

## CHARACTERIZATION OF SURFACE SPECIES ON MESOPOROUS TiO<sub>2</sub> PREPARED BY TiC OXIDATION

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Surface species responsible for low pH values of zero charge point and high sorption capacity of mesoporous TiO<sub>2</sub> powder obtained by TiC oxidation with nitric acid were studied by FTIR, EPR and XPS methods. It was found that during the titania synthesis the oxide surface was modified by nitrate-nitrite, carboxylic groups, NO<sub>x</sub> and ·C≡ radicals which determined adsorption properties of the TiO<sub>2</sub> powder.

### 1. Introduction

Titanium dioxide is used as a photocatalyst for UV decomposition of a wide variety of contaminants in water and air [1]. Mesoporosity and high surface area of TiO<sub>2</sub> powder enhances the efficiency of photocatalysis. Modification of the titania surface allows increasing the adsorption ability of TiO<sub>2</sub> powder and, thus, its activity in photodegradation processes can be improved.

This paper is focused on characterization of surface species on mesoporous TiO<sub>2</sub> powder obtained by TiC oxidation with nitric acid. FTIR, EPR, and XPS spectroscopies were applied for this purpose.

### 2. Experimental

Mesoporous TiO<sub>2</sub> powders were fabricated by oxidation of titanium carbide powder with nitric acid according to the method described in [2]. The samples were calcinated at 200 °C in air.

Fourier transform infrared spectra were collected on an AVATAR-330 spectrometer (Thermo Nicolet). XPS spectra were collected by Kratos DLD Ultrac spectrometer using AlK<sub>α</sub> radiation ( $E = 1486.6$  eV). Calibration was made relatively to C 1s line ( $E = 284.8 \pm 0.2$  eV). EPR spectra were recorded with

VARIAN E 112 spectrometer using the resonance frequency of 9.35 GHz (X-band) at 77 K and 298 K. Zeta-potential of TiO<sub>2</sub> particles was measured by Malvern Zetasizer S90.

### 3. Results and discussion

Oxidation of black TiC powder by concentrated nitric acid gives a yellowish powder with a fine-dispersed structure. Calcination of the powder at 200 °C results in a change of color to light-brown. X-ray diffraction pattern shows the presence only anatase TiO<sub>2</sub> phase. The crystallite size calculated using Debye-Scherrer equation is 4 nm. According to BET analysis the powder has mesoporous structure with an average pore size of 3.4 nm. The specific surface area is found to be 353 m<sup>2</sup>/g.

The synthesized TiO<sub>2</sub> particles have negative surface charge in a water suspension at pH > 3.5. Zero charge is observed at pH 3.5. This is lower than pH values commonly reported for TiO<sub>2</sub> formation [3].

It was found that the prepared titanium dioxide powder efficiently adsorbed positively charged molecules at neutral pH. Rhodamine B was chosen as a model pollutant for investigation of the sorption capacity of the TiO<sub>2</sub> powder. The maximum sorption capacity of the powder is near 40 mg/g (Fig. 1).

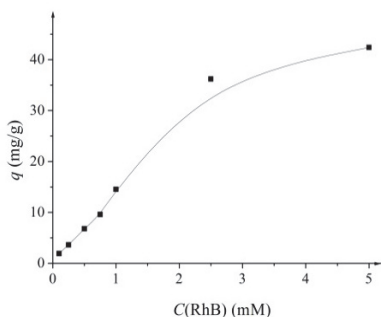


Figure 1. Sorption capacity of the synthesized TiO<sub>2</sub> powder to Rhodamine B.

High sorption activity of the synthesized powder is caused by large surface area, from one side, and the states at the TiO<sub>2</sub> surface, from the other side. Some nitrogen and carbon-containing species, which are produced during synthesis, might modify TiO<sub>2</sub> surface and influence adsorption properties of the TiO<sub>2</sub> powder. We used XPS, FTIR, and EPR spectroscopies for identification of these species.

The XPS results are collected in Table 1. Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub> single lines of symmetric shape are registered at the energies, which correspond to Ti<sup>4+</sup> ( $E_{bond}$  Ti 2p) in TiO<sub>2</sub>. O 1s, C 1s and N 1s peaks indicate that OH<sup>-</sup>, CO<sub>x</sub><sup>-</sup>, and NO<sub>x</sub><sup>-</sup> groups are present on the oxide surface. C 1s line has a complex shape which can be approximated by lines assigned to sp<sup>3</sup>- and sp<sup>2</sup>- carbon states and oxidized -CO and COO<sup>-</sup> species. XPS data show that Ti<sup>δ+</sup> and C<sup>δ-</sup> states, which

are characteristic for titanium carbide, are absent in the synthesized titania samples, indicating that TiC is completely oxidized during the synthesis.

Table 1. XPS data of TiO<sub>2</sub> obtained by oxidation of TiC with nitric acid.

Lines	$E_{\text{bonds}}$ , eV	Element species
O 1s	530.1	O <sup>2-</sup> (TiO <sub>2</sub> )
	531.6	HO <sup>-</sup> (TiO <sub>2</sub> )
C 1s	284.8	C-C, C-H
	286	>C=O
	288.8	-COO <sup>-</sup> , CO <sub>3</sub> <sup>-</sup>
Ti 2p <sub>(3/2)</sub>	458.7	Ti <sup>4+</sup> (TiO <sub>2</sub> )
N 1s	400.2	NO <sub>x</sub>

The FTIR spectrum of the sample is presented in Fig. 2. The dominating wide band at 400–850 cm<sup>-1</sup> is attributed to vibrations in octahedrons [TiO<sub>6</sub>]. It is a superposition of several normal  $\nu(\text{Ti-O})$  vibrations characteristic of TiO<sub>2</sub>. The

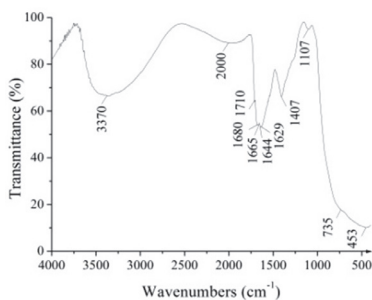


Figure 2. FTIR spectrum of TiO<sub>2</sub> obtained by oxidation of TiC.

spectrum shows two intensive bands related to deformation  $\delta(\text{H-O-H})$  vibrations at 1629 cm<sup>-1</sup> and asymmetric  $\nu_{\text{as}}(\text{O-H})$  vibrations at 3200–3400 cm<sup>-1</sup> of water molecules. The region from 800 to 1800 cm<sup>-1</sup> shows vibrations of nitro, nitrates and carboxylate groups. In this region there are vibrations from unbound nitrate groups (at 1680 cm<sup>-1</sup>), monodentate groups (at 1665 and 1680 cm<sup>-1</sup>) and bidentate ones (at 1407 and 1107 cm<sup>-1</sup>). The lines at 1407 and 1107 cm<sup>-1</sup> are the symmetric and asymmetric stretching vibrations of nitro groups, respectively. The broad absorption band at 2000 cm<sup>-1</sup> may be due to an appearance of complexes with CO adsorbed on the TiO<sub>2</sub> surface.

The EPR spectrum shows the central line with  $g$ -factor of 2.0025 and weakly resolved broadened neighboring lines (Fig. 3). The half width of the central line ( $\Delta B$ ) is 0.5 mT. The spectrum represents a superposition of two triplet signals of NO<sub>x</sub> radicals. The radicals include one unpaired electron ( $S=1/2$ ) and <sup>14</sup>N atom (nuclear spin  $I = 1$ , <sup>14</sup>N isotope abundance is 99.6 %). These two signals

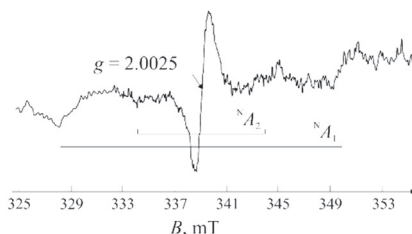


Figure 3. EPR spectrum of TiO<sub>2</sub> obtained by oxidation of TiC.

have a central line with  $g = g_e$  and different hyperfine structure (HFS) constants ( $A^N$ ). This constant characterizes magnetic interaction of the unpaired electron with  $^{14}\text{N}$  nuclear. The parameters of the EPR signals and corresponding paramagnetic centers (PCs) are presented in Table 2.

Table 2. Parameters of the EPR signals and nature of the corresponding PCs, which are observed in the titanium dioxide obtained by oxidation of TiC with nitric acid.

Parameters of the EPR signals	Paramagnetic centers
$g = 2.002; {}^N A_1 = 5.6 \text{ mT}$	$\cdot\text{NO}_2$
$g = 2.002; {}^N A_2 = 2.4 \text{ mT}$	
$g_{\text{iso}} = 2.002$	$\cdot\text{C}\equiv$

Intensity of the central EPR line exceeds the total intensity of the neighboring  $^{14}\text{N}$  HFS lines, which can be due to an existence of additional signals at  $g = g_e$  without hyperfine splitting.  $\cdot\text{C}\equiv$  radicals in the amorphous carbon phase have such type of EPR signal. They can be formed as a byproduct of TiC oxidation by nitric acid under heating. The total concentration of the PCs ( $\text{NO}_x + \cdot\text{C}\equiv$ ) is  $4 \times 10^{16}$  spin/g.

#### 4. Conclusion

Using XPS, FTIR and EPR methods the presence of hydroxyl, carboxylic, nitrate-nitrite groups,  $(\text{Ti})_2 > \text{CO}$ ,  $\text{Ti}-\text{CO}$  complex, and  $\text{NO}_x$  and  $\cdot\text{C}\equiv$  radicals in mesoporous  $\text{TiO}_2$  powder prepared by TiC oxidation with  $\text{HNO}_3$  are confirmed. The nitrogen and carbon-containing species modify the  $\text{TiO}_2$  surface, change the charge state of the surface and provide high sorption capacity of the  $\text{TiO}_2$  powder to a positively charged dye.

#### Acknowledgments

The work was supported by the project (645662 – SMARCOAT – H2020-MSCA-RISE-2014) of «HORIZON-2020» EU program.

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