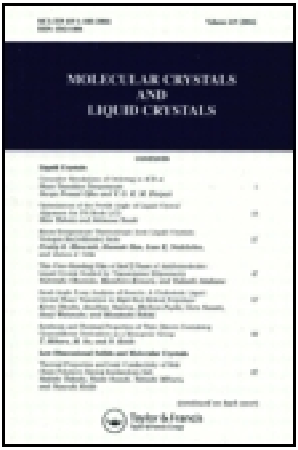

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5CB LIQUID CRYSTAL AS A SPECIFIC PROBE FOR SURFACE STUDIES OF METAL-DOPED TIO_2 (ANATASE) NANOPARTICLES

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5CB LIQUID CRYSTAL AS A SPECIFIC PROBE FOR SURFACE STUDIES OF METAL-DOPED TIO_2 (ANATASE) NANOPARTICLES

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Metal-doped Me^{n+}*-*TiO_2 *(where Me is* Cu^+, Mn^{2+}, Cr^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}*) anatase powders and heterogeneous systems* Me^{n+}*-*TiO_2*-4-pentyl-4′-cyanobiphenyl have been studied by FTIR spectroscopy method.* TiO_2 *samples have been produced by thermal hydrolysis of titanium chloride and as their spectroscopic data revealed, have different types of surface active centers and the amount of hydroxyl and hydrate covering. Doped metal cations increase a variety of possible active centers, disturbing surface OH-groups by coordination or ionic bonding. 5CB molecules, approaching* TiO_2 *surface, displace adsorbed water molecules and can create hydrogen bonds of -CN. . .HO-Ti≡ and π-electrons. . .HO-Ti≡ types. The influence of metal cations is a polarizing effect on 5CB molecules, which increases in a following row* $Cu^+ < Mn^{2+} < Cr^{2+} < Co^{2+} < Ni^{2+} < Fe^{3+}$*. This is in a perfect agreement with the polarizing activity of these cations. At that 5CB molecules change their orientation and possess some deformations, which is confirmed by the corresponding changes in spectral parameters of 5CB deformation modes.*

Keywords: 5CB; active centers; IR spectroscopy; metal-doped TiO_2 anatase

INTRODUCTION

In recent years, titanium dioxide (TiO_2) materials have been focused great interest because they exhibit many modified electronic and optical

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properties as well as extensive applications. TiO_2 is proved to be a good and perspective active component for different types of catalysts and photocatalysts. There are a number of publications describing its role in the destruction processes of many organic compounds. In comparison with other semiconductor catalysts, TiO_2 is biologically and chemically inertial, stable to photodegradation and also relatively cheap [1–3].

The experimental results showed that the synthesis techniques and the processing conditions have a strong influence on the microstructures, electronic and vibrational properties of TiO_2 powders. One of the numerous ways to modify these materials is to include doping atoms of various valences (for example, Fe, Co, Al etc.) to their crystalline structure [4,5]. This procedure leads to changes in electron-donor properties of TiO_2 surface, and also to considerable changes in its photocatalytic activity. It has been demonstrated [6–8], that TiO_2 photocatalytic activity depends on the concentration and type of doping atoms. Adatoms can result in the appearance of new energetic states in the energy gap of the bulk material. For instance, the presence of coordinationally non-saturated Fe-atoms in TiO_2 particle surface layer leads to new single electron levels, which decrease the frequency of the optical transition during electro-magnetic irradiation, and thus increase its catalyst photoactivity [9]. Al-doped TiO_2 has different acid-base properties of surface active centers, compared to those ones of pure titanium and aluminum dioxides [10].

Considering all mentioned above, investigations of interactions between different organic molecules and the photocatalyst surface (pure and doped) are of particular importance. In this work we use 4-pentyl-4′-cyanobiphenyl (5CB) as a specific organic probe, which allows to study the solid surface state and the interactions occurred between molecules and various surface active centers. 5CB liquid crystal has a considerable dipole moment concentrated on CN group and can create different bonds (mainly, of hydrogen types) with TiO_2 surface active centers.

In general, heterogeneous systems with a large area of the liquid-solid boundary are promising objects for investigations due to remarkable changes observed in their compound properties and structure compared to those of the bulk substances. In particular, materials with 5CB molecules as a filler have been found wide application in electronic devices. These may be either filled 5CB in aerosil-based systems or confined 5CB dispersed in inorganic porous matrices. Liquid crystals in these systems manifest new interesting physical properties that are absent in bulk material [11,12].

The aim of this work is to study two-component systems based on TiO_2 (anatase) crystalline powders and 5CB liquid crystal. TiO_2 surface has been modified different metal cations (Cu^{+}, Mn^{2+}, Cr^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}), in order to investigate their influence on the nature of surface active centers and their interaction with 5CB molecules. We used IR vibrational spectroscopy, which is proved to be particularly successful for the identification of local surroundings, changes in molecular interactions and phase structure.

EXPERIMENTAL

Titanium dioxide is known to exist in three crystalline modifications: rutile (tetragonal), brookite (orthorhombic) and anatase (tetragonal). For our experiments we prepared TiO_2powders with anatase crystalline constructions of particles, which have been produced with a high degree of the chemical purity (quantity of coloring admixtures, – Fe, Co, Cr, Cu, Ni, Mn, V – does not exceed 1×10^{-5}% mas.) [13]. The TiO_2 preparation method includes thermal hydrolysis of titanium tetrachloride ($TiCl_4$) initially digested in hydrochloric acid (HCl) and then diluted in distilled water [14]. The synthesis is carried out under normal pressure and temperature of 373 K in a presence of specially prepared titanium nuclei, which are added to control a process of crystal growth. Herewith, a polycrystalline sediment – hydrated titanium dioxide and hydrochloric acid, is obtained according to the following scheme:

$$\mathrm{TiCl_4 + 3H_2O \rightarrow TiO(OH)_2 + 4HCl}$$

$$\mathrm{TiO(OH)_2 \rightarrow TiO_2 + H_2O}$$

This technique allows to change physical-chemical features of TiO_2 materials, – their phase composition, the size and construction of particles, their surface state, porous structure and other properties by adjusting the synthesis conditions. Produced TiO_2 particles had almost a spherical shape with a typical size of 10–30 μm in diameter and consisted of grown together nanocrystallite aggregates (5–15 nm). Their anatase structure has been confirmed by X-ray phase analysis (DRON-2, $Cu_{k\alpha}$ radiation).

TiO_2 surface modification has been carried out by adsorption of metal cations (Cu^{+}, Mn^{2+}, Cr^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}) from the diluted solutions of the corresponding salts by the ion-exchange mechanism at $pH = 6–7$. The concentration of dopants included has been estimated, taking into account known amounts of initial substances. Metal cation content in the ending samples was 5–10%at. in relation to Ti-atoms. These data have been confirmed by X-ray fluorescence analysis method (XNAT-Control X-ray fluorimeter, Germany). Obtained titanium hydroxide suspensions were filtered and then annealed at $\sim$450 K during 24 hours. Further the samples were carefully treated with distilled water in order to remove adsorbed doping anions and additionally annealed at 573 K during 15 hours.

4-pentyl-4′cyanobiphenyl (5CB) C_5H_{11}-C_6H_4-C_6H_4-C≡N exists in nematic phase within the temperature range from 295,5 to 308 K. The structure and spectral features of this substance have been studied in details [15].

TiO_2-5CB heterogeneous systems have been obtained by loading TiO_2 particles of chosen modified structure into 5CB nematic liquid and mixing at room temperature.

IR absorption spectra of pure and metal-doped TiO_2 (anatase) powders, 5CB, and also heterogeneous systems TiO_2-5CB and Me^{n+}-TiO_2-5CB (where Me is Cu^+, Mn^{2+}, Cr^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}) have been recorded and analyzed.

FTIR spectra for all samples have been measured at room temperature on Bruker IFS-88 spectrometer in a region of 4000–400 cm^{-1}. The spectral slit width was 2 cm^{-1}, the number of scanning was 32. Pure TiO_2 powders have been suspended in Nujol.

RESULTS AND DISCUSSION

Anatase belongs to the space group $D^{19}{}_{4h}$ ($I4_1/amd$). Its crystallographic cell contains two primitive unit cells, each of which consists of two TiO_2 formula units. According to the factor group analysis [16], six modes, $A_{1g} + 2B_{1g} + 3E_g$, are Raman active and three modes, $A_{2u} + 2E_u$, are infrared active. One vibration, B_{2u}, will be inactive in both infrared and Raman spectra. All of these modes account for the 15 normal optical modes of vibrations.

IR spectra of all TiO_2 samples are characterized by strong broad bands at $\sim$400–700 cm^{-1}. Larbot *et al.* [17] and Chhor *et al.* [18] assigned it to $\nu_{\text{Ti-O}} = 550$–$653\,cm^{-1}$ and $\nu_{\text{Ti-O-Ti}} = 436$–$495\,cm^{-1}$ framework bonds. Spectral parameters of this band remain practically the same after loading TiO_2 particles into 5CB.

Anatase particles have a porous and defective surface, which contains active centers of different nature and amount. The problem of surface active centers on the polydispersive TiO_2 is quite difficult. According to the investigations carried out before [19], microcrystals of rutile and anatase have three the most pronounced crystalline planes similar to the bulk TiO_2 monocrystals. In the case of anatase, they are (001), (101) and (111) ones, i.e. its surface layers contain 2- and 3-coordinated O-atoms and 4- and 5-coordinated Ti-atoms. So in the first assumption, we can consider that active centers for TiO_2 powders are the same as for TiO_2 crystals. Presence of surface adsorbed water leads to the formation of ≡Ti-OH and ≡Ti-(OH)-Ti≡ groups. Their properties can differ from one crystalline plane to another. Doping TiO_2 with metal cations even increases a variety of possible active centers, which can realize on the surface.

The characteristic IR spectral region of TiO_2 surface active centers is presented in Figure 1. Spectrum of pure TiO_2 powder contains a very intensive broad band with absorption maxima at ~1122, 1138 and 1146 cm^{-1}. When metal cations are doped to TiO_2 surface, this band significantly transforms and simultaneously new absorption bands appear. Broad IR bands, which are present in spectra for all TiO_2 samples at ~1050, 1120, 1150, can be assigned to different surface active centers, connected with TiO_2 hydroxyl covering and adsorbed water molecules, such as ≡Ti-O-H and ≡Ti-(OH)-Ti≡. Their variety for different Me^{n+}-TiO_2 samples results in such a broadening of these bands and is indicated by different shapes of δ(OH) deformation vibration band (Fig. 2). Metal cations disturb surface OH-groups by coordination or ionic bonding, and in the case of Mn^{2+} can even substitute surface Ti-atoms, completing TiO_2 crystalline lattice. At that new surface groups appear, such as Mn-OH and Mn-(OH)-Ti≡, which have their spectral bands shifted to the long-wavelengths. In this

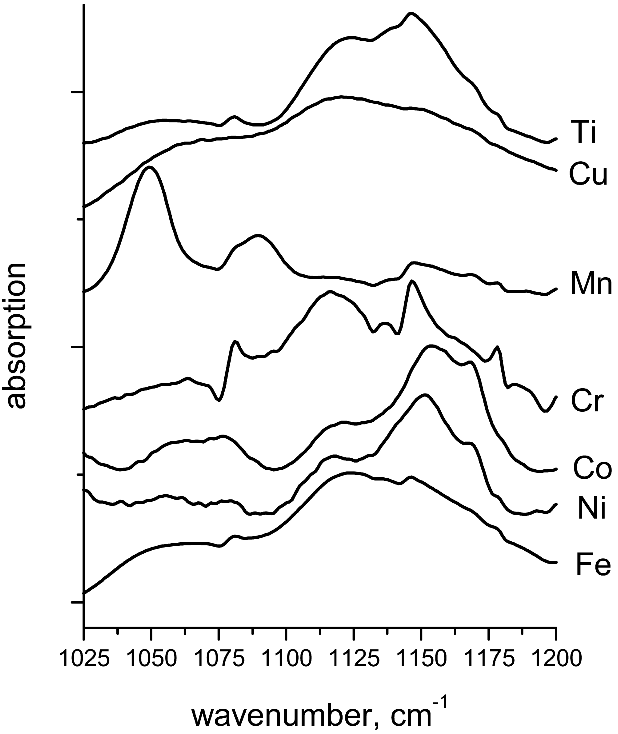

FIGURE 1 FTIR spectral region, characteristic for TiO_2 surface active centers, for pure TiO_2 powders, doped with different cations.

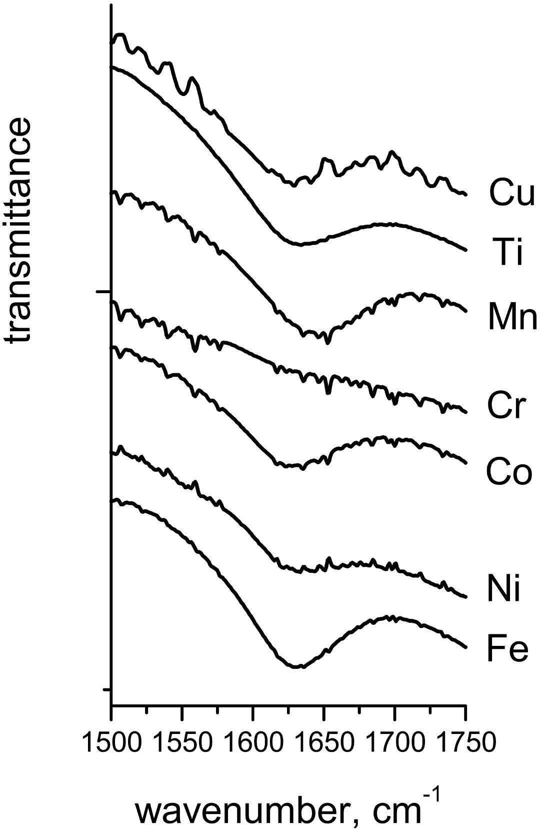

FIGURE 2 FTIR spectral region of deformation δ(OH) vibrations for pure TiO_2 powders, doped with different cations.

case broad bands at ~1120 and 1150 cm^{-1}, less or more seen for all other TiO_2 powders, are observed at ~1040 and 1080 cm^{-1}. Several narrow bands at ~1080, 1146, 1168 and 1178 cm^{-1}, which can be most clearly seen for Cr-TiO_2 sample, are also observed in this spectral region. These bands can be attributed to local active centers on Ti- or Me^{n+}-ions, which connected with the TiO_2 lattice deformations near the surface. Cr-TiO_2 powder has less hydroxyl and adsorbed water covering (Fig. 2), so there these bands are the most intensive and very pronounced.

Upon loading TiO_2 particles into 5CB very intensive in the case of pure titanium dioxide absorption bands at ~1120 and 1150 cm^{-1} significantly decrease, as well as long wavelength wings of δ(OH) and ν(OH) (~1600 and 3200 cm^{-1}, correspondingly). These facts are an evidence that 5CB molecules, approaching TiO_2 surface, displace adsorbed water and destroy water associates near the surface. It is interesting to notice, that the same result we obtained when we were investigating interactions in heterogeneous systems of similar TiO_2 particles and benzophenone [20].

In order to understand the mechanism of molecular interactions between 5CB molecules and influence of different metal cations doped, we carefully analyzed IR absorption bands corresponding to 5CB molecule vibrations. IR spectrum of the bulk 5CB was investigated and fully interpreted before [21].

We have found that only several IR adsorption modes of 5CB are sensitive to the presence of TiO_2 surface and metal cations (Table 1). These frequencies can be attributed to the stretching vibrations of CN group and to the stretching and deformation ring vibrations. Having nearly the same positions in all Me^{n+}-TiO_2-5CB systems, their broadening depends on the metal cation doped. For instance, we have the largest spectral width of these bands in the case of Fe^{3+} cation and the least one in the case of

TABLE 1 Spectral Parameters of Some 5CB Absorption Bands in its Heterogeneous Systems with Metal-doped TiO_2 Particles

Cation	ν_{max}, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}
ν(CN) stretching mode		
Cu^+	2227.1	9.2
Ti^{4+}	2226.9	9.8
Mn^{2+}	2226.9	10.0
Cr^{2+}	2226.3	10.9
Co^{2+}	2226.9	11.9
Ni^{2+}	2227.2	12.8
Fe^{3+}	2227.1	14.2
ν(CC) ring deformation mode		
Cu^+	1606.0	7.2
Ti^{4+}	1606.1	7.5
Mn^{2+}	1606.2	7.5
Cr^{2+}	1605.8	8.6
Co^{2+}	1605.9	8.8
Ni^{2+}	1606.0	10.6
Fe^{3+}	1605.7	12.4
γ(CH) perpendicular deformation mode		
Cu^+	855.7	14.2
Ti^{4+}	856.2	12.9
Mn^{2+}	856.6	10.0
Cr^{2+}	856.3	13.8
Co^{2+}	856.2	15.6
Ni^{2+}	856.1	17.2
Fe^{3+}	856.5	18.3

TABLE 2 Spectral Parameters of 5CB Absorption Bands

FTIR band	$\nu_{\max}$, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}
ν(CN) stretching mode	2225.9	9.1
ν(CC) ring deformation mode	1605.7	7.2
γ(CH) perpendicular deformation mode	856.1	11.9

Cu^{+} and Mn^{2+} (see Table 1). The whole row, in which metal cation influence increases, is the following: $Cu^{+} < Mn^{2+} < Cr^{2+} < Co^{2+} < Ni^{2+} < Fe^{3+}$. For comparison, Table 2 presents the same spectral parameters for pure 5CB substance. Near TiO_2 surface 5CB molecules can form hydrogen bonds of –CN…HO-Ti≡ and π-electrons…HO-Ti≡ types, which reflects in mentioned above changes in the corresponding CN-group and phenyl vibrations.

Forming of donor-acceptor bonds is accompanied with shifting of ν(CN) absorption band towards the high frequencies as a result of the C≡N bond strengthening due to the changes in hybridization of nitrogen orbitals [22]. We have not observed any shifts of this band within the limits of error. Thus we can suggest that the influence of metal cations, adsorbed on TiO_2 surface, is a polarizing effect of these cations on 5CB molecules. It is well-known that the polarizing activity of the ion abruptly increases with its charge increasing and its radius decreasing, but the structure of its external electron orbital is also of great importance [23]. Values of ion radii, ion potentials and relative polarizing potential for studied metal cations are listed in Table 3. These data are in perfect agreement with our results, described above. Changes in FTIR spectral parameters of described absorption bands for Me^{n+}-TiO_2-5CB heterogeneous systems well correlate with the polarizing effect of corresponding metal cations. During polarizing, 5CB molecules possess simultaneously orientation changes and deformation. At that, when the polarizing effect increases, the role of

TABLE 3 Values of Ion Radii, Ion Potentials and Relative Polarizing Potential for Metal Cations, Used in Metal-doped TiO_2 Samples

Cation	Ion radius, Å	Ion potential z/R	Polarizing potential, V
Cu^{+}	0.98	1.02	0.57
Mn^{2+}	0.91	2.20	0.85
Cr^{2+}	0.83	2.41	no data
Co^{2+}	0.78	2.56	0.92
Ni^{2+}	0.74	2.70	0.95
Fe^{3+}	0.67	4.48	1.34

molecule deformation becomes more significant. This is also confirmed by spectral changes, observed by us for ring deformation ν(CC) and perpendicular deformation γ(CH) modes (Table 1).

CONCLUSIONS

We have investigated metal-doped (Cu^{+}, Mn^{2+}, Cr^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}) TiO_2 anatase powders and their heterogeneous systems with 5CB liquid crystal by FTIR spectroscopy at room temperature. TiO_2 samples have been produced by thermal hydrolysis of $TiCl_4$. Titanium dioxide particles have a very defective surface, which contains active centers of different nature and amount. Doped metal cations increases a variety of possible active centers, disturbing surface OH-groups by coordination or ionic bonding, and in the case of Mn^{2+} even substituting surface Ti-atoms. ≡Ti-OH and ≡Ti-(OH)-Ti≡ groups are formed on the surface due to the presence of adsorbed water. 5CB molecules, approaching TiO_2 surface, displace adsorbed water molecules and can create hydrogen bonds of –CN…HO-Ti≡ and π-electrons…HO-Ti≡ types, which reflects in changes in the spectral parameters of corresponding CN-group and phenyl vibrations. The influence of metal cations, adsorbed on TiO_2 surface, is a polarizing effect of these cations on 5CB molecules and increases such as $Cu^{+} < Mn^{2+} < Cr^{2+} < Co^{2+} < Ni^{2+} < Fe^{3+}$, which is in a perfect agreement with the polarizing activity of these cations. At that 5CB molecules change their orientation and possess some deformations, which is confirmed by the corresponding changes in spectral parameters of deformation modes.

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