

Oxidation of 2-methyl-1-naphthol with H₂O₂ over mesoporous Ti-MMM-2 catalyst

Oxana A. Kholdeeva^{a,*}, Olga V. Zalomaeva^{a,b}, Alexander N. Shmakov^a, Maxim S. Melgunov^a,
Alexander B. Sorokin^b

^a Borekov Institute of Catalysis, Pr. Ac. Lavrentieva 5, Novosibirsk 630090, Russia

^b Institut de Recherches sur la Catalyse, CNRS, 2, avenue A. Einstein, 69626 Villeurbanne cedex, France

Received 15 July 2005; revised 16 September 2005; accepted 19 September 2005

Available online 17 October 2005

Abstract

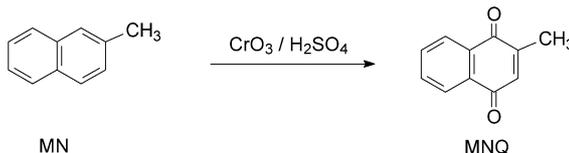
The catalytic oxidation of 2-methyl-1-naphthol (MNL) to 2-methyl-1,4-naphthoquinone (MNQ; menadione; vitamin K₃) using aqueous H₂O₂ as an oxidant and hydrothermally stable mesoporous mesophase titanium silicates Ti-MMM-2 as catalysts has been studied. The effects of mesopore diameter, temperature, solvent nature, reagent concentrations, and catalyst amount on the yield of MNQ were evaluated. Crucial factors affecting the MNQ yield include MNL concentration, H₂O₂/MNL molar ratio, reaction temperature, and the mode of MNL addition to the reaction mixture. Selectivity dramatically decreases with increasing MNL concentration and decreasing temperature. Stepwise addition of the substrate to the reaction mixture improves selectivity. Oxidation in the presence of ¹⁸O₂ provided 96.2 ± 0.1% of unlabeled MNQ, indicating H₂O₂ as an oxygen source. The Ti-MMM-2 catalyst allows one to obtain MNQ with selectivity as high as 78% at complete substrate conversion. The catalyst can be used repeatedly without loss of either activity or selectivity. The proposed method is convenient and environmentally benign. © 2005 Elsevier Inc. All rights reserved.

Keywords: 2-Methyl-1-naphthol; 2-Methyl-1,4-naphthoquinone; Oxidation; H₂O₂; Ti-MMM-2

1. Introduction

Quinone derivatives play an important role in biosystems and are useful intermediates and products of fine chemistry [1,2]. Thus the development of environmentally benign methods for the production of substituted quinones is a challenging goal. The elaboration of new methods for the production of synthetic vitamin K₃ (2-methyl-1,4-naphthoquinone [MNQ], menadione), which is widely used as a blood coagulating agent and is a key intermediate in the preparation of the other vitamins of group K, is of particular importance. Traditionally, MNQ is produced on industrial scale via stoichiometric oxidation of 2-methylnaphthalene (MN) by CrO₃ in sulfuric acid with a yield of 40–60%. This method produces about 18 kg of toxic inorganic waste per 1 kg of the target product [2–4]. No wonder this process is often cited as an example of a “dirty” fine

chemical industry process [3–5]:

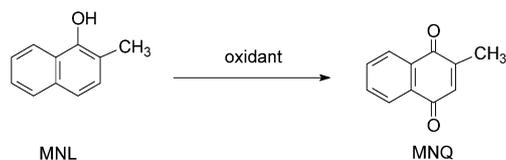


Over the last two decades, the development of clean catalytic methods for the MNQ production has received increasing attention. The catalytic procedures described in the literature are typically based on the oxidation of MN with hydrogen peroxide or *tert*-butyl hydroperoxide (TBHP) [6–13]. Among the reported catalytic systems are methyltrioxorhenium(VII) (CH₃ReO₃)/H₂O₂ [6,7], Fe(III) perchlorate or Fe(III) acetate/H₂O₂ [8], iron phthalocyanines/TBHP [9,10], Pd(II)–polystyrene sulfonic acid resin/60% H₂O₂ [11], and Ti- and Fe-containing zeolites/H₂O₂ [12,13]. The drawback of these catalytic methods is a moderate yield of the target product (typically 40–60%). Moreover, some of the systems use homogeneous catalysts, or catalysis becomes homogeneous as a

* Corresponding author. Fax: +7 3833 309573.
E-mail address: khold@catalysis.nsk.su (O.A. Kholdeeva).

result of leaching of the active species from a solid catalyst during the oxidation process. This entails the well-known problems with catalyst separation and inevitably leads to contamination of the product with traces of hazardous transition metals.

The use of 2-methyl-1-naphthol (MNL) instead of MN as a substrate allows one to increase the selectivity in MNQ formation by avoiding the formation of some byproducts, particularly 6-methyl-1,4-naphthoquinone:



In turn, MNL can be produced by a vapor-phase methylation of 1-naphthol in the presence of Al_2O_3 [14,15] or Fe_2O_3 modified by chromium, silicon, and potassium [16]. Methylation of 1-tetralone followed by the subsequent dehydrogenation of 2-methyl-1-tetralone in the presence of Pd/C catalyst also has been reported [17]. An alternative method includes dehydrogenation of 1-tetralone over Pd or Ni supported on Al_2O_3 to yield 1-naphthol [18,19], followed by the methylation procedure. One-step vapor-phase synthesis of MNL from 1-tetralone has been also reported [20]. Recently, a new cheap, efficient method of MNL preparation has been proposed [21]. In this method, vapor-phase methylation of 1-naphthol is performed over mixed oxides of Mg(II) and Fe(II) or Fe(III). Various cobalt complexes were reported to catalyze oxidation of MNL with molecular oxygen with the yield close to quantitative [22]. Unfortunately, poorly described experimental details do not allow reproduction of these results. Mo–V-phosphoric Keggin heteropoly acids can be used as reversibly acting oxidants to convert MNL to MNQ with a yield of up to 80–85% [23–26]. However, the excess V-containing compounds used precludes this method's consideration as an environmentally benign route to vitamin K₃. The development of an MNL oxidation process using an atom-efficient, clean oxidant and a true heterogeneous catalyst remains a challenge.

Over the past decade, considerable research was dedicated to the preparation of various mesoporous materials containing transition metal ions highly dispersed in inorganic, mostly silicate matrixes and their use as catalysts in selective oxidation of bulky organic substrates with hydroperoxides [27–38]. Different microporous and mesoporous titanium and iron silicates, including TS-1, Ti-Beta, Fe-Beta, Ti-MCM-41, and some others, were tested in MN oxidation with 30% H_2O_2 . The selectivity to MNQ attained 35–63% at 10–28% of MN conversion [12,13]. Previously, we found that mesoporous titanium silicates, both well-ordered and amorphous ones, effectively catalyze the oxidation of 2,3,6-trimethylphenol (TMP) to 2,3,5-trimethyl-1,4-benzoquinone (TMBQ; vitamin E precursor) [35,36]. However, most of these catalytic materials suffered from hydrolytic instability, restricting their practical use. Recently we reported the preparation and characterization of the novel highly active and hydrothermally stable titanium-silicate, Ti-MMM-2, and demonstrated its reusability in selective oxidations with aqueous H_2O_2 [37,38]. Here we report a new method for MNL

oxidation to MNQ using aqueous H_2O_2 as an oxidant and Ti-MMM-2 as a heterogeneous catalyst. Special attention was given to the factors governing the reaction selectivity and optimization of the reaction conditions. Catalyst stability and recyclability were demonstrated.

2. Experimental

2.1. Materials and catalysts

2-Methyl-1-naphthol (98%) was purchased from Aldrich and used as received. The concentration of hydrogen peroxide (28 wt% in water) was determined iodometrically before use. $^{18}\text{O}_2$ (>98.5%) was purchased from Eurisotope. All the other reactants were obtained commercially and used without further purification.

Ti-MMM-2 (samples 1, 2, and 3, containing 1.68, 1.78, and 2.16 wt% of Ti, respectively) were prepared under moderately acidic conditions as described previously [37,38] using $\text{Na}_2\text{Si}_2\text{O}_5$ and $\text{TiOSO}_4 \cdot \text{H}_2\text{SO}_4$ as silica and titanium sources, respectively, and cetyltrimethyl ammonium bromide (CTAB) as a template. Al,Ti-MMM-2 (sample 4, containing 2.28 wt% of Ti and 0.07 wt% of Al) was prepared by a similar procedure, using $\text{Al}_2(\text{SO}_4)_3$ as an aluminum source. Sample 5 (1.82 wt% of Ti) was prepared using a mixture of 95% of neutral triblock copolymer Pluronic $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (P123) and 5% of CTAB as a template. The surfactant was removed from as-synthesized forms by calcination in air flow at 550–560 °C for 3 h. 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 titanium state in the silicate matrix was characterized by diffuse reflectance UV spectroscopy (DR UV) at ambient conditions.

2.2. Catalytic experiments

Catalytic experiments were performed under vigorous stirring in thermostatted glass vessels at 60–80 °C. The reactions were initiated by adding 0.125–0.5 mmol of H_2O_2 to a mixture containing 0.025–0.1 mmol of MNL, 3.8–15 mg of catalyst (0.0013–0.0057 mmol of Ti), an internal standard (biphenyl), and 1 ml of MeCN. In the alternative procedure, a concentrated solution of MNL in MeCN was gradually added to the mixture, containing 3.8–7.5 mg of the catalyst (0.0013–0.0034 mmol of Ti) and 0.088–0.125 mmol of H_2O_2 . The total final amount of MNL was 0.025 mmol in 1 ml of MeCN. The oxidation products were identified by both gas chromatography–mass spectroscopy (GC-MS) and ^1H nuclear magnetic resonance (NMR). MNL conversions and MNQ yields were quantified by GC using biphenyl as an internal standard. In recycling experiments, catalysts were separated from the reaction mixture by filtration, washed with methanol, dried in air at 100 °C, and then reused. Labeling experiments were carried out under atmosphere containing a mixture of $^{18}\text{O}_2$ with argon in a ratio of 36.2:63.8 according to the following procedure. A 50-ml flask was charged with 1 ml of MeCN containing 0.025 mmol of MNL and 3.5 mg of solid catalyst (0.0017 mmol of Ti). The reaction mixture

was submitted to three freeze–pump–thaw cycles, and the reaction flask was filled with the $^{18}\text{O}_2$ –Ar gas mixture (36.2:63.8). The reaction was started by adding 35% H_2O_2 solution (0.125 mmol). The isotopic composition of products and the gas phase were determined by GC–MS after correction on ^{18}O natural abundance and isotopic purity of $^{18}\text{O}_2$ using an m/z ratio of 172/174 for MNQ.

2.3. Physical measurements

GC analyses were performed using a Tsvet-500 gas chromatograph equipped with a flame ionization detector and quartz capillary column (25 m \times 0.3 mm) filled with Carbowax 20 M. GC–MS analyses of organic products were conducted using a HP 5973/6890 system (electron impact ionization at 70 eV, He carrier gas, 30 m \times 0.25 mm cross-linked 5% PHME siloxane (0.25- μm coating) capillary column; HP-5MS) or a VG-7070 instrument. DR UV measurements were performed on a Shimadzu UV–vis 2501PC spectrometer at ambient conditions. Nitrogen adsorption isotherms at 77 K were measured using a Quantachrome Autosorb-6BKr instrument. 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 the Siberian Synchrotron Radiation Center (SSRC).

3. Results and discussion

3.1. Catalyst characterization

The sample codes and physicochemical characteristics of the prepared titanium-silicate catalysts are given in Table 1. Structural and textural characteristics of the calcined forms of the catalysts were determined from synchrotron XRD patterns and nitrogen adsorption isotherms and calculated as described previously [39,40]. The representative XRD patterns are given in Fig. 1. The XRD (100) reflections are of the symmetric shape with the full-width-at-half-maximum (FWHM) values in the 0.2 – 0.8° 2θ range. Comparing the FWHM values shows that

the sample ordering reduced as follows: $1 > 2 > 3$ and 4. The nitrogen adsorption isotherms of all samples were of type IV with a rather narrow interval of relative pressure $\Delta(P/P_0)$. According to the comparative analysis of nitrogen adsorption performed as described previously [39], samples 1–4 have no micropores and have high internal and low external surface areas. These samples have uniform mesopores with a diameter of 3 nm and a silicate wall thickness of about 1.0 nm. Thus all obtained structural and textural characteristics are in agreement with those that we had described previously for the Ti-MMM-2 material [37,38]. The appropriate mesopore diameter and silicate wall thickness ensure good accessibility of titanium for hindered reactants.

In contrast with samples 1–4, sample 5, prepared using 95% of nonionic template P123 and 5% of ionic CTAB, has both mesopores and micropores. The pore size distribution plots for samples 1 and 5 are shown in Fig. 2. Sample 5 is characterized by a mesopore volume size distribution in the 6–7 nm range. Thus its mesopores are significantly larger than those of Ti-MMM-2 (3 nm). The silicate wall thickness, calculated

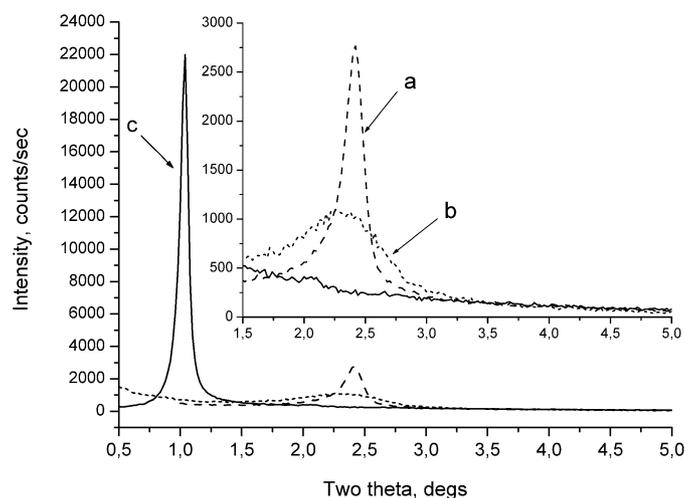


Fig. 1. XRD patterns for Ti-MMM-2: (a) sample 1; (b) sample 4, and (c) sample 5.

Table 1
Physicochemical properties of Ti-MMM-2 catalysts studied

Sample	Ti (wt%)	A_{Me}^{a} (m^2/g)	$A_{\text{ext}}^{\text{b}}$ (m^2/g)	V_{Me}^{c} (cm^3/g)	V_{m}^{d} (cm^3/g)	d_{Me}^{e} (nm)	h_{w}^{f} (nm)	a_0^{g} (nm)	FWHM ^h (2θ ($^\circ$))	$\lambda_{\text{max}}^{\text{i}}$ (nm)
1	1.68	1329	64	0.58	0	3.2	1.0	4.2	0.2	211
2	1.78	1119	75	0.57	0	3.2	1.0	4.4	0.4	206
3	2.16	922	66	0.46	0	3.2	1.0	4.2	0.8	204
4 ^j	2.28	1006	94	0.53	0	3.2	1.0	4.2	0.8	211
5	1.82	492	32	0.63	0.14	6.7	4.0	10.7	0.2	210

^a Specific mesopore surface area.

^b Specific external surface area.

^c Specific mesopore volume.

^d Micropore volume.

^e Mesopore diameter.

^f Wall thickness calculated from the equation $h_{\text{w}} = a - d$.

^g Unit cell parameter.

^h Full-width-at-half-maximum of the (100) reflection.

ⁱ Maximum in DR-UV spectrum.

^j 0.07 wt% of Al.

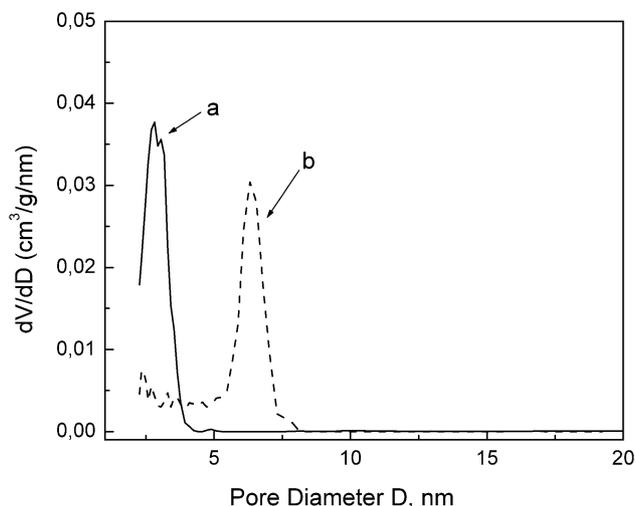


Fig. 2. Pore size distribution for Ti-MMM-2: (a) sample 2 and (b) sample 5.

as $a_0 - d_{Me}$, is about 4 nm. It is noteworthy that mesoporous titanium-silicate of this type has been prepared for the first time. The enhanced mesopore diameter is expected to ensure better accessibility of titanium for reactants, provided that the titanium centers are well-dispersed and not blocked inside thick silicate walls, as occurred earlier with the Ti-SBA-15 catalyst [41].

It is conventional that the absorption frequency in the DR UV spectra of titanium-silicates depends on the coordination number of Ti(IV) and its dispersion in the silicate matrix [27,29,31,34]. The band with λ_{max} at 205–208 nm, observed for anhydrous TS-1, indicates isolated tetrahedrally coordinated Ti sites [27,42,43]. After adsorption of water, 4-fold coordinated titanium transforms to a 5- and 6-fold coordinated titanium, reflected in a shift of the UV maximum to 215–225 nm [44–46]. A further shift to 250–270 nm indicates the formation of partially oligomerized or/and highly hydrated titanium species [27, 29,47]. A rather narrow band with maximum in the 204–211 nm range, observed in the DR UV spectra of Ti-MMM-2 (Fig. 3), shows that titanium is presumably in a site-isolated, most likely tetrahedral, form in all of the samples prepared. Importantly, no long-wave shift of the maximum was observed after treatment with aqueous H_2O_2 under the conditions of MNL oxidation (Fig. 3e). This is in a sharp contrast to what happened to Ti-Beta, Ti-MCM-41, TUD-1, Ti-MMM, TiO_2-SiO_2 mixed oxides, and many other titanium-silicate materials [35,36,44,47].

3.2. Catalytic oxidation of MNL

The results on MNL oxidation with H_2O_2 over the Ti-MMM-2 samples are given in Table 2. Under similar conditions, samples 1 and 2 showed similar results (MNQ yield of 68 and 66%, respectively), indicating that the sample ordering is not crucial for catalytic activity. Sample 3, which is even less ordered than samples 1 and 2, provided a 75% MNQ yield (Table 2, run 7). This could be due to the higher degree of titanium isolation in the silicate surrounding compared with the other samples (see Table 1). Note that the catalyst should be calcined before the catalytic experiment; otherwise, MNQ yield will decrease considerably (as in run 15). Sample 5, which has

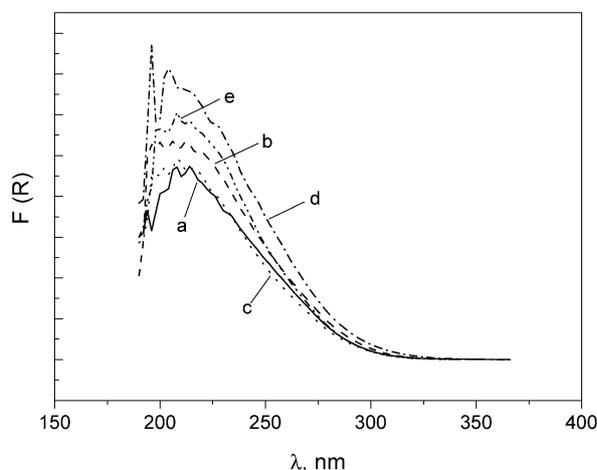


Fig. 3. UV-vis diffuse reflectance spectra of Ti-MMM-2: (a) sample 1, (b) sample 3, (c) sample 4, (d) sample 5, and (e) sample 1 after treatment with H_2O_2 (treatment conditions: Ti-MMM-2, 150 mg; H_2O_2 (35%), 0.7 M; MeCN, 10 ml; 80 °C, 1 h).

Table 2
MNL oxidation with 30% aqueous H_2O_2 over Ti-MMM-2 catalysts^a

Run	Sample ^b (mg)	[MNL] (M)	[H_2O_2] (M)	Selectivity to MNQ ^c (%)	MNL conver- sion (%)
1	1 ^d (15)	0.1	2.42	25	100
2	1 ^d (7.5)	0.05	1.11	32	100
3	1 ^d (3.8)	0.025	0.57	58	100
4	1 ^e (3.8)	0.025	2.42	68	100
5	2 ^e (3.8)	0.025	2.42	66	100
6	3 ^f (3.8)	0.025	2.42	58	100
7	3 ^e (3.8)	0.025	2.42	75	100
8	3 ^{e,g} (3.8)	0.025	2.42	64	89
9	3 ^e (3.8)	0.025	0.57	49	100
10	3 ^e (3.8)	0.025	1.47	52	100
11	3 ^e (3.8)	0.025	6.20	52	100
12	3 ^{e,h} (3.8)	0.025	2.42	27	100
13	3 ^{e,i} (3.8)	0.025	2.42	17	100
14	3 ^{e,j} (3.8)	0.025	2.42	38	96
15	3 ^{e,k} (3.8)	0.025	2.42	57	100
16	4 ^e (3.8)	0.025	2.42	67	100
17	5 ^e (3.8)	0.025	2.42	78	100
18	-e,l	0.025	0.57	0	51

^a Reaction conditions: [MNL]/[H_2O_2] = 1/5; MeCN, 1 ml, 80 °C, 30 min.

^b All the samples were calcined at 550 °C for 3 h prior to use.

^c GC yield based on MNL consumed.

^d H_2O_2 was added to the reaction mixture as one portion.

^e A solution of MNL in 500 μ l of MeCN was added to the reaction mixture by portion of 50 μ l every 2 min.

^f A solution of MNL in 500 μ l of MeCN was added at one portion.

^g [MNL]/[H_2O_2] = 1/3.5.

^h AcOH was used as solvent instead of MeCN.

ⁱ MeOH was used as solvent instead of MeCN.

^j Ethyl acetate was used as solvent instead of MeCN.

^k Not freshly calcined sample.

^l blank experiment without catalyst.

a larger mesopore diameter (6–7 nm) than the other samples (3 nm) produced MNQ with a yield of 78%. This is similar to the MNQ yield in sample 3 and superior to that in sample 1, which has a DR UV maximum at the same wavelength as in sample 3. It is noteworthy that the improved result that we obtained with sample 5 provides evidence in favor of good

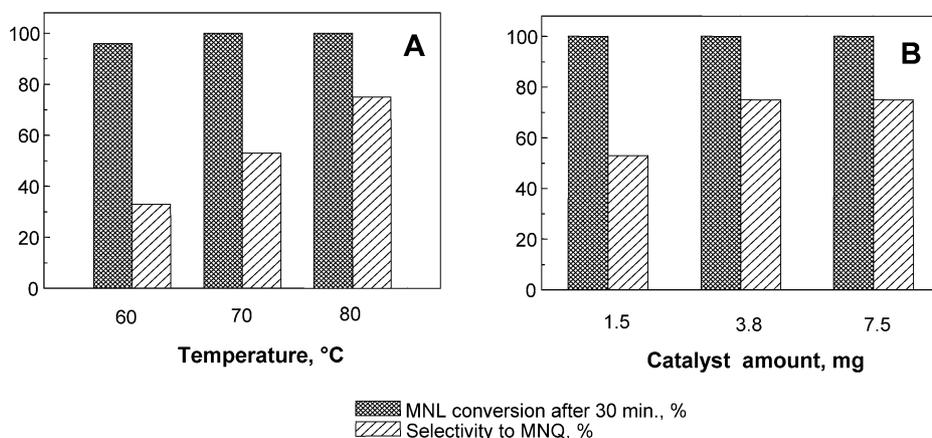
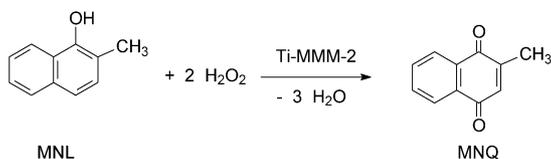


Fig. 4. The effect of temperature (A) and catalyst amount (B) on the selectivity to MNQ and MNL conversion. Reaction conditions: MNL, 0.025 M; H_2O_2 , 0.125 M, MeCN 1 ml, 30 min; (A) sample 2, 3.8 mg and (B) 80 °C. MNL solution in 250 μl of MeCN was added to the reaction mixture by portions 50 $\mu\text{l}/2$ min.

accessibility of titanium sites, despite the thick silicate walls (about 4 nm) in this sample. This finding is in sharp contrast to the Ti-SBA-15 catalyst, which had large mesopores (10 nm) but poor catalytic activity because of low titanium accessibility and dispersion [41]. Thus we may conclude that increasing mesopore size results in some increase in MNQ yield, provided that the other catalyst characteristics (primarily titanium dispersion and its accessibility) remain similar.

The stoichiometry of MNL oxidation with H_2O_2 to produce MNQ is 1:2:



However, even a 3.5 molar excess of H_2O_2 over MNL does not permit complete substrate conversion (Table 2, run 8). The selectivity to MNQ increases with increasing $[\text{H}_2\text{O}_2]/[\text{MNL}]$ ratio. The optimal $\text{H}_2\text{O}_2/\text{MNL}$ ratio is 5; taking into account that 2 equivalents of peroxide are needed to convert phenol to quinone, the real excess of peroxide is equal to 2.5.

The selectivity to MNQ increased significantly with increasing temperature: 32% at 60 °C, 53% at 70 °C, and 75% at 80 °C (Fig. 4A). The nature of the solvent greatly affects the selectivity of MNL oxidation. At 80 °C, the yield of MNQ was 75% for MeCN, 27% for AcOH, 17% for MeOH, and 38% for ethyl acetate (Table 2, runs 7, 12, 13, and 14). Augmentation of the amount of catalyst up to the optimal value of 5 mol% (mol Ti/mol MNL = 0.05) leads to growing selectivity of MNQ at 100% MNL conversion (Fig. 4B). It is worth to note that even without any catalyst, 51% of MNL was converted, but no MNQ was produced (Table 2, run 18).

The selectivity to MNQ essentially improved with decreasing MNL concentration at a constant $\text{H}_2\text{O}_2/\text{MNL}/\text{Ti}$ ratio (Table 2, runs 1–3). Because a lower concentration of H_2O_2 leads to a reduced amount of H_2O in the reaction mixture, we studied the effect of H_2O concentration on the reaction trend and found that MNQ selectivity initially increases with introducing additional water but decreases after reaching a maximum value

(runs 7, 9–11). A stepwise addition of MNL to the reaction mixture also favors enhanced reaction selectivity (compare runs 6 and 7). The same effect of temperature and substrate concentration for the oxidation of TMP to TMBQ with H_2O_2 over Ti-Si catalysts was found previously [35,36]. That allows us to suggest that the MNL oxidation over Ti-MMM-2 might proceed via a mechanism similar to that proposed for TMP and involve the formation of aryloxy radicals, ArO^\bullet [35,48]. The lower the ArOH concentration, the lower the possibility of ArO^\bullet coupling to yield dimeric and polymeric byproducts, which are typical of MNL oxidation [23]. We detected small amounts of 2-methyl-2,3-epoxy-1,4-naphthoquinone by GC-MS; however, the main byproducts were unidentified tars.

To probe the mechanism of MNL oxidation, we performed oxidation in the presence of $^{18}\text{O}_2$, controlling the isotopic composition of products and dioxygen in the gas phase during the entire reaction course. The initial isotopic composition of dioxygen determined by MS was 99.9% of $^{18}\text{O}_2$ and 0.1% of $^{16}\text{O}_2$. After a 30-min reaction, dioxygen left in the gas phase already contained 8.9% of $^{16}\text{O}_2$. By controlling the N_2 content in the gas phase, we ensured that this $^{16}\text{O}_2$ was not due to air entering the flask. This finding strongly indicates dioxygen formation from H_2O_2 . Our calculations show that about 50% of the $^{16}\text{O}_2$ formed came from H_2O_2 . This result explains the need to use a 2.5-fold excess of H_2O_2 with respect to the reaction stoichiometry to achieve the optimal MNQ yield. The isotopic composition of products and substrate were constant during the entire reaction, indicating no oxygen exchange between dioxygen and products. A very low ^{18}O labeling ($3.8 \pm 0.1\%$) was observed in the MNQ. Most of the MNQ ($96.2 \pm 0.1\%$) contained no ^{18}O label, consistent with the involvement of titanium-based active species and the absence of long-lived aryloxy radicals. Otherwise, significant ^{18}O content in MNQ should have been found. The absence of long-living aryloxy radicals is also consistent with high quinone yield, whereas coupling products should be obtained in the opposite case.

Previously, we demonstrated that Ti and Si materials behave as true heterogeneous catalysts and do not suffer from titanium leaching when oxidation is done by H_2O_2 in MeCN [35–38]. We performed the Ti-MMM-2 catalyst recycling experiments

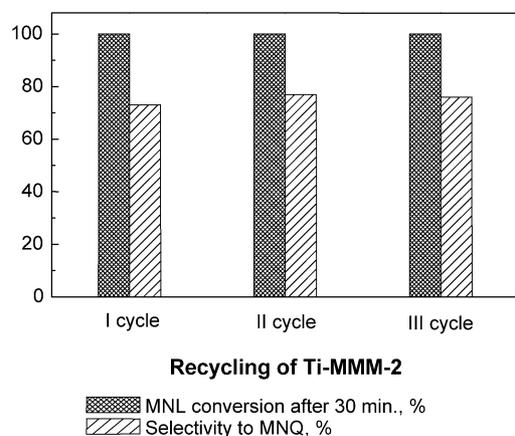


Fig. 5. Catalyst recycling. Reaction conditions: MNL, 0.025 M; H_2O_2 , 0.125 M; Ti-MMM-2 (sample 2) 3.8 mg, MeCN 1 ml, 80 °C, 30 min, MNL solution in 250 μ l of MeCN was added to the reaction mixture by portions 50 μ l/2 min.

using sample 3. No loss in either catalytic activity or selectivity was observed during at least three catalytic cycles (Fig. 5). The MNQ yields were 73, 77, and 76% in three consecutive oxidations. These results strongly support the absence of catalyst deactivation during the catalytic runs. If some amount of the catalyst were in fact deactivated, this would correspond to a diminishing effective catalyst/substrate molar ratio. In turn, this would lead to decreasing MNQ selectivity (at 100% conversion), as had been established in the experiments with decreasing catalyst amount (Fig. 4B).

4. Conclusions

The oxidation of MNL to MNQ by aqueous H_2O_2 effectively proceeds over mesoporous titanium silicates of the Ti-MMM-2 type. Crucial factors affecting MNQ yield are MNL concentration, H_2O_2 /MNL molar ratio, solvent nature, reaction temperature, and the mode of MNL addition to the reaction mixture. At optimal reaction conditions, MNQ yield attained 75–78% at 100% substrate conversion. The Ti-MMM-2 catalyst can be used repeatedly with no loss of catalytic activity or selectivity. The proposed method of MNQ production is environmentally benign and avoids product contamination by traces of transition metals. The catalytic material obtained with the mixture of ionic and nonionic surfactant (a representative of these materials is sample 5) is a novel type of mesoporous titanium silicate that should be studied in more detail.

Acknowledgment

OVZ acknowledges financial support from the Embassy of France in Moscow through a doctoral fellowship. Financial support of RFBR-CNRS (Grant 05-03-34760) is highly appreciated.

References

[1] P. Schudel, H. Mayer, O. Isler, in: W.H. Sebrell, R.S. Harris (Eds.), *The Vitamines*, vol. 5, Academic Press, New York, 1972, p. 165.

[2] L.F. Fieser, *J. Biol. Chem.* 133 (1940) 391.
 [3] R.A. Sheldon, *Top. Curr. Chem.* 164 (1993) 21.
 [4] R.A. Sheldon, *J. Dakka, Catal. Today* 19 (1994) 215.
 [5] W. Bonrath, T. Netscher, *Appl. Catal. A: Gen.* 280 (2005) 55.
 [6] W. Adam, W.A. Herrmann, W. Lin, Ch.R. Saha-Moller, R.W. Fischer, J.D.G. Correia, *Angew. Chem. Int. Ed.* 33 (1994) 2475.
 [7] W.A. Herrmann, J.J. Haider, R.W. Fischer, *J. Mol. Catal. A: Chem.* 138 (1999) 115.
 [8] J. Kowalski, J. Ploszynska, A. Sobkowiak, *Catal. Commun.* 4 (2003) 603.
 [9] A. Sorokin, A. Tuel, *Catal. Today* 57 (2000) 45.
 [10] A.B. Sorokin, S. Mangematin, C. Pergrale, *J. Mol. Catal. A: Chem.* 182–183 (2002) 267.
 [11] S. Yamaguchi, M. Inone, S. Enomoto, *Chem. Lett.* (1985) 827.
 [12] O.S. Anunziata, L.B. Pierella, A.R. Beltramone, *J. Mol. Catal. A: Chem.* 149 (1999) 255.
 [13] O.S. Anunziata, A.R. Beltramone, J. Cussa, *Appl. Catal. A: Gen.* 270 (2004) 77.
 [14] L.H. Klemm, J. Shabtai, D.R. Taylor, *J. Org. Chem.* 33 (1968) 1480.
 [15] B.E. Leach, C.M. Starks, *US Patent* 3 993 701 (1976).
 [16] H. Grabowska, W. Mista, L. Syper, J. Wrzyszczyk, M. Zawadzki, *J. Catal.* 160 (1996) 134.
 [17] S. Shimizu, T. Ishitoku, H. Nanbu, *Japanese Patent* 58 065 235 (1983).
 [18] I. Calinescu, R. Avram, *Rev. Chim.* 45 (1994) 865.
 [19] M.V. Kheifets, D.A. Sibarov, V.V. Sobolev, N.A. Petrova, *J. Appl. Chem. USSR* 59 (1986) 990.
 [20] I. Yuranov, L. Kiwi-Minsker, A. Renken, *Appl. Catal. A: Gen.* 226 (2002) 193.
 [21] F. Monteleone, F. Cavani, C. Felloni, R. Trabace, *European Patent* 014 832 (2004).
 [22] M. Frostin-Rio, D. Pujol, C. Bied-Charreton, M. Perree-Fauvet, A. Gaudemer, *J. Chem. Soc., Perkin Trans. 1* (1984) 1971.
 [23] K.I. Matveev, A.P. Krysin, T.F. Titova, B.M. Khlebnikov, V.F. Odjakov, T.G. Egorova, E.G. Zhizhina, V.N. Parmon, *Russian Patent* 2 022 958 (1994).
 [24] K.I. Matveev, E.G. Zhizhina, V.F. Odjakov, V.N. Parmon, *Russian Patent* 2 061 669 (1996).
 [25] K.I. Matveev, E.G. Zhizhina, V.F. Odjakov, *Russian Patent* 2 162 837 (2001).
 [26] K.I. Matveev, V.F. Odjakov, E.G. Zhizhina, *J. Mol. Catal. A: Chem.* 114 (1996) 151.
 [27] B. Notari, *Adv. Catal.* 41 (1996) 253.
 [28] A. Corma, M.T. Navarro, J. Perez Pariente, *J. Chem. Soc., Chem. Commun.* (1994) 147.
 [29] A. Corma, *Chem. Rev.* 97 (1997) 2373.
 [30] M. Schneider, A. Baiker, *Catal. Today* 35 (1997) 339.
 [31] W. Zhang, M. Froba, J. Wang, P.T. Tanev, J. Wong, T.J. Pinnavaia, *J. Am. Chem. Soc.* 118 (1996) 9164.
 [32] P.T. Tanev, M. Chibwe, T.J. Pinnavaia, *Nature* 368 (1994) 321.
 [33] A. Sayari, *Chem. Mater.* 8 (1996) 1840.
 [34] X. Gao, I.E. Wachs, *Catal. Today* 51 (1999) 233.
 [35] N.N. Trukhan, V.N. Romannikov, E.A. Paukshtis, A.N. Shmakov, O.A. Kholdeeva, *J. Catal.* 202 (2001) 110.
 [36] O.A. Kholdeeva, N.N. Trukhan, M.P. Vanina, V.N. Romannikov, V.N. Parmon, J. Mrowiec-Bialoń, A.B. Jarzebski, *Catal. Today* 75 (2002) 203.
 [37] O.A. Kholdeeva, M.S. Melgunov, A.N. Shmakov, N.N. Trukhan, V.V. Kriventsov, V.I. Zaikovskii, V.N. Romannikov, *Catal. Today* 91–92 (2004) 205.
 [38] O.A. Kholdeeva, M.S. Melgunov, A.N. Shmakov, N.N. Trukhan, M.E. Malyshev, V.B. Fenelonov, V.N. Parmon, V.N. Romannikov, *Russian Patent* 2 229 930 (2004).
 [39] V.B. Fenelonov, V.N. Romannikov, A.Yu. Derevyankin, *Microporous Mesoporous Mater.* 28 (1999) 57.
 [40] V.B. Fenelonov, A.Yu. Derevyankin, S.D. Kirik, L.A. Solovyov, A.N. Shmakov, J.-L. Bonardet, A. Gédéon, V.N. Romannikov, *Microporous Mesoporous Mater.* 44–45 (2001) 33.
 [41] N.N. Trukhan, V.N. Romannikov, A.N. Shmakov, M.P. Vanina, E.A. Paukshtis, V.I. Bukhtiyarov, V.V. Kriventsov, I.Yu. Danilov, O.A. Kholdeeva, *Microporous Mesoporous Mater.* 59 (2003) 73.
 [42] G.N. Vayssilov, *Catal. Rev.-Sci. Eng.* 39 (3) (1997) 209.

- [43] G. Petrini, A. Cesana, G. De Alberti, F. Genoni, G. Leofanti, M. Paolovan, G. Paparatto, P. Rofia, *Stud. Surf. Sci. Catal.* 68 (1991) 761.
- [44] A. Carati, C. Flego, E. Previde Massara, R. Millini, L. Carluccio, G. Bellussi, *Microporous Mesoporous Mater.* 30 (1999) 137.
- [45] E. Geobaldo, S. Bordiga, A. Zecchina, E. Giamelo, G. Leofanti, G. Petrini, *Catal. Lett.* 16 (1992) 109.
- [46] S. Bordiga, S. Coluccia, C. Lamberti, L. Marchese, A. Zecchina, F. Boscherini, F. Buffa, F. Genoni, G. Leofanti, G. Petrini, G. Vlaic, *J. Phys. Chem.* 98 (1994) 4125.
- [47] Z. Shan, J.S. Jansen, L. Marchese, Th. Maschmeyer, *Microporous Mesoporous Mater.* 48 (2001) 181.
- [48] N.N. Trukhan, O.A. Kholdeeva, *Kinet. Katal.* 44 (2003) 347.