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A new mesoporous titanium-silicate Ti-MMM-2: a highly active and hydrothermally stable catalyst for H_2O_2-based selective oxidations

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Abstract

Physicochemical characterisation and catalytic properties of a new hydrothermally stable mesoporous mesophase titanium-silicate, denoted as Ti-MMM-2, synthesised under moderately acidic conditions are reported. Structure and texture were characterised by using X-ray diffraction, N_2 adsorption and TEM. The state of titanium was characterised using DRS-UV and XANES techniques. Catalytic properties of Ti-MMM-2 were tested in oxidation of three large organic substrates, 2,3,6-trimethylphenol, caryophyllene and methyl phenyl sulfide, and compared with catalytic properties of TS-1 and Ti-MMM (titanium-silicate of the MCM-41-type synthesised under weakly alkaline conditions). The catalytic activity of Ti-MMM-2 is considerably higher compared to the activity of microporous TS-1 and similar to that of Ti-MMM. The performed physicochemical study implicated that Ti-MMM-2 combines marked accessibility of titanium and its high dispersion that ensure high catalytic activity of this material. By contrast to Ti-MMM, Ti-MMM-2 is hydrothermally stable and can be used repeatedly without deterioration of catalytic properties. A blend of high catalytic activity and hydrothermal stability allows to consider Ti-MMM-2 as a promising catalyst for the selective oxidation of large organic molecules with aqueous H_2O_2.

Keywords: Ti-MMM-2; Hydrothermal stability; Selective oxidation; H_2O_2

1. Introduction

The selective oxidation of organic compounds with an environmentally friendly oxidant, aqueous H_2O_2, in the presence of heterogeneous, easily recyclable catalysts is a challenging goal of fine chemistry [1–3]. Critical targets for catalytic technology using H_2O_2 are larger-pore analogues of titanium-silicate TS-1 [4]. In the past decade, a considerable amount of research was dedicated to the preparation of various titanium-containing mesoporous molecular sieves [5–12]. Nevertheless, the problem of catalyst deactivation in the presence of aqueous H_2O_2 still restricts practical applications of these materials [2,4,9–11].

Recently, we reported that the mesoporous mesophase material, Ti-MMM (highly ordered titanium-silicate of the MCM-41-type synthesised under weakly alkaline conditions), shows high activity in H_2O_2-based oxidation of bulky organic substrates [12–14]. Meanwhile, hydrolytic instability of this material leads to a structure collapse during the oxidation process, which in turn results in a decrease of the catalytic activity after recycling [12–14]. It has been reported that mesoporous silicates of the SBA-15 family synthesised under strong acidic conditions possess a hydrothermal stability [15–17]; however, introduction of a heteroelement into the silicate matrix under strong acidic conditions is problematic [8,16,17]. Recently, we reported the preparation of Ti-SBA-15 under weakly acidic conditions [18]. This material showed stable catalytic properties but the activity was rather low because of thick silicate walls and poor titanium dispersion. Here, we present physicochemical and catalytic properties of the new highly active and hydrothermally stable mesoporous titanium-silicate, denoted as Ti-MMM-2, synthesised under moderately acidic conditions.

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2. Experimental

2.1. Materials

2,3,6-Trimethylphenol (TMP), methyl phenyl sulfide (MPS), (−)-caryophyllene (CP) and cetyltrimethyl ammonium bromide (CTAB) were purchased from Fluka and used without additional purification. A solution of $TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$ (Aldrich) was used as received. Hydrogen peroxide (30%) was determined iodometrically prior to use. All the other reactants were obtained commercially and used without further purification.

2.2. Catalyst synthesis and characterisation

TS-1 (Si/Ti = 30, DRS-UV: $\lambda_{max} = 204$ nm) was prepared according to Ref. [19]. Ti-MMM (Si/Ti = 49) was synthesised as described in Ref. [12]. Ti-MMM-2 (Si/Ti = 46) was synthesised according to the procedure which generally included mixing of three solutions. The first solution consisted of 6.5 g of CTAB dissolved in 108 g of water. The second was 2.7 g of 0.5 M $TiOSO_4$. The third was 4.1 g of $Na_2Si_2O_5$ in 133 g of water. All three solutions were clear and transparent. The solutions were mixed and the final pH was adjusted to 3.0 using 4 M HCl. The mixture was kept overnight under ambient conditions and then hydrothermally treated at 50 °C for 24 h. The resulted precipitate was filtered off, washed, dried in air at 120 °C and calcined at 600 °C. Structure and texture characteristics were determined from synchrotron XRD patterns and nitrogen adsorption isotherms (77 K) according to Refs. [20,21]. To estimate the hydrothermal stability, Ti-MMM-2 was treated with boiled water for 6 h or with aqueous 30% H_2O_2 (15 mg Ti-MMM-2, 0.11 M H_2O_2, 3 ml MeCN, 25 °C, 1 h), dried in air and calcined at 500 °C before all measurements.

2.3. Catalytic experiments

Catalytic experiments were performed in thermostatic glass vessels under vigorous stirring at 20, 50 and 80 °C for oxidation of MPS, CP and TMP, respectively. Typically, the substrate concentration was 0.1 M and the catalyst amount was 15–31 mg. The H_2O_2 concentration was 0.12, 0.10 and 0.35 M for oxidation of MPS, CP and TMP, respectively. Acetonitrile (3 ml) was used as a solvent. The oxidation products were identified by GC–MS and ^1H NMR and quantified by GC. After the reactions, catalysts were filtered off, washed with methanol, dried, calcined in air at 500 °C for 1–2 h and then re-used. The leaching tests were performed as described earlier [12–14]. H_2O_2 consumption was determined by iodometric titration.

2.4. Instrumentation

GC analyses were performed using a gas chromatograph "Tsvet-500" equipped with a flame ionisation detector. Quartz capillary columns, 35 m × 0.3 mm filled with SE-54, 15 m × 0.3 mm filled with SE-30 and 25 m × 0.3 mm filled with Carbowax 20 M, were used for analyses of MPS, CP and TMP oxidation products, respectively. GC–MS analyses were conducted using a gas chromatograph Saturn 2000 equipped with a mass spectrometer CP-3800. ^1H NMR spectra were recorded on an MSL-400 Bruker spectrometer. The XRD measurements were performed on a URD-6 diffractometer with parallel beam ($\lambda = 0.154178$ nm) mounted on a channel of the VEPP-3 synchrotron radiation source at Siberian Synchrotron Radiation Center (SSRC). DRS-UV measurements were performed on a Shimadsu UV-Vis 2501PC spectrophotometer. The XANES spectra (fluorescent mode) of the Ti–K edge were obtained at the EXAFS Station at SSRC as described in Ref. [18].

3. Results and discussion

The physicochemical characteristics of Ti-MMM-2 are summarised in Table 1. According to XRD (Fig. 1) and nitrogen adsorption, the material has an ordered hexagonal arrangement of uniform mesopores with a diameter of $d = 3.2$ nm and silicate wall thickness $h = 1.0$ nm. Ordered mesopores are observed on the TEM image of Ti-MMM-2 (insert in Fig. 1). However, it should be mentioned that in general the structure of Ti-MMM-2 is less ordered compared to Ti-MMM and Ti-SBA-15, which is indicated by a larger value of the full-width-at-half-maximum of the (1 0 0) reflection observed for Ti-MMM-2 (Table 1). According to the comparative analysis of nitrogen adsorption, Ti-MMM-2 has no micropores and possesses high internal and low external surface areas. The corresponding comparative plot in the pressure range of $0.05 < P/Po < 0.3$ was linear and clearly extrapolated to origin. The silicate wall of Ti-MMM-2 is comparable with that of Ti-MMM but thinner than that of

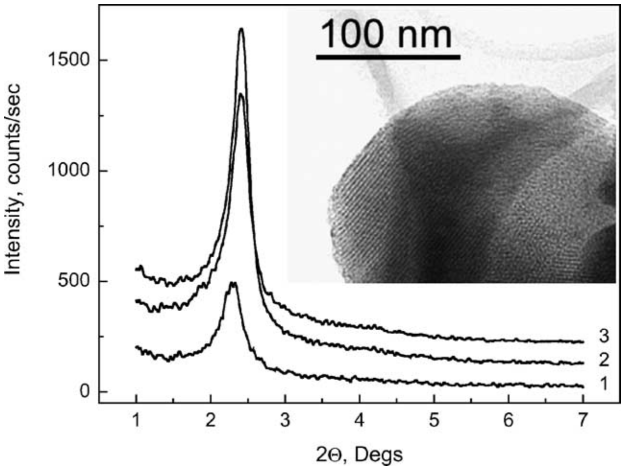


Fig. 1. X-ray diffraction patterns for Ti-MMM-2: (1) as-synthesised (with surfactant in pores), (2) calcined and (3) calcined after treatment with boiled water. The insert presents a TEM image of the calcined Ti-MMM-2 sample.

Table 1
Physicochemical properties of Ti-MMM-2

Sample no.	wt.% Ti (Si/Ti atomic ratio)	pH of synthesis	DRS-UV $\lambda_{\max}$ (nm)	Textual parameters					Structural parameters	
				A_{Me}[a] (m^2/g)	A_{ext}[b] (m^2/g)	V_{Me}[c] (cm^3/g)	d_{Me}[d] (nm)	h_{W}[e] (nm)	a_0[f] (nm)	FWHM[g], 2θ (°)
Ti-MMM-2	1.67 (46)	3.0	211	1147	51	0.74	3.2	1.0	4.2	0.36
1[h]			211	1069	50	0.65	3.2	1.0	4.2	0.30
2				1054	62	0.67	3.3			
4				1064	63	0.68	3.3			
8				1039	59	0.63	3.2			
Ti-MMM [12]	1.53 (49)	9.0	218	1059	53	0.908	3.8	0.8	4.6	0.078
Ti-SBA-15 [18]	2.05 (38)	3.2	248	573	30	1.34	10.6	1.7	12.2	0.054

[a] Total specific surface area.
[b] Specific external surface area.
[c] Specific mesopore volume.
[d] Mesopore diameter.
[e] Wall thickness calculated from the equation $a_0 = d_{\mathrm{Me}} + h_{\mathrm{W}}$.
[f] Unit cell parameter.
[g] Full-width-at-half-maximum of the (1 0 0) reflection.
[h] The number corresponds to the number of treatments of the Ti-MMM-2 sample with boiled water.

Ti-SBA-15 (Table 1). The appropriate mesopore diameter and the silicate wall thickness ensure a good accessibility of titanium for reactants. In sharp contrast to Ti-MMM [12–14], both structure and texture of Ti-MMM-2 remained unchanged after treatment with boiled H_2O (Fig. 1, Table 1).

The absorption frequency in DR-UV spectra of titanium-silicates depends on the coordination number of Ti(IV) and its dispersion in the silicate matrix [2,5]. The transition frequency at $\lambda_{\max} = 208$ nm, observed for anhydrous TS-1, serves as an indicative of the isolated tetrahedrally coordinated Ti sites [2]. After adsorption of water, four-fold-coordinated titanium transforms to a five- and six-fold-coordinated one. This reflects in shifting the UV-maximum to 215–220 nm. Further shifting to 250–270 nm indicates the appearance of partially oligomerised titanium species [2,5]. A narrow band with a maximum at 211 nm, observed in DR-UV spectrum of Ti-MMM-2 (Fig. 2), clearly signifies that titanium is mostly in a site-isolated form. Importantly, no long-wave shift of the maximum was observed after treatment with boiled water or aqueous H_2O_2, which is in sharp contrast to Ti-MMM and TiO_2–SiO_2 mixed oxides [13,14]. Note that the question about the titanium environment in mesoporous titanium-silicates is still under debates. Many authors attribute the transitions centred at 210–230 nm to 5-6-coordinated Ti(IV) [2,5], while few authors trend to 4-coordinated (probably, distorted) Ti(IV) [22,23].

The DRS-UV data are in agreement with XANES data obtained for Ti-MMM-2 (insert in Fig. 2). Analysis of the pre-edge peaks and features of the XANES Ti–K edge spectrum studied as a “fingerprint” [2,24–26] tends to indicate that Ti is isolated and mostly 5- to 6-coordinated. Thus, the performed physicochemical study implicated that Ti-MMM-2 combines marked accessibility of titanium and its high dispersion that ensure high catalytic activity of this material in selective oxidations with aqueous H_2O_2.

The oxidation of MPS, CP and TMP with H_2O_2 in the presence of Ti-MMM-2 afforded methyl phenyl sulfoxide (MPSO), caryophyllene 4,5-monoepoxide (CPO) and 2,3,5-trimethyl-1,4-benzoquinone (TMBQ) as the main oxidation products. The activity of Ti-MMM-2 was similar to that of Ti-MMM (Table 2) and considerably higher

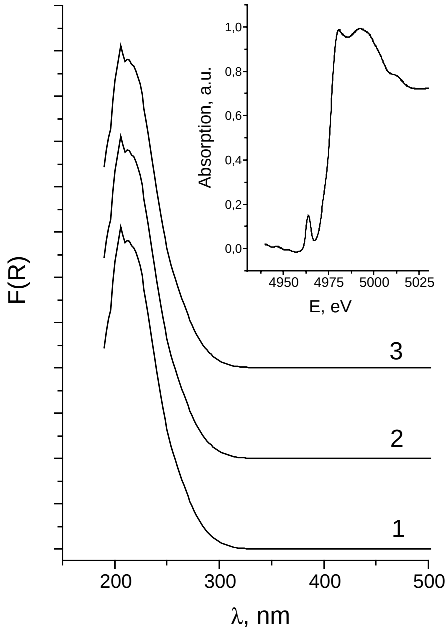


Fig. 2. DR-UV spectra for Ti-MMM-2: (1) before treatment, (2) after treatment with boiled water and (3) after treatment with 30% H_2O_2 in MeCN. The insert presents a XANES spectrum of the calcined Ti-MMM-2 sample.

Table 2
Catalytic properties of Ti-MMM-2

Catalyst (mg)	Conversion (%)	TOF[a] (h^{-1})	Yield[b]
MPS oxidation[c]			
Ti-MMM-2 (14)	98	100	75% MPSO
Ti-MMM (19)	99	85	74% MPSO
TS-1 (11)	29	25	15% MPSO
CP oxidation[d]			
Ti-MMM-2 (14)	75	11	52% CPO
Ti-MMM (19)	70	9	56% CPO
TS-1 (11)	16	2	5% CPO
TMP oxidation[e]			
Ti-MMM-2 (31)	100	66	81% TMBQ
Ti-MMM (41)	100	55	77% TMBQ
TS-1 (25)	7	4	4% TMBQ

[a] TOF: moles of substrate consumed/(moles of Ti × h).

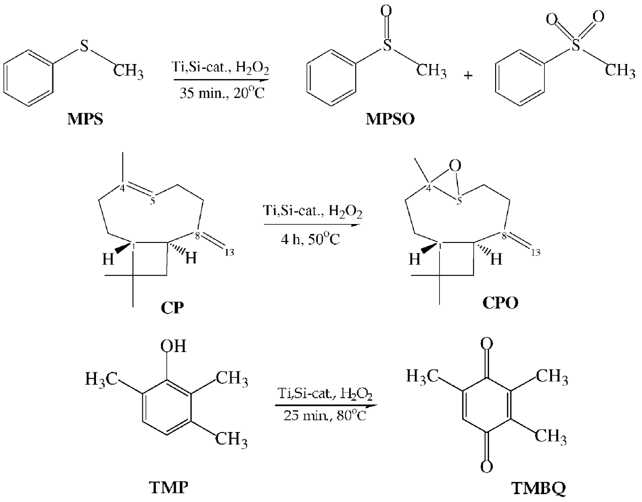
[b] GC yield based on initial substrate.

[c] Reaction conditions: 0.1 M MPS, $MPS/H_2O_2 = 1/1.2$, 20 °C, 3 ml MeCN, 35 min.

[d] Reaction conditions: 0.1 M CP, $CP/H_2O_2 = 1/1$, 3 ml MeCN, 50 °C, 4 h.

[e] Reaction conditions: 0.1 M TMP, $TMP/H_2O_2 = 1/3.5$, 80 °C, 3 ml MeCN, 25 min.

compared to the activity of microporous TS-1, for which diffusion limitations would be expected.



In the presence of MPS, the H_2O_2 decomposition over Ti-MMM-2 (as well as Ti-MMM) was not substantial and the selectivity with respect to H_2O_2 was rather high (>90%). In the case of the TMP oxidation (80 °C), the H_2O_2 decomposition was more pronounced and a 3.5-fold molar excess of the oxidant with respect to TMP was needed to reach a complete TMP conversion (the reaction stoichiometry is 2:1). All H_2O_2 was consumed during the reaction and the selectivity to TMBQ based on H_2O_2 consumed was quite moderate (50–60%). Thus the H_2O_2 selectivity depends on the substrate and/or reaction conditions.

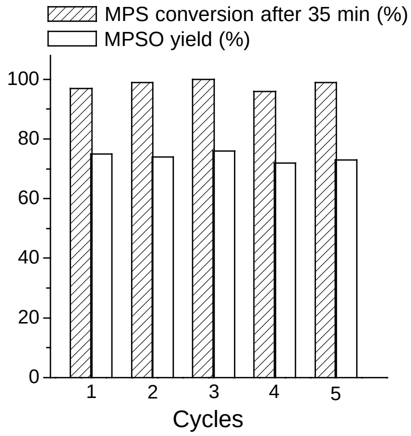


Fig. 3. MPS oxidation (five catalytic cycles) with aqueous H_2O_2 over Ti-MMM-2. Reaction conditions are given in Section 2.

Experiments with fast catalyst filtration at the reaction temperature performed during the MPS, CP and TMP oxidations over Ti-MMM-2 showed no further substrate conversion in the filtrate after removing the catalyst, which indicates that the oxidation takes place on the catalyst surface and is a true heterogeneous process. According to the elemental analysis data, the total titanium content in Ti-MMM-2 remained unchanged after several catalyst treatments with 30% aqueous H_2O_2 in MeCN. Note that this is exactly what has been observed for Ti-MMM [12–14]. Nevertheless, despite the absence of titanium leaching, substantial loss of catalytic properties occurred after recycling of Ti-MMM due to its low hydrothermal stability. Noteworthy, no loss of the catalytic activity was observed after recycling of Ti-MMM-2 (Fig. 3). Thus, the new mesoporous material Ti-MMM-2 combines high activity of Ti-MMM with stability of Ti-SBA-15. All these allow to consider Ti-MMM-2 as a promising catalyst for the selective oxidation of bulky organic substrates with aqueous H_2O_2.

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