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Upgrading bio-derived molecules through oxidative cleavage of C=C bonds over zeolite-based catalysts

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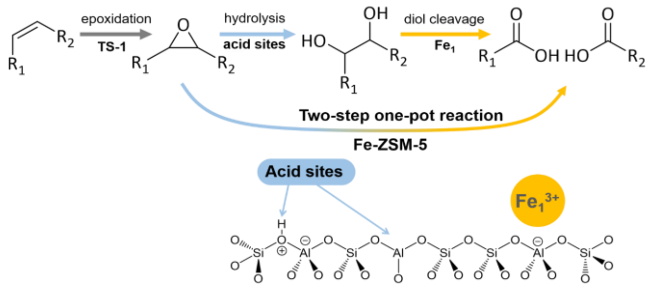
Abstract

The oxidative cleavage of C=C bonds in bio-derived unsaturated fatty acids to produce carboxylic acids involves three steps: epoxidation, hydrolysis, and vicinal diol cleavage (Scheme 1)[1]. Current methods use ozonolysis[2], homogeneous catalysts[3] or noble metals[4], which face challenges such as high costs and difficult separation. Recently, we showed that Fe-ZSM-5 zeolites with monomeric iron species and H_2O_2 can effectively catalyze the vicinal diol cleavage[5]. In this study, we extend the application of Fe-ZSM-5 as a bi-functional catalyst for a two-step, one-pot conversion of epoxides through hydrolysis and diol cleavage.

Fe-ZSM-5 catalysts were prepared by ion exchange, resulting in monomeric Fe-species confirmed by XAS and UV-Vis spectroscopy. NH_3-TPD and Py-ads-FTIR analyses indicated that Fe-exchange reduced the zeolite's Brønsted acidity while introducting Lewis acidity. Fe-ZSM-5 catalysts were active in hydrolyzing propylene oxide to 1,2-propane diol, driven by the zeolite intrinsic acidity. Addition of H_2O_2 and a temperature increase to 50°C, significantly boosted the vicinal diol cleavage activity, due to interactions between monomeric Fe-sites and H_2O_2. Expanding on these findings, we examined the complete cascade reaction for C=C bond cleavage starting with ethylene gas as a model substrate. While Fe-ZSM-5 alone was inactive in the epoxidation step, a physical mixture of TS-1 (for epoxidation) and Fe-ZSM-5 (for hydrolysis and cleavage) successfully catalyzed the entire sequence. These results highlight the potential of modified zeolite catalysts to streamline the conversion of bio-derived molecules with C=C bonds, reducing process steps and utilizing benign solvents and oxidizing agents.



Scheme 1. Schematic representation of the cascade oxidative cleavage reaction over bifunctional Fe-ZSM-5 catalyst.

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