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Grafting of V_2O_5 Monolayers onto TiO_2 from Alkoxide Precursors: A Diffuse Reflectance FTIR Study

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Vanadia layers are immobilized on a titania support by the selective reaction of the surface hydroxyl groups with the reagent vanadyl triisopropoxide. The impregnation and calcination processes are studied *in situ* by diffuse reflectance FTIR spectroscopy. The isopropoxide groups of the precursor are oxidized to acetone during calcination; this result is confirmed by acetone adsorption and isopropanol oxidation experiments. Calcination in an inert gas atmosphere (argon or nitrogen) generates a reduced state of the catalyst; UV–VIS reflectance spectroscopy shows that vanadium(IV) coexists with vanadium(V) in the first immobilized monolayer, which consists of polymeric arrays of distorted VO_6 coordination units. Observation of the overtones of the V=O stretching vibration yields valuable information on the coordination geometry, as well as on the oxidation and hydration state. An overtone band observed at 2060 cm^{-1} is attributed to VO^{2+} ions at an oxygen-deficient surface site. © 1990 Academic Press, Inc.

INTRODUCTION

Highly active catalysts for the selective catalytic reduction (SCR) of NO with NH_3 have recently been prepared (*1, 2*) by the specific reaction of vanadyl alkoxides $VO(OR)_3$ with the surface hydroxyl groups of TiO_2 (predominantly anatase), in a water-free solvent. Successive monolayers of vanadia can be selectively grafted to the support by this technique (*1*); in the most active catalyst a V_2O_5 layer of ~1-nm thickness is detected by high-resolution transmission electron microscopy. In a recent publication (*3*) Raman and FTIR spectroscopy have been used to characterize the structure of these catalysts. We have shown that during the first and second impregnation with vanadyl triisobutoxide, a vanadium concentration of 0.17 mmol/g, which is approximately equal to the OH-group concentration of 0.15 mmol/g determined on the support prior to impregnation, is immobilized, (*1*). This was defined as a "monolayer" of V_2O_5 on the carrier; Raman spectroscopy revealed that the vanadium(V) is present in the form of disordered polymeric arrays of octahedral coordination units anchored on the TiO_2 surface (*3*). Secondary hydroxyl groups bound to vanadium are created during calcination of these catalysts. Further layers of V_2O_5 can then be grafted on top of the first by subsequent impregnations with the vanadyl alkoxide reagent (*1, 2*). These second and possibly further layers are structurally different from the first layer which is bound directly to the support. This is evidenced most clearly by a shift in the highest frequency Raman band from 1030 to 996 cm^{-1} and by changes in IR overtone absorptions around 2000 cm^{-1} (*3*); this point will be addressed in detail in this paper. After four impregnations, the highest turnover rates for SCR were achieved (*2*). At this stage, the catalytically active second (and higher) layer(s) are structurally similar to (*3*), but not identical to, crystalline V_2O_5; in particular, they are reduced at significantly lower temperatures (*2*).

The aim of the present paper is to study the process of immobilization and the

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changes occurring during calcination of the catalysts, using FTIR spectroscopy. The reaction products released from the immobilized precursor are identified, and the assignments are confirmed by adsorption and partial oxidation experiments. Information on the state of the catalyst after calcination in an inert gas atmosphere is obtained by FTIR and diffuse reflectance spectroscopy.

The structural assignments are based on a large body of vibrational spectroscopic data (*4–13*) on V_2O_5/TiO_2 prepared by a variety of techniques, with loadings varying between ~0.1 and ~20 wt%. In particular, reference will be made to the work of Busca *et al.* (*9–11*), who have studied catalysts prepared by impregnation of TiO_2 with $VOCl_3$. These authors have successfully used isopropanol adsorption and partial oxidation as a test reaction (*10, 11*). Busca and Lavalley (*12*) have demonstrated that the observation of V=O overtone bands can be used to monitor the state of the catalysts; the sensitivity of these bands to the dehydration state was investigated (*13*). Our study of the calcination process in the temperature range between 300 and 500 K (*14*) complements recent experiments performed by Bond *et al.* (*15*) at higher temperatures.

EXPERIMENTAL

The pretreatment of the catalyst precursor (P25, Degussa, consisting of ~70% anatase and ~30% rutile) and the procedure used for the successive immobilization of V_2O_5 layers have been described in detail elsewhere (*1, 2*). Briefly, each impregnation cycle consists of precalcination of the precursor, reaction with the vanadyl alkoxide in dry hexane in an inert gas atmosphere (dry argon), washing, drying, and calcination (*1*). During this last step secondary V–OH groups are created, which can further react with the vanadyl alkoxide in the next impregnation cycle. Structural changes occurring during the first through fourth impregnation are studied. In particular, the process of calcination is monitored by diffuse reflectance FTIR during each step. Catalysts prepared in this manner will be denoted as TiO_2–nV-unc ($n = 1 \ldots 4$) prior to calcination and as TiO_2–nV after calcination, as in our previous communications (*1–3*).

To ensure an equal hydration state of the surface, the titania support and each precursor was calcined at 573 K for 1 h prior to impregnation. Note that in Ref. (*1*), vanadyl triisobutoxide was used as the impregnation reagent. In this study, the slightly more reactive vanadyl triisopropoxide $VO(O\text{–}iC_3H_7)_3$ (VTIP) has been employed, which is commercially available from Alfa Chemicals. The precursor material was suspended in ~40 ml of dry hexane, and 0.35 ml of VTIP was added with a syringe; this corresponds to a VTIP concentration of 1.5×10^{-2} *M* in the resulting solution. Subsequently the suspension was stirred for 12 h at 333 K in an argon atmosphere. Acetone and isopropanol were obtained in p.a. quality from Merck.

Diffuse reflectance IR spectra were recorded on an FTIR instrument (Digilab, Model FTS 80) equipped with an "environmental chamber" (Spectra Tech). Scans (256) have been accumulated for each spectrum. The cell was constantly purged with a small flow of argon during all experiments. The freshly impregnated sample TiO_2–nV-unc was introduced into the environmental chamber under inert gas and was slowly heated to 473 K under argon. Spectra were recorded at the temperatures indicated below, allowing for an equilibration time of 3 min after each temperature step. For comparison, impregnated samples were also calcined *ex situ* in oxygen at 573 K for 3 h.

Diffuse reflectance spectra are conventionally presented in the form of Kubelka–Munk plots (*16*), $f(R) = [1 - (R/R_0)]^2/2(R/R_0)$, where R and R_0 denote the reflectivities of sample and reference, respectively. This representation tends to emphasize strong peaks in the spectrum, at the expense of smaller features. In the present study, species are identified in terms of their vibrational frequencies and by temperature-dependent changes in the spectrum. As the line intensities are only used for qualitative interpretation, we have found it more convenient to plot the negative logarithm of the reflectivity change, $-\log (R/R_0)$, which will be referred to below as "absorbance." In the case of small reflectivity changes, $R/R_0 = 1 - \varepsilon$, the two representations become proportional to each other, i.e., $f(R) \approx \varepsilon/2$ and $-\log (R/R_0) \approx \varepsilon/2.3$.

RESULTS

(*a*) *Immobilization of* $VO(O\text{–}iC_3H_7)_3$ *and Calcination*

The spectrum of the TiO_2 support (top trace in Fig. 1) exhibits four resolved stretching vibrations in the 3710- to 3640-cm^{-1} range (*8*), of which the band at 3640 cm^{-1} is prominent in intensity. The reflectivity minimum (apparent absorbance maximum) at 930 cm^{-1} is due to a TiO_2 absorption centered at 820 cm^{-1}. As the undiluted TiO_2 support is being investigated, the intensive absorption band gives rise to a characteristic dispersion-type lineshape (*16*) in the reflection spectrum, with a reflectivity minimum at 930 cm^{-1}. This minimum shows up as a "peak" in the plot of $-\log (R/R_0)$ presented in Fig. 1.

Impregnation with vanadyl triisopropoxide results in very pronounced changes, as seen in the second trace in Fig. 1. The OH absorptions of the support have completely disappeared, showing that all TiO_2-bound surface hydroxyl groups have reacted with $VO(O\text{–}iC_3H_7)_3$. (Vanadyl triisopropoxide is apparently more reactive than the isobutoxide reagent $VO(O\text{–}iC_4H_9)_3$ used in Refs. (*1–3*), where two impregnation steps were required to achieve monolayer coverage). A series of well-resolved bands appears which can all be assigned to vibrations of vanadyl-bound isopropoxide groups, by reference to the spectrum of $VO(O\text{–}iC_3H_7)_3$ reported in the literature (*17*). Assignments of the more important bands are summarized in Table 1. The V═O stretching vibration around 1000 cm^{-1} is not detected due to the intense absorption of the support in this range. The broad absorption centered at 3250 cm^{-1} is due to physisorbed H_2O (*8*).

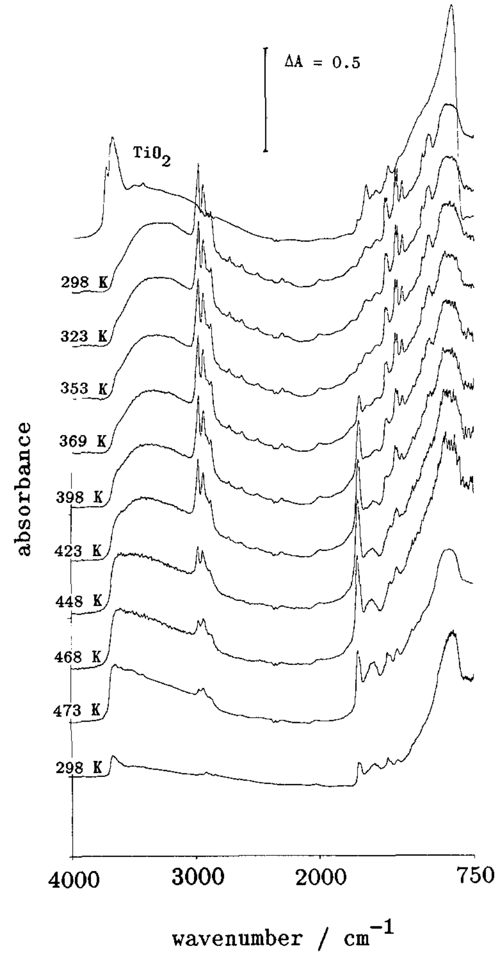


FIG. 1. Diffuse reflectance FTIR spectra recorded (at the temperatures indicated) during calcination of a catalyst prepared by single impregnation of TiO_2 (P25, Degussa) with $VO(O\text{–}iC_3H_7)_3$ in a stream of argon. Scans (256) have been accumulated for each temperature at a resolution of 4 cm^{-1}. The top trace represents the spectrum of the support; the bottom trace was obtained after cooling the calcined catalyst to room temperature. "Absorbance" spectra, i.e., the negative logarithm of the reflectivity change (R/R_0), are plotted in this and subsequent figures unless otherwise noted (see Experimental).

The calcination process was studied by increasing the temperature of the catalyst in

TABLE 1

Selected Vibrations of $VO(O\text{-}iC_3H_7)_3$

Wavenumber/cm^{-1}	Assignment (from Ref. (*17*))
2972, 2936, 2874	CH_3 stretching, asym. and sym.
1455, 1407, 1392, 1375	CH_3 deformation, asym. and sym.
1333	CH deformation
1174	CH_3 wagging
1125	C–O stretching

steps of 20 K in a continuous flow of argon. Little change is observed up to a temperature of 363 K (Fig. 1). At ~368 K the bands of the immobilized precursor start to disappear and a new band at 1680 cm^{-1} increases in intensity. At 448 K this feature represents the most intense absorption of the spectrum. On its low-frequency side, a broad band centered at 1560 cm^{-1} is discerned.

When the catalyst is held at 473 K for a longer period of time (15 min), the decomposition of the immobilized alkoxide precursor goes to completion and the absorption at 1680 cm^{-1} decreases in intensity to finally disappear. The latter peak must therefore be assigned to a volatile product of the calcination reaction. The frequency of the band suggests assignment to a chemisorbed carbonyl compound, i.e., acetone. To test this hypothesis, acetone adsorption and isopropanol oxidation experiments have been performed and these are described below in Sections (b) and (c).

After complete calcination the catalyst is cooled to room temperature, and the spectrum shown in the bottom trace of Fig. 1 is recorded. When compared to the spectrum of the support (top), several new bands are observed. The vibration at 3650 cm^{-1} is assigned to secondary hydroxyl groups bound to surface vanadyl species (*8*). A broad band centered at 1560 cm^{-1} is attributed to an overtone of the V–O–V stretching vibration at 820 cm^{-1}, in agreement with Busca *et al.* (*9*). Further bands are observed at 1550, 1445, and 1380 cm^{-1} (shoulder). These bands are clearly seen when the spectrum taken at 473 K (Fig. 1) is plotted on an expanded scale; they are also evident in the spectrum of the calcined catalyst at room temperature (top trace in Fig. 2). Hussein *et al.* (*18*) have assigned these bands to surface-bound acetate which is formed by oxidation of the chemisorbed acetone. This assignment is supported by our observation that the same group of bands appears in the isopropanol oxidation experiment at the highest temperature employed (373 K trace in Fig. 3).

Analogous runs have been performed studying the impregnation and calcination steps $TiO_2\text{–}1V \rightarrow TiO_2\text{–}2V\text{-unc} \rightarrow TiO_2\text{–}2V$

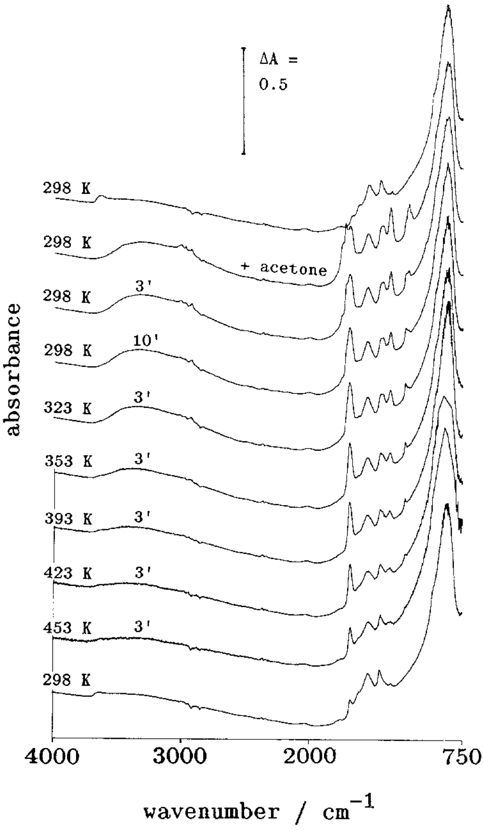


FIG. 2. Adsorption of acetone on the surface of a singly impregnated catalyst (TiO_2–1V). The spectrum of the catalyst is shown in the top trace. After adsorption of 10 μl of acetone, the second spectrum results, which changes with time (labels in minutes) while the catalyst is being purged with argon. Subsequently chemisorbed acetone is desorbed by the temperature program indicated.

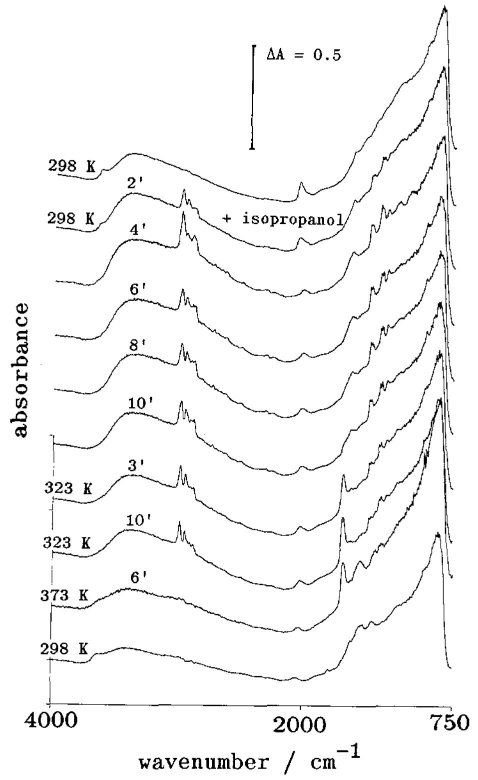


FIG. 3. Isopropanol oxidation on the surface of catalyst TiO_2–4V calcined in air. Top trace corresponds to the catalyst prior to adsorption; second and third trace represent isopropanol adsorption. During the temperature program, chemisorbed acetone is formed by oxidation of isopropanol; at higher temperatures all species are desorbed from the surface.

and TiO_2–3V → TiO_2–4V-unc → TiO_2–4V. Qualitatively, the same sequence of events is observed as described above; the spectra are therefore not reproduced but are available from the authors on request. For the calcined catalyst TiO_2–4V, the V=O stretching absorption is clearly discernible as a shoulder at 1035 cm^{-1} (cf. Ref. (*3*).

(*b*) *Acetone Adsorption*

To confirm the assignment of the abovementioned peak at 1680 cm^{-1} to chemisorbed acetone, 10 μl of acetone were evaporated and adsorbed onto the surface of the freshly calcined catalyst TiO_2–1V at room temperature (Fig. 2). The top trace refers to the surface before adsorption. After adsorption (second trace), three bands appear in the carbonyl stretching region at 1740 (shoulder), 1710, and 1680 cm^{-1}, as well as further bands at 1565, 1420, 1365, and 1215 cm^{-1}. When the temperature is raised, the doublet of bands at 1740 and 1710 cm^{-1} first decreases in intensity (298 K, spectra taken after 3 and 10 min) and then disappears completely at 323 K. At 353 K only a sharp band at 1680 cm^{-1} remains visible in the carbonyl stretching region. At 423 K the corresponding species starts to desorb and has mostly disappeared at 473 K, at which temperature the spectrum corresponds again to that of the calcined catalyst prior to acetone adsorption.

The assignment of these observations is straightforward by reference to the spectrum of acetone in the liquid phase (e.g., in CCl_4: 1740, 1720, 1412, 1365, and 1218 cm^{-1} (*19*)). Thus the pair of bands at 1740 and 1710 cm^{-1} is assigned to physisorbed acetone, which desorbs between 298 and 323 K. The absorption at 1680 cm^{-1} corresponds to the more strongly bound chemisorbed acetone which desorbs at 453 K, i.e., right in the range that was also observed for the product of calcination discussed in Section (a). The assignment to surface-bound acetone is supported by a recent normal coordinate analysis (*20*), where it was found that the frequency of the C=O stretching vibration is significantly lowered when the terminal oxygen is bound to a surface coordination site, in the direction of the C=O bond.

(*c*) *Isopropanol Oxidation*

In Section (a) it was suggested that acetone is formed by oxidation of isopropoxide groups during calcination. As a second experiment to test this hypothesis, 10 μl of isopropanol was evaporated and adsorbed onto the surface of a TiO_2–4V catalyst, which had previously been calcined in oxygen at 573 K for 3 h. The spectrum of this catalyst before the adsorption (top trace in Fig. 3) exhibits a V=O fundamental vibration at 1020–1035 cm^{-1} and an intensive overtone absorption at 1950–2050 cm^{-1}. Upon isopropanol adsorption, the spectrum shown in the second trace of Fig. 3 results. A comparison with Fig. 1 and with the data of Ref. (*17*) shows that the vibrations can be assigned to surface-bound isopropoxide groups, while the characteristic ν(OH) and δ(OH) bands of undissociated alcoholic hydroxyl groups are completely absent.

Spectra were first recorded at 298 K 2 and 10 min subsequent to isopropanol injection; the intensity of the isopropanol absorption increases somewhat during that time. After 10 min a weak shoulder at 1680 cm^{-1} is detected, which develops into a pronounced peak upon raising the temperature to 332 K. Upon further heating, the intensity of this peak decreases; it disappears at 423 K. In view of the results of Section (b), this absorption can be readily assigned to chemisorbed acetone formed by the oxidation of the adsorbed isopropoxide.

Note that isopropanol oxidation is only observed for catalysts that have previously been calcined in air or oxygen. If one performs the same experiment on a freshly impregnated catalyst not exposed to O_2, no conversion of isopropanol is observed. This point will be addressed more fully below.

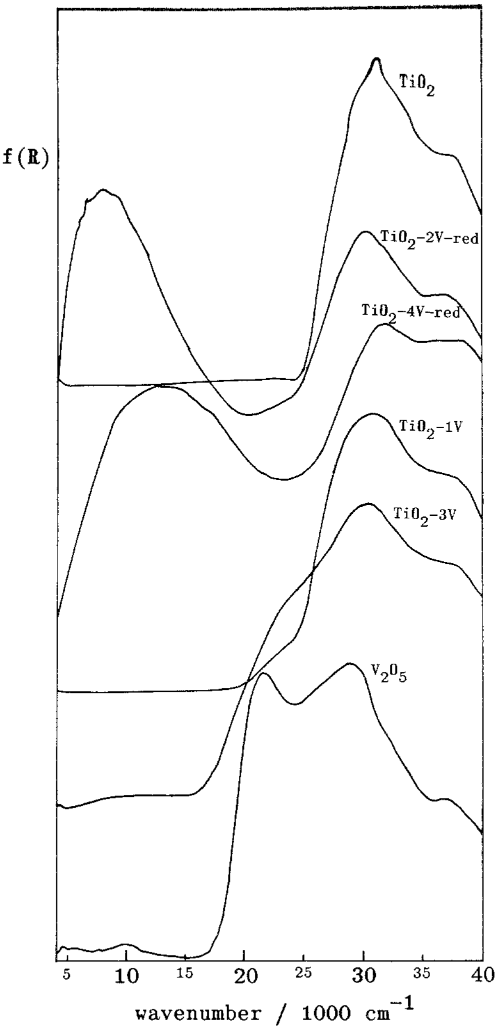


FIG. 4. UV–VIS diffuse reflectance spectra of the catalysts investigated in this work. The Kubelka–Munk function *f*(*R*) (*16*) is plotted for the following samples (top to bottom traces): TiO_2 support; TiO_2–2V-red; TiO_2–4V-red; TiO_2–1V; TiO_2–1V; TiO_2–3V; crystalline V_2O_5. For nomenclature of the samples, see text.

(*d*) *UV–VIS Diffuse Reflectance Spectra*

The white color of the TiO_2 support changes to dark blue during impregnation with $VO(O\text{–}iC_3H_7)_3$. When the catalyst is calcined in argon in the environmental chamber up to a temperature of 473 K, oxygen being excluded, the catalyst retains its blue color. These catalysts will be referred to as TiO_2–*n*V-red. However, when the catalyst is calcined in air or oxygen at 573 K, the color changes to yellow, with the intensity of coloration changing from pale yellow (TiO_2–1V) to orange (TiO_2–4V). For comparison, microcrystalline V_2O_5 powder exhibits the well-known brown color.

For a quantification of these color changes, UV–VIS diffuse reflectance spectra have been recorded. The corresponding Kubelka–Munk functions *f*(*R*) (*16*) are presented in Fig. 4. The anatase support (top trace) is characterized by an absorption edge at 26,200 cm^{-1}. The blue catalyst TiO_2–2V-red shows absorptions at 9,000 cm^{-1}, 11,000 cm^{-1}, and a shoulder at 13,000 cm^{-1}; for TiO_2–4V-red one observes a broad band with a maximum between 13,000 and 16,000 cm^{-1}. In contrast, the air-calcined (yellow) catalysts are character-

TABLE 2

Overtone Bands of the V=O Stretching Vibration

Catalyst	Wavenumber/cm^{-1}				
1V-red	2056	2035	—	—	
1V-ox	—	2040	—	—	
1V-hyd			2020 -	1890	(Broad)
2V-red	2060	2035	—	—	
2V-ox	—	2042	—	—	
2V-hyd			2020 -	1890	(Broad)
3V-red	2058	2035	2020	1990	
3V-ox	—	2045	2020	1990	
3V-hyd			2020[a]	1975	1950
4V-red	2061	2043	2020	1990	
4V-ox	—	2043	2020	1990	
4V-hyd			2020	1975	1950

[a] Weak.

ized by a broad band between 20,000 and 25,000 cm^{-1}, which appears as a shoulder for TiO_2–1V and as a pronounced absorption for TiO_2–3V. The reference spectrum of crystalline V_2O_5 powder is shown in the bottom trace.

(*e*) *Overtone Absorptions*

Monitoring the overtone region around 2000 cm^{-1} of the V=O stretching motion has proven to be a valuable tool to elucidate the structure and oxidation state of the surface-bound vanadia, as well as the hydration state of the surface (*12, 13*). We have therefore measured the FTIR spectra for all catalysts after heating in argon at 473 K (TiO_2–nV-red) and after heating in oxygen at 573 K (TiO_2–nV-ox). Results are compiled in Table 2. For completeness, we have also added the data for catalysts TiO_2–nV exposed to ambient air for several days, whereafter the surface is equilibrated with atmospheric water (TiO_2–nV-hyd).

The changes occurring upon the transition from the low-coverage TiO_2-bound VO_x surface phase to the two- and multilayer structure, which structurally resembles crystalline V_2O_5, are clearly reflected in the overtone spectra. The systems TiO_2–2V and TiO_2–4V are shown as an example. The catalyst TiO_2–2V-red (Fig. 5, top trace) exhibits two absorptions: in addition to the 2035-cm^{-1} band (which probably corresponds to the 2045-cm^{-1} band reported by Busca *et al.* (*9*), another strong absorption is detected at 2060 cm^{-1}, which, to our knowledge, has not been previously observed. After calcination in oxygen (Fig. 5, bottom) this additional peak is absent; the catalyst exhibits a single absorption at 2042 cm^{-1}. The system TiO_2–4V exhibits the same behavior (cf. Fig. 6 and Table 2), but in addition, another strong band at 2020 cm^{-1} and a shoulder at 1990 cm^{-1} are observed both in the reduced (TiO_2–4V-red) and in the oxidized catalyst. Note that after the isopropanol oxidation experiment described in Section (c), an overtone spectrum is observed (bottom trace in Fig. 6) which matches that of the reduced catalyst (top).

DISCUSSION

The results presented above will be interpreted to derive information on the processes occurring during calcination and on the primary products formed. The temperature program shown in Fig. 1 clearly demonstrates that the immobilized precursor decomposes when the temperature is raised

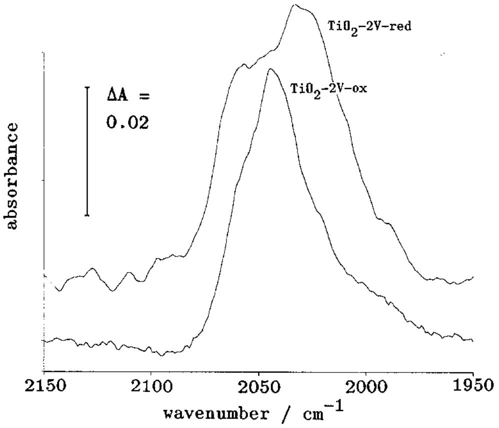


FIG. 5. Diffuse reflectance FTIR overtone spectra of catalyst TiO_2–2V after calcination in argon (473 K, top) and in oxygen (573 K, bottom). Both spectra correspond to the dehydrated surface.

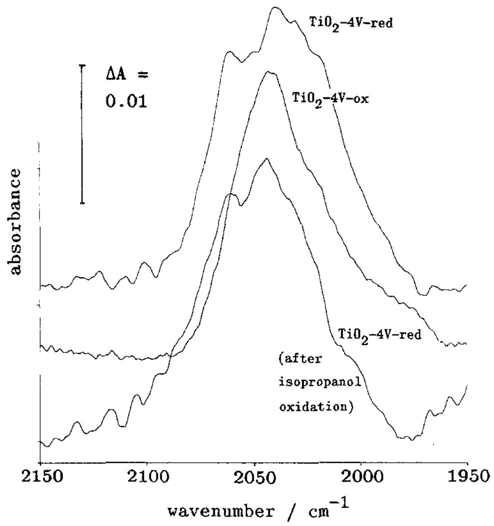
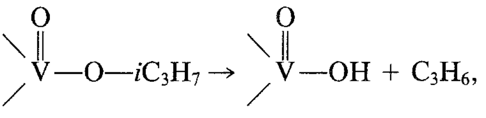


FIG. 6. Diffuse reflectance FTIR overtone spectra of the dehydrated catalyst TiO_2–4V after calcination in argon (top), after calcination in air (middle), and after experimentation with isopropanol oxidation (bottom).

above 363 K. This finding may be supplemented with another observation: when the impregnated catalyst is stored under inert gas at room temperature for a week, and then transferred to the environmental chamber, a small but unambiguous peak of chemisorbed acetone at 1680 cm^{-1} is also detected. This shows that the decomposition reaction, which apparently is characterized by a low activation energy, is already proceeding at room temperature, albeit at a low rate. The onset of decomposition at 363 K also explains why Bond and Flamerz (*15*) observed little change in the FTIR spectrum after "drying" the impregnated catalyst at 393 K.

The second point concerns the product of calcination, acetone, which was identified unambiguously from the experiments described in Sections (b) and (c) (acetone adsorption and isopropanol oxidation). Oxidation of the isopropoxide group to acetone and acetate necessarily implies that at least part of the vanadium (V) present on the surface must be reduced during calcination. Two observations are in accordance with this statement: the catalysts remain blue when calcined in inert gas, and they fail to oxidize isopropanol in this state. The combination of isopropoxide oxidation and vanadium (V) reduction differs from the mechanism proposed earlier (*1*) that specifies olefin formation,


$$(\text{O}{=})\text{V}{-}\text{O}{-}i\text{C}_3\text{H}_7 \rightarrow (\text{O}{=})\text{V}{-}\text{OH} + \text{C}_3\text{H}_6,$$

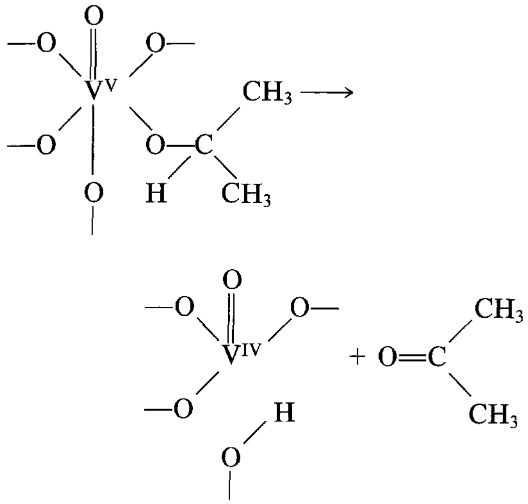
which would involve no change in oxidation state. Due to its high volatility, propene would not be detected in our dynamic FTIR experiments, such that propene formation may be occurring in parallel to acetone formation. In this context, it is interesting to note that Busca *et al.* (*9*) have detected both V(IV) and V(V) on the surface of their catalysts (prepared by impregnation of TiO_2 with $VOCl_3$) after calcination in air at 720 K. However, the fact that the catalysts calcined in argon do not oxidize isopropanol suggests that the reduction of vanadium (V) during calcination prevails under these conditions.

This leads to the question as to what information can be derived on the oxidation state and local coordination geometry of vanadium after calcination in our catalysts, which have been prepared from a different precursor than the systems studied by Busca *et al.* (*9, 10*). UV–VIS diffuse reflectance and FTIR overtone results are most informative in this respect. The catalysts calcined in air are discussed first. Vanadium(V) in an octahedral oxygen environment (VO_6) exhibits a charge transfer transition in the range from 20,000 to 25,000 cm^{-1}, while for tetrahedrally coordinated vanadium(V) the corresponding band occurs between 30,000 and 35,000 cm^{-1}. We do observe a shoulder between 20,000 and 25,000 cm^{-1} for TiO_2–1V and a pronounced band in the same range for TiO_2–3V (Fig. 4). This fact is in complete agreement with our earlier analysis (*3*) that V(V) is present in the form of distorted polymeric arrays of VO_6 in the first monolayer immobilized on the TiO_2 support, and that the second and subsequent layers resemble the crystal structure of V_2O_5 where the local coordination is octahedral as well.

As for the reduced catalysts, a broad band peaking between 13,000 and 16,000 cm^{-1} has been observed for TiO_2–4V-red, in excellent agreement with the literature data for the vanadyl cation VO^{2+} (oxidation state IV) in octahedral environment (*21*). There is significant absorption in the 20,000 to 25,000-cm^{-1} range, which is characteristic for octahedrally coordinated vanadium(V), although no separate peak is resolved. The observation of V(IV) and V(V) is in complete agreement with recent XPS studies on model titania/vanadia interfaces (*22*).

Most revealing is the spectrum of TiO_2–2V-red (Fig. 4) where, in addition to a shoulder at 13,000 cm^{-1}, a strong absorption in the near infrared region at 9,000 cm^{-1} is found. Flynn and Pope (*23*) have assigned this band to an "intervalence charge transfer transition" in mixed valence compounds; there V(IV) ions are neighboring V(V) centers in structures consisting of edge-sharing octahedra (e.g., in isopolydecavanadates $V_{10}O_{28}{}^{6-}$). Thus the observation of an absorption near 9,000 cm^{-1} points again to the simultaneous presence of V(IV) and V(V) in the reduced catalysts, in agreement with the remarks made above and with the results of Busca *et al.* (*9*).

The observation of an overtone band for the reduced catalysts at the unusually high frequency of ~2060 cm^{-1} (Table 2) is particularly noteworthy. It appears reasonable to postulate that the V═O bond strength, and thus the frequency of oscillation, is increased in the process where an isopropoxide group is removed from the local coordination unit. Thus the formation of acetone could be represented schematically in the following way:

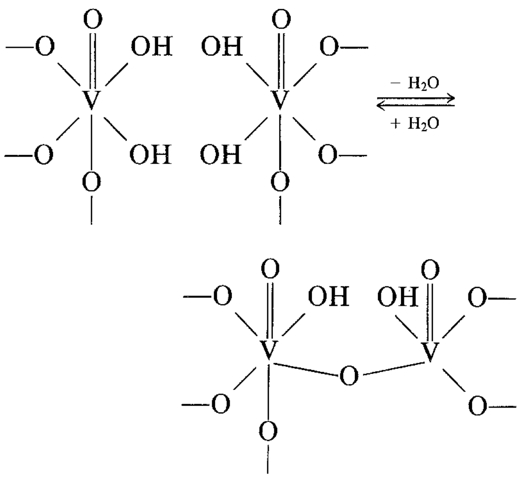


Note that this diagram only suggests the geometrical connectivity and does not imply a model of electronic structure or bond order. In essence, the reduction of V(V) and the release of acetone results in an oxygen deficiency in the local coordination octahedron and hence in a higher VO^{2+} overtone frequency.

Some final remarks concern structural information on the first and second layer of vanadia on our catalysts, which can be derived from the overtone spectra. The layered structure resembling crystalline V_2O_5 reveals itself by the following characteristic feature pointed out by Cavani *et al.* (*11*). There are two fundamentals at 1020 and 985 cm^{-1} (shoulder), and hence three overtone bands at 2020, 1990, and 1975 cm^{-1}. Three overtone bands are seen for our catalysts TiO_2–3V and TiO_2–4V in the oxidized and hydrated state but not for the systems TiO_2–1V and TiO_2–2V which exhibit a single overtone. Our earlier statement (*3*) that these catalysts contain a single layer of octahedrally coordinated vanadium bound directly to the support is thus fully confirmed. This layer cannot contain a dioxo species, a model supported by Bond and Flamerz (*15*), because again, such a structure would give rise to three overtone bands.

It is only recently that the importance of the hydration state of the surface on the overtone spectrum has been realized (*13*).

Let us discuss the monolayer catalysts for clarity. Upon heating under vacuum, the V=O fundamental shifts from 900 to 1035 cm^{-1}, and the corresponding overtone from 1950 to 2045 cm^{-1} (*10, 12, 13*). (The 1950-cm^{-1} band has also been reported in our earlier communication (*3*) where hydrated catalysts have been investigated.) This shift is attributed to the reversible dissociative adsorption (low temperature) and desorption (high temperature) of water,



The V=O bond strength and hence ν(V=O) are higher in the dehydrated form.

In this context it is worthwhile to point to the observation of the broad band at 1560 cm^{-1} in the calcination experiments (Fig. 1). In pure V_2O_5 a broad absorption at 820 cm^{-1} is attributed to an asymmetric stretching vibration of V–O–V structural units. The fundamental is not observable for the supported catalysts; Busca *et al.* (*9*) have attributed the 1560-cm^{-1} band to an overtone of this vibration. The fact that we do observe an increase in this band during calcination is in agreement with the model that more V–O–V bridges are formed during H_2O desorption by condensation of neighboring V–OH groups.

CONCLUSIONS

From the results of the present study, the following picture of the immobilization process of vanadia on the titania support emerges. During first impregnation, a quantitative reaction of the hydroxyl groups of TiO_2 (anatase) with the reagent VO (O–$i$$C_3H_7$) is observed. The calcination in argon involves the oxidation of isopropoxide to acetone, with a concomitant reduction of V(V) to V(IV). Vandium(IV) is present in the form of VO^{2+} ions in an environment which is oxygen-deficient after desorption of the calcination product, acetone. UV–VIS reflectance spectroscopy indicates that V(IV) coexists with V(V). A distorted octahedral coordination sphere (VO_6) is inferred from the electronic transitions and the vibrational spectrum (V=O fundamental and overtones), in full agreement with previous ESR investigations (*24*).

The V=O overtone region around 2000 cm^{-1}, which was previously investigated by Busca *et al.* (*10, 12, 13*), has provided valuable information on the layer structure of the grafted V_2O_5/TiO_2 catalysts. First, the distinction between single and multiple layers of vanadia is easily made from the number of overtone bands observed. Second, the position of the ν(V=O) overtone vibration(s) is strongly influenced by the hydration state of the surface. The lowering of the frequency from ~1035 cm^{-1} (freshly oxidized catalysts) to ~980 cm^{-1} for catalysts stored in air is mainly a result of dissociative water adsorption, rather than an effect of vanadia–support interaction, as had been suggested earlier (*3, 6*). Finally, the oxygen-deficient VO^{2+} groups in the reduced catalyst are characterized by an unusually high overtone frequency of 2060 cm^{-1}.

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