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Direct incorporation of B, Al, and Ga into medium-pore ITH zeolite: Synthesis, acidic, and catalytic properties

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Direct crystallization of B-, Al- and Ga-substituted medium-pore **ITH** zeolites was carried out using hexamethonium hydroxide (HMH) and N,N,N′,N′,-tetramethyl-1,6-hexanediamine (TMHDA) as structure-directing agents. The type of organic SDA was found determining the crystal size and the nature of Brønsted acid sites in isomorphously substituted **ITH** zeolites. The use of HMH resulted in formation of tiny (length of 0.5–3 μm) needle-like **ITH** crystals having bridging $\equiv$Si—(OH$^+$)—E($^-$)$\equiv$ (E = B, Al, Ga) groups with acidic strength increasing in the following sequence B < Ga < Al. In contrast, **ITH** zeolites with bulky (length of 40–50 μm) crystals prepared using TMHDA possess loosely bond framework and $[(SiO)_3Al—OH]^-H^+$ and $(SiO)_2B—OH$ groups (absorption band at 3670 cm^{-1}) perturbing upon interaction with pyridine. B-, Al- and Ga-ITH possessing tiny crystals showed improved catalytic performance in tetrahydropyranylation of 1-hexanol in comparison with non-acidic heteroelement-free germanosilicate zeolites and isomorphously substituted **ITH** zeolites with bulky crystals. The yield of target ether is enhanced with increasing strength of acid sites (e.g. B- < Ga- < Al-ITH) or with growth in their concentration.

1. Introduction

Zeolites form an important group of crystalline microporous metallosilicates with well-defined pores and cavities being intensively applied in industry. While small-pore zeolites (with pore openings limited by 8 atoms in tetrahedral coordination, i.e. 8-ring) play a significant role in gas separation [1], medium- (10-ring) and large-pore (12-ring) zeolites are applied as solid catalysts in large-scale processes [2]. Such useful properties of zeolites as (1) surface areas in the order of 400–700 m^2 g^{-1}; (2) high adsorption capacity presenting besides a concentration effect enhancing the rate of bimolecular reactions; (3) the possibility of introducing isolated, well defined acid, base, and/or redox active sites in accessible framework positions; and (4) easy tuning of acid strength of the Brønsted acid sites by incorporating different T^{III} atoms into the framework provide their advantageous catalytic behavior. However, the most remarkable feature of zeolites as heterogeneous catalysts lies in the possibility of shape-selective control of reaction selectivity, firstly discovered for medium-pore zeolites [3].

Medium-pore **MFI** is the most versatile solid-acid catalyst used in more than 50 processes in petroleum refining, petrochemicals and aromatics processing. One of the reasons for its catalytic versatility is a broad range of compositions, in which it can be prepared. In particular, it is possible to synthesize **MFI** zeolite with Si/Al ratios from about 8 to infinity [4]. This flexibility allows tuning the catalytic properties of Al-MFI to the desired optimum. Isomorphous substitution of silicon for different 3- and 4-valent element broadened the field of **MFI** application even more. Ti-substituted **MFI** (TS-1) presenting one of the most important innovation in heterogeneous catalysis over the last decades appeared as a brilliant catalyst for the oxidation of various organic substrates (e.g. alkanes, alkenes, alcohols, and aromatics) with H_2O_2 under mild conditions [5–7], while the breakthrough of Ga-bearing **MFI** zeolite was found in the aromatization of lower alkanes (Cyclar process) [8].

Due to the high potential of medium-pore zeolites in shape-selective catalysis, there is still a continuous effort to synthesize new structures, especially containing 2- and 3-dimensional channel systems, as well as to modify the characteristics of the existing ones.

Recently, a new zeolite **ITH** possessing interconnecting medium-pore 9- (4.0 × 4.9 Å), 10- (4.8 × 5.7 Å) and 10- (4.7 × 5.1 Å) ring channels was synthesized using hexamethonium hydroxide (HMH) as structure-directing agent (SDA) [9]. The introduction

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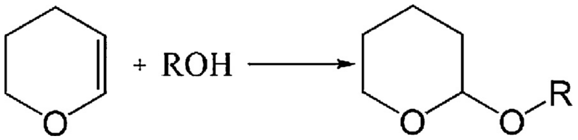

Scheme 1. Tetrahydropyranylation of alcohols.

of acid sites was attempted by direct synthesis of borosilicate and aluminosilicate **ITH** zeolites [10]. While crystallizing smoothly in borosilicate systems, zeolite **ITH** was not obtained from aluminosilicate reaction mixtures (RMs). Later on, the structure-directing propensity of Ge toward zeolites containing D4R SBUs was exploited to increase the rate of **ITH** crystallization, which allowed preparing Al-substituted germanosilicate **ITH** zeolite exhibiting strong acid centers (63 and 48 μmol/g of Brønsted and Lewis acid sites, respectively) [11]. Synthesized Al-**ITH** was shown as shape selective catalyst in the aromatics conversion [12] and the catalytic cracking of vacuum gas oil producing propylene [11].

In contrast to HMH providing the formation of **ITH** zeolites having tiny needle-like crystals in Ge-poor ($Si/Ge = 6–\infty$) concentrated ($H_2O/T \leq 10$) gels [11,13], the use of N,N,N′,N′-tetramethyl-1,6-hexanediamine (TMHDA) was recently reported favoring formation of **ITH** zeolites with large platelet-like crystals in Ge-enriched ($1 \leq Si/Ge \leq 4$) diluted ($H_2O/T^{IV} = 22–66$) medium [14].

To the best of our knowledge, systematic investigation of the synthesis conditions leading to **ITH** zeolites isomorphously substituted with different 3-valent elements with tunable acidic properties and variable size of the crystals has not been performed.

This contribution focuses on the understanding of the crucial factors impacting generation of acid centers by incorporation of B, Al, Ga into **ITH** zeolite using HMH and TMHDA as SDAs in germanosilicate reaction mixtures. The influence of synthesis conditions, the nature of SDA, and 3-valent element on the textural characteristics (e.g. the size and shape of the crystal, porosity) and acidic properties (nature, concentration and strength of acid sites) in B-, Al- and Ga-substituted **ITH** zeolites is carefully addressed. Catalytic activity of **ITH** zeolites containing different 3-valent elements was tested in tetrahydropyranylation of 1-hexanol (Scheme 1). The activity of various heterogeneous catalysts in the tetrahydropyranylation of alcohols may be attributed to both Brønsted and Lewis acid sites [15,16], while the yield in this reaction usually enhances with increasing strength of the acid sites [17]. Thus, the choice of tetrahydropyranylation reaction offers us to diversify B-, Ga- and Al-substituted **ITH** zeolites according to their catalytic ability and to verify relation between activity and acidity of the catalysts.

2. Experimental part

2.1. Materials

1,6-Dibromohexane (96%), trimethylamine solution (31–35 wt.% in ethanol), TMHDA (99%), boric acid (H_3BO_3, 99.97%), aluminum hydroxide (≥98.5%), gallium nitrate hydrate (99.9%), germanium oxide (99.99%), tetraethylorthosilicate (TEOS, 98%), hydrofluoric acid (48 wt.% in H_2O, ≥99.99%) were used for the synthesis of SDAs and zeolites. 3,4-Dihydro-2*H*-pyran (DHP, 97%), 1-hexanol (≥99.5%), mesitylene (≥99%), and hexane (≥97%) were used in catalytic experiments. All reactants and solvents were obtained from Sigma–Aldrich and used as received without any further treatment.

Hydrofluoric acid (48 wt.% in H_2O, ANALPURE®), nitric acid (67 wt.% in H_2O, ANALPURE®), hydrochloric (36 wt.% in H_2O, ANALPURE®) supplied by Analytika spol. s.r.o. were used for digestion of zeolites.

2.2. Preparation of hexamethonium dihydroxide (HMH)

Hexamethylene-bis (trimethylammonium) dibromide was prepared according to Ref. [18] and transformed into hydroxide form using Ambersep® 900(OH) anion exchange resin. The solution of HMH was concentrated under low pressure (20 Torr) at 40 °C until the hydroxide concentration grown to >1.0 M.

2.3. Synthesis of *ITH* zeolites

The synthesis of tiny crystals of isomorphously substituted **ITH** zeolites was performed using HMH as SDA similarly to Ref. [10] replacing a part of silica source for the required amount of 3-valent element. Molar compositions of reaction mixtures were varied in the ranges 0.80–0.91 SiO_2 : 0–0.06 $EO_{1.5}$: 0.09–0.2 GeO_2 : 0.25 HMH: 0.5 HF: 5 H_2O (E = B, Al, Ga). Typically, a certain amount of a source of 3-valent element (e.g., boric acid, aluminum hydroxide or freshly precipitated gel of gallium hydroxide) and germanium oxide were dissolved in a solution of HMH (1.0 M). TEOS was then added and the mixture was gently stirred until complete evaporation of the excess of water and alcohol formed. A certain amount of hydrofluoric acid was then added to reaction mixture. The resulting fluid gel was charged into 25 ml Teflon-lined autoclave and heated at 175 °C for 10 days under agitation (~60 rpm). The solid product was separated by filtration, washed with distilled water and dried overnight at 95 °C.

The occluded HMH was removed from the samples by calcination from room temperature to 300 °C at a rate of 1 °C/min, and that latter temperature was maintained for 3 h. The next step involved increasing the temperature at a rate of 1 °C/min up to 580 °C; the product was kept at this temperature for 3 h, to burn off the remaining organics.

Isomorphously substituted **ITH** zeolites having large crystals were prepared according to Ref. [14]. TMHDA was used as the structure-directing agent. The synthetic suspension had the composition of 0.5–0.8 SiO_2 : 0–0.2 $EO_{1.5}$: 0.2–0.5 GeO_2 : 7 TMHDA: 1.4 HF: 55 H_2O (E = B, Al, Ga). The suspension was heated at 175 °C for 10 days under static condition. The as-synthesized **ITH** samples were washed with distilled water, dried at 65 °C for 12 h and calcined at 650 °C for 8 h with a temperature ramp of 1 °C/min under air flow.

Obtained zeolites were designed as *x*E-ITH-*n*, where E – B, Al or Ga; *x* – concentration of the respective heteroelement in the reaction mixture ($T^{III}/(T^{III} + T^{IV})$), mol%; *n* – Si/Ge in the gel.

2.4. Characterization

The crystallinity of all samples under investigation was determined 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 at a scan rate of $0.25^\circ\ 2\theta\ min^{-1}$.

Al, Ga, B, Si and Ge contents were analyzed using ICP (ThermoScientific iCAP 7000). For Al, Ga, Si, Ge determination ca. 50 mg of the material was digested in a mixture of HF, HNO_3, and HCl. The samples were placed in the microwave in a closed vessel at $T = 140$ °C for 35 min. Saturated solution of H_3BO_3 was then added for complexation of the excess of HF. B was extracted off the sample (200 mg) with 0.1 M HCl according to Ref. [19]. After digestion/extraction, solutions under analysis were collected in 250 ml flasks and the volume was measured with ultra pure water.

Nitrogen adsorption/desorption isotherms were measured using an ASAP 2020 (Micromeritics) static volumetric apparatus at liquid nitrogen temperature (−196 °C). Prior to the sorption measurements, all samples were degassed with a turbomolecular pump at 300 °C for 8 h.

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