Journal of Catalysis 266 (2009) 79–91

Contents lists available at ScienceDirect

Journal of Catalysis

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

The role of the zeolite channel architecture and acidity on the activity and selectivity in aromatic transformations: The effect of zeolite cages in SSZ-35 zeolite

Naděžda Žilková [a], Martina Bejblová [a], Barbara Gil [b], Stacey I. Zones [c], Allen W. Burton [c], Cong-Yan Chen [c], Zuzana Musilová-Pavlačková [a], Gabriela Košová [a], Jiří Čejka [a,*]

[a] J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic v.v.i., Dolejškova 3, CZ-182 23 Prague 8, Czech Republic
[b] Department of Chemistry, Jagiellonian University, Ingardena 3, PL-30 060 Krakow, Poland
[c] Chevron Energy and Technology Company, Richmond, CA 94 802, USA

ARTICLE INFO

Article history:
Received 1 August 2008
Revised 16 May 2009
Accepted 20 May 2009
Available online 2 July 2009

Keywords:
Zeolite architecture
Cage effect
Acidity
Alkylation
Disproportionation
SSZ-33
SSZ-35
MCM-58
MCM-68

ABSTRACT

A series of zeolites differing in the channel architecture and acidity was investigated in toluene disproportionation, together with toluene and *p*-xylene alkylation with isopropyl alcohol. Zeolites with one- to three-dimensional 10-ring and 12-ring channels with and without cages, and those having 12–12–10 and 12–10–10-ring channel systems were studied. It was shown that general relationship of increasing zeolite activity with increasing pore diameter and pore connectivity is not valid as the size of some 12-ring channels (Beta, MCM-68) is comparable with 10-ring channels (ZSM-5, SSZ-35). In addition, the presence of cages in the structure of SSZ-35 and MCM-58 attributes the unusual catalytic behavior of these zeolites. SSZ-35 and MCM-58 zeolites behave in both toluene reactions such as three-dimensional large-pore zeolites. Subtle differences between zeolites of similar pore sizes and dimensionality can be usually explained based on the differences in the acidity of the individual zeolites. In *p*-xylene alkylation SSZ-35 exhibited high conversion with the highest selectivity to 1-isopropyl-2,5-dimethyl benzene and a low rate of deactivation. The presence of 18-ring cages in the channels of 10-ring zeolite SSZ-35 (STF) gives rise to an unusual catalytic behavior of this zeolite by comparison to other 10-ring zeolites. SSZ-35, possessing channels of 0.54 × 0.57 nm in diameter, exhibits catalytic activity in transformation of aromatic hydrocarbons that is similar to large-pore zeolites. 18-Ring cages enable the formation of relatively bulkier transition states while the diffusion of the product molecules out of the 10-ring channel system is not slowed down due to 10-ring windows. In addition, the channel system of SSZ-35 prevents the formation of coke precursors.

1. Introduction

More than 180 different structural types of zeolites were already recognized by the International Zeolite Association. The individual types of zeolites differ in the size of the channels (8-, 10-, 12-, 14-, or even larger rings), connectivity of the channels, and the presence or absence of cages in channel intersections or along the channel itself [1]. In addition to zeolite acidity, the size of channels and their dimensionality influence the activity and selectivity in transformations of organic compounds [2–4]. Reactions of alkyl and dialkyl aromatic hydrocarbons represent an interesting group of reactions both from the practical petrochemical viewpoint as well as model reactions usually influenced by shape selectivity [5,6]. Zeolites with 10 rings usually exhibit *restricted transition-state* and *product shape* selectivity being particularly important in *para*-selective reactions such as toluene disproportionation, xylene isomerization, and toluene alkylation with methanol, ethylene/ethanol, and propylene/propanol [7–14]. Diffusion coefficients of individual *ortho*, *meta*, and *para* isomers differ in several orders of magnitude, which completely changes the product mixture composition in comparison with conventional non-microporous catalysts [15].

The crystal size of zeolites is expected to substantially influence the conversion of aromatic hydrocarbons as well as the resulting selectivity, especially when related to the *para*-selectivity [16–19]. Unfortunately, most of the papers published show these selectivities for different conversions, which makes it impossible to provide clear conclusions. In this respect, Melson and Schűth showed, for ethylbenzene disproportionation, that external acidity plays a very important role due to the enrichment of aluminum in the crystal rim. Thus, the external acidity of zeolites increases substantially when decreasing the size of the crystals [18].

Zeolites represent the most important inorganic materials for catalysis, finding applications in dozens of technological processes from petroleum refining and petrochemistry up to fine chemical

---

* Corresponding author.
E-mail address: jiri.cejka@jh-inst.cas.cz (J. Čejka).

0021-9517/$ - see front matter © 2009 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2009.05.017

synthesis [5,9]. The synergism in zeolite synthesis and prediction of new zeolite structures increase the opportunities for their further application and deepen our knowledge on their behavior in catalytic reactions [20,21]. For a long time it was believed that zeolite activity increases mainly with increasing channel dimensions and connectivity of the channels. A typical example of this relationship is represented by the so-called Constraint Index, a test presented in a paper by Frillette et al. [22]. The Constraint Index relates the activity and selectivity of a zeolite to the ratio of the cracking rates of *n*-hexane to 3-methylpentane under standard reaction conditions. Various researchers have attempted to rationalize this relationship using this and other test reactions [23]. Novel zeolites with previously unknown structural features frequently show unexpected catalytic behavior. On the other hand, these 'standard' catalytic reactions can be used to characterize the internal pore architecture of unknown zeolites [24].

In a similar way, reactant conversions usually increase with the concentration of active sites while in some reactions the selectivity can be deteriorated by the presence of a high concentration of Lewis acid sites [5].

To differentiate the catalytic behavior of zeolites we investigated a series of different structural types of zeolites. Medium pore zeolites are represented by ZSM-5 (3-D channel structure with 10-ring channels) and SSZ-35 (1-D structure with 10-ring channels and 18-ring cages [25]). Typical large pore zeolites studied are Mordenite (1-D structure), MCM-58 (isostructural with ITQ-4 and SSZ-42 with undulating 1-D 12-ring system with cages [26]), and zeolite Beta (3-D 12-ring channel system). MCM-68 (3-D 12–10–10-ring channel system [27]) and SSZ-33 (3-D 12–12–10-ring system [28]) are examples of zeolites combining large and medium pore channels. Our knowledge on the catalytic behavior of zeolites with different structural types can provide a deeper insight when studying zeolites with yet unknown structures. It was already predicted for the, at that time unknown, structures of IM-5 and SSZ-57 [24]. In this case, catalytic results were combined with adsorption studies using 2,2-dimethylbutane as a probe molecule [29].

Finding the relationship among zeolite channel architecture, zeolite acidity, and activity and selectivity in toluene disproportionation as well as toluene and *p*-xylene alkylation with isopropyl alcohol is the main objective of this investigation. This relationship is influenced by two types of factors: (i) those associated to parameters of catalytic reaction (reaction temperature, space velocity, concentration of reactants, and thermodynamic equilibrium), and (ii) those related to the properties of the catalysts used (crystal size, channel size, and dimensionality of the channel system, type and strength of acid sites and their density and coking). While factors ad (i) were maintained constant during all measurements, we tried to analyze in more detail variables ad (ii) thus, those depending on the zeolites themselves. These include Si/Al ratio, concentration of Brønsted and Lewis sites, and their density as well as crystal size, because those are factors that cannot be adjusted completely in the same way for all zeolites under study. On the other hand, detailed analysis of acidic properties of zeolites under study provides us with a nice opportunity to correlate the catalytic behavior of these zeolites and their structural features.

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 mechanism, but also the product selectivity for preferential xylene formation [5,30,31]. 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 such as *n*-propyl toluene requiring a particular channel arrangement [32,33]. As for the *p*-xylene alkylation, the product of the first alkylation step is always 1-isopropyl-2,5-dimethyl benzene and all other products can be formed via secondary reactions. The details of their channel systems are provided in Table 1. In addition, this contribution evidences the importance of 18-ring cages in the 1-D 10-ring channel system of zeolite SSZ-35. This zeolite exhibits higher reaction rates than those for other three-dimensional 10-ring or even large-pore zeolites. SSZ-35 has a system of 1-D 10-ring channels that periodically open into wide, shallow cavities that are circumscribed by an 18-ring (Fig. 1) [25]. Only a few zeolites with such interesting structures have been described up-to-date in the literature [34], but the effect of their cages on the catalytic behavior has not yet been reported.

Table 1
Structural features of zeolites under study. Reference samples are marked with asterisks.

Zeolite	IZA code	Channel dimensionality	Channel entrances	Channel diameter (nm)
MOR*	MOR	2-D	12–8	0.65 × 0.70 0.26 × 0.57
BEA*	BEA	3-D	12–12–12	0.66 × 0.76 0.56 × 0.56
ZSM-5*	MFI	3-D	10–10–10	0.53 × 0.56 0.51 × 0.55
MCM-58	IFR	1-D	12	0.62 × 0.72
MCM-68	MSE	3-D	12–10–10	0.64 × 0.68 0.52 × 0.58 0.52 × 0.52
SSZ-33	CON	3-D	12–12–10	0.64 × 0.70 0.70 × 0.59 0.51 × 0.45
SSZ-35	STF	1-D	10	0.54 × 0.57

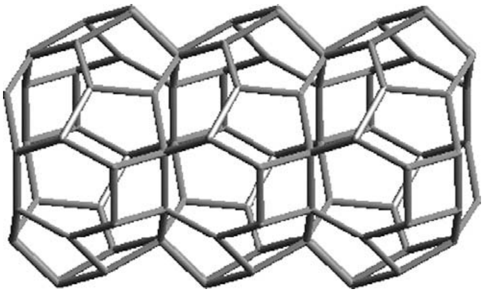

Fig. 1. View of 3 STF cages that stack to form the 1-dimensional pore in SSZ-35.

2. Experimental

2.1. Catalysts under study

Synthesis, properties and characterization of all zeolites under study were already reported, e.g. SSZ-33 and SSZ-35 [35,36], Beta and Mordenite [37], and MCM-58 and MCM-68 [38]. As an essential interest has been paid here to SSZ-35, its synthesis is briefly discussed. The SSZ-35 zeolite was prepared according to Ref. [39]. The synthesis of SSZ-35 itself was carried out in a 4-l reactor containing a Hastelloy C liner. Into the liner 0.45 mol of the SDA in 727 g of water (plus additional 950 g) was introduced. Then 300 g of 1 M KOH solution was added. Reheis F2000 (hydrated aluminum hydroxide containing 50–53 wt% Al_2O_3) was used as a source of aluminum. 7.31 g (37 mmol) of it was added to the reaction mixture and finally 185 g of Cab–O–Sil M5 (97% SiO_2, Cabot) was introduced to give 3 mol of SiO_2. The reaction was seeded at the 0.9 wt% level. The resultant mixture was heated to 160 °C (15 °C/min ramp up), and stirred at 150 rpm for 2.5 days. The synthesized SSZ-35