5}O_{0.75}$ and $La_{0.5}Pr_{0.5}O_{1.75}$ supported Ru catalysts showed high ammonia synthesis rate under mild conditions (300 - 400 ºC, 1.0 MPa), when the catalysts were pre-reduced at unusually high temperature, 650 ºC. Furthermore, we found that $Ru/Ba_{0.1}La_{0.45}Ce_{0.45}O_{1.68}$ reduced at 700 ºC showed the comparable to or better activity than other reported oxide supported Ru catalysts.

Such design concept of catalyst was applied to development of Co catalysts. We discovered that Co/BaO/MgO reduced at 700 ºC exhibited higher ammonia synthesis rate than bench-mark Ru catalysts at 350 ºC and 1.0 MPa. At the same temperature the ammonia synthesis rate of Co/BaO/MgO was increased drastically with increase in pressure to 3.0 MPa and was higher than that of active Ru-based catalyst such as $Ru/La_{0.5}Ce_{0.5}O_{0.75}$. This is because Co/BaO/MgO is free from hydrogen poisoning, which is typical drawback for Ru catalysts. It was uncovered that the Co nanoparticles are encapsulated by nano-fractions of BaO and all the surface-available Co sites contact with the low-crystalline nano-fractions, and electrons are effectively donated from the nano-fractions *via* Co to antibonding π-orbital of N_2, which results in weakening of N≡N bond, rate determining step for ammonia synthesis.