

**SYNTHESIS AND STRUCTURAL STUDIES
OF MCM-41 AND SBA-15 TYPE
MESOPOROUS SILICATES**

Ph.D. Theses

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Introduction

For the development of modern civilization chemistry and the chemical industry is of utmost importance. Chemical science itself and the industry utilizing its results have indispensably contributed both to the improvement of living conditions and the increase of material prosperity. Although the chemical industry is responsible for the deterioration of the environment, at the same time through applying the latest results of chemistry research it is a major player in environmental protection.

Catalytic technologies constitute an important part in production of the chemical industry and, thus, they contribute to economical development to a large extent. The more and more rigorous environmental legislation requires the development and application of new “clean technologies” largely based on the heterogeneous catalysts. While heterogeneous catalytic processes have been used in petroleum chemistry for a long time, the synthesis of many fine chemicals or specialty compounds is performed in homogeneous catalytic processes taking place in the liquid phase. A large number of these processes were developed in the first half of the last century concentrating on productivity and neglecting the harmful environmental effects of the inorganic wastes or toxic by-products. Nowadays, the decomposition costs of these wastes also have to be taken account, and, of course, these are included in the price of the products. Recent technological development more and more turns toward the application of heterogeneous catalysts, since they offer easier separation from the product mixture, possible recycling and smaller amounts of waste material, thus, ultimately, cheaper products.

In the last decades, preparation of tailored catalyst having pores and channels with given sizes and structures has come into the limelight. In these pore structures the reactant molecules are constrained to assume conformations favourable for the reaction. The first family of catalysts with tailored pore structure was that of the zeolites. They found many applications in the petrochemical industry, and a large number of papers and patents proved their suitability for the synthesis of fine chemicals and specialty compounds. However, their relatively small pore openings (0.5-1.2 nm) limit their use, because larger molecules cannot enter into the structure and thus, the active centres are inaccessible. More recently, catalysis research was extended to develop materials with larger pore openings and wider channels. As a result a new, mesoporous silicate family

(M41S) was discovered with members having the MCM-41 structure. MCM-41 (and the other members of this family) has ordered pore system and (unlike zeolites) amorphous pore walls, thus, the pore openings as well as the quality and the quantity of heteroatoms can be widely varied. Right after the synthesis of MCM-41 research started on the applicability of various metal-containing MCM-41 as acidic and redox catalysts. Soon after the finding of MCM-41 a new mesoporous silicate with larger pore diameters but similar ordering, SBA-15 that is, was discovered.

For the synthesis of both molecular sieves surface-active organic material (template) is needed with the role of directing structure formation. The final step in the synthesis of mesoporous silicates is the removal of this organic template. The conventional template removal processes may injure the structure, therefore intensive research work has started to develop alternative template removal procedures.

Aims

In the Department of Applied and Environmental Chemistry of the University of Szeged, the synthesis, characterization and application of these two mesoporous silicate families is one of the research topics studied intensively.

The results of earlier studies proved the advantageous structural and catalytic properties of the samples treated with ozone at lower temperature in comparison with samples prepared by the conventional template removal process. In order to complement our knowledge concerning the template removal process we aimed to use two additional oxidants (NO_2 , N_2O) beside O_2 and O_3 and the reaction conditions of template removal was also planned to vary. To complete the study full-scale structural and reactivity characterisations were planned too.

Experimental methods

During the development of catalysts and catalytic technologies the synthesis, the characterization and the applications are equally important. All these aspects were studied concerning the MCM-41 and SBA-15 mesoporous silicates.

Following literature data, both structures (MCM-41 and SBA-15) have been

prepared in pure siliceous or in framework-substituted forms using transition metals (titanium, zirconium, vanadium or iron) as isomorphous substitutes. For the synthesis of most materials conventional methods were used, however, in the preparation of SBA-15 samples the transition metal sources were dissolved tetrahydrofuran (THF) to assure homogeneous distribution of the modifier ions.

The final step in the synthesis of mesoporous silicates is the removal of the organic template used for the development of the given porous structure. Since this process can affect the catalytic performance, we studied various oxidation agents and reaction conditions. They were pure oxygen, ozone, nitrogen dioxide or dinitrogen oxide in the temperature range of 200 – 540 °C. The starting („as synthesized”) materials, the intermediates and the final products of the treatment procedures were characterized with all available instrumental methods. They were as follows: X-ray diffractometry, surface area determination, thermal analysis, IR spectrometry, UV-VIS spectrometry in the diffuse reflectance mode, transmission electron microscopy, solid-state NMR spectroscopy and catalytic measurements with gas-chromatographic product analysis.

Novel scientific results

From the work leading to these Theses the following novel scientific results can be concluded:

1. The results confirmed that at 200 °C the organic template could be removed totally with ozone, while in the presence of the other oxidation agents part of the organic material remained in the silicate structure. The BET surface areas of the samples treated with ozone at 200 °C were the same as the materials using other oxidants at 400 °C. Comparing the values of the measured BET surface areas, pore diameters, basal plane distances and wall thicknesses of the samples treated by the various oxidants, no significant differences could be detected indicating that at 400 °C each oxidation agent removed the organic template from the channel system.
2. The X-ray diffraction patterns, as well as the results of nitrogen adsorption measurements have unambiguously proven that the decrease in the pore diameter, i.e. the shrinkage of pores are affected by the temperature in much larger extent

than that of the nature of the oxidation agent.

3. On the TEM micrographs both the ordered hexagonal channel system, i.e. the honeycomb structure of MCM-41 and the parallel pores characteristic of SBA-15 can be distinguished clearly proving that samples treated by the oxidation agents remained intact, i.e. there was no observable morphological change.
4. The BET surface areas of the SBA-15 samples synthesized in the presence of THF are larger than those of the materials prepared by the conventional method, however, the pore diameters are the same. At the beginning, THF was assumed to have similar role as mesitylene has in the synthesis of MCM-41 – to increase the pore diameter –, however, on the basis of more recent results a different picture emerged. The role of THF is established to keep the transition metal ions in the synthesis solution to assure uniform distribution.
5. It is well known that originating from the different sizes of the substituent ions the geometrical parameters of the lattice differs from the pure siliceous form. These changes, either a decrease or an increase depending on the size of the substituent, may be suitable for determining the concentration of the substituent atoms in the lattice. On the basis of our X-ray diffraction study of mesoporous silicates containing substituent atoms we established that the relative differences between the T-atoms and the silicon atom were levelled off, these changes were not detected in the pore diameters. Consequently, this technique cannot be applied for the estimation of T-atom concentration in the structure.
6. The IR spectra revealed that there was no detectable difference in the intensity of the band at around 960 cm^{-1} , moreover, considering the substituent ion or the template removal agent no systematic alteration of this band was observed. In our spectra only one, not separable band could be identified in this region both for the pure siliceous and the substituted materials. We suppose that origin of this band – in every case - is the Si-O-Si bonds formed in the new molecular environment. In the crystalline materials with ordered pore system the T atoms exist in tetrahedral positions, therefore, the characteristic UV-VIS bands can generally be distinguished from the specific bands of octahedral extra-framework formations or

from the bands characteristic of the transition metal oxide. In the mesoporous materials the possibility of movements is higher in comparison with the zeolites resulting in more complex UV-VIS spectra. Considering our results, it could be established that during the template removal procedure at 400 °C using each oxidation agent, certain part of the T-atoms exited the framework.

7. Performing catalytic test reactions, it was established that the modified mesoporous silicates containing substituent atoms catalyze both the Friedel-Crafts type alkylation and the redox type reactions. These measurements testify that both acidic and redox type active centres can be formed inside the mesoporous structure during template removal.

Conference presentations

1. Méhn, D., Meretei, E., Halász, J., Kónya, Z., Kiricsi I.:
Comparison of the possible preparation, characterization methods and catalytic test reactions for isomorphously substituted MCM-41 catalysts,
5th Pannon. Intern. Symp. Catal., Kazimierz Dolny nad Wisla, 2000, Book of Abstracts P03
2. Méhn, D., Meretei, E., Halász, J., Kónya, Z., Kiricsi, I.:
Investigation of isomorphously substituted MCM-41 materials as selective oxidation catalysts,
5th Intern. Symp. Exhib. Environ. Contam. Centr. East. Eur., Prague, 2000
3. Meretei E.:
Titán-, vanádium- és zirkóniumtartalmú MCM-41 katalizátorok szintézise, vizsgálata és alkalmazása,
XXIII. Kémiai Előadói Napok, Szeged, 2000
4. Meretei, E., Méhn, D., Halász, J., Kiricsi, I.:
Novel method for soft template removal in the synthesis of MCM-41 mesoporous materials,
SSC2002, Solid State Chem. Conf., Bratislava, 2002
5. Meretei, E., Halász, J., Méhn, D., Kónya, Z., Korányi, T.I., B.Nagy, J., Kiricsi, I.:
Structural consequences of mild oxidative template removal in the synthesis of modified MCM-41 silicates,
XXVI Eur. Conf. Molec. Spectr. (EUCMOS), Lille, 2002
6. Halász, J., Nyári, W., Meretei, E., Hannus, I., B.Nagy, J., Kiricsi, I.:
Structural properties and catalytic activity in selective oxidation of In-containing ZSM-5 catalysts,
XXVI Eur. Conf. Molec. Spectr. (EUCMOS), Lille, 2002

7. Solymár E.:
Spektroszkópiás módszerek alkalmazása mezopórusos szilikátok szerkezetvizsgálatában,
46. Magyar Spektrokémiai Vándorgyűlés, Szeged, 2003
8. Meretei, E., Szegedi, Á., Pál-Borbély, G., Kónya, Z., Kiricsi, I.:
Acidic and redox behaviour of transition metal ion substituted spherical mesoporous MCM-41 silicates,
EuropaCat–VI, Innsbruck, 2003
9. Szegedi, Á., Pál-Borbély, G., Meretei, E., Kónya, Z., Kiricsi, I.:
Acidic and redox behaviour of iron substituted spherical mesoporous MCM-41 silicates,
14th Intern. Zeolite Conf., Cape Town, 2004
10. Szegedi, Á., Pál-Borbély, G., Meretei, E., Kónya, Z., Horváth, Zs. E., Biró, L. P., Kiricsi, I.:
Synthesis and characterization of spherical mesoporous MCM-41 materials containing transition metals,
14th Intern. Zeolite Conf., Cape Town, 2004