Influence of intimacy and micropore size on the catalytic performance of bifunctional catalysts

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Bifunctional catalysts are crucial for the upgrading of hydrocarbons to transportation fuels and chemicals and may also enable new routes of renewable synthetic fuel production. For optimal catalytic performance, it is generally accepted that a close intimacy between the metal sites and acid sites is desired. However, recent studies report detrimental effects on selectivity when Pt nanoparticles are located inside zeolite micropores, in closest proximity with zeolite acid sites. Catalysts with nanometer scale intimacy between metal sites and acid sites displayed a higher selectivity towards isomers and less secondary cracking.\(^1\), \(^2\) Here, we varied the location of Pt nanoparticles at the nanoscale while using zeolite based catalysts with medium to large pores: ZSM-5, zeolite Beta and zeolite Y. The location of Pt nanoparticles in zeolite/Al\(_2\)O\(_3\) composite supports was controlled by using different Pt precursors: a cationic Pt(NH\(_3\))\(_4^{2+}\) (aq) complex that exchanges with protons from the zeolite or an anionic PtCl\(_6^{2-}\) (aq) complex that adsorbs on positively charged Al\(_2\)O\(_3\) in acidic conditions (pH ~ 3). Results of n-C\(_7\) hydroisomerisation tests show slight differences in catalytic activity for ZSM-5 and zeolite Beta based catalyst, while no beneficial effects were observed for zeolite Y catalysts. For ZSM-5 based catalysts selectivity towards monobranched products was identical for both catalysts, whereas no dibranchd isomers were observed, as can be seen in figure 1. For large pore zeolites (zeolite Beta, zeolite Y) locating Pt nanoparticles on the Al\(_2\)O\(_3\) binder had a beneficial effect on isomer selectivity, especially towards desired dibranched C\(_7\) isomers. The higher isomer selectivity for the large pore zeolites is tentatively attributed to the shorter diffusion pathway of olefinic intermediates through zeolite micropores, which is slower than their paraffinic counterparts due to strong adsorption on Brønsted acid sites. For ZSM-5 these effects are overshadowed by the slow diffusion of the skeletal isomers of heptane.

The ratio between dibranchd isomers vs. cracked products as a function of conversion. Large pore zeolite catalyst with Pt nanoparticles located on the alumina binder - in red - outperform catalysts with Pt nanoparticles in the zeolite shown in green.


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