Support Pretreatment Effect on the Catalytic Properties and Reusability of Silica-Supported Titania Catalysts in 2,3,6-Trimethylphenol Oxidation with Hydrogen Peroxide

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Abstract—The effects of some variants for silica support pretreatment on the catalytic properties and reusability of silica-supported titania in the liquid-phase oxidation of 2,3,6-trimethylphenol (TMP) into 2,3,5-trimethyl-1,4-benzoquinone (TMBQ) with hydrogen peroxide, a green oxidizer, have been investigated. The support pretreated with aqueous ammonia and then evacuated demonstrates the optimal activity, selectivity, and reusability of catalysts. The TMBQ selectivity reaches 93% at a TMP conversion of 90% in at least four cycles for the catalyst prepared.

The selective liquid-phase oxidation of organic compounds is widely used in the production of large-scale products and fine organic synthesis products and intermediates [1, 2]. The advantages of solid-phase catalysts are that they are easily separable from reaction mixtures and can potentially be reused [2, 3]. However, frequently encountered serious problems are the leaching of the active component into the solution during the reaction and/or the agglomeration of the active component on the support surface, which leads to a decline in the activity and selectivity of the catalyst as it is reused [3, 4]. Mesoporous titanium silicate catalysts show a high catalytic activity and selectivity in 2,3,6-trimethylphenol (TMP) oxidation into 2,3,5-trimethyl-1,4-benzoquinone (TMBQ, the key intermediate in the synthesis of vitamin E) with hydrogen peroxide [5–8], an environmentally friendly oxidizer. Catalysts having dimeric or small oligomeric Ti sites uniformly distributed on the surface of the silicate support allow >99% TMBQ formation selectivity to be attained at a practically 100% conversion of the initial phenolic substrate [9–12]. However, the problem of achieving an optimal balance between the catalytic activity (selectivity) and reusability of mesoporous titanium silicate catalysts in reactions involving aqueous hydrogen peroxide is still unsolved [8]. In order to develop new approaches to this problem, we investigated the effects of some variants of pretreatment of the silicate support on the catalytic properties and reusability of silica-supported titania catalysts in the liquid phase oxidation of TMP with hydrogen peroxide.

EXPERIMENTAL

Chemicals

Support samples were synthesized as-received tetraethyl orthosilicate (Acros Organics), 25% aqueous ammonia (special-purity grade, Russia), and concentrated nitric acid special-purity grade, BioMedKhim, Russia). Toluene (special purity grade, Vekton, Russia), and titanium tetraisopropoxide (99%, Sigma-Aldrich) were vacuum-distilled just before the synthesis. Acetonitrile (special-purity grade, Acros, Russia) was additionally dried and stored over activated molecular sieve 4 Å. 2,3,6-Trimethylphenol (97%, Fluka) was used as received.

The hydrogen peroxide concentration in the initial reactant (~30 wt %) was determined by iodometric titration just before use.

Preparation of Supports and Catalysts

The initial catalyst support was prepared by the sol–gel process [13]. Concentrated nitric acid (ρ = 1.41 g/mL, 3 mL) and distilled water (40 mL) were added to tetraethyl orthosilicate (35 mL). The mixture was stirred at 25°C for 2 h. After stirring, the sol was placed in hermetically sealed plastic containers. The silica gel was kept at 50°C for 3 days. Thereafter, the gel was washed with distilled water and was immersed into a 25% ammonia solution and was kept there for 3 days. Next, the gel was dried at room temperature for 1 day and was then subjected to stepwise heat treatment between 100 and 600°C, being kept at each temperature point for 1 h.
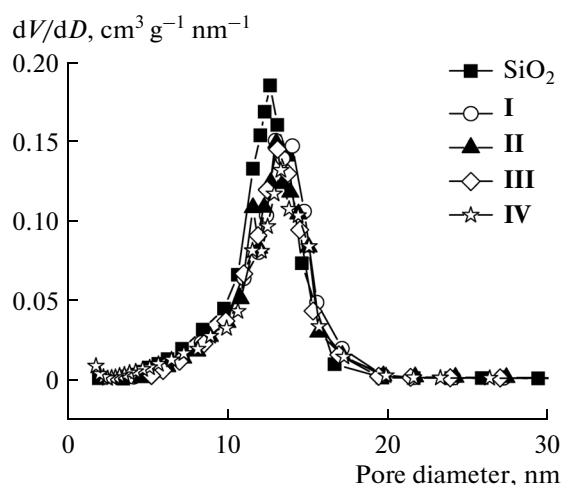
dV/dD, cm³ g⁻¹ nm⁻¹

Fig. 1. Pore size distribution in the SiO₂ support and in samples **I–IV** of the TiO₂/SiO₂ catalysts.

One part of the support prepared in this way was directly loaded with the active component (samples **I** and **IV**). The other part of the support was additionally treated, before active component deposition, with aqueous ammonia at 25°C for 2 h to restore the hydroxyl cover of the surface and was then heat-treated at 100°C (sample **II**) and kept in a vacuum at 80°C for 20 min and at 100°C for 40 min (sample **III**).

The active component was deposited onto the SiO₂ surface via grafting [14]. The synthesis was performed at 107°C. The titanium dioxide precursor—titanium tetraisopropoxide—was added in 200-μL portions to a suspension of the support in toluene, and the mixture was kept at the synthesis temperature for 1 h. The product was washed with toluene, dried at 25°C for 1 h, and calcined at 600°C for 6 h. Four samples of the TiO₂/SiO₂ catalyst (**I–IV**) were prepared in this way. Sample **IV** differed from sample **I** in that it had a low titanium content (0.27 wt %).

Catalyst Characterization

The titanium content of catalysts and reaction mixtures was determined by inductively coupled plasma atomic emission spectroscopy (AES-ICP) on an OPTIMA 4300 DV spectrometer (PerkinElmer, United States) and on an Agilent 4100 microwave plasma atomic emission spectrometer (Agilent, United States).

The textural characteristics of supports and catalysts were determined by low-temperature nitrogen adsorption on a Tristar II 3020 analyzer (Micromeritics, United States). Before measurements, all samples were degassed in a vacuum at 200°C for 2 h. The diffuse reflectance UV spectroscopic (DR-UV) and Raman spectroscopic characterization of supported catalysts was carried out on Shimadzu UV–VIS 2501 PC (Shimadzu, Japan) and Bruker RFS 100/S (Bruker, Germany, Nd:YAG laser, 1064 nm) spectrometers, respec-

tively. Before these physicochemical measurements, the catalysts were calcined at 550°C.

The chemical composition of materials was studied by IR spectroscopy on a Nicolet 6700 Fourier-transform IR spectrometer (Thermo Scientific, United States) in the 400–4000 cm⁻¹ wavenumber range.

Catalytic Tests

Catalytic TMP oxidation was carried out in temperature-controlled glass reactors at 80°C under vigorous stirring with a magnetic stirrer (500 rpm). The reaction was initiated by adding 0.35 mmol H_2O_2 to a mixture containing 0.1 mmol TMP, 0.014 g of the catalyst (0.008 mmol Ti), and 1 mL of acetonitrile. Biphenyl as the internal standard was added to the reaction mixture. During the reaction, the reaction mixture was sampled with a syringe and was analyzed by GC-MS (to determine the qualitative composition of the products) and by GC (to determine the TMBQ yield and TMP conversion). Each run was repeated three or four times. The structure of the reaction products was confirmed by ¹H NMR spectroscopy.

The catalyst was reused at a larger reaction mixture volume of 15–20 mL. After the completion of the reaction, the catalyst was filtered and was washed with hot acetonitrile and acetone and was then dried in air at room temperature. Prior to being used in the next operation cycle, the catalyst was calcined at 250°C for 2 h and at 550°C for 4 h. To elucidate the nature of catalysis, we carried out an experiment in which the catalyst was separated out by hot filtration and the substrate conversion in the filtrate was monitored [3].

GC analyses were performed on a Tsvet-500 chromatograph fitted with a Khromos IRM-10 control unit (Khromos, Russia), a flame-ionization detector, and a BPX5 quartz capillary column (30 m × 0.25 mm). GC-MS analyses were carried out on an Agilent 7000B chromatograph (30 m × 0.25 mm HP-5ms capillary column, Agilent MSD 5973 quadrupole mass-selective detector). ¹H NMR spectra were recorded on a Bruker Avance-400 spectrometer operating at 400.13 MHz).

RESULTS AND DISCUSSION

The titanium content and textural properties of the initial support and those of supported catalysts **I–IV** are given in Table 1. All samples are mesoporous. The pore size distribution for the support (SiO₂) and catalysts **I–IV** is plotted in Fig. 1. The deposition of the active component only insignificantly decreases the specific surface area and mesopore volume. According to the data presented in Table 1, the pretreatment of the support with aqueous ammonia makes it possible to slightly increase the amount of supported titanium in the samples. This is quite natural, because the number of H-bonded silanol groups on the surface (absorption

Table 1. Textural characteristics of the SiO_2 support and TiO_2/SiO_2 catalysts

Sample	Support pretreatment	Ti, wt %	S_{BET}, m^2/g	V_{pore}, cm^3/g	D_{pore}, nm
Support	–	–	235	0.77	12.6
I	–	2.46	198	0.72	13.3
I*			203	0.71	12.2
II	NH_3	2.94	190	0.70	13.0
II*			197	0.71	12.6
III	NH_3 + pumping	2.74	167	0.66	13.0
III*			188	0.72	12.7
IV	–	0.27	200	0.64	13.3
IV*			185	0.61	12.6

Reaction conditions: [TMP] = 0.1 mol/L, [H_2O_2] = 0.35 mol/L, catalyst weight of 14 mg, 1 mL of CH_3CN, 80°C.
* After the first TMP oxidation cycle.

bands at 951 and 3454 cm^{-1}) increases as a result of this treatment (Fig. 2, spectra *1*, *2*), and these groups are involved in the formation of Ti−O−Si bonds on the surface [15, 16]. Note that the number of hydroxyl groups showing themselves in the 3000−3600 cm^{-1} range is larger for sample **I**, which was obtained by titanium isopropoxide deposition on calcined SiO_2 without additional treatment (Fig. 2, spectrum *3*). This may be due to the anchoring of Ti-containing sites through the formation of monopodal and dipodal Ti−O−Si bonds with the support surface.

For samples **II** and **III**, which were prepared using SiO_2 pretreated with aqueous ammonia (**II**) and then vacuum-dried (**III**), this absorption band is stronger than the same band for the supports but is weaker than that for Sample **I**. This fact can be explained by the formation of a larger number of dipodal and tripodal Ti−O−Si bonds at the titanium isopropoxide−SiO_2 surface interaction stage. In situ IR spectroscopic studies of the interaction between the titanium alkoxide and the SiO_2 surface [17] demonstrated that isolated OH groups (absorption band at 3837 cm^{-1}) interact weakly with the titanium alkoxide, while H-bonded OH groups form stronger bonds. Since the pretreatment with aqueous ammonia generates H-bonded hydroxyl groups on the SiO_2 surface, this procedure ensures the formation of Ti-containing sites highly coordinated to the surface in samples **II** and **III**.

The vacuum treatment of the support at 80°C for 20 min (after treatment with aqueous ammonia) followed by drying at 100°C in air for 40 min does not remove all adsorbed H_2O molecules from the SiO_2 surface [18]. The presence of adsorbed water leads to the formation of anatase clusters on the support surface. This is expected to make the Ti-containing sites more resistant to hydrolysis under the action of hydrogen

peroxide. Note also that the support pretreatment exerts only a slight effect on the textural characteristics of the Ti-containing samples.

It is well known that the state of Ti-containing sites (their local geometry and coordination environment) in titanium silicates has a strong effect on their catalytic properties [4, 7, 8]. The synthesized catalyst samples were characterized by DR-UV spectroscopy, which is a readily available and reliable method of determining the state of titanium sites in titanium silicates and provides means to distinguish isolated sites
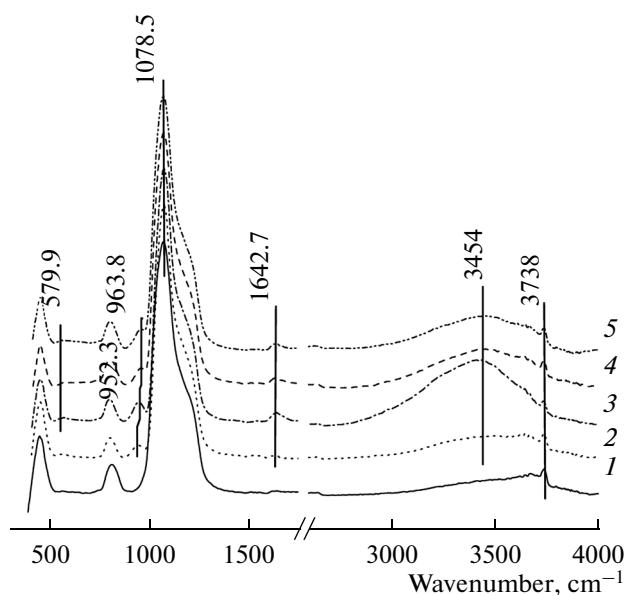
Fig. 2. IR spectra of (*1*, *2*) calcined SiO_2 support before and after its interaction with aqueous ammonia and (*3−5*) samples **I**−**III** of the TiO_2/SiO_2 catalyst.
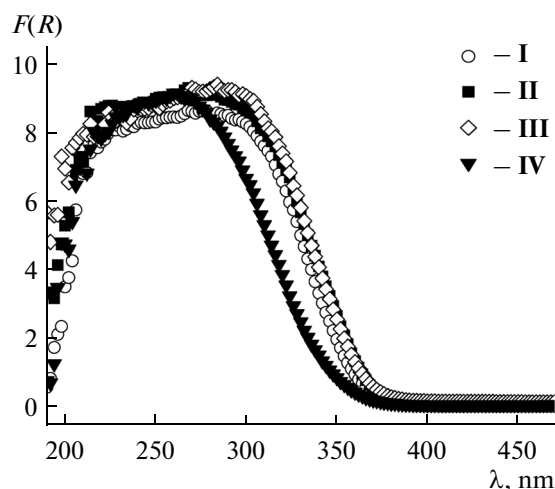
Fig. 3. DR-UV spectra of calcined samples **I**–**IV** of the TiO$_2$/SiO$_2$ catalyst.

(205–230 nm), di/oligomerized sites (240–300 nm), and anatase microcrystallites (330–340 nm) [7, 12, 15, 19–21]. The DR-UV spectra of catalysts **I**–**IV** are shown in Fig. 3. Absorption in the 330–340 nm range indicates the presence of anatase clusters on the surface of catalysts **I**–**III**. The edge of the absorption band occurs at 360–370 nm, which, according to the literature [19], suggests that the cluster size is over 1.2–1.6 nm (30–70 TiO$_2$ units). In addition, the Raman spectrum of catalyst **III** exhibits an absorption band at 145 cm^{-1}, which clearly indicates the presence of the anatase phase [15, 19, 20]. Thus, the existence of anatase-like particles on the SiO$_2$ surface in sam-

ples **I**–**III** is beyond any doubt. Concerning the similarity of the DR-UV spectra of catalysts **I**–**II**, it can be concluded that the support pretreatment variants considered here exert no significant effect on the state and degree of dispersion of the active component (TiO$_2$). For the sake of comparison, we examined sample **IV**, which had a low titanium content of 0.27 wt %. Its DR-UV spectrum is also presented in Fig. 3. The absorption band of sample **IV** in the 200–350 nm range is considerably shifted to shorter wavelengths relative to the same band for samples **I**–**III**, indicating a lower degree of clustering in this sample [7, 12, 15, 19–21]. The edge of this absorption band is below 350 nm, which indicates a domination of clusters smaller than 1.2 nm [19]. Similar spectra were earlier recorded for silica-supported titania samples prepared by grafting of titanocene dichloride Ti(Cp)$_2$Cl$_2$ tp the surface of commercial silica gels [9, 10], although the titanium content of these materials was one order of magnitude higher (2–3 wt %). Thus, the method used in this study to deposit titanium onto the SiO$_2$ surface affords a lower degree of dispersion of the active component than the method involving the organometallic precursor Ti(Cp)$_2$Cl$_2$. (It will be demonstrated below that this fact has serious implications both for the catalytic activity and for the reusability of the catalysts.)

The catalytic properties of samples **I**–**IV** in TMP oxidation with 30% hydrogen peroxide in acetonitrile are listed in Table 2. For all samples, the major oxidation product is TMBQ. The minor products of this reactions are 2,2',3,3',5,5'-hexamethyl-4,4'-bisphenol (BP) and products of further TMBQ oxidation, namely, isomeric epoxy derivatives and 2-hydroxy-3,5,6-trimethyl-1,4-benzoquinone (scheme).
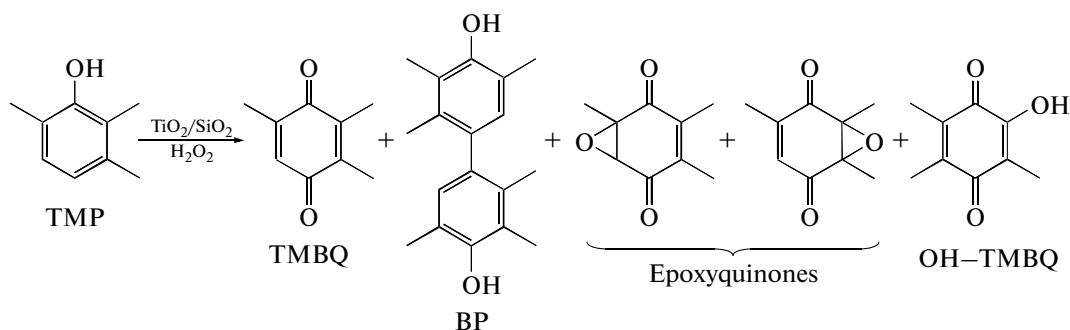
Scheme. 2,3,6-Trimethylphenol oxidation products.

The data presented in Table 2 demonstrate that the pretreatment of the support exerts a marked effect both on the catalytic activity and on the target product (TMBQ) formation selectivity. In the first cycle, the TOF of the catalysts per titanium amount in the sample decreases in the following order: **IV** > **III** > **I** > **II**. Sample **IV** is similar in activity to the samples prepared earlier by Ti(Cp)$_2$Cl$_2$ grafting [9]. This is in agreement with the similarity of their DR-UV spectra. The lower

activity of samples **I**–**III** is explained by the lower degree of dispersion of titanium on their surface and, accordingly, by the lower accessibility of the Ti sites. At the same time, the TMBQ formation selectivity changes as follows: **IV**, **I** ~ **III** > **II**. The highest TMP conversion (92 and 90%) and TMBQ yield (87 and 84%) are attained with samples **I** and **III**, respectively. The reaction time is 35 min for sample **III** and 50 min for sample **I**. According to the stoichiometry of the

Table 2. TMP oxidation over TiO$_2$/SiO$_2$ catalysts **I–IV**

Sample	Cycle	Time, min	TMP conversion, %	TMBQ selectivity*, %	TOF**, min^{-1}
I	1	50	92	95	0.7
	2	90	85	94	0.3
	3	90	86	94	0.3
II	1	80	80	81	0.3
	2	105	84	82	0.16
	3	110	76	83	0.15
	4	120	73	82	0.13
III	1	35	90	93	0.9
	2	60	90	91	0.3
	3	70	90	92	0.3
IV	1	80	76	95	1.9
	2	240	75	91	0.6
	3	450	60	60	0.2

Reaction conditions: [TMP] = 0.1 mol/L, [H$_2$O$_2$] = 0.35 mol/L, catalyst weight of 14 mg, 1 mL of CH$_3$CN, 80°C.

 * Yield on the reacted substrate casis.

** TOF = (number of moles of reacted TMP) × (number of moles of Ti)$^{-1}$ × (time)$^{-1}$, derived from initial TMP disappearance rate data.

reaction, two H$_2$O$_2$ molecules are needed for the oxidation of one TMP molecule into TMBQ, so the efficiency of the oxidizer (TMBQ yield on the H$_2$O$_2$ basis) for these samples is estimated at about 50%.

Table 2 presents reuse data for catalysts **I–IV** in the TMP oxidation reaction. Although catalyst **IV** is the most active one in the first cycle, its activity decreases progressively from one cycle to another. The same happens to the selectivity of this catalyst: in the third cycle, it is no higher than 60%. The substrate conversion decreases from 76% in the first cycle to 60% in the third one. At the same time, catalysts **I–III** show a much higher performance if used repeatedly. Although

the specific activity of these catalysts decreases after the first operation cycle, in subsequent cycles it comes to a constant value. It is significant that both the selectivity (and also the substrate conversion for sample **III**) and the target product yield remain invariable (Fig. 4). The reusability of sample **III** under the catalytic conditions is confirmed by the invariance of its DR-UV spectrum throughout three operation cycles (Fig. 5) and by the preservation of its textural characteristics (Table 1). Thus, sample **III**, which combines a high selectivity and a high performance resistance, seems to be the optimum catalyst for TMP oxidation into TMBQ.
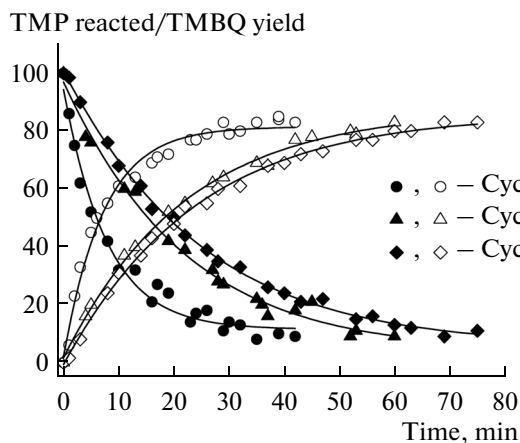

Fig. 4. Reuse data for catalyst **III** (dark symbols—TMP conversion data; open symbols—TMBQ yield). Reaction conditions: [TMP] = 0.1 mol/L, [H$_2$O$_2$] = 0.35 mol/L, catalyst weight of 14 mg, 1 mL of CH$_3$CN, 80°C.
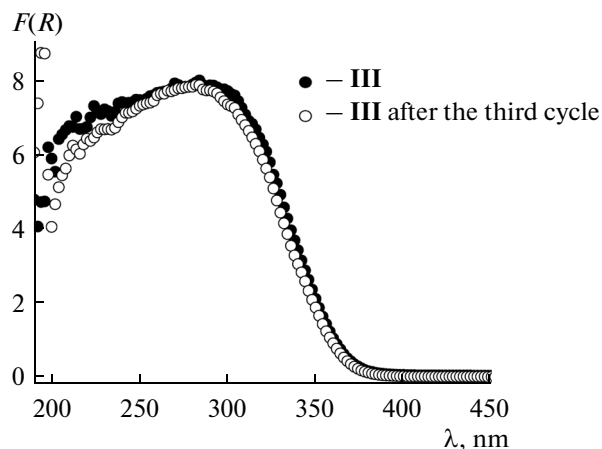

Fig. 5. DR-UV spectra of calcined samples of initial catalyst **III** and the same catalyst that has operated in three cycles of the TMP oxidation reaction. The reaction conditions are the same as specified in Fig. 4.
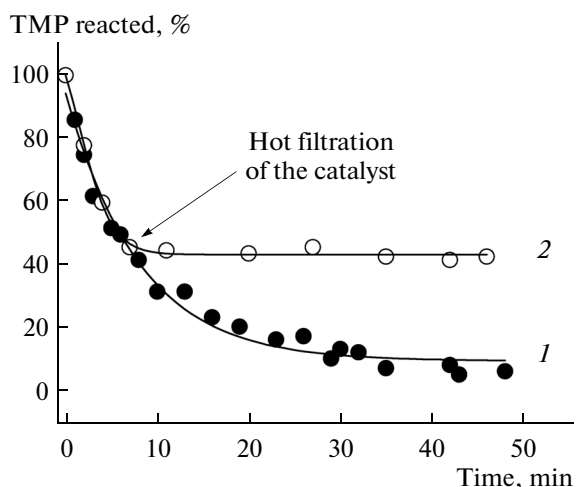
TMP reacted, %

Fig. 6. Kinetics of TMP conversion in the presence of catalyst **III**: (*1*) catalyst is not removed from the reaction mixture; (*2*) catalyst is filtered out during the reaction. The reaction conditions are the same as specified in Fig. 4.

In order to prove the heterogeneous nature of catalysis in the system examined, we carried out an experiment in which catalyst **III** was quickly removed by hot filtration during the reaction and substrate conversion in the filtrate was then monitored. The results of this experiment are presented in Fig. 6. It can be seen that, after the removal of the catalyst, the reaction ceases completely, indicating the heterogeneous nature of catalysis. For all catalysts, we determined the titanium content of the filtrates after the first operation cycle. The amount of titanium in the filtrate was no higher than 0.1 ppm for samples **III** and **IV** and was 0.12 ppm. Therefore, the active component practically does not leach from the catalyst into the solution during the reaction.

Thus, the study of the effects of different pretreatments of the silicate support prepared by the sol−gel method on the catalytic properties and reusability of the supported titanium silicate catalysts in the liquid-phase oxidation of 2,3,6-trimethylphenol with aqueous hydrogen peroxide into 2,3,5-trimethyl-1,4-benzoquinone demonstrated that the support that was pretreated with aqueous ammonia and was then evacuated is optimal for preparing a catalyst simultaneously showing high activity, a high selectivity, and reusability. With this catalyst, in at least four operation cycles the target quinone formation selectivity is 93% at a phenolic substrate conversion of 90%.

ACKNOWLEDGMENTS

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