



Porosity and accessibility of acid sites in desilicated ZSM-5 zeolites studied using adsorption of probe molecules



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ARTICLE INFO

Article history:

Received 13 March 2013

Received in revised form 8 June 2013

Accepted 29 August 2013

Available online 8 September 2013

Keywords:

Thermodesorption of hydrocarbons

Desilicated zeolite ZSM-5

Micropores

Mesopores

Hierarchical materials

ABSTRACT

Porosity of zeolites ZSM-5 (Si/Al = 32 or 164) desilicated with NaOH or NaOH/TBAOH (tetrabutylammonium hydroxide) solutions was studied by means of quasi-equilibrated temperature programmed desorption and adsorption (QE-TPDA) of selected hydrocarbons. QE-TPDA of *n*-nonane confirmed substantial formation of mesopores upon desilication, observed also in N₂ adsorption/desorption isotherms. Very narrow mesopore size distributions with maxima at about 4 nm, typical for partially constricted mesopore networks, were obtained for all desilicated zeolites. It was also observed that desilication with NaOH/TBAOH results in formation of additional slightly larger mesopores (ca. 4–6 nm) while even larger mesopores (6–10 nm) were found after leaching with NaOH only. Thermodesorption of *n*-hexane revealed that the micropores in the desilicated zeolites remained unchanged. Acidity of the zeolites was characterized by quantitative IR measurements of pyridine and collidine (2,4,6-trimethylpyridine) adsorbed on acid sites. Increased numbers of Brønsted acid sites accessible for large collidine molecules found for the modified zeolites indicate that during desilication redistribution of the framework Al atoms to the surface of mesopores occurred. The influence of TBAOH presence in desilicating mixture on porosity and accessibility of the acid sites was also discussed.

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1. Introduction

Zeolites are crystalline aluminosilicates containing systems of channels and cavities of molecular dimensions within their structures. Due to their unique properties like high surface area, well-defined pore sizes and topology, high thermal and hydrothermal stability, intrinsic acidity and shape selectivity, zeolites are widely used in industrial catalytic technologies [1,2]. However, application of zeolite catalysts in reactions which involve large molecules is limited due to restricted access and slow mass transfer to and from the active sites located within the micropores. Desilication, extensively developed in recent decade [3–6], was found to be very effective and reproducible method for preparation of mesoporous zeolites without significant damages in both crystallinity and acidity of the parent material. Crucial factors in this process are temperature and time of treatment, type and concentration of the desilication agent, type of the zeolite framework and Si/Al ratio, as well as presence of so called pore directing agents (PDA) [4,5,7–11].

Our earlier studies on desilicated ZSM-5 zeolites showed that use NaOH/TBAOH (tetrabutylammonium hydroxide) mixture as leaching agent produced mesopores of higher surface area and

pore volume but of smaller diameter than using NaOH alone [12]. On the other hand, IR studies of pivalonitrile (t-butyl nitrile) sorption showed that desilication improved also accessibility of acid sites in the studied zeolites, implying redistribution of the framework Al atoms [13]. These findings indicated that more detailed characterization of porosity and acidity of the desilicated zeolites is necessary, as changes in their micropore geometry as well as number and location of the acid sites may influence their catalytic properties. For this purpose two methods based on adsorption of probe molecules i.e. quasi-equilibrated temperature desorption and adsorption of *n*-nonane, *n*-hexane and cyclohexane and quantitative IR measurements of pyridine and collidine (2,6-dimethylpyridine) adsorbed on acid sites were employed in this work.

Quasi-equilibrated temperature programmed desorption and adsorption (QE-TPDA) of volatile hydrocarbons, a novel experimental method developed for characterization of porous materials [14,15], allows detection of the micro- and mesopores as well as determination of their volume. The QE-TPDA profiles of *n*-alkanes observed for zeolites, characteristic to the type of framework [16], are also influenced by the extraframework cations [17]. Based on the adsorption enthalpy of *n*-alkanes, calculated from the QE-TPDA profiles, the micropore size of zeolites may be estimated with good accuracy [18]. Additionally, the mesopore size distributions may be obtained from the low temperature QE-TPDA profiles of *n*-nonane

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[19]. The QE-TPDA method has been already successfully applied for characterization of zeolites [16,20,14], mesoporous silicas [19,21] and their carbon replicas [22], active carbons and metal-organic frameworks.

The QE-TPDA of *n*-alkanes is especially well suited for porosity characterization of hierarchical zeolites, since depending on the adsorbate and experimental conditions, the observed effects may be limited to the micropores only. On the other hand, N₂ physisorption which is most often used as a standard method for porosity analysis, does not give reliable results related to the micropore region. Due to quadrupole interactions between nitrogen molecules and extraframework cations or the framework Al atoms, values of pressure in the low pressure range of the N₂ adsorption isotherm do not correlate with actual sizes of the micropores which are being filled. Adsorption of argon at 87 K gives better results in characterization of the zeolites' microporosity, but so far it is not widely available as a standard technique [23].

IR spectroscopy is a powerful tool for systematic studies of acidity of hierarchical zeolites providing information on the influence of different desilication conditions on location, content, acid strength and accessibility of both Brønsted and Lewis sites. Various probe molecules, differing in basicity and/or size, are widely employed for characterization of the external and internal acid sites in hierarchical zeolites [24,25]. Using pivalonitrile for this purpose was proposed by Busca et al. [26]. These semi-quantitative IR investigations of the accessibility of the Si–OH–Al groups were performed by monitoring the band of Si–OH–Al group, disappearing upon the sorption of the hindered pivalonitrile molecules. Our previous study [27], being a continuation and extension of the earlier work by Busca et al., was focused on the accessibility of both Brønsted and Lewis sites in desilicated zeolites. A novel method of quantitative IR measurements of pivalonitrile sorption employed in this study was proven suitable for investigation of the accessibility of the acid sites in zeolites of various structure and acidity. However, for better discrimination between the acid sites located inside the micropores and those present on the mesopore surface application of larger basic probe molecule is necessary. Therefore in this work the recently developed method of quantitative IR measurements was employed for determination of accessibility of the acid sites by adsorption of collidine.

2. Experimental

The studied materials were commercial zeolites ZSM-5 with Si/Al ratio 32 and 164 (Zeolyst International, CBV 5524G and CBV 28014, respectively). The parent NH₄ZSM-5 zeolites were desilicated at 65 °C for 30 min according to two different paths: with use of 0.2 M NaOH solution and the mixture of 0.2 M NaOH and 0.2 M TBAOH (tetrabutylammonium hydroxide) combined in 3:2 ratio. Details of the desilication treatment have been described elsewhere [12].

Porosity of the parent and alkaline treated samples were characterized by means of N₂ adsorption and desorption at –196 °C (ASAP 2010, Micromeritics) and quasi-equilibrated temperature programmed adsorption and desorption of *n*-hexane, cyclohexane and *n*-nonane with use of the thermodesorption apparatus equipped with thermal conductivity detector (Micro Volume TCD, Valco) presented more into detail elsewhere [14,15,28,29,21].

N₂ physisorption measurements were preceded by outgassing the sample in vacuum at 350 °C for 12 h. Values of the BET surface area were calculated from the adsorption branches. The micro- and mesopore volumes (V_{micro} , V_{meso}) were determined using the α_s -plot method (with Aeorosil 200 taken as a reference material). Mesopore size distributions were obtained from the desorption branches of the isotherms using the BJH model.

Prior QE-TPDA experiment a sample (ca. 10 mg) was activated by heating in He flow (10 °C/min, to 500 °C). Adsorption was carried in room temperature by replacing pure helium used as the carrier gas with helium containing small admixture of a hydrocarbon (ca. 0.4 vol.%). After completed adsorption the QE-TPDA experiment was performed by cyclic heating and cooling the sample (10 °C/min, to 400 °C) in He/HC flow (6.5 cm³/min). Desorption–adsorption cycles were separated with 1 h isothermal segments at room temperature. In the micro- and mesopore volume calculations, the experimental desorption maxima were integrated and related to the calibration data. Density of the adsorptive was assumed as equal to that of the liquid.

Prior to FTIR studies, all studied materials were pressed into the form of self-supporting discs (ca. 5 mg/cm²) and activated in situ in an IR cell at 550 °C under vacuum ($p < 10^{-6}$ mbar) for 1 h. Spectra were recorded with a Bruker Tensor 27 spectrometer equipped with a MCT detector. The spectral resolution was of 2 cm⁻¹. Total concentration of both the Brønsted and Lewis acid was determined in quantitative IR studies of pyridine (Py) sorption according to the procedure described in Ref. [12]. The acid strength of the Brønsted acid sites was measured by thermodesorption of pyridine (Py). The excess pyridine was adsorbed at 170 °C, then the physisorbed Py was removed by evacuation at the same temperature. The chemisorbed pyridine was subsequently desorbed at 350 and 550 °C. The ratios A_{350}/A and A_{550}/A , where A as well as A_{350} and A_{550} are the intensities of IR bands of pyridinium ions PyH⁺ upon the evacuation at 170 °C and upon the desorption at 350 and 550 °C, respectively, were taken as the measure of the acid strength of the Brønsted acid sites.

The pivalonitrile (Pn) sorption was performed at room temperature according to procedure described in Ref. [27]. The excess of collidine (Coll) was adsorbed at room temperature, then physisorbed molecules were subsequently removed by the evacuation at 200 °C. All the spectra presented in this work were normalized to 10 mg of sample.

3. Results

3.1. N₂ adsorption and desorption

Low temperature nitrogen physisorption isotherms measured for the studied MFI zeolites were showed in Fig. 1. Larger slopes of the hysteresis loops indicate higher adsorption capacity of the samples treated with alkaline solutions in comparison to the parent zeolites. Adsorption–desorption isotherms for each samples are typical for materials which consist micro and mesoporosity in their structure and can be classified as type IV isotherms with H3 type hysteresis loops closing at p/p_0 of about 0.4. Values of the BET surface area as well as the micro- and mesopore volume determined with the α_s -plot method were shown in Table 1.

3.2. QE-TPDA of *n*-nonane

QE-TPDA profiles of nonane recorded for the parent and the desilicated zeolites are shown in Fig. 2. As desorption temperature increases with the decreasing pore size, distinct maxima and minima observed in low temperature range (<100 °C) and in high temperature range (150–300 °C) should be attributed to desorption and adsorption of *n*-nonane molecules from/in the mesopores and micropores, respectively. While the micropore related peaks (with maximum at 230 °C) seem to be not affected by the alkaline treatment, the low temperature desorption from the mesopores significantly increased after desilication. For all Si/Al = 164 zeolites and the parent Si/Al = 32 one a two step desorption from the mesopores occurred, with one desorption maximum below 50 °C and

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