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Titanium Dioxide Xerogel Modified with Powder Cellulose in Oxidation of Trimethylhydroquinone

A. B. Shishmakov, Yu. V. Mikushina, M. S. Valova,
O. V. Koryakova, and L. A. Petrov

Institute of Organic Synthesis, Ural Division, Russian Academy of Sciences, Yekaterinburg, Russia

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Abstract—A procedure was developed for modification of titanium dioxide xerogel by addition of powder cellulose in the stage preceding hydrolysis of tetramethoxytitanium. The resulting catalytic systems based on the new material were studied in a model liquid-phase catalytic process of oxidative dehydrogenation of trimethylhydroquinone with atmospheric oxygen.

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Titanium dioxide is widely used as a sorbent and a catalyst support. The efficiency of its application is mainly governed by the structural and texture characteristics, development of the surface, and accessibility of its active centers throughout the entire volume.

Synthesis of xerogels of element oxides by any method is accompanied by their shrinkage and, as a result, by a decrease in the specific surface area on drying. There are several ways to eliminate this phenomenon: variation of the composition of dispersion medium, drying for longer time, and the use of special additives [1–9].

The aim of this study was modify titanium dioxide with powder cellulose (PC) and to study the resulting materials in a model catalytic process of oxidative dehydrogenation of trimethylhydroquinone (TMHQ) with atmospheric oxygen.

EXPERIMENTAL

Powder cellulose was prepared by hydrolysis of kraft cellulose produced at the Baikal Paper and Pulp Plant (Technical Specification OP 13-027 94 88-08–91) in 2.5 N hydrochloric acid at 100°C. Hydrolysis was performed for 2 h. The resulting product was washed with distilled water on a filter until neutral pH of the aqueous extract. The product was dried at 100°C.

Three samples of titanium dioxide xerogels K1, K2, and K3 were prepared as follows: 1.5, 3, and 9 ml of tetrabutoxytitanium (TBT), respectively, was dissolved in 20 ml of methanol. Hydrolysis was performed with 500 ml of water at 20°C. The precipitate was washed on a filter until the absence of butanol in the wash water and dried at 100°C.

To prepare modified xerogels (MXs) with the $TiO_2 : PC$ ratios of 0.45 : 0.55, 0.26 : 0.74, and 0.06 : 0.94, 9-, 3-, and 1.5-ml portions of TBT, respectively, were dissolved in 20 ml of methanol. To each of these solutions, 1 g of PC was added. Hydrolysis was performed at 20°C in 500 ml of water with stirring. The solutions were kept for 10 min and by this time the major fraction of the precipitate settled. The aqueous phase was decanted from the modified TiO_2. The precipitate was treated as described above.

The TiO_2 and $TiO_2 : PC$ gels of compositions 0.31 : 0.69, 0.62 : 0.38, and 0.81 : 019 were prepared from a solution of 9 ml of TBT in 20 ml of methanol. Modification was performed by addition of 2, 1, and 0.5 g of PC, respectively, to the solution. Hydrolysis was performed in 500 ml of water. The precipitate was separated on a filter without preliminary decantation and washed. After completion of washing, the paste was placed in a flask filled with 50 ml of water.

The IR spectra of the samples in the form of solid powders were recorded on a Perkin-Elmer Spectrum One IR Fourier spectrophotometer in the range 4000–370 cm^{-1} using diffuse reflection attachment (DRA). The sorption of 1,4-hydroquinone (HQ) was performed by addition of a solution of HQ in methanol into MX [weight ratio HQ : MX = 1 : (0.25–8)], followed by drying of the sample at room temperature for 3 days. The bands were assigned on the basis of reference data [10]. The intensities of the spectra were processed using the spectrometer software.

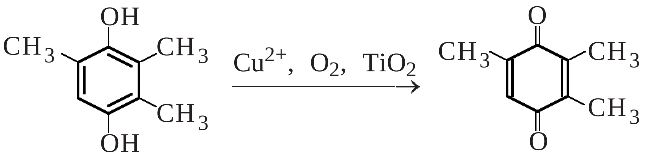
The kinetic experiments were carried out in a temperature-controlled reactor equipped with a reflux condenser, with stirring of the aqueous-methanol solution (volume ratio water : methanol = 1 : 1) by air bubbling. The air flow rate was 3.1 $l\,h^{-1}$.

TMHQ was oxidized at 50 ± 0.2°C. The concentration of the substrate was 66, and that of $CuCl_2 \cdot 2H_2O$, 6 mM.

The kinetic measurements were performed by stopping the reaction and determining the content of the starting substance. The resulting functions of concentrations were subjected to polynomial approximation. The initial reaction rates were found by numerical differentiation and interpolation. The error in their determination was no more than 10%. The TMHQ content was determined by gas-liquid chromatography on a Chrom-4 chromatograph [11].

The resulting cellulose-inorganic materials were studied by IR spectroscopy. The IR spectrum of titanium dioxide xerogel contains a strong absorption band peaked at 340 and 560 cm^{-1}, which can be regarded as a superposition of vibrations of the Ti–O bonds and water librations. In the range 1000–1200 cm^{-1}, there are three extremely weak peaks, which can be assigned to bending modes of the Ti–OH groups (1192, 1168, and 1090 cm^{-1}). For modified samples of TiO_2, there are no changes in the range of vibrations of the Ti–O bonds. Weak peaks corresponding to the Ti–OH groups are not observed on the background of the bands of PC. The IR spectrum of cellulose is mainly determined by absorption of three hydroxy groups incorporated in a glucopyranose unit. In the spectrum of PC there are the following absorption bands: 3348 cm^{-1}, stretching modes of hydroxy groups; in the range 3000–2800 cm^{-1}, stretching modes of methylene and methine groups of cellulose; 1640 cm^{-1}, δ_{HOH}, bending modes of water of crystallization. The band at 1451 cm^{-1} corresponds to δ(OH); 1427, to $\delta(CH_2)$ + δ(CH); 1369, to δ(CH); 1335, to δ(OH) (in-plane); 1315, to $\delta(CH_2)$ (wagging vibrations); 1281, 1248, 1235, and 1203, to δ(OH) + δ(CH) [12]. According to published data [13], the band at 1159 cm^{-1} corresponds to asymmetric stretching modes of the C–O–C bridge; however, in some publications [14] this band is assigned to the C–O stretching or O–H bending modes of the C–OH group. The band at 1054 cm^{-1} is assigned to the stretching modes of the C–O bond in the C^3H–OH group, and the band at 1035 cm^{-1}, to the stretching modes of the primary alcoholic group in various conformations. In the spectrum of PC in the range 860–400 cm^{-1}, there is a broad diffuse absorption on whose background a series of ill-defined bands characterizing various vibrations of the pyranose ring and bending modes of hydroxy groups are observed. The interaction of PC with hydrated titanium dioxide in the modified samples results in variation of the intensities of the absorption bands corresponding to hydroxy groups (the band ν_{as} at 2900 cm^{-1} was used as an internal reference). The most significant increase in the intensity (by a factor of 1.2–2) is observed for the bands at 1159, 1054, and 1035 cm^{-1}. Variations in the spectrum of PC increase with the fraction of the inorganic component in the sample. Thus, variation of the spectral characteristics of PC suggests that its hydroxy groups are involved in interparticle interaction with TiO_2 via hydrogen bonds.

Previously, [15] we have studied the model catalytic liquid-phase oxidation of TMHQ with atmospheric oxygen in the medium of TiO_2 gel:



It has been established by ESR spectroscopy [16] that, depending on the Cu(II)/TiO_2 ratio, several types of Cu(II) compounds are formed in the titanium dioxide phase: mono complexes, associates of mono complexes, copper(II) hydroxide, and polynuclear bridged compounds. The last kind of compounds was the most reactive.

Addition of powder cellulose does not affect the course and parameters of the catalytic process. Apparently, Cu(II) does not react with PC under the reaction conditions.

The dependences of the initial rate of TMHQ oxidation on the Cu(II) content of the MX phase for the samples of various compositions are shown in Fig. 1. The dependences are nonlinear because of the formation of various Cu(II) compounds and also because of limitations imposed by the sorption capacity of xerogel for Cu^{2+} ions. The maximum observed in the dependences is caused by the formation of the most catalytically active Cu(II) species on the surface of titanium dioxide. The number of these compounds increases with the fraction of PC in the sample. The sample of the composition of TiO_2 : PC = 0.06 : 0.94 did not affect the reaction due to the small amount of TiO_2 in the weighed portion, whose increase hampers stirring of the reaction mixture.

One of the ways to produce gels of element oxides with various specific surface areas is to vary the concentrations of substances being hydrolyzed [17]. However, these distinctions are lost in the course of drying to the xerogel state (Fig. 1, curve *1*). Modification of PC allows us to prevent to a certain extent these undesirable changes.

To elucidate the interactions occurring in the system MX–substrate, we studied the sorption of hydroquinone on MX by IR spectroscopy. The choice of HQ is caused by its resistance to air, minimal overlapping of the spectra of HQ and MX, fairly simple spectrum of HQ, and higher intensity of its bands, allowing detection of HQ in the analytical range of optical densities even at its low content in the system. The absorption bands of the aromatic ring, ν 1515 and 1470 cm^{-1}, are manifested fairly clearly in the IR spectra, and analysis using these bands presents no problems.

The absorption bands of hydroquinone were assigned on the basis of published data [10]. The absorption bands corresponding to the skeleton vibrations of aromatic rings are manifesed at 517, 1009, 1470, and 1515 cm^{-1}. The stretching absorption bands of OH groups appear at 3255 cm^{-1}; the absorption bands of C–OH group appear at 1240 (C–O stretching modes) and 1210 cm^{-1} (bending modes).

In the spectrum of HQ sorbed on $TiO_2 : PC = 0.45 : 0.55$ at the ratio HQ : MX = 1 : 0.5, we observed redistribution of the intensities of the absorption bands corresponding to the skeleton vibrations of the aromatic ring of HQ, ν 1515 and 1470 cm^{-1}. At the ratio HQ : MX = 1 : 1, a shoulder at 1500 cm^{-1} appears in the band at 1514 cm^{-1}; at the ratio HQ : MX = 1 : 4 the band at 1515 cm^{-1} is shifted to 1500 cm^{-1} and the intensity of the band at 1470 cm^{-1} decreases. The apparent variation of the intensities of the bands corresponding to vibrations of the C–C bonds of HQ suggests that the MX surface interacts with the π-electron system of the ring. Analysis of the other bands of HQ is difficult because of super-position of the spectra of HQ and PC.

The spectral changes observed are in good agreement with data on sorption of HQ on previously obtained TiO_2 gels [15]. Based on this fact and also on the insensitivity of the homogeneous catalytic reaction to addition of PC, we can conclude that the sorption-active component in MX is its inorganic component.

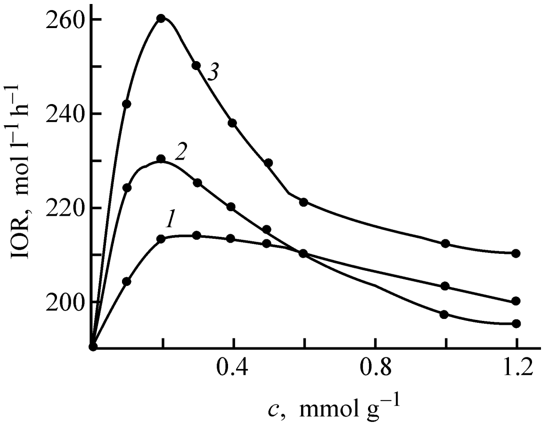


Fig. 1. Initial rate of TMHQ oxidation (IOR) vs. the Cu(II)/MX ratio *c* in the reaction area. Concentration of Cu(II) 6 mM; the same for Fig. 3. (*1*) K1-K3, (*2*) PC : TiO_2 = 0.35 : 0.45, and (*3*) PC : TiO_2 = 0.74 : 26; the same for Fig. 3.

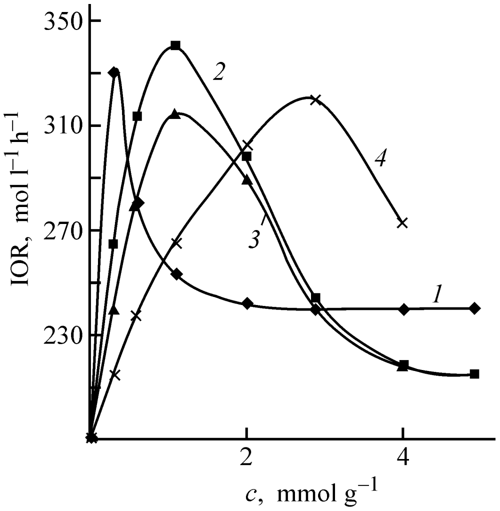


Fig. 2. Initial rate of TMHQ HCO oxidation (IOR) vs. the Cu(II)/TiO_2 ratio *c* in the reaction area. Gel: (*1*) TiO_2, (*2*) TiO_2 : PC = 0.81 : 0.19, (*3*) TiO_2 : PC = 0.62 : 0.38, and (*4*) TiO_2 : PC = 0.31 : 69.

The kinetic data recalculated to TiO_2 are presented in Fig. 2. For the samples of MX, the maximum of copper activity is shifted to higher Cu(II)/TiO_2 ratios as the PC fraction increases, i.e., the most catalytically active polynuclear Cu(II) compounds in the material phase are formed at a lower amount of TiO_2. This fact is caused by an increase in the specific surface area of titanium dioxide in MX with increasing PC/TBT ratio in the stage of hydrolysis.

To elucidate which stage of xerogel formation is influenced by the modifying additive, it was of interest

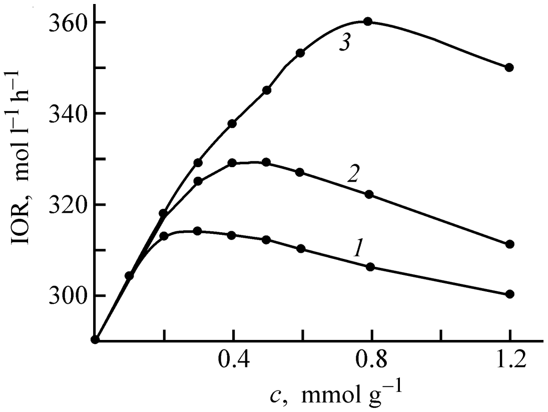


Fig. 3. Initial rate of TMHQ HCO oxidation (IOR) vs. the Cu(II)/TiO_2 ratio c in the reaction area.

to perform the model reaction with the modified TiO_2 gels. The data obtained are presented in Fig. 3.

For the modified gels, the effect similar to that for xerogels is observed, i.e., the maximum of the activity is shifted to higher Cu^{2+}/TiO_2 ratios. Thus, the influence of PC goes beyond the stage of drying, but is manifested even in the stage of gel formation and results in the formation of more sorption-active TiO_2 particles of a smaller size.

CONCLUSIONS

(1) Samples of titanium dioxide xerogels modified with powder cellulose with various ratios of TiO_2 to the modifying additive were prepared.

(2) The activity of Cu(II) in the matrix of modified samples in catalysis of oxidative dehydrogenation of trimethylhydroquinone is higher than that in the process occurring in the presence of unmodified titanium dioxide xerogel.

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