



## Post-synthetic improvement of H-ZSM-22 zeolites for the methanol-to-olefin conversion



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### ABSTRACT

Microporous ZSM-22 zeolites (structure type TON) were modified by treatments with different alkaline solutions for introducing mesopores. This surprisingly affected the nature and the density of both SiOH groups and Brønsted acid sites significantly, while the Brønsted acid strength was maintained. The catalyst lifetime in the methanol-to-olefin (MTO) conversion could be enhanced by a factor of up to 2 for an optimum Brønsted acid site density of 0.34 mmol/g, which was also accompanied by the highest propene selectivity of 48%. The product distributions of the parent microporous and the modified mesoporous ZSM-22 catalysts were very similar. This indicates that the shape selectivity of the modified ZSM-22 zeolites in the MTO conversion is mainly determined by the 10-ring pore system and not affected by introduced mesopores. Therefore, it can be excluded that catalysis near the pore mouths plays a significant role in the MTO conversion on ZSM-22 zeolites.

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## 1. Introduction

In the past years, the introduction of mesopores into zeolite catalysts by desilication gained a rising attention, e.g., for improving the activity of ZSM-5 zeolites applied as catalysts in the methanol-to-olefin conversion (MTO) [1–3]. Like ZSM-5 zeolites (structure type MFI) with crossing 10-ring pores (pore diameters of 0.51 nm × 0.55 nm and 0.53 nm × 0.56 nm), also ZSM-22 zeolites (structure type TON), having unidimensional 10-ring pores (pore diameter of 0.46 nm × 0.57 nm) [4], are interesting catalysts for the MTO conversion [5,6]. Until now, however, the rapid deactivation of ZSM-22 zeolites, probably caused by a rapid blocking of the unidimensional pore system due to coke formation, is a strong limitation for their application in the MTO conversion. The introduction of mesopores could be, therefore, a promising modification procedure, which, on the other hand, also may influence the catalyst acidity and product selectivity [7] and could lead to improvements as were demonstrated for comparatively unidimensional ZSM-12 catalysts in isomerization reactions [8]. The aim of the present work was the development of hierarchical ZSM-22 zeolites

containing mesopores and, for the first time, their application as MTO catalysts. By this way, also the role of heterogeneous catalysis at Brønsted acid sites on the external surface and near the pore mouth, as discussed for ZSM-22 and ZSM-23 zeolites, could be clarified [9].

## 2. Experimental

### 2.1. Sample preparation

The parent ZSM-22 zeolite P0 was synthesized in a dynamically rotating autoclave according to literature [10] and NH<sub>4</sub>-exchanged. For the desilication procedure, the unexchanged parent zeolite P0 was dissolved (30 cm<sup>3</sup>/g) in aqueous solutions of 0.4 M NaOH (sample P1), 0.4 M KOH (sample P2), or 0.8 M KOH (sample P3) at 358 K for 1 h. Subsequently, the desilicated materials were stirred in an aqueous solution of 0.1 M HCl (100 cm<sup>3</sup>/g) at 338 K for 6 h and, subsequently, washed two times with demineralized water. All catalysts were in their acidic form.

### 2.2. Characterization methods

X-Ray diffraction was conducted on a Bruker D8 diffractometer with CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) in a  $2\theta$  range of 5–50° and with

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a scan rate of 6.0°/min. The Chemical composition of the catalysts was determined by an ICP-OES instrument Varian VISTA-MPX. Physisorption of N<sub>2</sub> was conducted at 77 K on a Quantachrome Autosorb 3B instrument. Before the measurement, the samples were evacuated for 16 h at 623 K. <sup>1</sup>H and <sup>27</sup>Al MAS NMR measurements were performed with samples in the dehydrated and hydrated state on a Bruker Avance III 400WB spectrometer at resonance frequencies of 400.1 and 104.3 MHz, upon  $\pi/2$  and  $\pi/6$  single pulse excitation, repetition times of 20 s and 0.5 s, respectively, and with a sample spinning frequency of 8 kHz (MAS). The dehydration was carried out at 673 K in vacuum (pressure below 10<sup>-2</sup> Pa) for 12 h. For quantitative <sup>1</sup>H MAS NMR measurements, a dehydrated zeolite H,Na-Y (ammonium exchange degree of 35%) was used as an external intensity standard. Dehydrated samples were filled into the MAS NMR rotors inside a glove box purged with dry N<sub>2</sub> gas. Some of the samples were loaded with 70 mbar acetonitrile-*d*<sub>3</sub> (99.9% deuterated, ACROS) by using a vacuum line and, subsequently, evacuated at 293 K for 12 h. Other samples were loaded with 100 mbar ammonia (Westfalen) for 10 min by using a vacuum line and subsequently evacuated at 453 K for 2 h in order to remove physisorbed ammonia molecules. The MAS NMR spectra were evaluated using the Bruker software WINNMR and WINFIT.

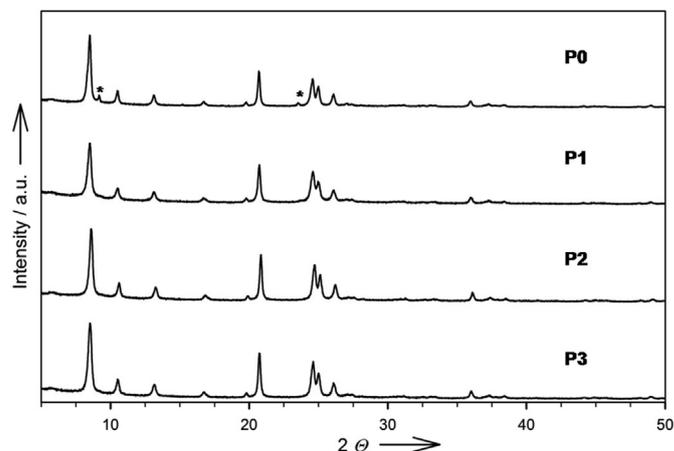
The catalytic conversion of methanol was investigated at atmospheric pressure in a fixed-bed glass reactor (inner diameter 5 mm) with 0.2 g catalysts and a sieve fraction of 0.25–0.6 mm. Prior to the catalytic methanol conversion, the catalysts were activated under flowing nitrogen gas at 723 K for 4 h. The reactant methanol was introduced by loading nitrogen gas ( $p_{\text{MeOH}} = 3.2$  kPa) inside a saturator, corresponding to a weight hourly space velocity of  $\text{WHSV} = 0.5 \text{ h}^{-1}$ . The reaction products were analyzed by on-line gas chromatography on a HP5890/II gas chromatograph equipped with a Poraplot Q column (50 m, Agilent). Dimethyl ether (DME) in the product distribution was considered as unconverted methanol.

### 3. Results and discussion

#### 3.1. Effect of desilication and acid treatment on the morphology, framework composition, and acidity

The yields of solid materials (catalysts P1 to P3) obtained after the modification and the parameters describing their morphological properties are given in Table 1. The yields of the modified ZSM-22 zeolites are decreasing upon applying a stronger desilication step, while the bulk  $n_{\text{Si}}/n_{\text{Al}}$  ratio of these materials slightly increased from 30 to 34 (see Table 1, column 3).

X-ray diffraction patterns and SEM pictures of the catalysts are given in Figs. 1 and 2, respectively. The observed reflexes verified the pure ZSM-22 structure of the mesoporous catalysts P1 to P3, while in the patterns of the parent catalyst P0 also weak reflexes of a ZSM-5 phase occur, which disappear upon modification. The crystallinity of the samples relative to the parent material was largely maintained (>92% relative crystallinity). This confirms a high resistance against desilication, as already published for ZSM-



**Fig. 1.** XRD powder patterns of parent (P0) and desilicated ZSM-22 zeolites (P1 to P3). Small reflexes (marked by asterisks\*) indicate the presence of ZSM-5 phases, which occur exclusively for the parent ZSM-22 zeolite (P0).

22 [7] and the similar unidimensional ZSM-12 [8]. The ZSM-22 crystals are agglomerated, needle-like rods of less than 1  $\mu\text{m}$  length, and no visible changes appear upon desilication and acid treatment (Fig. 2).

The N<sub>2</sub> physisorption experiments indicated a growing BET surface area and pore volume for the mesoporous ZSM-22 catalysts P1 to P3 in comparison to the parent material P0 (see Table 1). Treatment with KOH is introducing more mesopore volume into the ZSM-22 zeolite than treatment with NaOH, which is in contrast for ZSM-5 zeolites treated under same conditions [11]. The <sup>27</sup>Al MAS NMR spectra of the ZSM-22 catalysts in Fig. S1 of the Supplementary material indicate that only negligible contents of octahedrally coordinated extra-framework aluminum (<sup>27</sup>Al MAS NMR signals at 0.5 ppm) exist in the samples P0 to P3. The dominating signals at 55.5 ppm are due to tetrahedrally coordinated framework aluminum, responsible for the formation of Brønsted acidic Si(OH)Al groups [12]. The different <sup>1</sup>H MAS NMR signals (head of Table 2) in the spectra of Fig. 3 were assigned according to literature [13,14]. Their quantitative evaluation gave the hydroxyl densities (in mmol/g) summarized in columns 2 to 5.

The hydroxyl densities in Table 2 indicated that the mesoporous ZSM-22 samples P1 to P3 have a significant smaller content of disturbed Si(OH)Al groups (<sup>1</sup>H MAS NMR signals at 6.0 ppm) than the parent zeolite P0. This decrease could be caused by removing strained framework aluminum sites as reported for ZSM-5 zeolites [15]. For the sample P1, the increase of the common Si(OH)Al groups (<sup>1</sup>H MAS NMR signal at 4.2 ppm) may be due to the dissolution of siliceous framework contents and also by the reinsertion of aluminum during the HCl treatment [7]. The increase of the <sup>1</sup>H MAS NMR signals at 1.8 ppm hints at an increasing number of defect SiOH groups as a result of the desilication.

**Table 1**

Yields of the ZSM-22 samples after the modification and their morphological properties.

Catalyst	Yield (wt%)	$n_{\text{Si}}/n_{\text{Al}}$ ratio <sup>a</sup>	BET surface (m <sup>2</sup> g <sup>-1</sup> )	Pore volume <sup>b</sup> (μg <sup>-1</sup> )	Mesopore volume <sup>c</sup> (μg <sup>-1</sup> )
P0	—	30	209	132	46
P1	74	34	284	267	224
P2	65	34	255	343	278
P3	42	34	267	418	362

<sup>a</sup> Determined via ICP-OES.

<sup>b</sup> Determined at  $p/p_0 = 0.99$ .

<sup>c</sup> Pore volume minus micropore volume via t-plot method.

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