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## Highly monodisperse sub-nanometer and nanometer Ru particles confined in alkali-exchanged zeolite Y for ammonia decomposition

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## ABSTRACT

Nanometer- and sub-nanometer-sized Ru particles were deposited on four different alkali-exchanged zeolite Y supports (H-Y, Na-Y, K-Y, and Rb-Y) by an ion-exchange method followed by a calcination treatment under vacuum. The average particle size of the Ru-based catalysts (Ru/M-Y: M = H, Na, K, and Rb) was approximately 1 nm, with the majority of Ru particles being highly monodisperse with a size in the sub-nanometer range. The oxygen-deficient environment during calcination and the well-defined repeated pore structure of zeolite are thought to have strongly affected the formation of Ru particles by restraining particle growth inside the upper/sodalite cages of the zeolite Y matrix. X-ray absorption spectroscopic analysis revealed that the Ru particles were highly reducible at low temperatures and were low coordinated with short Ru—O bonds. The effect of surface acidity on the catalytic activity of Ru/M for ammonia decomposition was investigated. Ammonia temperature-programmed desorption analysis suggested that the acidity of the alkali-exchanged zeolite Y increased (H > Na > K > Rb) with an increase in the electronegativity of the alkali cation. Among all the catalysts, H-Y exhibited the highest acidity because of the presence of strong Brønsted acid sites. The catalytic activities of the Ru/M-Y catalysts for ammonia decomposition in the gas phase decreased in the order of Ru/Rb-Y > Ru/K-Y > Ru/Na-Y > Ru/H-Y, that is, the lower the acidity, the higher is the catalytic activity. This was correlated to increased electron density of the surrounding Ru active sites, which likely facilitated nitrogen desorption from the catalyst surface. Finally, the surface intermediates formed under ammonia decomposition conditions were identified by *in situ* diffuse reflectance infrared Fourier transform spectroscopy. NH/NH<sub>2</sub> surface intermediates were identified in the presence of Ru with weaker N—H bonds in the case of Ru/Rb-Y compared to the case of Ru/H-Y. Overall, the high catalytic activity of the Ru/Rb-Y catalyst for ammonia decomposition was mainly because of the high basicity of the Rb-Y zeolite and the confined nanometer- and sub-nanometer-sized Ru particles, which led to a high Ru dispersion, open pore structure of the zeolite, and strong metal to support interaction between the Ru active sites and the Rb-Y zeolite support.

## 1. Introduction

With increasing global energy demands, the consumption of fossil fuels has increased, and that not only leads to the depletion of carbon-based fuels, but also negatively affects the environment due to the greenhouse gas emissions resulting from the use of fossil fuels. Therefore, clean and sustainable energy sources are being extensively explored to mitigate the energy and environmental problems.

Renewable energy production from numerous potential renewable sources (e.g., solar and wind) is expected to increase significantly to help realize a sustainable energy society in the future. However, because of the unpredictable and intermittent nature of renewable energy sources, electricity generated from renewable sources needs to be stored in a carrier to be used at a desired site. Hydrogen has been recognized as a promising large-scale (>1 GW h) renewable energy carrier because of its high gravimetric energy density (ca. 33.3 kW h kg<sup>-1</sup>; 120 MJ/kg-H<sub>2</sub>).

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