In-situ observation of N_2 and H_2 adsorbed on Ru/MgO catalyst using modulation excitation-infrared spectroscopy

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Ru catalysts were reported to exhibit high catalytic activity under milder conditions than Fe-based catalysts used in Haber-Bosch process.[1] This is because both adsorption of N_2 molecules and desorption of products on Ru surfaces proceed smoothly due to the moderate binding energy between Ru and N species.[2] On the other hand, the strong binding energy between Ru and H species causes hydrogen poisoning, which diminishes the catalytic activity under high pressure conditions. To extend availability of Ru catalysts, the adsorption behavior of N_2 and H_2 under reaction conditions should be clarified. In this study, we examine the adsorption behavior of reactants on Ru nanoparticle catalysts surface under N_2 or H_2 atmosphere by employing modulation-excitation infrared spectroscopy (MEIRS), which enables highly sensitive and time-course observation of their adsorption states.

We prepared MgO supported Ru nanoparticle catalyst with 4-5wt% of Ru loading (Ru/MgO) by impregnation, thermal decomposition and hydrogen reduction according to the report.[3] Fig. 1 shows the time-domain spectrum of MEIRS while alternately introducing N_2 and Ar at 250 °C under 0.1 MPa. The absorbance increased with time to exposure to N_2 and decreased after introduction of Ar. We observed two sharp peaks at 2071 and 1932 cm^{-1} and broad peaks at 1631, 1427, 1211 and 980 cm^{-1}. From the density functional theory (DFT) calculations, the sharp and broad peaks were assigned to vertical and horizontal adsorption of N_2 on Ru nanoparticles, respectively.[4] In addition, each peaks were attributed to the adsorptions on different sites, which hold N_2 by different number of Ru atoms. The newly observed adsorption states of N_2 are possibly ascribed to hidden intermediate species formed on Ru/MgO and this finding would contribute to the elucidation of the reaction mechanism in catalytic ammonia synthesis.

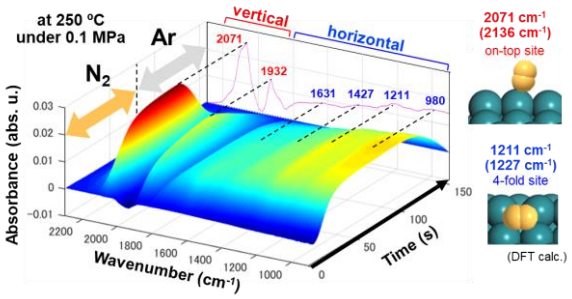

Fig. 1. Time-domain spectrum of MEIRS for Ru/MgO measured in the modulation of N_2 and Ar at 250 °C under 0.1 MPa.

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