Journal of Energy Chemistry 25 (2016) 318–326

Contents lists available at ScienceDirect

Journal of Energy Chemistry

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

http://www.journals.elsevier.com/journal-of-energy-chemistry/

Tuning of textural properties of germanosilicate zeolites ITH and IWW by acidic leaching

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ARTICLE INFO

Article history:
Received 22 October 2015
Revised 3 December 2015
Accepted 5 December 2015
Available online 18 December 2015

Keywords:
Textural properties
ITH
IWW
Degermanation

ABSTRACT

The possibility to adjust textural properties of **ITH** and **IWW** zeolites by the variation of conditions (e.g. temperature, pH, duration) of acidic leaching was shown. While the growth of the temperature of acid treatment caused the increasing amount of leached Ge atoms and enhancing volumes of both micro and mesopores at 80 °C, the mesopore volume in **ITH** (Si/Ge = 3.4 and 5.8) and **IWW** (Si/Ge = 3.3) zeolites changed with the duration of the treatment ($pH = 2$; $T = 80$ °C) as follows: 96 h < 1 h < 24 h. Independently on the chemical composition and zeolite topology, the treatment of germanosilicate zeolites at pH = 2–7 resulted in development of both micro and mesoporosity accompanied by the extraction of substantial amount of Ge atoms, while the increasing acidity up to pH = 0 resulted in some reduction of Ge extraction and in the development of mesopores at maintained value of micropore volume when compared with initial germanosilicates. The higher activity (i.e. number of reactant molecules converted per active site) of germanosilicate with modified micro-mesoporous channel system in comparison with parent **IWW** zeolite in esterification of levulinic acid was attributed to enhanced accessibility of active sites.

1. Introduction

Zeolites, crystalline microporous materials, have a decisive impact on high number of technological applications including large-scale processes in heterogeneous catalysis, separation and adsorption [1]. Catalytic applications of aluminosilicate zeolites, possessing strong acidic centers, encompass oil refining and petrochemistry, fine chemical synthesis and environmental catalysis [2,3]. Though being extremely beneficial in shape-selective catalysis [4], micropores impose restrictions on the use of conventional zeolites in fine chemical or pharmaceutical synthetic applications involving transformations of bulky molecules due to mass transfer limitations [5,6].

Last decade has brought a number of different strategies to accomplish the synthesis of zeolites with additional mesoporosity. Highly ordered hexagonal aluminosilicates with walls containing primary and secondary structural building units, similar to those of microporous zeolites have been successfully synthesized in Ref. [7] from assembly of preformed aluminosilicate precursors with cetyltrimethylammonium bromide surfactant.

The generation of secondary intercrystalline porosity in zeolites was achieved using different types of organosilanes taking advantage of their high affinity for reaction with silicate and aluminosilicate species [8–12]. The control over the mesopore diameters by changing the chain length in surfactant organosilane $[(RO)_3SiC_3H_6\text{-}N^+(CH_3)_2C_nH_{2n+1}]Cl$ ($n = 16$–22) was demonstrated on zeolites **MFI**, **LTA**, **MOR**, **CHA** and **FAU** [8,12].

An innovative approach to the direct crystallization of hierarchical zeolites was recently proposed by Ryoo and co-workers [13]. It consists in using a specially designed amphiphilic structure-directing-agent (SDA) composed of polyquaternary ammonium part and long hydrophobic tail. The single-tail SDA like $C_{22}H_{45}-N^+(CH_3)_2-C_6H_{12}-N^+(CH_3)_2-C_6H_{12}$ leads to a formation of **MFI** nanosheets of irregular arrangement or regular stacking into an ordered multilamellar mesostructure, which could be maintained by generating silica or organic pillars between zeolite layers [14]. In contrast, gemini-type multiammonium surfactants $[C_nH_{2n+1}-(N^+(R)_2-C_6H_{12})_m-N^+(CH_3)_2-C_nH_{2n+1}$ ($n = 18, 22$; $m = 2, 3$)] generate thin zeolite layers with regular mesostructure ordering [15]. Produced hierarchical **MFI** zeolites exhibited high catalytic activity and long lifetime in the liquid-phase Friedel–Crafts alkylation and acylation of aromatics, annulation of phenols with 2-methyl-3-buten-2-ol, Pechmann condensation of phenols [16–19].

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http://dx.doi.org/10.1016/j.jechem.2015.12.003
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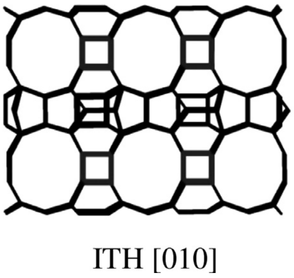

Fig. 1. The structure of zeolite **IWW** and **ITH** in 010 projections.

Demetallation of zeolites can be considered as the most cost effective way of the fabrication of hierarchical materials, lacking however in the intelligent designing of pore architecture formed. Non-uniform mesopores facilitating diffusion of reactants to the active centers of the zeolite catalysts were shown to be easily generated by post-synthesis treatments as dealumination (e.g. steaming, acid leaching or their combination) [20,21], desilication (e.g. base leaching) [22–26], or detitanation [27,28].

Recently, new zeolite structures, containing double four-ring (D4R) units, were synthesized by introducing germanium into the reaction mixtures [29–33]. Germanosilicate zeolite **IWW** possessing interconnecting 8 – (4.6 × 3.3 Å), 10 – (4.9 × 4.9 Å) and 12 – (6.0 × 6.7 Å) ring channels (Fig. 1) was firstly prepared by Corma and coworkers [34] in concentrated reaction mixtures ($H_2O/T^{IV} = 3.5$, where T is the zeolite framework tetrahedral atom) using 1,5-bis-(methylpyrrolidinium)-pentane as structure-directing agent (SDA). Similarly to the most of other germanosilicate zeolites, more than 95% of Ge atoms were found preferentially occupying T sites in D4R units of **IWW** framework [35]. The structure analysis of Ge-rich (Si/Ge = 3.1) and Ge-poor **IWW** (Si/Ge = 6.4) samples performed in [36] allowed to find the composition of the D4Rs being [6Ge,2Si] and [4Ge,4Si], respectively. Another germanosilicate zeolite **ITH** with a set of interconnected 9 – (4.0 × 4.9 Å), 10 – (4.8 × 5.7 Å) and 10 – (4.7 × 5.1 Å) ring channels (Fig. 1) can be synthesized using hexamethonium [37] or *N*,*N*,*N*′,*N*′-tetramethyl-1,6-hexanediamine [38] as SDA. In contrast to **IWW**, **ITH** zeolites were found containing Ge atoms in $[4^15^26^2]$ cages in the layers and in D4R units [39,40].

Hydrolytic instability of Si–O–Ge and Ge–O–Ge linkages combined with regioselective location of Ge atoms in D4R units shown for a number of germanate and germanosilicate structures [41–43] enabled the development of a new top-down strategy for producing zeolitic layers by selective disassembly of appropriate (in terms of topology and chemical composition) germanosilicate **UTL, IWW, ITH, ITR** zeolites in acid environment [39,44]. Further manipulations with fabricated crystalline **UTL**-like layers (including swelling [45], pillaring [46,47], intercalation [48], condensation [49]) opened the way to novel expanded layered structures or even new zeolites, not yet prepared by conventional hydrothermal synthesis. As for the hydrolytic "weakness" of germanosilicate zeolites [50], regioselective location of Ge in their frameworks [41–43] was exploited in Ref. [51] to generate transport pores in **IWW** zeolite. Formation of additional micro and mesopores after the treatment of **ITH** zeolites with $Al(NO_3)_3$ solution (pH = 2) was reported in Ref. [52].

This work is aimed to address the influence of treatment conditions as well as chemical composition and topology of germanosilicate zeolites on the textural characteristics of materials produced by applying acid leaching. With this purpose, the effect of pH, T, and duration of the treatment on the outcome of acid leaching of germanosilicate **ITH** zeolites differing in chemical compositions (e.g. Si/Ge = 3.4 and 5.8) and **IWW** zeolite (Si/Ge = 3.3) was investigated.

2. Experimental

2.1. Materials

1,6-Dibromohexane (96%, Sigma Aldrich), trimethylamine solution (31–35 wt% in ethanol, Sigma Aldrich), *N*,*N*,*N*',*N*'-tetramethyl-1,6-hexanediamine (TMHDA) (99%, Sigma Aldrich), *N*-methylpyrrolidine (97%, Sigma Aldrich), 1,5-dibromopentane (97%, Sigma Aldrich), germanium oxide (99.99%, Sigma Aldrich), tetraethyl orthosilicate (TEOS, 98%, Sigma Aldrich), hydrofluoric acid (48 wt% in H_2O, ≥ 99.99%, Sigma Aldrich), acetone (99%, Fisher Chemical) were used for the synthesis of SDAs and zeolites. 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 decomposition of zeolites.

Levulinic acid (99%, Sigma Aldrich), ethanol (> 99.8%, Sigma Aldrich) and mesitylene (98%, Sigma Aldrich) were used for catalytic experiments.

All reactants and solvents were used as received without any further treatment.

2.2. Syntheses of SDAs

2.2.1. Preparation of hexamethonium dihydroxide (HMH)

Hexamethylene-bis (trimethylammonium) dibromide was prepared according to the Ref. [53]. 37.4 g of 1,6-dibromohexane was mixed with 82.5 g of trimethylamine solution (31–35 wt% in ethanol) and 200 mL of ethanol with a magnetic stirrer for 2 days at room temperature. Then, the mixture was directly washed with ethyl acetate and diethyl ether and the final product was separated by filtration and dried at room temperature for 12 h.

Hexamethylene-bis (trimethylammonium) dibromide was transformed into hydroxide form using Ambersep® 900(OH) anion exchange resin (0.4 mmol of SDA per 1 g of anion exchange resin). The solution of HMH was concentrated under low pressure (35 Torr) at 30 °C until the hydroxide concentration grown to > 1.0 mol/L

2.2.2. Preparation of 1,5-bis-(methylpyrrolidinium) pentane dihydroxide ($MPP(OH)_2$)

The preparation of structure directing agent for IWW synthesis followed the procedure in the Ref. [34]. The SDA, 1,5-bis-(methylpyrrolidinium)pentane (MPP) dibromide, was synthesized by reaction of 40 g of *N*-methylpyrrolidine with 37.5 g of 1,5-dibromopentane in 300 mL of acetone under reflux during 24 h.

The hydroxide form of MPP was obtained by ion-exchange with Ambersep® 900(OH) anion exchange resin and was concentrated under low pressure (35 Torr) at 30 °C until the hydroxide concentration was equal to approximately ∼ 1.0 mol/L.

2.3. Syntheses of ITH and IWW zeolites

The zeolite samples synthesized in this study were designated as ITH-*n* and IWW-*n* where *n* stands for the Si/Ge ratio in the reaction mixture.

2.3.1. Syntheses of ITH zeolites

Ge-rich zeolite ITH-2 was obtained according to Ref. [38] from the reaction mixture with the following composition: $0.66SiO_2 : 0.33GeO_2 : 7TMHDA : 1.4HF : 44H_2O$, using N,N,N′,N′-tetramethyl-1,6-hexanediamine (TMHDA) as the SDA. Certain amount of