Catalysis Today 227 (2014) 26–32

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Modification of textural and acidic properties of -SVR zeolite by desilication

Martin Kubů*, Maksym Opanasenko, Mariya Shamzy

J. Heyrovsky Institute of Physical Chemistry of the ASCR, v. v. i., Dolejškova 3, CZ-182 23 Prague 8, Czech Republic

ARTICLE INFO

Article history:
Received 14 June 2013
Received in revised form 16 October 2013
Accepted 25 November 2013
Available online 28 January 2014

Keywords:
-SVR zeolite
Desilication
Hierarchical materials
Textural and acidic properties

ABSTRACT

Desilication conditions (concentration of NaOH and TPAOH solution, duration of the treatment) of -SVR zeolite were varied and related to the textural and acidic properties of the obtained materials. The treatment of -SVR zeolite with NaOH solution led to the formation of mesopores and also the increasing of the concentration of surface acid sites, accessible for bulky molecules (e.g. 2,6-ditertbutyl-pyridine). The volume of mesopores as well as the concentration of accessible acid centres in desilicated materials depends mainly on the concentration of the alkaline solution. The increase in the pH of the treatment resulted in moderate decrease of both micropore volume and Brønsted acid sites concentration, while the volume of mesopores increased significantly. Independently of the duration and pH of the treatment with NaOH solution, all desilicated -SVR zeolites are characterized by broad pore-size distribution in the range of 5–20 nm with the maximum around 14 nm. At fixed pH of the treatment with TPAOH, the volume of mesopores and their average size decreased, while the Si/Al ratio and the concentration of Brønsted acid sites in desilicated materials increased which indicates the inhibiting effect of TPA^+ cations on the extraction of Si from -SVR zeolite.

1. Introduction

Zeolites, crystalline aluminosilicates with ordered networks of micropores, are utilized in numerous large-scale chemical technologies as heterogeneous catalysts due to their unique properties such as high surface area, high thermal stability, adjustable acidity and shape-selectivity [1,2]. Catalytic applications of zeolites cover a wide range of reactions, from oil refining, petrochemistry, fine chemical synthesis to biomass upgrade and separation processes [3–6]. Despite that, zeolites generally suffer from intracrystalline diffusion limitations because of the molecular dimensions of micropores. The size of zeolite pores (0.3–1.0 nm) also limits the accessibility of the active sites located in the channels for bulky reactants [7], which may negatively impact their catalytic performance for transformation of large molecules.

In relation to this issue, big hopes were connected with the mesoporous molecular sieves, firstly synthesized in 1992. However, low thermal and hydrothermal stability as well as the low acidity of mesoporous molecular sieves strongly limit their application in catalysis [8–10].

At the same time, great efforts have been undertaken to obtain zeolites possessing micropores with the diameter higher than 0.85 nm (extra-large pores), which are promising for catalytic transformation of bulky molecules [11–18]. However the synthesis of such zeolites requires specially prepared templates. Recently, it was shown that a lamellar MFI zeolite is formed when using "gemini-type" poly(quaternary ammonium)surfactants composed of a long-chain alkyl group (C_{18}–C_{22}) and several quaternary ammonium groups spaced by a C_6 alkyl linkage [19].

Significant effort has been devoted to develop the approaches for the introduction of mesopores in zeolites to combine the perfect properties of both micro- and mesoporous materials. The creation of new materials, including zeolite nanosheets, by post-synthesis modification of layered materials was proposed. However, the application of this strategy is limited to several zeolite structures including MCM-22 precursor [20], pre-ferrierite [21] and germanosilicate UTL zeolite [22,23].

A substantial mesoporosity of zeolite crystals can be obtained by using carbon templating approach where carbon particles are included in the synthesis of the zeolite, thereby leaving pores in the zeolite matrix after combustion [24,25]. Although in this case the optimization of the synthesis parameters is usually required to obtain the material with an appropriate crystallinity. Recently, microwave-assisted hydrothermal method has been reported not only to provide distinct advantages over the conventional synthesis (e.g. rapid heating, homogeneous nucleation, supersaturation by the rapid dissolution of precipitated gels, shorter crystallization time) but also is an efficient way for mesopore generation by desilication [26,27]. Direct synthesis of carbon-templating mesoporous ZSM-5 using microwave heating was shown by Park et al. [25].

---

* Corresponding author.
E-mail address: martin.kubu@jh-inst.cas.cz (M. Kubů).

0920-5861/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cattod.2013.11.063

At the same time, mesopores in zeolite crystals can also be easily created by post-synthesis treatments resulting in dealumination (e.g. steaming, acid leaching or their combination [28]) or in desilication (e.g. base leaching [8]). While removal of aluminium from the framework results in decreasing concentration of acid centres in zeolites, silicon extraction is known as an effective approach to create transport mesopores in various zeolites by preferential extraction of framework Si, preserving the Al environment and the related acidic properties.

Unfortunately, the major drawback of desilication remained in limited applicability to zeolites with Si/Al ratio 25–50 in the framework [29], until Verboekend has shown the controlled formation of mesopores in high-silica zeolites through pore-directing agents (PDA, e.g. Al(OH)$_4^-$, TPA$^+$) [30]. Since that time, desilication methods were intensively investigated to generate mesopores in zeolites of various chemical compositions and structure types (e.g. MFI [31], Y [32], IFR [33]).

Recently synthesized high silica -SVR zeolite is a member of the medium pore zeolite family. It possesses 3-dimensional 10-ring pore system with ordered silicon vacancies – structure defects in tetrahedron surrounding four hydroxyl groups [34]. The aluminosilicate -SVR was active in alkylation and transalkylation reactions of aromatic hydrocarbons, isomerization of C_4–C_7 hydrocarbons and olefins to aromatics [35]. The development of intracrystalline mesopores within -SVR crystals upon framework silicon extraction may open new perspectives in the application of this zeolite in catalysis.

In this work, we present a detailed study of the influence of the desilication conditions (e.g. NaOH and TPAOH concentration, duration of the treatment) of zeolite -SVR (Si/Al = 41) on the structural, textural and acidic properties of the formed micro/mesoporous materials to identify the crucial parameters for the formation of intracrystalline mesopores, while preserving the original acidity of the zeolite.

2. Experimental part

2.1. 2.1 Synthesis of hexamethylene-1,6-bis-(N-methyl-N-pyrrolidinium) hydroxide

3.5 g of N-methylpyrrolidine (97%, Aldrich) was dissolved in 50 ml of acetone. Then 4.9 g of 1,6-dibromohexane (98%, Aldrich) was added, and the resulting solution was stirred for 3 days at room temperature. The formed solid product was recovered by filtration, washed with diethyl ether and dried. Hexamethylene-1,6-bis-(N-methyl-N-pyrrolidinium) bromide was converted into hydroxide form by ion exchange with AG1-X8 (Bio-Rad) resin. The successful synthesis of the structure-directing agent (SDA) was confirmed by ^{1}H NMR spectroscopy after dissolution in methanol-d_4 (Fig. 1). 6 signals, attributed to differently shielded hydrogen atoms in the SDA molecule, were found. ^{1}H NMR (300 MHz, CD_3OD): δ 1.51 (m, 4H), 1.88 (m, 4H), 2.24 (m, 8H), 3.12 (s, 6H), 3.44 (m, 4H), 3.60 (t, 8H). The signal at 3.34 ppm (marked with asterisk) belongs to the solvent.

2.2. Synthesis of -SVR zeolite

The synthesis of parent -SVR zeolite was performed according to the Ref. [36]. The starting gel had the following composition: 40 SiO_2:1 $AlO_{1.5}$:6 $SDA(OH)_2$:1200 H_2O. In particular, 4.2 g of deionised water, 5.3 g Ludox LS-30 (30% SiO_2), 11.9 ml of 0.33 M hexamethylene-1,6-bis-(N-methyl-N-pyrrolidinium) hydroxide solution and 1.67 g of 15% $Al(NO_3)_3$ solution were mixed and stirred for 30 min. The resulting fluid gel was charged into 25 ml Teflon-lined autoclave and heated at 160 °C for 15 days under agitation (~25 rpm). The solid product was separated by filtration, washed with distilled water and dried overnight at 95 °C. The SDA was removed by calcination. Products were heated from room temperature to 120 °C at a rate of 1 °C/min, and the temperature was maintained for 2 h. The next step involved increasing temperature up to 540 °C for 5 h at a rate of 1 °C/min. Finally, the temperature was increased up to 580 °C at a rate of 1 °C/min and the product was kept at this temperature for 5 h.

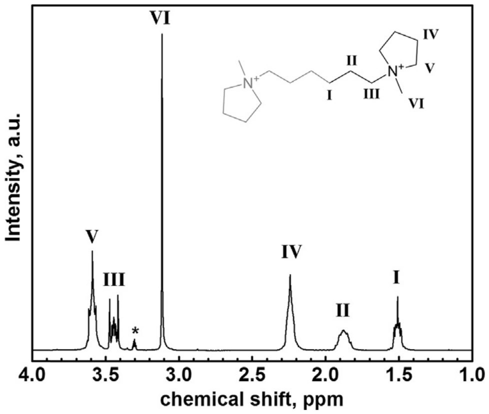

Fig. 1. ^{1}H NMR spectrum of hexamethylene-1,6-bis-(N-methyl-N-pyrrolidinium) bromide.

2.3. Desilication

Desilication procedure was based on Refs. [31,37]. Treatments were performed in 10 cm^3 glass flasks. The alkaline solution (5 cm^3) was stirred and heated to 65 °C, after which the zeolite sample (0.167 g) was added. The resulting mixture was left to react under reflux for different periods of time (Table 1) followed by quenching. The solid product was centrifugated and extensively washed out with distilled water to reach neutral pH and then dried overnight in an oven at 60 °C. In the case of TPAOH presence in the alkaline solution, calcination at 550 °C for 5 h (heating rate 5 °C/min) was applied after the treatment to remove occluded TPA$^+$ species. Na$^+$ forms of -SVR samples were converted to NH_4^+ form by three-fold treatment with 1.0 M NH_4NO_3 solution at room temperature for 3 h.

The samples, treated with NaOH solution, are designated according with the expression: -SVR/NaOH conc. (M)/time (min). When treated with the mixture of NaOH and TPAOH, the samples are designated as -SVR/NaOH conc. (M) + TPAOH conc. (M)/time (min).

2.4. Characterization

^{1}H NMR spectrum of the organic SDA was recorded on a Varian Mercury 300 spectrometer at 300.0 MHz in CD_3OD solutions at 25 °C. Chemical shifts (δ/ppm) are given relative to residual CHD_2OD signals (δ_H 3.34 ppm).

The crystallinity of all samples under investigation was checked by X-ray powder diffraction (XRD) using a Bruker AXS-D8 Advance diffractometer with a graphite monochromator and a position sensitive detector Våntec-1 using CuKα radiation in Bragg–Brentano geometry.

The size and shape of zeolite crystals were examined by scanning electron microscopy (SEM, JEOL JSM-5500LV microscope). For the measurement crystals were coated with a thin platinum layer by sputtering in vacuum chamber of a BAL-TECSCD-050.

Nitrogen adsorption/desorption isotherms were measured on a Micromeritics GEMINI II 2370 volumetric Surface Area Analyzer at