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Three-dimensional 10-ring zeolites: The activities in toluene alkylation and disproportionation

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ABSTRACT

Three-dimensional 10-ring zeolites TUN, IMF, –SVR, MFI and MEL were investigated as for their acid properties, adsorption of 2,2-dimethylbutane and in toluene disproportionation and its alkylation with isopropyl alcohol. The results were compared against zeolite *SFV, the structure of which consists mainly of MEL zeolite with some additional 12-ring channel system. With exception of –SVR synthesized with high Si/Al ratio, all other zeolites provided Si/Al ratios in a narrow region. Novel zeolites TUN, IMF, and –SVR exhibited higher conversions than MFI and MEL in toluene alkylation. TUN and IMF were substantially more active in toluene disproportionation indicating less diffusion restrictions of channel structure on the disproportionation reaction. *SFV showed a similar catalytic behavior to MEL with much lower selectivity to *p*-xylene and *p*-cymene. This could indicate that both toluene disproportionation and alkylation proceed in reaction space of *SFV being similar to those of MFI and MEL. *SFV and TUN exhibited much faster adsorption of 2,2-dimethylbutane than MFI, MEL, IMF, and –SVR. It was concluded that the presence of some larger transport pores in *SFV than in other zeolites is responsible for fast adsorption of 2,2-dimethylbutane and transport of products resulting in a low selectivity to *p*-xylene and *p*-cymene.

1. Introduction

Transformations of aromatic hydrocarbons represent one of the most important groups of reactions in petrochemical processes [1–3]. Alkylation, disproportionation, isomerization, and transalkylation reactions usually carried out over zeolite catalysts allow upgrading of low value chemicals like benzene or toluene to those of higher practical interest, such as ethylbenzene, *p*-xylene or cumene [4,5]. In this respect, zeolite channel structures and types and concentration of acid sites play the decisive role as for the zeolite activities and selectivities are concerned. In addition to the practical application of zeolites as catalysts in industrial processes, zeolites can serve as model catalysts for investigating reaction mechanisms and structure–acidity–activity relationship for novel zeolites [6–10].

225 different structural types of zeolites were already recognized by the International Zeolite Association [11]. The individual types of zeolites differ in the size of the channels (8-, 10-, 12- or 14-rings), their connectivity and the presence or absence of cages in channel intersections or along the channel itself [12–15]. Zeolite acidity and channel architecture control the activity and selectivity in transformations of organic compounds [7,9,16,17]. In addition to conventional three-dimensional zeolites, novel zeolite morphologies including layered [18–21], pillared [22], self-pillared [23], hierarchical [24,25], or nanosponge [26] zeolites have been also synthesized and their properties described in detail. Activity and selectivity of zeolite catalysts in catalytic reactions are directly related to the structure, texture and chemical composition of a particular zeolite under study.

In this contribution we investigated the relationship among the pore structure of several novel medium-pore zeolites (TUN, IMF, –SVR, *SFV) and their acidity in toluene alkylation with isopropyl alcohol and in toluene disproportionation. Toluene disproportionation was chosen as one of these reactions because it reflects not only the structural features and acidity of the zeolite catalysts under study, due to the possibility of monomolecular and bimolecular

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Table 1
List of zeolites under study and their structural characteristics.

Sample	Reference	Dimensionality of the channels	Type of the channels	Size of the channels (nm)
TUN	[27]	3D	(10 + 10) × 10	0.55 × 0.60 + 0.52 × 0.60; 0.54 × 0.55
IMF	[28]	3D	10 × 10	0.55 × 0.56; 0.53 × 0.59
–SVR	[29]	3D	10 × 10 × 10	0.55 × 0.57; 0.52 × 0.59; 0.52 × 0.56
SFV	[17]	3D	12 × 10 × 10	0.51 × 0.82; 0.56 × 0.56; 0.50 × 0.55
MFI		3D	10 × 10	0.51 × 0.55; 0.53 × 0.56
MEL		3D	10	0.53 × 0.54

mechanism, but also the product selectivity for preferential xylene formation [9]. Toluene alkylation provides even more information about the reaction volume and acidity of zeolites due to the parallel alkylation/disproportionation reactions, selectivity to cymenes, *p*-cymene and also a possible formation of secondary products like *n*-propyl toluene requiring a particular channel arrangement [6]. All zeolites were characterized by XRD, adsorption isotherms, SEM, and FTIR spectroscopy with different probe molecules.

TUN, IMF, –SVR, and *SFV zeolites were recently synthesized and they possess rather complex structures consisting of intersecting 10-rings, their structural features are listed in Table 1. TUN zeolite was synthesized by group of Hong [27]. Structure of zeolite IMF was determined by Baerlocher et al. [28] describing it as two-dimensional system of 10-ring channels with limited third dimension along (0 1 0). Unit cell of –SVR zeolite has 24 different crystallographic sites, one of them forms ordered Si vacancy [14,29]. Synthesis of TUN, IMF, and –SVR is carried out using diquaternary alkylammonium ions based on N-methyl pyrrolidine. The only difference among the individual SDAs (structure directing agents) is the length of the carbon chain between two heterocyclic rings. TUN is prepared with 1,4-bis-(N-methyl-pyrrolidinium) butane (1,4-MPB), whereas IMF and –SVR with pentane (1,5-MPP) and hexane (1,6-MPH) analogs, respectively.

2. Experimental

2.1. *SDA preparation*

The divalent SDA cations were prepared, purified and characterized as follows:

The synthesis is generally carried out according to Fig. 1. 0.48 mol (20% excess) of N-methyl pyrrolidine (MP, 98% Acros) was mixed with 200 ml of methanol (99+%, Acros) and stirred while drop-wise adding of 0.2 mol of 1,*n*-dibromoalkane ($n = 4$–6). Final mixture was stirred at room temperature for 4 days. Unreacted amine and solvent were evaporated, obtained white sediment dissolved in boiling isopropyl alcohol (99.5%, Lachner) and yellowish solution put into the fridge for recrystallization. After 2 days, trituration with acetone (99.5%, Lachner) and its consecutive evaporation to dryness finished the procedure. Due to high sensitivity to moisture, all SDAs were stored closed in a flask before using in the synthesis. The purity was determined by ^{1}H NMR.

2.2. *Zeolite synthesis*

2.2.1. *TUN*

TUN zeolite was synthesized from the reaction gel with the following molar composition: 4.5(1,4-MPB-Br$_2$)·11Na$_2$O·0.75Al$_2$O$_3$·30SiO$_2$·1200H$_2$O [27]. Distilled water, 1,4-MPB dibromide, Al(NO$_3$)$_3$·9H$_2$O (p.a., Lachner), NaOH (98%, Lachner) and fumed silica (Aldrich) were mixed together exactly in the written order. Each chemical was added after dissolving the previous ones. After being stirred at room temperature for 1 day, the mixture was transferred to Teflon-lined 500 ml autoclave and heated at 160 °C for 12 days under agitation and autogenous pressure.

2.2.2. *IMF*

For IMF synthesis [30], the aqueous solution of 1,5-MPP dibromide was prepared. Then NaAlO$_2$ (52% Al$_2$O$_3$, 42.5% Na$_2$O, Riedel de Haën), NaOH, NaBr (99+%, Acros) and fumed silica were added. The mixture with the molar composition 10(1,5-MPP-Br$_2$)·17Na$_2$O·6NaBr·Al$_2$O$_3$·60SiO$_2$·2400H$_2$O was stirred for 2 h to form an uniform gel [31]. Crystallization proceeded in Teflon-lined 25 ml autoclaves at 175 °C for 10 days under static conditions.

2.2.3. *–SVR*

High silica –SVR zeolite was synthesized in fluoride media in the presence of 1,6-MPH hydroxide [32]. For that purpose, 1,6-MPH dibromide (11.1 g), distilled water (56.1 g) and AG1-X8 resin (28.7 g) were put together and stirred overnight at room temperature for exchanging 1,6-MPH to its hydroxide form. After filtration, 64 g of the obtained solution was mixed with 12.6 g of tetraethyl orthosilicate (TEOS, 98.5%, Aldrich). Water and ethanol formed from TEOS hydrolysis were allowed to evaporate to evident dryness in a hood for 5 days. 0.2 g of LZ-210 zeolite (partially dealuminated Y zeolite) as a potential contributor of aluminum, 0.1 g of as-made pure-silica –SVR as seeds, 3.7 g of distilled water and 1.25 g of 40% HF (p.a., Lachner) were added and stirred with plastic spatula until thick gel was formed. Resulting gel was placed in Teflon-lined stainless steel 25 ml autoclaves and heated at 170 °C under agitation for 9 days.

2.2.4. **SFV*

*SFV zeolite was synthesized using N-butyl-N-cyclohexylpyrrolidinium hydroxide as a template [33]. The resulting gel in a 25 ml Teflon liner was capped off and placed in a Parr bomb Steel reactor and heated in an oven at 170 °C, while rotating at 43 rpm, for 18 days. The mixture was filtered through a fritted-glass funnel, the obtained solids were washed generously with water, then rinsed with a small amount of acetone and allowed to air-dry overnight and further dried in an oven at 120 °C [17].

2.2.5. *MFI*

MFI zeolite was purchased from PQ Corporation (CBV-8020) in NH$_4$-form with Si/Al = 34.5.

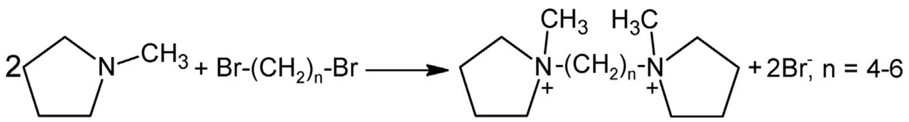

Fig. 1. SDA preparation.