Abstract

Conventional zeolites are important shape-selective heterogeneous acid catalysts due to the presence of acid sites accessible through uniform micropores. Recently designed hierarchical zeolites with combined micro-mesoporosity also contain acid sites on the external surface or in mesopores. These highly accessible acid sites are promising active centres for the transformation of bulky molecules, which cannot pass through the micropore openings of conventional zeolites. An example of a reaction that can benefit from the use of zeolites is the one-pot cascade Prins-Friedel-Crafts (PFC) reaction of an aldehyde, homoallylic alcohol, and aromatic compound, which yields valuable heterocyclic compounds containing 4-aryltetrahydropyran moieties.

In this work, the acidic characteristics of a series of hierarchical aluminium- and gallium-containing **MFI** and **MWW** zeolites were evaluated by FTIR-monitored thermodesorption of probe molecules and further related to the catalytic properties of zeolites in the PFC reaction of butyraldehyde, 3-buten-1-ol, and anisole.

The nature, strength, and total concentration of acid sites in the catalysts were evaluated using thermodesorption of pyridine (kinetic diameter 0.54 nm), while the characteristics of the external surface Brønsted acid sites were probed using 2,6-di-tertbutylpyridine (kinetic diameter 0.79 nm). The results revealed the crucial role of the strength of acid sites and their distribution between the internal and external surfaces of the crystals, as well as the important impact of zeolite structure on the butyraldehyde conversion and selectivity toward targeted products of the PFC reaction. Among the catalysts investigated, Al-containing **MWW** zeolites with high total concentration of acid sites (0.41 mmol/g), remarkable fraction of strong acid centers (66%) and notable fraction of highly accessible external acid sites showed the highest values of butyraldehyde conversion (90% after 24 h) and selectivity toward the targeted products of the PFC reaction (37% at 50% conversion).

Keywords: heterogeneous catalysis, zeolites, Prins-Friedel-Crafts reaction