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An IR Spectroscopy Study of the State and Localization of Vanadium–Oxo Species Adsorbed on TiO_2 (Anatase)

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The state and localization of vanadium–oxo species adsorbed on anatase have been studied by IR spectroscopy of probe molecules, UV–vis spectroscopy, XPS, and chemical analysis. The adsorption was carried out from acidic solutions of ammonium vanadate. Two samples were used as adsorbents: (i) pure anatase, characterized by the presence of two kinds (strong and weak) of Lewis acid sites and two kinds of surface hydroxyl groups, and (ii) anatase treated with hydrogen peroxide where physically and chemisorbed peroxides exist. It was established that the active sites for adsorption were, in the first case, the surface hydroxyl groups and the strong Lewis sites only. The catalyst thus obtained (VT1) was characterized by a Lewis acidity, mainly due to the weak acid sites of the support, as well as by a small amount of Brønsted acid sites representing surface V–OH groups. When the adsorption proceeded on the peroxide-treated sample, the vanadium coverage was higher, since all Lewis acid sites of anatase participated in the process. A protonic acidity was also observed on this sample (VT2), but, contrary to VT1, the Lewis acidity was associated with the existence of V^{5+}. On the basis of the results obtained, structures of the surface species are proposed. Some possibilities of using the samples as catalysts are discussed. © 1991 Academic Press, Inc.

INTRODUCTION

Vanadia–titania catalysts possess high activity and selectivity in processes of industrial importance such as oxidation of *o*-xylene (*1–8*), naphthalene (*9*), and butadiene (*10*), oxidative ammonolysis of various aromatic hydrocarbons (*11–13*), and selective reduction of nitric oxides with ammonia (*14–16*).

It is generally accepted (*1–6, 17, 18*) that the active phase is the vanadia part of the catalysts and the most appropriate support is the low-temperature modification of titanium dioxide, anatase. The structure of the active phase strongly depends on the vanadia content as well as on the preparation conditions. The most used method for synthesis is deposition of V_2O_5 by impregnation (*1–4, 18–25*). In a series of cases, vanadia–titania catalysts are obtained by the so-called "ion exchange" method. The adsorption of $VOCl_3$ (*3, 18, 21, 22, 26–28*), $VO(OiBu)_3$ (*18, 29*), and $VO(acac)_2$ (*18, 30, 31*) from organic solutions on anatase are widely used. These syntheses are complex since the processes occur in completely nonaqueous media. Roozeboom *et al.* (*32, 33*) have shown the possibility of preparation of catalysts with a very low vanadium content using adsorption of vanadate ions from weakly acid aqueous solutions. In all these cases it is assumed that the active sites for adsorption are surface hydroxyl groups (*18, 21, 22, 26, 29–33*). The catalysts prepared by ion exchange are especially interesting due to their high catalytic activity (*18, 21, 26*) as well as from a commercial viewpoint owing to the low content of the active phase.

The vanadium oxide compounds on the anatase surface are different depending mainly on the degree of coverage. It is established (*3, 20, 21, 25, 26, 32, 33*) that the monolayer vanadium oxide catalysts contain two types of surface compounds: (i)

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isolated monooxo–vanadyl groups that interact strongly with the titanium dioxide surface and (ii) bidimensional vanadium oxide clusters bonded weakly to the support. The presence of a separate V_2O_5 phase (*1, 3, 13, 18, 19, 21, 25*) or polyvanadate ions (*34*) is also observed at higher coverages. It is interesting that coordinatively unsaturated (c.u.s.) titanium cations are present on the surface with a theoretically calculated monolayer or even at higher coverages (*19, 22, 26*). The inhomogeneous distribution of the active phase is also confirmed by studies with a high-resolution electron microscope (*24*).

A number of hypotheses are proposed for the explanation of the unique catalytic properties of vanadia–titania catalysts. Thus, Vejux and Courtine (*35*) have noted the crystallographic fitting between the (010) face of V_2O_5 and the prevailing (according to (*35*)) anatase planes: (001), (100), and (010). Thus, there is a possibility of epitaxial growth of V_2O_5 during its deposition with predominant exposure of the (010) vanadia face characterized by the presence of V=O groups (*36*). These groups are responsible for the processes of selective oxidation. Polish authors (*27, 28*) have proposed a model, according to which isolated VO_4 groups with two terminal and two bridge oxygen atoms are situated on the (001) anatase face. The specific effect of the support consists of favoring the formation of dioxovanadate groups containing reactive oxygen. The disadvantage of this model is that the other faces characteristic of a real anatase crystal are not considered. Bond *et al.* (*5, 18*) suppose that at a low V_2O_5 content isolated tetrahedral hydroxovanadyl groups are formed. The precious catalytic properties of such catalysts are due to the joint effect of an easily reducible V=O bond and an acid hydroxyl group from the same active center (*5*). Gryzbowska (*6*) supposes the better catalytic properties of anatase-supported vanadia catalysts in comparison with those of bulk V_2O_5 to be due to the weaker acid properties of the monolayer coverage caused by the effect of the support.

Obviously, various vanadium oxide compounds are formed on anatase depending on the concentration of the supported vanadia and on the preparation conditions. The structure, localization, and reactivity of these species determine the activity and selectivity of the catalysts. The full elucidation of the question about the properties of vanadia–titania catalysts requires studying each kind of surface compounds separately.

The purpose of the present paper is to establish the structure, localization, and reactivity of the VO_x compounds formed after adsorption on anatase of vanadium–oxo species from aqueous solutions.

EXPERIMENTAL

Hydrated titanium dioxide was prepared by hydrolysis of titanium tetrachloride at pH 9 (*37–39*), followed by calcination in air at 400°C for 2 h. The substance obtained had, according to XRD data, the structure of anatase.

Part of this preparation was suspended in 5% H_2O_2 solution, filtered, and dried in air at room temperature.

Samples of pure and hydrogen peroxide-treated anatase (5 g each) were suspended in 100 ml 0.06 *M* solutions of V^{5+} at different pH values. After 2 h the precipitates were filtered and washed several times with distilled water to remove unadsorbed ions, then dried at 120°C and calcined in air at 400°C for 1 h.

The V^{5+} solutions were prepared by dissolving ammonium vanadate in nitric acid (1 : 1). The desired pH value was attained by alkalization with ammonia.

To carry out the adsorption IR experiments the samples were pressed into pellets with a suitable thickness and placed in the IR cell. This cell was directly connected to a vacuum apparatus ensuring residual pressure below 10^{-4} Torr[1].

IR spectra were registered with UR-20 and Specord M-80 apparatuses. For the adsorption measurements the samples under-

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[1] Torr = 133.3 $N \cdot m^{-2}$.

went *in situ* thermal treatments under vacuum better than 10^{-4} Torr at 400°C and in oxygen (100 Torr) at the same temperature. X-ray phase analysis was performed with a DRON-3 apparatus using a Cu$K\alpha$ radiation source. The diffuse reflectance UV–vis spectra were registered with a Shimadzu-300 apparatus. The ESR spectra were recorded with a Bruker ER 200 DSRC apparatus using a DPPH marker. The XPS measurements were carried out with an ESCALAB MkII (VG Scientific, Ltd.) apparatus using Mg$K\alpha$ radiation. Chemical analysis was made by atomic absorption analysis with a Pye Unicam SP 1950 apparatus at the corresponding resonance wavelength. The specific surface area was determined by conventional low-temperature nitrogen adsorption according to the BET method.

RESULTS

Preliminary Remarks

The preliminary experiments have shown that the adsorption of vanadium-containing ions from aqueous solutions of ammonium vanadate proceeds within a wide range of pH values but with different coverages. The highest vanadium content was reached during adsorption from solutions with pH $\leq$ 1. For that reason, "molecular deposition" was carried out at pH of ca. 0.5. Under these conditions, adsorption was irreversible and the surface compounds obtained were not able to be washed off by neutral or acid solutions. The treatment with a 25% ammonia solution at room temperature for 24 h also did not cause leaching of the supported active phase, which indicated that the latter was directly connected with the support surface (*3*, *13*, *21*).

Characterization of the Samples

Some characteristics of the samples investigated are presented in Table 1. Notation VT1 will be used for the sample prepared in the absence of hydrogen peroxide, whereas the sample synthesized using peroxide-treated TiO_2 will be denoted by VT2. The X-ray phase analysis has shown, in all cases, presence of anatase alone. This is normal for low-coated vanadia–titania catalysts (*7*). According to XPS, the V : Ti ratio higher than that observed using the results of AAA is indicative of the surface localization of the adsorbed species. The vanadium content in sample VT1 is lower than that of sample VT2 but in both cases it does not exceed a monolayer coverage (according to Ref. (*18*)). The calculated surface concentrations of V atoms are significantly lower than the average concentration of c.u.s. titanium cations on anatase (ca. 5 Ti^{4+} nm^{-2} (*37*)).

The positions of the V $2P_{3/2}$ peaks (518.3 and 519.3 eV for VT1 and VT2, respectively) are indicative of a five valent state of the vanadium (*23*). This is in agreement with the absence of a signal from the ESR spectra of the samples (*40*).

Diffuse-reflectance UV–vis spectra of samples VT1 and VT2 (using anatase as a reference) are shown in Fig. 1. In the spectra of both samples there is a band with a maximum at 400–415 nm, which corresponds to LMCT characteristic of compounds of octahedrally coordinated vanadium(V) (*41*, *42*). The absence of reflectance at the higher frequencies, where the *d-d* transitions are observed (*41*), shows that the samples contain no tetravalent vanadium. This fact coincides with the XPS and ESR results described above. Some diffuse reflectance in the region 450–700 nm, typical of V^{4+} compounds (*41*), is observed in the spectrum of sample VT2 after its calcination at 550°C in air; i.e., the thermal treatment leads to reduction of part of V^{5+} to V^{4+} (*21*).

IR Spectroscopic Studies

All IR spectra were taken after preliminary activation of the samples (1 h vacuum treatment at 400°C, followed by 1 h heating in 100-Torr oxygen atmosphere at the same temperature and evacuation after cooling). This activation was performed to eliminate the adsorbed water and eventual organic impurities.

1. Anatase supports. The IR spectra of pure and peroxide-treated titanium dioxide,

TABLE 1

Some Characteristics of the Samples Investigated

Sample	Adsorbent	*S* (m^2/g)	V : Ti ratio on the surface layers[a]	Surface concentration (V^{5+}/nm^2)[b]
TiO_2	—	165	—	—
VT1	Anatase	136	4.3 : 100	1.6
VT2	Anatase treated with H_2O_2	142	7.2 : 100	2.2

[a] According to XPS data.

[b] Calculated according to atomic absorption analysis data.

registered after activation, contain two adsorption bands with maxima at 3740 and 3700 cm^{-1} (Fig. 2). These bands, in agreement with data from the literature (*38, 43, 44*), correspond to two types of surface hydroxyl groups. The adsorption of CO on both samples (Fig. 2) leads to the formation of two kinds of Ti^{4+}—CO carbonyls (IR bands at 2206 and 2186 cm^{-1}), which correspond to two types, α and β, of Ti^{4+} Lewis acid sites, respectively (*38, 43, 45*). The higher frequency and stability of the carbonyls manifesting band at 2206 cm^{-1} are indicative of the greater acidity of the respective sites. The fact that the surface properties of pure and peroxide treated anatase are identical after activation is due to the low thermal stability of the adsorbed peroxide groups; as shown earlier (*39*), their decomposition begins at about 80°C.

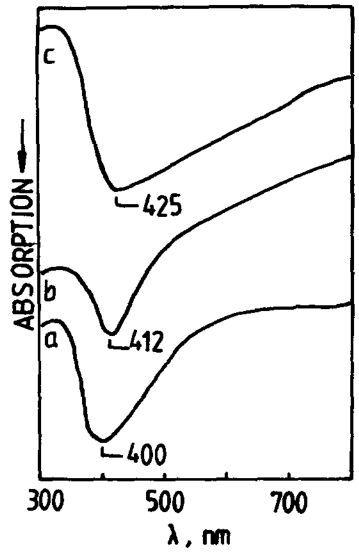


FIG. 1. Diffuse-reflectance UV–vis spectra of samples VT1 (a) and VT2 (b), calcined at 400°C in air, and sample VT2 after heating in air at 550°C (c).

2. *Sample VT1.* The IR spectrum of the sample VT1 is shown on Figs. 3 and 4. An absorption band at 3660 cm^{-1} with a low-frequency shoulder is observed in the ν(OH) region after thermal treatment of the sample (Fig. 3) and can be ascribed to the stretching modes of V—OH surface hydroxyl groups (*21, 22, 26*). A very weak and broad absorbance in the 3600–3000 cm^{-1} region shows the existence of some H-bonded hydroxyls. At a lower wavenumber there is a band at 2504 cm^{-1} (Fig. 4), which corresponds to the first overtone of the V=O stretching mode observed at 1034 cm^{-1} (*21, 22, 26, 46*).

The surface acidity of sample VT1 has been studied using ammonia and CO adsorption. The introduction of ammonia (5 Torr) at room temperature, followed by 15-min evacuation to eliminate H-bonded molecules, leads to the appearance in the IR spectrum of a series of new bands (Figs. 3 and 4). In the high-frequency region overlapping bands due to symmetric and asymmetric N—H stretching vibrations of NH_4^+ and coordinatively bonded NH_3, as well as the Fermi resonance of $2\delta_{as}(NH_3)$ with $\nu_s(NH_3)$ (*43, 47*), are observed. The band at 3576 cm^{-1} can be attributed to

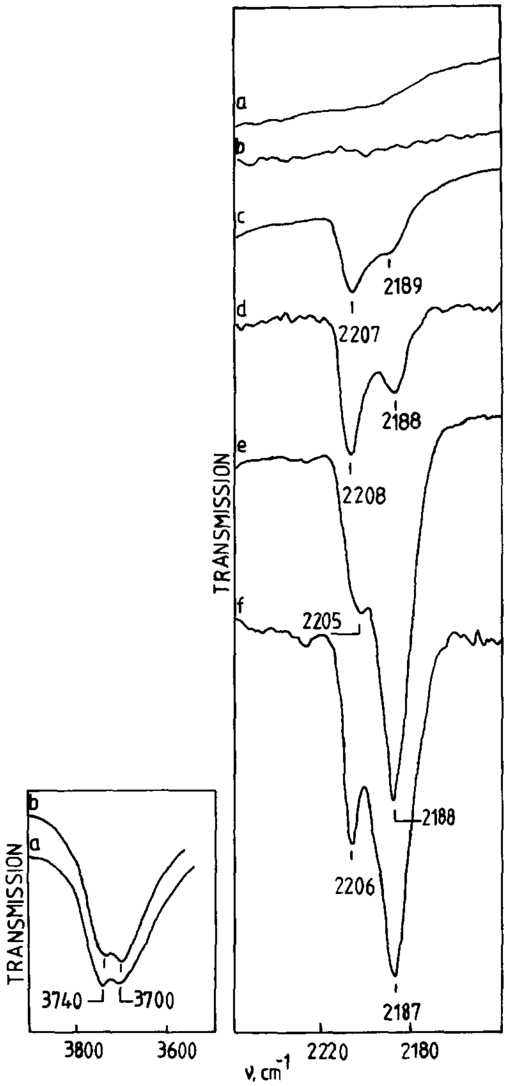


FIG. 2. IR spectra of: anatase after activation at 400°C (a), and after adsorption of 1- (d) and 20- (f) Torr CO; hydrogen peroxide pretreated anatase after activation at 400°C (b) and after adsorption of 1- (c) and 20- (e) Torr CO.

ν(NH) stretching modes of NH^+ groups formed after dissociation of part of the ammonia molecules during adsorption (*48*, *49*).

Two intense bands at 1600 and 1172 cm^{-1}, the latter having a high-frequency shoulder, characterize $\delta_{as}(NH_3)$ and $\delta_s(NH_3)$ modes of coordinatively bonded ammonia (*38*) and evidence the existence of Lewis acidity on the sample surface (Fig. 4). The broad low-intensity band at 1452 cm^{-1} is assigned to $\delta_{as}(NH_4)$ vibrations. The position of this band is indicative of weak or moderate acidity of the protonic sites (*43*). Simultaneously, the band at 3660 cm^{-1}, due to V—OH groups, decreases in intensity, which indicates the reversible ammonia adsorption and supports the conclusion of a moderate Brønsted acidity.

It is worth noting that the band at 1034 cm^{-1}, which characterizes the V=O stretching modes, as well as the corresponding overtone at 2054 cm^{-1}, disappears from the spectrum after adsorption of ammonia (Fig. 4).

The adsorption of CO on the sample leads to the appearance of a band, whose maximum shifts from 2194 to 2190 cm^{-1} with increasing CO coverage (Fig.5). The decrease in equilibrium CO pressure causes the decrease in the band intensity and its disappearance after brief evacuation. This

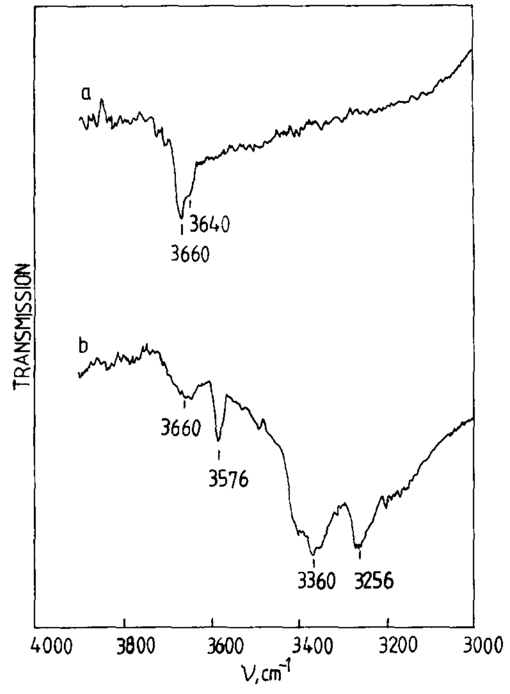


FIG. 3. IR spectra of sample VT1 (for the symbols see text) after activation at 400°C (a) and after adsorption of NH_3 (5 Torr, followed by 15-min evacuation) (b).

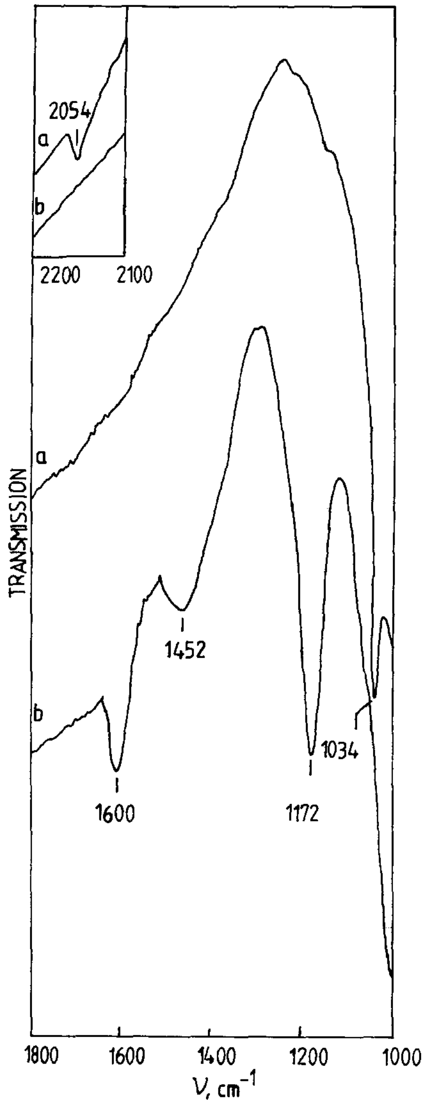


FIG. 4. IR spectra of VT1 after activation at 400°C (a) and after adsorption of NH_3 (5 Torr, followed by 15-min evacuation) (b).

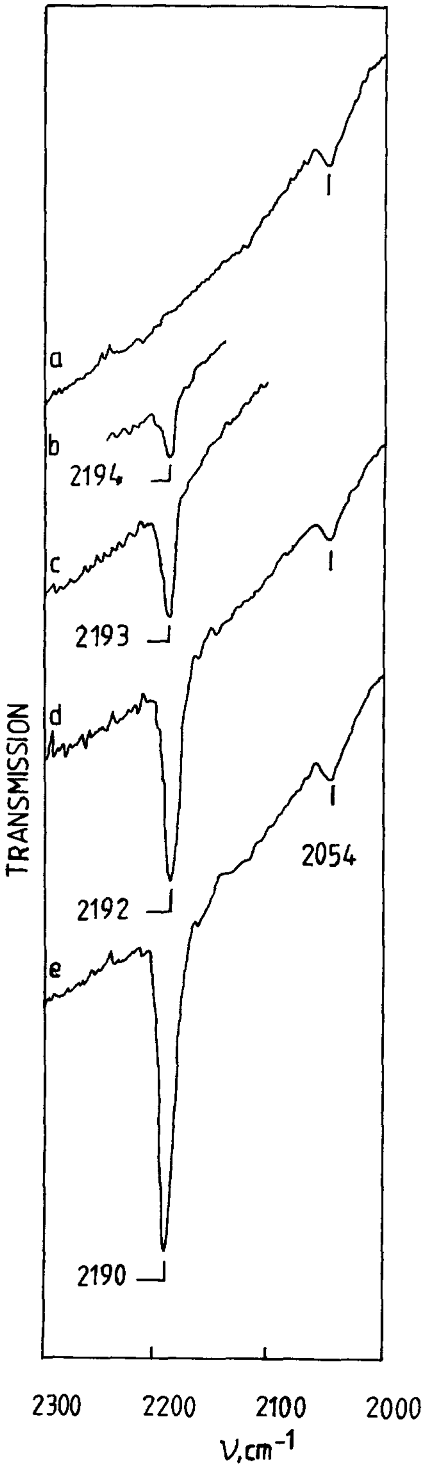


FIG. 5. IR spectra of VT1 after activation at 400°C (a) and after adsorption of 3- (b), 7- (c), 20- (d), and 45- (e) Torr CO.

band has been assigned to CO coordinated on surface c.u.s. ions (*43*).

The experimental results obtained show that, contrary to TiO_2 sample, VT1 is characterized by only one type of Lewis acid sites, able to coordinate CO. Moreover, this sample also possesses a Brønsted activity.

3. Sample VT2. The IR spectrum of sample VT2 (Figs. 6 and 7) is similar to that of VT1. A band at 3680 cm^{-1}, which corre-

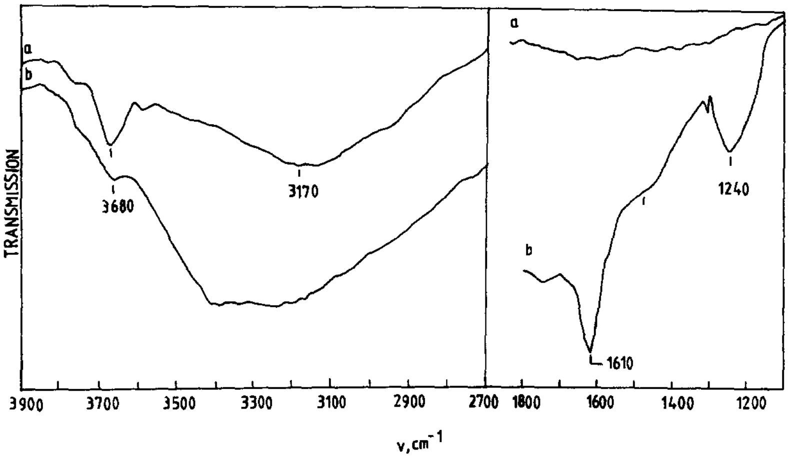


FIG. 6. IR spectra of VT2 after activation at 400°C (a) and after adsorption of NH_3 (5 Torr, followed by 15-min evacuation) (b).

sponds to the ν(OH) of isolated V—OH groups, and a broadband with a maximum centered around 3170 cm^{-1}, due to H-bonded hydroxyl groups, are observed (Fig. 6). However, the latter is much more intense than in the case of the VT1 sample. The higher frequency of the isolated V—OH groups in this case is probably due to the influence of the extra deposited vanadium–oxo species. In the 2500–2000 cm^{-1} region there is a band with a maximum at 2060 cm^{-1}, which is assigned to the first overtone of the V^{5+}=0 stretching modes (*21, 22, 26, 46*).

The adsorption of ammonia (5 Torr, followed by 15-min evacuation), in addition to the bands due to N—H stretching modes, leads to appearance of two bands with maxima at 1610 and 1240 cm^{-1} (Fig. 6). They correspond to $\delta_{as}(NH_3)$ and $\delta_s(NH_3)$ modes of coordinatively bonded ammonia, respectively (*43*). A low-intensity band at about 1460 cm^{-1}, which is typical of ammonium ions, is also observed. This and the fact that the band due to V—OH groups at 3680 cm^{-1} decreases in intensity indicate that the observed Brønsted acidity is due to isolated V—OH groups again. Disappearance of the band at 2060 cm^{-1}, assigned to the first overtone of V=O stretching modes, is observed after adsorption of ammonia as in the case of VT1 sample.

The introduction of CO at room temperature produces no substantial changes in the spectrum (Fig. 7). Moreover, the spectrum is preserved even after heating the sample in a CO atmosphere at 400°C or in oxygen at 500°C. The adsorption of CO at room temperature after precalcination of the sample at 500°C leads to the appearance of weak bands at 2200 and 1940 cm^{-1} which indicate that during the treatment some changes in the surface state have occurred.

In contrast to sample VT1, the absorption of CO does not reveal the presence of c.u.s. cations on the surface of VT2. However, a Lewis acidity, different from that of VT1 sample and both pure and H_2O_2 pretreated titania, was detected by ammonia adsorption. A certain amount of protonic sites was also observed.

The acidity of the isolated V—OH groups is measured by the so called "hydrogen bond" method as well. According to it (*50*), the value of the ν(OH) spectral shift after adsorption of weak bases is a quantitative characteristic of the hydroxyl group acidity. When the VT2 sample comes in contact with benzene vapor (20 Torr), the frequencies of the surface hydroxyl groups are shifted down

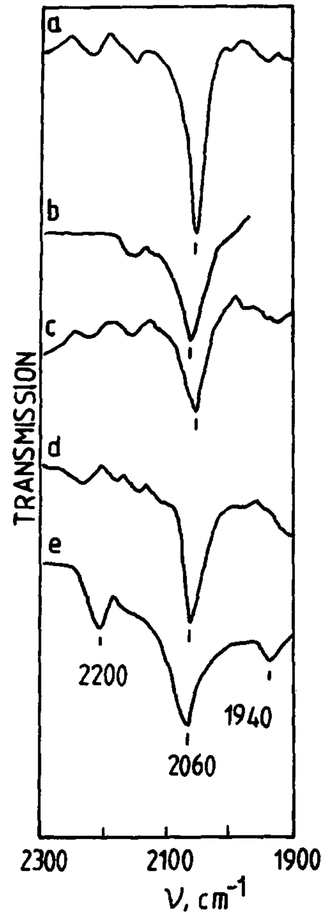


FIG. 7. IR spectra of VT2 after activation at 400°C (a), subsequent introduction of 30-Torr CO in the cell (b), after heating in the same atmosphere at 400°C (c), pumping off and heating in 100-Torr oxygen at 500°C (d), evacuation and introduction of 20-Torr CO at room temperature (e).

from 3680 to 3470 cm^{-1}, i.e., $\Delta\nu(OH) = 210$ cm^{-1} (Fig. 8). This corresponds to a moderate Brønsted acidity. However, it should be noted that the observed shift may be due to a secondary interaction between a surface hydroxyl group and a benzene molecule adsorbed on other sites. A similar effect has been observed earlier on pure anatase (*48*).

DISCUSSION

The c.u.s. titanium cations on the anatase surface can be divided into several groups (*37, 38*):

1. Inert Ti^{4+} cations, inactive toward CO adsorption at room temperature.
2. strong (α) and weak (β) Lewis acid sites;
3. titanium ions associated with surface hydroxyl groups.

The results of the present paper show that the localization of vanadium–oxo compounds on the anatase surface depends on the presence or absence of preadsorbed hydrogen peroxide during the synthesis.

Sample VT1

The results of surface testing with ammonia have revealed the existence of both Brønsted and Lewis acidity on the VT1 sample surface. The value of $\delta_s(NH_3)$, which is sensitive to the type of the coordination sites, corresponds to the Ti^{4+}—NH_3 complexes (*38, 43, 45, 48*). The high-frequency shoulder of the latter band, however, might be related to the $\delta_s(NH_3)$ of either Ti^{4+}—NH_3 species formed on α-Lewis acid sites of anatase (*38, 45*) or V^{5+}—NH_3 complexes (*43, 51*). Comparison with the results of the CO adsorption study supports the second assumption. The position of the corresponding carbonyl band and its behavior during the change of the CO equilibrium pressure show that this band may be as-

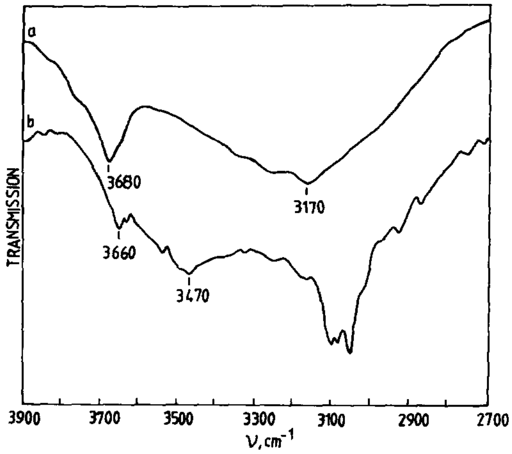


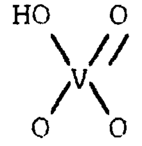
FIG. 8. IR spectra of VT2 after activation at 400°C (a) and subsequent contact with 20-Torr benzene vapor (b).

signed to carbonyls of the Ti^{4+}—CO type formed with the participation of the β-Lewis acid sites of anatase (*38, 43–45*). The somewhat higher frequency is probably due to the influence of vanadia on the electron state of the support. A similar effect is observed for Co^{2+}/TiO_2 samples (*44*). In this case, the α-Lewis acid sites, which are characteristic of TiO_2, are not observed; i.e., after the vanadia deposition they are blocked, whereas the β-sites remain free. The Ti—OH groups of the support have disappeared, which indicates their participation in the synthesis process. The Lewis acidity of the VT1 is mainly due to the presence of c.u.s. β-Ti^{4+} ions on the sample surface.

Hence, the vanadium–oxo species on the activated VT1 sample are localized (i) on the planes characterized by four-coordinated titanium cations, which represent the α-acid sites, (e.g., (110), (111), and (113) (*38, 45*)) and (ii) on some edges, where the surface OH groups are situated mainly (*38*).

The high values of ν(V=O) and the corresponding overtone (2054 cm^{-1}) indicate the absence of polymer structures. As shown by Frederickson and Hausen (*52*), crystalline polyvanadates manifest V=O stretching frequencies in the 1000–950 cm^{-1} region. The value of 2ν(V=O) is also an indication of the absence of a separate V_2O_5 phase (*20, 21, 46*), which is in agreement with the absence of ammonia-soluble surface vanadium compounds on the sample. The V=O vibrations for the VT1 sample coincide with those for $VOCl_3$ (1035 cm^{-1} (*53*)), where isolated V^{5+}=O groups exist and V^{5+} ions are four-coordinated. The higher coordination of V^{5+}, obtained from the UV–vis spectroscopy data, may be due either to the complete saturation of the coordination sphere by oxygen ions or to the presence of adsorbed water molecules on the air-dry samples used. The thermovacuum treatment causes the formation of c.u.s. species, the presence on the surface of which has been detected by ammonia adsorption. The fact that only one frequency of V=O vibrations is observed suggests that O=V=O fragments are not characteristic of the surface species, since in the other case both symmetric and asymmetric stretching vibrations should be observed.

The above considerations and the presence of isolated surface V—OH groups permit the assumption about the existence of monomeric surface species with the following structure:



(I)

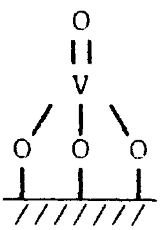
Scheme 1

localized near the α-acid sites.

This structure is similar to that proposed by Bond *et al.* (*18*). However, these authors are of the opinion that the electrons in the O=V–OH fragments are delocalized, which is not observed with our samples.

It is known that, under the adsorption conditions used (pH < 1 and below 1 wt% NH_4VO_3) vanadium is present in the solution only in the form of hydrated mononuclear cation $VO_2^+ \cdot nH_2O$ (*54, 55*). Most probably the adsorption of these cations on anatase proceeds on the c.u.s. oxygen ions situated in vicinity of the α-Lewis acid sites and the structures proposed above are formed after dehydration during the calcination.

When the surface hydroxyl groups of anatase participate in the adsorption, the following species are probably formed after the calcination:



(II)

Scheme 2

It should be noted that Scheme 2 is identical to the structures proposed by Went *et al.* (25). Our results evidence that the formation of structures of type **(I)** or **(II)** is determined by the site where the vanadium–oxo species are localized.

The question whether a V—OH group exists in the structures **(I)** and **(II)** is discussed further on.

Sample VT2

The data on the Lewis acidity of sample VT2 are, at first site, contradictory. The results on CO adsorption have shown the complete absence of this kind of acidity. On the other hand, ammonia adsorption has revealed the presence of Lewis acid sites: the band position of $\delta_{as}(NH_3)$ is characteristic of ammonia coordinated to V^{5+} ions (*43, 51*); no Ti^{4+}—NH_3 complexes are detected. A similar behavior has been described for V^{5+}-containing systems (*22, 43, 51*) and explained by both the weak electron donor properties of the CO molecules and the weak electron acceptor properties of the vanadium(V) ions, probably due to their high coordinative saturation (*51, 56*). Being a strong base, ammonia is able to be coordinated to vanadyl species. This results in the disappearance of the V═O overtone from the spectrum.

Busca (*22*) has interpreted the strong Lewis acidity on vanadia–titania catalysts by the presence of V^{4+} ions. It is known (*43, 56*) that these ions are able to interact with CO forming carbonyls with IR bands in the region 2205–2170 cm^{-1}. Such bands are not registered on sample VT2 after introduction of CO, which is why we think that the Lewis acid sites observed by ammonia adsorption are due to the presence of c.u.s. V^{5+} ions on the sample surface.

The weak absorption at 2200 cm^{-1} registered after CO introducing to sample, preheated at a higher temperature in oxygen, may be due to carbonyls formed on the α-acid sites of anatase (*38, 45*). The existence of these sites can be explained by migration of VO_x species on the surface during the calcination. As a result, part of the α-acid sites of the support is liberated. However, the probability for the observed carbonyls to be of a V^{4+}—CO type should also be noted (*43, 56*). This possibility is supported by the presence of a band at 1940 cm^{-1}, which may be assigned to $2\nu(V^{4+}{=}O)$ vibrations and is in agreement with the results of UV–vis spectroscopy, which have revealed the appearance of V^{4+} after heating the samples at high temperatures.

The experimental results show that, in contrast to sample VT1, the surface vanadia compounds on VT2 block both types of Lewis acid sites on the anatase. The surface hydroxyl groups of the support have also participated in adsorption, similarly to the case of VT1. Besides the species observed on VT1, additional vanadium–oxo groups exist on the sample surface. They are located on the anatase planes on which the β-sites (five-coordinated Ti^{4+} ions) are situated, namely (100), (010), (101), and (011) (*38*). The structure of the species formed is of type **(I)**. This fact is supported by the higher hydroxyl coverage of the sample VT2 than that of VT1.

The presence of H_2O_2 on anatase during the adsorption of VO_x species from aqueous solutions permits the formation of peroxide bridges between the titanium and vanadium ions. It is known that peroxocomplexes are characteristic of both elements. This possibility may explain the blocking of the β-Lewis sites in this case. However, some differences are observed between the species formed near the α- and β-sites. The latter are characterized by H-bonded hydroxyl groups. This may be explained by the higher density of c.u.s. Ti^{4+} ions on the planes where the β-sites are situated (*37*).

The observed distribution of vanadia on VT1 and VT2 samples is in agreement with the results of XPS and the chemical analysis. The higher vanadium coverage on the VT2 sample is due to the blocking of the β-sites of anatase in addition to the sites where vanadium species are localized on the VT1 sample. Moreover, the calculated values of vanadium surface concentrations (see Table 1) coincide very well with the expected concentration of the respective active sites for adsorption on the anatase surface (ca. 1.5 Lewis sites nm^{-2} and 0.6 Ti—OH nm^{-2} (*38, 39*).

It is of interest to discuss the eventual catalytic behavior of the samples VT1 and VT2 with respect to the *o*-xylene oxidation. It is shown (*1, 4*) that Ti^{4+} Lewis acid sites favor the complete combustion of some intermediates of the reaction. Hence, the VT1 sample, containing exposed β-Ti^{4+} ions, should possess a selectivity lower than that of VT2. Indeed, a similar behavior has been described by Wachs *et al.* (*1*) and Cavani *et al.* (*3*). These authors have observed a better selectivity for vanadia–titania catalysts having a higher vanadium content.

Catalysts prepared by adsorption from aqueous solutions (see for example Refs. (*32, 33*) and sample VT1) are characterized by a vanadia coverage insufficiently high to block all Ti^{4+} Lewis acid sites. On the contrary, the proposed method of synthesis in the presence of hydrogen peroxide combines the simplicity of the catalyst preparation and the desired distribution of the surface vanadate species.

CONCLUSIONS

1. A new method of synthesis of vanadia–titania catalysts, based on adsorption from aqueous solutions of ammonium vanadate, is proposed.

2. The sample obtained after adsorption of VO_2^+ on pure anatase and subsequent calcination, is characterized by blocking of the strong Lewis sites of the support. The Ti–OH surface hydroxyl groups are absent, whereas isolated V–OH groups are formed. The weak Lewis acid sites of anatase remain free.

3. When anatase is preliminary treated with hydrogen peroxide, the weak Lewis acid sites are also occupied.

4. The surface vanadium(V) species formed after calcination possess one vanadyl group each. When localized at the Lewis acid sites, they also contain a V–OH group. No hydroxyl groups are characteristic of vanadates formed after exchange with anatase surface OH groups.

5. Both samples have a small amount of Brønsted and a higher amount of Lewis acid sites. The Lewis acidity of the sample prepared by adsorption on pure anatase is mainly due to c.u.s. Ti^{4+} cations, whereas in the other case c.u.s. V^{5+} only are observed.

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