



## Effective hierarchization of TS-1 and its catalytic performance in cyclohexene epoxidation



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### ABSTRACT

The presented data showed that the chemical treatment of TS-1 with alkaline medium resulted in the formation of highly developed hierarchical structures. The esterification of the hydroxyl groups by methanol allowed modifying the hydrophobicity of TS-1 surface and obtaining truly micro/mesoporous material. The preservation of microporous characteristics was confirmed by XRD and low temperature nitrogen sorption studies. Detailed information on acidic properties of mesoporous titanosilicalites was delivered by IR studies of pyridine sorption and implicitly from <sup>29</sup>Si MAS NMR investigations. Well-developed internal mesoporosity together with the retaining of Ti<sup>4+</sup> atoms in tetrahedral framework positions offered 7-fold higher catalytic activity for the conversion of cyclohexene molecules than the native microporous TS-1. The selectivity to epoxide reached the value of 96% for the most efficient mesoporous titanosilicate.

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### 1. Introduction

Among features responsible for unique catalytic properties, the MFI zeolite shows versatility towards isomorphous substitution of Al and/or Si atoms by metal ions such as B<sup>3+</sup>, Ga<sup>3+</sup> or Ti<sup>4+</sup> [1,2]. Thus, the MFI structure is an excellent starting point for the developing of the group of new zeotype catalysts where one of the most important materials is titanosilicalite (TS-1). The TS-1, synthesized for the first time in 1983 by Taramasso et al. [3], is a crystalline zeotype material, characterized by the presence of Ti<sup>4+</sup> replacing silicon atoms in framework positions. The presence of tetrahedrally coordinated titanium species implies high catalytic activity, thus TS-1 is widely applied to numerous oxidation reactions such as aromatic hydroxylation, cyclohexanone ammoxidation and alkene epoxidation using mild conditions [4,5]. However, the applicability of TS-1 in catalytic reactions involving large molecules is extremely limited by its narrow pore structure which impose the diffusional limitations, especially for the reaction

undergoing in liquid phase. Many efforts have been devoted to introduce intracrystalline mesoporosity into TS-1 structure in order to reduce the micropore environment restrictions, e.g. modified crystallization methods [6], hard [7] and soft [8] templating and demetalation [9,10]. In group of post-synthetic methods of modification of zeolitic materials one of the most effective and most economical seems to be desilication process. The desilication is identified with the process of selective extraction of silicon from the framework in the alkaline medium. The effectiveness of Si extraction from the framework depends on a number of parameters, including the value of Si/M ratio, framework topology, type and concentration of the desilication agent, temperature and time of process [11]. There is common agreement that titanium in the active catalyst is present in the tetrahedral environment, both in microporous (TS-1, TiBeta) and mesoporous (TiMCM-41) catalysts. Thus all modification approaches are focused on retaining of Ti atoms in tetrahedral environment.

The interaction of alcohols with oxide surfaces, in particular with SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, as well as with zeolites has been extensively investigated and reviewed by Knözinger [12] and others [13–15]. Regardless of the weak proton-donor character of the SiO<sub>2</sub> surface it has been found that, even at room temperature, a chemisorption of methanol led to the formation of the –OCH<sub>3</sub> methoxy groups [16].

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The esterification of the silanol groups was reported to be enhanced as the temperature increased and the  $\equiv\text{SiOCH}_3$  bond were resistant to temperatures of  $\sim 400^\circ\text{C}$  in vacuum or  $150^\circ\text{C}$  in air [17,18]. This work was attempted to show that the chemical treatment of TS-1 with alkaline medium resulted in the formation of intracrystalline mesoporosity. As the formation of methoxy species strongly modified the hydrophobicity of the surface such procedure was employed for the TS-1 material influencing its utility for desilication process especially with regard to retaining of tetrahedral or pseudo tetrahedral Ti atoms in TS-1 framework. Additionally, the textural and acidic characteristics were faced with catalytic data of cyclohexene epoxidation.

## 2. Experimental section

### 2.1. Catalyst preparation

A commercial titanium silicalite-1 (TS-1) from ACS Materials (Ti–Si Molecular Sieve; protonic form, Si/Ti  $\sim 30$ ) was used as a native material.

The post-synthesis treatment of TS-1 material was carried out according to two different procedures. First modification route was a typical desilication in (i) a solution of sodium hydroxide (NaOH) or (ii) mixture of NaOH and TBAOH (tetrabutylammonium hydroxide; Sigma-Aldrich, 40% solution).

Desilication of the native TS-1 was carried out in the solutions of 0.2 M NaOH or the mixtures of 0.2 M NaOH and 0.2 M TBAOH at  $65^\circ\text{C}$  for half an hour. For the mixture of TBAOH/(NaOH + TBAOH) ratio was 0.4. The 100 ml of solution was added to 3.0 g of titanium silicalite-1. After desilication suspension was cooled down in ice-bath, filtered and washed with distillate water until neutral pH. Subsequently, all studied samples were ion-exchanged to the ammonium form by fourfold treatment with 0.5 M  $\text{NH}_4\text{NO}_3$  at  $60^\circ\text{C}$  for 1 h. Finally, the achieved materials were again filtrated, washed and dried at room temperature.

Another modification was aimed to increase hydrophobicity of native TS-1 material by methanol ( $\text{CH}_3\text{OH}$ ; Sigma Aldrich, 99% anhydrous) treatment. The 20 ml of  $\text{CH}_3\text{OH}$  was added to 6.0 g of TS-1 and vigorously stirred at  $70\text{--}80^\circ\text{C}$  for 60 h until the evaporation of the liquid phase. The resulting methanol-treated material M-TS was immediately contacted with NaOH solution and desilicated according to the procedure described above. The notation of all samples and information on modification conditions are summarized in Table 1.

### 2.2. Characterization methods

The powder X-ray diffraction (XRD) measurements were carried out using a PANalytical Cubix diffractometer, with  $\text{CuK}_\alpha$  radiation,  $\lambda = 1.5418 \text{ \AA}$  and a graphite monochromator in the  $2\theta$  angle range of  $5\text{--}50^\circ$ . Powder X-ray patterns were used for structural

identification of the relative crystallinity value (%Cryst) for all TS-1 materials. The determination of the relative crystallinity value was based on the integral intensity of the characteristic peaks in the range between  $22^\circ$  and  $26^\circ$ .

Si and Ti concentrations in all studied TS-1 materials were determined by the ICP OES method with an Optima 2100DV (PerkinElmer) spectrometer.

The  $\text{N}_2$  sorption processes at  $-196^\circ\text{C}$  were studied on an ASAP 2420 Micromeritics after activation in vacuum at  $400^\circ\text{C}$  for 12 h. Surface Area ( $S_{\text{BET}}$ ) and micropore volume ( $V_{\text{micro}}$ ) were determined by applying the BET and  $t$ -plot methods, respectively. Pore size distribution and volume of mesopores ( $V_{\text{meso}}$ ) were obtained by applying the BJH model to the adsorption branch of the isotherm. The mesopore surface area ( $S_{\text{meso}}$ ) was calculated in the range between 2 and 30 nm with BJH model and it denotes external surface area.

The STEM micrographs were obtained using transmission electron microscope (JEOL 2100F UHR) working at 200 KV, with Field Emission Gun (FEG), EDX analysis and STEM detectors for bright and dark mode.

The solid state  $^{29}\text{Si}$  MAS NMR spectra were acquired on an APOLLO console (Tecmag) at the magnetic field of 7.05 T (Magnex). The  $3 \mu\text{s}$  rf pulse ( $\pi/2$  flipping angle) was applied, 4 kHz spinning speed, and 256 scans with the delay of 40 s were acquired. The frequency scales in ppm were referenced to TMS. The spectra were normalized to the same mass of sample.

The diffuse reflectance (DR) UV–vis spectra were measured on a Jasco V-550 UV–vis spectrophotometer with a  $\text{BaSO}_4$  plate as the reference.

Prior to the FTIR study all samples were pressed into the form of self-supporting wafers (ca.  $5\text{--}10 \text{ mg cm}^{-2}$ ) and pre-treated in situ in homemade quartz IR cell at  $450^\circ\text{C}$  under vacuum conditions for 1 h. Pyridine (Avantor Performance Materials Poland S.A.) and carbon monoxide (Linde Gas, 99.95%) were used as adsorbates. The CO adsorption was performed at  $-100^\circ\text{C}$ . The pyridine (Py) was adsorbed at  $170^\circ\text{C}$ . The concentration of Brønsted and Lewis acid sites was determined in quantitative IR studies of pyridine adsorption, according to the procedure given in Refs. [19,20]. The values of  $0.110 \text{ cm}^2/\mu\text{mol}$  and  $0.061 \text{ cm}^2/\mu\text{mol}$  were obtained for the  $1450 \text{ cm}^{-1}$  band of pyridine coordinatively bonded to Lewis sites (PyL) and for the  $1545 \text{ cm}^{-1}$  band of pyridinium ion ( $\text{PyH}^+$ ), respectively. The IR spectra were recorded with a Bruker Tensor 27 spectrometer equipped with a MCT detector. The spectral resolution was  $2 \text{ cm}^{-1}$ .

### 2.3. Catalytic tests

Catalytic studies were performed using cyclohexene (99%, Sigma-Aldrich) as substrate and hydrogen peroxide as the primary oxidant. Before the reaction, the solid was dried overnight at  $110^\circ\text{C}$  to remove adsorbed moisture. The reactions were performed in a

**Table 1**  
Treatment conditions and sample notation.

Sample	Sample symbol	Treatment conditions
Native	TS	Native H-form
Desilicated with NaOH	TS/NaOH	The 3 g of native TS-1 was modified with 100 ml of 0.2 M NaOH at $65^\circ\text{C}$ for 30 min. Fourfold ion exchange with 0.5 M $\text{NH}_4\text{NO}_3$ at $60^\circ\text{C}$ for 1 h.
Desilicated with NaOH&TBAOH	TS/ NaOH&TBAOH	The 3 g of native TS-1 was modified with 100 ml of 0.2 M NaOH&TBAOH at $65^\circ\text{C}$ for 30 min. Fourfold ion exchange with 0.5 M $\text{NH}_4\text{NO}_3$ at $60^\circ\text{C}$ for 1 h.
Treated with $\text{CH}_3\text{OH}$	M-TS	The 6 g of native TS-1 was modified with 20 ml of $\text{CH}_3\text{OH}$ at $70\text{--}80^\circ\text{C}$ , for 60 h. Fourfold ion exchange with 0.5 M $\text{NH}_4\text{NO}_3$ at $60^\circ\text{C}$ for 1 h.
Treated with $\text{CH}_3\text{OH}$ /desilicated with NaOH in $65^\circ\text{C}$	M-TS/NaOH	The 3 g of methanol-treated TS-1 was modified with 100 ml of 0.2 M NaOH at $65^\circ\text{C}$ , for 30 min. Fourfold ion exchange with 0.5 M $\text{NH}_4\text{NO}_3$ at $60^\circ\text{C}$ for 1 h.

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