

POST-SYNTHESIS CREATION OF MESOPORES IN MFI, FAU AND BEA ZEOLITES: INFLUENCE ON ADSORPTIVE AND CATALYTIC BEHAVIOR

Vladislav Rac¹, Vesna Rakić¹, Dušan Stošić^{2,3}, Ljiljana Damjanović⁴, Aline Auroux²

¹Faculty of Agriculture, University of Belgrade, Nemanjina 6 Zemun, Belgrade, Serbia

²Institut de Recherches sur la Catalyse et l'Environnement de Lyon, 69626 Villeurbanne Cedex, France.

³Laboratoire Catalyse & Spectrochimie, UMR 6506, ENSICAEN, 6, boul. Maréchal Juin, 14050 Caen, France

⁴Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12-16, Belgrade, Serbia

E-mail: vrac@ffh.bg.ac.rs

ABSTRACT

The influence of mesopore formation, via alkali induced desilication process, on the adsorptive and catalytic properties of ZSM-5, USY and Beta zeolites was investigated. The investigated zeolites were characterized using low temperature N₂ adsorption, X ray diffraction, microcalorimetry of NH₃ adsorption, and microcalorimetry of 2-phenylethylamine adsorption. The influence of mesopore formation on the adsorptive capabilities of ZSM-5, USY and Beta zeolites was investigated using phenol, salicylic acid, sodium diclofenac and atenolol as adsorbates. Catalytic properties of the investigated zeolites were evaluated in fructose dehydration reaction.

Keywords: hierarchical zeolites, adsorption, fructose dehydration, acidity.

INTRODUCTION

Hierarchical zeolites, containing at least two levels of porosity (usually micropores and mesopores), have been in the spotlight of the scientific attention during the last decade. It has been shown that the existence of mesoporosity in zeolitic structures results in significant improvements of their adsorptive and catalytic properties [1]. In this work, a post-synthesis approach [2] using alkaline leaching was used for mesopore introduction in ZSM-5, USY and Beta zeolites. The adsorptive capabilities of thus obtained hierarchical zeolites were tested using adsorbate molecules belonging to an increasingly interesting group of pharmaceutically active substances, which are now considered to be water and soil pollutants of emerging concern [3]. Also, the investigated zeolitic samples were tested for fructose dehydration, an acid catalyzed reaction, which is a promising route for the production of 5-hydroxymethylfurfural (HMF), an important building block for the production of fuels and fine chemicals [4].

EXPERIMENTAL

Mesopore formation in zeolites ZSM-5 (Zeolyst, SiO₂/Al₂O₃ = 23, 50 and 80), USY (Zeolyst, SiO₂/Al₂O₃ = 60) and Beta (Zeolyst, SiO₂/Al₂O₃ = 25) was performed through silicone extraction by sodium hydroxide (0.2 M), using procedure reported in reference [5]. Textural properties of the samples were determined by N₂ adsorption at 78 K on a Micromeritics 2010 apparatus, after heating of the samples at 400 °C for 4 hours. The t-plot method was used for discrimination between micropores from mesopores. XRD patterns were recorded on a Bruker

D5005 (Cu K α , 2° to 80° (2 θ), 0.02° s⁻¹). Adsorption of salicylic acid, diclofenac-Na, atenolol and phenol was studied in batch experiments: typically, 50 mg of zeolite was added to an adsorbate solution (0.0002 – 0.002 M) and the suspension was stirred in a sealed flask during 1 h at 30 °C. The 1h contact time was determined in separate kinetic experiments as long enough for adsorption to reach equilibrium. Liquid phase was separated by centrifugation (Minispin, Eppendorf, 13400 rpm, during 30 minutes). Equilibrium adsorbate concentrations were determined using Shimadzu UV-1650PC spectrophotometer and the adsorbed amounts were calculated from the difference between the initial and equilibrium concentrations of the adsorbate. Fructose dehydration was performed at 130 °C, in a 100 ml stainless still autoclave. In a typical procedure, 600 mg of fructose was dissolved in 60 ml of water and then 80 mg of solid catalyst was added. At 1 h intervals samples were withdrawn from the reaction mixtures and concentrations of fructose and HMF were determined by collecting ¹H NMR spectra, using liquid NMR technique (Bruker AVANCE 250).

RESULTS AND DISCUSSION

The desilication treatment resulted in mesopore formation in all investigated zeolites. The largest mesoporous surface was developed in USY zeolite, but this was accompanied by a significant degree of destruction of microporous structure [6]. Among the ZSM-5 samples, the largest relative increase of mesoporous surface was obtained for the sample having SiO₂/Al₂O₃=50 [5].

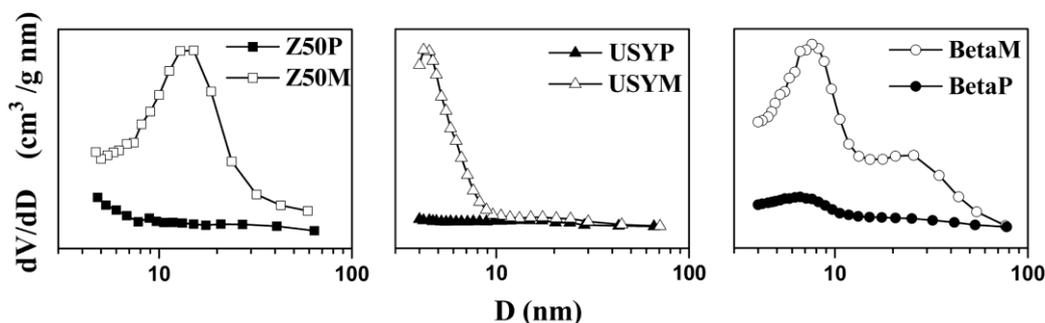


Figure 1. Pore size distributions of ZSM-5 (SiO₂/Al₂O₃=50), USY and Beta zeolites.

Mesopore formation in the investigated zeolites resulted in significant diminishing of the acid site strength in zeolites USY and ZSM-5 (SiO₂/Al₂O₃=23), partial decrease of acid site strength in zeolite Beta, while the acidities of ZSM-5 (SiO₂/Al₂O₃=50 and SiO₂/Al₂O₃=80) were only slightly affected by the modification [5,6]. The diffractograms of the mesoporous samples show that their structures were preserved after the alkaline treatment but, in all cases, also indicate decreased crystallinities, compared to the parent analogues (91%, 76% and 84% for ZSM-5 with SiO₂/Al₂O₃ = 23, 50 and 80, respectively; 68% for USY; 89% for Beta). Relative crystallinities were estimated from diffraction peaks intensities, taking the parent zeolite's crystallinity to be 100% [2].

Adsorption investigations showed that, for molecules with dimensions similar to or larger than zeolitic micropore diameters (sodium diclofenac and atenolol), mesopore introduction can result in significantly increased adsorption capacities. These results indicate that mesoporous zeolites can widen the domain of use of zeolites as adsorbents. However, adsorption capacities

for all investigated adsorbate molecules were also proven to be strongly dependent on the acidity of the zeolites. Our results show that decreased acidity, which can appear as a result of the mesopore formation process, can result in diminished adsorptive capabilities of a zeolite, when basic molecules are used as adsorbates. Therefore, further fine tunings of the applied mesopore formation process are needed in order to achieve control over not only textural, but also acidic properties of hierarchical zeolites.

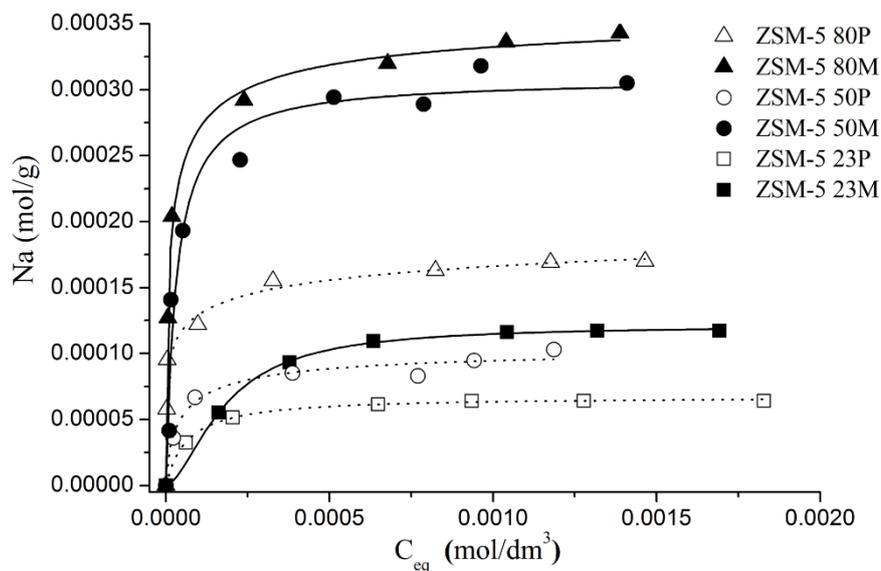


Figure 2. Isotherms of atenolol adsorption on parent and mesoporous ZSM-5 zeolites with different $\text{SiO}_2/\text{Al}_2\text{O}_3$.

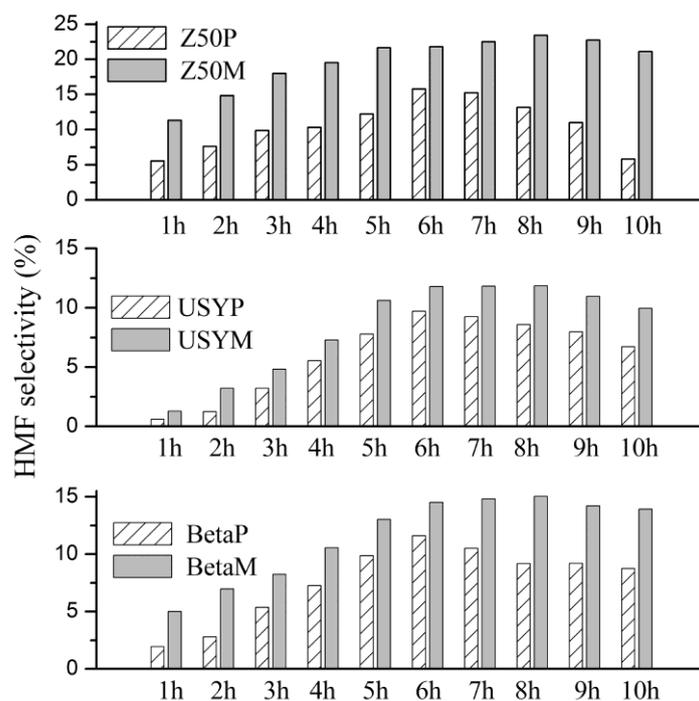


Figure 3. Selectivities towards HMF in fructose dehydration for parent and mesoporous ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3=50$), USY and Beta zeolites.

In fructose dehydration reaction, increased selectivity towards formation of the desired product, 5-hydroxymethylfurfural, was detected for mesopore containing zeolites, compared to the microporous ones. This selectivity increase was measured for all investigated mesoporous samples, regardless of acidity changes caused by the modification [6]. Zeolites containing mesopores exhibited not only increased selectivities towards the desired product, but also extended durations of reaction periods with maximal selectivity, compared to their microporous analogues. These improvements in catalytic behavior can be attributed to facilitated diffusion of reactants and products which can lead to suppression of the unwanted side reactions. Furthermore, within the series of hierarchical samples, as well as within parent samples series (analyzed separately), significant influence of the strength of the acid sites was observed: the stronger the acid sites, the larger the selectivity. This is in accordance with already published results [7], which highlighted the importance of acid sites strength for HMF selectivity when microporous zeolites (MOR, ZSM-5, BEA) were concerned.

CONCLUSION

Introduction of mesopores into initially microporous zeolites ZSM-5, USY and Beta significantly altered their adsorptive and catalytic properties. Due to the existence of mesopore structure, modified zeolites exhibited larger capacities for the adsorption of substances whose molecular diameters are comparable to or larger than micropore framework openings. In the investigated catalytic reaction, fructose dehydration, mesoporous structure within the zeolites enabled larger selectivity towards the desired product, most probably via lowering the diffusional limitations of the solid material. However, both adsorptive and catalytic properties investigated in this work were also shown to be dependent on the acidity changes induced by the modification procedure. Hence, further efforts are necessary in order to ensure better control of the mesopore formation process itself and the final properties of the hierarchical zeolites obtained.

ACKNOWLEDGEMENTS

Serbian ministry of Education and Science (Project 172018) is acknowledged for financial support.

REFERENCES

- [1] M. S. Holm, E. Taarning, K. Egeblad, C. H. Christensen, *Catal. Today*, 2011, **168**, 3–16
- [2] D. Verboekend, G. Vile, J. Perez-Ramirez, *Cryst. Growth Des.*, 2012, **12**, 3123–3132.
- [3] S.K. Khetan, T.J. Collins, *Chem. Rev.*, 2007, **107**, 2319–2364.
- [4] J. Kruger, V. Choudhary, V. Nikolakis, D. Vlachos, *ACS Catal.*, 2013, **3** 1279-1291.
- [5] V. Rac, V. Rakić, Z. Miladinović, D. Stosić, A. Auroux, *Thermochim. Acta*, 2013, **567**, 73-78.
- [6] V. Rac, V. Rakić, D. Stošić, O. Otman, A. Auroux, *Micropor. Mesopor. Mater.*, 2014 **194**, 126–134.
- [7] V. Ordonsky, J. van der Schaaf, J. Schouten, T. Nijhuis, *J. Catal.*, 2012, **287**, 68–75.