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Tailoring mesoscopically structured H-ZSM5 zeolites for toluene methylation

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ABSTRACT

Mesoscopically structured zeolites based on H-ZSM5 were designed and synthesized as highly active and shape selective catalysts for methylation of toluene by tuning diffusion and acid site concentration of the catalysts. This was achieved by combining desilication, subsequent dealumination and chemical deposition of a mesoporous SiO_2 overlayer of several nanometer thickness. The decreasing effective diffusion length in zeolite crystals achieved by desilication and dealumination increased the turnover rate of toluene by favoring activation of methanol and facilitating desorption of the produced xylenes, albeit with some loss in p-xylene selectivity. The presence of the SiO_2 overlayer increased the p-xylene selectivity by enhancing the tortuosity of the zeolite, randomly blocking pore openings at the surface, and increasing the effective diffusion path length. The final material combines the higher catalyst utilization with enhanced selectivity leading to rates comparable to the parent zeolite, but at significantly higher selectivity.

1. Introduction

The reaction of toluene with methanol to xylenes has great potential to become an important process in the chemical industry [1]. Among the three xylene isomers, p-xylene has the highest demand as a key intermediate for the production of terephthalate, which itself is an intermediate for polyester synthesis [2]. Methylation of toluene on commercially available medium pore zeolites, however, often yields thermodynamic mixtures of the xylene isomers [3–5] (i.e., ortho:meta:para xylene ratio of ~22:53:25 at 650 K [6]). As the xylene isomers have similar boiling points, energy intensive processes, such as adsorption or fractional crystallization, are required for separation [1,2].

The para-selectivity with H-ZSM5 has been reported to be enhanced by increasing the zeolite crystal size [7–9], by impregnating with phosphorous or boron compounds [4,8,10,11], and by chemical vapor (CVD) [12] or liquid deposition (CLD) [13,14] of tetraethyl orthosilicate (TEOS). In particular, TEOS deposition on the zeolite particle surface is an attractive method to increase the shape selectivity by partially blocking the pore openings as well as by reducing the concentration of Brønsted acid sites in pore mouth region [3,12,14]. The modification decreases the diffusivity of o- and m-xylene, while it increases for p-xylene [15]. On the other hand, the desilication and subsequent dealumination of H-ZSM5 shorten the diffusion path length and increase the transport rates of all aromatic molecules [16,17], leading to enhanced activity [18–20], albeit with lower shape selectivity compared to the parent material [20].

In this work, the strategy to synthesize small crystal zeolites with a mesoporous SiO_2 overlayer for efficient catalyst utilization and high shape selectivity is reported. The synthesis of materials structured on a meso-scale level is described, together with the characterization of intermediate and final materials, and the investigation of their catalytic impact on the toluene methylation kinetics.

2. Experimental

2.1. Materials

Zeolite H-ZSM5 (Si/Al = 36; Süd-Chemie) was used as parent material, and five different hierarchical samples were prepared by desilication (DS), subsequent dealumination (DS–DA) and by surface modification (SM) by CLD of TEOS, as shown in Scheme 1.

The desilicated DS sample was prepared by heating the parent H-ZSM5 in a 0.2 M NaOH (>98%, Sigma–Aldrich) solution (30 cm^3 per gram of zeolite) at 340 K under stirring for 0.75 h [21]. The solution was transferred into vials, and the solid phase was centrifuged at

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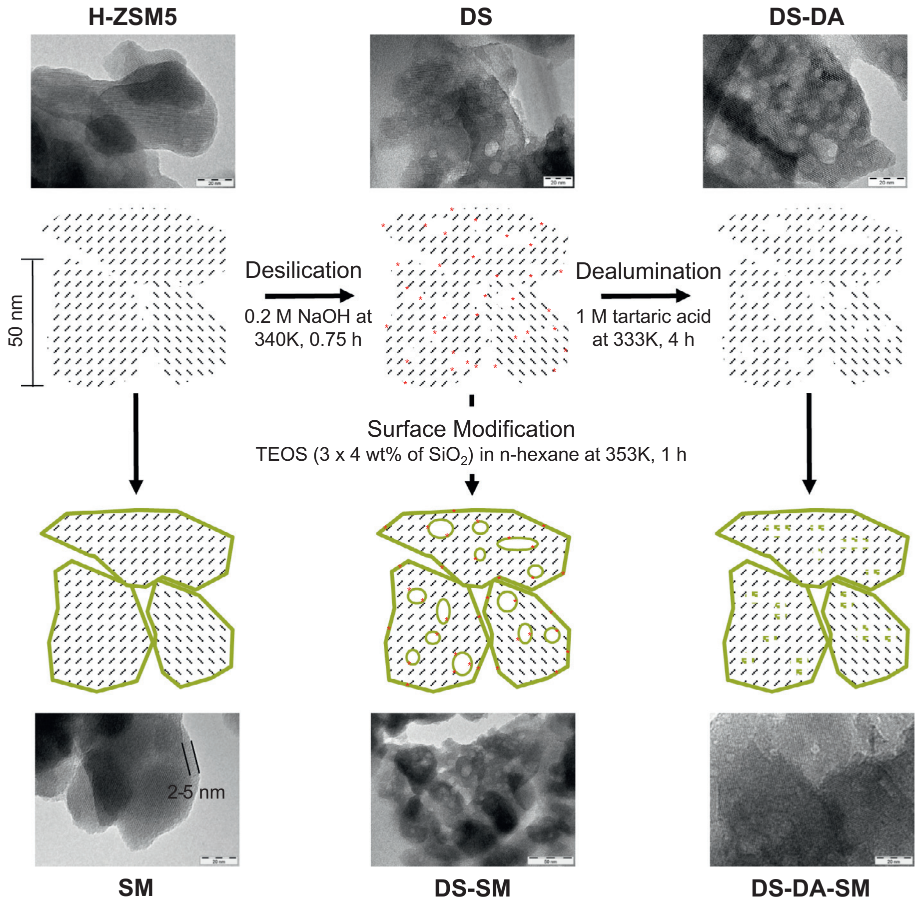

Scheme 1. Schematic representation and TEM images of the hierarchical samples prepared from the parent H-ZSM5 zeolite. DS = desilicated H-ZSM5, DS–DA = dealuminated DS sample, SM = surface modified sample by chemical liquid deposition of tetraethyl orthosilicate (TEOS). *Indicates the location of extra-framework Al species (EFAl).

4000 rpm for ~0.5 h and washed with deionized water. The washing procedure was repeated three times. The sodium form of the DS zeolite was exchanged into the ammonium form in 0.2 M NH_4Cl (>99.5%, Sigma–Aldrich) solution (30 cm^3 per gram of zeolite) at 353 K under stirring for 6 h. The solid was separated and the ion exchange with fresh 0.2 M NH_4Cl solution was repeated three times. After the third ion exchange, the zeolites were separated by centrifugation, washed with deionized water and dried (at 353 K) before the sample was treated in a synthetic air (flowing at 1.7 $cm^3\ s^{-1}$; 20.5% O_2 in N_2, Westfalen) at 823 K (heating rate of 0.05 K s^{-1}) for 10 h to obtain the Brønsted acidic form of the zeolite.

The desilicated and dealuminated (DS-DA) sample was prepared from the DS sample in a 1 M 2,3-dihydroxybutanedioic acid (L-tartaric acid; >99.5%, Sigma–Aldrich) solution (20 cm^3 per gram of zeolite) at 333 K under stirring for 4 h [22]. This solution was separated, washed, and dried as described above, before it was calcined in synthetic air (flowing at 1.7 $cm^3\ s^{-1}$) at 823 K (0.05 K s^{-1}) for 10 h.

The surface modified SM samples were prepared by heating the parent H-ZSM5, the DS or the DS–DA sample in hexane (25 cm^3 per gram of zeolite; 97%, Sigma–Aldrich) with TEOS (4 wt% SiO_2 per gram of zeolite; >99.0%, Sigma–Aldrich) at 353 K under stirring for 1 h [13]. Hexane was removed with a rotary evaporator under vacuum, and the materials were dried at 353 K, before the treatment in a synthetic air (flowing at 1.7 $cm^3\ s^{-1}$) at 353 K (0.083 K s^{-1}) for 2 h, 453 K (0.033 K s^{-1}) for 3 h, and finally 823 K (0.033 K s^{-1}) for 5 h. This procedure was repeated three times for all samples (i.e., H-ZSM5, DS, and DS–DA) to obtain the final material (total deposition amount of 12 wt% of SiO_2).

2.2. Catalyst characterization

The elemental composition and the crystal size distribution of the materials were determined by atomic absorption spectroscopy (AAS) using Unicam M Series Flame-AAS equipped with an FS 95 auto-sampler and a GF 95 graphite furnace and by dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS system, respectively. The powder X-ray diffraction (XRD; Philips X'Pert Pro system, $\lambda_{CuK\alpha}$ = 0.154056 nm, 40 kV/40 mA) patterns were recorded between 2θ angles of 5–70° (step size of 0.017° and a scan speed of 0.3 s per step). The signals between ~5–10° and 22–25° after background correction were integrated and compared to the parent H-ZSM5 to estimate the relative crystallinity of the hierarchical samples (see Table S1). The TEM images were taken by a Hitachi H-7100 with a maximum acceleration of 120 kV after cutting through the cross section of the sample.

The N_2 physisorption was carried out at 77 K on a PMI automated sorptometer after outgassing the samples under vacuum at 523 K for 2 h. The BET isotherm [23] was used to evaluate the apparent specific surface area over a relative pressure range from 0.01 to 0.1 p/p_o. The micro- and meso-pore volumes were evaluated by using the α_s comparative plot [24] with non-porous hydroxylated silica [25] as the reference adsorbent. The macropore volume was calculated by subtracting micro- and meso-pore volumes from the total pore volume determined at p/p_o = 0.95. The pore size distribution of the zeolites was evaluated by the DFT method (cylindrical pore, NLDFT equilibrium model).

Infrared (IR) spectroscopy (Thermo Nicolet 5700 FT-IR spectrometer, resolution 4 cm^{-1}) with pyridine (99.8%, Sigma–Aldrich)