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An EPR Study of the Surface Chemistry of the V_2O_5–WO_3/TiO_2 Catalyst: Redox Behaviour and State of V(IV)

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A series of catalysts built up by V_2O_5 and WO_3 overlayers on TiO_2 anatase which have shown remarkable activity and selectivity in the selective catalytic reduction (SCR) of nitric oxide have been investigated by electron paramagnetic resonance spectroscopy. All the systems exhibit spectra due to the presence of both isolated and magnetically interacting V(IV) ions whose amount has been monitored as a function of the temperature of progressively reducing vacuum treatments. By comparison with binary systems (V_2O_5/TiO_2 and WO_3/TiO_2) evidence has been provided for the structural features of V(IV) ions isolated at the surface of the ternary systems. Although the two supported phases mainly interact with the TiO_2 matrix, the present investigation reveals the existence of a mutual (structural and electronic) interaction between the two supported bidimensional phases which determines the special redox properties of the ternary systems. These properties are remarkably different from that of V_2O_5/TiO_2 systems and can contribute to an understanding of the catalytic behaviour of the V_2O_5–WO_3/TiO_2 systems in the SCR reaction. © 1997 Academic Press

INTRODUCTION

Heterogeneous catalysts consisting of a mixed overlayer of vanadium and tungsten oxides on a TiO_2 support are active in the selective reduction of nitrogen oxides by ammonia (de-NO_x reaction) (1, 2). They are closely related to the well known vanadia/titania binary systems widely used in the selective oxidation of hydrocarbons but which are also active in the de-NO_x reaction. It is generally believed that the inclusion of tungsten oxide in the commercial catalysts is due to the special role of this latter component in the stabilization of the catalyst and in quenching the oxidation of SO_2 (usually present in nitrogen oxides containing emissions) to SO_3 (3).

Despite an apparent simplicity, the binary vanadia/titania is a complex system, as witnessed by the large number of experimental studies directed at obtaining a satisfactory characterisation of the surface and of the active sites (4–6). The complexity of the system is enhanced if tungsten oxide is added to vanadia in the TiO_2 overlayer. It is usually accepted that in vanadia/titania both monomeric and polymeric vanadium oxide species (vanadates and polyvanadates) are present on the surface (4). The first type prevails at low coverage of the TiO_2 surface. The second type (polyvanadates) prevails when the active phase coverage is near the monolayer. For loadings of the active phase beyond the monolayer, crystallites of V_2O_5 are also formed (5, 6). An analogous situation has been described for WO_3/TiO_2 systems (7) (monomeric and polymeric tungstates). By comparison, the ternary systems have been studied much less (8).

The electron paramagnetic resonance (EPR) technique has often been employed to investigate the V_2O_5/TiO_2 system (9–11). The application of the technique to vanadia/titania is limited in practice to the detection of the spectra due to V(IV) ions; however, it provides a detailed description both of the nature of the species (V^{4+} or VO^{2+}, for instance) and of their coordination which proves extremely useful for a deep understanding of the whole system. The values reported for the spectral parameters (the spin-Hamiltonian parameters) of V(IV) on TiO_2 are rather spread. This is certainly due to the complexity of the system (heterogeneity of the surface with simultaneous presence of several species of V(IV)) but also, in same cases, to a poor accurancy in deriving the parameters from the experimental spectra. The EPR spectra of V(IV) in fact are complicated by the high number of hyperfine levels (the levels generated by the interaction of the unpaired electron with the $I = 7/2$ ^{51}V nucleus) and by the second order effects that tend to produce an asymmetric hyperfine structure with unequal separation of the various lines (12). In this situation the use of computer simulation to correctly derive the parameters from the experimental spectra is needed but has been seldom used (as far as V(IV)/TiO_2 is concerned) in the past.

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Concerning the presence of V(IV) ions at the surface of V_2O_5/TiO_2 catalysts, different opinions appear in the literature: some authors indicate that the V(IV) state is preferentially formed in the first overlayer over TiO_2 (13, 14), whereas other authors indicate that nearly all vanadium centres are in the form of V(V) and that V(IV) constitutes a very minor and insignificant fraction of the surface active sites in catalytic conditions (15). Also in this case it has to be noted that a systematic evaluation of the amount of V(IV) (via EPR) in the vanadia/titania systems has never been attempted in the past, essentially because the derivation of quantitative results by EPR is not straightforward. Only recently have detailed reports on the applications of quantitative EPR to catalyst characterisation appeared in the literature (16).

Whatever the amount of V(IV) actually present at the solid–solid interface, it should be kept in mind that the oxidation number, the coordination, and the structural properties of surface vanadium ions in V_2O_5/TiO_2 mixed oxides depend, in principle, on several factors, namely:

(a) the amount of the vanadia phase on the support and the surface area of the support;

(b) the nature of the TiO_2 support phase: anatase, rutile, or brookite;

(c) the method adopted for the preparation of the system (impregnation, anchoring, or solid state reaction between TiO_2 and V_2O_5) (Evidence of abundant V(IV) content at the TiO_2 interface has been reported, for instance, in the case of samples prepared by direct reaction at high temperature of the two oxides (6) which is, in terms of physico-chemical conditions, a method very different from the classic and more widely employed impregnation of the support); and

(d) the nature of the chemical and thermal treatments undergone by the catalyst after preparation.

It will be shown in the following that the presence of the second supported WO_x phase, in the ternary system, also influences the state and the abundance of V(IV) at the surface.

The present paper reports an EPR investigation on the redox behaviour of a series of ternary V_2O_5–WO_3/TiO_2 systems containing a fixed amount of WO_3 and a variable V_2O_5 loading. A first general characterisation of the system was reported in Ref. (8). In the present work attention is mainly devoted to the state of V(IV) and to the changes produced in the spectra by various thermal treatments in vacuo aimed at obtaining solids whose features (in terms of both surface hydration and redox state) are as close as possible to those of the working catalyst. An evaluation by EPR of the amount of V(IV) in the various stages of the thermal treatments is also performed.

To correctly understand the special features of the ternary samples the various thermal redox treatments have also been carried out on the pure TiO_2 matrix and on binary WO_3/TiO_2 and V_2O_5/TiO_2 reference samples having a content of the supported oxide corresponding to that of the ternary systems and prepared according to the same procedure.

EXPERIMENTAL

The various samples employed in the present work will be labelled by letters indicating the oxidic phases present in the sample (TWV indicating the ternary samples, TV, TW, and WV the binary ones) and with the loading of the vanadia phase expressed as V_2O_5 weight percent (wt%). All the investigated ternary samples have a fixed WO_3 weight percentage (9%) and a V_2O_5 percentage varying between 0.3 and 1.4%. Accordingly, their composition is quite close to that adopted for commercial SCR catalysts. Titanium dioxide (anatase phase) was first impregnated with an aqueous solution of ammonium paratungstate and then calcined at 873 K. The WO_3/TiO_2 (TW) samples thus obtained or the bare TiO_2 were impregnated with a solution of ammonium metavanadate and oxalic acid, then dried and calcined at 873 K to obtain the TWV samples and the TV binary samples respectively. The samples obtained by this procedure are indicated with a C (for calcined). Other samples underwent a final reducing treatment at 423 K under vacuum and will be hereafter labelled with R (for reduced). A third type of solid (the binary vanadium pentoxide/tungsten oxide system, 1.4% in V_2O_5, labelled VW) was also investigated and was prepared as follows. A solution of oxalic acid and ammonium metavanadate was mixed with ammonium paratungstate and citric acid. After evaporation of the solvent the solid component was dried and calcined at 773 K under O_2 for 3 h.

More details on the sample preparation and on the morphological characterisation of the samples are reported in Ref. (8). The support coverage of the various ternary samples varies from 0.6 to 0.8 of a theoretical monolayer.

The samples employed for EPR investigations were transferred into a vacuum cell holding an EPR tube and analysed after thermal treatments in vacuo at various temperatures or after gas adsorption. EPR spectra were recorded by a Varian E-109 spectrometer equipped with a dual cavity and connected to a personal computer for data handling and elaboration. Several spectra for all types of sample were recorded both at room temperature and at 77 K. No qualitative difference in the spectral profile was observed by comparing the spectra at these two temperatures. The experimental spectra were simulated by a version of the SIM14S program (from QCPE) adapted for personal computers.

Quantitative estimation of V(IV) was performed by comparing the spectral intensity at 77 K of each sample (which is the result of a double integration of the experimental first derivative spectrum) with a calibration curve obtained by recording the spectral intensity at 77 K of several frozen aqueous solutions of $VOSO_4 \cdot 5\,H_2O$ as a function of the V(IV) content. In the range of concentration adopted (which was related to the possible V(IV) content of our samples) the calibration was linear.

RESULTS

1. *EPR Spectra of Samples in Various Redox States*

All ternary TWV samples exhibit after the final calcination in air (C-samples) an EPR spectrum due to V(IV). Tetravalent vanadium is a $S = 1/2$ system (the electronic configuration of the ion is $3d^1$) which displays a quite complex electron resonance spectrum. This is due, first of all, to the high number of hyperfine lines arising from the interaction of the unpaired electron with the ^{51}V nucleus (nuclear spin = 7/2, natural abundance close to 100%) and, second, to the anisotropy of both g and A tensors leading to a complex overlap of different spectral lines. An example of the spectra is shown in Fig. 1a for the TWV1.4 (C) sample. A similar, but more intense, spectrum is shown by the corresponding (R) sample which underwent the reducing treatment. The spectrum in Fig. 1a is representative of the ternary samples even though, on a large number of samples analysed in the present work, some differences in the profile were found from one spectrum to another, mainly due to the different relative amounts of the various species combining to determine the spectral shape.

The occurrence of V(IV) in an oxidized material such as the calcined samples is typical of ternary samples. The V(IV) EPR spectrum shows a negligible intensity or is not observed at all in the case of the corresponding binary reference TV samples after calcination.

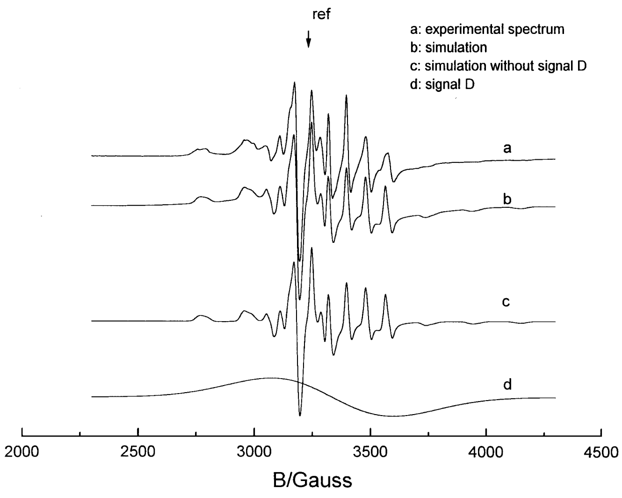


FIG. 1. EPR spectra of TWV1.4 outgassed at 298 K. The experimental spectrum has been recorded at 298 K.

TABLE 1

Spin Hamiltonian Parameters and Abundances of the Various V(IV) Species as Derived by Computer Simulation of the Spectra

Oxide	Species	Nature	Abund. (%)	$g_{\parallel}$	$g_{\perp}$	g_{iso}	$A_{\parallel}$	$A_{\perp}$	A_{iso}
TWV	A	isolated	7.0	1.9124	1.9824	1.96	198.8	74.1	115.7
	B	isolated	7.0	1.9147	1.9831	1.96	193.2	69.9	111.0
	C	isolated	13	1.8967	1.9778	1.95	195.7	69.2	111.4
	D	interact.	73*			1.981	—	—	unres.
TV	E	isolated	30	1.940	1.97	1.96	172	52	92.05
	F*	interact.	70*			1.981	—	—	unres.
VW	G	isolated	23	1.89	1.96	1.94	178	52	94
	H	isolated	7	1.83	1.94	1.91	178	52	94
	I	interact.	70	—	—	1.93	—	—	—

* Due to the large linewidth of signals D and F this figure represents only a rough indication of the abundance of the species. For further details and explanation see the text of the Results section.

The experimental spectral profile in Fig. 1a has been reproduced by computer simulation (Fig. 1b) in terms of the contribution of four distinct V(IV) signals (Table 1). One of them (labelled species D in Table 1 and also reported in Fig. 1d) is due to interacting V(IV) centres whose (magnetic) interaction is large enough to smear out the hyperfine structure and to give rise to a broad line (500 gauss linewidth, 1 gauss = 0.1 mtesla). The abundance of the interacting species introduced in the parameter set of the computer simulation is about 70% of the total tetravalent vanadium (Table 1). Such a high value, which at first sight could appear surprising, is basically due to the large linewidh of the signal. In this type of symmetric signal the intensity (which results from the double integration of the first derivative signal) is in fact roughly proportional to the amplitude multiplied by the *square* of the linewidth. To show the full effect of the D signal on the simulation (Fig. 1b), the latter has to be compared with the profile in Fig. 1c which has been derived by eliminating the contribution of species D to the simulation. The effect of the broad line related in interacting D species is that of reproducing the rising trend of the baseline at the wings of the spectrum. One should therefore pay attention to taking the abundance of species D introduced in the simulation as a true measure of the percentage of the interacting V(IV) since very similar effects on the profile of the spectrum could also be obtained using quite different values of linewidth and abundance of the species D. For the same reason an evaluation by means of an EPR spectra simulation of the amount of interacting species present in the various TWV and TV samples is meaningless.

The resolved signals are three and correspond to three relatively isolated species that represent about 30% of the total V(IV). Two of them (species A and B in Table 1) have spin-Hamiltonian parameters very close to one another.

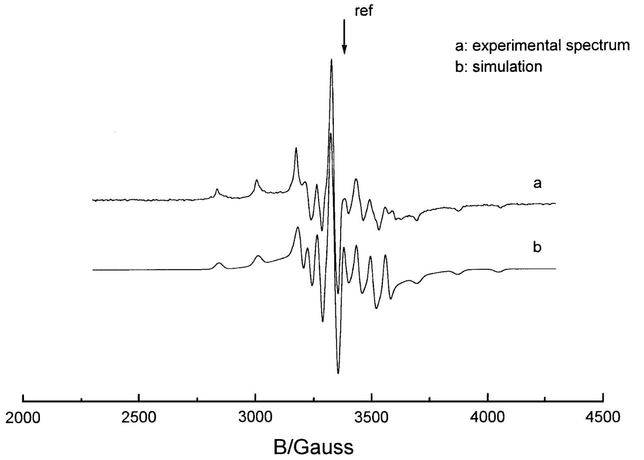


FIG. 2. Experimental and computer simulated spectra of TV1.4 outgassed at 423 K. The experimental spectrum has been recorded at 298 K.

The species labelled C in Table 1 is the most abundant isolated species. The three isolated species (A, B, C) are characterized by a relatively high value of the hyperfine constant, the $A_\parallel$ value ranging between 193 and 198 Gauss.

The calcined TV binary samples either do not exhibit an EPR spectrum or, in some cases, have an extremely weak EPR line. Only after an annealing treatment at $T = 423$ K for 1 h does an EPR spectrum due to V(IV) show up. The spectrum observed in these conditions in the case of a TV1.4 binary calcined sample is reported in Fig. 2a together with its computer simulation (Fig. 2b). It should be noted that also in the case of binary TV samples the analysis of a large number of experimental results indicates a certain variability in the spectral shape which can be explained, as before, in terms of different abundances of the various species. The imperfect reproducibility of the EPR spectra of samples having the same composition is related to the sample history (in particular to the age of the sample and to the degree of surface contamination by atmospheric agents) and to small random variations in the preparation procedure. In the case of some binary TV samples, traces of the species A, B, and C, typical of ternary samples, are also observed. The spin-Hamiltonian parameters used to simulate the spectrum in Fig. 2 are reported in Table 1. Also in this case the isolated vanadium ions (species E) are around 30% of the whole amount of V(IV) but the parameters of the isolated species are different from those observed for ternary samples, and in particular, the $A_\parallel$ value is lower (172 G).

The spectrum of TWV samples is slightly modified by interaction at room temperature with diamagnetic basic molecules such as ammonia and water. The effect of adsorption is basically a reversible modification of the relative intensities of the various components. This indicates that at least a fraction of the surface vanadium (IV) ions exhibits a coordinative unsaturation that enables the ion to interact with the basic donor molecules. A similar effect (which concerns isolated V(IV) species visible in the EPR) has not been observed in the case of TV samples even though this does not allow one to exclude the existence of interactions between ammonia and other components of the vanadia phase. FT-IR measurements have in fact provided evidence for perturbations on the V=O stretching bands upon interaction with NH_3 for both TWV and TV samples (8).

For the sake of completeness the EPR spectra of binary VW samples have also been recorded. Tetravalent vanadium tends to diffuse into the bulk of WO_3, giving rise to the EPR spectrum reported, with the corresponding simulation, in Fig. 3. Two distinct species of isolated V(IV) are easily distinguished in the spectrum and their parameters are also reported in Table 1 (species G and H). A signal due to interacting V(IV) species is also present (signal I in Table 1), having a linewidth of about 300 G. The parameters of VW spectra are unambiguously different from those of samples supported on TiO_2. In particular, the g values are markedly lower than those recorded for isolated species in TWV and TV samples (see Table 1).

The calcined TWV and TV samples have been submitted to successive thermovacuum treatments to follow the behaviour of the V(IV) EPR signal intensity as a function of the temperature in the range 298–620 K. Analogously to the situation reported above concerning the spectral shape, these quantitative results also are not totally reproducible in that they are highly sensitive to the initial state of the material which, in its turn, depends on the age of the sample and on its degree of surface contamination by atmospheric agents. In particular, the time elapsed between the calcination and the thermal treatment in vacuo plays a basic role in determining the amount of V(IV) detected in the first run of the treatment. Work is in progress in our laboratories to

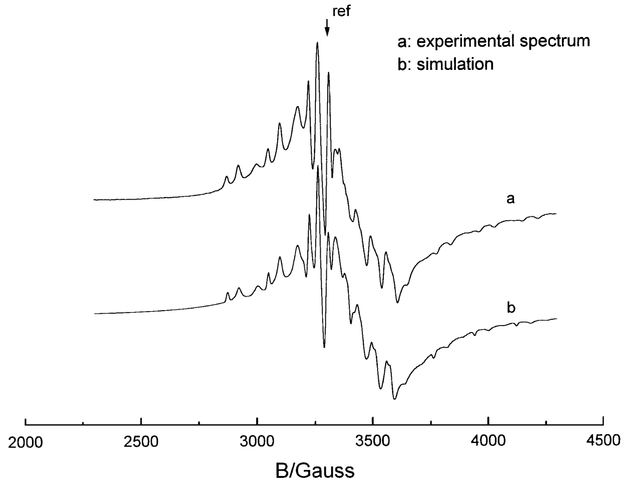


FIG. 3. Experimental and computer simulated spectra of a VW reference sample (containing 1.4% V_2O_5) outgassed at 298 K. The experimental spectrum has been recorded at 298 K.

clarify this point. Despite these facts, however, some data emerge clearly from the quantitative analysis and can be summarised as follows:

(i) The initial amount of V(IV) in calcined samples (recorded after removing the atmosphere from the EPR tube at room temperature) is always much higher for ternary TWV samples than for the corresponding binary TV ones for which, in some instances, no EPR spectrum at all is observed. The amount of tetravalent vanadium initially present on the calcined TWV samples is small but nonnegligible in that it ranges (according to the sample) between 2 and 8% of the total vanadium (vide infra).

(ii) The EPR intensity increases with increasing evacuation temperature and reaches a maximum around 423 K. Figure 4 reports the V(IV) amount (in terms of fraction of the total vanadium) for three typical ternary samples having different vanadia loadings. On binary TV samples the described signal appears upon annealing at temperature higher than room temperature. The maximum intensity (which remains lower than that observed on the corresponding TVW sample) is also attained at 423 K.

(iii) The fraction of V(IV) is higher for those samples having a lower vanadium loading. As shown in Fig. 4, the quantitative analysis of the EPR spectra indicates that for same samples, upon dehydration in mild conditions, the fraction of V(IV) attains the remarkable value of 20–25% of the total vanadium.

(iv) The EPR signal of V(IV) decreases upon annealing at $T > 423$ K. Since in such experimental conditions the hypothesis of mobility of the surface anchored species to form diamagnetic aggregates can be discarded, the decrease of the V(IV) signal intensity has to be assigned to a further reduction of the system with a possible formation of V(III) centres. No information about the redox state of the tungsten oxide phase can be derived from the present data except that no paramagnetic W(V) seems to be present at the surface.

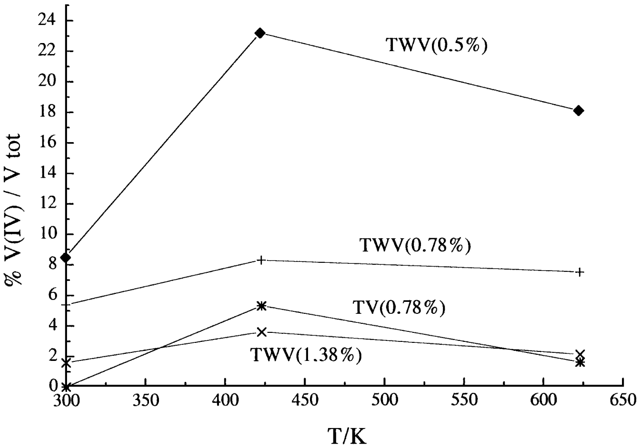


FIG. 4. Intensity of the V(IV) signal for various ternary TWV and binary TV samples as a function of the temperature of the thermovacuum treatment.

Reoxidation of the ternary samples in O_2 atmosphere at 623 K causes a change in the colour of the reduced grey samples such that they recover their original yellow-brown colour. The signal of V(IV), initially present on the calcined samples, is however not restored, indicating that the reoxidation probably leads to the formation of a complete V(V) surface layer. It should be noted that the result of reoxidation with pure oxygen in the vacuum manifold could be different from that of calcination in air, which is the last step of the preparation procedure. A second annealing treatment after reoxidation gives a different result in comparison with the first one since the V(IV) amount remains, at all temperatures, lower than that observed by outgassing the calcined samples and reported in Fig. 4.

To check whether the described effect is due to a different hydration degree of the two solids (the reductive annealing treatment of the as-prepared samples also brings about a loss of surface water which is, of course, not restored upon reoxidation in O_2), a sample was rehydrated by contact for few seconds with water vapour at room temperature after reoxidation and before the second treatment of annealing in vacuo. No variation, however, was observed between the two types of reoxidised sample, both being more reluctant to reduce to V(IV) than the fresh samples.

All the ternary samples and the reference samples have also been submitted to a more drastic reducing treatment consisting of outgassing at 823 K for 1 h. The effects of the reduction on pure TiO_2 (an *n*-type semiconductor) are well known and have already been described since they consist in a net enrichment of the amount of electrons present in the conduction band (CB) of the oxide involving, inter alia, the appearance of a grey colour and a dramatic decrease of the transmission in the infrared spectrum of the reduced material. The effect is observed by EPR in terms of a net decrease of the quality factor of the cavity that causes the practical impossibility of tuning the system and therefore of recording any spectrum. This situation (which, for the sake of clarity, is totally different from the absence of an EPR signal) is a kind of fingerprint of the reduction of the whole sample with a consequent increase of the electron population in the conduction band. The same effect shown by TiO_2 was also observed in the case of TW (9% WO_3) and in that of TWV0.3 and TWV1.0, whereas it was not observed for *all* TV samples and for TWV with V_2O_5 loading higher than 1% (TWV1.4). For these latter types of sample the EPR spectrum exhibits a signal due to V(IV) whose intensity is, however, slightly lower than that of the spectra recorded after annealing at 423 K.

2. *Interaction of Deeply Reduced Samples with O_2*

When the TiO_2 sample reduced by outgassing at 823 K is contacted with oxygen at room temperature, the grey

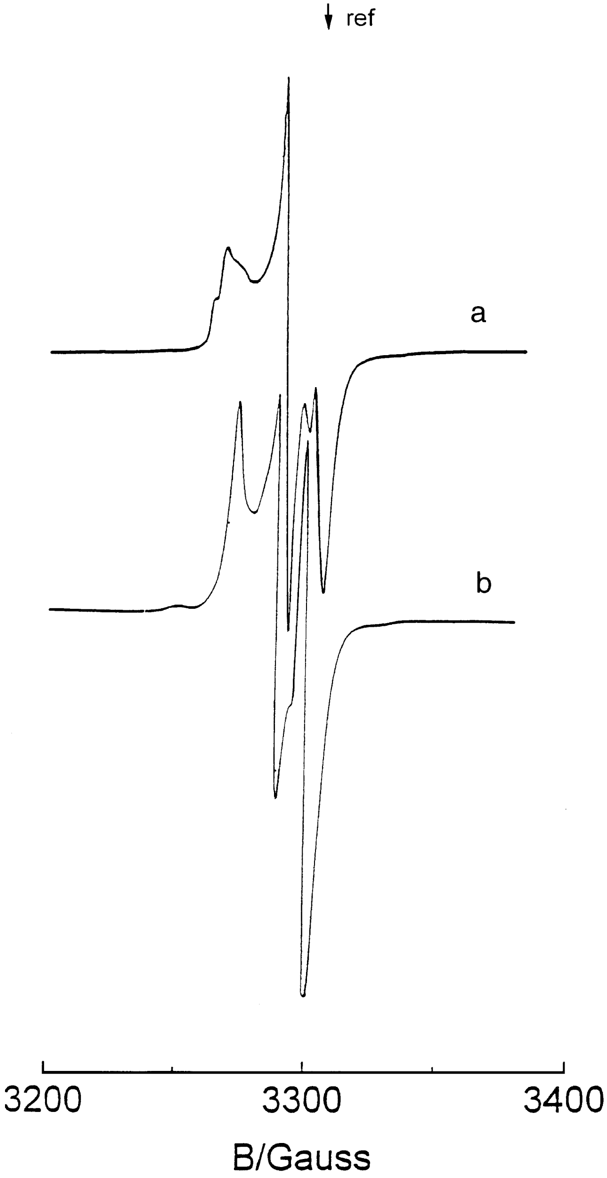


FIG. 5. EPR spectra (recorded at 77 K) of superoxide radical ions at the surface of (a) previously reduced TiO_2, and (b) previously reduced WO_3/TiO_2.

colour immediately vanishes and the solid no longer perturbs the quality factor of the EPR cavity. In such conditions the sample exhibits an EPR spectrum (Fig. 5a) which is easily assigned to surface adsorbed O_2^- ions stabilized on Ti^{4+} cations at the solid surface and is strictly similar to those previously reported in the literature (17).

The spectrum of the surface O_2^- ions is characterized by anisotropy of the g tensor with $g_{zz} > g_{yy} > g_{xx}$. The g_{zz} resonance is the most sensitive to the nature and charge of the adsorption site (18); in the present case the main g_{zz} value is at 2.023 with minor contributions (shoulders) at 2.027 and 2.020. Also, the binary TW sample reduced in the same way reacts with oxygen at room temperature, leading to the EPR spectrum in Fig. 5b whose features are different from those of the spectrum in Fig. 5a: in particular, in the g_{zz} region only one sharp component is present at $g_{zz} = 2.019$ and it should be noted that the height of this component with respect to the central ones (g_{yy} and g_{xx}) is higher than in the previous case.

Although the g_{zz} values observed in Figs. 5a and 5b are quite close, it seems very reasonable to indicate that O_2^- in the second case (Fig. 5b) is not stabilized on the same Ti^{4+} sites as those available on bare TiO_2 but is stabilized, very probably, on W^{6+} ions of the tungsten oxide overlayer (vide infra). The g_{zz} value is in fact in agreement with that reported by Howe for superoxide ions on WO_3/SiO_2 (19).

The ternary TWV samples with lower vanadia loading (0.3 and 1.0% V_2O_5, respectively), which are deeply reduced by thermal treatment at 823 K, are not able to transfer electrons to adsorbed oxygen at room temperature (RT). However, after reoxidation in an O_2 atmosphere at 623 K, a weak O_2^- signal is observed. This superoxide species is similar to that in Fig. 5b ($g_{zz} = 2.019$) and should be again assigned to O_2^- on tungsten ions. An O_2^- molecule adsorbed on a vanadium ions must, in fact, exhibit a superhyperfine structure due to the interaction of the unpaired electron with the ^{51}V nucleus. This interaction has been previously observed for O_2^- on V_2O_5/SiO_2 (20).

Finally, those samples whose electron population in the CB is not affected by vacuum treatment at 823 K (TV samples and TWV samples with more than 1% V_2O_5 by weight) do not form superoxide ions upon contact with oxygen at RT and at 623 K.

DISCUSSION

(a) *Nature of the Surface Vanadium Species*

As mentioned in the Introduction, a careful simulation of the spectra is very useful for extracting reliable spin-Hamiltonian parameters from complex spectra of heterogeneous systems such as those reported in the present work. Hence the values reported in Table 1, due to the goodness of the fit (Fig. 1), can be considered quite reliable and can be confidently compared with those of well defined molecular complexes or with those of systems in the solid state determined with similar accuracy. The V(IV) species observed in systems containing V_2O_5 anchored on TiO_2 (TV and TVW samples) exhibit, despite the differences between the various spin-Hamiltonian parameters, a clear vanadyl character. This means that one of the vanadium–oxygen bonds is particularly short and can be described in terms of a double V=O bond. All the isolated species observed on TWV (A, B, and C) and TV (E) samples are characterised by average values of g and A principal components ($g_{iso} = (g_{\parallel} + 2g_{\perp})/3$; $A_{iso} = (A_{\parallel} + 2A_{\perp})/3$) which, if reported in the (A_{iso} vs g_{iso}) empirical correlation diagram proposed by Davidson and Che (21), fall in the region of vanadyl species. This diagram

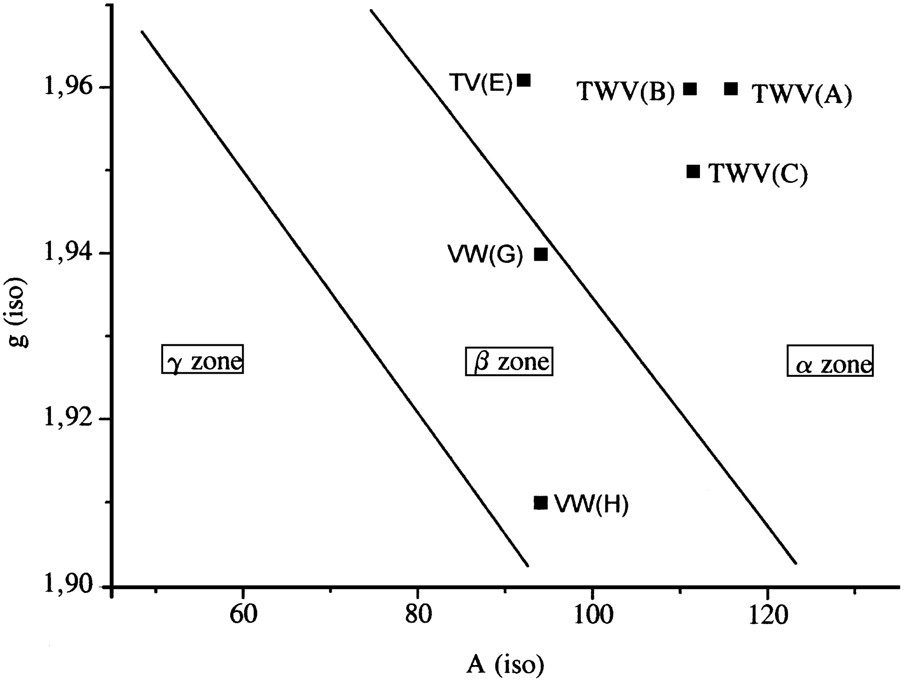
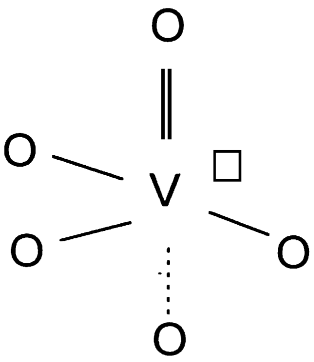


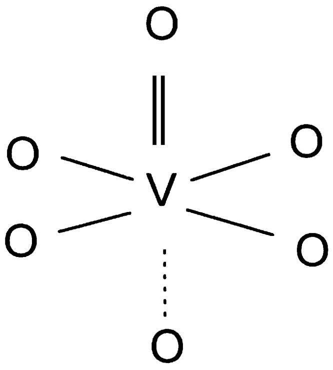
FIG. 6. Correlation diagram (g_{iso} vs a_{iso}) for the various isolated V(IV) species present on TWV, TV, and VW samples.

(21) has been derived on the basis of the analysis of a long series of well defined molecular vanadyl complexes. The frame of the diagram is reported in Fig. 6. The lines defining the α, β, and γ zones are the same as those of the original diagram and the experimental points correspond to the isolated V(IV) species in Table 1. The α zone (within which species A, B, C, and E are contained) is typical of 5-coordinated and 6-coordinated vanadyl species, whereas the β zone is typical of tetracoordinated V^{4+} ions. The first group of species (A, B, and C) observed and TVW samples correspond to surface vanadyl species slightly differing in the coordinative environment. The ability of a fraction of these species to adsorb water or ammonia suggests an assignment to a 5-coordinated vanadyl group having a distorted octahedral structure and one coordination vacancy in the equatorial plane (Scheme 1).

The lower a_{iso} value observed for the species on TV samples (species E) indicates a partial attenuation of the vanadyl character in comparison to the species on TWV. The g and A values of species E are very close to those reported for a tetravalent vanadium species in TiO_2 anatase by Gallay *et al.* (22) and assigned to interstitial V(IV). As this latter assignment is not totally unambiguous (another case of interstitial V(IV) in TiO_2 monocrystals was reported (23) as having lower A values), we hypothesize that species E is a vanadyl hexacoordinated species whose coordinative saturation is due to a deeper interaction (in comparison with A, B, and C) with the matrix (shown in Scheme 2).



SCHEME 1



SCHEME 2

The *g* and *A* values observed for WV binary systems (G, H) fall in the β region of the diagram in Fig. 6, typical of tetracoordinated V^{4+} ions. The two species are thus assigned to isolated V^{4+} ions in tetrahedral bulk sites of the WO_3 matrix. A detailed analysis of the V^{4+}–WO_3 system will be the object of a future paper; however, this result is relevant also to the present work since it indicates that, in the ternary TVW systems, the vanadyl ions interact with the titania matrix and not with a WO_3 *bulk matrix* that should not be present in the ternary samples. In other words, the WO_y surface phase dispersed on TiO_2 has different features from bulk WO_3.

The model proposed by some of us in a previous paper (8) for the ternary system (a mixed bidimensional overlayer of VO_x and WO_y oxidic phases supported on the TiO_2 surface) is confirmed by the present findings. The WO_y phase, however, plays a role in stabilizing the VO_x phase at the surface. Since ternary and binary samples have been submitted to the same thermal treatments, the above discussed difference between species A, B, C (TVW) and species E (TV) can be explained by hypothesizing some structural interaction between the tungsten oxide and the vanadia bidimensional phases; this very probably causes the formation of a polymeric mixed V–W surface bidimensional overlayer stable enough to prevent a deeper interaction (at the calcination temperature of 873 K) between the V ions and the TiO_2 matrix. This interaction on the contrary occurs in the case of the TV samples in the absence of a W overlayer leading to the formation of species E.

As far as the magnetically interacting species are concerned (species D and F in Table 1), the corresponding signal profile (Fig. 1d) does not permit an accurate evaluation of the nature of the species and of the V(IV)–V(IV) distance. The evaluation of this latter parameter on the basis of the linewidth is possible only for homogeneous systems (for instance, a solid solution) with regular spacing between the paramagnetic centers. This is not the case of a mixed supported oxide like the TWV system. It can be inferred, however, that the observed linewidth of signal D (500 G) is compatible with an average distance of 4–5 Å, a value which in its turn is compatible with that of a surface polymeric species containing V(IV) centers in vicinal position. As a basis for reference it can be recalled that crystals of $VOSO_4 \cdot 5\,H_2O$ display a symmetric unstructured signal with a linewidth of 350 G.

(b) *Redox Behaviour of the Samples*

The samples studied in the present work have been submitted to two types of outgassing–reducing treatments:

(i) weak reduction (by evacuation in the range 300–620 K)
(ii) stronger reduction (by evacuation at 823 K).

The quantitative results reported in Fig. 4 concern the former method and indicate that a non-negligible amount of V(IV) can be stabilized on TVW systems by evacuating in mild conditions. Furthermore, the presence of a tungsten oxide overlayer at the TiO_2 surface seems to favour the presence of tetravalent vanadium, as this oxidation state is more abundant in ternary samples than in binary ones. Remarkably, V(IV) is present in ternary samples that underwent the final calcination in air and is not present in the corresponding TV binary samples. Its amount increases upon pumping at 420–450 K. The origin of the reduction of vanadium ions by outgassing in mild conditions is rather puzzling as the phenomenon, easily observed in the first reduction run, is no longer observed on samples that have been reoxidized (even if in pure oxygen) and also on samples reoxidized and successively rehydrated by water adsorption. An explanation of this phenomenon is based on the presence of highly hydrated vanadium oxide and tungsten oxide species in the starting calcined catalyst exposed to ambient moisture for a certain period of time. These hydrated species, already described by Vuurman *et al.* (9), might have a particular reductive pathway during desorption of moisture, leading to an abundant formation of V(IV) which parallels the formation of the dehydrated two-dimensional overlayer occurring upon outgassing at high temperature.

The initial state of hydration of the supported oxide phases is probably not attained by readsorption of water vapour as performed in our experiments, so that simply reoxidized samples and reoxidized–rehydrated samples have in the same way upon a second thermal treatment under vacuum. A possible interpretation of the results of the second reduction run is that of a different reduction pathway being followed by the system and leading directly to V(III) formation (with stabilisation of a minor amount of V(IV)). This is suggested by the change of colour of the samples during the annealing, indicating that the sample indeed undergoes reduction in the second run also. Work is currently in progress in our laboratories in order to clarify the rôle of the hydration of the supported oxide species in the redox behaviour of the catalyst and in order to evaluate the fraction of the reduced vanadium species present at the surface under reaction condition.

The behaviour of the samples upon outgassing at high temperature (823 K) can be discussed in terms of energy levels of the various reduced states attained by the systems under investigation.

The electronic structure of titanium dioxide (anatase) is well known (24). The valence band (VB) is generated by the 2*p* oxygen orbitals while the conduction band (CB) is essentially due to the 3*d* orbitals of titanium. The energy gap is about 3.5 eV and is easily detected by UV-vis spectroscopy. Upon outgassing, anatase tends to become slightly nonstoichiometric with loss of tiny amounts of molecular oxygen. The energy of the orbitals of trivalent titanium formed in parallel with oxygen depletion lies in the band gap in close proximity to the lower limit of the conduction band and act as donor levels. The solid thus behaves as an *n*-type semiconductor. Paramagnetic Ti^{3+} can be observed by EPR at 77 K in such slightly nonstoichiometric samples. However, by increasing the degree of reduction of the solid the partially occupied *d* orbitals of the reduced titanium centers tend to overlap, causing the lower limit of the CB to shift downwards. In such conditions a non-negligible amount of electrons occupy the CB even at 77 K and the EPR spectrum, as described in the Results section, cannot be recorded for instrumental reasons. The three situations are illustrated in Figs. 7a–7c.

The samples containing a tungsten oxide overlayer on TiO_2 (TW) behave similarly to bare TiO_2. The extended surface overlayer (9% WO_3 by weight, corresponding to a surface coverage of about 0.6) does not protect the solid from a deep reduction. On the contrary, the small vanadium amount present in all TV samples (0.3–1.4%) is preferentially reduced, in the same conditions, with respect to the TiO_2 matrix. Surprisingly, the ternary TVW samples are also easily reduced if the V_2O_5 content is lower than 1% and for higher vanadia loading only (1.3–1.4%) they show the same behaviour as TV systems.

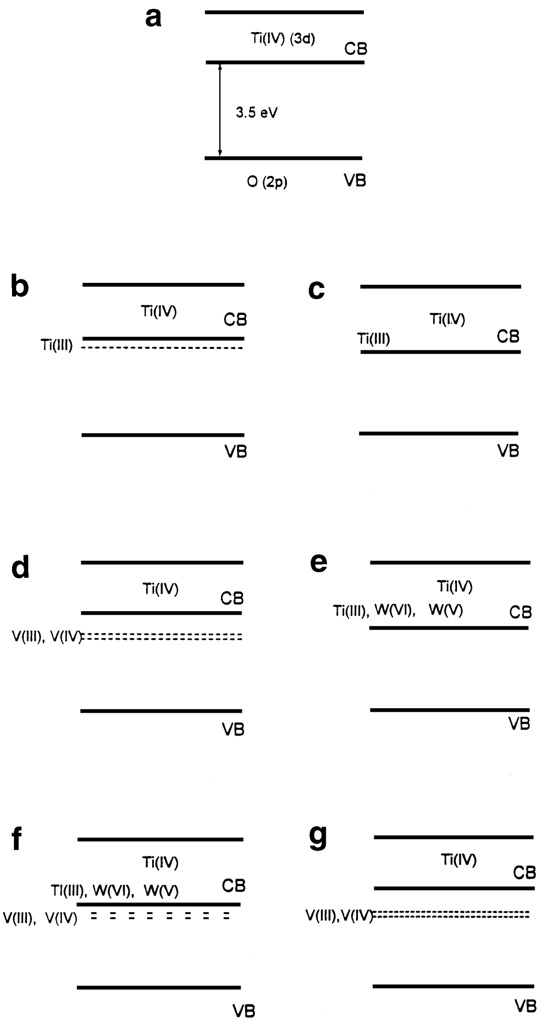


FIG. 7. Schematic representation of the energy bands and levels in the various oxide systems discussed in the text. In the cases represented in c, e, and f, the modification of the conduction band (CB) width and the presence of an electron population in the band experimentally correspond to the impossibility of recording EPR spectra (see text).

The behaviour of TV samples indicates that these solids undergo reduction following a different pathway with respect to pure titania. The *d* orbitals of V(IV) have lower energies than those of Ti(III), so they still fall in the energy gap but at values not as close to the CB limit. Consequently, the excess electrons in slightly reduced vanadia–titania are localized on vanadium and are detected by EPR as a paramagnetic tetravalent V species (Fig. 7d). Furthermore, on the basis of the trend shown in Fig. 4 (which indicates that the concentration of V(IV) centers reach a maximum upon outgassing at 423 K, i.e., well before the strongest reduction treatment undergone by the solid) a role for lower valence vanadium centers not visible in EPR (V(III) in Fig. 7d) seems very likely. When tungsten oxide species are in contact with TiO_2 in the TW samples the *d* orbitals of pentavalent tungsten species should fall at higher energy than those of V(IV) species (in TV ones) lying therefore close to (or into) the CB of TiO_2. For this reason the behaviour of the sample upon reduction is similar to that of bare TiO_2 with electrons delocalized into the CB and no W(V) species visible by EPR (Fig. 7e).

When small amounts of vanadia are also present in the solid (TWV0.3, TWV1.0), the number of suitable low lying V(IV) and V(III) centers is probably too low to trap all excess electrons, some of which, at least, still lie in the CB, causing the behaviour of the sample to be unmodified with respect to the TW samples (Fig. 7f). This is not the case for the sample with the highest vanadium loading (TWV1.4) in which the number of V centres suitable for electron trapping is enough to form EPR-active V(IV) and to prevent the increase of the electron population in the conduction band (Fig. 7g). As vanadium amounts corresponding to 0.3–1.0 wt% of V_2O_5 are, in the case of binary samples, capable of preventing the reduction of the whole solid and the increase of population in the CB, one can infer that the behaviour of the ternary sample also indicates the existence of an electron interaction between the surface vanadia and tungsten oxide phases (vide infra) which limits the electron trapping ability of a fraction of the vanadium ions.

A further comment is devoted to the reaction with O_2 at room temperature of the deeply reduced TiO_2, TW, and TVW samples. The reaction causes the reduction of O_2 to O_2^- (superoxide radical anion) because of the rapid electron transfer from the electron-rich solid to the adsorbed O_2 molecule. As is well known, the stabilisation of O_2^- occurs, for bare TiO_2, on top of surface-exposed Ti^{4+} ions

(17, 25). However, when a surface W overlayer is present (TW) the tungsten oxide species provides a preferential adsorption site. This indicates (since a fraction of free TiO_2 surface is still present on the TW samples) that the tungsten oxide species at the reduced surface has some coordinative unsaturation that allows the contact between the O_2^- ion and a positive W^{6+} centre. Furthermore, these latter centres are capable of a stronger electrostatic interaction with O_2^- in comparison with that of surface Ti^{4+} ions and thus act as preferential adsorption sites. When the presence of vanadia (TV samples and TVW with V_2O_5 loading higher than 1%) protects the TiO_2 matrix from reduction, the vanadium reduced centres are stable towards oxygen at RT and do not exhibit any propensity to reduction of O_2 to O_2^-. This observation, too, is in agreement with the description proposed in Fig. 7 since it indicates the relatively low energy of the electronic states in the band gap associated with V(IV) centers in TV and high loading TWV samples.

(c) *Reactivity of the Binary and Ternary Systems and Comparison between EPR Spectra and Other Experiments*

The EPR results reported in the present paper basically indicate that the presence of tungsten oxide significantly affects both the amount and the nature of V(IV) surface species and the redox behaviour of the catalysts. The results clearly show that:

(a) the amount of V(IV) in the calcined sample is higher in the ternary catalysts than in the binary ones with the same V loading, indicating that the presence of WO_3 probably increases the catalyst reducibility and in particular the reduction of V(V) to V(IV);

(b) the vanadyl species present on the surface of TWV catalysts exhibit different structural features with respect to those present on TV, and the interaction of the vanadyl species with the TiO_2 matrix is deeper in the latter case than in the former one;

(c) the redox behaviour of the TW samples upon outgassing at high temperature (823 K) is similar to that of bare TiO_2 and is not modified by small amounts (up to 1% by weight) of added vanadia: higher amounts of vanadia are needed in the case of ternary TWV samples to observe the same effect (prevention of the matrix reduction) observed for all binary TV samples.

All these results converge in indicating that electronic and structural interactions occur between the V and W species on the TiO_2 surface and are in agreement with the results of previous characterisations (by FT-IR, laser Raman, and UV-vis spectroscopies) on the same samples (8).

Evidence for the existence of interactions between V and W surface species has also been provided by catalytic tests in the SCR reaction. The catalytic measurements in fact have shown that TWV samples are more active in NO conversion than TV and TW samples with the same V or W loading, maintaining a high selectivity to N_2 even at high temperature where almost complete NO consumption occurs (8). Moreover, the activity of a given ternary TWV sample remains higher than that calculated in terms of a simple additive model, e.g. by adding the activities of V and W measured in the case of the two TV and TW samples having the same V and W loadings of the ternary sample.

The complex interplay of the three components of the TWV samples is clearly reflected, as shown by the data in the present paper, in a particular redox behaviour of the systems which has also been observed by temperature programmed surface reaction (TPSR) experiments involving adsorbed NH_3 and gaseous NO performed at both high (1 wt%) and low (≈30 ppm) oxygen concentrations and by temperature programmed reaction (TPR) experiments performed using the same gases (26). It has been shown that, under transient conditions and for low oxygen concentration, O_2 is consumed at temperatures well above those corresponding to the onset of the SCR reaction. Accordingly, a role for lattice oxygen (O_{lat}) has been inferred, and a redox mechanism has been proposed for the SCR reaction which implies at first the reduction of the solid,

$$2\,NH_3 + 2\,NO + O_{lat} \rightarrow 2\,N_2 + 3\,H_2O,$$

followed by catalyst reoxidation by gas-phase oxygen. Reoxidation is monitored by the consumption of gas-phase oxygen and incidentally is the rate determining step of the SCR process (26). The temperature threshold for the occurrence of SCR reaction without consumption of gas-phase oxygen is therefore an indicator of the catalyst reducibility. In the case of the ternary TWV1.4 catalyst the temperature threshold is lower than in the case of the corresponding TV sample (26) indicating, in agreement with EPR data, the easier reducibility of the ternary systems.

In conclusion, the EPR data presented here, together with the other spectroscopic and catalytic measurements recalled in this section (8, 26), seem to indicate that the redox behaviour of the solid is one of the crucial parameters for a system active in SCR reaction. In this view the use of titania as the optimal support of vanadia and tungsten oxide phases in SCR (and in some hydrocarbon oxidations as well) should be related to the correct energy gap which originates from interaction of the various oxidic phases and which has been schematically depicted in Fig. 7. In particular, the energy of the *d* orbitals of vanadium-reduced centers falls in a region not far from the limits of the conduction band of TiO_2 or of WO_3/TiO_2 while in the case of other supports with a wider band gap such as silica or alumina they are not as close to the lower limit of the conduction band. The particular conduction properties of the systems based on vanadia/titania or on vanadia–tungsten oxide/titania should allow an easy electron flow through the solid at the reaction temperature (which is of course much higher than that of spectra recording) with efficient redox cycles at the active vanadium center. This is not the case of vanadia/alumina or vanadia/silica systems (less active in the same reaction) where the vanadium centers are electronically isolated. The whole solid is an insulator and the redox cycles must take place, less efficiently, on each isolated site. The data reported in the present paper indicate, however, that significant differences exist between the vanadia/titania systems containing or not containing tungsten oxide overlayers which consist in an enhanced reducibility of the solid having a nearly full monolayer of tungsten oxide phases with respect to the binary TV systems. We have provided, both in the present paper and in other papers from our laboratories (8, 26), evidence of the structural and electronic interactions between tungsten oxide and vanadia phases which, in spite of the existence of a primary interaction of both phases with the titania support, seems to play a crucial role in the redox behaviour of the ternary solids. It is impossible, however, on the basis of the data collected up to now, to clarify unambiguously whether such interactions also determine the enhanced catalytic activity of the ternary V_2O_5–WO_3/TiO_2 in comparison with that of V_2O_5/TiO_2. Recent studies seem to suggest, for instance, that this enhanced catalytic activity is simply due to the presence in the ternary system of a second site (W) close to the principal catalytic center that favours the onset of a particular two-site catalytic mechanism (27).

We recall, however, that the idea of a correlation of the conductivity properties and redox behaviour of a system with its catalytic properties in SCR has been advanced also by other authors (10, 28, 29). The high conductivity of the W-containing titania, for instance, has been reported years ago (28) as well as the idea of the regulation of the semiconductor properties of vanadia/titania via insertion of extra ions (29) with the aim of modifying the catalytic activity in the SCR process.

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