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ZrO_2–TiO_2 Materials

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Abstract—The magnetic, electrical, catalytic, and photocatalytic properties of ZrO_2–TiO_2 materials were studied. The ZrO_2–TiO_2 system was shown to contain ZrO_2-, TiO_2, and $ZrTiO_4$-based solid solutions. Procedures for the preparation of high-activity ZrO_2–TiO_2 photocatalysts and photostable pigments were developed.

INTRODUCTION

ZrO_2–TiO_2 materials are potential candidates for the fabrication of refractory ceramics [1, 2] and development of advanced coating processes [3]. The ZrO_2–TiO_2 system is known to contain both TiO_2- and ZrO_2-based solid solutions, but there is no general agreement as to their extents. The existence of zirconium titanate, $ZrTiO_4$, was first reported in [4] and then confirmed in [5]. At 590 K, $ZrTiO_4$ reacts eutectoidally with monoclinic ZrO_2. The purpose of this work was to investigate the electrical, magnetic, catalytic, and photocatalytic properties of ZrO_2–TiO_2 samples with the aim of preparing photosensitive materials and photostable pigments.

EXPERIMENTAL

Samples for this investigation were prepared via coprecipitation of zirconium and titanium hydroxides obtained by reacting ammonia with $ZrOCl_2$ and $TiCl_4$, followed by washing with water to remove the ammonium salts. The residual ammonia was removed by calcination at 870 K. Next, the hydroxide mixtures were heat-treated in a muffle furnace at 1070 K for 6 h. The resultant materials were ground in a ball mill to the preset particle size.

The photocatalytic performance of the materials was characterized by their activity for the reduction of methylene blue to a leuco form [6]. We also assessed their catalytic activity for chemical metallization of composites [7]. Magnetic susceptibility was measured by the Faraday method in a stabilized magnetic field using an automatic balance. Electrical conductivity was measured at dc. Phase composition was determined on a DRON-3.0 x-ray diffractometer (Ni-filtered CuK_α radiation) at room temperature. Modifiers were introduced by impregnating ZrO_2–TiO_2 samples with appropriate metal salts, followed by calcination in air at 770 K for 4 h, or in the course of flame hydrolysis at 1370 K. The specific surface area S_{sp} was determined by low-temperature argon BET measurement.

RESULTS AND DISCUSSION

According to x-ray diffraction data (Fig. 1), the phase composition of the ZrO_2–TiO_2 materials was dependent on TiO_2 content. The samples containing 1.0 and 5.0 wt % TiO_2 were single-phase and consisted of monoclinic ZrO_2-based solid solutions. The diffraction patterns of the samples containing 20.0 wt % TiO_2

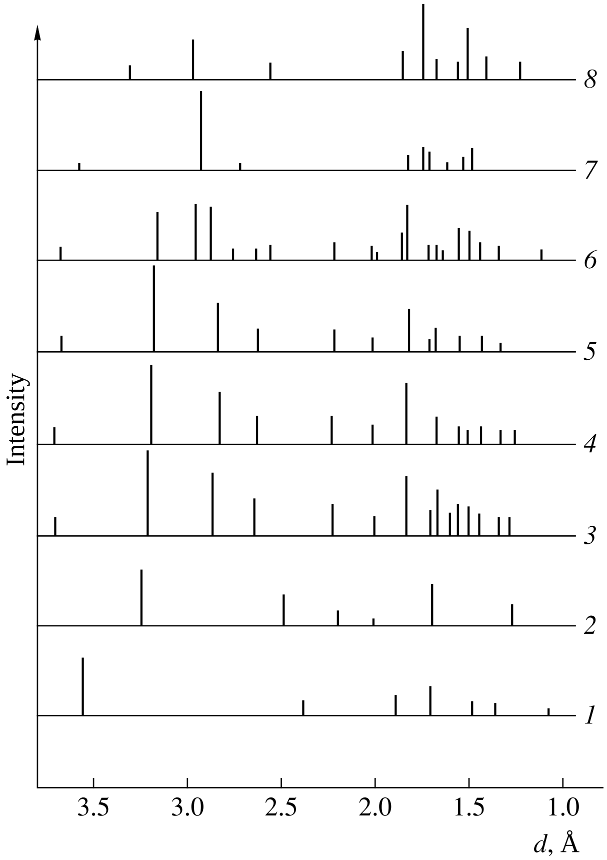

Fig. 1. Schematic diffraction patterns of (*1*) anatase, (*2*) rutile, (*3*) ZrO_2, and (*4*–*8*) ZrO_2–TiO_2 samples containing (*4*) 1.0, (*5*) 5.0, (*6*) 20.0, (*7*) 40.0, and (*8*) 60.0 wt % TiO_2.

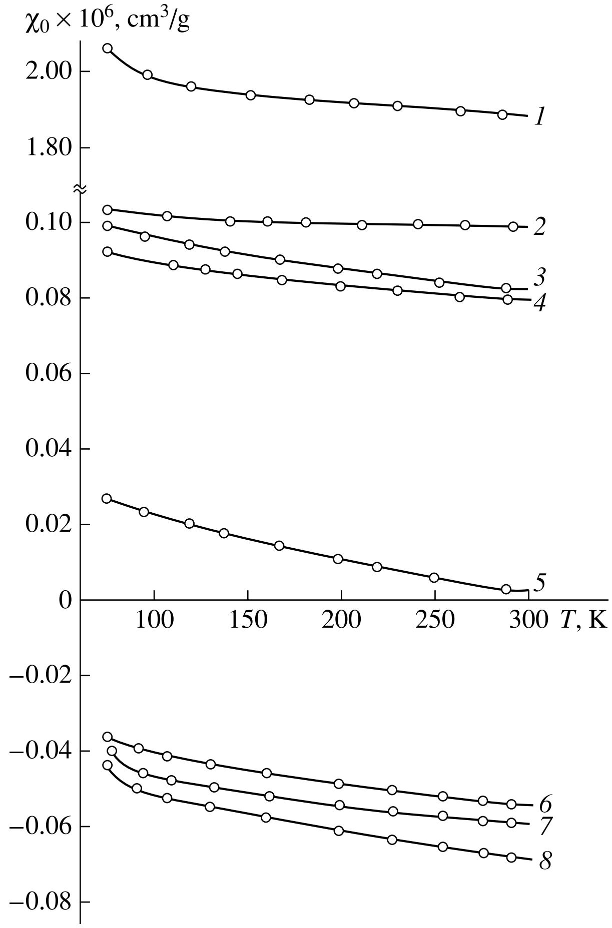

Fig. 2. Magnetic susceptibility as a function of temperature for (*1*, *2*) TiO_2 prepared by flame and liquid-phase hydrolysis, respectively; (*6*) ZrO_2; and (*3–5*, *7*, *8*) $ZrO_2–TiO_2$ samples containing (*3*) 40.0, (*4*) 60.0, (*5*) 20.0, (*7*) 1.0, and (*8*) 5.0 wt % TiO_2.

showed, along with peaks from monoclinic ZrO_2, reflections from $ZrTiO_4$. The relative intensity and number of such reflections increased with TiO_2 content. At 40.0 wt % TiO_2, the samples were again single-phase and consisted of a $ZrTiO_4$-based solid solution. The diffraction patterns of the samples containing 60.0 wt % TiO_2 showed reflections from $ZrTiO_4$ and rutile.

The data in Table 1 demonstrates that the catalytic and photocatalytic activity of TiO_2 prepared by high-temperature heat treatment is much higher than that of ZrO_2, TiO_2, or $ZrO_2–TiO_2$ prepared by liquid-phase hydrolysis. The likely reason is the presence of hydrogen during flame hydrolysis, which leads to a defect-rich structure of the material, as supported by magnetic susceptibility measurements (Fig. 2), which indicate a high concentration of paramagnetic centers.

It can be seen from Table 1 that, in the $ZrO_2–TiO_2$ system, the catalytic and photocatalytic activity reaches a maximum at 40.0 wt % TiO_2 and slightly decreases as the TiO_2 content increases to 60.0 wt %, which is likely associated with the formation of the rutile phase, as evidenced by x-ray diffraction data (Fig. 1). According to earlier studies [8], rutile has a low activity. Reducing the TiO_2 content to 20.0 wt % leads to a sharp drop in catalytic and photocatalytic activity. Note that the paramagnetic contribution also decreases with increasing TiO_2 content. The magnetic susceptibility depends strongly on TiO_2 content (Fig. 2). The samples containing more than 20.0 wt % TiO_2 are paramagnetic, and those containing less than 20.0 wt % TiO_2 are diamagnetic.

These findings indicate that the paramagnetism is mainly due to TiO_2. Given that, in the reactions studied, photocatalysis is due to [Ti^{3+}] paramagnetic centers [9, 10], the TiO_2-rich materials, unstable under UV irradiation, would be expected to exhibit high photocatalytic activity, whereas the ZrO_2-rich materials, stable to UV irradiation, must have low photocatalytic activity, as observed in experiment.

The electrical conductivity of the materials studied depends on the preparation procedure and TiO_2 content (Table 1). The titania prepared by high-temperature heat treatment and consisting of defect-rich anatase and

Table 1. Photocatalytic activity (PCA), catalytic activity (CA), and conductivity of TiO_2, ZrO_2, and $ZrO_2–TiO_2$ (numbers in parentheses indicate wt % TiO_2)

Phase composition	Preparation procedure	S_{sp}, m^2/g	Specific PCA, g/(l min m^2)	CA, %	σ, S/cm
TiO_2 (50% anatase + 50% rutile)	Flame hydrolysis of $TiCl_4$	50	1.4	70.0	3.6×10^{-6}
Anatase	Liquid-phase hydrolysis of $TiCl_4$	26	3.2×10^{-1}	45.2	9.8×10^{-8}
Rutile	"	20	1.6×10^{-2}	30.6	8.7×10^{-9}
Monoclinic ZrO_2	Liquid-phase hydrolysis of $ZrOCl_4$	28	1.3×10^{-2}	28.6	8.1×10^{-9}
$ZrO_2–TiO_2$ (1%)	Hydroxide coprecipitation	20	1.2×10^{-2}	27.5	7.1×10^{-9}
$ZrO_2–TiO_2$ (5%)	"	22	1.0×10^{-2}	23.0	6.7×10^{-9}
$ZrO_2–TiO_2$ (20%)	"	24	1.8×10^{-2}	34.0	9.3×10^{-9}
$ZrO_2–TiO_2$ (40%)	"	27	2.7×10^{-2}	43.8	12.9×10^{-9}
$ZrO_2–TiO_2$ (60%)	"	25	2.1×10^{-2}	41.3	11.3×10^{-9}

Table 2. Effect of impurities on the photocatalytic activity of ZrO_2 (I), TiO_2 prepared by high-temperature heat treatment (II), and ZrO_2–60.0 wt % TiO_2 (III)

Weight percent impurity	Photocatalytic activity, g/(l min m^2)								
	W			V			Al		
	I	II	III	I	II	III	I	II	III
0.001	1.5×10^{-2}	9.5×10^{-1}	2.4×10^{-2}	1.3×10^{-2}	7.2×10^{-1}	2.5×10^{-2}	9.7×10^{-3}	2.1×10^{-2}	9.9×10^{-3}
0.01	1.7×10^{-2}	1.2	2.9×10^{-2}	1.8×10^{-2}	9.1×10^{-1}	2.8×10^{-2}	8.2×10^{-3}	4.5×10^{-3}	8.7×10^{-3}
0.1	2.8×10^{-2}	1.5	3.6×10^{-2}	2.2×10^{-2}	1.1	3.4×10^{-2}	7.1×10^{-3}	1.3×10^{-3}	7.2×10^{-3}
1.0	3.2×10^{-2}	1.8	4.2×10^{-2}	2.7×10^{-2}	1.4	3.8×10^{-2}	9.0×10^{-4}	4.0×10^{-4}	9.5×10^{-4}
5.0	6.4×10^{-3}	4.3×10^{-2}	8.7×10^{-3}	2.1×10^{-3}	3.5×10^{-2}	7.2×10^{-3}	0	0	0

Note: The photocatalytic activity of unmodified ZrO_2, TiO_2, and ZrO_2–TiO_2 samples is 1.3×10^{-2}, 6.0×10^{-1}, and 2.1×10^{-2} g/(l min m^2), respectively; impurities were introduced by impregnation.

rutile phases has a high conductivity, whereas the σ of rutile TiO_2 prepared by liquid-phase hydrolysis, whose structure is stabilized by Al^{3+} ions, is fairly low [11]. The samples containing 1.0–5.0 wt % TiO_2 have the lowest conductivity, below the σ of pure ZrO_2 (Table 1). As the TiO_2 content increases to 40 wt %, σ rises. Since the measurements were performed at dc on powder compacts, they yielded surface conductivity [12].

Previous studies of TiO_2–M_nO_m materials showed that, depending on its nature, M_nO_m may act as an inert support (Li_2O, Al_2O_3, SiO_2, V_2O_5, WO_3) or exhibit catalytic activity (ZnO, ZrO_2) [13, 14]. It was found that the catalytic properties of such materials depend on their phase composition, TiO_2 content, and specific surface.

As shown above, the catalytic and photocatalytic properties of ZrO_2–TiO_2 materials depend on the Zr/Ti ratio, since the activity of ZrO_2 is notably lower than that of TiO_2. The catalytic, photocatalytic, magnetic, and electrical properties of ZrO_2 and TiO_2 depend strongly on the preparation procedure, heat-treatment conditions, and sample purity. High-purity, close-to-stoichiometry ZrO_2 and TiO_2 exhibit neither photocatalytic not catalytic activity and have low χ. Such materials are good insulators [15].

The introduction of metal impurities into TiO_2-containing materials, followed by calcination at 1270 K, changes their conductivity. The dopants with a valence below 4+ act as acceptors, and those with a valence above 4+ act as donors [8]. Since heat treatment at 1270 K yields monolithic materials, measurements on such samples allow one to determine their bulk conductivity. The specific surface of the samples is very small and has no effect on the measurement results. At the same time, if the calcination temperature does not exceed 770 K, impurities present in low concentrations act as donors, regardless of their valence, thereby reducing the work function and enhancing the catalytic activity [16]. The impurities have no effect on the S_{sp} of TiO_2 and accumulate in the surface layer.

Our results obtained on ZrO_2–TiO_2 samples doped with metals via impregnation demonstrate that small amounts of V^{5+} and W^{6+} raise the catalytic activity (Table 2) and σ of the material. Heterovalent impurities would be expected to change the carrier concentration. The likely location of impurities in the TiO_2 lattice was considered in [15]. It was shown that substitutionally incorporated vanadium and tungsten raise the carrier concentration in titania. Based on this conclusion and our experimental results and taking into account that the ionic radii of the dopants ($r_{V^{5+}}$ = 0.59 Å, $r_{W^{6+}}$ = 0.65 Å) are close to that of Ti^{4+} ($r_{Ti^{4+}}$ = 0.64 Å), we believe that, in the materials studied, the V and W ions are incorporated substitutionally. Since the catalytic and photocatalytic properties are determined mainly by TiO_2, it seems likely that the W^{6+} and V^{5+} dopants influence, for the most part, the concentration of active centers in TiO_2, thereby altering the properties of the material as a whole. With increasing dopant concentration, the photocatalytic activity of the samples decreases,

Table 3. Effect of impurities introduced during flame hydrolysis of $TiCl_4$ vapor on the photocatalytic activity of TiO_2

Photocatalyst	Specific surface, m^2/g	Photocatalytic activity, g/(l min m^2)
Unmodified TiO_2	50	1.4
TiO_2 + W^{6+}	52	2.8
TiO_2 + V^{5+}	49	2.1
TiO_2 + Bi^{5+}	120	2.3
TiO_2 + Al^{3+}	54	1.4×10^{-4}
TiO_2 + Cu^{2+}	46	1.0×10^{-4}
Unmodified TiO_2 prepared by liquid-phase hydrolysis of $TiCl_4$	20	1.6×10^{-2}

Note: Impurity content of 1.0 wt %.

which suggests that V^{5+} and W^{6+} may be present in a separate phase and that the active sites may be blocked. Doping of ZrO_2–TiO_2 with Al^{3+} ions ($r_{Al^{3+}}$ = 0.57 Å) reduces the photocatalytic activity of the samples over the entire range of dopant concentrations (Table 2) owing to the formation of a substitutional solid solution, which reduces the concentration of structural defects [15]. This finding was used to prepare photostable Al-modified ZrO_2–TiO_2 materials. However, fine-particle doped materials cannot be prepared by impregnation, which reduces the specific surface as a result of particle aggregation in water and during heat treatment. In view of this, we developed a technique for doping TiO_2 and TiO_2-based materials via high-temperature hydrolysis of dissolved metal salts in air–hydrogen flames [17].

The materials thus obtained have a high specific surface (Table 3). By introducing different impurities and adjusting the process parameters, we can obtain materials with a high photocatalytic activity, potentially attractive as photocatalysts and photosensitive components of insulators in photoadditive printed circuit manufacture, as well as materials with zero photocatalytic activity, which can be used as stable white pigments for UV-reflecting coatings.

The ZrO_2–TiO_2 materials precalcined at 1070 K in air exhibit no catalytic activity for the photoreduction of methylene blue to a leuco form or chemical metallization of composites. Heat treatment in a reducing atmosphere between 770–870 K has no effect on their catalytic and photocatalytic properties, while the samples calcined in hydrogen at 1070 K exhibit high catalytic activity and can be used as efficient photocatalysts. The χ of such materials is one order of magnitude higher than that of as-prepared samples.

Using the most active materials, we fabricated a set of catalyzed textolites and metallized their surfaces by the additive method. The high catalytic activity and small particle size of the materials prepared by high-temperature heat treatment ensured good adhesion both in total plating and photopatterning of the insulator. The use of the materials containing 1.0 and 5.0 wt % TiO_2 (with and without Al additions) as pigments makes it possible to obtain extremely weatherproof and thermally stable coatings.

CONCLUSION

The electrical, magnetic, and catalytic properties of ZrO_2–TiO_2 materials were studied. The effects of different modifiers were examined, and procedures for the preparation of high-activity photocatalysts and photostable pigments were developed.

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