CATL 21 Mechanism and isotope effect of ammonia synthesis over Fe and Ru catalysts

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Ammonia synthesis mechanism (dissociative or associative route?) is a never ending problem. The deuterium isotope effects in ammonia synthesis over both iron-based catalysts, the unpromoted Fe catalyst and double-promoted Fe catalyst (A110-3), and ruthenium-based catalysts, the Ru/γ-Al_2O_3, Ru/MgO, K-Ru/MgO and Ba-Ru/MgO, were evaluated with $N_2/3H_2$ and $N_2/3D_2$ under reaction conditions of 0.2 MPa, GHSV = 12000 h^{-1} or 24000 h^{-1} and 633 K ~ 773 K. A strong deuterium inverse isotope effect, about 2 of r_D/r_H , was observed for above catalysts in which the r_D/r_H is 1.75 ~2.07 for unpromoted Fe, 1.93~2.44 for double-promoted Fe, 1.12~2.03 for Ru/γ-Al_2O_3, 1.38~1.75 for Ru/MgO, 1.76 ~2.40 for K- Ru/MgO and 1.76 ~ 2.55 for Ba-Ru/MgO catalyst, respectively. It indicated that hydrogen should take part in a rate-determining step. The thermodynamic or dynamic isotope effect and the ammonia synthesis mechanism over iron and ruthenium catalysts were discussed.

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