

Brønsted-Lewis Acid Pairs in Ga/H-ZSM-5 for Alkane Conversion

M. W. Schreiber, M. Baumgärtl, A. Jentys, R. Bermejo-Deval, J. A. Lercher*

Catalysis Research Center, Technische Universität München, Garching, Germany

Abstract

On bifunctional catalysts (e.g., Ga/H-ZSM-5) propane dehydrogenation is the rate determining step of dehydrocyclodimerization¹. Brønsted-Lewis acid pairs formed by protonic sites in zeolite H-ZSM-5 and Ga, respectively, have shown to increase the rates of light alkane dehydrogenation. However, the state and the role of the Ga cation on alkane dehydrogenation has not been discerned. Here, we will identify the proximity of Ga⁺ and BAS to be the key for an efficient reaction pathway in the dehydrogenation of propane.

The addition of Ga into H-ZSM-5 indicated the stoichiometric replacement of one BAS by one Ga⁺ cation, as in situ IR spectroscopy showed the decrease of the Si(OH)Al stretching band (of BAS) at 3616 cm⁻¹. Therefore, the rate of propane dehydrogenation increased as a function of Ga concentration, reaching a maximum at a ratio of Ga/Al = 1/2, while the rate of the cracking decreased, which can relate to the loss of protonic sites. Three active sites for dehydrogenation were deduced from IR spectroscopy (Si(OGa)Al, BAS, and isolated Ga species), however, the observed maximum in the dehydrogenation rate does not follow the superposition of the rates on each of the sites. Thus, we infer that the interaction between one Si(OGa)Al species and one neighboring free BAS facilitates the dehydrogenation of propane.

The well-defined catalyst 1/2 Ga/ Al, containing mainly (kinetically dominating, but not exclusively) homotopic Lewis Brønsted acid pairs, allowed us to study the mechanism and the kinetics of the alkane dehydrogenation on these Lewis–Brønsted acid pairs experimentally and via DFT calculations. The highest rates in propane dehydrogenation were, thus, found at equal concentrations of Brønsted and Lewis acid Ga⁺ sites. While a reasonably high concentration of such pairs are kinetically dominating (the rate increased by more than 300 times compared to the two extreme cases of pure H-ZSM-5 and the fully exchanged Ga-ZSM-5), statistics of site distribution dictates that also some isolated Brønsted acid sites and Ga sites must exist. At the highest rate in propane dehydrogenation (1/2 Ga/Al Ga/H-ZSM-5), the Lewis–Brønsted acid pairs were estimated to have two additive contributions: one at low propane partial pressure on sites that bind propane rather strongly, but have a limited concentration; and a second with significantly weaker interaction with propane on sites that are by far more abundant on the studied catalyst. These findings provide a new high-activity reaction pathway for dehydrogenation of light alkanes and provide fundamental insight into the mechanism of alkane dehydrogenation over Lewis–Brønsted acid site pairs. The insight allows in general a new perspective on cooperative catalysis by Lewis and Brønsted acid sites in heterogeneous catalysis.