

Zeolite shaping: control of the zeolite acid properties and description of the zeolite/binder interface

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Abstract:

The commercial application of zeolites requires millimeter-sized bodies. The aim of this work is to rationalize the impact of shaping on zeolites and the nature of binder/zeolite interface. ZSM-5 of different crystal sizes (100 nm and 2 μm) with similar bulk Si/Al ratios were shaped with different binders and modifications on their textural properties are visible. Their acid properties are dependent on the zeolite crystal size but the behavior of shaped materials with small and large crystal is qualitatively the same. The catalytic results on isomerization of meta-xylene suggests that the reaction occurs at zones close to external surface.

Keywords: Zeolite ZSM-5, shaping, binder

1. Introduction

Acid properties of zeolites are commonly used in refining and petrochemical processes, as well in pollution abatement, and are promising for biomass conversion. Their commercial application as acid catalysts requires millimeter-sized bodies generally obtained by milling-extrusion. Catalyst scale-up step by shaping from “research catalysts” to complex multi-component systems - “technical catalysts” - (active phase, binder, additives) is often undervalued while is a key step for the viability of the processes^{1,2}. Zeolite-based catalysts, due to shaping, may differ strongly in textural, acid and catalytic properties depending on their preparation conditions. The aim of this work is to study and rationalize the physicochemical impacts of shaping on the concentration, the strength and the accessibility of acid sites and the nature of binder/zeolite interface.

2. Experimental

Zeolites ZSM-5 of different crystal sizes (100 nm and 2 μm) with similar bulk Si/Al ratios (25 and 22 respectively, provided by Zeolyst) were shaped with different binders and binder sources (boehmite from Sasol, silica from Nyacol: Nyasil 20 or Degussa : Ultrasil). The milling was done with 50 wt% of zeolite and 50 wt% of binder with (or without) base or acid peptization. Then, the homogeneous paste was extruded with a cylindrical shape and dried at 80°C overnight prior to calcination at 600°C for 2h. Textural analyses (nitrogen physisorption and mercury intrusion) were performed to characterize the micro, meso and macroporosity, specific area and external surface. ²⁷Al NMR MAS spectra were acquired and SEM images of polished extrudates section were taken. FTIR of adsorbed pyridine was conducted and the concentration of Brønsted and Lewis acid sites were determined after desorption at 423 K from the bands at 1545 cm^{-1} and 1445 cm^{-1} using extinction coefficient of 1.67 $\text{cm}\cdot\mu\text{mol}^{-1}$ and 2.94 $\text{cm}\cdot\mu\text{mol}^{-1}$ respectively. Fluorescence microscopy combined with fluorogenic probe molecules (oligomerization of furfuryl alcohol) was performed. Catalytic tests of meta-xylene isomerization with or without coupling with IR operando were performed at 573 K on the zeolites and shaped materials (crushed at 350 – 500 μm).

3. Results and discussion

Shaped materials presented in Figure 1 with ZSM-5 large crystals were made with boehmite or pre-calcined boehmite (γ -alumina). The modifications of textural properties are visible with the formation of macropores and big aggregates of binder for shaped materials with alumina instead of well-dispersed zeolite-binder mixture in the shaped materials with boehmite.

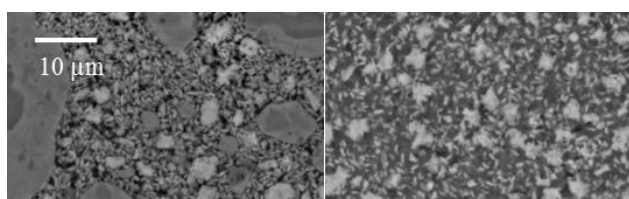


Figure 1 : SEM images of shaped ZSM-5 large crystals with γ -alumina (left) and with boehmite (with peptization, right)

According to FTIR spectroscopy of adsorbed pyridine, the large crystals are twice as acidic (in terms of number of Brønsted acid sites in $\mu\text{mol.g}_{\text{zeolite}}^{-1}$, BAS) compared to the small crystals (Figure 2). Part of the BAS from the small crystals may not be acidic enough to protonate or desorb pyridine below 423K. An investigation of Lewis acid sites (LAS) is necessary as it may help in the understanding of the phenomenon.

Catalytic tests of the isomerization of meta-xylene have shown difference in terms of catalytic activity: large crystals are twice less active than small crystals (Figure 2), which is not in agreement with the concentration of active BAS measured. This suggests that the reaction occurs in zones close to the external surface rather than in the core of the crystal. However, the ratio of activities of the two zeolites does not fit with the ratio of their external surface (between 3.7 from BJH method and 13 from theoretical calculation of external surface), suggesting the participation of sites at a certain depth from the external surface. In order to determine the concentration of acid sites participating while the zeolite is working in the meta-xylene isomerization reaction, IR *operando* measurement was performed. In that case, we observe that the Brønsted bridged acid sites (νOH at 3600 cm^{-1}) are not all involved in the reaction with meta-xylene at 573 K, confirming that only a part of the BAS is involved in the reaction (and especially for large crystals; work under progress).

For shaped catalysts, acidity and activity are normalized by the zeolite weight in the final material. Both large and small crystals have qualitatively the same behavior depending on the binder source. As shown in Figure 2, pre-calcined boehmite based materials are less acid (BAS concentration from pyridine adsorption and desorbed at 423 K calculated in $\mu\text{mol.g}_{\text{zeolite}}^{-1}$) and less active (activity in meta-xylene isomerization calculated in $\text{mmol.g}_{\text{zeolite}}^{-1}$) than those prepared with boehmite with or without peptization. Shaping with γ -alumina might imply dissolution/precipitation and modify the interface between the zeolite and the binder. For acidic and catalytic properties of silica based materials, the Na content initially present in the binder has a strong impact: the catalytic activity for shaped materials with Ultrasil (4500 ppm of Na) is twice lower compared to the expected results (parent zeolite) and compared to Nyasil 20 (silica source with a lower Na content, 600 ppm) (Figure 2).

As bulk measurements give averaged signals, we looked at the isolated zeolite crystals to visualize the impact of shaping on their acid sites using super resolution fluorescence microscopy. Using the oligomerization of furfuryl alcohol the location of BAS within the single crystals were mapped³. As shown in Figure 3, activity is present in the whole pellet of ZSM-5 large crystals shaped with boehmite without acid peptization but some edges are more active than others.

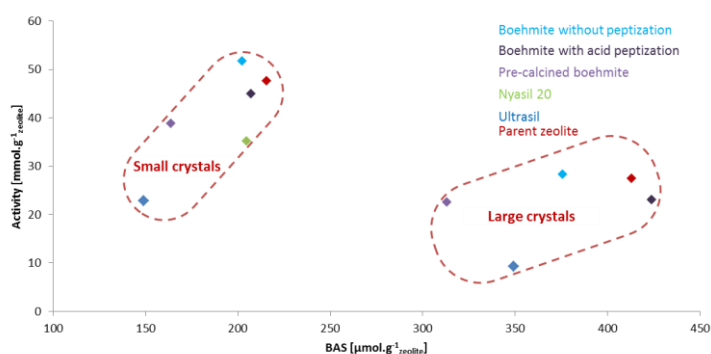


Figure 2 : Correlation of catalytic activity vs BAS of zeolites (small and large crystals) and zeolite-based catalysts

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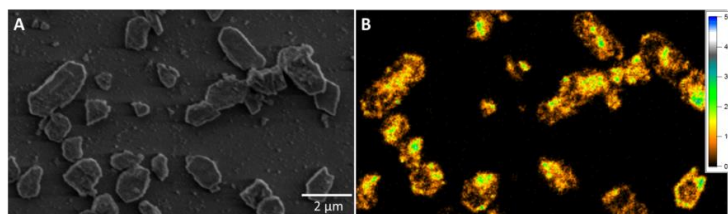


Figure 3 : NASCA measurements on crushed pellets made with ZSM-5 large crystals + boehmite without peptization

4. Conclusions

This work provides clues for important effects to be taken into account after shaping of zeolites (alumina source, Na content) and a first indication of the location of active sites. It also reminds of the complexity to properly characterize these effects on shaped materials.

References

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