

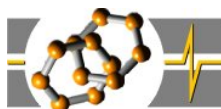


**The Faculty of Science and Informatics of the University of Szeged
Doctoral School of Environmental Sciences**

Preparation, physico-chemical and catalytic properties of MCM-22 type zeolite catalysts of hierarchical pore structure

Ph.D. Thesis

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Introduction and objectives

Because the mass transport of reactants and products is hindered in the micropores of zeolite catalysts, the conversion rate can be governed by the rate of diffusion. In fact, the diffusion rate limitation implies that only a fraction of the catalyst is involved in the reaction. The effectiveness of the catalyst can be enhanced either by accelerating the diffusion rate in the pores (e.g. by increasing the pore size) or by shortening the diffusional path in the micropores.

Zeolites are applied in numerous large-scale petrochemical processes (fluid catalytic cracking, hydrocracking, hydroisomerization, hydrodewaxing, alkylation, esterification, etc.) as heterogeneous catalysts, so apparently minor improvement of the catalytic process, such as application of a slightly more effective catalyst, can result in high ecological and economical benefit.

At the beginning of 1990's silica materials with ordered mesopores having pore diameter of 1.5-50 nm were discovered (e.g. MCM-41, SBA-15). The diffusion of molecules in these mesopores is faster than in the micropores of zeolites. However, incorporation of aluminum into the amorphous structure of the mesoporous silica materials results in the formation of weaker acid centers than the acid centers of zeolites. Sometimes the thermal and hydrothermal stability of the mesoporous silicates is also insufficient. Actually, the mesoporous silicates could not fulfill the expectations as regards their better catalytic properties in petrochemical reactions.

In order to develop more effective catalysts, synthesis, characterization, and investigation of catalytic behavior of zeolites with hierarchical pore system became a focal research topic in zeolite chemistry in the last decade. The hierarchical porous materials are expected to integrate the advantageous catalytic properties of zeolites (high thermal and hydrothermal stability, strong Lewis and Brønsted acid centers) with the favorable diffusional characteristics of meso and macropores. A possible approach of the problem is to synthesize microporous zeolite containing meso/macropores running across the zeolite crystallites. My work focused on the latter research topic.

Part of my research concerned the preparation of catalyst with micro and mesopores consisting of layered MCM-22 type zeolite and MCM-41 type mesoporous silica. Another aspect of my work was to obtain bifunctional zeolite catalyst with high selectivity to hydroisomerization taking advantage of the hierarchical pore structure.

A novel, two-step preparation method was developed applying first a delamination step on an MCM-22 precursor under alkaline condition, which step was followed by the hydrothermal synthesis of the MCM-41 component. The changes of the chemical and phase composition, structure, morphology, and textural properties of the MCM-22 zeolite were studied. Also, the effect of crystallite size of the MCM-22 precursor on the above changes and properties were examined.

Only few studies relate to the structural changes occurring during the formation of hierarchical pore system in zeolites, especially to the changes in the local environment of the framework aluminum. It is important to know how and in what extent the tetrahedral coordination of the aluminum atoms changes in the delaminated layers of MCM-22 during the applied treatments.

The activity in the disproportionation of toluene can inform us about the number of MCM-22 supercages, which cages were substantiated as active locations of the reaction. The conversion of a larger molecule, such as, 1,2,4-trimethylbenzene (1,2,4-TMB) provides information about the acid centers accessible on the outer surface of the catalysts, including the cup-shape pores on the surface of the MCM-22 crystallites.

Ni/H-form bifunctional catalysts were prepared and investigated in the hydroconversion of n-heptane, in order to learn about the influence of Ni concentration and the presence of mesopores on the catalytic activity and product selectivity.

The physico-chemical and catalytic properties of micro/mesoporous samples were compared with those of the parent MCM-22 zeolite, the delaminated MCM-22, and the aluminum-containing mesoporous MCM-41 silica.

Relationships were established between the pore structure and the other properties, such as, acidities, catalytic activity and selectivity.

The layer-structured MCM-22, first synthesized in 1990, was chosen as subject of my study because of the significant research interest in this zeolite. Relations between the specific channel system (channels with ten-membered ring openings, supercages with ten-membered ring entrances, surface cups with twelve-membered ring openings) and the catalytic properties were already thoroughly examined. The possibilities to prepare new types of aluminosilicates from the layered MCM-22 precursor also attracted much interest. The industrial application of MCM-22 is also significant. It is used as catalyst in the production of ethyl-benzene and cumene, the two major products made from benzene.

Preparation and catalytic application of a hierarchical material containing delaminated precursor of MCM-22 zeolite was published first by our research group in 2007.

Synthesis and experimental methods

Two different MCM-22 precursor materials were used. One of them consisted of small crystallites. It was prepared by hydrothermal synthesis in a stirred reactor (145 °C, 10 days) from water glass and aluminum sulphate using hexamethylene imine as structure directing template. The other precursor contained large crystallites and was made in a non-stirred (static) reactor among the same synthesis conditions the one above. In the first step of making catalyst, having hierarchical pore structure the individual layers of the template-containing MCM-22 precursor were separated, and in the next step an MCM-41 type mesoporous silica was synthesized in the presence of the delaminated product under hydrothermal conditions. In order to delaminate the precursor was refluxed in alkaline media with cetyltrimethylammonium bromide (CTMABr) at 80 °C. The swelled solid was washed with distilled water and treated in ultrasonic bath. Then, after addition of water glass and CTMABr to the delaminated solid, the mixture was hydrothermally treated (100 °C, 3 days). For comparison, zeolite MCM-22 and delaminated MCM-22 (dl-MCM-22) were also prepared by the heat treatment of the precursor and the delaminated precursor, respectively, at 540 °C. Besides the zeolites an aluminum-containing mesoporous MCM-41 sample was also prepared.

Structural changes were followed by X-ray powder diffraction (XRD). Chemical composition of the samples was determined by atomic absorption spectrophotometry (AAS). Morphological changes were studied by scanning electron microscopy (SEM). The specific surface area, pore size distribution, and the pore volume of the template-free catalysts were determined from the isotherms of nitrogen physisorption. The chemical environment of aluminum atoms were investigated by ^{27}Al -MAS-NMR spectroscopy.

The number, type and strength of acid centers (Brønsted, Lewis) was determined either by temperature-programmed ammonia desorption, using the NH_4^+ -forms of the zeolites (NH_3 -TPD). Fourier transform infrared spectroscopy (FT-IR) was also applied to examine the adsorption of pyridine on the H-form of the zeolites. In order to get information about the acid centers, out of the micropores the FT-IR was applied to study the adsorption of a molecule with kinetic diameter larger than the micropore size, such as, 2,4-dimethylquinoline.

Conversion of toluene and 1,2,4-TMB on H-form of zeolites were studied using a flow-through microreactor at atmospheric pressure, different space times, and 300 °C. Hydroconversion of n-heptane was investigated on Ni/H-form bifunctional catalysts in the

temperature range of 210-280 °C at 5 bar total pressure. Products were analyzed by on-line gas chromatography.

Theses

1. It was found that a composite material (dl-MCM-22/MCM-41) with hierarchical pore system can be obtained applying a two-step preparation method. In the first step the layered-structure MCM-22 precursor material was delaminated by treatment with tetrapropylammonium hydroxide and cetyltrimethylammonium bromide (CTMABr). In the second synthesis step mesoporous MCM-41 silica was synthesized by hydrothermal method in the presence of the delaminated MCM-22, additional silica source, and CTMABr.
2. It was pointed out that upon delamination most of the individual zeolitic layers of the MCM-22 precursor material remains intact and only a small fraction becomes amorphous during the swelling procedure. It was also found that the structure of our delaminated and calcined sample resembles rather to the MCM-56 type material, disordered in direction c , than to the ITQ-2, having a 'house-of-cards' structure. The MCM-56 structure was evidenced by XRD results. The XRD pattern showed that the long-range order in the crystallographic c direction decreased. The intensity of reflections, having Miller indices of $(hk0)$ hardly changed, whereas the (101) and (102) lines were broadened and decreased in intensity. The decreased specific surface area and micropore volume relative to those of the parent MCM-22 also support the structural assignment of the delaminated and calcined product to MCM-56.
3. It was shown that the delaminated zeolite MCM-22 contains a smaller number of supercages than the zeolite MCM-22. This conclusion was supported by the decreased rate of toluene disproportionation, known to proceed on the acid centers in the supercages of MCM-22. It was also shown, that partial desilication occurs as a result of treatment in alkaline media.
4. The extent of delamination strongly depends on the crystal size of the zeolite MCM-22 precursor. Due to fewer bonds between the individual layers of smaller crystals ($\sim 0.5 \times 0.5 \times 0.1 \mu\text{m}$) the delamination was more effective. It was also found that the presence of very small crystals, like those obtained by delamination, hinder the formation mesoporous MCM-41 in the synthesis mixture of the second preparation step.
5. It was found that a fraction of the framework aluminum in the delaminated MCM-22 and the composite material is three-coordinated. During alkaline delamination and in the

following hydrothermal treatment the tetrahedral coordination of the framework aluminum atoms become damaged, resulting in decreased Brønsted acidity.

6. It was shown that the trigonally coordinated framework Al atoms become tetrahedrally coordinated upon liquid-phase NH_4^+ ion exchange by taking up NH_4^+ ion into their coordination sphere. Thus, the Brønsted acidity of these samples is overestimated by temperature-programmed NH_3 desorption measurements (NH_3 -TPD). However, the Brønsted acidity of the H-form catalysts determined by FT-IR spectroscopic investigations of adsorbed basic molecules, such as pyridine and 2,4-dimethyl-quinoline, correlates well with the catalytic properties of the samples.
7. It was shown that in the disproportionation of 1,2,4-trimethylbenzene the composite catalyst was more active than the parent or the delaminated zeolite. It indicates that the presence of mesopores favors the transformation of larger molecules.
8. It was evidenced that the Ni/Brønsted acid site ratio in bifunctional catalysts significantly influences the hydroconversion of n-heptane in the range of 0.5-1.0. With increasing nickel content the activity and the rate of isomer formation is increasing, whereas the formation rate of cracking products becomes suppressed.
9. We pointed out that the heptane isomer selectivity of the composite catalyst (dl-MCM-22/MCM-41) relative to that of the zeolite MCM-22 is higher due to its lower diffusion resistance. The monobranched heptane isomers can leave the active catalyst particles through the mesopores before getting cracked.
10. It was found that Ni/Al-MCM-41 is not active in the hydroconversion of n-heptane. It becomes active at higher temperatures than the zeolite-containing catalysts, over 300 °C, and are active mainly in hydrogenolysis. It was proved that strong Brønsted acid centers like those in the micropores of zeolites can not be obtained by incorporating aluminum into mesoporous silica.
11. Our salient conclusion is that intersecting the zeolite channels by mesopores result in partially damaged zeolite active sites.

Application of results

The aim of my research work, focusing on the reduction of diffusion limitation in catalyst zeolite MCM-22, was primarily to gain knowledge about an interesting scientific topic. However, applying our new, two-step preparation method, utilizing relatively cheap templates (e.g. Pluronic type copolymer), more effective catalysts can be developed for the petrochemical industry.

Publications related to the thesis:

- 1. *Micro/mesoporous aluminosilicate composites from zeolite MCM-22 precursor***
M. Kollár, R.M. Mihályi, G. Pál-Borbély, J. Valyon
Microporous and Mesoporous Materials, 2007, 99, 37-46
IF₂₀₀₇: 2.210, *number of independent citations*: 9
- 2. *Activity and selectivity of zeolite MCM-22 catalysts in the disproportionation of toluene***
R.M. Mihályi, I. Kolev, V. Mavrodinova, C. Minchev, **M. Kollár**, J. Valyon
Reaction Kinetics and Catalysis Letters, 2007, 92, 345-354
IF₂₀₀₇: 0.584, *number of independent citations*: 2
- 3. *Comparative catalytic studies on alkylaromatics transformations over [Al]MCM-22 and boron-substituted [Al, B]MCM-22***
I. Kolev, V. Mavrodinova, R.M. Mihályi, **M. Kollár**
Microporous and Mesoporous Materials, 118, 2009, 258-266
IF₂₀₀₉: 2.652
- 4. *Silica and aluminosilicate catalysts of hierarchical porous structure***
M. Kollár, R.M. Mihályi, J. Valyon
Silica and Silicest in Modern Catalysis, ISBN: 978-81-7895-455-4 Editor I. Halasz,
2010, 171-186
- 5. *n-Heptane hydroconversion on bifunctional hierarchical catalyst derived from zeolite MCM-22***
M. Kollár, R.M. Mihályi, József Valyon
Studies in Surface Science and Catalysis, 175, 2010, 727-730
IF:-
- 6. *Acidic and catalytic properties of zeolite MCM-22 and its composite***
M. Kollár, R.M. Mihályi, S.D. Burton, J.H. Kwak, J. Szanyi
Proceedings of 10th Pannonian International Symposium on Catalysis, Eds.: M.
Derewinski, B. Sulikowski, A., Wegrzynowicz, ISBN: 978-83-929430-4-4, 2010, 183-191

7. *Transformations of alkyl aromatics over delaminated MCM-22 zeolites and their composites with mesoporous MCM-41 silicate*

M. Kollár, I. Kolev, R.M. Mihályi, V. Mavrodinova

Applied Catalysis A: General, 2011, 393, 59-70

IF₂₀₁₀: 3.383

Presentations and posters related to the thesis:

1. *Preparation and characterization of zeolite-containing micro- and mesoporous aluminosilicates*

M. Kollár, R.M. Mihályi, J. Valyon

1st International Workshop on in-situ study and development of processes involving nanoporous solids, La Grande Motte, France, 2006

2. *Preparation and Characterization of composites consist of nanocrystalline zeolites and mesoporous aluminosilicates*

M. Kollár, M.R. Mihályi, J. Valyon

12th International Conference of Chemistry, Csíkszereda-Miercurea Ciuc, Romania, 2006

3. *Preparation and characterization of micro/mesoporous composites from delaminated zeolite MCM-22 precursors having different crystallite size*

M. Kollár, M.R. Mihályi, J. Valyon

6th International Mesostructured Materials Symposium, Belgium, Namur, 2008,

4. *n-Heptane hydroconversion on bifunctional hierarchical catalyst derived from zeolite MCM-22*

M. Kollár, M.R. Mihályi, J. Valyon

10th International Symposium on the Scientific Bases for the Preparation of Heterogeneous Catalysts, Louvain-la-Neuve, Belgium, 2010

5. *1,2,4-Trimethylbenzene transformation over hierarchical catalyst assembled of delaminated zeolite MCM-22 precursor and mesoporous MCM-41 silicate*

M. Kollár, I. Kolev, R.M. Mihályi, V. Mavrodinova

16th International Zeolite Conference joint with the 7th International Mesoporous Materials Symposium, 2010

Other publications:

1. *Structural and acidic characteristics of X-ray amorphous and partially crystalline zeolite Beta*

M. Kollár, R.M. Mihályi, J. Valyon

Proceedings of the 8th Pannonian International Catalysis Symposium, Ed.: I. Pálinkó, ISBN: 963-06-0138-9, Hungarian Zeolite Association, Szeged, 2006, 190-195

2. *Structure, acidity and redox properties of MCM-22 ferrisilicate*

R.M. Mihályi, K. Lázár, M. Kollár, F. Lónyi, G. Pál-Borbély, Á. Szegedi

Microporous and Mesoporous Materials, 2008, 110, 51-63

IF₂₀₀₈: 2.555 number of independent citations: 1

3. *Toluene and 1,2,4-trimethylbenzene conversion on [Al]MCM-22 zeolite partially substituted by boron*

R.M. Mihályi, I. Kolev, M. Kollár, V. Mavrodinova, Ch. Minchev, T.I. Korányi

Studies in Surface Science and Catalysis, 174, 2008, 1215-1218

4. *Effect of the partial substitution of Al by B in MCM-22 zeolite on the selectivity and catalytic activity in toluene disproportionation*

M.R. Mihályi, I.N. Kolev, V.P. Mavrodinova, M. Kollár, T. Korányi, Ch.I. Minchev

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Materials, Eds.: K. Hadjiivanov, V. Valtchev, S. Mintova, G. Vayssilov, ISBN: 978-954-580-239-3, Heron Press, Sofia, Bulgaria, 2008, 363-371

5. *The mechanism of the Fischer–Tropsch reaction over supported cobalt catalysts*,
M. Kollár, A. De Stefanis, H.E. Solt, R.M. Mihályi, J. Valyon, A.A.G. Tomlinson
Journal of Molecular Catalysis A: Chemical, 2010, 333, 37-45
IF₂₀₁₀: 2.872

6. *The effect of mesopore formation on the acidity and catalytic behavior of zeolite ZSM-5*
M. Kollár, R.M. Mihályi, V. Kolev, V. Mavrodinova
Advanced Micro- and Mesoporous Materials -Book of Abstracts, Eds.: K. Hadjiivanov, V.
Valtchev, S. Mintova, G. Vaysilov, Heron Press, Sofia, Bulgaria, ISBN: 978-954-323-
558-2, 2010, 200-210

Sum impact factor (Σ_{IF}): 14.256

Other presentations and posters:

1. *Esterification of acetic acid with ethanol using zeolite membrane*
M. Kollár, M.R. Mihályi, A. Patis, V. Nikolakis
3rd International Workshop on in-situ study and development of processes involving
nanoporous solids, Alicante, Spain, 2007

2. *The Fischer-Tropsch Mechanism in Nanoporous Catalysts. In-situ Investigations*
M. Kollár, A. De Stefanis, H.E. Solt, R.M. Mihályi, J. Valyon, A.A.G. Tomlinson
1st International Conference on Nanoporous Materials in Energy and Environment,
Chania, Greece, 2008

3. *Effect of mesopore formation on the acidity and catalytic behavior of zeolite ZSM-5*
M. Kollár, M.R. Mihályi, J. Valyon
3rd International Symposium “Advanced Micro- and Mesoporous Materials”, Albena
resort, Bulgaria, 2009