

Effects of crystal size and Si/Al ratio on the surface properties of H-ZSM-5 zeolites

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Abstract

Highly crystalline H-ZSM-5 zeolite samples with crystal sizes from 0.5 to 5 μm and Si/Al ratios ranging from 20 to 70 have been prepared and characterized by IR spectroscopy, SEM and XRD techniques. The surface properties of these materials have been compared with those of conventional small crystal size materials by using FT-IR spectroscopy of the surface hydroxyl groups and of adsorbed carbon monoxide. The external surface has been investigated using pivalonitrile (2,2-dimethyl-propionitrile) as an adsorption probe. Data show that the basic structure of the zeolite active sites do not depend significantly on the crystal size. Brønsted acid sites of high acid strength are constituted by bridging OH groups located inside the zeolite channels, while Lewis acid sites and weakly acidic silanol groups are found on the external surface in all cases. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Protonic zeolites find industrial applications as acid catalysts in several hydrocarbon conversion reactions [1,2]. The activity of these materials is associated to two main properties: shape selectivity effects due to the molecular sieving properties associated to the well defined crystal pore sizes, where at least a part of the catalytic active sites are located; and a strong Brønsted acidity of bridging Si–(OH)–Al sites generated by the presence of aluminum inside the silicate framework.

The main factor allowing molecular sieving and, consequently, the shape selectivity is generally considered to be exclusively a steric effect, i.e., only molecules having a critical kinetic diameter lower than the channel diameter are allowed to enter the pores and to react on an active site or, in case, to exit them and to be recovered as a product of the reaction. Alternatively, transition state shape selectivity effects limit the formation of bulky transition state intermediates inside

the pores and avoid the formation of some unwanted reaction products.

On the other hand real zeolite catalysts are frequently pretreated in various ways such as steaming and are not “perfect” structures: extra-framework aluminum sites (EFAl) are frequently present and can also have a role either as active sites or as material hindering the molecular diffusion into the cavities. Additionally, different preparation methods of the same zeolite can give rise to quite different properties, due to several additional effects such as, e.g., different particle morphologies [3], active site densities or different distribution of framework aluminum and, consequently, of protons from surface to bulk [4]. In most cases the role of shape selectivity and of pretreatments, such as dealumination, are still imperfectly known or under debate.

Catalytic active sites also exist on the external surface and at the pore mouth of zeolite crystals. For shape selective reactions, these sites are considered to be responsible for unwanted non-selective catalysis [5]. A possible strategy to avoid unwanted unselective reactivity is to limit the external surface and the extra-framework material by producing large well crystallized zeolite crystals. The possible role of extra-

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framework species should also be limited by reducing the Al content in the zeolite.

Previous studies have been performed on the characterization and on the distinction of internal, external and extra-framework acid sites in H-MFI type zeolite structures with usual particle size [6–10]. In this paper, we report the comparative characterization of a small particle size sample with large particle highly crystalline samples, in order to confirm the previous data and to have additional information on the internal versus external surface acidity in zeolites.

2. Experimental

ZSM-5 crystals with increasing size from several tens of nanometers up to 5 μm have been synthesized by varying initial reactants and synthesis parameters.

Small particle size ZSM-5 (sample A) was obtained using aluminum isopropoxide (98%, Aldrich), tetraethylorthosilicate (Aldrich) and doubly distilled water as initial sources. The reactants were mixed under vigorous stirring and aged on an orbital shaker at ambient temperature for 24 h prior to the hydrothermal (HT) treatment. The composition of the clear initial solution was as follows: $25\text{SiO}_2:0.5\text{Al}_2\text{O}_3:4.5(\text{TPA})_2\text{O}:480\text{H}_2\text{O}$ (TPA = tetrapropylammonium). The syntheses were performed at 373 K for 5 days. The small size crystals resulting from the hydrothermal treatment of colloidal solutions were purified by three steps of high centrifugation (20,000 rpm, 60 min) of the solid, decanting of the supernatant and redispersion in doubly distilled water using an ultrasonic bath for 2 h.

Micrometer sized ZSM-5 crystals were synthesized from a gel with chemical composition: $1.0\text{SiO}_2:x\text{Al}_2\text{O}_3:0.1\text{Na}_2\text{O}:0.05(\text{TPA})_2\text{O}:40\text{H}_2\text{O}$, where x was 0.0065, 0.01 and 0.02. The initial reactants used for this preparation were: sodium aluminate (Carlo Erba, 54% Al_2O_3 ; 37% Na_2O), Aerosil 130 (Degussa), tetrapropylammonium bromide (Fluka), sodium hydroxide (97%, Merck), and doubly distilled water. The initial mixture was stirred at room temperature for 45 min and subjected to HT treatment at 473 K for 2 days. The solid was recovered by suction filtration, washed with distilled water and dried at 363 K overnight.

The obtained solids were studied by X-ray diffraction (XRD) using a STOE STADI-P diffractometer in Debye–Scherrer geometry equipped with a linear position-sensitive detector (6° in 2θ) and Ge monochromated $\text{Cu K}\alpha_1$ radiation.

Electron micrographs were taken on a Philips XL30 FEG scanning electron microscope (SEM). The elemental analyses of the solids were performed on an X-ray fluorescence spectrometer MagiX (Philips). Prior to the analysis the powdery sample was melted with $\text{Li}_2\text{B}_4\text{O}_7$ at 1573 K. The resultant glass bead was analyzed under vacuum with a Rhodium anticathode (2.4 kW).

The morphological features of the synthesized materials were studied using a Philips XL30 FEG scanning electron microscope (SEM).

The IR spectra (resolution 2 cm^{-1}) were recorded on a Nicolet Nexus Fourier transform instrument, using pressed

disks of pure zeolite powders, activated into the IR cell. A conventional gas manipulation/outgassing ramp connected to the IR cell was used. The adsorption procedure involves contact of the activated sample disk with gases and vapors at a known pressure and outgassing at increasing temperature. Pivalonitrile was purchased from Aldrich, CO cylinders were purchased from Siad. Experimentally, a small amount of pure zeolite powder is pressed to form a thin pellet (15 mg ca., 2.5 cm diameter). The pellet is thermally treated directly inside the IR cell at 773 K under vacuum in order to study the surface free from adsorbed water and eventually other adsorbed molecules. The “activated” surface is successively contacted with vapors of the probe molecule, pivalonitrile (PN) or with carbon monoxide (CO).

FT-IR spectra were collected after activation, after contact with the probe molecule (performed at r.t. and 2 Torr for PN, 130 K and 20 Torr for CO) and after evacuation in steps at increasing temperature (see figure legends), in order to investigate the surface species evolution. Skeletal spectra have also been recorded using the KBr pressed disk technique.

The Raman spectra were recorded using a Jobin Yvon LamRAM HR spectrometer. An argon laser at 514 nm is focused on the sample powders by a microscope using a $50\times$ objective. The power of the laser beam is about 4 mW. The back-scattered radiations are collected and the spectral resolution is about 0.5 cm^{-1} .

3. Results and discussion

Four samples were prepared for this study. Samples A and B were synthesized in order to compare the impact of crystal sizes on the ZSM-5 acidity, while samples C and D, together with the sample B, were synthesized in order to compare the effect of Si/Al ratio on the ZSM-5 acidity.

The physico-chemical characterization of the samples are summarized in Table 1. Samples A and B have similar Si/Al ratios of 18.5 and 23.8, respectively but the crystal size of the sample A, evaluated by SEM, is around 10 times lower than the one of the sample B, i.e., 0.5 and 5 μm , respectively. Samples B–D have similar particle sizes of 5 μm but increasing Si/Al ratios, 23.8, 43.0 and 68.3, respectively.

The XRD patterns of the samples in Fig. 1 show well crystallized materials corresponding to the MFI structure [11]. One can notice that the patterns of the sample A has a much lower intensity. The decrease in the XRD crystallinity of sample A is most probably due to the much smaller crystals and thus to higher number of framework defects with respect to micrometer-sized ones due to the milder HT conditions

Table 1
Data on the ZSM-5 samples under study

Sample name	Si/Al (FX, mol ratio)	Crystal size (SEM, μm)	^{27}Al NMR	S_{BET} (N_2 , m^2/g)
A	18.5	0.5	96% Al^{IV}	416
B	23.8	5	98% Al^{IV}	353
C	43.0	3–4	100% Al^{IV}	357
D	68.3	4	100% Al^{IV}	346

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