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Modification of Unsaturated Fatty Acids Derived from Tall Oil Using Micro/Mesoporous Materials Based on H-ZSM-22 Zeolite

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Abstract : Iso-stearic acid as a saturated fatty acid with a branched chain shows a low pour point, high oxidative stability and great biodegradability. The industrial production of iso-stearic acid involves first isomerizing unsaturated fatty acids into branched-chain unsaturated fatty acids (BUFAs), followed by hydrogenating the branched-chain unsaturated fatty acids to obtain iso-stearic acid. However, the production yield of iso-stearic acid is reportedly less than 30%. In recent decades, extensive research has been conducted on branched fatty acids. Most research has replaced acidic clays with zeolites due to their high selectivity, good thermal stability, and renewability. It was reported that isomerization of unsaturated fatty acid occurred mainly inside the zeolite channel. In contrast, the production of by-products like dimer acid mainly occurs at acid sites outside the surface of zeolite. Further, the deactivation of catalysts is attributed to the pore blockage of zeolite. In the present study, micro/mesoporous ZSM-22 zeolites were developed. It is clear that the synthesis of a micro/mesoporous ZSM-22 zeolite is regarded as the ideal strategy owing to its ability to minimize coke formation. Different mesoporosities micro/mesoporous H-ZSM-22 zeolites were prepared through recrystallization of ZSM-22 using sodium hydroxide solution (0.2-1M) with cetyltrimethylammonium bromide template (CTAB). The structure, morphology, porosity, acidity, and isomerization performance of the prepared catalysts were characterized and evaluated. The dissolution and recrystallization process of the H-ZSM-22 microporous zeolite led to the formation of approximately 4 nm-sized mesoporous channels on the outer surface of the microporous zeolite, resulting in a micro/mesoporous material. This process increased the weak Brønsted acid sites at the pore mouth while reducing the total number of acid sites in ZSM-22. Finally, an activity test was conducted using oleic acid as a model compound in a fixed-bed reactor. The activity test results revealed that micro/mesoporous H-ZSM-22 zeolites exhibited a high isomerization activity, reaching >70% selectivity and >50% yield of BUFAs. Furthermore, the yield of oligomers was limited to less than 20%. This demonstrates that the presence of mesopores in ZSM-22 enhances contact between the feedstock and the active sites within the catalyst, thereby increasing catalyst activity. Additionally, a portion of the dissolved and recrystallized silica adhered to the catalyst's surface, covering the surface-active sites, which reduced the formation of oligomers. This study offers distinct insights into the production of iso-stearic acid using a fixed-bed reactor, paving the way for future research in this area.

Keywords : Iso-stearic acid, oleic acid, skeletal isomerization, micro/mesoporous, ZSM-22
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