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REGULAR ARTICLE

Synthesis and characterization of hierarchical titanium-containing silicas using different size templates

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Abstract. The development of hierarchical catalytic heterogeneous catalytic systems with a controlled micro/mesopore ratio is an important issue in catalysis. The main purpose of the paper is to the establish influence of the size of the template molecule on the main characteristics of hierarchical titanium-containing silicas (H-TS). The H-TS were successfully synthesized by a bi-template method using tetrapropylammonium hydroxide (TPAG) as permanent template of MFI topology and tetramethylammonium bromide (TMAB), tetraethylammonium bromide (TEAB), tetrabutylammonium hydroxide (TBAG), dodecyltrimethylammonium bromide (DTMAB), cetyltrimethylammonium bromide (CTAB), didecyldimethylammonium chloride (DDAC), tetradecylbenzyldimethylammonium bromide (TBDAB) as variable structure-directing agent (SDA) of a different size. The structure and morphology were characterized by X-ray diffraction, a Fourier transform infrared spectroscopy, a Raman spectroscopy, a scanning electron microscopy and low-temperature nitrogen adsorption-desorption. The catalytic properties of the prepared titanium-containing micro-mesoporous silicas for hydroxylation of phenol with H_2O_2 have been evaluated, and their activities have been compared with those of TS-1 with only micropores. The findings of the research illustrate that with an increase in the molecule volume of the structure-directing agent, there is a decrease in the proportion of the crystalline phase and in the degree of the inclusion of Ti^{4+} atoms in the structure of the zeolite material. Increase in the volume of the structure-directing agent leads to the decrease of the crystallinity of the samples and decrease in the specific surface area of the material and in the specific volume of micropores. The result of this research will be used to create a theoretical model of controlled micro-/mesoporous ratio in silicas and it may open new perspectives for their potential application in selective oxidation reactions involving large molecules.

Keywords. Hierarchical silica; titanium silicalite; bi-template synthesis; mixed templates.

1. Introduction

Selective oxidation of organic compounds into targeted products using 'green' oxidizing agents is a priority for catalysis. Despite numerous achievements and discoveries in the area of oxidation processes, unsustainable methods for producing oxygenated compounds still persist in the industry. Generally, manufacturers rely on acids and soluble metal complexes as catalysts for their processes, both of which involve increased energetic and economic costs for their isolation and recovery processes, as well as the formation of significant amounts of waste.[1] The lack of universally heterogeneous catalyst systems, being of considering steric, and other factors is the main reason for the complete abandonment of the use of homogeneous catalysts.[2]

Zeolite materials are the most relevant catalytic systems in the field of oxidation of organic compounds. Zeolites are crystalline substances with a developed internal system of pores and channels, which are regularly repeated in three-dimensional space.[3] The availability and variety of the primary components needed for the synthesis of zeolite materials makes it possible to obtain materials with the necessary properties and structure.[4]

A genuine breakthrough in the field of liquid-phase oxidation was made by a microporous titanium silicalite (TS-1), developed by the company Enichem in 1986. Due to the titanium centers in its structure, this catalyst allows selectively and under mild conditions to oxidize secondary alcohols into ketones,[5] alkanes into alcohols,[6] epoxidation alkenes and unsaturated acids,[7,8] etc., using an 'environment-friendly' hydrogen peroxide oxidizer. However, the use of TS-1 is severely limited due to its microporosity and is only suitable for substrates with a kinetic size of up to 6 Å (linear alkanes and olefins). Therefore, the problem of selective oxidation of large organic molecules remains. Thereby, the creation of catalysts with an extensive network of pores is required.

An attempt to solve this problem was made in the 1990s by developing mesoporous catalytic systems based on materials MCM-41 and MCM-48 containing titanium atoms and other transition metals in the crystalline structure.[10,11] Despite the significant advantage of the diffusion of large molecules in mesoporous silicate materials, their catalytic activity is lower than that of microporous ones.[12] Therefore, in the last fifteen years, there has been increased development in the synthesis methods of zeolite materials with a hierarchical structure, which apart from micropores also have an additional material treatment system formed by meso and/or macropores.

The most common method for creating large pores in zeolite materials consists of the partial destruction of the structure. However, such a method leads to a chaotic formation of pores of uncontrolled size a significant material loss.[13–18]

An innovative solution is the direct template synthesis of catalyst systems.[19–23] The use of various structure directing agents at the stage of synthesis of zeolite material followed by removal through ignition makes it possible to achieve a uniform and controlled distribution of pores which is vital for diffusing processes occurring in the catalyst grain.

In this work, we prepared hierarchical titanium-containing silicas with micro-mesoporous structure by the dual-templating method. We used the SDA different size for regulation micro-, mesoporous ratio. The catalytic activity of the materials in the hydroxylation of phenol is reported and compared with that of a conventional TS-1 sample.

2. Experimental

2.1 *Materials*

The chemicals and reagents used for the synthesis were obtained from commercial sources. Tetrapropylammonium hydroxide (TPAOH) (1M in H_2O), tetramethylammonium bromide (TMAB) (98%), tetraethylammonium bromide (TEAB) (98%), tetrabutylammonium hydroxide (TBAOH) (40% wt. in H_2O), dodecyl trimethylammonium bromide (DTMAB) (98%), cetyltrimethylammonium bromide (CTAB) (98%), titanium butoxide (TBOT) (97%) were purchased from Merck. Didecyldimethylammonium chloride (DDAC) (95%) was procured from Supelco. Tetradecylbenzyldimethylammonium bromide (TBDAB) (50% wt. in H_2O) was procured from Vecos. Tetraethoxysilane (TEOS) (99%), phenol (99%), hydrogen peroxide (36.5%), titanium dioxide (anatase) (98%) were procured from Vekton. All the chemicals were of analytical grade and were used as obtained without further purification.

2.2 *Synthesis of hierarchical titanium silicas*

Samples of the titanium-containing silicas were synthesized by the dual-templating method using mixed structure-directing agents. We used two structure-directing agents, where TPAOH acted as a permanent structure-directing agent (SDA) and TMAB, TEAB, TBAOH, DTMAB, CTAB, DDAC, TBDAB as variable templates. The synthesis of micro-mesoporous titanium silicalites was carried out according to the following procedure. An exact amount of TEOS was loaded in a temperature-controlled glass reactor with a capacity of 100 mL. The reactor was purged with nitrogen to create an inert atmosphere and, with stirring, an exact amount of TBOT was introduced. The resulting mixture was cooled to the temperature of about 1.0 °C. Then, with vigorous mixing, the calculated amounts of templates and deionized water were added. The final stoichiometric composition of micro-mesoporous titanium silicalites samples had the following form of $SiO_2 : 0.02TiO_2:0.5TPAG:0.5X:50H_2O$, where X = TMAB, TEAB, TBAOH, DTMAB, CTAB, DDAC, TBDAB. By comparison, the titanium silicalite was synthesized by the same method without a variable template; the silicalite-1 was synthesized by the same method without TBOT and variable template.

The obtained gel-sol was subjected to hydrothermal treatment in a steel autoclave with a volume of 250 mL at 170 °C for 50 h.

The crystallized titanium silicalite was separated from the mother liquor, washed with deionized water to neutral pH and dried at 120 °C and the residual pressure of

40–60 mm Hg, and then calcinated in the air for 6 h at 550 °C.

2.3 *Characterization of the samples*

Fourier-transform infrared (FTIR) spectra were recorded in the $400-4000\,cm^{-1}$ range on an FTIR spectrometer Shimadzu IRAffinity-1 using the KBr pellet technique. X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-7000 with Cu-K α radiation (40 kV, 50 mA) in the range 2 teta of 6° and 50° with the angular step size of 0.02°.

The specific surface area and volume pore of the samples were determined by nitrogen adsorption-desorption measurements at 77 K on the nitrogen adsorption apparatus Sorbi-MS. Before the measurements, the samples were outgassed at 110 °C in vacuum for 1 h. The specific surface area was calculated using method Brunauer-Emmett-Teller (BET). The volume of the micropores and the surface of the mesopores were determined by the Bour-Lippens (STSA) method.

The scanning electron microscopy (SEM) was performed on the scanning electron microscope JEOL JSM-IT300LV with an accelerating voltage of 20 kV.

Raman spectra were recorded by using a NTEGRA Spectra instrument equipped with laser line 473 nm. Laser power was kept at 3.6 mW.

For calculating molecule volume, there was used a method developed at Molinspiration.[24]

2.4 *Hydroxylation of phenol*

The liquid-phase catalytic reaction was performed in a 50 mL two-necked glass reactor fitted with a water condenser at 60 °C under vigorous stirring. A typical reaction involves 2.4 mmol of the substrate, 0.8 mmol of H_2O_2, 38.0 mL H_2O and 0.2050 g samples H-TS. The progress of the reaction was monitored by analyzing the products obtained at different intervals through the capillary gas chromatograph (Chromos GH-1000, VB-5 30 m x 0.32 mm columns with flame ionization detector). The products were identified by GC–MS (Shimadzu GCMS-QP2020) splitting pattern. The concentration of residual H_2O_2 was determined by an iodometric titration with sodium thiosulphate (0.1 N) in the presence of starch as an indicator. The aliquot of the samples was withdrawn during the reaction and was quickly subjected to titration.

3. Results and Discussion

3.1 *Molecule volume*

The samples of micro-mesoporous titanium-containing silicate materials were obtained by the method of direct synthesis using structure-directing agents of various volume. The volume of the template molecule was

Table 1. The volume of the template molecule.

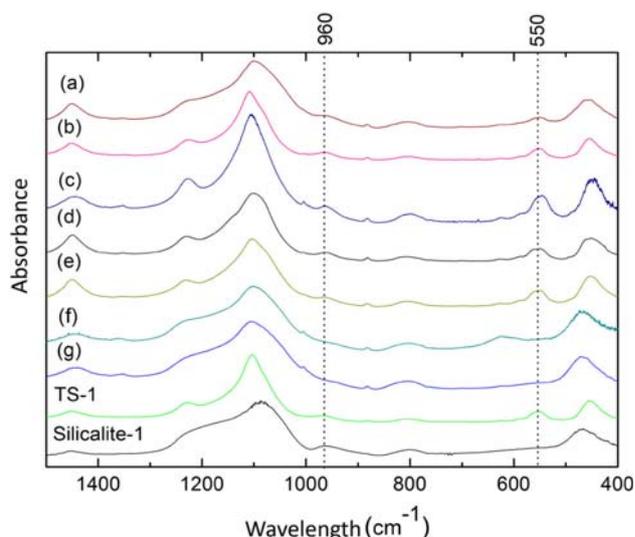| Template	Molecule volume (nm^3)
TMAB	0.0951
TEAB	0.1623
TPAG	0.2295
TBAG	0.2967
DTMAB	0.2799
CTAB	0.3471
TBDAB	0.3684
DDAC	0.3975

Figure 1. The fragment of the infrared spectrum of the samples. a – TMAB, b – TEAB, c – DTMAB, d –TBAOH, e – CTAB, f – TBDAB, g – DDAC.

calculated using the program.[24] The results of the calculation are shown in Table 1.

3.2 *FT-IR analysis*

In the infrared spectrum of the obtained materials, the absorption bands characteristic of titanium silicates are observed: $\nu_{as}(Si-O-Si)$ at $1040-1080\,cm^{-1}$, $\nu(Si-O-Ti)$ and $\delta(Si-O-Ti)$ at $960-980\,cm^{-1}$, $\nu_s(Si-O-Si)$ at $810\,cm^{-1}$ and $\delta(Si-O-Si)$ at $435\,cm^{-1}$, $(Si-O-Ti)$ and $(Si-O-Si)$ at $540-550\,cm^{-1}$.[25] For a rough estimate of the feeding rate of Ti^{4+} atoms in the framework of zeolite material, the ratio of the peak intensities at $960\,cm^{-1}$ and $550\,cm^{-1}$ (I960/I550) was used. Figure 1 shows the infrared spectrum of the obtained samples.

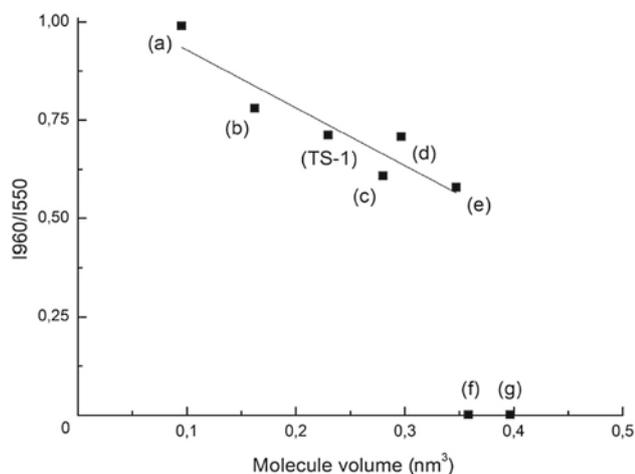Figure 2 shows the graph of the inclusion of Ti^{4+} ions in the frame samples.

Figure 2. The graph of the inclusion of Ti^{4+} ions in samples according to the template molecule volume. a – TMAB, b – TEAB, c – DTMAB, d –TBAOH, e – CTAB, f – TBDAB, g – DDAC.
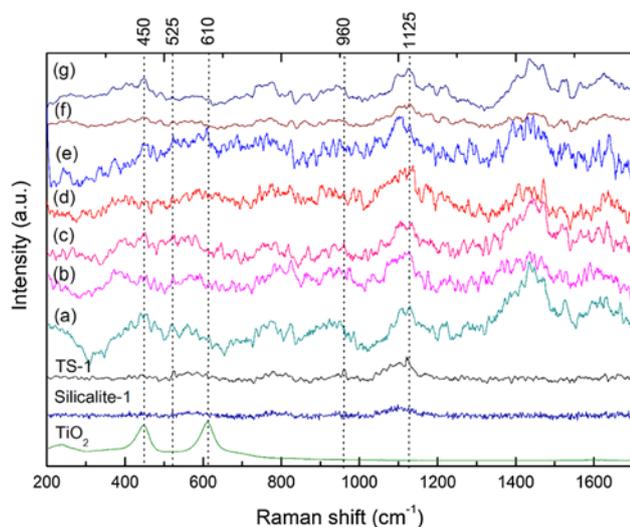

Figure 4. XRD pattern of samples a – TMAB, b – TEAB, c – DTMAB, d –TBAOH, e – CTAB, f – TBDAB, g – DDAC.

Figure 3. Raman spectra of samples H-TS (a-g), anatase (TiO$_2$), silicalite-1 and TS-1. a – TMAB, b – TEAB, c – DTMAB, d –TBAOH, e – CTAB, f – TBDAB, g – DDAC.

Figure 5. The graph of crystallinity on the template molecule volume. a – TMAB, b – TEAB, c – DTMAB, d –TBAOH, e – CTAB, f – TBDAB, g – DDAC.

It was found that an increase in the size of the template leads to a decrease in the degree of inclusion of Ti^{4+} ions. Probably, this dependence is due to the fact that when using a template with a small molecule size, a denser 'packing' of crystals occurs, leading to the fact that the structure contains more titanium atoms per unit volume, in contrast to crystals with mesopores.

3.3 *Raman spectroscopy*

Raman spectra of the samples H-TS are shown in Figure 3. The spectra of the H-TS samples were compared with anatase (TiO$_2$), silicalite-1 and TS-1.
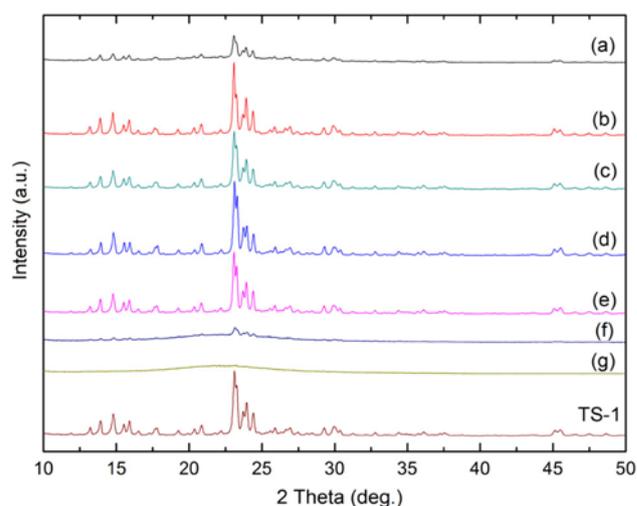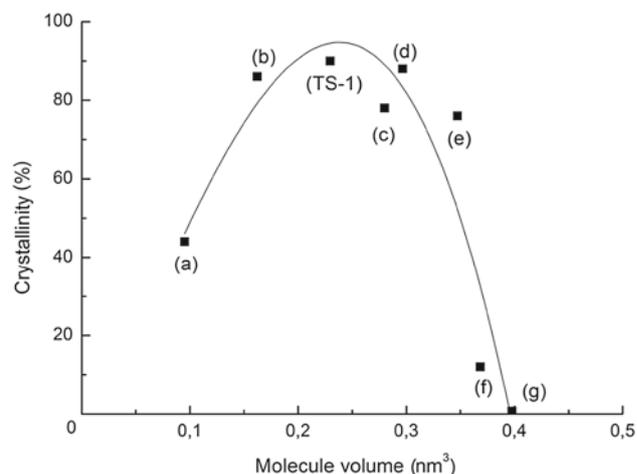
The characteristic bands of TiO$_2$ at 473 nm are 230, 450, 610 cm^{-1}. For TS-1, 525–530, 960, 1125 cm^{-1} are considered. These bands are associated with framework Ti and it doesn't attribute to silicalite-1. The first band (525−530 cm^{-1}) assigned to the symmetric stretching vibration of framework Ti–O–Si species. Both the 960 and 1125 cm^{-1} bands attribute to the Ti^{4+} active sites of TS-1.[26–28]

From the data obtained it could be concluded that samples (a–e) contain titanium in the form of isolated atoms in the crystal structure of the silicalite material with small amounts of anatase. In the samples with TBDAB and DDAC templates is predominantly in the form of TiO$_2$, as indicated by the absence of absorption bands at 960 and 1125 cm^{-1}.

Table 2. Textural data of the samples.

Samples	Second template	$S_{BET}(m^2/g)$	$V_{micro}(cm^3/g)$	$S_{meso}(m^2/g)$
TS-1	-	349.5	0.156	9.1
a	TMAB	171.7	0.072	13.7
b	TEAB	338.5	0.136	47.1
c	DTAB	289.2	0.106	58.5
d	TBAG	319.2	0.145	6.0
e	CTAB	264.3	0.105	34.0
f	TBDAB	120.3	0.026	61.3
g	DDAC	102.9	0.004	92.7

3.4 *XRD analysis*

Figure 4 illustrates the powder XRD patterns of samples. The MFI (TS-1) crystal structure appears on the radiograph in the form of several intense peaks in the region of the average angles $2\theta = 7$ to $50°$, which characterize the crystal structure of the orthorhombic unit cell TS-1.[29]

The sorted peaks of the samples (a) and (f) (Figure 4) have a low intensity which indicates low crystallinity of the structure, and in the case of the sample (g), full amorphousness of material is observed.

We can see that the nature of the spectrum of sample 2 in the region $2\theta = 45°-45.5°$ is slightly different from the others. The presence of a more intense peak of $2\theta = 45°$ in the $45.0°$ and $45.5°$ doublet indicates the presence of an orthorhombic crystal structure MEL. It was found that in sample (b) there are two types of crystal structures MFI and MEL with the phase ratio MEL/MFI of 40.9/59.1. Only the MFI crystal structure was found in the other samples.

Figure 5 indicates the dependency of crystallinity on the template molecule volume. It was found that with an increase of the volume of the template, the fraction of the crystal phase in the samples decreases. The use of TMAB led to the formation of a structure with low crystallinity and probably the use of this structure-forming component affects the method of particle aggregation during crystal growth.

3.5 *Textural properties*

The combination of meso- and microporosity was proven by nitrogen adsorption-desorption. Textural properties are summarized in Table 2.

It has been discovered that with an increase of the volume of the structure-directing agent molecule, the specific surface area of the material, as well as the specific volume of micropores, decrease. This is explained by the fact that large molecules of the template form larger mesopores, which leads to a decrease in the total surface area due to the presence of voids. Confirming this theory, the surface area of mesopores naturally increases. However, the use of tetramethylammonium ion as a template leads to the formation of a nonporous or supermicroporous system due to poor coordination of the template and precursors of silicon and titanium.

Figure 6 indicates two types of pore size distributions. Samples (a), (b), (e), (f) and (g) there are wide distribution of pores without prevailing pore size. Samples (c) and (d) show the relatively narrow distribution of pores with peaks centered on 27 nm, 141 nm (c) and 41 nm, 140 nm (d).

3.6 *Morphology study by SEM*

The SEM images in Figure 7 are consistent with the XRD data discussed above.

SEM images depict a change in the shape of crystals of H-TS samples with varying templates. It can be concluded that the increase in the size of SDA sterically hinders the uniform growth of a symmetric crystal, which leads to the formation of structures with a chaotic size and the decrease in crystallinity.

3.7 *Catalytic test*

Table 3 presents the results of the catalytic performance of the synthesized H-TS using H_2O_2 as the oxidant in the hydroxylation of phenol.

Among the synthesized H-TS materials, sample (c) shows the highest performance in the hydroxylation of phenol reaction due to the optimal volume of the mesopore and relatively high crystallinity. The substrate conversions are 10,93% and dihydroxybenzene (hydroquinone (HQ) and catechol (CAT)) selectivity are 59,57% which are larger than those other samples H-TS and TS-1.
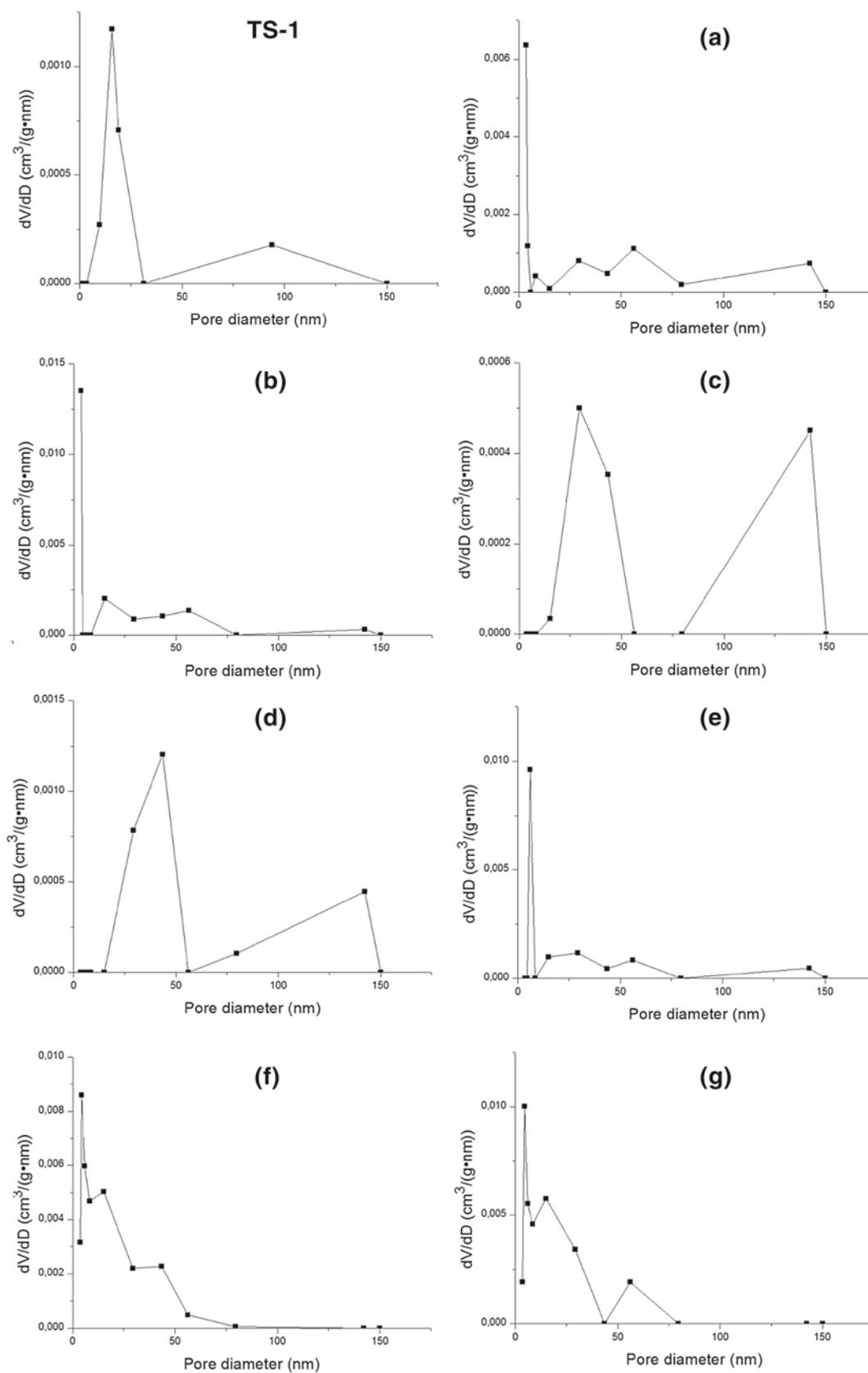
Figure 6. The graph of pore distribution in the samples a – TMAB, b – TEAB, c – DTMAB, d –TBAOH, e – CTAB, f – TBDAB, g – DDAC.
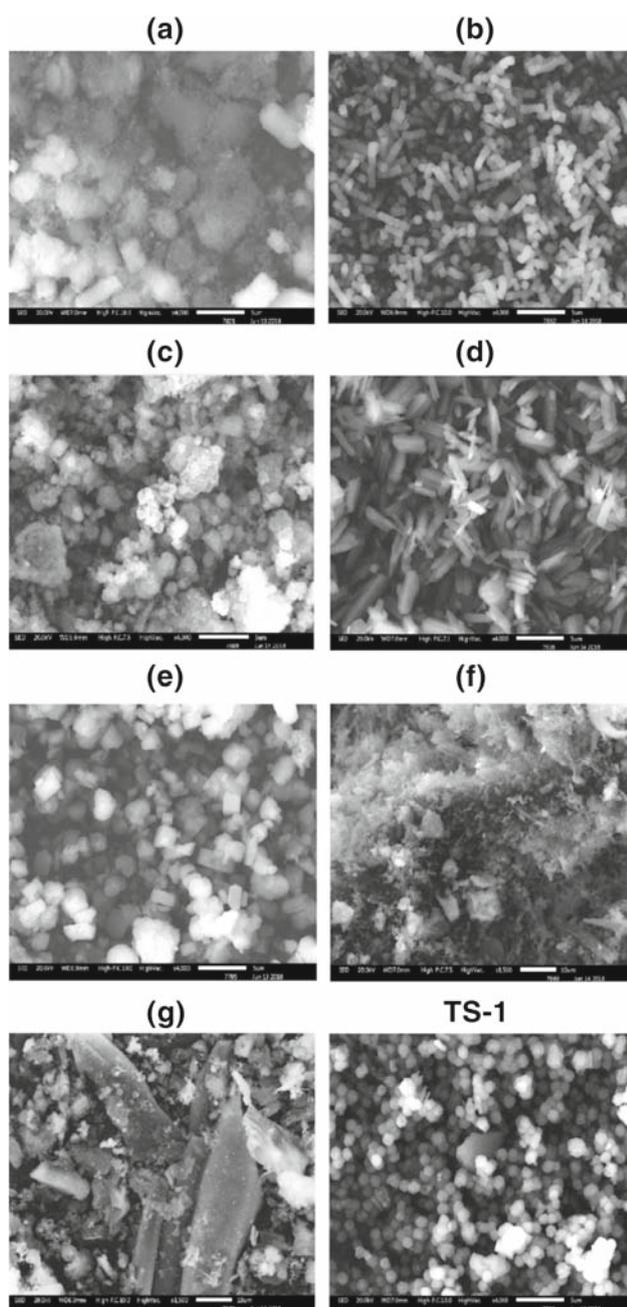
Figure 7. SEM image of samples a – TMAB, b – TEAB, c – DTMAB, d –TBAOH, e – CTAB, f – TBDAB, g – DDAC.

As for samples (a), (b), (c), their lower framework crystallinity and lower external surface area cause their inferior catalytic performance. From the data obtained it could be observed that the size of the secondary template allows changing the composition of the reaction products in a fairly wide range. This fact confirms the hypothesis that using a certain combination of SDA, it is possible to obtain the desired reaction products.

4. Conclusions

In summary, hierarchical titanium-containing silicas were successfully synthesized using dual templates: TPAG with TMAB, TEAB, TBAOH, DTAB CTAB, DDACl, TBDAB. The hierarchical structure of the as-synthesized samples was confirmed by the XRD and low-temperature nitrogen adsorption. The catalytic activity of the samples was successfully studied in the reaction of phenol hydroxylation.

It was discovered that with an increase of the size of the molecule of the template, the decrease in the proportion of the crystalline phase and in the degree of inclusion of Ti^{4+} atoms in the structure of the zeolite material are observed; with the increase in the size of the SDA, the crystallinity of the samples decreases; the increase in the volume of the molecule of the template leads to the decrease in the specific surface area of the material and in the specific volume of micropores. It was found that the size affects the size and shape of the resulting zeolite crystals.

Supplementary Information (SI)

All additional information related to characterization H-TS using FT-IR (Figure S1, Figure S2), XRD pattern (Figure S3, Figure S4), SEM (Figure S5) are given in the supplementary information available at www.ias.ac.in/chemsci.

Table 3. Phenol hydroxylation of over various catalysts.

Samples	Second template	Conv. phenol (%)	Product selectivity (%)		
			HQ	CAT	BQ
TS-1	-	10.65	34.06	29.89	5.10
a	TMAB	3.64	0.08	2.04	5.89
b	TEAB	8.95	14.58	20.69	13.04
c	DTAB	10.93	17.05	29.22	13.30
d	TBAG	9.93	12.33	21.43	14.05
e	CTAB	4.74	2.65	20.79	21.32
f	TBDAB	2.22	0.06	0.75	2.70
g	DDAC	1.16	1.16	1.28	3.88

Acknowledgements

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