CHARACTERIZATION OF MICRO- AND MESOPOROUS Ti -CATALYSTS

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Abstract

Titanium catalysts are important materials for many types of oxidation reactions. Conventionally prepared microporous titanosilicate, namely TS-1, is well-known catalyst used in oxidation reaction with hydrogen peroxide. Since the size restriction of pores in microporous catalysts limits their wide application, large effort has been invested in order to prepare new types of catalysts with expanded surface area and pore size. Such new type of catalyst, mesoporous TS-1, was compared with conventional microporous TS-1 in our study. Besides the typical reactions, e.g. epoxidations, oxidation of sulfides represents another important branch of application. This type of reaction leads to the preparation of organic sulfoxides and sulfones, which are important chemical intermediates and building blocks of pharmaceutical and agrochemical compounds. Our study is focused on the testing of both types of catalysts, i.e., microporous TS-1 and mesoporous TS-1, in the oxidation of methyl phenyl sulfide with 30% hydrogen peroxide, and the influence of the structure in conversions of reagents and the selectivity to products was described. Samples were studied using BET analysis and X-ray powder diffraction analysis. The morphology of the samples was observed by atomic force microscopy.

Keywords: TS-1, titanosilicate, oxidation, atomic force microscopy, catalysis

1. INTRODUCTION

Titanosilicate zeolites are industrially used mostly for oxidation and epoxidation of organic compounds such as alkanes, alkenes and aromatics [1,2]. Due to the titanium as a center of catalytic activity it is possible to use aqueous hydrogen peroxide as an oxidizing agent which provides active oxygen [3].

Selective oxidation of organic sulfides is important chemical reaction, which produces sulfoxides and sulfones. These compounds are known to be valuable intermediates and building blocks of pharmaceuticals and agrochemicals. Sulfoxides are used as well as intermediates for preparation of chemically and biologically active molecules [4].

Usage of titanosilicate zeolites as catalysts is restricted on reactions of small molecules because of active centers situated in pores of relatively small diameters. Herein microporous titanium silicalite-1 (TS-1) was used [5]. TS-1is zeolite with MFI structure [6] having three-dimensional channel system of intersecting elliptical 10-ring pores with diameters of 5.3 × 5.5 and 5.1 × 5.5 Å and containing titanium isomorphously substituted silicon in the framework [7]. In our reactions we compared the microporous TS-1 with so-called hierarchical type of zeolites possessing micro- and mesopores, named as mesoporous TS-1. Additional porosity in the mesopore size region (pore diameters in the range 2-50 nm) [8], can be created with the help of secondary templating [9]. The main aim of this study was to answer the question whether this simple structural modification causes changes in the course of oxidation (mainly selectivity of products) and whether the mesoporous TS-1 will behave as the conventional microporous TS-1 or rather as the TS-1 modified in different and more difficult ways (layered or pillared).

2. EXPERIMENTAL

Conventional microporous titanosilicate (TS-1), titanosilicate with secondary prepared mesopores (TS-1 / Meso) and top-down prepared layered titanosilicate after Si-source pillaring (TS-1 / PiliSi), were prepared according to Wilde et al. [10]. Phase composition was determined using SmartLab (Rigaku) X-ray powder diffractometer equipped with Co tube (CoKα, λ = 0.1789 nm). The XRD patterns were collected in a 2θ range 1° - 40° with a step size of 0.02° and speed 1.5 $\text{deg}\cdot\text{min}^{-1}$. The textural properties were determined from nitrogen sorption isotherms. The isotherms were recorded at liquid nitrogen temperature (-196 °C) with Gemini II 2370 (Micromeritics) volumetric instrument. BET area was evaluated using adsorption data in the range of a relative pressure p/p_0 from = 0.05 to 0.20, the t-plot method [11] was applied to determine the specific volume of micropores (V_{micro}). Chemical composition of the materials (expressed hereafter as the n_{Si} / n_{Ti} ratio) was determined using Philips PW 1404 X-ray fluorescence spectrometer (Philips) with the analytical program UniQuant. Morphology of the powder samples was studied using atomic force microscope SolverNEXT (NT-MDT). The scanning of the samples took place in semicontact mode with noncontact probes NSG30 (NT-MDT). Before the measurement, the powder sample was dispersed into ethanol, applied on the mica substrate and fixed by drying. The images of morphology obtained by atomic force microscopy (AFM) were evaluated using Image Analysis software (NT-MDT).

Catalytic experiments were carried out in the liquid phase in a round-bottom glass batch reactor (V = 25 cm^3) equipped with a magnetic stirrer (500 rpm) at the laboratory temperature. Methyl phenyl sulfide (99%, Sigma-Aldrich) was used as a substrate, hydrogen peroxide (30 wt.% aqueous solution, Mach Chemicals) was used as the oxidant, acetonitrile (99.9%, Sigma-Aldrich) as a solvent and 1,3,5-trimethylbenzene / mesitylene (98%, Aldrich) was used as an internal standard. In a typical experiment, 10 cm^3 of acetonitrile was loaded into the reactor, followed by the addition of the substrate (0.5 cm^3, 4 mmol), and mesitylene (0.25 cm^3, 2 mmol). Finally 50 mg of catalyst was added. The reaction was started by addition of 30% hydrogen peroxide solution (0.23 cm^3, 2 mmol). Samples were taken periodically from the reaction mixture; liquid phase was separated from solid catalyst and analyzed by capillary gas chromatography. The conversion of methyl phenyl sulfide was calculated as the ratio of converted and initially present methyl phenyl sulfide. The selectivity for methyl phenyl sulfoxide / methyl phenyl sulfone is given as the mass of sulfoxide / sulfone formed relative to the converted mass of the substrate, methyl phenyl sulfide.

3. RESULTS AND DISCUSSION

3.1. Catalyst characterization

For the evidence that we have tested and compared different types of titanosilicate structures, the results of XRD analysis are presented in **Figure 1**. The XRD patterns of conventional TS-1 and mesoporous TS-1 prepared only by adding the secondary template to the synthesis gel of microporous one, clearly demonstrate the presence of the MFI structure, typical for TS-1. In connection with catalytic activity, TS-1 / Meso was further compared to another type of material with mesopores, namely TS-1 / PiliSi, prepared by so-called Assembly-Disassembly-Organisation-Reassembly - ADOR strategy [12], prepared from as-synthetized layered material by pillaring it with amorphous silica [13]. For pillared TS-1, a strong diffraction line is present at low 2θ = 1.7°. This line characterizes a regular organization of the layers within these pillared materials. The diffraction lines are less intense due to the presence of amorphous pillars in these materials.

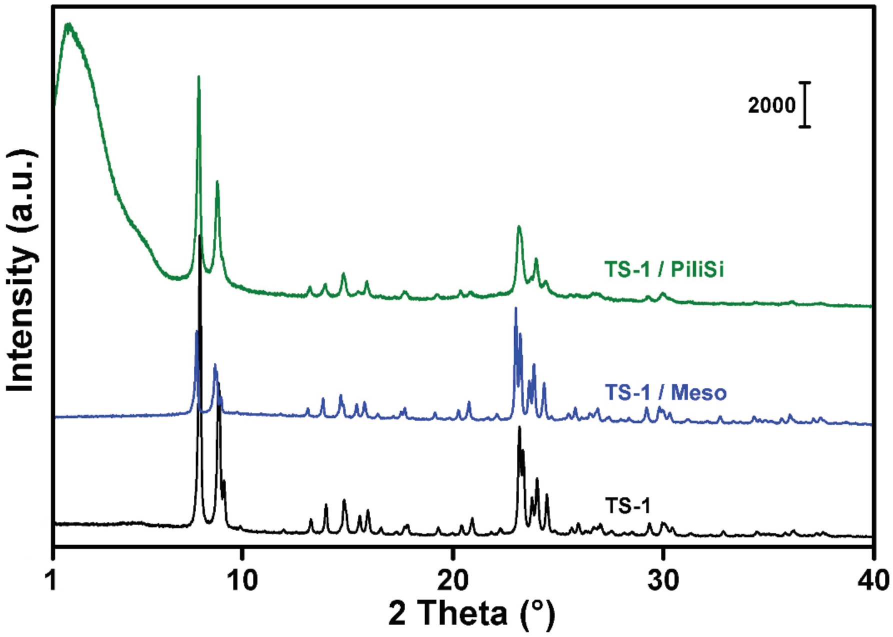

Figure 1 X-ray powder diffraction patterns of calcinated Ti-catalysts. Conventional microporous titanosilicate (TS-1), titanosilicate with secondary prepared mesopores (TS-1 / Meso), top-down prepared layered titanosilicate after Si-source pillaring (TS-1 / PiliSi)

Textural properties of the three titanosilicates are shortly summarized in **Table 1**. It can be seen that the content of titanium is comparable, around n_{Si} / n_{Ti} = 48. In the case of total surface areas it can be summarized that TS-1 and mesoporous TS-1 possess similar values opposite to the top-down synthesized layered counterpart TS-1 / PiliSi in which the surface area is visibly larger. The evidence that all three materials are based on microporous material is proven by similar volume of micropores. On the other hand, the benefit of hierarchical structures TS-1 / Meso and TS-1 / PiliSi is the increased amount of mesopores.

Table 1 Textural properties of Ti-catalysts determined by nitrogen adsorption and chemical analysis

Catalyst	n_{Si} / n_{Ti}	S_{TOT} ($m^2 \cdot g^{-1}$)	V_{micro} ($cm^3 \cdot g^{-1}$)	V_{meso} ($cm^3 \cdot g^{-1}$)
TS-1	49	460	0.12	0.03
TS-1 / Meso	40	465	0.10	0.16
TS-1 / PiliSi	55	575	0.11	0.29

With respect to the much simpler preparation of TS-1 / Meso compared to TS-1 / PiliSi, we further focused our attention to the TS-1 / Meso sample. In order to observe how morphology of conventional TS-1 and TS-1 / Meso differs and to find whether the secondary created mesopores can be seen, the AFM analysis using semicontact mode was involved. AFM images of the samples TS-1 and TS-1 / Meso are presented in **Figure 2**. Average sizes and roughnesses of grains were calculated by detailed analysis of AFM images. The grains of TS-1 are visible in the **Figure 2A**. This sample forms small and smooth grains with mean diameter ($d_{\varnothing}$) 212 ± 8 nm and average roughness (R_a) 1.9 ± 0.3 nm. In comparison with TS-1, the grains of TS-1 / Meso (**Figure 2B**) have six times larger mean diameter, i.e., $d_{\varnothing}$ = 1275 ± 142 nm, and the detailed scanning of grain showed that the surface of grains is rougher (R_a = 60 ± 13 nm) and contains non-spherical pores with average size 20.4 ± 8.2 nm (**Figure 2C**). This fact is in accordance with the **Table 1**. In both samples TS-1 (**Figure 2A**) and TS-1 / Meso (**Figure 2B**), the grains have distinct borders and are clearly recognizable from one another.

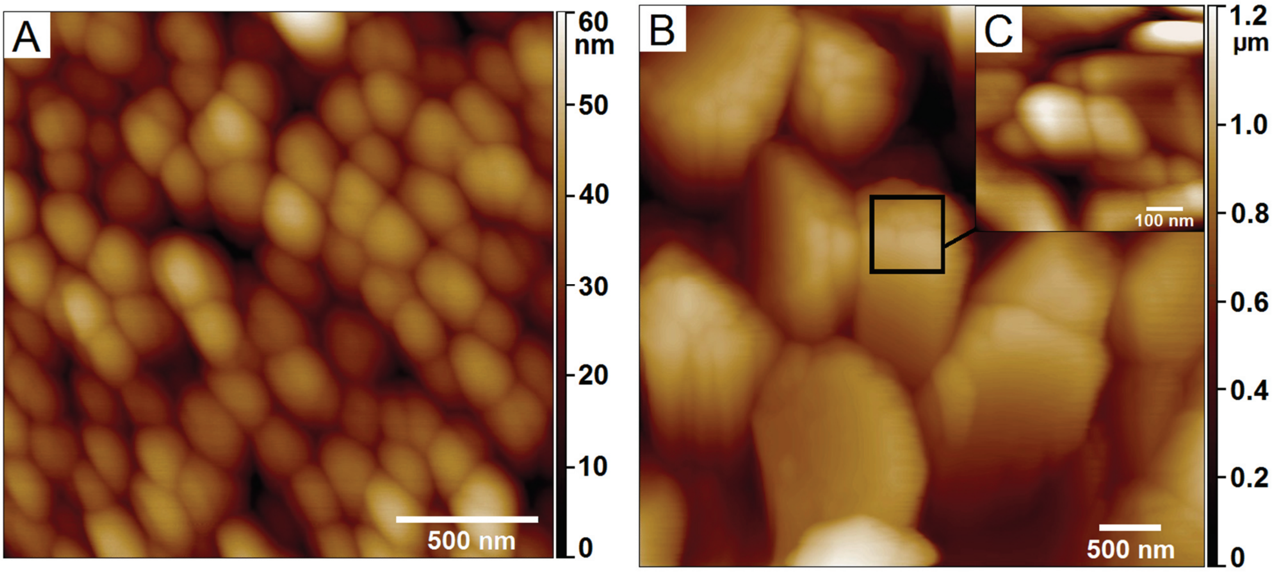

Figure 2 AFM images of samples: microporous titanosilicate TS-1 (A), titanosilicate with secondary prepared mesopores TS-1 / Meso (B), and detailed view on surface of TS-1 / Meso grain showing mesopores (C)

3.2. Oxidation of methyl phenyl sulfide

We have tested a relatively small molecule of sulfide, namely methyl phenyl sulfide, to compare the effects of a mesoporous material (TS-1 / Meso) whose preparation is relatively easy, only by adding the secondary template to the synthesis gel of microporous one. This leads to creation of mesopores, which are beneficial in the catalytic reactions. Our interest was to monitor the catalytic activity of such prepared sample and to determine whether the properties differ from the original microporous form. Moreover, in order to evaluate the possible effects of mesopores itself, we compared the results with layered counterpart.

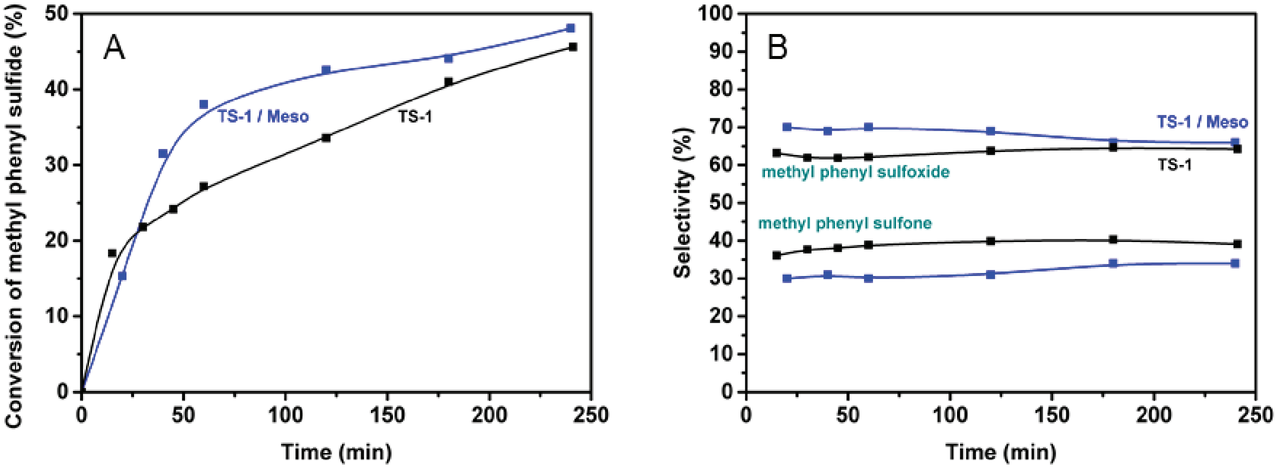

Figure 3 Oxidation of methyl phenyl sulfide on microporous titanosilicate (TS-1) and titanosilicate with secondary prepared mesopores (TS-1 / Meso); conversion of methyl phenyl sulfide (A) and selectivity to the reaction products (B)

The progress of the oxidation of methyl phenyl sulfide with hydrogen peroxide at laboratory temperature for TS-1 and TS-1 / Meso is shown in **Figure 3A**. It is obvious that in both cases almost maximum conversion of substrate was achieved, and, furthermore, that the initial progress of reaction is almost the same during 40 minutes. After this period, slow increase in substrate conversion is obvious during all reaction times in the case of TS-1, while the reaction progress with TS-1 / Meso is still steep until 60 minutes, then the reaction process is slowed down. This can be attributed to transport effects when mesopores possess a positive effect on substrate transportation. Similar features were observed in the case of layered material. It is good to note that in the absence of a catalyst the substrate conversion was less than 20 %.

Nature of the materials was more revealed by related selectivity to the reaction products. In the case of top-down prepared pillared catalyst, selectivity to methyl phenyl sulfoxide was almost 100 %. Behavior of the TS-1 / Meso and TS-1 samples differs from this pillared catalyst (**Figure 3B**). For both TS-1 / Meso and TS-1, selectivity to the first reaction product, methyl phenyl sulfoxide, and the following product, methyl phenyl sulfone, was comparable, around 60-70 % and 30-40 %, respectively. Although the TS-1 / Meso contains mesopores positively affecting the transport of the substrate, ubiquitous micropores and irregular mesopores (as opposed to unblocked mesopores in layered material) lead to slower transport of the first product to allow the encounter the active center and thus cause the oxidation to the second step.

4. CONCLUSION

Various forms of titanosilicates as catalysts possessing different structural features with increased accessibility of active Ti-sites were studied in the liquid-phase, in oxidation reaction of methyl phenyl sulfide with 30% hydrogen peroxide to produce methyl phenyl sulfoxide and subsequent oxidation to methyl phenyl sulfone.

We have focused on the comparison of the Ti-catalyst prepared only by secondary templating of the synthesis gel of conventional TS-1 to create mesopores besides micropores (named TS-1 / Meso) to see whether its catalytic activity would be comparable to the conventional microporous TS-1 or rather to more complex structure of layered catalyst prepared by top-down synthesis.

The AFM scanning showed the differences between the grain size and grain roughness of TS-1 and TS-1 / Meso and confirmed the presence of pores with average size 20 nm on TS-1 / Meso grains. AFM operated in semicontact mode thus proved to be a suitable technique for study the morphology of mesoporous zeolites in powder form, i.e., without necessity to prepare pressed pellets prior to the analysis.

In the absence of a catalyst the substrate conversion was less than 20 %. For all catalysts, the highest possible conversion of substrate achieved during 4 hours was almost 50 % (due to the hydrogen peroxide equivalent). More interesting was the situation around the selectivity to the products of the reaction. Although it can be assumed that the resulting mesopores allow faster transport of both, substrate and products, it has been shown that TS-1 / Meso has exhibited progress of reaction comparable with the layered material in terms of conversion. However, in comparison with the layered material exhibiting almost 100 % selectivity to the first reaction product, the TS-1 / Meso is more comparable to microporous TS-1 (selectivity to the first product, i.e., methyl phenyl sulfoxide, was around 65 %). This phenomenon can be explained by transport influences. Whereas any unblocked mesopores of layered material allow rapid transport of product, the ubiquitous micropores in conventional TS-1 and TS-1 / Meso slow the transport, and, therefore, another possible encounter with the active site and subsequent reaction to the second step can be expected.

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