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Titanium-Doped Solid Core-Mesoporous Shell Silica Particles: Synthesis and Catalytic Properties in Selective Oxidation Reactions

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Abstract Near monodisperse spherical particles composed of a nonporous silica core covered by a Ti-doped hexagonally arranged mesoporous silica shell, Ti-SCMS, as well as spherical submicron-size particles of Ti-MCM-41, have been synthesized for the first time and characterized by elemental analysis, N_2 adsorption, XRD, TEM and DR-UV spectroscopy. The mesoporous Ti,Si-shell has a thickness of about 45 nm and incorporates isolated Ti centers in tetrahedral coordination. Catalytic properties of Ti-SCMS and Ti-MCM-41 have been studied in selective oxidation of three representative bulky organic substrates, 2,3,6-trimethylphenol, methyl phenyl sulfide and caryophyllene, with aqueous H_2O_2 in MeCN medium. Ti-SCMS appeared to be more active and selective in the H_2O_2-based selective oxidation reactions compared to Ti-MCM-41, thus demonstrating an advantage of conducting a catalytic process in a thin mesoporous Ti,Si-shell.

Keywords Core-shell structure · Monodisperse silica particles · Site-isolated Ti centers · Selective oxidation · H_2O_2

1 Introduction

There is an everlasting conviction that a blend of different synthetic approaches can lead to new results in acquiring materials with new properties. Nowadays, this is one of the main trends in nanoscience and nanotechnology. As long ago as 1968, Stöber and co-workers worked out an approach to the synthesis of monodisperse nonporous spherical SiO_2 particles, the size of which could be varied in a micron range from 0.1 to 2 μm [1]. In 1992, Mobil company presented MCM-41 family of highly ordered mesoporous materials with high surface area and uniform structure of mesopores-channels [2]. This type of materials has attracted great attention due to a wide range of potential applications in catalysis, chromatography, adsorption, drug release, chemical and biochemical sensor and analytical application, nanocomposites, etc. [3–10].

Recently, these two approaches were combined to prepare monodisperse hybrid spherical SiO_2 particles consisting of a solid nonporous core covered by a well-ordered mesoporous silica shell with a uniform thickness [11]. Such a well-organized mesoporous structure, having not only a regular diameter of pores-channels but also a uniform, easily tuned length of the channels, cannot be accomplished using traditional MCM preparation routes. Hence, this is an attractive approach for designing novel heterogeneous catalysts for selective transformations of

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bulky organic molecules because uniform size of mesopores ensures regular conditions of molecular mass transfer, which could be crucial for both catalytic activity and selectivity.

However, the transformation of a mesoporous material to a catalytically active one requires application of a third, subnanometer-scale approach to introduce an active component and to achieve a homogeneous distribution of spatially well separated catalytic sites within an inert matrix [12]. Syntheses of mesostructured titanium-silicates, such as Ti-MCM-41 [13, 14], Ti-HMS [15], Ti-TUD-1 [16], Ti-MMM-2 [17] and some other, can serve as an example of the successful utilization of such an approach. These materials have attracted considerable attention as catalysts for selective oxidation of bulky organic substrates using green oxidant—aqueous hydrogen peroxide [18–24].

In this work, we applied the three nanotechnological approaches—on micro, nano and subnano levels—to synthesize for the first time near monodisperse spherical silica particles with a solid inert core covered by a hexagonally arranged titanium-silicate mesoporous shell, Ti-SCMS. We also prepared spherical submicrometre-size particles of Ti-MCM-41. Both materials were characterized with physicochemical techniques, and their catalytic properties were assessed in selective H_2O_2-based oxidation of three bulky substrates relating to different classes of organic compounds.

2 Experimental

2.1 Materials

Cetyltrimethylammonium bromide from Acros (CTAB, 99+%) was used as structure directing agent. Tetraethylorthosilicate Aldrich (TEOS, 98+%) was used as SiO_2 precursor. Titanium (IV) isopropoxide from Aldrich was used as titanium source. 2,3,6-Trimethylphenol (TMP) and methyl phenyl sulfide (MPS) were purchased from Fluka and used without additional purification. (−)-Caryophyllene (CP, >99%) was isolated from the oil of *Eugenia caryopyllata* by vacuum rectification. Aqueous ammonia (28%) was purchased from Sigma. Acetonitrile (Fluka) was dried and stored over activated 4A molecular sieves. All other reactants were obtained commercially and used without further purification. The concentration of hydrogen peroxide (~30% in water) was determined iodometrically prior to use.

2.2 Catalyst Synthesis

The synthesis of Ti-SCMS was carried out by a two-step one-pot route adapting the procedure described for Ti-free core-shell silica particles [11]. To prepare near monodisperse solid beads, TEOS was added to the solution containing ethanol and aqueous ammonia and stirred for 6 h at room temperature. The molar composition of the suspension was as follows: $TEOS:EtOH:NH_3:H_2O = 1:70.1:2.1:19.5$. To form a mesoporous shell around the preliminarily prepared cores, the resulting suspension was diluted with water and a solution of CTAB in water/ethanol = 2:1 (v/v) was added under vigorous stirring. After 30 min, an extra portion of TEOS and titanium isopropoxide, modified with acetylacetone (acac) to prevent titanium agglomeration to TiO_2-like species, was added dropwise, and the suspension was additionally stirred for 16 h at ambient temperature. The resulting molar composition was: $TEOS:EtOH:NH_3:H_2O:CTAB:Ti(OiPr)_4:acac = 1:54.9:1.46:339:0.086:0.0062:0.0125$. The as-synthesized particles were isolated by centrifugation, redispersed by means of ultrasonic irradiation in distilled water, centrifuged again and dried under ambient conditions. The dry composite material was calcined for 1.5 h at 250 °C and then 4 h at 550 °C in air in order to remove the structure-directing agent (CTAB) from the mesoporous shell. The resulting material was designated as Ti-SCMS.

The synthesis of Ti-MCM-41 particles was carried out according to the method analogous to modified Stöber route [25]. To synthesize Ti-MCM-41 submicron-size particles, a solution of CTAB in water/ethanol = 2:1 (v/v) was added under vigorous stirring to the solution containing absolute ethanol, aqueous ammonia and water. After 30 min, TEOS and titanium isopropoxide modified with acetylacetone (acac) were added dropwise simultaneously, and the reaction mixture was stirred for 16 h at room temperature. The resulting molar composition was: $TEOS:EtOH:NH_3:H_2O:CTAB:Ti(O^iPr)_4:acac = 1:187.3:5:1157:0.3:0.021:0.042$. The as-synthesized particles were isolated by centrifugation and dried at ambient conditions. The dry material was calcined for 1.5 h at 250 °C and then 4 h at 550 °C in air.

2.3 Characterization

The freshly calcined samples of Ti-SCMS and Ti-MCM-41 were studied by means of low angle powder XRD using VEPP-3 synchrotron radiation source. Nitrogen adsorption isotherms were measured using ASAP-2400 instrument (Micromeritics) at 77 K. Textural characteristics were calculated using the previously reported comparative method [26]. Average mesopore diameters were estimated by means of the combined adsorption—XRD approach reported elsewhere [26, 27]. Transmission electron microscopic (TEM) images were obtained using JEM-2010 electron microscope (JEOL, Japan). The average size of particles was determined from TEM images by averaging diameters of more than 100 particles. Local elemental analysis was performed by EDX method using an energy-dispersive X-ray Phoenix spectrometer EDAX equipped with a Si (Li) detector with an energy resolution not worse than 130 eV. Titanium state in the catalysts was probed by DR-UV spectroscopic technique (Shimadzu UV-VIS 2501 PC) under ambient conditions.

2.4 Catalytic Tests

Catalytic oxidation with H_2O_2 was performed under vigorous stirring (500 rpm) in thermostated glass vessels. The rate of substrate consumption remained constant when the stirring rate varied in the range of 200–1,000 rpm, indicating no external diffusion limitation. Typical reaction conditions were as follows: TMP, 0.1 M; H_2O_2, 0.35 M; Ti 0.006 mmol; MeCN, 1 mL, 80 °C, 30 min; MPS, 0.1 M; H_2O_2, 0.12 M; Ti 0.002 mmol; MeCN, 1 mL 20 °C, 30 min and CP, 0.1 M; H_2O_2, 0.1 M; Ti 0.002 mmol; MeCN, 1 mL 50 °C, 2 h. Samples of the reaction mixture were withdrawn periodically during the reaction course by a syringe through a septum. Each experiment was reproduced 4–6 times. The oxidation products were identified by GS-MS and ^{1}H NMR. Product yields and substrate conversions were quantified by GC using internal standard.

3 Results and Discussion

3.1 Ti-Doped Solid Core-Mesoporous Shell Particles

The XRD pattern of a typical Ti-SCMS sample is shown in Fig. 1. It clearly exhibits a relativly sharp most intensive primary (100) reflection along with weak, poorly resolved higher order (110) and (200) reflections, indicating that the material has a hexagonal structure [28]. Unfortunately, it is hard to estimate the degree of order from the reflection pattern since the thickness of mesoporous layer is small and broardening of the reflexes can have different origins, namely it can be caused by reflection from curved channels (disordered hexagonal packing) or by reflection from ordered but small regions. The XRD pattern of solid cores, which were peaked out at the first step of synthesis, is also given in Fig. 1. One can see that the cores do not possess any ordered long period structure, and therefore, the observed reflections appear due to the mesoporous shell.

The nitrogen adsorption–desorption isotherm of Ti-SCMS is presented in Fig. 2a. It has a IV type shape according to IUPAC nomenclature which is characteristic of mesoporous materials and reveals no hysteresis loop in the region of mesopores filling. The narrow interval of relative pressure $\Delta(P/Po) = 0.08$, within which the nitrogen capillary condensation occurs, agrees with a narrow pore size distribution (Fig. 2b). For the sake of comparison, the nitrogen adsorption-desorption isoterm of solid cores is given in Fig. 2a. No doubt, the isotherm is characteristic of a non-porous material. The surface area of the cores is

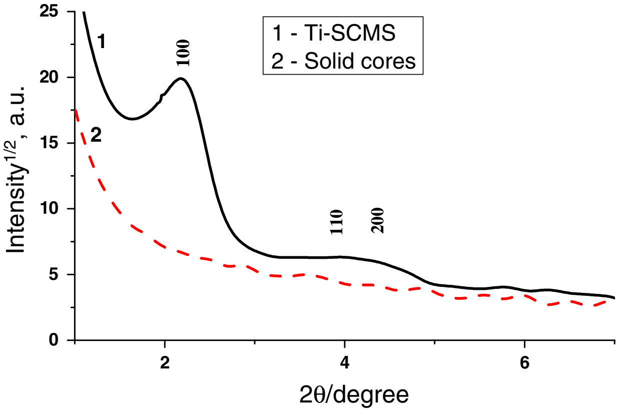


Fig. 1 XRD patterns of Ti-SCMS and solid cores

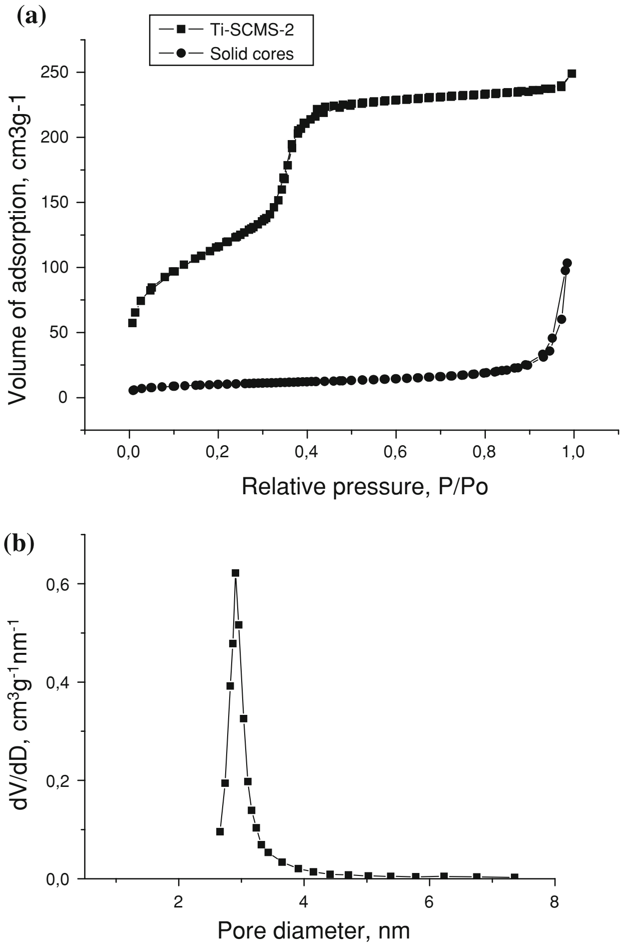


Fig. 2 (**a**) Nitrogen adsorption–desorption isotherms for Ti-SCMS and solid cores and (**b**) pore size distribution for Ti-SCMS

Table 1 Textural and stuctural characteristics of Ti-SCMS and Ti-MCM-41

Catalyst	Ti content (wt.%)	Structural parameters		Textural parameters			
		a_0^a (nm)	FWHM[b] (2θ degs)	A_{me}^c (m^2/g)	A_{ext}^d (m^2/g)	V_{me}^e (cm^3/g)	D_{me}^f (nm)
Ti-SCMS	0.3 (1.6)[g]	4.63	0.3	406	19	0.34	3.2
Ti-MCM-41	2.4	3.77	0.7	1375	105	0.76	3.0

[a] Unit cell parameter; [b] Full width at half maximum of the (100) reflection; [c] Specific mesopore surface area; [d] Specific external area; [e] Mesopore volume; [f] Mesopore diameter; [g] Ti content in mesoporous shell

36 m^2/g that corresponds to a submicrometer particles size. Typical textural and structural characteristics of Ti-SCMS are given in Table 1 along with Ti content determined by elemental analysis. The values of the specific surface area and pore volume of the Ti-SCMS material are close to the corresponding characterictics of the pure siliceous material reported ealier [11]. Hence, the results acquired from N_2 adsorption measurements together with the XRD data strongly support the formation of a material of the MCM-41 type with hexagonal arrangement of mesopores-channels. The diameter of mesopores in Ti-SCMS can be varied by altering the structure directing agent as well as by employing a special hydrothermal treatment. This work is in progress in our group.

The TEM images of the Ti-SCMS material are shown in Fig. 3a. One can see spherical particles of a uniform size consisting of a nonporous core and a mesoporous shell with channels oriented perpendicularly to the core surface. The hystogram of particles size distribution (Fig. 3b) confirms near monodispersity of the obtained core-shell particles of Ti-SCMS. The thickness of the shell was estimated to be 45 nm, while the average particle diameter equals to 510 nm. The thickness of the mesoporous shell and the avarage particle diameter of Ti-SCMS are in good agreement with the respective parameters of the Ti-free core-shell particles [11].

EDX spectra taken from two regions are shown in Fig. 4. The root spectrum corresponds to the particle center and gives the value of bulk wt.% of Ti in the sample, while the tip spectrum belongs to mesoporous shell and gives wt.% of Ti in the shell. The bulk amount of Ti (0.3 wt.%) obtained by EDX agrees with the data of elemental analysis (0.3 wt.%). In turn, the amount of titanium in the shell (1.6 wt.% according to EDX) is consistent with the amount of Ti-precursor which was added at the second step of the synthesis. Thus the local elemental analysis performed by EDX confirmed that entire titanium is located within the mesoporous shell.

The DR-UV spectrum of the freshly calcined sample of Ti-SCMS containing totally 0.3 wt.% of Ti (1.6 wt.% in the shell) is presented in Fig. 5. It shows a rather sharp band with a maximum centered at 210 nm. According to the literature, this band is attribured to oxygen to Ti(IV) charge transfer transitions and indicates the presence of site-isolated, most likely, tetra-coordinated titanium atoms [14–16, 29, 30].

3.2 Ti-MCM-41 Spherical Particles

Ti-doped MCM-41-type shperical particles were synthesized under basic conditions using low sufractant concentration. TEOS was used as SiO_2 sourse and aqueous ammonia was used as catalyst. This procedure gives spherical silica particles with radial pore arrangement, in contrast to the reported dilute solution route [31] which produces nanosized elongated spherical particles with hexagonally ordered parallel channels.

The TEM microphotograph of the Ti-MCM-41 material revealed sherical particles with the radial pores arrangement and the size between 100 and 250 nm (Fig. 6).

The XRD pattern of the Ti-MCM-41 material prepared in this work is shown in Fig. 7. The spectrum exibits only relatively sharp primary (100) peak with FWHM = 0.7, no higher order reflections. This may be caused by cylindrical channels bend and twist, without preferred direction, close to the particle core [32]. It contrasts with XRD patterns of nanoparticles with parallel channels which typically exibit three diffraction peaks [31].

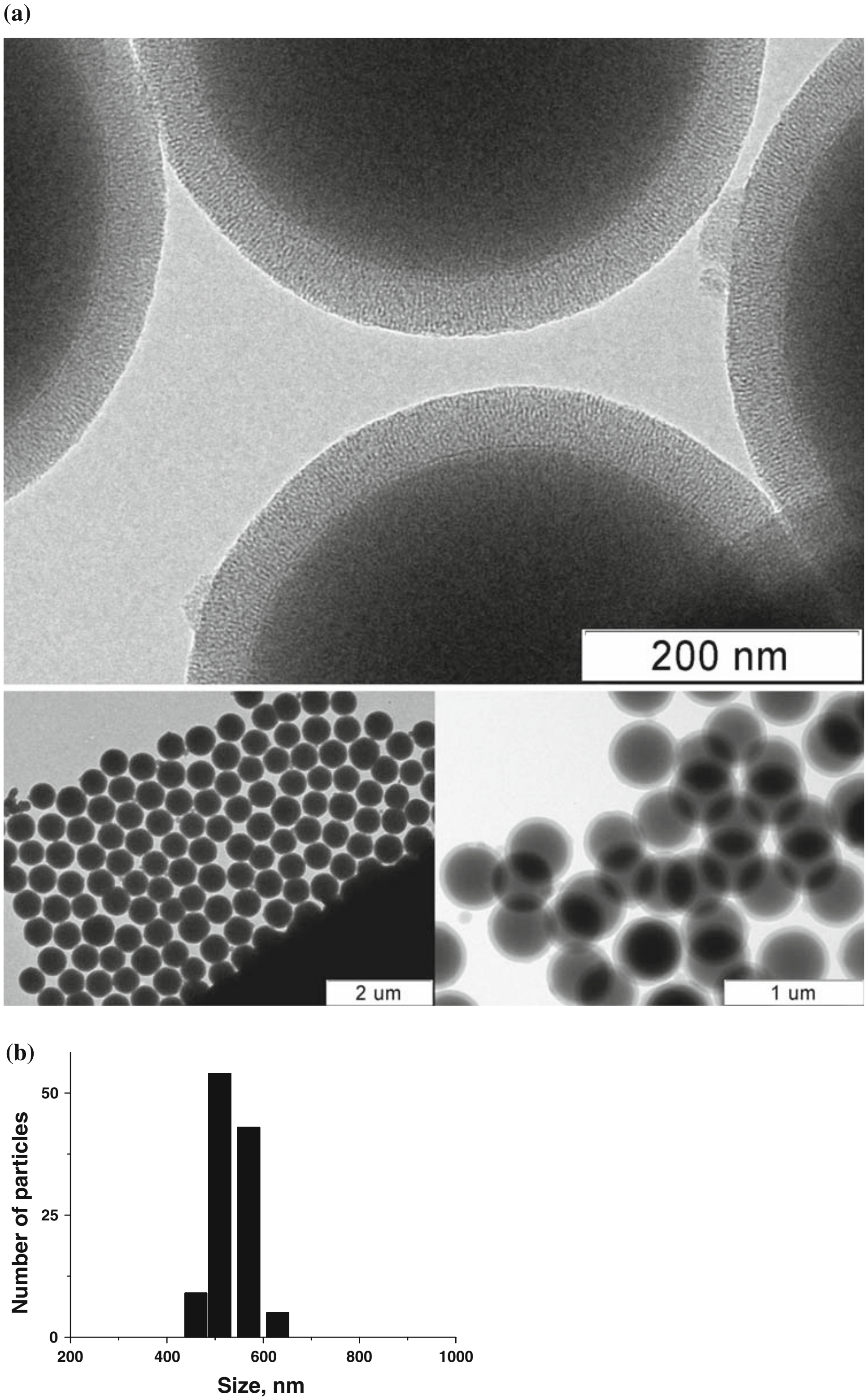
The typical adsorption isotherm of the calcined Ti-MCM-41 sample is presented in Fig. 8. N_2 adsorption–desorption isoterm corresponds to the IV type showing sharp inflection at the relative pressure $P/P_0 > 0.2$. The textural and structural characteristics of this material along with the elemental analysis data are given in Table 1. Both XRD and N_2 adsorption data are consistent with the formation of the hexagonally packed mesoporous structure in the Ti-MCM-41 particles.

The DR-UV spectrum is typical of Ti-MCM-41 and shows a band with a maximum centred at 230 nm which is attributed to site-isolated titanium species (Fig. 5) [14].

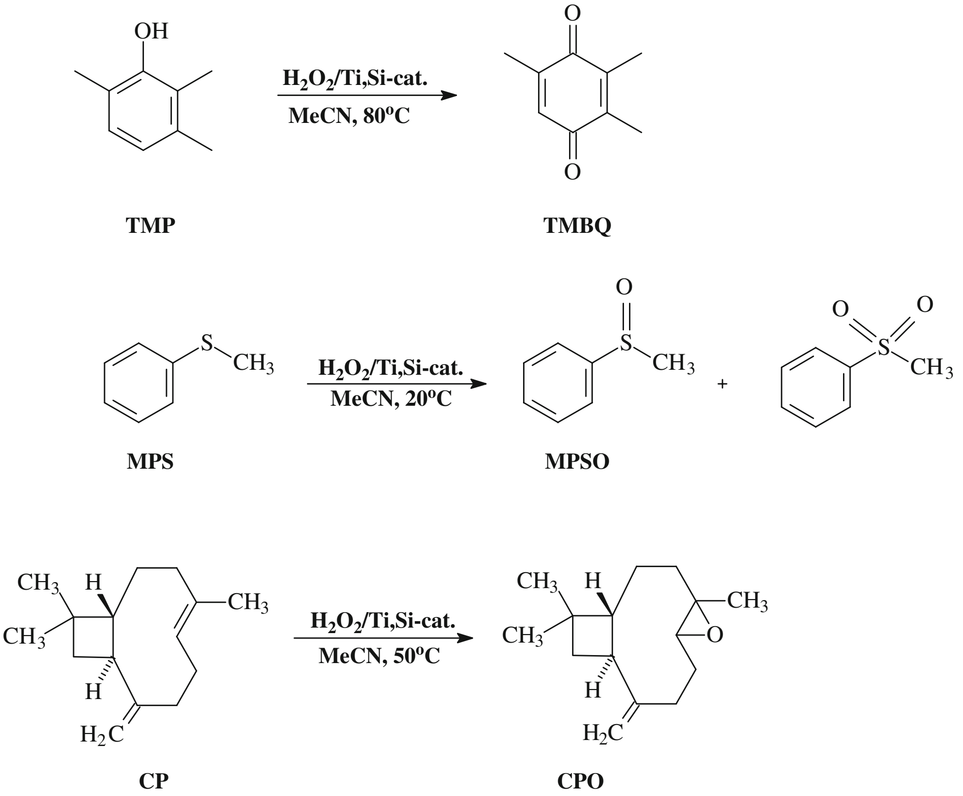
3.3 Catalytic Results

Catalytic properties of the Ti-SCMS and Ti-MCM-41 materials were examined in H_2O_2-based oxidation of three representative organic substrates, 2,3,6-trimethylphenol

Fig. 3 TEM images of Ti-SCMS



(TMP), methyl phenyl sulfide (MPS) and (−)-caryophyllene (CP).



The results of the catalytic tests are presented in Table 2. The oxidation reactions produce the corresponding quinone, sulfoxide and epoxide, which are useful intermediates in fine chemicals synthesis. Thus TMP oxidation yields 2,3,5-trimethyl-1,4-bezoquinone (key intermediate in the synthesis of Vitamin E [33]), while oxidation of the natural terpene CP gives caryophyllene oxide, which has been approved by FDA as a food and cosmetic stabilizer [34]. The main by-products were 2,2′,3,3′,5,5′-hexamethyl-4,4′-biphenol, methyl phenyl sulfone and diol in the oxidation of TMP, MPS and CP, respectively.

One can judge from the data presented in Table 2 that the catalytic performance of Ti-SCMS is superior to that of the Ti-MCM-41 submicrometre-size particles. For all the substrates, the catalytic activity related to Ti active centre (TOF) determined from the initial rates of the substrate consumption was about twice as high as the activity feasible with Ti-MCM-41. Furthermore, Ti-SCMS allows one to attain higher substrate conversions compared to Ti-MCM-41. The larger the substrate molecule, the more pronounced the difference in the achievable substrate conversion. While 60% conversion of caryophyllene was observed over Ti-SCMS, only 14% of this substrate was converted in the presence of Ti-MCM-41 under the same reaction conditions. This may be explained by a better mass transfer conditions implemented in the short channels of the Ti-SCMS mesoporous shell compared to the longer and radially arranged channels of the Ti-MCM-41 spherical particles. Yet, it is reasonable to anticipate that the time of the attendance of the primary oxidation products (or intermediates) inside pores should be lower in short channels and this might supress the processes leading to by-products, such as overoxidation (MPS), di/polymerization (TMP) and hydrolysis (CP), and thus increase the selectivity. Indeed, we found better selectivities with respect to the target products for Ti-SCMS compared to Ti-MCM-41 (see Table 2). Again, the more pronounced difference in selectivities over these two catalytic materials was observed for the formation of caryophyllene oxide, which is known to be extremely prone to epoxide ring opening.

4 Conclusions

Near monodisperse spherical silica particles consisting of a non-porous core covered by a titanium-silicate mesoporous shell (thickness of 45 nm) with hexagonal structure as well as spherical submicron-size particles of Ti-MCM-41 have been synthesized and characterized for the first time. The Ti-SCMS material revealed better catalytic performance in liquid phase H_2O_2-based oxidation of bulky organic

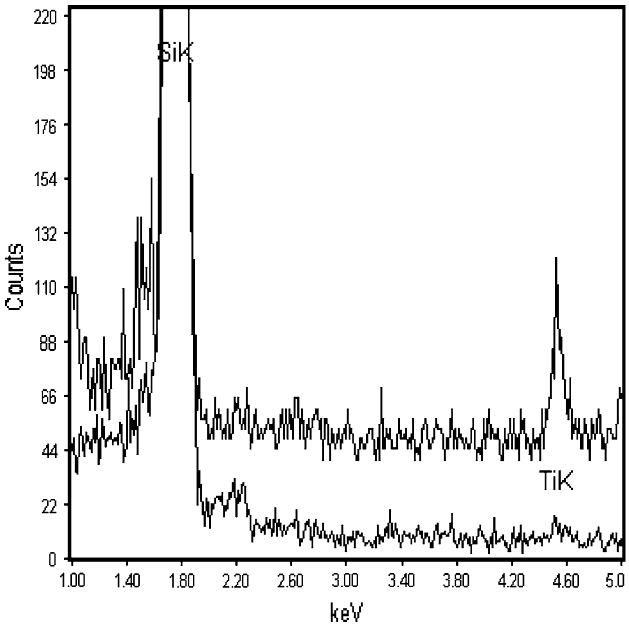


Fig. 4 EDX spectra for the mesoporous shell (tip line) and for the center of particle (root line). Spectra are normalized to the maximum peak (SiK)

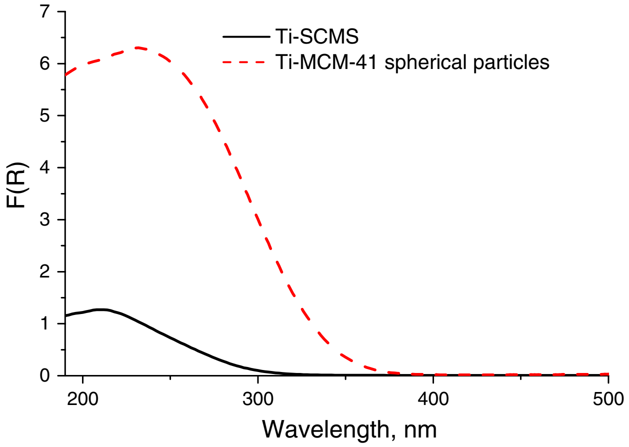
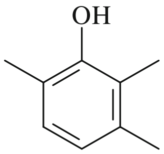
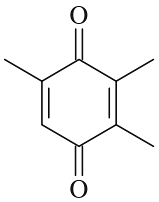
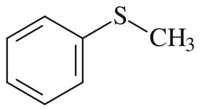
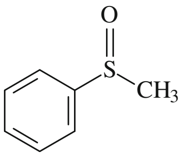
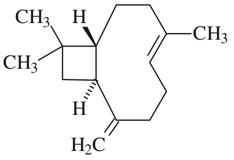
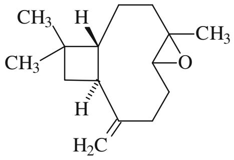


Fig. 5 DR-UV spectrum of Ti-SCMS containing totally 0.3 wt.% of Ti and Ti-MCM-41 spherical particles

Table 2 Selective oxidations with H_2O_2 over Ti-SCMS and Ti-MCM-41 catalysts[a]

Catalyst	Substrate	Substrate conversion (%)	Product	Selectivity[b] (%)	TOF[c] (min^{-1})
Ti-SCMS		99		77	2.5
Ti-MCM-41		92		72	1.2
Ti-SCMS		100		77	15.7
Ti-MCM-41		75		73	8.7
Ti-SCMS		60		60	0.5
Ti-MCM-41		14		43	0.2

[a] Reaction conditions are given in the Experimental; [b] GC yield based on the substrate consumed; [c] TOF = (moles of substrate consumed)/(moles of Ti) × (time); determined from the initial rates of substrate consumption

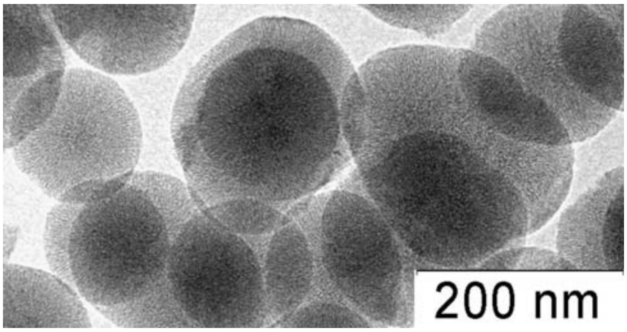


Fig. 6 TEM image of Ti-MCM-41 submicron-size particles

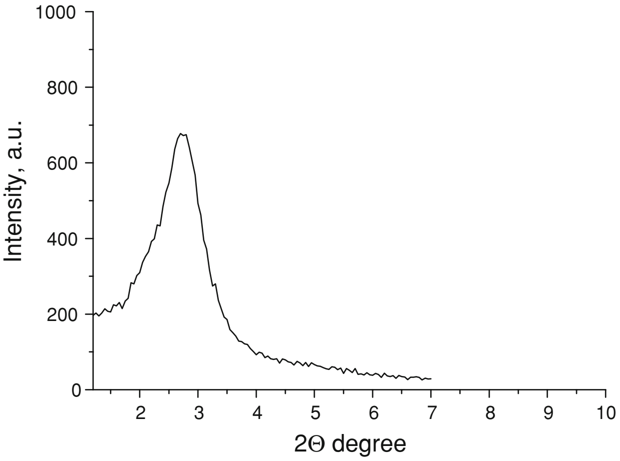


Fig. 7 XRD pattern of Ti-MCM-41

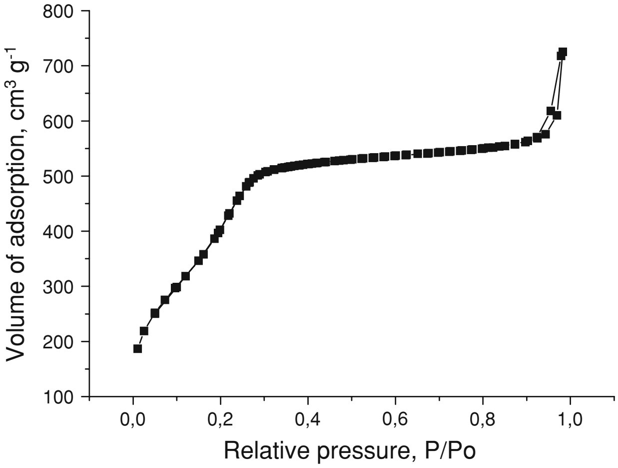


Fig. 8 Nitrogen adsorption–desorption isotherm for Ti-MCM-41

substrates compared with the Ti-MCM-41 submicron-size particles, demonstrating advantages of conducting a catalytic process in a thin mesoporous Ti,Si-shell.

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