

## SYNTHESIS STRATEGIES TOWARDS MICRO/MESOPOROUS SILICATE COMPOSITES

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### INTRODUCTION

Ordered mesoporous silica based molecular sieves are attractive materials for adsorption and catalytic applications, due to their large pore sizes (2-50 nm) and high surface areas (~1000 m<sup>2</sup>/g). [1,2] However, amorphous nature of the walls causes poor hydrothermal stability and low activity toward catalytic processes of these materials, which represents a major drawback. [3] This drawback could be overcome by combining interconnected microporous (zeolite) networks with structured mesopores thus producing micro/mesoporous composites. Search for synthesis procedures which could lead to the catalytically most efficient micro/mesoporous silicate composite material is intensively studied for more than a decade. [4] For understanding of structural characteristics of these materials which enable catalytic properties, detailed structural characterization is required. Here we report on different synthesis approaches for the preparation of microporous/mesoporous silica based composites and their detailed structural investigations. [5,6]

### EXPERIMENTAL

#### Syntheses

(Ti, Al)-Beta/MCM-48 composite was prepared by two-step synthesis. In first step colloidal solution containing zeolite (Ti, Al)-Beta was prepared by hydrothermal treatment at 408 K for 3 days. In the presence of surfactants (cetyltrimethylammonium bromide and Triton X-114) added into colloidal solution in the second step, reorganization of zeolitic nanoparticles in the walls of cubic MCM-48 mesoporous matrix was achieved.

Re-crystallization (zeolitization) was used in the synthesis of ZSM-5/SBA-15 composite. Al-SBA-15 matrix was impregnated with template tripropylammonium bromide, which directs the formation of ZSM-5 zeolite phase, and hydrothermally treated in microwave oven at 413 K from 1.5 to 5 hours.

Ti-Beta/SBA-15 composite was synthesized by post-synthetic deposition of zeolitic nanoparticles inside the channels of SBA-15 matrix. SBA-15 mesoporous matrix was dry-impregnated (incipient wetness) by colloidal solution containing nanoparticles of zeolite Ti-Beta prepared hydrothermally at 408 K.

All prepared composite materials were calcined at 823 K in order to remove structure directing agents from pores and thus activate the products.

### RESULTS AND DISCUSSION

#### Structural properties

The presence of 3-D cubic mesostructure in (Ti, Al)-Beta/MCM-48 and 2-D hexagonal mesostructure in ZSM-5/SBA-15 and Ti-Beta/SBA-15 was proven by low-angle XRD (not

shown). Diffractograms also show weak intensity and broad reflection peaks at higher angles corresponding to zeolite Beta phase in (Ti, Al)-Beta/MCM-48 and ZSM-5 phase in ZSM-5/SBA-15 indicating the presence of nanosized zeolitic domains in mesoporous matrix.

Structural parameters of composite materials obtained from N<sub>2</sub> sorption analysis are collected in Table 1. In the case of (Ti, Al)-Beta/MCM-48 micropore volume and BET surface area are increased whilst mesopore diameter remains the same in comparison with MCM-48 matrix. This implies the presence of zeolitic domains inside the mesoporous walls. Zeolitization of mesoporous SBA-15 walls in synthesis of ZSM-5/SBA-15 leads to increased micropore volume and wall thickness, in comparison with Al-SBA-15 matrix, due to the presence of zeolitic domains in amorphous walls. Decrease of pore diameter and surface area can be caused by partial destruction of mesostructure during zeolitization process, observed also by TEM measurements. Deposition of Ti-Beta nanoparticles inside SBA-15 channels, thus producing Ti-Beta/SBA-15 composite, leads to increased wall thickness and decreased pore diameter in comparison with SBA-15 matrix. In contrast with SBA-15, which lacks the micropore content, the micropore volume of Ti-Beta/SBA-15 composite samples tends to increase due to the micropores located in the Ti-Beta zeolite plugs. This indicates that zeolitic nanoparticles are deposited on the inner walls of mesochannels. Decreasing of BET surface area can be explained by partial blocking of mesopores with zeolitic nanoparticles.

Structural correlations between mesoporous and zeolitic phases were investigated by HR-TEM. IFFT TEM micrograph of (Ti, Al)-Beta/MCM-48 shown on Figure 2a revealed faint, but characteristic self-assembled cubic arrangement of mesopores. Mesostructure walls have microporous characteristics. Lattice pattern of microporous phase coincides with pattern of mesopores, implying that both phases are structurally correlated. TEM measurements are in agreement with N<sub>2</sub> sorption analysis. From micrograph of ZSM-5/SBA-15 shown on Figures 2c and d dark spots on partially destroyed mesoporous matrix can be observed, representing spherical crystalline ZSM-5 precursors that start to grow from amorphous aluminosilicate wall. Similar features can be observed in HRTEM micrograph of Ti-Beta/SBA-15 (Figure 2b). It can be seen that some Ti-Beta nanoparticles are located inside the mesopore channels of the SBA-15 matrix and some bigger crystallites which probably cause blocking of the mesopores.

#### Active sites

Titanium sites in (Ti, Al)-Beta/MCM-48 and Ti-Beta/SBA-15 composites were investigated by XANES/EXAFS analysis. Normalised Ti K-edge XANES spectra and Fourier transform of Ti EXAFS spectra of composites are shown on Figure 2 and Figure 3 respectively. Titanium(IV) in (Ti, Al)-Beta/MCM-48 occurs in slightly distorted tetrahedral environment with one oxygen atom at the distance of 1.73(1) Å and three at the distance of 1.86(1) Å. Titanium in Ti-Beta/SBA-15 is five-fold coordinated. Four oxygen atoms are at the distance of 1.88(2) Å and one at the distance 2.48(3) Å. The latter oxygen atom corresponds to additionally coordinated OH group or water molecule. In both cases silicon atoms were found in second Ti coordination sphere. This is direct proof of the presence of isolated titanium(IV) cations in silicate framework and thus the presence of catalytically active oxidation sites in composites.

Aluminium sites in aluminosilicate frameworks of (Ti, Al)-Beta/MCM-48 and ZSM-5/SBA-15 composites were investigated by <sup>27</sup>Al NMR spectroscopy (spectra not shown). In both cases the presence of tetrahedral aluminium was found. Framework aluminium presents Lewis or Brønstedt acid sites in the form of bridging hydroxyls Si(OH)Al.

Table 1. Textural properties of composite materials and mesoporous matrixes. ( $S_{\text{BET}}$  - BET surface area,  $V_{\text{mi}}$  – micropore volume,  $W_{\text{T}}$  – wall thickness,  $D$  – pore diameter).

Material	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_{\text{mi}}$ (cm <sup>3</sup> /g)	$W_{\text{T}}$ (nm)	$D$ (nm)
MCM-48	609	-	5.7	2.2
(Ti, Al)-Beta/MCM-48	805	0.013	5.7	2.2
Al-SBA-15	855	-	3.6	8.0
ZSM-5/SBA-15	464	0.026	4.8	7.0
SBA-15	726	-	1.2	10.7
Ti-Beta/SBA-15	695	0.029	4.4	7.5

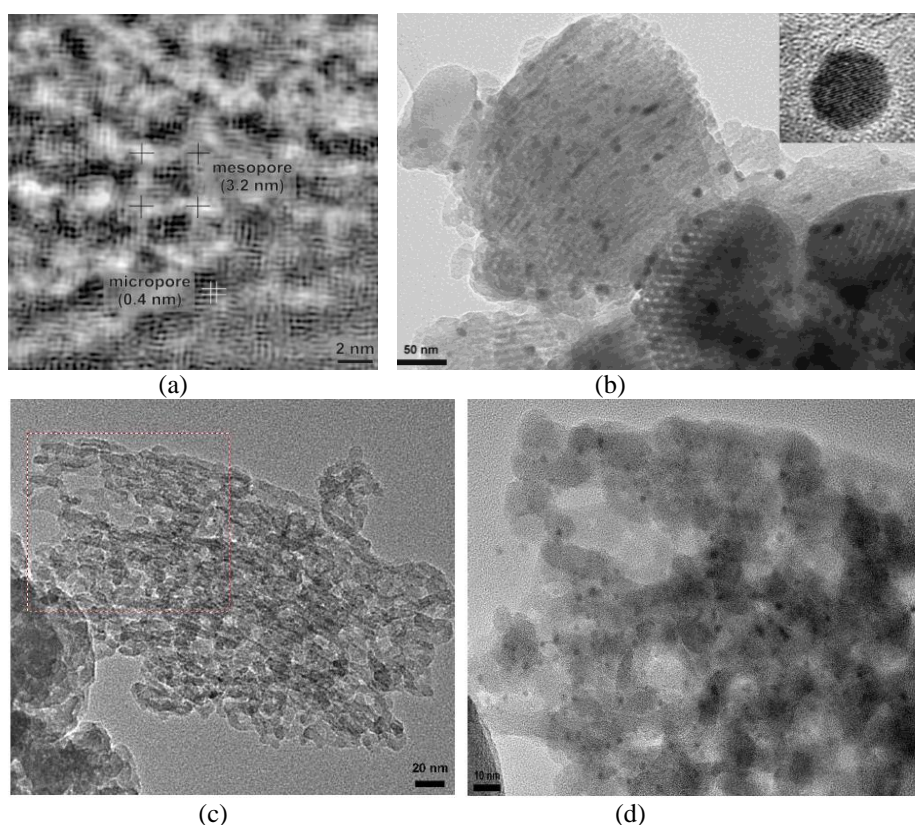
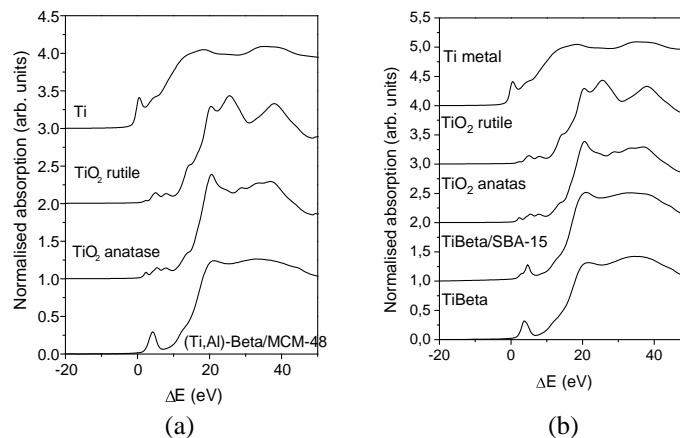


Figure 1. TEM micrographs of (a) (Ti, Al)-Beta/MCM-48 (IFFT image), (b) Ti-Beta/SBA-15, (c) ZSM-5/SBA-15, (d) magnified inset area marked in image c.


 Figure 2: Normalised Ti K-edge XANES spectra of (a) (Ti, Al)-Beta/MCM-48, (b) Ti-Beta/SBA-15 samples and references (Ti, TiO<sub>2</sub> anatase, TiO<sub>2</sub> rutile, Ti-Beta).

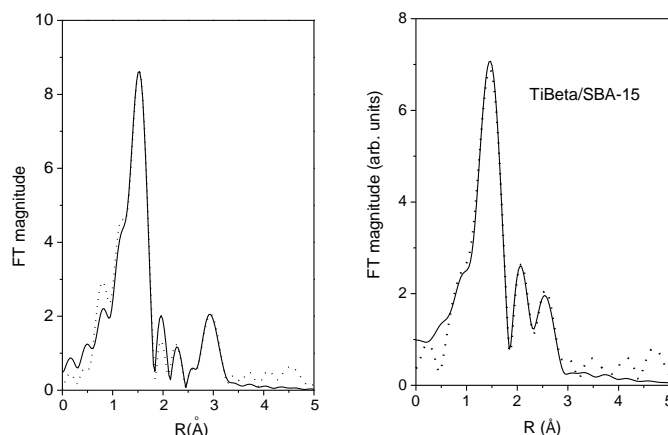


Figure 3: Fourier-transform magnitude of the  $k^3$ -weighted Ti EXAFS spectra of (a) (Ti, Al)-Beta/MCM-48 and (b) Ti-Beta/SBA-15 samples (dotted line – experiment, solid line - EXAFS model).

## CONCLUSIONS

Three different micro/mesoporous composite materials were synthesized using different synthesis approaches. We showed that all synthesis approaches are effective and lead to thermally stable bimodal porous materials. By choosing proper synthesis procedure location of zeolitic nanodomains in mesoporous matrix can be manipulated. By reorganization of zeolitic nanoparticles into mesoporous matrix (two-step synthesis) and post-synthetic zeolitization of mesoporous walls incorporation of zeolitic phase into mesoporous walls can be achieved. By post-synthetic deposition (incipient wetness) zeolitic nanoparticles can be deposited inside mesoporous channels as plugs. Also by choosing different zeolitic systems (zeolite (Ti, Al)-Beta, Ti-Beta and ZSM-5) structural properties of composite materials can be varied. (Ti, Al)-Beta/MCM-48 is a potential bifunctional catalyst with isolated oxidation and acid sites whereas Ti-Beta/SBA-15 and ZSM-5/SBA-15 materials are potential monofunctional catalysts with oxidation and acid (Lewis or Brønsted) sites, respectively.

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