

Abstract

Meerwein-Ponndorf-Verley (MPV) reduction is a selective hydrogen transfer reaction that converts carbonyl compounds to the corresponding alcohols under mild conditions, offering a safer alternative to conventional hydrogenation by avoiding the use of molecular hydrogen. Recently, Lewis acid zeolites, particularly Zr- and Sn-substituted beta zeolites, have been identified as effective catalysts. Although MPV reduction is typically highly selective, its selectivity can decrease when the substrate structure allows competing Lewis catalysed reactions. In such cases, the addition of organic bases can increase selectivity by forming zeolite-amine complexes, although the mechanism as well as the base structure-activity correlations are unknown.

This study focuses on the MPV reduction of citronellal, a bio-derived aldehyde, in the presence of Zr- and Sn-beta catalysts, which suffers from side reactions like carbonyl-ene cyclization and acetalization. Small nitrogen-containing organic bases such as pyridine and N-methylpiperidine were used to increase the citronellol selectivity and to disclose the structure-activity correlations between the base and the selectivity improvement. A series of pyridine-derived bases shifted selectivity in favour of citronellol except 2,6-ditert-butylpyridine, which is unable to coordinate. Regarding overall conversion, pyridine and 2,5-lutidine caused only a slight decrease (83% conversion after 6 hours) compared to the base-free system (97 %). In contrast, bulkier 2,4,6-collidine resulted in significantly lower conversion (48 %), likely due to restricting diffusion and limiting access to the active sites. This highlights that coordination to the Lewis sites is essential, as only bases that can coordinate, form the zeolite-amine complexes and modulate the reaction selectivity. Notably, the presence of the base accelerated citronellol formation, suggesting that the zeolite-amine complex modifies the active sites rather than poisons them, as is often observed with aluminosilicate zeolites.

Building on these observations, apparent activation energies of individual reaction pathways were determined with added bases. Kinetic studies, performed between 40 and 80 °C using N-methylpiperidine and pyridine over Zr- and Sn-beta zeolites, showed that the pyridine addition decreased the apparent activation energy for citronellol formation from 56 kJ · mol⁻¹ (base-free system) to 44 kJ · mol⁻¹, while that for isopulegol remained unchanged (26 kJ · mol⁻¹). The reaction with N-methylpiperidine was diffusion-limited, as formation of both products exhibited values below 30 kJ · mol⁻¹. These findings highlight that the zeolite-amine complex influences intrinsic reaction mechanism, likely through active site modification and change in internal diffusion.

Key words: catalysis, Lewis acid, zeolite, amine, Meerwein-Ponndorf-Verley reduction, hydrogen transfer, stereoselectivity