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Study of the Influence of the Preparation Method on the Formation of the Phase Composition and Structure of V–Ti–O and W–Ti–O Catalysts for Selective Catalytic Reduction of NO by NH_3

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Abstract—The influence of the preparation method on the structure and phase composition of V–Ti–O and W–Ti–O catalysts for selective catalytic reduction of NO by NH_3 was studied. The preparation conditions were found to insignificantly affect the structure of the resulting V–Ti–O catalysts, whereas in the case of W–Ti–O catalysts, such an influence was distinctly observed. The introduction of tungsten ions into the lattice of titanium dioxide leads to the formation of both local defects (solid solutions of the substitution type) and extended, so-called Wadsley's defects in the framework of TiO_2. The concentrations of the defects of both types depend on the catalyst preparation conditions.

INTRODUCTION

Three-component V_2O_5–WO_3/TiO_2 systems are widely used as catalysts for selective catalytic reduction (SCR) of NO_x by NH_3. Unfortunately, the number of publications devoted to the study of V–W–Ti–O catalysts is limited [1–8]. The results obtained by different authors are sometimes contradictory to each other. Most likely, this is a result of the strong dependence of the catalyst properties on their preparation conditions. Moreover, the influence of tungsten on the formation of the catalyst structure is elusive because of the quite complicated composition of such three-component catalysts. To clarify the role of vanadium and tungsten in the process of the catalyst formation, model V–Ti–O and W–Ti–O systems prepared under conditions typical for the preparation of the three-component catalyst were studied.

EXPERIMENTAL

Catalysts

Preparation of V_2O_5/TiO_2 and WO_3/TiO_2 catalysts by impregnation. The initial TiO_2 support (anatase) was prepared by hydrolysis of a $TiCl_4$ solution in concentrated HCl using an ammonia aqueous solution (25 wt % NH_3) at 70°C and pH 5–6. The resulting precipitate was washed with distilled water and then dried at room temperature and 110°C for 2 and 4 h, respectively.

V_2O_5/TiO_2 catalysts were prepared by impregnation of TiO_2 with a VOC_2O_4 solution. These samples are further denoted as (wt %)V-i.

WO_3/TiO_2 catalysts were prepared by impregnation of TiO_2 with an ammonium tungstate solution in aqueous ammonia. These samples are further denoted as (wt %)W-i.

Preparation of V_2O_5/TiO_2 and WO_3/TiO_2 catalysts by coprecipitation. The catalysts were prepared by hydrolysis of a $TiCl_4$ solution in concentrated HCl at 70°C and pH 5–6 in the presence of

(a) an ammonium vanadate solution in 25 wt % aqueous ammonia; these samples are further denoted as (wt %)V-c;

(b) an ammonium tungstate solution in 25 wt % aqueous ammonia; these samples are further denoted as (wt %)W-c; and

(c) a mixture of ammonium vanadate and ammonium tungstate solutions in 25 wt % aqueous ammonia; these samples are further denoted as (wt %)V-(wt %)W-c.

The resulting precipitates were washed with distilled water and dried at room temperature and 110°C for 2 and 4 h, respectively, and then calcined at 350 and 450°C for 4 h.

Preparation of grafted V_2O_5/TiO_2 catalysts. The initial TiO_2 support was prepared in the same way as for the impregnated samples. Before grafting, the carrier was dried at 110°C and calcined at 350°C for 6 h. The catalysts were prepared by grafting vanadium on the surface of TiO_2 using $VOCl_3$ according to the procedure described elsewhere [9]. These samples are further denoted as (wt %)V-g.

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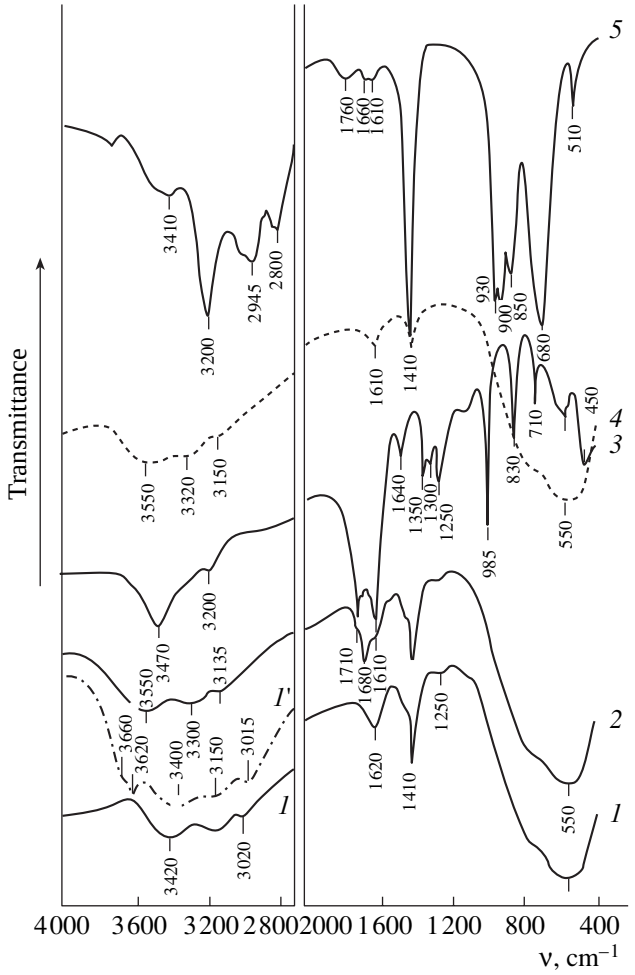

Fig. 1. IR spectra of (*1*) TiO_2 prepared by hydrolysis of $TiCl_4$, (*1'*) the suspension of TiO_2 in fluorinated oil, (*2*) sample 2V-i, (*3*) VOC_2O_4 precursor, (*4*) sample 2V-c, and (*5*) NH_4VO_3 precursor. Samples *1*, *2*, and *4* were dried at 110°C for 4 h.

Catalyst Characterization

XRD analysis was performed using a HZG-4C diffractometer (Freiberger Praezisionsmechanik GmbH, Germany) with CuK_α irradiation equipped with a graphite monochromator. Diffraction patterns were obtained in the interval of diffraction angles 5°–60°. The parameters of the TiO_2 framework were determined using the (101) and (200) reflections for the anatase structure in the region of diffraction angles 22°–30° and 46°–52°, respectively. The sweep rate was 1°C/min for standard measurements and 0.25°C/min for precision measurements. The parameters of the coherent scattering area were determined from the broadening of the diffraction lines using the Selyakov–Sherrer equation.

Diffuse-reflectance UV–visible spectra of powdered samples were measured using a Specord M-40 spectrometer equipped with a conventional diffuse-reflectance attachment consisting of a photometric sphere. MgO was used as a reference sample in all cases except for the case of V/TiO_2 samples prepared by impregnation, coprecipitation, and adsorption from the gas phase. In the case of vanadium-containing samples, the spectrum of the initial TiO_2 calcined at the same temperature as the V/TiO_2 catalysts was subtracted from the spectra of the samples under study. In this case, the cell with TiO_2 was placed instead of MgO.

IR spectra were recorded using a Specord 75 IR spectrometer. The samples were pelleted with CsI before measurements. The catalyst/CsI ratio was 2 mg : 800 mg; the pellet thickness was 267 mg/cm^2; and the pressure was 8.3×10^4 kg/cm^2. To exclude the influence of water traces on the spectra of initial TiO_2, it was also prepared and measured as a suspension in fluorinated oil (Fig. 1, spectrum *1'*).

RESULTS

V–Ti–O System

The IR spectrum of TiO_2 prepared according to the procedure described above and dried at 110°C is shown in Fig. 1 (spectrum *1*). Absorption bands at 3150, 3020, and 1410 cm^{-1} attributed to NH_4^+ [10] are observed in the spectrum of initial TiO_2, besides the own absorption bands of the support located in the range of 1000–400 cm^{-1}. This means that NH_4^+ ions are strongly adsorbed at the surface of TiO_2 during the hydrolysis of $TiCl_4$.

The IR spectrum of the TiO_2 suspension in fluorinated oil (Fig. 1, curve *1'*) contains narrow absorption bands at 3620 and 3660 cm^{-1} corresponding to OH groups and an absorption band at 3400 cm^{-1} assigned to the vibrations of weakly bound water molecules. This indicates that the product of $TiCl_4$ hydrolysis represents titanium hydroxide with the composition described by the chemical formula $TiO_{2-x}(OH)_x \cdot nH_2O$ rather than hydrated titanium dioxide. The composition of this hydroxide obviously depends on the preparation conditions. After the impregnation of $TiO_{2-x}(OH)_x \cdot nH_2O$ with a solution of VOC_2O_4 (sample 2V-i), a set of new absorption bands appears in the spectrum at 1710, 1680, and 1610 cm^{-1} (Fig. 1, curve *2*). These absorption bands presumably correspond to the antisymmetric stretching vibrations of the C=O bond in the oxalate anion [10]. Two of these absorption bands (at 1710 and 1610 cm^{-1}) are also observed in the spectrum of the initial VOC_2O_4 salt (curve *3*). Therefore, a part of the vanadium at the surface of TiO_2 could exist in the form of VOC_2O_4. The presence of an additional intense absorption band at 1680 cm^{-1} indicates that some oxalate anions are present in a different state after the synthesis. This could be explained by the formation of new V–Ti–C_2O_4 species bound to the TiO_2 surface with the oxalate anion serving as a bridge [10]. Taking into account a rather low content of the supported component (2 wt %), a more detailed study of the catalysts is

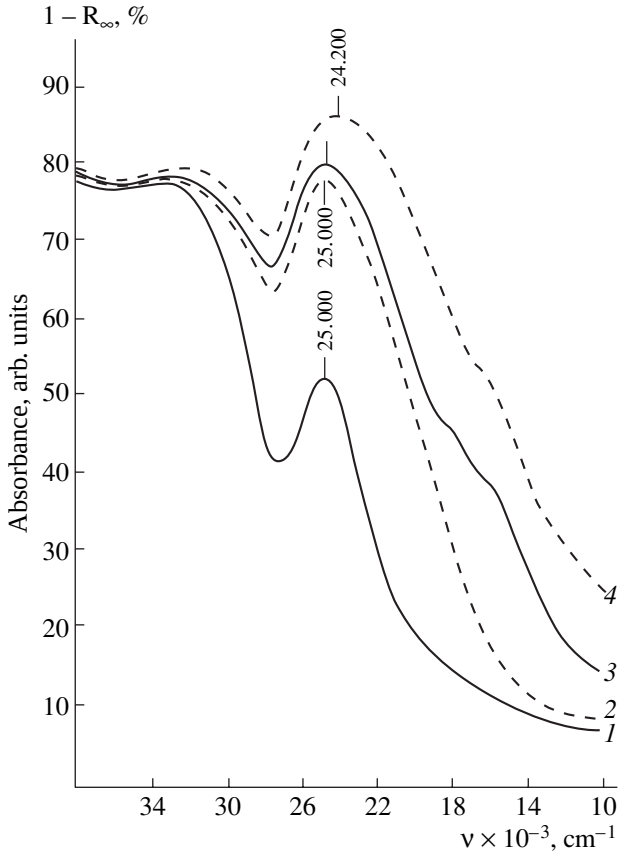

Fig. 2. Diffuse-reflectance UV–visible spectra of the samples V_2O_5/TiO_2 (measured with the subtraction of the spectrum of TiO_2): (*1*, *3*) $2\%V_2O_5/TiO_2$-i (2V-i); (*2*, *4*) $2\%V_2O_5/TiO_2$-c (2V-c). Samples *1*, *2* were air dried at 110°C for 4 h, samples *3*, *4* were then calcined at 450°C.

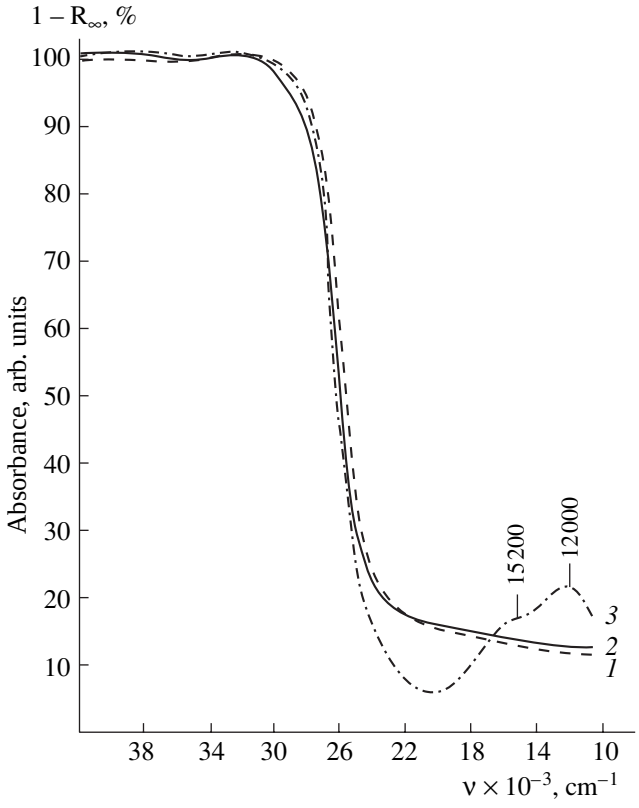

Fig. 3. Diffuse-reflectance UV–visible spectra of (*1*) TiO_2 prepared by hydrolysis of $TiCl_4$ and dried at 110°C for 4 h (*2*) a mechanical mixture of TiO_2 and NH_4VO_3, and (*3*) a mechanical mixture of TiO_2 and VOC_2O_4.

hardly possible because of the rather low intensity of the other absorption bands corresponding to oxalate anions.

Several absorption bands attributed to the absorption of NH_4^+ (at 3150, 3020, 1410 cm^{-1}) and intrinsic absorption of TiO_2 (at 1000–400 cm^{-1}) are also observed in the IR spectrum of sample 2V-i.

In the case of sample 2V-c (Fig. 1, curve *4*), the absorption bands at 3320, 3150, and 1410 cm^{-1}, corresponding to the absorption of the NH_4^+ ion in the starting NH_4VO_3 salt (Fig. 1, curve *5*), are characterized by a rather low intensity. This implies that the dried sample prepared by the coprecipitation technique contains vanadium either as its hydrated oxide or as a surface V–Ti species.

Diffuse-reflectance UV–visible spectra of samples 2V-i and 2V-c obtained by subtraction of the spectrum of the initial TiO_2 and the spectrum of the mechanical mixture of initial salts with titanium dioxide are shown in Figs. 2 and 3. Comparison of the spectra of samples 2V-i and 2V-c with the spectra of the model compounds reveals a sharp difference between them. A new absorption band at 25000 cm^{-1} is observed in the spectra of the dried samples and sample 2V-c (Fig. 2, curves *1*, *2*), which is not present in the spectra of the mechanical mixture (Fig. 3, curves *2*, *3*).

It should be pointed out that the spectra of sample 2V-i does not contain any absorption band at 18000–11000 cm^{-1} corresponding to the *d*–*d* transitions in the V^{4+} ion. This fact could be presumably explained by the oxidation of the part of vanadium ions.

The absence of the absorption band at 25000 cm^{-1} in the spectrum of the mechanical mixture of the initial salts with titanium dioxide and the appearance of this band in the spectrum of the sample 2V-c could be accounted for by strong chemical interaction of vanadium ions with the surface of the support. Thus, this absorption band could be ascribed to the band of charge transfer from surface O^{2-} ions to the V^{5+} ions. The intensity of this absorption band is expected to be dependent on the amount of vanadium ions chemically bonded with the surface of TiO_2.

Diffuse-reflectance UV–visible spectra of samples 2V-i and 2V-c are compared in view of the above hypothesis in Fig. 2 (curves *1* and *2*). These spectra are

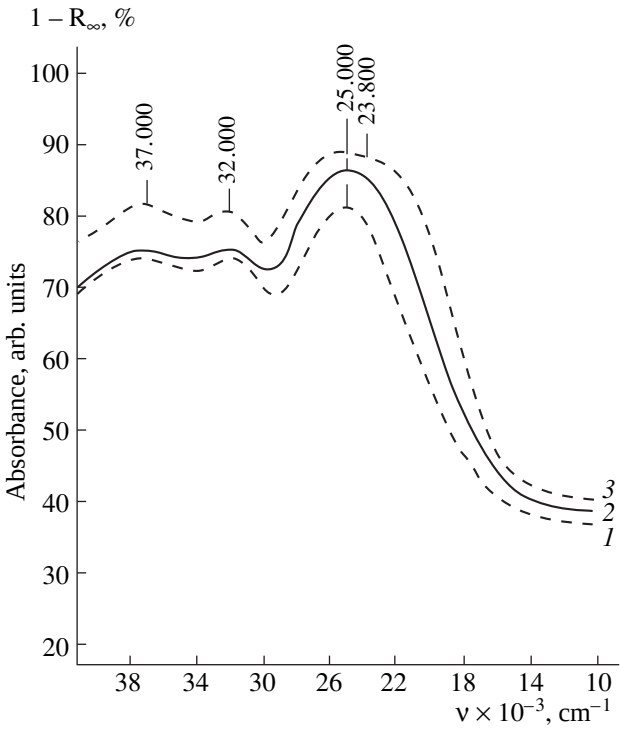

Fig. 4. Diffuse-reflectance UV–visible spectra of V_2O_5/TiO_2-grafted (measured with the subtraction of the spectrum of TiO_2): (*1*) 0.93V-g, (*2*) 1.6V-g, (*3*) 2.4V-g.

very similar to each other except for the intensity of the absorption bands at 30000–11000 cm^{-1}. The intensity of these absorption bands is considerably higher in the case of the samples prepared using the coprecipitation technique. The higher intensity of the absorption band at 25000 cm^{-1} in the spectrum of sample 2V-c (Fig. 2, curve *2*) indicates that the procedure of coprecipitation is favorable for the formation of the chemical bonds between vanadium ions and the surface of the carrier, unlike the sample prepared by the impregnation technique. The results obtained are in perfect agreement with IR spectroscopic data: the dried samples prepared by the impregnation technique contain vanadium mostly in the molecular form, as a chemical salt, and only a small part of the vanadium ions are bonded to the surface of the support through the bridging oxygen atoms. At the same time, in the case of the coprecipitation of NH_4VO_3 and $TiCl_4$, hydrolysis leads to the formation of hydrated vanadium and titanium oxides, which can react with each other with the buildup of solid solutions already at the stage of coprecipitation and drying.

Nevertheless, despite such a difference in the intensities of curves *1* and *2*, the similar character of the absorption for the samples under study indicates that the state of the part of vanadium ions in the dried samples is the same for the samples prepared using different techniques and different vanadium precursors.

Calcination of sample 2V-i at 450–500°C leads to an increase in the intensity of the absorption band at 25000 cm^{-1} and to the broadening of this absorption band (Fig. 2, curve *3*). This can presumably be a result of the interaction of vanadium ions with the surface of the carrier upon the decomposition of the vanadium salt chemically adsorbed on the surface of TiO_2. In the case of sample V-c, calcination cause no considerable change in the intensity of the absorption band at 25000 cm^{-1} (Fig. 2, curve *4*) in agreement with the hypothesis that vanadium forms surface compounds with TiO_2 already at the stage of coprecipitation. It should be noted that calcination of both samples at 450°C results in an increase in the intensity of absorption bands in the region 18000–11000 cm^{-1}, which can be attributed to *d–d* transitions of V^{4+} in VO^{2+} ions [11]. The growth of the V^{4+} concentration in samples 2V-i and 2V-c can be accounted for by the migration of a part of the V^{5+} ions into the framework of TiO_2 at elevated calcination temperatures and by the redistribution of the electron density between Ti^{4+} and V^{5+} ions followed by the electron localization on the vanadium ion.

To confirm the interpretation of the absorption band at 25000 cm^{-1} as the band arising from the vanadium chemically bonded to the TiO_2 surface, V/TiO_2 samples prepared by vanadium grafting from the gas phase were studied. The electron spectra of these samples are shown in Fig. 4 (curves *1–3*). Grafting of vanadium from $VOCl_3$ to the surface of TiO_2 resulted in the appearance of the absorption band at 25000 cm^{-1}. The intensity of this absorption band grows in parallel with an increase in the vanadium content from 0.93 to 2.4 wt %. The considerable broadening of this absorption band in the case of sample 2.4 wt % could be explained by the presence of another absorption band in the low-frequency region, which could be ascribed to the increase of the dimensions of V_xO_y clusters chemically bonded to the surface of TiO_2.

It should be noted that the diffuse-reflectance UV–visible spectra of the samples prepared by grafting do not contain any absorption bands which could be ascribed to the V^{4+} ions. This means that such a preparation procedure is not characterized by the migration of vanadium ions into the bulk of the carrier.

According to the results of the XRD analysis, samples 2V-i and 2V-c do not contain the bulk phase of V_2O_5. This result is rather typical for the case when vanadium in these samples is present either as dispersed vanadium oxide particles or as surface oxide clusters and isolated ions. Strong chemical binding of vanadium to the surface of TiO_2 and its migration to the interior of the carrier seem to prevent the formation of a bulky V_2O_5 phase upon calcination of the samples.

A W–Ti–O System

To clarify the role of tungsten in the process of the catalyst formation, a series of model W–Ti–O samples

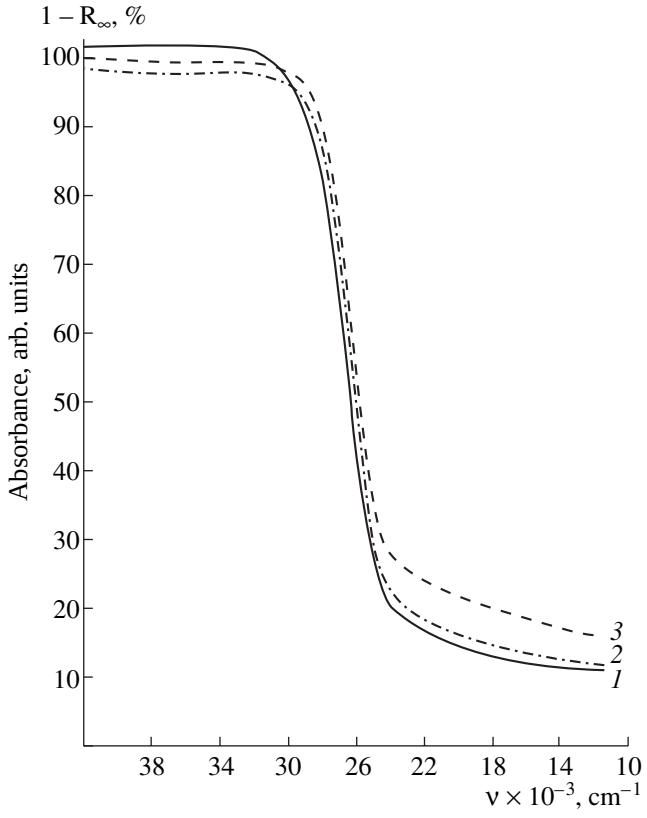

Fig. 5. Diffuse-reflectance UV–visible spectra of: (*1*) TiO_2, (*2*) WO_3/TiO_2-i (samples 6.96W-i, 17.4W-i, 24W-i), and (*3*) WO_3/TiO_2-c (sample 7W-c). Samples were dried at 110°C for 4 h.

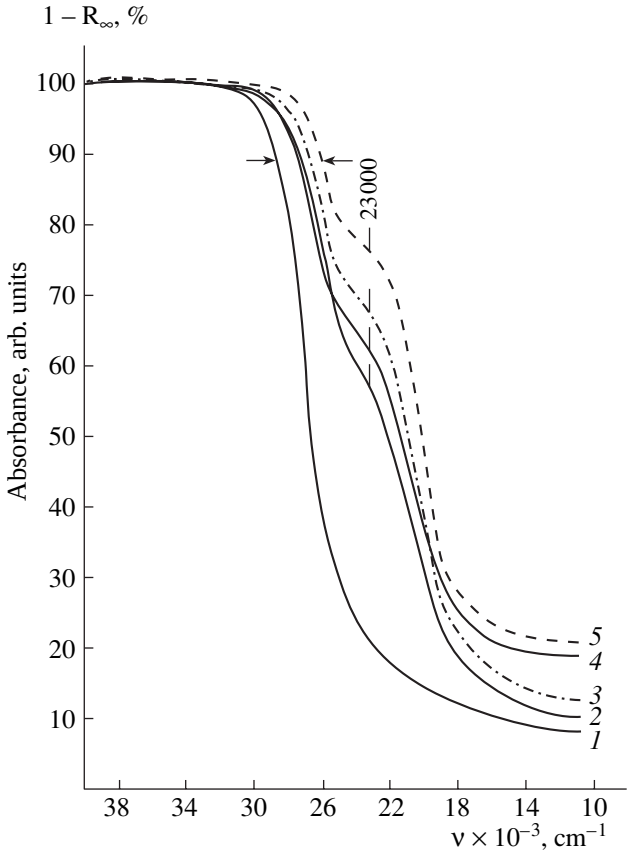

Fig. 6. Diffuse-reflectance UV–visible spectra of (*1*) TiO_2, (*2*) 6.96W-i, (*3*) 17.4W-i, (*4*) 24W-i, and (*5*) 7W-c. Samples were dried at 110°C for 4 h and then calcined at 350°C.

with different tungsten contents was studied. The samples were prepared according to the procedure used in the case of 2V-i and 2V-c samples. Diffuse-reflectance UV–visible spectra of the samples dried at 110°C are shown in Fig. 5. Curve *1* in this figure corresponds to the pure TiO_2 phase, curve *2*, to the samples prepared by impregnation (samples 6.96W-i,17.4W-i, and 24W-i), and curve *3*, to the sample prepared by coprecipitation (sample 7W-c). All these spectra are quite similar to each other even at high tungsten content. Calcination of the samples at 350°C leads to a shift of the edge of the basic absorbance toward lower frequencies and to the appearance of a new absorption band at 23000 cm^{-1} with an intensity depending on both the preparation conditions and tungsten concentration (Fig. 6, curves *2–4* correspond to the samples prepared by impregnation, curve *5*, to the sample prepared by coprecipitation).

The appearance of a similar absorption band has been observed earlier in [9] in studying the influence of the preparation procedure on the formation of the crystal structure of pure TiO_2. It was found that in several cases an additional absorption band at 23000 cm^{-1} is observed in the spectral region corresponding to the band gap of TiO_2. The intensity of this absorption band depends on the preparation conditions, and the growth of its intensity is accompanied by a progressive shift of the edge of the basic absorbance toward lower frequencies. Both the intensity and the shift reach their maximum values when $TiCl_3$ is used as a starting compound. Characterization of this sample using high-resolution electron microscopy reveals the presence of extended defects (ordered shear structures) in the structure of the resulting TiO_2 [9]. The nonhomogeneity of this sample is probably connected with the presence of significant amounts of admixed Ti^{3+} ions leading to the formation of so-called Wadsley's defects. In this case, the absence of oxygen in the framework is compensated by the change in the way in which the oxygen polyhedrons are connected to each other without significant changes in the coordination of the cation with the formation of the ordered shear structures [12].

It is known that the crystallization of TiO_2 is followed by the formation of regular and disordered Wadsley's defects. The extent of ordering of such defects depends on the concentration of Ti^{3+}. The shear ordered structures are only observed for samples that are characterized by the maximum values of the shift of the basic absorbance and the intensity of the absorption band at 23000 cm^{-1}. Therefore, these parameters can be

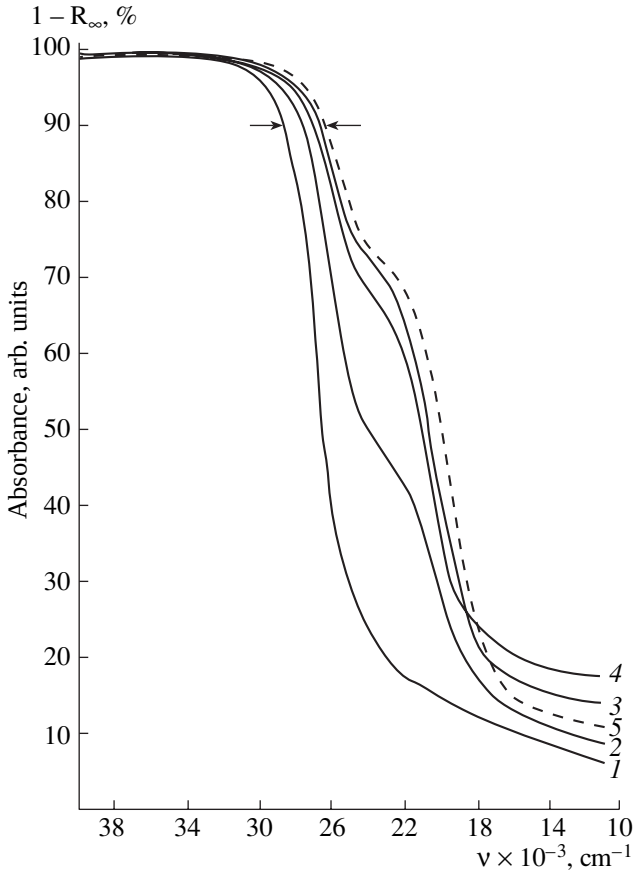

Fig. 7. Diffuse-reflectance UV–visible spectra of (*1*) TiO_2, (*2*) 6.96W-i, (*3*) 24W-i, (*4*) 17.4W-i, (*5*) 7W-c. Samples were dried at 110°C for 4 h and then calcined at 350 and 450°C.

used to estimate the regularity of Wadsley's defects. Obviously, the higher the intensity of the edge of basic absorbance at 23000 cm^{-1} and the greater the shift of the absorption band, the greater the regularity of the defects.

Diffuse-reflectance UV–visible spectra of TiO_2 containing tungsten and the spectrum observed for TiO_2 prepared from $TiCl_3$, i.e., for the sample in which the formation of the ordered shear structures [9] takes place, are quite similar to each other. This fact indicates the formation of ordered shear structures in the case of W-containing samples. The maximum values of the shift of the basic absorbance and the intensity of the absorption band at 23000 cm^{-1} are observed for samples 17.4W-i and 7W-c (Fig. 6, curves *3* and *5*, respectively). A further increase in the calcination temperature up to 450–500°C (Fig. 7) leads to some decrease in the intensity of the absorption band at 23000 cm^{-1} in the spectra of sample 6.96W-i (Fig. 7, curve *2*) and to a slight growth of its intensity in the spectra of sample 24W-i (Fig. 7, curve *3*). These changes could be connected with a partial annealing of the defects in the case of sample 6.96W-i and their further ordering in the case of sample 24W-i. Taking into account these results, it could be claimed that the samples with a high tungsten content prepared by impregnation and the samples with a low tungsten content prepared by coprecipitation reveal the highest extent of regularity of Wadsley's defects. Thus, the samples with the same tungsten content prepared by different methods (samples 6.96W-i and 7W-c) contain different amounts of defects.

According to the results of XRD analysis, no bulk WO_3 phase was observed for the system W–Ti–O even at a high tungsten concentration (24 wt %). The results of physicochemical characterization of W–Ti–O catalysts are summarized in Table 1. Modification of TiO_2 with W^{6+} ions leads to considerable changes in the TiO_2 unit cell parameters, especially at high tungsten contents (sample 24W-i). In this case, the increase in the parameters *a* and *c* can be accounted for by an increase in the concentration of tungsten ions in the lattice of TiO_2. This may be one of the reasons behind the absence of the bulk WO_3 phase at the surface of TiO_2 even at rather high concentrations of tungsten.

DISCUSSION

The results obtained for V–Ti–O and W–Ti–O systems indicate that the method of their preparation influences the state of vanadium and tungsten, on the one hand, and the structure of TiO_2 on the other hand. This effect may be explained by the peculiarities of these oxides, with their properties being determined by their own and admixed defects. The ability of transition metals to change their valence state, the high mobility of oxygen in the oxides of transition metals, and the presence of diverse admixed centers are responsible for such a variety of defects that they create discrete electron levels in the band gap and substantially influence the physicochemical properties of the resulting systems. Therefore, it is expected that different preparation conditions would dramatically affect the properties of such compounds.

In the case of the catalysts prepared by coprecipitation, the hydrolysis process is often complicated by the occurrence of polymerization and complex formation processes in the solution. This leads to the micrononhomogeneity of the precursor solution. Upon coprecipitation, the disorder in the starting solution causes the formation of defects in the solids.

The pH values of hydroxide precipitation for coprecipitation method are considerably different for various hydroxides, and the colloid particles of hydroxide having the lowest value of precipitation pH are formed first. These colloid particles capture some amount of hydroxide with a higher value of precipitation pH. Only with a further increase in pH does complete precipitation of this hydroxide take place. The resulting hydrogel often represents a conglomerate of particles with a radially nonuniform composition. The inner part of the particle contains predominantly hydroxide with a low

precipitation pH, while the outer surface of the particle is enriched by the element with a high precipitation pH [13, 15].

Taking into account the results of diffuse-reflectance UV–visible and IR spectroscopy, as well as the above reasoning, it is possible to deduce that the coprecipitation of vanadium and titanium should proceed from the precipitation of titanium hydroxide particles with adsorbed vanadium hydroxide to the formation of a solid solution at the surface of titanium hydroxide. It should be noted that the size of such particles is rather small (50–70 Å), and the definitions of surface and volume of the particle are quite different in this case and for big particles, because for very small particles the number of surface and bulk atoms may differ 10–100 times.

In the preparation of V–Ti–O catalysts by impregnation, the formation of a solid solution of vanadium ions in titanium dioxide occurs mostly at the stage of the calcination. Nevertheless, according to the results of electron spectroscopy, the state of vanadium in the final catalysts prepared by impregnation is quite similar to that in the catalysts prepared by coprecipitation. The main difference is observed in the intensities of absorbance in the region of 30000–11000 cm^{-1} attributed to V^{4+} ions and vanadium species chemically bonded to the TiO_2 surface. In the case of the catalysts prepared by coprecipitation, the intensities of these absorption bands are higher. The difference between the spectra of the samples prepared by different techniques is probably related with the higher concentration of V^{5+} ions in the lattice of TiO_2 in the case of the samples prepared by impregnation. The charge transfer bands corresponding to the lattice V^{5+} ions overlap with the TiO_2 absorption and, thus, cannot be taken into account [11].

The pattern is quite different in the case of W–Ti–O catalysts. The absence of the absorption bands originated from the interaction between tungsten and titanium hydroxides in the dried samples, if any interaction takes place at all, is probably the result of the amorphous state of hydroxides. The additional absorption band at 23000 cm^{-1} and the shift of the edge of the basic absorbance toward lower frequencies is observed only in the case of calcined samples. The absorption band at 23000 cm^{-1} appears upon crystallization of the samples and, therefore, can be assigned to the absorption by the defects in the lattice of TiO_2. It can be anticipated that coprecipitation of tungsten and titanium salts leads to the formation of a composite hydroxide with definitely alternating titanium and tungsten ions. The high intensity of the absorption band at 23000 cm^{-1} and the significant value of the shift of the edge of the basic absorbance for sample 7W-c indicate the nonhomogeneity of this sample and the formation of ordered shear structures even at low tungsten concentrations. Taking into account the complexity of the processes occurring in the solution during the coprecipitation procedure, the degree of the nonhomogeneity of the sample would be dramatically dependent on the preparation conditions.

Physicochemical properties of V–Ti–O and W–Ti–O systems

Sample*	V_2O_5, wt %	WO_3, wt %	$T_{calcination}$, °C	Cell parameters, Å		Coherent scattering region, Å
				a	*c*	
2V-i	2.0	–	450	–	–	–
2V-c	2.0	–	450	–	–	–
TiO_2	–	–	350	3.7936	9.39	70
6.96 W-i	–	6.96	350	3.801	9.54	60
17.4 W-i	–	17.4	350	3.807	9.504	50
24 W-i	–	24.0	350	3.821	9.534	50
7 W-c	–	7.0	450	3.794	9.565	85

* i stands for impregnation, c stands for coprecipitation.

In the case of the W–Ti–O catalysts prepared by impregnation, the noticeable nonhomogeneity of the samples is observed only for the samples with rather high tungsten contents (17–24 wt %).

On the other hand, the nonhomogeneity of the W–Ti–O sample prepared by coprecipitation and characterized by the low tungsten concentration (7 wt %) indicates that the formation of defects of different types in the lattice of TiO_2 depends to a large extent on the distribution of tungsten across the particle. The higher homogeneity of the samples prepared by impregnation can be probably explained by the quite different localization of tungsten ions in the lattice of TiO_2. This leads to different types of excessive positive charge compensation such as formation of Ti^{3+} ions or cation vacancies.

Thus, the results of this work can be summarized as follows. In the case of V–T–O catalysts, the preparation procedure does not significantly influence the state of vanadium and titanium (except for the grafted samples), while in the case of W–Ti–O catalysts the preparation technique strongly affects the state of W and Ti in the resulting catalysts. This is probably the most important reason for the dependence of the catalytic and physicochemical properties of three-component V–W–Ti–O systems on the preparation conditions. The results of the study of such three-component catalysts will be presented in the next communication.

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