

Mesoporous ZSM-5 zeolites prepared by desilication as catalysts for synthesis of dimethyl ether

M. Rutkowska*, D. Macina, L. Chmielarz, N. Mirocha-Kubieñ
Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland

*corresponding author: rutkowsm@chemia.uj.edu.pl

Introduction

Desilication by alkaline treatment is an effective method to generate mesopores in the MFI framework. The development of mesopores in ZSM-5 zeolite via desilication should improve the accessibility of active sites and facilitate the transport of reactants and products within the zeolite matrix. We expect that such modification will be crucial for improvement of catalytic activity, especially in case of reactions in which bulky molecules take part [1].

Dimethyl ether (DME) synthesis from methanol is acid-catalyzed, exothermic reaction, which is carried out commercially in the temperature range of 180-400°C and at pressures up to 18 bars [2]. Catalysts, typically used for methanol dehydration, are solid acidic materials, such as γ -Al₂O₃ or zeolites. The surface acidity of the catalyst is a very important parameter which determines the selectivity of the process. Catalysts with strong acid sites produce light olefins and promote coke formation, while catalysts with weak acid sites convert methanol mostly to DME.

Materials and Methods

The catalysts were prepared using commercial H-form of ZSM-5 (Si/Al \approx 17) supplied by Eka Chemicals. In each synthesis (according to recipe described in [3]), 150 mL of 0.2 M NaOH (Chempur) per 2 g of zeolite was used. The resulting slurry was stirred under reflux at 358 K for 1, 2 or 4 h, yielding micro-mesoporous materials denoted as ZSM-5/*x*h, where *x* stands for duration of alkaline treatment. The obtained samples were modified with Fe and Cu and physicochemically characterized (N₂-sorption, XRD, IR-DRIFT, UV-vis-DRS).

Results and Discussion

The obtained materials were characterized by low temperature N₂ sorption (using 3Flex v1.00, Micromeritics). The textural parameters of ZSM-5 and desilicated samples (ZSM-5/1h, ZSM-5/2h and ZSM-5/4h) are given in Table 1. After desilication the BET and external surface areas, as well as meso+macropore volumes increased. It proves the successful

Table 1. Textural properties of the samples determined from N₂-sorption measurements

Sample code	S _{BET} /m ² ·g ⁻¹	Micropore area /m ² ·g ⁻¹	External surface area /m ² ·g ⁻¹	Micropore volume /cm ³ ·g ⁻¹	Meso+macropore volume /cm ³ ·g ⁻¹
ZSM-5	443	254	189	0.100	0.128
ZSM-5/1h	503	231	272	0.096	0.383
ZSM-5/2h	583	218	365	0.091	0.660
ZSM-5/4h	452	153	299	0.064	0.601

generation of mesoporosity in the samples. Alkaline treatment of ZSM-5 for 2 hours generated optimal textural parameters. Extended duration of desilication process led to decrease in textural parameters what can be connected with too invasive structure modification (too far-conducted zeolite matrix destruction).

In our studies modified ZSM-5 zeolites were tested as catalysts for the synthesis of DME from methanol (using gas chromatograph SRI 8610C). The best catalytic results were obtained for the desilicated samples modified with Fe (FeZSM-5/2h and FeZSM-5/4h). These materials are characterized by a high methanol conversion, which reached about 90% at 250°C and a very high selectivity to DME even at higher temperatures. Due to the relatively high mesoporosity of these materials the transport of the reagents through the catalyst bed is facilitated, which allows significantly decrease the coke formation and extend the operating time of catalyst. The other catalysts were also active in this process, but methanol conversion as well as selectivity to DME were lower in comparison to FeZSM-5/2h and FeZSM-5/4h. Results obtained for the iron-modified samples are shown in Figure 1.

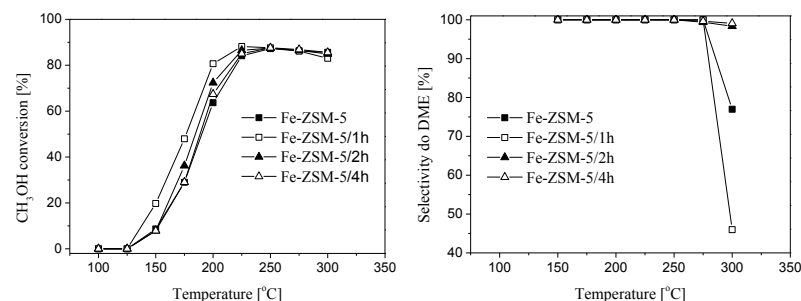


Figure 1. Results of CH₃OH conversion and selectivity to DME for the samples modified with Fe.

Significance

Two series (exchanged with Fe and Cu) of alkaline modified ZSM-5 zeolite were tested in the process of methanol conversion to DME. Especially, the iron modified samples were found to be very active and selective catalysts in the examined process.

References

1. Groen, J.C.; Moulijn, J.A.; Pérez-Ramírez, J. *Journal of Materials Chemistry* **2006**, 16, 2121
2. Moradi, G. R.; Yaripour, F.; Vale-Sheyda, P. *Fuel Processing Technology* **2010**, 91, 461
3. Melián-Cabrera, I.; Espinosa, S.; Mentrut, C.; Kapteijn, F.; Moulijn, J.A. *Catalysis Communications* **2006**, 7, 100

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