

Enhanced Acid Site Accessibility in Hierarchical Zeolites

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Introduction

Due to their frequent operation in the transport limitation regime, the activity, and occasionally also the selectivity and lifetime of zeolites in catalytic reactions are largely limited. It is of great importance to increase the accessibility and molecular transport to/from the active sites in zeolites to reach their full catalytic potential. During the last decade, hierarchically structured zeolites have emerged as an important class of materials leading to improved catalytic performance compared to their microporous parents [1]. This is due to the integration in the same material of the catalytic properties of the native micropores and the facilitated transport brought by interconnections with a complementary mesopore network. Diffusion studies have demonstrated the enhanced transport in mesoporous zeolites with respect to their purely microporous counterparts [2]. However, the enhanced access to the active sites in hierarchical zeolites has never been proven in a direct and quantitative way, i.e. what fraction of available sites can be additionally utilized upon introducing extra porosity in the zeolite crystal. This understanding is vital for rational catalyst design since it correlates materials properties, diffusion data, and catalytic performance.

Herein, infrared spectroscopy of substituted pyridines with different kinetic diameter (pyridine: 0.50 nm, lutidine: 0.67 nm, and collidine: 0.74 nm) and basic strength is demonstrated as a simple and powerful methodology to quantify the enhanced accessibility of acid sites in hierarchically structured ZSM-5 prepared by desilication. This leads to the newly defined *accessibility index* (ACI), which can be widely used to rank the effectiveness of hierarchical zeolites in catalysis.

Materials and Methods

Commercial ZSM-5 (Si/Al = 42) was used as the parent zeolite (P). Hierarchical zeolites were prepared by alkaline treatment of P in 0.2 M NaOH for 30 min at 318 K (H1), 328 K (H2), and 338 K (H3). Pyridine, lutidine, and collidine were adsorbed on the zeolites at 300 K followed by evacuation at 473 K to remove the excess of probe molecules. Infrared spectra were recorded with a Nicolet Magna 550 FTIR spectrometer at 2 cm⁻¹ optical resolution. Molar extinction coefficients were determined for spectral quantification.

Results and Discussion

Desilication of the parent zeolites by NaOH treatment at different temperatures led to hierarchical zeolites with mesopore surface areas (S_{meso}) ranging from 128 to 324 m² g⁻¹. As shown in Figure 1, the original type I isotherm in P transformed into combined type I and IV isotherms, characteristic of hierarchical porous systems coupling micro- and mesoporosity. The hierarchical zeolites possess intracrystalline mesopores of ca. 10 nm (see pore size distribution in Figure 1).

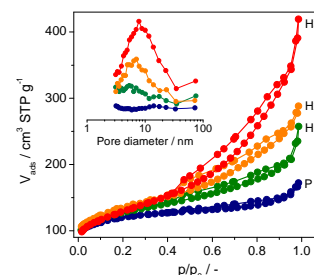


Fig. 1. N₂ isotherms of the parent and hierarchical zeolites. Inset: BJH pore size distributions.

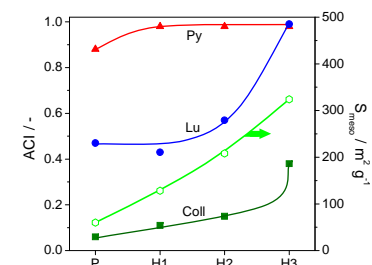


Fig. 2. Accessibility index of the zeolites for pyridine, lutidine, and collidine, and correlation with the mesopore surface area of the samples.

The *accessibility index* (ACI) for a given probe molecule (pyridine, lutidine, and collidine) is defined as the number of sites detected by adsorption of the probe divided by the total amount of acid sites in the sample as quantified by infrared spectroscopy (Figure 2). As expected from the micropore size of ZSM-5 (ca. 0.56 nm), pyridine (Py) probes a large fraction of the acid sites in the parent zeolite and therefore only a slight increase in accessibility is observed in the hierarchical zeolites. Lutidine (Lu) probes <50% of the sites in the purely microporous zeolite. Collidine is too large to enter the ZSM-5 micropores and reaches nearly no sites in the parent zeolite. Upon desilication, the accessibility of the bulky molecules is spectacularly enhanced. ACI(Lu) reaches the maximum value of 1, while the ACI(Coll) increases from nearly 0 in P to 0.4 in H3. The creation of mesopores by desilication shortens the average micropore length, thereby increasing the available acid sites at the pore mouths. The accessibility index is intimately related to the effectiveness factor in acid-catalyzed reactions and can be used as a first indication of the utilization of the zeolite. Our results show that desilication can potentially transform off-the-shelf zeolites in superior catalysts by introduction of intracrystalline mesoporosity. We will compare the effectiveness of synthetic strategies towards hierarchical zeolites, including the above-explained desilication as well as (solid and supramolecular) templating and controlled crystallization.

Significance

An infrared spectroscopic method unequivocally demonstrates the enhanced accessibility of acid sites in hierarchically structured zeolites. This leads to significant flexibility in the rational design of zeolites in which porosity and acidity can be precisely engineered to perform the selective conversion of specific feedstocks maximizing the catalyst effectiveness.

References

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