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VANADIA LAYERS SUPPORTED ON TiO_2/SiO_2 MIXED OXIDES – AN ESR AND RAMAN INVESTIGATION

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ESR and Raman spectroscopy have been used to characterize monolayers of vanadia, which had been immobilized on titania and on a 20% TiO_2/80% SiO_2 mixed oxide support from a vanadyl alkoxide precursor. Characteristic vibrations observed in the Raman spectrum, as well as UV-visible reflection data, indicate that the most abundant vanadia species on the surface consists of disordered polymeric arrays: the central vanadium ion is surrounded by the tightly bound vanadyl oxygen, four oxygen ions in the basal plane, and a distant sixth oxygen ligand in bridging position to the support. From the ESR spectra the principal values of g and A tensors are obtained, and their dependence on the support material and on the vanadia loading is investigated. Comparison with TPR measurements indicates that for structurally and chemically similar catalysts, the ESR-derived deviation $\Delta g_{\perp} = g_{\perp} - g_e$ from the free electron g value provides a useful measure of the V=O bond strength.

1. Introduction

The controlled grafting of vanadia layers on the surface of oxidic supports [1] is an attractive route to prepare highly active catalysts for the selective catalytic reduction (SCR) of nitric oxides. Recently we have proposed [2] the used of molecularly mixed oxide carriers to tune the interaction between the support and the active phase; a significant increase in SCR activity and a high selectivity to N_2 have been achieved [2]. In this letter ESR [3] and Raman spectroscopy are used to study the interaction between the TiO_2/SiO_2 mixed oxide support and the active vanadia phase.

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The mono- and multilayers of V_2O_5 are immobilized by the reaction of surface hydroxyl groups of the support with vanadyltrialkoxides [1,2]. Titania (anatase) as a support interacts strongly with the first immobilized vanadia layer, which results in a comparatively low SCR activity. Raman spectroscopy has shown [4] that this layer mainly consists of disordered polymeric arrays of "VO_6" local coordination units. The distorted octahedron of oxygen ligands surrounding the vanadium(V) center consists of a short V=O double bond perpendicular to the surface, four singly bound oxygen ions in the basal plane, and a sixth oxygen ligand in a bridging position between V(V) and the support. This coordination geometry prevailing in the first layer of V_2O_5 immobilized on TiO_2 has been confirmed by ESR spectroscopy [5]. The activity of the catalyst is strongly increased by anchoring further vanadia layer on top of the first one [1,4]. Raman spectroscopic investigations [4] reveal that the catalytically most active centers are located in a second vanadia layer anchored on top of the first one. This second layer exhibits structural similarities with the stacked layer architecture of crystalline V_2O_5, although distinct differences between the surface phase and the properties of bulk V_2O_5 are observed.

When silica is used as the support material, its interaction with immobilized vanadia layers is weaker, and the properties of the vanadia are modified to a lesser extent. A disadvantage of the weaker bonding to the silica carrier is a higher tendency for thermally induced aggregation.

In search for a method to combine the desirable properties of TiO_2 and SiO_2 supports, mixed oxides have been synthesized by the sol-gel process [2]. Titania and silica hydrosols are mixed in appropriate proportions; after drying and calcination amorphous materials are obtained. TPR measurements reveal that the reducibility of the immobilized vanadia can be continuously tuned in this manner [2]. From SCR activity measurements an optimum titania content of 20% in the support material was determined; for this catalyst (denoted as TiO_2/SiO_2–1V in the following) the SCR activity at 400 K is about 500 times higher [2] than for the monolayer catalyst on pure titania (TiO_2-1V). These systems have been characterized by X-ray diffraction and high resolution electron microscopy [2]. The SiO_2 matrix is X-ray amorphous. In the support containing 20% TiO_2, small crystalline domains of TiO_2 in the anatase modification have been detected.

ESR spectroscopy was shown to be a valuable source of structural information on the local coordination geometry of vanadium ions [3]; usually ions in the oxidation state +IV (one d-electron) are probed. We have previously performed ESR measurements [2,5] to characterize our layer catalysts; more extensive references to the literature are compiled in ref. [5]. In this letter ESR spectra from titania- and titania/silica-supported systems are compared, in order to gain further insight into the nature of the interaction between vanadia and the amorphous mixed oxide support. From the analysis of the measured powder spectra, the principle values of the g and A tensors are determined. The deviation of the perpendicular component from the free electron g value, $\Delta g_\perp$, was found

[5] to represent a useful measure of tetragonal distortion of the local coordination octahedron. A decrease in $|\Delta g_{\perp}|$ was established to correlate with a strengthening of the V=O bond.

This letter is organized as follows. First, UV-visible reflection data and Raman spectra are presented to characterize the local coordination geometry of the vanadium. On the basis of these results, a model for the analysis of the ESR powder patterns is summarized, and the relevant parameters are evaluated and discussed. Finally, some conclusions regarding the structure of the catalysts are drawn, and correlations with the reducibility of V(V) derived from TPR measurements are discussed.

2. Experimental

The preparation of the samples has been described elsewhere in detail [1,2]. The monolayer catalysts (1V) were impregnated once with vanadyl-triisobutoxide (VTIB), while the preparation of the multilayer catalysts (4V) consisted of four impregnation steps with VTIB. The mixed gel carrier consisted of 20 mol% TiO_2 and 80 mol% SiO_2 [2].

UV-visible reflection spectra were recorded on a conventional spectrophotometer (Beckman, model DK-2) equipped with an integration sphere. Raman spectra were excited with the 488 nm line of an argon ion laser. Plasma lines from the laser were eliminated with a filter monochromator (Applied Photophysics, model 2300). To avoid a thermal dehydration of the surface due to the incident laser beam [6,7], and to guarantee equal conditions as in the ESR experiment, a beam expander and a cylindrical focussing lens have been used. An area on the catalyst wafer of 100 μm width and 5 mm height was illuminated, and the laser power on the sample was confined to 20 mW.

The ESR measurements have been performed on a conventional X-band spectrometer (Bruker) with 100 kHz modulation at room temperature. The microwave frequency was 9.412 GHz for the V_2O_5 monolayer on TiO_2, and 9.761 GHz for the other samples. Signals due to ^{51}V with $I = 7/2$ were observed from all the catalysts and attributed to V^{4+} ions.

3. Results and discussion

3.1. UV-VISIBLE REFLECTION SPECTRA

UV-visible reflection spectra for $TiO_2(20\%)/SiO_2(80\%)$–4V are shown in fig. 1 both for the catalyst stored in ambient atmosphere (top trace), and for a sample dehydrated in oxygen at 573 K for one hour (bottom trace). The latter spectrum has been deconvoluted into three bands. These spectra are assigned as follows.

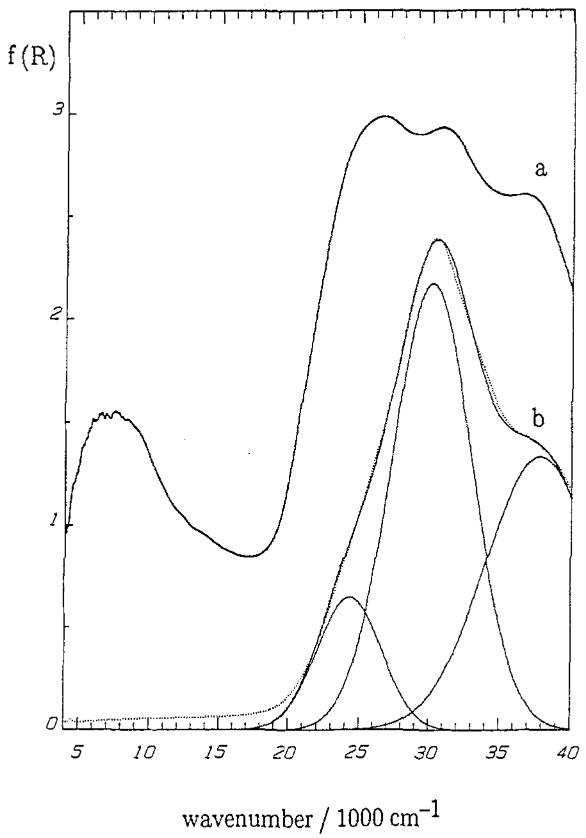

Fig. 1. UV-visible reflection spectra of the catalysts prepared by fourfold impregnation of the TiO_2(20%)/SiO_2(80%) support with vanadyl-triisobutoxide. The Kubelka-Munk function $f(R)$ is shown (a) for the catalyst stored under atmospheric conditions (hydrated form) and (b) after dehydration of the catalyst at 573 K in oxygen for one hour. In (b), the experimental spectrum (dotted line) has been deconvoluted into three peaks. The calculated spectrum is shown as the full line.

Bands at 30′500 cm^{-1} and 37′800 cm^{-1} are due to the anatase component of the support [8]. The broad band centered at ≈ 8000 cm^{-1} seen in the spectrum of the hydrated catalyst (top) is attributed [9,10] to a vanadium(V)-vanadium(IV) intervalence charge transfer band, demonstrating that both oxydation states are coexisting in a polymeric layer of surface vanadia.

Finally, the vanadia charge transfer band observed at 26′200 cm^{-1} (hydrated sample) and 24′200 cm^{-1} (dehydrated sample) provides important information on the local coordination of the vanadium. Comparison with data from the literature [11,12] suggests a coordination sphere for the vanadium center that consists of five nearest neighbor oxygen ions. The vanadium ion is situated at the center of a square pyramidal structure, with a distant oxygen from the support representing the sixth ligand. In the model compound α-VPO_5, with a vanadium coordination number of 5, this charge transfer band is found at 24′300 cm^{-1} [12]. Note that this band experiences only a modest shift upon dehydration, which demonstrates that the coordination polyhedron is only slightly modified. By comparison, in submonolayers of VO_x on SiO_2, for which tetrahedrally coordinated vanadium oxide species are proposed, adsorption of water changes the coordination number from four to six; this process is accompanied by a shift of the charge transfer band from 30′300 cm^{-1} (tetrahedral coordination) to 21′000 cm^{-1} (octahedral coordination). From the failure to observe such a shift on our sample, we can conclude that the coordination number of the vanadium centers does not change upon dehydration.

3.2. RAMAN SPECTRA

The laser Raman spectrum of the catalyst prepared by four impregnations of the TiO_2 (20%)/SiO_2(80%) support with the vanadyl triisobutoxide reagent is shown in fig. 2. No Raman bands that would correspond to crystalline SiO_2 are detected, in full agreement with the X-ray diffraction measurements that showed the SiO_2 to be amorphous. The TiO_2 (anatase) fraction of the support exhibits strong Raman bands [13] at 144, 400, 517, and 640 cm^{-1}. Weak and broad second order features appear at 320 and 790 cm^{-1}. According to literature [13] the rutile modification of titania exhibits Raman bands at 611 and 448 cm^{-1}, with an additional weak feature at 828 cm^{-1}. The only indication of any rutilization is a weak shoulder on the low wavenumber side of the band at 640 cm^{-1}.

The remaining bands are due to the supported VO_x phase. An intensive band at 703 cm^{-1} is attributed to a stretching vibration of oxygen ions in bridging position between three vanadium centers ($\mathrm{V{-}O}\big\langle{}^{\mathrm{V}}_{\mathrm{V}}$). This band, together with the corresponding deformational motion at 306 cm^{-1}, is also found in crystalline

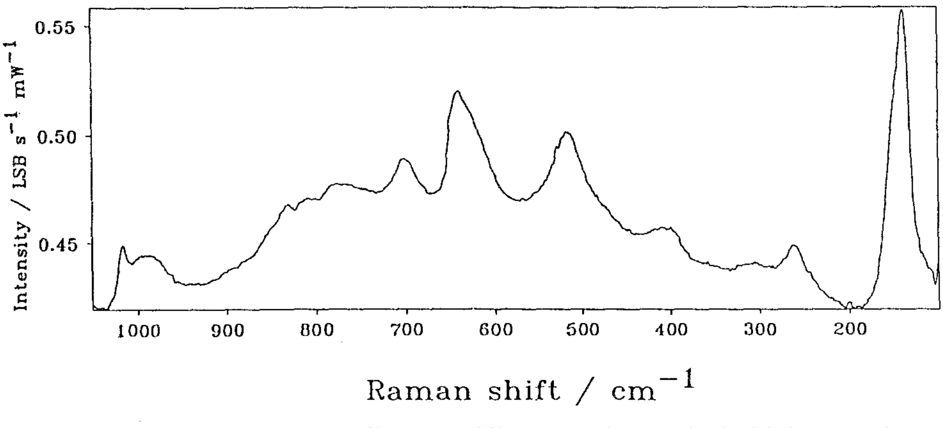

Fig. 2. Raman spectrum of the TiO_2(20%)/SiO_2(80%)–4V catalyst, excited with 20 mW of power at 488 nm from an argon ion laser. For experimental details, see text.

V_2O_5, and is characteristic for the layer structure found in this oxide. Oxygen ions situated between two vanadium centers given rise to a Raman band at 483 cm^{-1} in V_2O_5. A weak shoulder on the low wavenumber side of the support band at 517 cm^{-1} can be attributed to this vibration in our catalyst.

The most informative features of the spectrum are the vibrations around 1000 cm^{-1}, which are due to stretching vibrations of vanadium-oxygen double bonds [14]. We recognize a broad band centered around 990 cm^{-1}, and a peak at 1025 cm^{-1} of medium intensity. Generally the peak position is influenced by two factors, of which the vanadium-oxygen bond order is most important [4,15]. For example, in crystalline V_2O_5 the bond order is slightly less than two, with a characteristic sharp and intensive Raman band at 996 cm^{-1}. The second factor that influences the peak position, which has been recognized only recently [6,10], is the hydration state of the surface. In a moist atmosphere water molecules may be physisorbed to vanadium centers, thereby donating electron density to the vanadyl bonds, and potentially increasing the coordination number. Chemisorption of water molecules to form vanadium hydroxyl bonds both influences the bond order and creates structural heterogeneity.

In our spectrum the features that are characteristic of double- and multilayer V_2O_5, i.e. a strong and sharp ν (V=O) band at 996 cm^{-1} and the corresponding deformation δ(V=O) at 285 cm^{-1}, are absent. Spectra similar to ours have recently been obtained by Busca et al. [6]. In a study of VO_x monolayers supported on titania the authors observed a broad Raman band centered at 995 cm^{-1}. On increasing the laser power, this band decreased in intensity, and a new peak appeared at 1035 cm^{-1}. From a combined Raman and FTIR study, Busca et al. [6] have attributed the broad 995 cm^{-1} band to hydrated, and the 1035 cm^{-1} band to dehydrated surface mono-oxo vanadyl groups [6]. With this information, and the supporting evidence from the UV-visible reflection spectra mentioned above, we attribute the broad Raman band at 995 cm^{-1} (fig. 2) to a hydrated, and the 1025 cm^{-1} band to a dehydrated surface VO_x species, with predominant fivefold coordination and a distant sixth ligand on the support. This polymeric vanadia surface phase is formed by the condensation of surface V–OH groups followed by the desorption of water. The band at 265 cm^{-1} is attributed to the deformational mode of the surface vanadyl groups.

In addition, we observe two weak bands at 835 cm^{-1} and at 850 cm^{-1} which are tentatively ascribed to monomeric, tetrahedrally coordinated vanadate ions that are singly bound to the mixed oxide support. This assignment is the subject of further investigation, and will be reported at another place.

3.3. ANALYSIS OF THE ESR SPECTRA

In order to evaluate the observed data in a quantitative way, the experimental spectra were fitted to calculated powder spectra by a nonlinear least-squares

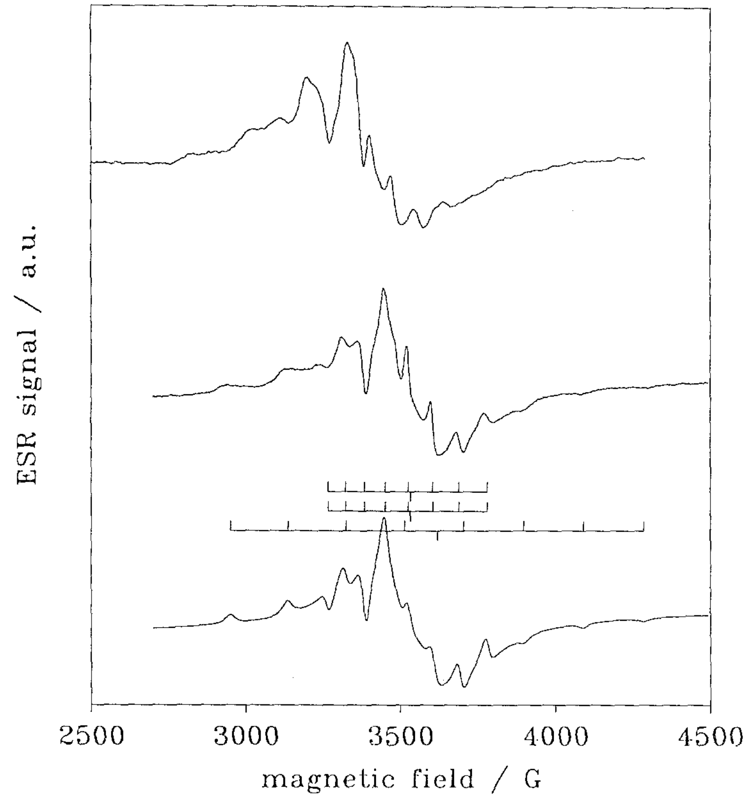

Fig. 3. ESR spectra of V_2O_5 monolayer supported on TiO_2 and $TiO_2(20\%)/SiO_2(80\%)$ mixed gel (TiO_2-1V, upper trace, and TiO_2/SiO_2-1V, middle trace). A simulated spectrum of the mixed gel catalyst is included (bottom trace), where a Lorentzian line width of 23 G was obtained from the fit.

method. The procedure used is based on a modified Gauss-Newton method, and is described in detail in ref. [16].

As in our previous investigations [5], an axially symmetric spin Hamiltonian was assumed, in agreement with the distorted octahedral coordination geometry of C_{4v} symmetry [17]. The short vanadyl double bond (V=O), which is directed perpendicular to the surface, defines the axis of symmetry. The lineshape of the derivative spectrum is described by a Lorentzian, of peak to peak width w. Thus there are six parameters that describe the vanadium signal ($g_{\|}$, $g_{\perp}$, $A_{\|}$, $A_{\perp}$, w, and an overall amplitude).

From figs. 3 and 4 it is evident that the signals of interest appear superimposed onto a broad and unstructured background derivative signal. To obtain a reasonable fit, this signal had to be taken into account; it is defined by three parameters (position, width, and amplitude). Finally, a linear baseline correction was included (2 parameters).

The best fit values of the *linear* parameters (i.e., the two amplitudes and the baseline parameters) were obtained analytically for each set of the *nonlinear* parameters (positions, widths, hyperfine splittings). In searching the *minimum* of the sum of squared deviations of the multiparameter function from the experimental spectrum, the nonlinear parameters were varied in an alternating and iterative fashion.

Some simulations are presented in figs. 3 and 4. The corresponding stick spectra are included, indicating the magnetic field positions corresponding to $g_{\parallel}$, with an eightfold hyperfine splitting due to $A_{\parallel}$, and the magnetic field positions corresponding to $g_{\perp}$, with an eight-line multiplet pattern due to $A_{\perp}$, respectively.

The parameters determined from the computer simulations are given in table 1. These were used to calculate the deviations from the free electron g value, $\Delta g_{\parallel} = q_{\parallel} - g_e$ and $\Delta g_{\perp} = g_{\perp} - g_e$. As mentioned above, $|\Delta g_{\perp}|$ is a sensitive indicator of tetragonal distortion of the local coordination octahedron of oxygen ligands surrounding the vanadium ions [5,18,19]. For the principal components of the g tensor, one finds [18] from second order perurbation theory (neglecting small terms)

$$\Delta g_{\parallel} = -8\lambda\beta_1^{*2}\beta_2^{*2}/\Delta E_{x^2-y^2} \quad \text{and} \quad \Delta g_{\perp} = -2\lambda\epsilon_{\pi}^{*2}\beta_2^{*2}/\Delta E_{xz}. \tag{1}$$

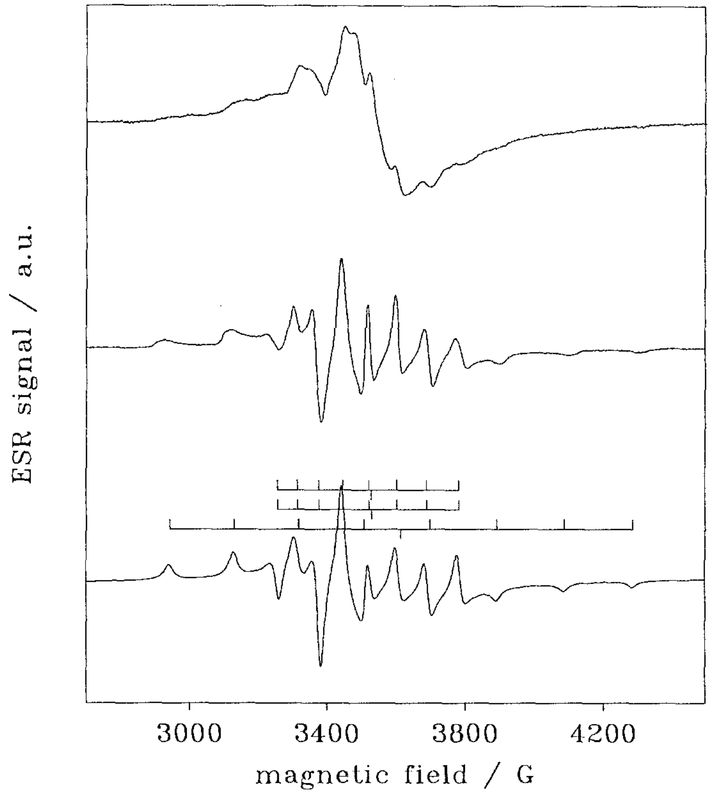

Fig. 4. ESR spectra of V_2O_5 multilayer structure supported on TiO_4 and TiO_2/SiO_2 mixed gel (TiO_2-4V, upper trace, and TiO_2/SiO_2-4V, middle trace). A simulated spectrum of the mixed gel catalyst is included (bottom trace), where a Lorentzian line width of 18 G was obtained from the fit.

Here λ denotes the spin-orbit coupling parameter of the free vanadium ion ($\sim 170\ \mathrm{cm}^{-1}$), β_1^*, β_2^*, and ϵ_π^* are MO coefficients [18], $\Delta E_{x^2-y^2}$ is the excitation energy from ψ^* (b_2) to ψ^* (b_1), and ΔE_{xz} denotes the excitation energy from ψ^* (b_2) to ψ^* (e_π). Note that $\Delta E_{x^2-y^2}$ is independent of a tetragonal distortion of the coordination octahedron, and is determined by the splitting parameter 10 Dq of an average octahedral environment [20]. On the other hand, ΔE_{xz} increases with tetragonal distortion, i.e. with a compression of the vanadium-oxygen distance along the z-axis *relative* to the bond lengths in the xy plane. As pointed out in ref. [5], this can be due *either* to a shortening of the V=O double bond, *or* to an increase in the V–O bond distances in the basal plane of the distorted octahedron. With either of these two changes, $|\Delta g_\perp|$ is decreasing according to eq. (1). A larger distance between the four electron rich ligands and the central vanadium ion will in turn result in a stronger Coulomb attraction of the vanadyl oxygen [5], and therefore in a strengthening of the V=O bond.

Furthermore, the electron delocalization over the ligand orbitals was determined from the ESR data. The squared MO coefficient [18]

$$\beta_2^{*2} = \tfrac{7}{6}\Delta g_\parallel - \tfrac{5}{12}\Delta g_\perp - \frac{7}{6}\,\frac{A_\parallel - A_\perp}{P}, \tag{2}$$

with $P = 184.5$ G, expresses the fraction of unpaired d-electrons localized at the vanadium ion [18]. The quantity $C = 1 - \beta_2^{*2}$ is a measure of delocalization over the ligand orbitals. Table 1 is supplemented by the values of the Fermi contact term for the vanadium ion, which is given by [18]

$$K_{\mathrm{eff}} = \frac{|A_\perp|}{P} + \tfrac{2}{7}\beta_2^{*2} + \tfrac{11}{14}\Delta g_\perp . \tag{3}$$

Table 1
Parameters characterizing the ESR spectra of the investigated catalysts

catalyst	$g_\parallel$	$g_\perp$	$\lvert\Delta g_\perp\rvert$	$\lvert A_\parallel\rvert$ (G)	$\lvert A_\perp\rvert$ (G)	β_2^{*2}	K_{eff}	T_{max} [a] (K)
TiO_2–1V	1.921±0.008	1.969±0.004	0.033	187	70	0.66	0.54	694
TiO_2–4V	1.912±0.009	1.970±0.006	0.032	196	69	0.71	0.55	713
TiO_2/SiO_2–1V	1.926±0.006	1.974±0.002	0.028	191	73	0.67	0.57	745
TiO_2/SiO_2–4V	1.929±0.004	1.976±0.002	0.026	191	75	0.66	0.57	759
SiO_2–1V [b]	1.934±0.010	1.974±0.005	0.028	193	73	0.69	0.57	805
after TPR	1.930	1.979	0.023	194	71	0.70	0.57	

[a] The ‘reduction temperature’ T_{max} is defined as the temperature of maximum hydrogen consumption in a TPR experiment. Note that the values of T_{max} may be shifted if TPR measurements are performed under conditions other than those specified in ref. [1]. Data are taken from refs. [1] and [2].

[b] Data from ref. [5].

3.4. PARAMETERS DERIVED FROM THE ESR SPECTRA

The ESR parameters obtained from our analysis permit the estimation of changes in the local coordination geometry and in the V=O bond strength. From table 1 we see that $|\Delta g_\perp|$ is consistently smaller in the multilayer structure (4V) than in the monolayer (1V). This holds true for both supports, TiO_2 and TiO_2/SiO_2.

In our earlier studies of V_2O_5 layer catalysts by ESR [5] we have shown that there is a correlation between the V=O bond strength, as reflected by $|\Delta g_\perp|$, and the reducibility of vanadium(V), which in turn has a strong impact on the catalytic properties. As a measure of reducibility, we shall use the temperature T_{max} of maximum hydrogen consumption in temperature programmed reduction (TPR) [21]; this quantity is also included in table 1. The correlation between $|\Delta g_\perp|$ and T_{max} is confirmed by the present study. For example, if we compare the catalysts TiO_2–1V and TiO_2–4V, the reduction temperature changes from 694 K to 713 K, and the ESR-derived quantity $|\Delta g_\perp|$ decreases from 0.033 to 0.032. This holds also true for the mixed gels TiO_2/SiO_2–1V and TiO_2/SiO_2–4V: $|\Delta g_\perp|$ changes from 0.028 to 0.026, while T_{max} shows an increase from 745 K to 759 K (table 1).

As mentioned above, one of the motivations for the use of TiO_2/SiO_2 mixed gel supports is that the vanadia-support interaction can be tuned between the values on TiO_2 (comparatively strong interaction) and SiO_2 (weaker interaction). In fact, if we compare the catalysts TiO_2–1V and TiO_2/SiO_2–1V, T_{max} increases from 694 to 745 K, and the bond strength parameter $|\Delta g_\perp|$ changes from 0.033 to 0.028. This smooth variation can be extended by including the results of an ESR-investigation of a silica-supported catalysts (SiO_2–1V) after TPR [5]. The value $|\Delta g_\perp| = 0.023$, which is the smallest in the series of the singly impregnated catalysts, is reflected by a high reduction temperature, $T_{max} = 805$ K.

The correlation is also confirmed if we compare TiO_2–4V and TiO_2/SiO_2–4V: T_{max} increases from 713 K to 759 K, and $|\Delta g_\perp|$ decreases from 0.032 to 0.026. To summarize, for all investigated systems we observe a consistent parallelism of larger values of T_{max} with decreasing values of $|\Delta g_\perp|$.

The electron delocalization $(1 - \beta_2^{*2})$ onto the ligand orbitals shows no significant changes for the investigated catalysts (see table 1), and the values of the Fermi contact term K_{eff} can be regarded as independent from the support material and the immobilization of further layers. A mentioned above, two types of geometrical changes can give rise to an increase in tetragonal distortion. The constancy of K_{eff} suggests that the rigid V=O bond length is affected to a lesser extent than the V–O bond length in the basal plane, which in turn influences the catalytically relevant 'bond strength' of the vanadyl group.

The results of the present study confirm that ESR is a useful probe to characterize the structure of supported V_2O_5 catalysts. Here this method has been applied to test the novel concept of tuning support properties by the use of mixed oxide carriers, which are prepared by the sol-gel process. The continuous variation of the interaction between support and active phase, which has been deduced earlier from TPR [2] and Raman/FTIR data [10], is fully confirmed by the smooth variation of the ESR parameters for the monolayer catalysts on TiO_2, TiO_2(20%)/SiO_2(80%) and SiO_2. The molecularly mixed nature of the amorphous oxides [2] obtained by the sol-gel route is clearly supported by this result.

4. Conclusions

The vanadyl (V=O) bond strength increases with addition of silica to the titania support, as reflected by the reduction temperature T_{max}. As discussed above, a stronger bond may be associated with a shorter V=O bond distance and/or a stronger tetragonal distortion of the coordination octahedron. We are aware of the fact that structural information from ESR spectra, recorded under ambient conditions, are not directly comparable to the dehydrated state of the catalyst at 700 K, at which temperature reduction takes place in the TPR experiments. Yet, the present results demonstrate that within a range of structurally similar catalysts, there exists a useful correlation between the quantity $|\Delta g_{\perp}|$ derived from ESR, and the V=O bond strength as reflected in the reduction temperature and catalytic properties.

Finally, it is worthwile to summarize the structural information which emerges from this study for the catalyst prepared by four impregnations with vanadyl triisobutoxide (TiO_2/SiO_2–4V), and to draw a comparison with the corresponding catalyst where a pure TiO_2 support has been subject to the same impregnation cycle [1,4]. In the latter system, we had found [4] a multilayer vanadia phase (but not crystalline V_2O_5), with the vanadium ions in a distorted octahedral coordination sphere. Note that the BET surface area of the TiO_2/SiO_2 support (250 m^2/g) is about five times larger than that of the pure titania used in the previous investigations [1,4]. Therefore, it is not surprising to find no multilayer VO_x phase on our mixed metal oxide support, although the amount of immobilized vanadium is approximately the same. Bands typical of the multilayer structure in V_2O_5 are absent. The most informative feature of our Raman spectrum (fig. 2) are the bands at 703 cm^{-1} and 305 cm^{-1} (weak). These bands are characteristic of oxygen ions in bridging positions between three vanadium centers within one layer of V_2O_5. Thus we draw the conclusion that the dominant VO_x phase on our catalyst is present in the form of a monolayer. This layer consists of vanadium centers surrounded by five oxygen ions, resulting in a distorted square pyramidal coordination of the vanadium ion. A more distant oxygen ion from the support supplements the coordination sphere, which can therefore also be regarded as a highly distorted octahedron.

Acknowledgments

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