Catalytic Ozonation of 4-Nitrophenol in the Presence of Magnetically Separable Titanium Dioxide – Magnetite Composite

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Article info

Nomenclature

A – catalytic activity;
C_0 and C – initial and current total organic carbon concentrations in aqueous phase, respectively, mol/l;
$k_{eff,c}$ and k_{eff} – effective rate constants of 4-nitrophenol mineralization during ozonation with and without a catalyst, respectively, min^{-1};

t – time, min.

Abstract

This paper deals with determining catalytic activities of titania (TiO_2) with various crystalline structures and magnetite (Fe_3O_4) during mineralization of 4-nitrophenol in aqueous media by ozonation. Among the titania samples under study, amorphized TiO_2 was shown to have the highest catalytic activity, while magnetite was characterized by the lowest catalytic activity. A procedure is proposed to synthesize a magnetically separable composite (TiO_2/Fe_3O_4) including amorphized titania and magnetite phases, which involves deposition of a catalytically active titania phase on preformed magnetite particles. We also studied the effect of mass ratio of titania and magnetite phases in the composite on its catalytic activity during 4-nitrophenol mineralization by ozonation. It was found that catalytic activity of composite increased as the amorphized titania phase was doped with magnetite phase up to 30% wt but as the magnetite portion in the composite catalyst was further increased, its activity decreased. According to Fourier transform infrared (FTIR) spectroscopy, content of catalytically active sites (hydroxyl groups of titania) in the composite catalyst decreases as compared to the pure phase of amorphized titania. Increase in catalytic activity of the composite as its magnetite content increases to 30% wt can be attributed to increase of accessibility of catalytically active sites (OH groups) for ozone, because specific surface area and total pore volume of the composite catalyst as determined by BET increase as compared to amorphized TiO_2 and catalytically active titania phase is located mostly on surface of magnetite particles which is indicated by scanning electron microscopy (SEM) results and electrophoretic light scattering (ELS) data. It was shown that the obtained composite catalyst of optimized composition, in spite of its fine particles, can be easily recovered from aqueous phase by magnetic field and used repeatedly in ozonation in order to promote water purification process.

1. Introduction

Nitroaromatic compounds, including 4-nitrophenol (4-NP), are widely used in production of dyes, pesticides, herbicides, plasticizers and explosives which results in relevant environmental protection issues. Nitrophenols are toxic, cancerogenic and mutagenic [1]. Therefore, their environmental release must be prevented. To remove organics from waste water, biological treatment has been used usually. However, nitrophenols are biodegraded very slowly due to their toxicity for microorganisms [2]. This calls for studies developing efficient methods to remove nitrophenols from waste water. As one of such methods, ozonation is proposed [1]. Mineral-ization of most organics, including 4-NP, by ozone is a complex, multistage process [3]. Initial stages of 4-NP oxidation by ozone are rather fast, ozone fed into the reaction medium being used efficiently in oxidation processes. As oxidation progresses, a number of carboxylic acids are formed as intermediate products, such as oxalic, glyoxalic and formic acids [3]. Further mineralization of these acids by ozone is slow which makes the water-treating process considerably longer and costlier. Oxidation rate of ozone-resistant organics, as reported in paper [2], can be improved by using heterogeneous catalysts such as: MnO_2, Al_2O_3, ZnO, TiO_2. Paper [4] demonstrates titania (TiO_2) with anatase structure to be one of the most efficient catalysts in ozonolytic organics

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mineralization process. A major drawback of solid catalysts which can be used in water-treatment processes is that they are difficult to be recovered from aqueous phase after ozonation where they are used in form of fine particles. One of possible ways to simplify recovery of fine catalyst particles from liquid media could be introducing of magnetic component in their composition. Such component, for example, can be magnetite (Fe_3O_4). However, catalytic activity of magnetite in mineralization of ozone-resistant organics is unknown, and doping TiO_2-based catalyst with it may have a substantial effect on its activity. Thus, further studies are required to obtain an efficient magnetically separable titania – magnetite composite catalyst.

This study deals with synthesis and compositional optimization of a magnetically separable titania – magnetite composite catalyst, and with its catalytic activity in ozonolytic mineralization of hard-to-degrade organics, illustrated by one of them, 4-NP. Particular goals of the study are as follows: to determine catalytic activity of titania with various crystalline modifications and magnetite in 4-NP mineralization, to prepare a TiO_2/Fe_3O_4 composite catalyst with optimal composition and macrostructure, and use this catalyst to perform complete mineralization of 4-NP.

2. Experimental

Catalytic mineralization of 4-NP during ozonation was studied in a glass cylindrical reactor of 500-cm^3 useful volume and 5 cm inner diameter. The experiments were performed at 30 ± 0.1 °C. Ozone-air mixture with ozone concentration of 10 mg/l was bubbled into the reactor via a porous glass sparger at 0.8 l/min flow rate. Ozone was produced from oxygen of air in a laboratory ozonator OGVK-02V (MELP CJSC, Russia). Gas-phase concentration of ozone at the reactor inlet was measured by spectrophotometry, using ozone meter ICO-01 (MELP CJSC, Russia). Residual ozone at the reactor outlet was removed from the gas phase using ozone decomposer DTK-10 (MELP CJSC, Russia). The initial aqueous 4-NP concentration in all experiments was 400 mg/l. Catalyst concentration in aqueous phase was 1.2 g/l.

To determine 4-NP mineralization (complete decomposition to CO_2, H_2O and NO_3^-) rate in the course of ozonation, total organic carbon (i.e. carbon of total organics dissolved in aqueous phase) was measured periodically in liquid-phase samples from the reactor, using TOC-L analyzer (Shimadzu, Japan). The resulting kinetic curves of the mineral-

ization process, as recommended by paper [5], were processed using first-order reaction rate Eq. (1).

$$\frac{dC}{dt} = k_{eff} C \qquad (1)$$

where k_{eff} – effective rate constant of 4-NP mineralization, min^{-1}; C – current total organic carbon concentration in aqueous phase, mol/l, and t – time, min.

As a kinetic parameter describing 4-NP mineralization process, effective mineralization rate constant (k_{eff}) was used, which was determined in accordance with Eq. (2) as a ln(C_0/C) versus t line slope.

$$\ln (C_0/C) = k_{eff} t \qquad (2)$$

where C_0 – initial total organic carbon concentration in aqueous phase, mol/l.

Catalytic activity (A) of the test catalyst samples in organic carbon mineralization during 4-NP ozonation was calculated as ratio of effective mineralization rate constants with and without a catalyst under equal conditions [6]:

$$A = \frac{k_{eff,c}}{k_{eff}} \qquad (3)$$

where $k_{eff,c}$ and k_{eff} – effective rate constants of 4-NP mineralization during ozonation with and without a catalyst, respectively, min^{-1}.

Amorphized titania (sample T-1) was obtained by hydrolysis of titanium tetra-tert-butoxide (TTB) in isopropyl alcohol as described in paper [7]. Titania with crystalline structures of anatase and rutile was obtained by calcination of amorphized TiO_2 at 600 °C (sample T-2, anatase) and 1000 °C (sample T-3, rutile), respectively.

Magnetite was obtained by alkaline (pH = 10÷11) co-hydrolysis of $FeSO_4$ and $FeCl_3$ at 80 °C as described in paper [8].

When synthesizing the magnetically separable composite catalyst, we intended to deposit titania on surface of preformed magnetite particles. Magnetite particles were suspended in isopropyl alcohol. The weight of magnetite particles to be added to isopropyl alcohol was calculated from the required final magnetite contents of the composite catalyst samples: sample C-10 (10% wt Fe_3O_4); sample C-30 (30% wt Fe_3O_4); sample C-50 (50% wt Fe_3O_4). TTB at 1.25 mol/l was added to the resulting magnetite suspension. Then TTB was slowly hydrolyzed. To do so, isopropyl-alcohol solution of distilled water (water concentration 1.75 mol/l) was added to the TTB – containing magnetite suspension while

mixing vigorously, so that water-to-TTB molar ratio amounts to 1. After that, the reaction mixture was maintained at 60 °C for 2 h while mixing, then cooled to 25 °C and, to complete TTB hydrolysis distilled water was introduced to the reaction mixture, so that final water-to-TTB molar ratio amounts to 25. The suspension was maintained at 60 °C for 1 h while mixing. The resulting precipitate was filtered under vacuum, rinsed by isopropyl alcohol, and dried at 105 °C.

The X-ray diffraction (XRD) patterns of catalyst samples were obtained on XRD-7000 diffractometer (Shimadzu, Japan) using Cu Kα radiation in the 2θ range from 10 to 80°.

Specific surface area and total pore volume of the catalyst samples were measured by Brunauer–Emmett–Teller (BET) method, using Nova 1200e analyzer (Quantachrome Instruments, USA).

Morphology and average particles size of the catalyst samples were determined by scanning electron microscopy (SEM) using microscope S-3400N (Hitachi, Japan).

Fourier transform infrared (FTIR) spectra of the catalyst samples were recorded with FTIR spectrometer, Nicolet-380 (Thermo, USA), using samples tableted with KBr.

Zeta-potentials of catalyst sample particles were measured by electrophoretic light scattering (ELS), using ZetaSizer analyzer (Malvern, USA).

3. Results and Discussion

3.1. Catalytic activities of titania with various crystalline structures and magnetite in ozonolytic 4-NP mineralization

First of all, titania samples of various crystalline structure and a magnetite sample were obtained.

XRD patterns of the prepared samples are shown in Fig. 1a-d. It can be seen (Fig. 1a) that sample T-1 is highly amorphized TiO_2, weak and broad peaks can be attributed to beginning of anatase phase formation. The diffraction peaks of samples T-2 (Fig. 1b) and T-3 (Fig. 1c) were assigned to the well crystallized anatase and rutile phases respectively. The diffraction peaks of magnetite sample (Fig. 1d) can be attributed to the cubic structure of crystalline Fe_3O_4.

Catalytic activities of obtained samples in ozonolytic 4-NP mineralization were measured. It can be seen (Fig. 2a) that 4-NP mineralization rate increases in the presence of the titania samples, however, to various degrees. Catalytic activities of TiO_2 samples decreasing as follows: T-1 > T-2 > T-3 (Fig. 2b), are attributable to substantial reduction of their specific surface areas (Table 1). Among the test samples, Fe_3O_4 exhibits the lowest catalytic activity.
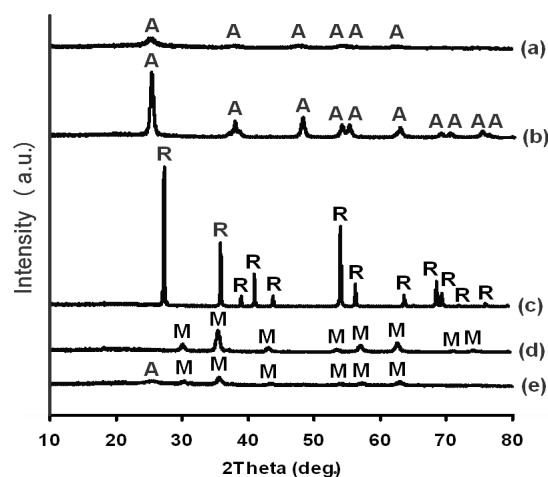

Fig. 1. XRD patterns of the catalyst samples: a – T-1; b – T-2; c – T-3; d – Fe_3O_4; e – C-30. Designation of diffraction peaks: A – anatase; R – rutile; M – magnetite.
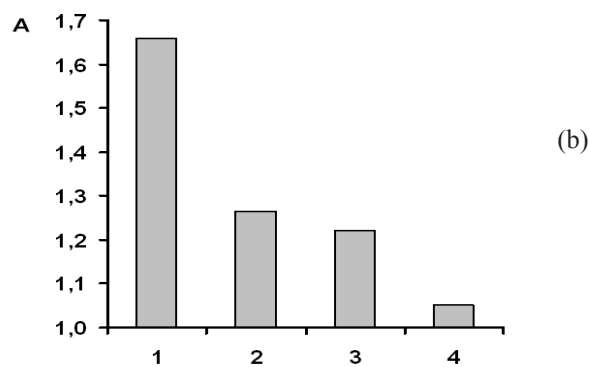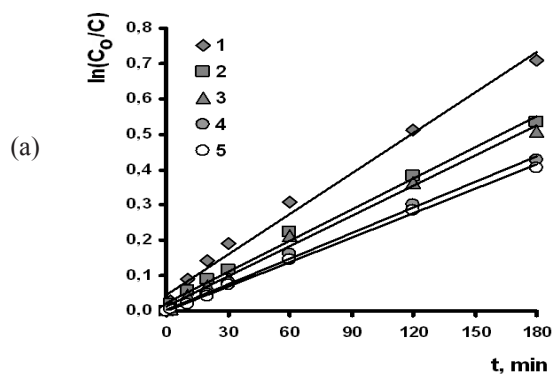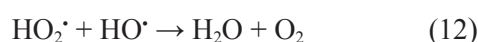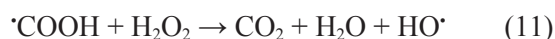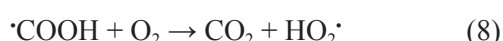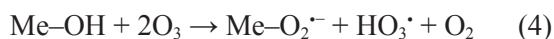

Fig. 2. Effects of titania samples with various crystalline structures and magnetite on mineralization rate of 4-NP during ozonation (a – kinetic curves; b – catalytic activity (A)): 1 – T-1; 2 – T-2; 3 – T-3; 4 – Fe_3O_4; 5 – ozonation without a catalyst.

Table 1

Specific surface areas, total pore volumes, ζ-potentials and average particles sizes of the test samples

Sample	Specific surface area, m^2/g	Average particles size, nm	ζ-potential, mV (pH = 7)	Total pore volume, cm^3/g
T-1	350	105	-9.2 ± 2.1	0.61
T-2	55	-	-	-
T-3	8	-	-	-
Fe_3O_4	68	62	16.2 ± 1.9	-
C-30	457	144	-2.6 ± 1.8	0.74

Data in paper [4] and FTIR spectroscopy results obtained by us indicate that calcination of amorphized titania leads to decrease of OH groups concentration on its surface. This may be responsible for crystalline TiO_2 modifications (T-2, T-3) have lower catalytic activities than amorphized TiO_2 (T-1). Chemical Eqs. (4) to (6) [9] show OH groups are active sites of catalyst (Me–OH) which speed up decomposition of ozone dissolved in aqueous phase to produce $HO^\bullet$ radicals. These radicals are involved in mineralization of molecular-ozone-resistant organics. Chemical Eqs. (7) to (12) [10] demonstrate the way of $HO^\bullet$ radicals interaction with organic substances as illustrated by oxalic acid, one of the most molecular-ozone-resistant intermediates which are produced during mineralization of many hard-to-degrade organic compounds [11], including 4-NP [3].

$$Me–OH + 2O_3 \rightarrow Me–O_2^{\bullet-} + HO_3^\bullet + O_2 \quad (4)$$

$$Me–O_2^{\bullet-} + O_3 + H_2O \rightarrow Me–OH + O_2 + HO_3^\bullet \quad (5)$$

$$HO_3^\bullet \rightarrow HO^\bullet + O_2 \quad (6)$$

$$OOC–COOH + HO^\bullet \rightarrow CO_2 + H_2O + {}^\bullet COOH \quad (7)$$

$$^\bullet COOH + O_2 \rightarrow CO_2 + HO_2^\bullet \quad (8)$$

$$HO^\bullet + HO^\bullet \rightarrow H_2O_2 \quad (9)$$

$$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2 \quad (10)$$

$$^\bullet COOH + H_2O_2 \rightarrow CO_2 + H_2O + HO^\bullet \quad (11)$$

$$HO_2^\bullet + HO^\bullet \rightarrow H_2O + O_2 \quad (12)$$

Paper [12] shows that activity of heterogeneous catalysts in ozone decomposition producing $HO^\bullet$ radicals to be determined not only by its surface OH groups concentration but also by acid-base properties of these groups. Catalytic activity is enhanced as OH groups increase in acidity [12], i.e., as deprotonation and negative charges on metal-oxide particle surfaces become more likely. Zeta-potential values of amorphized titania (T-1) and magnetite (Fe_3O_4)

are given in Table 1. ζ-potential of amorphized TiO_2 (T-1) is negative which goes with negative charge of potential-determining ions on titania particles surface. However, magnetite has positive ζ-potential at the same pH value (pH = 7) which was used to measure zeta-potential of sample T-1. This is likely to result from Fe_3O_4 being more basic than amorphized TiO_2. Lower OH groups acidity in Fe_3O_4 allows to expect that magnetite will exhibit lower catalytic activity in 4-NP mineralization than amorphized titania (T-1). According to our data (Fig. 2), magnetite really displays weak catalytic action in ozonolytic 4-NP mineralization as compared to titania samples.

Our experiments allowed to conclude that, while synthesizing a magnetically separable TiO_2/Fe_3O_4 composite catalyst, it is expedient to maintain amorphized state of the titania phase, and to deposit TiO_2 on Fe_3O_4 particles surface when producing the composite, i.e., to facilitate access of ozone molecules to the active sites of titania phase.

3.2. Synthesis and compositional optimization of magnetically separable titania-magnetite composite catalyst

To provide the required component distribution throughout the catalyst particle cross-section such that TiO_2 phase covers Fe_3O_4 particles, preformed magnetite particles were suspended in the liquid phase (isopropyl alcohol). Then TTB was slowly hydrolyzed in liquid phase of the suspension. After hydrolysis was completed, the composite particles were separated from the liquid phase and dried at 105 °C to prevent TiO_2 from crystallization and maintain amorphized state of this phase. XRD pattern of the composite sample C-30 is shown in Fig. 1e. The peaks with 2θ values of 30.09°, 35.44°, 43.07°, 53.43°, 56.96°, 62.54° correspond to the crystalline Fe_3O_4. TiO_2 phase in the composite is highly amorphized, broad and weak peak with 2θ value of 25.26° can be attributed to beginning of anatase phase formation.
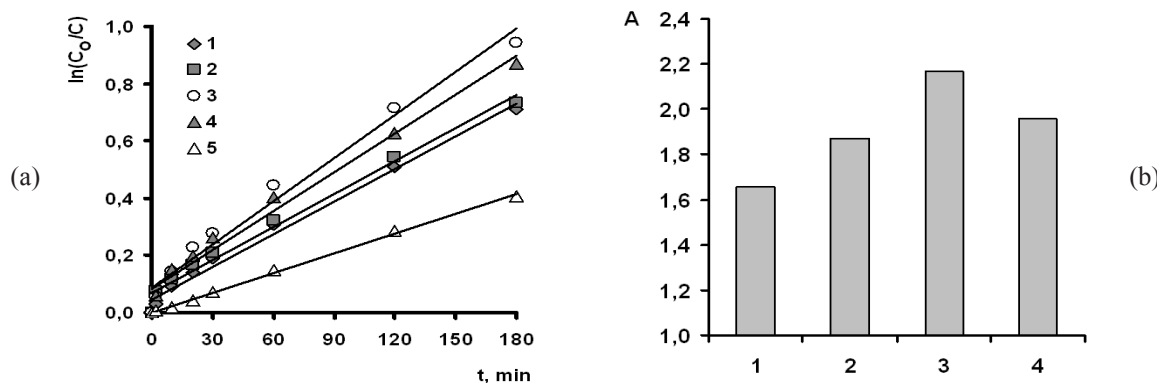
Fig. 3. Effect of composite catalyst samples with various magnetite contents on mineralization rate of 4-NP during ozonation (a – kinetic curves; b – catalytic activity (A)): 1 – amorphized TiO_2 without Fe_3O_4 (T-1); 2 – C-10; 3 – C-30; 4 – C-50; 5 – ozonation without a catalyst.

To optimize the catalyst composition, a number of amorphized titania-magnetite (TiO_2/Fe_3O_4) composite samples with varying magnetite contents were obtained, and their effect on ozonolytic 4-NP mineralization rate was studied (Fig. 3a). According to the findings (Fig. 3b), when titania phase is doped with up to 30% wt magnetite phase, catalytic activities of the composite catalyst samples increase as compared to pure amorphized titania, in spite of decrease in TiO_2 portion of the catalyst. However, as magnetite portion of the composite further increases, its catalytic activity falls. Thus, optimal magnetite content of the composite catalyst is 30% wt. (sample C-30).

To explain the observed increase in catalytic activity of the composite as the low-active magnetite phase content increase up to 30% wt. as compared to amorphized titania in more detail, C-30, T-1 and Fe_3O_4 samples were examined by FTIR spectroscopy (Fig. 4). FTIR spectra of pure amorphized TiO_2 and Fe_3O_4 phases are as reported in publications [13, 14]. All absorption bands of TiO_2 and Fe_3O_4 are preserved in the composite sample (Table 2, Fig. 4) which suggests that individual oxide phases still exist in the composite. However, as to intensity of

absorption bands, the composite is more similar to TiO_2 which can be explained by its higher content in the composite catalyst. Particular attention should be paid to the absorption bands corresponding to bending vibrations δ(TiOH) and δ(FeOH), their intensity being a measure of OH groups content in the sample which, as noted above, are responsible for catalytic activity.

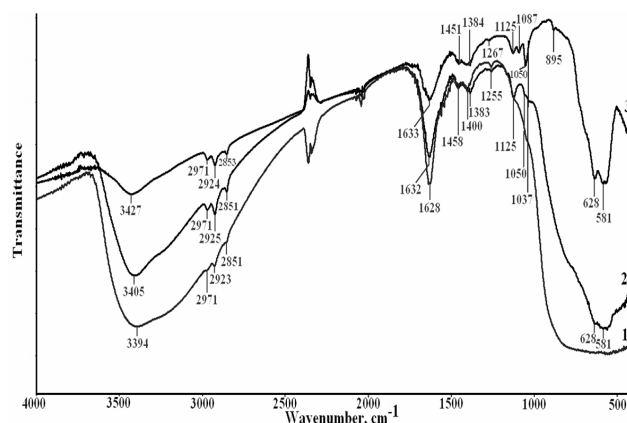Fig. 4. FTIR spectra of samples: 1 – T-1; 2 – C-30; 3 – Fe_3O_4.

Table 2

Important absorption bands in FTIR spectra of samples of the composite (C-30), amorphized titania (T-1), magnetite (Fe_3O_4), and their interpretation

| Wavenumber, cm^{-1}			Interpretation of absorption bands according to [13, 15]
C-30	T-1	Fe_3O_4	
3405	3394	3427	v(OH) stretching vibrations of hydrogen-bonded OH protons
1632	1628	1633	δ(HOH) bending vibrations of water molecules
1458, 1400	1458, 1400	-	δ($\equiv$Ti–O–Ti$\equiv$) bending vibrations
1037	1037	-	δ(TiOH) bending vibrations
-	-	895	δ(FeOH) bending vibration
500 to 800	500 to 800	-	v(TiO) stretching vibrations
628	-	628, 581	v(FeO) stretching vibrations

(a)

(b)

(c)
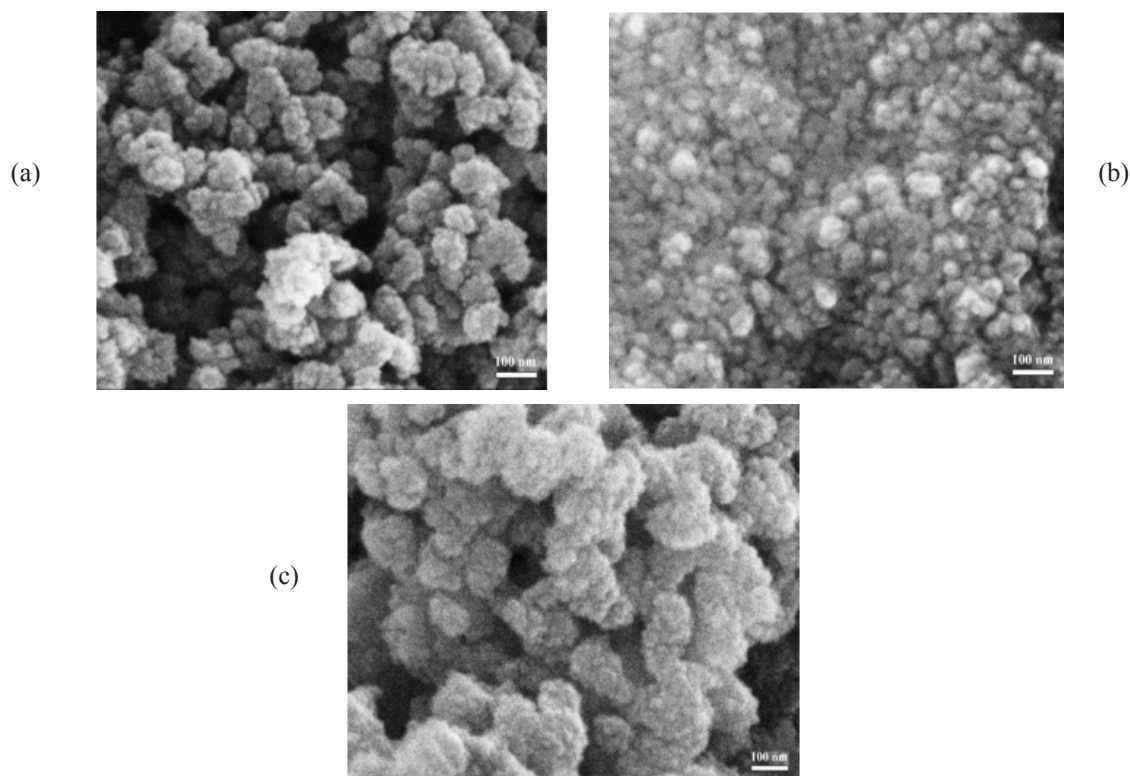
Fig. 5. SEM images of samples: a – T-1; b – Fe$_3$O$_4$; c – C-30.

Figure 4 shows that the absorption band δ(FeOH) in the composite FTIR spectrum cannot be observed due to high intensity of a wide absorption band of stretching vibrations ν(TiO). The absorption band δ(TiOH) is somewhat less intense in the composite than in titania. This suggests that OH groups concentration in the magnetically separable catalyst is less in comparison with amorphized TiO$_2$. Absorption band of stretching vibrations ν(OH) generated by surface OH groups and adsorbed water molecules, and band of bending vibrations δ(HOH) of adsorbed water molecules, decrease in intensity as follows: T-1 > C-30 > Fe$_3$O$_4$ (Fig. 4) which confirms indirectly that there are less OH groups in the composite than in amorphized titania because adsorbed water amount is considerably dependent on OH groups concentration on oxide particle surfaces.

Thus, increase in catalytic activity of the composite as compared to amorphized titania cannot be explained by the increase of total amount of active sites (OH groups) in the composite. However, according to BET data (Table 1), the specific surface area and total pore volume of C-30 are 1.3 and 1.2 times respectively higher than in amorphized titania sample (T-1). This can be a reason of the increase in accessibility of active sites in the composite catalyst for ozone molecules. The findings allow to conclude that, though total amount of active sites in the composite catalyst decreases, increase in their availability due to increase in specific surface area and porosity enhances catalytic activity of the composite as compared to pure amorphized titania.

To determine morphology and average particles size, C-30, the composite catalyst sample with the highest catalytic activity, and samples of amorphized titania (T-1) and magnetite (Fe$_3$O$_4$) were examined by scanning electron microscopy. Figure 5 shows that these samples consist of agglomerated irregular-shaped particles rather homogeneous in size. The measured average particles sizes for the test samples are given in Table 1. Average particles sizes of the composite catalyst (C-30), amorphized titania (T-1) and magnetite (Fe$_3$O$_4$), and comparisons of their SEM images suggest that amorphized titania phase was formed during synthesis of the composite on magnetite particles surface mostly which resulted in formation of larger-sized composite catalyst particles (Fig. 5, Table 1). Electrophoretic light scattering demonstrated (Table 1) that composite particles (C-30) are more similar in ζ-potential to amorphized TiO$_2$ particles (T-1), and rather different from Fe$_3$O$_4$ particles which indicates that the titania phase is situated mostly on surfaces of the composite catalyst particles.

Observed decrease in activities of the composite catalyst samples with increase in magnetite content over 30% wt (Fig. 3b) can be explained by increases Fe$_3$O$_4$ portion on composite particles surface.
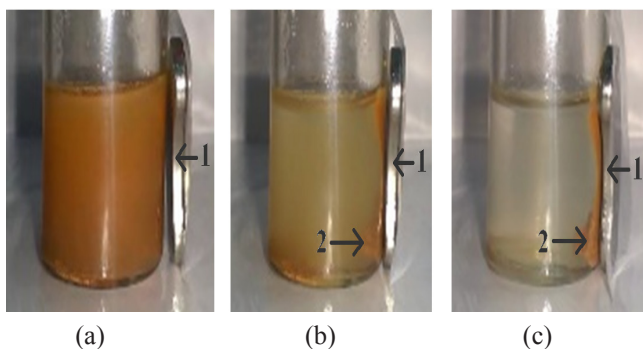
Fig. 6. Magnetic separation of the composite catalyst (C-30): (a) – suspension in water before separation; (b) – after exposition to magnetic field for 30 s; (c) – after exposition to magnetic field for 3 min; 1 – magnet; 2 – composite catalyst concentrated at the magnet poles.

As confirmed by visual observations (Fig. 6), the compositionally optimized composite catalyst (C-30) can be readily separated from the suspension by magnetic field after ozonation which allows to recover it from the liquid phase much simpler. It was found that catalyst recovered from the liquid can be used repeatedly in ozonation and loses its catalytic activity rather slowly, at 4% per cycle on average.

Thus, the studies allowed to perform synthesis, compositional and structural optimization of fine magnetically separable composite catalyst which includes phases of amorphized titania and magnetite. The catalyst can increase mineralization rate of hard-to-degrade and bioresistant organic compound (4-NP) during catalytic ozonation. Complete mineralization of 4-NP can be achieved. It can be expected that the catalyst will be efficient in ozonation of other hard-to-degrade organics, which produce molecular-ozone-resistant organic intermediates during mineralization. This statement is undergoing further experimental validation. Particles of the compositionally optimized composite catalyst were found to be structured so that catalytically active amorphized titania phase was found to concentrate mostly on their surface. Higher catalytic activity of the composite in comparison with pure amorphized titania can be explained by its higher specific surface area and larger pore volume. This provides higher accessibility of active sites (OH groups) for ozone molecules. The composite catalyst particles, though fine, can be readily recovered from liquid phase by magnetic field and used repeatedly to intensify water purification by ozonation.

4. Conclusions

1. We examined catalytic activity of titania samples with various crystalline structures and magnetite in ozonolytic mineralization of 4-nitrophenol. Amorphized titania was shown to have the highest catalytic activity among TiO_2 test samples. Magnetite was found to exhibit low catalytic activity in 4-nitrophenol mineralization. The findings allowed to solve the problem of selecting phase composition for the composite catalyst and hypothesize that the best catalytic properties will be observed if the most catalytically active phase, amorphized titania, will be situated on the composite particles surface and the low-active magnetite phase within it.

2. We solved the problem of synthesizing a magnetically separable composite catalyst for 4-nitrophenol mineralization and optimize its composition and macrostructure. To provide the required distribution of titania and magnetite throughout the catalyst particle cross-section, such that TiO_2 phase covers Fe_3O_4 particles, the composite was synthesized by slow hydrolysis of titanium tetra-tert-butoxide in the presence of suspended magnetite particles which act as phase formation sites for titania. When optimizing the composite catalyst compositionally, the highest catalytic activity was observed in the sample which contained 30% wt magnetite. The composite catalyst with optimized composition has higher catalytic activity than pure amorphized titania which results from higher accessibility of active sites (OH groups) for ozone due to higher specific surface area and total pore volume of the composite. Catalytically active titania phase in the composite sample (30% wt magnetite) of the highest catalytic activity was found to concentrate mostly in surface layer of the composite particles which is in line with the data from scanning electron microscopy and electrophoretic light scattering.

3. Using 4-nitrophenol as an example, we showed that this composite catalyst can be used to intensify ozonolytic mineralization of hard-to-degrade organics which produce stable intermediates during oxidation. The composite catalyst can be easily separated in magnetic field and re-used in ozonation process.

Acknowledgements

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