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Oxidation of 2,3,6-Trimethylphenol over Ti- and V-Containing Mesoporous Mesophase Catalysts: Structure–Activity/Selectivity Correlation

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The oxidation of 2,3,6-trimethylphenol (TMP) has been carried out over well-organized Ti- and V-containing mesoporous mesophase silicate catalysts (Ti- and V-MMM) using hydrogen peroxide and *tert*-butyl hydroperoxide (TBHP) as oxidants. Vanadium leaching was observed in the V-MMM/H_2O_2 and V-MMM/TBHP systems, whereas no titanium leaching occurred for Ti-MMM with both oxidants. TMP oxidation runs on a surface of Ti-MMM catalyst, producing 2,3,5-trimethyl-1,4-benzoquinone (TMBQ) with selectivity as high as 86% at 100% TMP conversion. Titanium content in Ti-MMM determines the state of the active catalytic site and influences the structure regularity, thus affecting the catalytic behavior. The catalysts with titanium loading in the 1.5–2 wt% range show the highest activity and selectivity. Some loss of catalytic properties observed after recycling may occur due to collapsing of the catalyst structure caused by water. The lower the water concentration in the reaction mixture, the more stable the catalyst. © 2001 Academic Press

Key Words: **titanium; vanadium; mesoporous mesophase catalysts; oxidation; 2,3,6-trimethylphenol; 2,3,5-trimethyl-1,4-benzoquinone; H_2O_2; TBHP.**

INTRODUCTION

The selective oxidation of 2,3,6-trimethylphenol (TMP) is of great interest as a method for the preparation of 2,3,5-trimethyl-1,4-benzoquinone (TMBQ), a key intermediate in the synthesis of vitamin E (1, 2). Until recently, stoichiometric oxidation of TMP with MnO_2, HNO_3, or other hazardous reagents (3, 4) was the main route for TMBQ industrial production. In the past decade, the development of environmentally friendly catalytic methods has become a challenging goal. A few catalytic systems have been developed using "clean" oxidants, such as molecular oxygen and hydrogen peroxide: (1) copper halides and other copper salts/O_2, (5–7); (2) cobalt complexes with Schiff bases/O_2 (8, 9); (3) ruthenium salts/H_2O_2 (10); and (4) heteropoly acids/O_2 or H_2O_2 (11, 12). However, all the above-mentioned systems are based on the use of homogeneous catalysts that leads to the known problems with catalyst separation and, therefore, contamination of the goal product with transition metal compounds. An efficient method for TMBQ production based on the employment of a solid, heterogeneous catalyst has not yet been reported. Recently, an attempt was made to use Fe(III) phthalocyanine dimeric catalyst immobilized onto amorphous SiO_2 in TMP oxidation with TBHP; however, the selectivity with this catalyst was good (72–80%) only in the first catalytic cycle (13).

To date titanium-silicalites TS-1 and TS-2 are the most efficient catalysts for H_2O_2-based oxidations of organic compounds with kinetic diameter <6 Å (14, 15 and references therein); however the steric restriction in the microporous zeolite (pore size ca. 0.55 nm) prevents its application in the field of fine chemistry. Mesoporous silicate materials, containing transition metal ions (M) in a heterogeneous matrix (M-MCM-41, M-MCM-48, M-HMS, M-Si-mixed oxides, etc.) have attracted much attention as catalysts for selective oxidation of bulky organic substrates (16–34). Among other reactions, oxidation of 2,6-di-*tert*-butyl phenol to a mixture of corresponding monoquinone and diphenoquinone over M-HMS and M-MCM-41 ($M =$ V, Ti) has been reported (19, 23, 26, 27). Recently, oxidations of 2,3,5-trimethylphenol with H_2O_2 over (Cr)MCM-41 (35) and TiAPO-5 (36) have been reported to give TMBQ with yield's of 64 and 85%, respectively. However, substantial chromium leaching was observed in the former system, while the heterogeneity of the latter system has not been demonstrated and seems to be problematic (29).

Recently, we reported the alkene and thioether oxidation with H_2O_2 over well-organized mesoporous mesophase silicate materials (Ti- and V-MMM) (37, 38). In the present work, we considered the possibility of TMP oxidation to TMBQ by cheap and environmentally friendly oxidants, H_2O_2 and TBHP, in the presence of Ti- and V-MMM catalysts. Special attention was devoted to the problem of transition metal leaching during the oxidation process. The question on structure/activity and structure/selectivity relationships has been addressed. Note that when we started

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our investigation, no works concerning TMP oxidation over Ti-containing catalysts had been reported (39). While we were working on this paper, Sorokin and Tuel published the paper devoted to TMP oxidation over anchored phtalocyanine catalysts (40), where they briefly advertised the results on TMP oxidation with H_2O_2 in the presence of Ti-containing silica-based molecular sieves. However, since no experimental details or catalyst characterization were reported, the results manifested in (40) cannot be compared with our results and thus collectively discussed.

EXPERIMENTAL

Materials

2,3,6-TMP (Fluka) was recrystallized from hexane. Hydrogen peroxide (30%) was concentrated in vacuum up to 84% and was determined iodometrically prior to use. TBHP (6.95 M solution in decane, Aldrich) was commercial sample and was titrated prior to experiments. All the other reactants were obtained commercially and used without further purification.

Catalyst Synthesis and Characterization

Ti-MMM (samples **1**, **2**, **3**, **4**, **5**, and **6**, containing 4.32, 2.50, 1.90, 1.53, 1.00, and 0.58 wt% of Ti, respectively) and V-MMM (sample **7**, 0.88 wt% of V) were prepared by the procedure described in (37, 38) under weakly alkaline conditions by hydrothermal synthesis at 140°C for 40 h (titaniumsilicates) and for 140 h (vanadiumsilicate) in the presence of $C_{16}H_{33}N(CH_3)_3Br$. The surfactant was removed from as-synthesized forms by calcination in air flow at 550–600°C. The calcined forms of the catalysts were characterized by X-ray diffraction (XRD) using synchrotron radiation, nitrogen adsorption at low temperature, and elemental analysis. The state of the transition metal ions before and after treatment with H_2O_2 was characterized by DRS-UV at ambient conditions. To estimate hydrostability, samples were treated with water at room temperature for 2 h. All the samples were calcined at 560°C before running UV spectra and before XRD measurements.

Catalytic Experiments

Catalytic experiments were performed under vigorous stirring in thermostated glass vessels at 30–80°C. Typically, the reactions were initiated by adding 0.33–2.64 mmol of H_2O_2 (as 30–84% aqueous solution) or 1.16 mmol of TBHP (7 M solution in decane) to a mixture, containing 0.3–0.15 mmol of TMP, 25–107 mg of a catalyst (0.013 mmol of M), an internal standard (biphenyl), and 3 ml of a solvent. The oxidation products were identified by GC-MS, UV-Vis and ^{1}H NMR. TMP conversion and TMBQ yield were quantified by GC. After the reaction, catalysts were filtered off, washed with methanol, dried in air at room temperature, and then reused. Pure TMBQ as well as by-products were separated from the reaction mixture by means of adsorption column chromatography on silica gel using gradual elution (hexane/ethyl acetate). ^{1}H NMR and UV–Vis spectra of the obtained TMBQ coincided completely with the reference spectra.

Instrumentation

Gas chromatographic analyses were performed using a gas chromatograph "Tsvet-500" equipped with a flame ionization detector and a quartz capillary column (25 × 0,3) filled with Carbowax 20 M. GC-MS analyses of organic products were conducted using an LKB-4091 instrument. ^{1}H NMR spectra were recorded on an MSL-400 Bruker spectrometer. DRS-UV measurements were performed on a Shimadsu UV–VIS 2501PC spectrophotometer.

RESULTS AND DISCUSSION

Catalyst Characterization

The synthesis and characterization of the most of Ti-MMM (samples **1–6**) as well as the V-MMM (sample **7**) used in this study were reported elsewhere (37, 38). The sample codes and basic physical characteristics are listed in Table 1. Textural parameters were calculated as described in (41, 42). In previous work (38), we have shown that XRD reflections observed for Ti- and V-MMM are of highly symmetric shape with the full-width-at-half-maximum (FWHM) values of about 0.08–0.09° 2θ. This allowed us to describe the mesostructure of these samples as highly ordered hexagonal arrangement of mesopores. This was supported also by a narrow interval of relative pressure $\Delta(P/P_o) = 0.06–0.08$, along with relatively small values of the external surface area (37). For samples **1–3**, which have higher Ti loading, the structure perfection is less. However, comparing XRD patterns of all the Ti-MMM samples with XRD patterns reported for other mesoporous silicate materials, like Ti-MCM-41 and Ti-HMS (16, 18–20, 24, 27, 28, 33), one can point out considerably more regular structure of Ti-MMM. The DR-UV spectra for samples **2–6** (λ_{max} at 215–228 nm) indicated site-isolated titanium species according to (14, 16, 18, 27). For sample **1**, the UV absorption maximum was shifted to longer wavelengths, and the band was broader, thus indicating the appearance of partially olygomerized titanium-oxygen species (14, 16, 27, 33).

Catalytic Results

Experimental data on the catalytic oxidation of TMP with H_2O_2 and TBHP over the V-MMM catalyst are summarized

TABLE 1

Structural and Textural Parameters of Ti- and V-MMM Catalysts

Sample no. (M)	Si/M atomic ratio (wt% M)	Structural parameters		Textural parameters					λ_{max} in DR–UV spectra (nm)
		a_o[a] (nm)	FWHM[b] (deg. 2θ)	A_{Me}[c] (m^2/g)	A_{ext}[d] (m^2/g)	V_{Me}[e] (cm^3/g)	d_{Me}[f] (nm)	h_W[g] (nm)	
1 (Ti)	19 (4.32)	4.47	0.117	911	86	0.738	3.50	0.97	240
H-**1**[h]	19 (4.32)	—	0.62	841	81	0.615	—	—	—
2 (Ti)	29 (2.50)	4.23	0.183	1209	32	0.852	3.42	0.81	228
3 (Ti)	39 (1.89)	4.23	0.110	1260	29	0.903	3.45	0.78	226
4 (Ti)	49 (1.53)	4.64	0.078	1059	53	0.908	3.79	0.85	218
5 (Ti)	70 (1.00)	4.40	0.090	—	—	0.900	3.59	0.81	215
6 (Ti)	124 (0.58)	4.68	0.086	1068	48	0.932	3.84	0.84	216
H-**6**[h]	124 (0.58)	—	0.46	927	38	0.704	—	—	—
7 (V)	70 (0.88)	5.18	0.090	922	34	0.877	4.20	0.98	255, 370

[a] Unit cell parameter.

[b] Full-width-at-half-maximum of the (100) reflection.

[c] Specific mesopore surface area.

[d] Specific external surface area.

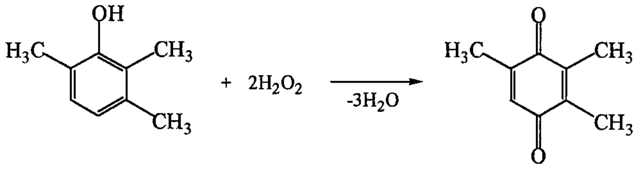
[e] Specific mesopore volume.

[f] Mesopore diameter.

[g] Wall thickness calculated from the equation $a_o = d_{Me} + h_W$.

[h] After treatment with water.

in Table 2. The stoichiometry of TMP oxidation with H_2O_2 to produce TMBQ is 1 : 2.



2,3,6-TMP **TMBQ**

Only 90% of TMP were converted when twofold excess of H_2O_2 was employed. This indicated some unproductive decomposition of the oxidant in the presence of V-MMM. Threefold or higher excess of H_2O_2 was needed to achieve complete TMP conversion. The selectivity to TMBQ was moderate (46%) and decreased with increasing peroxide concentration. The use of TBHP instead of H_2O_2 gave only 31% of TMBQ, the reaction time being increased (Table 2).

TABLE 2

TMP Oxidation with 30% Aqueous H_2O_2 over V-MMM Catalyst[a]

Molar ratio [TMP]/[H_2O_2]	Yield[b] of TMBQ (%)	TMP conversion (%)
1/2	47	90
1/3	46	99
1/5	38	100
1/7	27	100
1/3.5[c]	31	98

[a] Reaction conditions: TMP 0.1 M, sample 7, 35 mg, MeCN 3 ml, 50°C, 1 h.

[b] GC yield based on TMP consumed.

[c] TBHP was used instead of H_2O_2; reaction time 2.7 h.

The problem of transition metal ion leaching from mesoporous catalysts has been addressed in many papers (23, 26, 28, 29, 33). We examined the V-MMM catalyst using experiments with fast catalyst removal by filtration during the oxidation process and found the same activity both in the presence of V-MMM and in the filtrate. This was evidence that vanadium leaching takes place, and the reaction actually proceeds in the solution. With TBHP used as the oxidant, the reaction also proceeded in the filtrate but the oxidation rate was lower compared to the reaction in the presence of V-MMM (Fig. 1a). Thus, the leaching of vanadium active species occurs with both oxidants under the conditions studied and the problem of vanadium leaching from MMM as well as other mesoporous matrixes has yet to be solved.

In sharp contrast to V-MMM-based systems, no further activity was exhibited in the filtrate after fast removal of Ti-MMM during TMP oxidation in both Ti-MMM/H_2O_2 and Ti-MMM/TBHP catalytic systems, even at 80°C. The catalyst filtration was carried out at the reaction temperature in order to prevent readsorption of metal ions from the solution on cooling. Figure 1b clearly shows that the TMP oxidation process is truly heterogeneous. Additionally, no titanium leaching was found when comparing the elemental analysis data of the catalyst before and after several catalytic cycles. Taking into account that titanium leaching was observed for Ti-MCM-41/H_2O_2 by other research groups (28, 33), the present work unambiguously

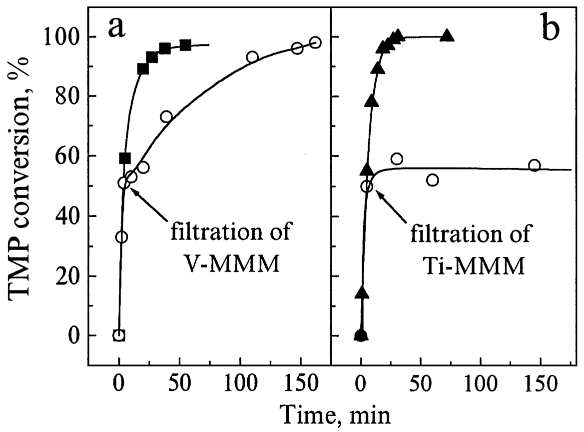


FIG. 1. TMP oxidation with TBHP over V-MMM (a) (sample **7**) and with H_2O_2 over Ti-MMM (b) (sample **4**). Reaction conditions: TMP 0.1 M, TBHP 0.35 M (or H_2O_2 0.7 M), V-MMM 35 mg (or Ti-MMM 42 mg), MeCN 3 ml, 80°C.

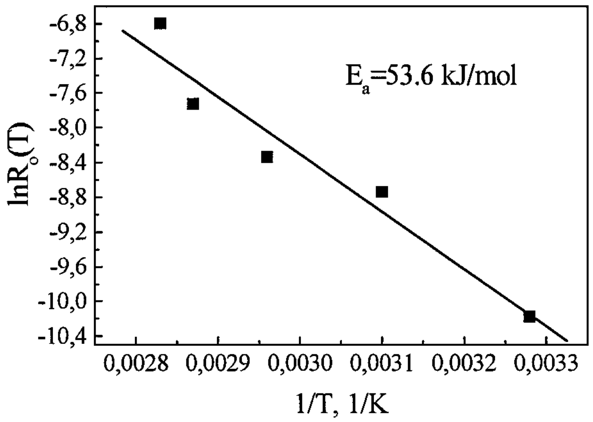


FIG. 2. $\ln R_o$ vs $1/T$ plot for the TMP oxidation with H_2O_2 over Ti-MMM (sample **4**). Reaction conditions: TMP 0.1 M, Ti-MMM 42 mg, $[TMP]/[H_2O_2] = 1/7$, MeCN 3 ml.

demonstrates the advantage of the well-organized Ti-MMM materials. The data on the catalytic TMP oxidation with H_2O_2 and TBHP over Ti-MMM (sample **4**) are given in Table 3. Since the selectivity of TMBQ formation was considerably higher with H_2O_2 than with TBHP (77 and 32%, respectively), our attempts to optimize reaction conditions were directed to the reaction with H_2O_2. Like V-MMM, the Ti-MMM catalyst induced some unproductive peroxide decomposition, and thus a more than stoichiometric amount of H_2O_2 was needed to attain complete TMP conversion (runs 1–3).

The selectivity to TMBQ considerably increased with increasing temperature: 55 and 70% at 65 and 80°C, respectively (runs 5 and 6). Effective activation energy E_a estimated from the $\ln R_o - 1/T$ plot (Fig. 2) was 53.6 kJ/mol. This shows that the reaction rate is not limited by the diffusion of reactants to the active catalytic sites, because E_a for diffusion-limited process should be expected to be considerably lower.

Generally, the nature of the solvent affected the selectivity of TMP oxidation. At 65°C, the yield of TMBQ was found to be 55, 63, and 71% for MeCN, AcOH, and MeOH,

TABLE 3

TMP Oxidation with 30% Aqueous H_2O_2 over Ti-MMM Catalyst[a]

Run	[TMP] (M)	$[TMP]/[H_2O_2]$ (molar ratio)	Solvent	T (°C)	Time (h)	Yield[b] of TMBQ (%)	TMP conversion (%)
1	0.1	1/3	MeCN	50	8	39	86
2	0.1	1/5	MeCN	50	8	47	95
3	0.1	1/7	MeCN	50	8	51	97
4	0.1	1/7	MeCN	30	6	48	33
5	0.1	1/7	MeCN	65	6	55	98
6	0.1	1/7	MeCN	80	6	70	100
7	0.1	1/7	AcOH	65	6	63	98
8	0.1	1/3	MeOH	65	6	71	98
9	0.1	1/7	AcOH	80	6	70	99
10	0.1	1/3	MeCN	80	0.4	71	90
11	0.1	1/3.5	MeCN	80	0.4	77	100
12	0.1	1/3.5[c]	MeCN	80	3.3	32	97
13	0.05	1/3.5	MeCN	80	0.4	82	100
14	0.05	1/3.5[d]	MeCN	80	0.5	86	100
15	0.1	1/3.5[d]	MeCN	80	0.8	82	100

[a] Sample **4**, 42 mg.

[b] GC yield based on TMP consumed.

[c] TBHP was used instead of H_2O_2.

[d] TMP solution was added by portions to the reaction mixture.

respectively (runs 5, 7, and 8), whereas at 80°C the selectivity attained 70% for both MeCN and AcOH (runs 6 and 9). While TMBQ was fairly stable to overoxidation at 50°C and thus the TMP/H_2O_2 ratio did not affect the selectivity (runs 2 and 3), at 80°C some further oxidation of TMBQ took place when sevenfold molar excess of H_2O_2 was employed. As a result, the selectivity value passed through a maximum (82 and 70% at 93 and 99% conversion, respectively). Therefore, high excess of H_2O_2 should be avoided when the temperature is raised. The optimal TMP/H_2O_2 molar ratio to get complete TMP conversion at high selectivity was found to be 1/3.5 (run 11). At a lower ratio the phenol conversion was not complete (run 10).

It has been well-documented that the first step in alkylphenol oxidation by one-electron oxidants is the formation of phenoxyl radical $ArO^\bullet$ (43):

$$ArOH + Ox \rightarrow ArO^\bullet + Red + H^+.$$

The following routes of $ArO^\bullet$ transformations lead to different oxidation products:

(1) $ArO^\bullet + Ox \rightharpoonup \ldots\ldots \rightharpoonup$ quinone

(2) C–C coupling: $2ArO^\bullet \rightharpoonup$ biphenol $\xrightarrow{+Ox}$ diphenoquinone

(3) C–O coupling: $nArO^\bullet \rightharpoonup$ polyphenylene oxide

The tail-to-tail dimer, 2,2′,3,3′,5,5′-hexamethyl-4,4′-biphenol (BP), and the head-to-tail polymer, polyphenylene oxide, have been established to be typical by-products formed in TMP oxidations to TMBQ (11 and references cited therein). Note that the corresponding diphenoquinone, which could in principal result from further oxidation of BP, had never been found in TMP oxidation processes. At the same time, the formation of 3,3′,5,5′-tetramethyldiphenoquinone from 2,6-dimethylphenol is well-precedented (19, 23, 26, 27, 41–45). Sterical reasons are most likely responsible for this phenomenon. Moreover, we have found earlier that BP can be an intermediate in TMP oxidation to TMBQ (11). The only product of TMP oxidation in the Ti-MMM/H_2O_2 system detected by GC-MS was TMBQ. Meanwhile, the comparison of UV–Vis spectra of a reference TMBQ and the reaction mixture clearly showed the presence of a yellow product (or products) different from TMBQ (Fig. 3). The by-product fraction was separated on silica gel and BP was identified by ^{1}H NMR (11). However, the strong absorption in the visible region (Fig. 3) could not be due to BP, which is colorless. The yellow by-product could not result from TMBQ overoxidation because the quinone was found to be stable at the reaction conditions (50°C). We suppose that this is, probably a C–O-coupling product, polyphenylene oxide, or another nonvolatile polymeric compound.

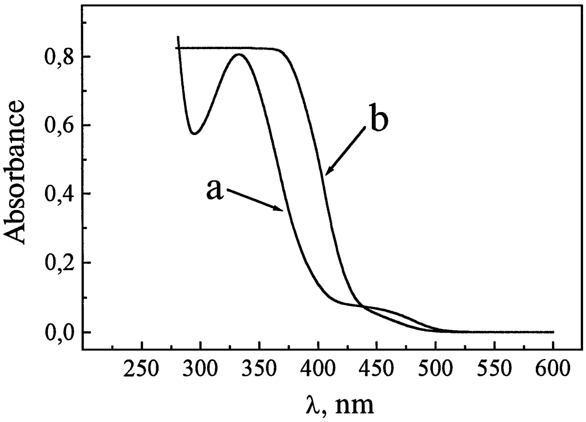


FIG. 3. UV–Vis spectra (l = 1 cm): (a) TMBQ (2.06×10^{-3} M) in MeCN; (b) reaction mixture after 3 h. Reaction conditions: TMP 0.1 M, Ti-MMM 42 mg (sample **1**), [TMP]/[H_2O_2] = 1/6, MeCN 3 ml, 50°C. Before running spectra the catalyst was separated and the reaction mixture was 25-fold diluted with MeCN.

The formation of C–C and C–O coupling products allowed us to suggest that TMP oxidation in the Ti-MMM/H_2O_2 catalytic system proceeds via the formation of phenoxyl radical. Taking this hypothesis in mind, it was reasonable to expect that lowering TMP initial concentration would result in suppression of the polymerization process, thus increasing TMBQ yield. Indeed, the selectivity to TMBQ raised from 77 to 82% when TMP concentration was twice reduced (runs 11 and 13). In turn, stepwise addition of TMP to the reaction mixture also enhanced the selectivity (runs 14 and 15), while slow dosing of H_2O_2 gave an opposite effect. Meanwhile, we cannot exclude that an alternative mechanism, involving TMP electrophylic hydroxylation with titanium hydroperoxocomplex, takes place to yield TMBQ. It should be mentioned, however, that the mechanism of interaction of titanium hydroperoxocomplex with organic substrates, including phenol, still remains a matter of discussion (14). Probably, whether homolytic or heterolytic route takes place, depends on the substrate nature. A heterolytic mechanism seems to be more or less proved for alkene epoxidation (14, 15, 29), while a homolytic mechanism most likely operates in alkane (14, 29) and thioether (46, 47) oxidations. Moreover, the reaction mechanism seems to be dependent on the catalyst nature. Thus when using amorphous titanosilicate, the oxidation of the side chain in toluene was found to predominate thus indicating a radical mechanism, while TS-1 and TS-2 produced only cresols indicating electrophylic hydroxylation (21). To elucidate the actual mechanism of TMP oxidation in the Ti-MMM/H_2O_2 system, a thorough mechanistic study is needed.

Optimization of the reaction conditions allowed us to produce TMBQ with the yield of 86% at 100% TMP conversion using Ti-MMM/H_2O_2 system. Note that this selectivity value is similar to that observed for the best homogeneous

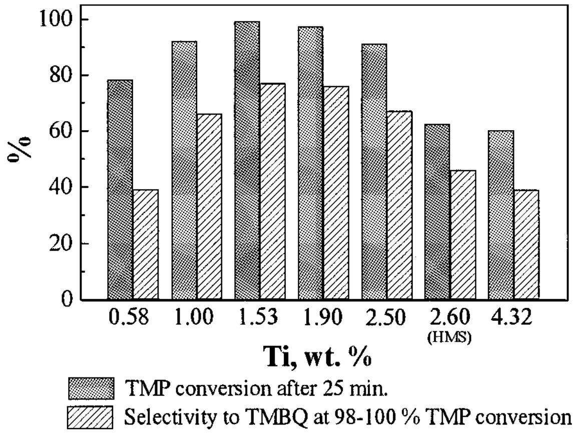


FIG. 4. Oxidation of TMP with H_2O_2 over Ti-MMM samples with different Ti loading. Reaction conditions: TMP 0.1 M, Ti 1.3×10^{-2} mmol, $[TMP]/[H_2O_2] = 1/3.5$, MeCN 3 ml, 80°C.

catalytic systems known to date for TMP oxidation (5, 9–11).

Structure/Activity and Selectivity Relationships

In order to establish the factors which determine the catalyst activity and selectivity in the reaction studied, we have tested a series of Ti-MMM samples with different Ti content (Fig. 4). In all experiments, specified amounts of catalyst were used in order to introduce 0.013 mmol of Ti to each reaction. The most active samples were found to be the most selective samples. Samples **3** and **4** with titanium loading in the 1.5–2 wt% range exhibited superior catalytic properties (Fig. 4). A similar trend was previously observed for cyclohexene oxidation with H_2O_2 over Ti-MMM (37, 38) and grafted Ti-MCM-41 (48). It has been reported that the increase of titanium content in Ti-MMM as well as Ti-MCM-41 results in the loss of structure regularity (33, 37, 38, 49) and the formation of less reactive Ti–O–Ti bonds (16, 33, 48). Both structure perfection of Ti-MMM catalyst and high dispersion of titanium in the silicate matrix were proposed to be crucial factors determining catalytic behavior (37, 38). The structure regularity seems to be important from the point of view of titanium accessibility. The Ti-MMM wall-thickness values calculated as described in (41, 42) are given in Table 1. Taking into account that silica tetrahedron size was estimated to be about 0.4 nm (50), most of the introduced titanium should be expected to be accessible to reactants for samples **2–6**. With increasing titanium loading, the wall-thickness also increases according to (49) and our results (sample **1**) and thus a part of titanium species is expected to be located inside the silica walls. Indeed, the reaction selectivity to TMBQ was found to be 76 and 39% for the Ti-MMM samples, containing 1.89 and 4.32 wt% of Ti, respectively, while the reaction time was increased in the same order (Fig. 4). However, since both structure regularity loss and partial titanium oligomerization occur with increasing titanium content, it seems to be problematic to estimate separately the effect of each of these two factors on the Ti-MMM catalytic properties. We believe that a comparison of Ti-MMM samples with Ti-HMS may be profitable. Thus we have found that the Ti-HMS catalyst with 2.60 wt% Ti, which has a titanium dispersion very close to that of sample **1** according to the DR-UV data, but does not have a regular structure (37), showed considerably poorer activity and selectivity compared sample **1**. Thus, we may conclude that both the titanium state and structure regularity (titanium accessibility) determine catalytic activity and selectivity of Ti-MMM catalysts in the TMP oxidation.

Less understandable was the decrease in the catalytic activity and selectivity observed for samples with low Ti content (66 and 39% selectivity for samples with 1.00 and 0.58% Ti, respectively), given the fact that the structure of these Ti-MMM samples has been established to be perfect and site-isolated titanium species have been found to predominate (Table 1). Therefore, structure perfection and high dispersion of titanium are necessary but not sufficient factors which determine the catalytic performance of Ti-MMM catalysts. We suppose that the reason for the reduced activity of Ti-MMM samples with low titanium content might be their lower hydrolytic stability compared to the samples with high Ti content. The problem of the hydrolytic unstability, resulting in collapsing of silicate walls of MMM and MCM-41, has been addressed in few papers (28, 30, 51–53). XRD patterns (Fig. 5) and N_2 adsorption data for hydrated Ti-MMM samples (Table 1) show that after treatment with water the structure of Ti-MMM samples is considerably damaged. However, this process seems to be less pronounced for the sample with higher titanium content if one compares intensity values of the [100] reflections. Recently, it has been found that introduction of about 5 wt%

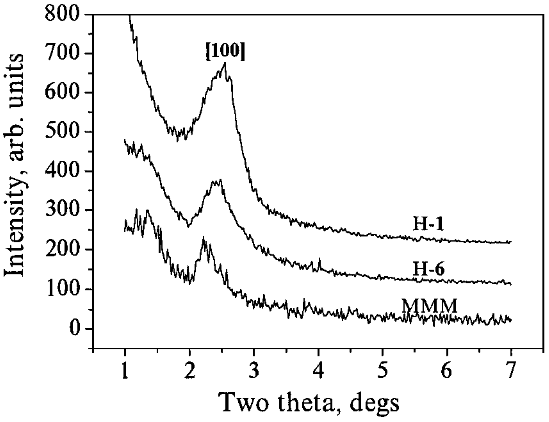


FIG. 5. The XRD patterns for hydrated and recalcined forms of sample **1** (H-**1**), sample **6** (H-**6**), and pure siliceous MMM.

Al largely enhanced hydrostability of MMM compared to pure siliceous MMM (51, 52). We suppose that a similar relationship may exist between titanium content and hydrolytic stability of Ti-MMM. However, a combined XRD and kinetic study is needed to confirm the difference in the rates of structure damage for Ti-MMM samples with different Ti loading under the conditions used for TMP oxidation.

Catalyst Recycling

Ti-MMM catalysts can be easily separated by simple filtration and then reused. We finally investigated the possibility of catalyst recycling using the best Ti-MMM samples (**3** and **4**) and found that stability of the catalytic behavior depends on H_2O_2 and, therefore, H_2O concentration employed. When using 30% H_2O_2, at $[H_2O_2] = 0.175$ M, both the reaction rate and TMBQ yield remained unchanged during three catalytic cycles, whereas at $[H_2O_2] = 0.35$ M, subsequent activity and selectivity decay was observed (Table 4). Again, contrary to the Ti-MCM-41/H_2O_2 system (28, 33), no titanium leaching occurred from the Ti-MMM catalysts. The total titanium content in the sample remained unchanged according to the elemental analysis data. We suppose that the catalyst deactivation results most likely from the Ti-MMM structure collapsing during the oxidation process caused by water (*vide supra*). The structure collapse, in turn, may result in the blockage of some of the active titanium sites inside the silica walls as well as the formation of titanium–oxygen clusters. Indeed, DR-UV spectra of the Ti-MMM catalyst (sample **3**) recorded after treatment with 30% aqueous H_2O_2 showed the long-wave shift of the absorption maximum to 270 nm (Fig. 6). Noteworthy, after treatment with 74% H_2O_2 the spectrum remained practically unchanged (Fig. 6). Since all the samples were calcined before running UV spectra and the conditions used to record the spectra were identical for the initial sample and the treated samples, the long-wave shift cannot be attributed to simple hydration of titanium species and can be ascribed to the appearance of partially oligomerized titanium species (14, 16, 27, 33). To verify the hypothesis, concerning negative effect of water on the catalyst stability, we performed the oxidation using 84% H_2O_2, instead of 30% H_2O_2 (0.35 M H_2O_2 in the reaction mixture in both cases), and found that the stability of the Ti-MMM catalysts enhanced and they can be reused repeatedly for at least three catalytic cycles without suffering a loss in activity and selectivity (Table 4). However, it should be mentioned that complete TMP conversion was not achieved when using 1/3.5 TMP/H_2O_2 molar ration and the reaction rate was lower for concentrated H_2O_2 than for dilute one. The latter fact is consistent with our results obtained earlier for H_2O_2-based oxidation in the presence of Ti-containing polyoxometalate (54). Thus, water seems to play two contradictory roles: on one hand, it enhances catalytic activity in the first catalytic cycle but, on the other hand, it destroys the catalyst structure and thus worsens the catalytic properties in the following cycles. Therefore, a compromise should be achieved between the catalyst activity and its hydrolytic stability.

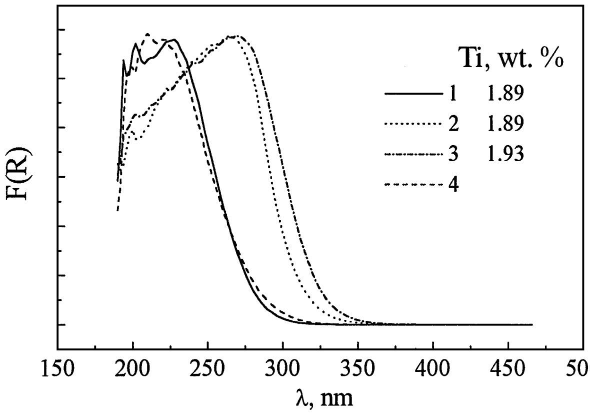


FIG. 6. UV–Vis diffuse reflectance spectra for Ti-MMM (sample **3**): (1) before treatment; (2) after first treatment with 30% H_2O_2; (3) after second treatment with 30% H_2O_2; (4) after first treatment with 74% H_2O_2; Ti-MMM 33 mg, H_2O_2 0.35 M, MeCN 3 ml, 80°C, 1 h.

TABLE 4

The Effect of H_2O_2 Concentration on TMP Oxidation over Ti-MMM[a]

% H_2O_2	$[H_2O_2]$ (M)	Cycle	Time (h)	TMP conversion (%)	Yield[b] of TMBQ (%)
30	0.175	I[c]	0.4	100	82
		II	0.4	100	79
		III	0.4	100	79
30	0.35	I[c]	0.4	100	77
		II	1.2	99	60
		III	1.8	99	47
30	0.35	I	0.6	100	76
		II	2.5	97	37
		III	5.7	95	32
84	0.35	I	1.7	77[d]	64
		II	1.7	80	68
		III	1.7	79	66

[a] Reaction conditions: $[TMP]/[H_2O_2] = 1/3.5$, sample **3**, 33 mg, MeCN 3 ml, 80°C.

[b] GC yield based on TMP consumed.

[c] Sample **4**, 42 mg.

[d] Complete TMP conversion was not achieved.

CONCLUSIONS

The well-organized Ti-MMM are effective catalysts for TMP oxidation to TMBQ with aqueous H_2O_2. High selectivity (up to 86% at 100% TMP conversion) can be attended at optimal reaction conditions. This is a rare example of really heterogeneous process, producing TMBQ. The catalysts with titanium content in the 1.5–2 wt% range possess the best catalytic properties. No titanium leaching takes place during the oxidation process; however, some loss of the catalytic properties may occur, which is most likely due to collapsing of the catalyst structure caused by water. The catalyst stability increases with reducing concentration of water in the reaction mixture.

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REFERENCES

1. Schudel, P., Mayer, H., and Isler, O., *in* “The Vitamins” (W. H. Sebrell and R. S. Harris, Eds.), Vol. 5, p. 165. Academic Press, New York, 1972.
2. Yamada, S., Takeshita, T., and Tanaka, J., *J. Syn. Org. Chem. Jpn.* **40**, 268 (1982).
3. Bushmilyev, V. A., Kondratyeva, T. A., Lipkin, M. A., and Kondratyev, A. V., *Khim-Farm Zh.* **5**, 65 (1991). [In Russian]
4. Constantini, M., Krumenaker, L., and Igersheim, F., French Patent 2552425 (1983).
5. Chao-Yang, H., and Lyons, J. E., European Patent 93540 (1983).
6. Türk, D., European Patent 0 127 888 B1 (1987).
7. Chiba, K., and Fukuoka, N., Japanese Patent 202297 A2 (2000).
8. Tomaja, D. L., Vogt, L. H., and Wirth, J. G., *J. Org. Chem.* **35**, 2029 (1970).
9. Laas, H., Tavs, P., and Hannebaum, H., Dt. Patent 3302498 (1984).
10. Ito, S., Aihara, K., and Matsumoto, M., *Tetrahedron Lett.* **24**, 5249 (1983).
11. Kholdeeva, O. A., Golovin, A. V., Maksimovskaya, R. I., and Kozhevnikov, I. V., *J. Mol. Catal.* **75**, 235 (1992).
12. Shimizu, M., Hayakawa, T., and Takehira, K., *Tetrahedron Lett.* **30**, 4711 (1989).
13. Sorokin, A., and Tuel, A., *New. J. Chem.* **23**, 473 (1999).
14. Notari, B., *Adv. Catal.* **41**, 253 (1996).
15. Clerici, M. G., and Ingallina, P., *J. Catal.* **140**, 71 (1993).
16. Corma, A., *Chem. Rev.* **97**, 2373 (1997).
17. Schneider, M., and Baiker, A., *Catal. Rev. Sci. Eng.* **37**(4), 515 (1995).
18. Corma, A., Navarro, M. T., Perez-Pariente, J., and Sanchez, F., *Stud. Surf. Sci. Catal.* **84**, 69 (1994).
19. Tanev, P. T., Chibwe, M., and Pinnavaia, T., *Nature* **368**, 321 (1994).
20. Blasco, T., Corma, A., Navarro, M. T., and Perez-Pariente, J., *J. Catal.* **156**, 65 (1995).
21. Keshavaraja, A., Ramaswamy, V., Soni, H. S., Ramaswamy, A. V., and Ratnasamy, P., *J. Catal.* **157**, 501 (1995).
22. Contier, S., and Tuel, A., *J. Catal.* **157**, 124 (1995).
23. Reddy, J. S., and Sayari, A., *J. Chem. Soc., Chem. Commun.* 2231 (1995).
24. Corma, A., Iglesias, M., and Sanchez, F., *Catal. Lett.* **39**, 153 (1996).
25. Zhang, W., and Pinnavaia, T. J., *Catal. Lett.* **38**, 261 (1996).
26. Reddy, J. S., Liu, P., and Sayari, A., *Appl. Catal. A: General* **148**, 7 (1996).
27. Zhang, W., Fröba, M., Wang, J., Tanev, P. T., Wong, J., and Pinnavaia, T. J., *J. Am. Chem. Soc.* **118**, 9164 (1996).
28. Rhee, C. H., and Lee, J. S., *Catal. Lett.* **40**, 261 (1996).
29. Sheldon, R., *Stud. Surf. Sci. Catal.* **110**, 151 (1997).
30. Koyano, K. A., and Tatsumi, T., *Micropor. Mater.* **10**, 259 (1997).
31. Kochkar, H., and Figueras, F., *J. Catal.* **171**, 420 (1997).
32. Van der Waal, J. C., Rigutto, M. S., and van Bekkum, H., *Appl. Catal. A: General* **167**, 331 (1998).
33. Chen, L. Y., Chuah, G. K., and Jaenicke, S., *Catal. Lett.* **50**, 107 (1998).
34. Di Wei, Wei-Te Chueh, and Haller, G. L., *Catal. Today* **51**, 501 (1999).
35. Mahalingam, R. J., Badamali, S. K., and Selvam, P., *Chem. Lett.* 1141 (1999).
36. Mahalingam, R. J., and Selvam, P., *Chem. Lett.* 455 (1999).
37. Kholdeeva, O. A., Derevyankin, A. Yu., Shmakov, A. N., Trukhan, N. N., Paukshtis, E. A., Tuel, A., and Romannikov, V. N., *J. Mol. Catal. A: Chemical* **158**, 417 (2000).
38. Trukhan, N. N., Derevyankin, A. Yu., Shmakov, A. N., Paukshtis, E. A., Kholdeeva, O. A., and Romannikov, V. N., *Micropor. Mesopor. Mater.* **44–45**, 603 (2001).
39. Kholdeeva, O. A., Romannikov, V. N., Trukhan, N. N., and Parmon, V. N., RU Patent Application 2000105325. Priority 03.03.2000.
40. Sorokin, A., and Tuel, A., *Catal. Today* **57**, 45 (2000).
41. Fenelonov, V. N., Romannikov, V. N., and Derevyankin, A. Yu., *Micropor. Mesopor. Mater.* **28**, 57 (1999).
42. Romannikov, V. N., Fenelonov, V. B., Nosov, A. V., Derevyankin, A. Yu., Tsybulya, S. V., and Kryukova, G. N., *Russ. Chem. Bull.* **48**, 1821 (1999).
43. Taylor, W. I., “Oxidative Coupling of Phenols.” Dekker, New York, 1967.
44. Gorodetskaya, T. A., Kozhevnikov, I. V., and Matveev, K. I., RU Application 1155580 (1985).
45. McNelis, E., *J. Org. Chem.* **31**, 1255 (1966).
46. Kholdeeva, O. A., Kovaleva, L. A., Maksimovskaya, R. I., and Maksimov, G. M., *J. Mol. Catal. A: Chemical* **158**, 223 (2000).
47. Kholdeeva, O., Maksimov, G. M., Maksimovskaya, and Kovaleva, L. A., *Kinet. Catal.* **42**, 217 (2001).
48. Marchese, L., Gianotti, E., Dellarocca, V., Maschmeyer, T., Rey, F., Coluccia, S., and Thomas, M., *Phys. Chem. Chem. Phys.* **1**, 585 (1999).
49. Alba, M. D., Becerro, A. I., and Klinowski, J., *J. Chem. Soc., Faraday Trans.* **92**(5), 849 (1996).
50. Iler, R. K., “The Chemistry of Silica,” Vol. 1. Wiley, New York, 1979.
51. Solovyov, L. A., Kirik, S. D., Shmakov, A. N., and Romannikov, V. N., *Micropor. Mesopor. Mater.* **44–45**, 17 (2001).
52. Kodenev, E. G., Shmakov, A. N., Derevyankin, A. Yu., Lapina, O. B., and Romannikov, V. N., *J. Mol. Catal. A: Chemical* **158**, 349 (2000).
53. Zhao, X. S., Lu, G. Q., and Hu, X., *Micropor. Mesopor. Mater.* **41**, 37 (2000).
54. Kholdeeva, O. A., Maksimov, G. M., Maksimovskaya, R. I., Kovaleva, L. A., Fedotov, M. A., Grigoriev, V. A., and Hill, C. L., *Inorg. Chem.* **39**, 3828 (2000).