Mechanistic insight into heterogeneous hydrogenation of methylenecyclobutane with the use of parahydrogen

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In spite of all the accumulated knowledge there is still a number of unanswered questions regarding the mechanisms of hydrogenation reactions. Parahydrogen-induced polarization (PHIP) can provide unique information about the mechanisms of reactions involving hydrogen. PHIP is based on pairwise addition of two H atoms from the same parahydrogen (p-H_2) molecule to the same substrate molecule. This leads to significant enhancement and characteristic antiphase lineshape of NMR signals of the corresponding ^{1}H nuclei.

In this work PHIP technique was applied for a mechanistic study of methylenecyclobutane (MCB) hydrogenation over Rh, Pt and Pd catalysts supported on TiO_2 [1]. The reaction leads to formation of up to 11 products. At lower temperatures (150–350 °C) the major reaction product was methylcyclobutane while higher temperature of 450 °C favors branched products isoprene, 2-methyl-1-butene and 2-methyl-2-butene. Based on the absence of PHIP effects for isoprene we propose that it is produced via direct cleavage of C_4 ring without adsorption of MCB via C=C bond. Formation of other products starts with adsorption of the reactant via the C=C bond. PHIP results show that cyclic products 1-methylcyclobutene and methylcyclobutane are formed via sequential steps of H atoms addition and elimination. Acyclic products are obtained through fission of C_4 ring to 1,4-pentanediyl and 2-methyl-1,4-butanediyl species which then may isomerize to adsorbed alkenes followed by either desorption, pairwise hydrogen replacement or H_2 addition. The differences in PHIP signal patterns of 2-methyl-1-butene formed from MCB and 2-methyl-2-butene allowed to establish that 2-methyl-1-butene is produced from MCB via 2-methylbutylidene species, while in case of 2-methyl-2-butene as a reactant 2-ethyl-1,3-propanediyl species serves as an intermediate. Altogether, the obtained results demonstrate the unique features of PHIP technique as a tool for mechanistic studies of hydrogenation reactions.

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[1] O.G. Salnikov et al., *ChemPhysChem* **2022**, *23*, e202200072.