

FROM ZEOLITES TO MESOPOROUS MATERIALS

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INTRODUCTION

Porous silicates are classified into three categories, microporous with pore diameters from 0.3 to 2 nm, mesoporous having pores diameters between 2 and 50 nm, and macroporous with pores greater than 50 nm¹. Their large surface areas and a variety of structure types make them useful as catalysts supports.

Transition-metal functionalised microporous silicates (zeolites) are widely used as heterogeneous catalysts in oxidation reactions². These catalysts display a remarkable catalytic activity due to the unique atomic architecture of the transition-metal centres, which are isolated in the microporous aluminosilicate framework of zeolites. The pore size limitations of microporous catalysts can be overcome by using mesoporous silicates when larger reactants have to be processed. However, transition-metal functionalised mesoporous silicates do not exhibit catalytic properties that are comparable to transition-metal functionalised microporous ones³. The hydrothermal stability of the former is rather low and the leaching of transition-metal species from the solid makes the recovery of the catalyst difficult.

For overcoming this problem we prepared transition-metal functionalised silicates with hierarchical porous structure (microporous/mesoporous composites). This preparation is based on the use of zeolitic seeds containing small crystalline domains instead of fully-crystalline zeolitic particles^{4,5}. These zeolitic seeds were organized into mesoporous structures by using different types of surfactants. The essential and the most difficult part of the method is to achieve the successful functionalisation of the small zeolitic seeds by transition-metals which is rather much difficult as to functionalised fully crystalline zeolitic particles. This part of the method was developed by our group using zeolite (Ti,Al)-Beta and mesoporous silicates MCM-41 and MCM-48^{6,7} and it is reported here. Such solids may exhibit great improvements with respect to internal diffusion limitations compared with conventional mesoporous molecular sieves.

EXPERIMENTAL

Titanium functionalised zeolitic seeds (Ti,Al)-Beta, mesoporous silicates (Ti-MCM-41, Ti-MCM-48) and silicates with hierarchical porous structure ((Ti,Al)-Beta/MCM-41, (Ti,Al)-Beta/MCM-48) were synthesized hydrothermally^{6,7}. The catalytic properties of these materials depend both on structure and transition-metal, i.e. its location and oxidation state, and also on thermal and hydrothermal stability of these materials. The characterization process of the potential catalyst consists of basic characterization, detailed structural study of local environment of titanium and catalytic tests.

The basic characterisation of titanium containing products were performed by using X-ray diffraction (XRD), thermal analysis (TG/DSC), elemental analysis (EDAX - Energy Dispersion Analysis by X-rays), scanning electron microscopy (SEM), transmission electron microscopy (TEM), nitrogen physisorption and nuclear magnetic resonance spectroscopy (NMR).

The nature and location of titanium in prepared materials were investigated by X-Ray Absorption Spectroscopic (XAS) techniques: X-ray Absorption Near-Edge Structure

(XANES) and Extended X-ray Absorption Fine Structure (EXAFS). XANES analysis identifies local symmetry and the average oxidation number of transition metal atoms. EXAFS analysis provides the description of a short-range order for selected transition metal in terms of the number of neighbours, distances, and thermal and static disorder within the range of those distances. XAS techniques are decisive methods for the following of synthesis pathways and also for the recognition of structural properties that are relevant to the overall optimal performance of a synthesis product that could be a potential catalyst.

New potential catalysts with hierarchical porous structures in comparison with mesoporous structures are currently being tested in oxidation reactions. Catalytic tests are currently being performed in the French laboratory (Laboratoire des Systèmes Interfaciaux à l'Echelle Nanométrique (SIEN), Université Pierre et Marie Curie, Paris, France) in the frame of Slovenia-France bilateral collaboration and in one of the network laboratories of the FP6 INSIDE PORES European Network of Excellence (2004-2008, Coordinator: National Center for Scientific Research "Demokritos", Athens, Greece, <http://www.inside-pores.gr>).

RESULTS AND DISCUSSION

Thermally stable titanium containing microporous/mesoporous composite (Ti,Al)-BETA/MCM-41 was synthesized hydrothermally in the presence of structure-directing agents cetyltrimethylammonium bromide (CTABr) and tetraethyl ammonium hydroxide (TEAOH). Microporous/mesoporous structure of the product was successfully characterized by XRD (Figure 1) and HRTEM. Local environment of titanium incorporated into the microporous/mesoporous silicate material was investigated by X-ray absorption spectroscopy. XANES studies showed the presence of tetrahedrally coordinated Ti^{4+} cations in the template-free sample. EXAFS analysis revealed that titanium cations were coordinated to 4 oxygens in the first coordination shell at a distance of 1.84 Å. The preliminary catalytic test of the potential catalyst was the epoxidation of cyclooctene using *tert*-butyl hydroperoxide (TBHP) as the oxidant. The new composite material proved to be as efficient catalyst as (Ti,Al)-Beta zeolite. Titanium leaching from the composite was not observed. NMR investigations showed that acid sites related to framework aluminum were generated by removal of potassium and sodium ions from the (Ti,Al)-BETA/MCM-41 pores.

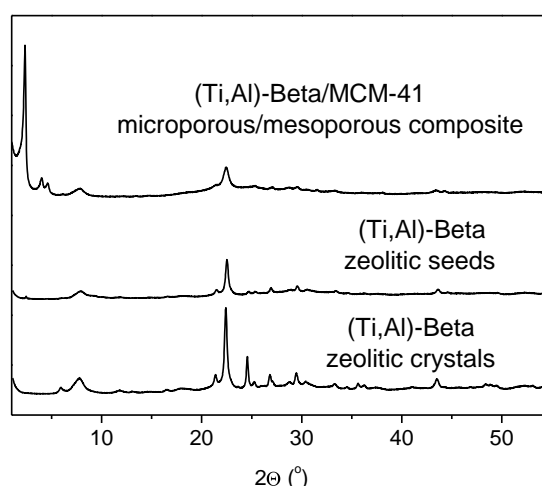


Figure 1. XRD pattern of the template-free microporous/mesoporous composite (Ti,Al)-Beta/MCM-41 confirms the presence of both mesoporous MCM-41 and microporous zeolite Beta phases. The four peaks at 2.33 °, 4.00 °, 4.60 ° and 6.16 ° 2θ were assigned to hexagonal mesoporous structure with $a_0 = 4.39$ nm. The peaks at 7.80 °, 22.45 ° and higher are typical for zeolite Beta structure.

Thermally stable titanium-containing microporous/mesoporous composite (Ti,Al)-Beta/MCM-48 was synthesised hydrothermally in the presence of structure-directing agents cetyltrimethylammonium bromide (CTABr), polyoxyethylene(8) isooctylhexyl ether (Triton[®] X-114) and tetraethylammonium hydroxide (TEAOH) in the absence of sodium cations. The presence of both microporous and mesoporous phases was determined by XRD and HRTEM (Figure 2 and Figure 3) and by the analysis of nitrogen adsorption isotherm based on the α -plot method. The mass percentage (μ) of the microporous material in the composite is approximately 6.5 %. NMR investigations showed that acid sites related to framework aluminium were generated by calcination of the as-synthesised (Ti, Al)-Beta/MCM-48. Local environment of titanium incorporated into the microporous/mesoporous silicate material was investigated by X-ray absorption spectroscopy. XANES studies showed the presence of tetrahedrally-coordinated Ti^{4+} cations in the template-free sample. EXAFS analysis revealed that titanium cations were coordinated to four oxygens in the first coordination shell, to one oxygen at 1.73(1) Å and three oxygens at 1.86(1) Å. In the second coordination sphere three silicon atoms were found at distances 3.18(2) Å and 3.48(2) Å, respectively. These results indicated framework Ti and thus the presence of Ti oxidation centres within the composite material.

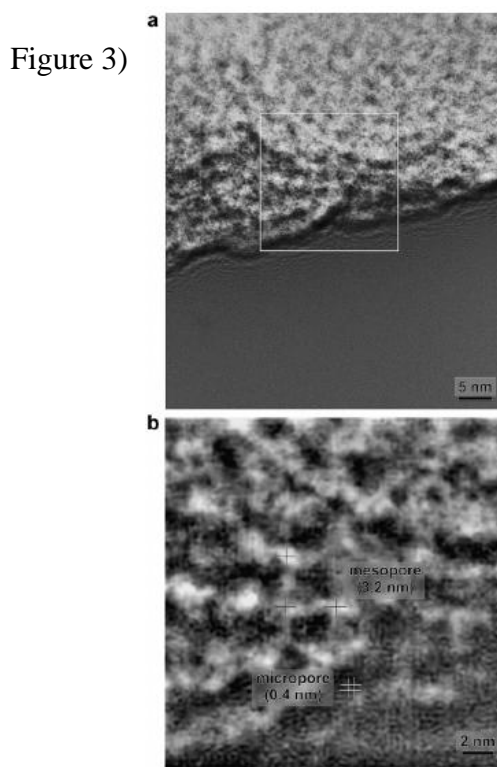
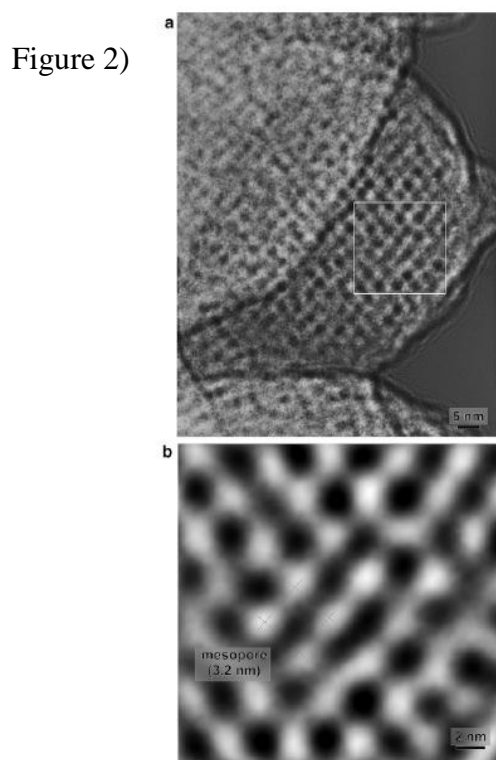


Figure 2. (a) A HRTEM image of the template-free TiMCM-48 viewed along [001] direction. (b) FFT filtered magnified image of the inset outlined in Figure 2a clearly shows a cubic arrangement of mesopores and lack of the microporous features in the walls.

Figure 3. (a) HRTEM image of the template-free (Ti,Al)-Beta/MCM-48 composite with a distorted cubic arrangement of mesopores. (b) FFT filtered image of the inset from Figure 3a shows a delocalised micropore pattern having narrower lattice spacing than the hosting mesoporous matrix.

CONCLUSION

The pore size limitations of transition-metal functionalized zeolites can be overcome by using transition-metal functionalized mesoporous silicates with pore openings from 2 to 10 nm. However, these materials do not exhibit catalytic properties that are comparable to zeolitic ones. Their hydrothermal stability is rather low and the leaching of transition-metal species from the solid makes the recovery of the catalyst difficult. Our research was focused on the preparation of novel titanium containing catalysts with hierarchical porous structure that combine good catalytic properties and thermal stability of microporous- and pore openings of mesoporous silicates. In the first part, we have successfully prepared titanium containing small zeolitic seeds of zeolite Beta ((Ti,Al)-Beta). Further on, we have synthesized titanium-modified microporous/mesoporous silicates (Ti,Al)-Beta/MCM-41 and (Ti,Al)-Beta/MCM-48 with hierarchical porous structure. Microporous (zeolite Beta) structure and mesoporous (MCM-41, MCM-48) structures were confirmed by X-ray powder diffraction (XRD) and High Resolution Transmission Electron Microscopy (HRTEM). Tetrahedral coordination of titanium was determined by X-ray absorption spectroscopy that confirmed the incorporation of titanium into silicate framework and announced its catalytic function. Catalytic tests of prepared and characterized potential catalysts are in progress.

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OD ZEOLITA DO MEZOPOROZNIH MATERIJALA

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SAŽETAK

Mikroporozni silikati (zeoliti) funkcionalizirani prijelaznim metalima i otvorima pora 0.3 do 2 nm se naširoko koriste kao heterogeni katalizatori u oksidacijskim reakcijama. Ovi katalizatori pokazuju izvanrednu katalitičku aktivnost zahvaljujući centrima prijelaznih metala koji su izolirani unutar silikatne rešetke. Katalitička svojstva ovih materijala ovisi o strukturnom tipu, lokaciji i prirodi inkorporiranog metala. Limitiranost veličinom pora kod mikroporoznih katalizatora se može izbjeći uporabom mezoporoznih silikata s otvorom pora od 2 do 10 nm, kada se trebaju procesirati reaktanti većih molekula. Međutim, oni ponekad ne pokazuju katalitička svojstva zeolita. Ispuštanje čestica prijelaznih metala iz mezoporoznih silikata onemogućava regeneraciju katalizatora. U svrhu prevladavanja ovog problema, priredili smo zeolitno cjepivo funkcionalizirano prijelaznim metalima koje sadrži male kristalinične djelove i inkorporirali ih u mezoporozni materijal. U ovom radu pokazujemo sintezu i karakterizaciju mikroporoznog/mezoporoznog kompozitnog materijala, koji se sastoji od zeolita (Ti,Al)-Beta i mezoporoznog MCM-41 i MCM-48.

Ključne riječi: mikroporozni/mezoporozni kompozit, silikat, titanij, katalizator, oksidacijske reakcije