

Vanadium Oxide Monolayer Catalysts

II. A Laser Raman Spectroscopic Study of Oxidic Vanadium/ γ -Alumina Catalysts [1]

By

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Laser Raman spectroscopy is used to study the structure of vanadium ions in V(V)oxide/ γ -Al₂O₃ catalysts. From a comparison with spectral data of V in known structures it is concluded that on wet impregnated catalysts at least three V species may be present. At low surface concentration isolated monomeric vanadate tetrahedra are present on the alumina surface, as well as a twodimensional polymeric network of distorted vanadate octahedra sharing corners and/or edges. At higher concentrations V₂O₅ crystallites are formed.

The dominant species in a monolayer catalyst, prepared by exchange of surface hydroxyl groups for vanadate anions, is again the twodimensional network of distorted vanadate octahedra, together with a minor amount of isolated VO₄ tetrahedra.

Mit Hilfe der Laser-Raman-Spektroskopie wurde die strukturelle Anordnung der Vanadiumionen in Vanadium(V)-oxid/ γ -Aluminiumoxid-Katalysatoren untersucht. Durch Vergleich mit Spektraldaten von V in bekannten Strukturen ergab sich, daß auf imprägnierten Katalysatoren mindestens drei Formen von Vanadiumoxid anwesend sind. Bei niedriger Oberflächen-Konzentration liegen isolierte, monomere Vanadat-Tetraeder auf der Oberfläche des Aluminiumoxids vor, zusammen mit einem zweidimensionalen polymeren Netzwerk von verzerrten Vanadat-Oktaedern, die über gemeinsame Ecken und/oder Kanten miteinander verknüpft sind. Bei höheren Konzentrationen werden V₂O₅-Kristallite gebildet.

Bei einem Monoschichtkatalysator, der durch Austausch von Oberflächen-Hydroxylgruppen gegen Vanadatanionen hergestellt wurde, liegt überwiegend wieder das zweidimensionale Netzwerk von verzerrten Vanadat-Oktaedern vor, zusammen mit einer geringen Menge von isolierten VO₄-Tetraedern.

Introduction

In recent years there has been a growing emphasis on the study of the structure and composition of catalytically active surface phases containing

transition metal ions, their dependence on the method of preparation and on the degree of surface coverage and their relation to catalytic properties. Sometimes distinct phases may coexist [2–7].

For example, for molybdenum oxide on γ - Al_2O_3 four different Mo species were found [6, 7]. Increasing the coverage of the surface with molybdenum oxide resulted in the formation of isolated molybdate tetrahedra, of a polymolybdate phase with octahedrally surrounded Mo, of subsurface $\text{Al}_2(\text{MoO}_4)_3$ and of 'free' MoO_3 in succession.

The formation of different surface phases of vanadium oxide on some supporting oxides has also been the subject of various studies [8–11]. Yoshida *et al.* [8] studied the properties of vanadium oxide supported on silica and γ -alumina. From their ESR-studies they concluded that vanadium oxide is stabilized on the silica surface as isolated tetrahedrally coordinated (VO_4) -species at first, followed by the formation of a $(\text{VO}_5)_n$ network of distorted square pyramidally coordinated vanadium ions and finally by the formation of massive V_2O_5 crystals by accumulation of vanadium oxide on top of these small networks. Similarly, on γ -alumina the vanadium oxide was concluded to be present as an isolated square pyramidally coordinated (VO_5) -species (which resembles the (VO_5) -unit in crystalline V_2O_5), a $(\text{VO}_5)_n$ network and massive V_2O_5 , respectively, with increasing vanadium content.

Later, other authors reported similar results on the basis of *reflectance spectroscopic* investigations. Hanke *et al.* [9, 10] found on SiO_2 (aerosil) two different dispersed vanadium(V)oxide phases: a δ' phase of tetrahedrally coordinated vanadium(V) with low activity for the oxidation of butene and alcohol and a δ'' phase with octahedrally coordinated vanadium(V) being considerably more active as a catalyst. These findings were confirmed by Horvath *et al.* [11]. Praliaud and Mathieu [12] investigated reduced and unreduced vanadium oxides supported on magnesia, alumina and silica. Depending on the method of preparation they found vanadium species of mainly 5- and 6-coordination for magnesia and alumina and one of mainly 4-coordination for silica.

Finally Khalif *et al.* [13] measured by *adsorption microcalorimetry* the heats of adsorption of oxygen on pre-reduced V-oxide/ SiO_2 of the monolayer type. They found several types of adsorption centers on the surface, viz. $V_{C_{3v}}^{3+}$ and $V_{T_d}^{4+}$, which adsorb oxygen without activation energy to form $V_{T_d}^{5+}$ and $V_{C_{4v}}^{5+}$, and $V_{C_{4v}}^{4+}$ which requires a significant activation energy to oxidize to $V_{O_h}^{5+}$. These symmetries were deduced by ESR.

Some of the techniques, listed above, suffer from the fact that the coordination is determined indirectly. Furthermore, reflectance spectra are sometimes poorly resolved [12]. These problems are overcome to a large extent by Raman spectroscopy. Recently the use of this technique to study catalyst structures and catalytic phenomena has been reviewed by Cooney *et al.* [14] and by Egerton and Hardin [15]. Using this technique a number of

authors [6, 7, 16–22] has obtained valuable information about the structures of supported molybdenum- and tungsten oxide catalysts.

The present paper describes investigations on vanadium(V)-oxide/ γ - Al_2O_3 catalysts by laser Raman spectroscopy.

Raman spectra of two types of catalyst have been recorded. The first one is a series of wet-impregnated vanadia/alumina samples with various amounts of vanadium oxide of which the structural changes with composition have been studied. The second catalyst type was prepared by anionic exchange of the surface hydroxyl groups of the alumina carrier for polymeric and/or monomeric vanadate anions [1]. In order to interpret the results the Raman spectra of some pure reference compounds of known structures were recorded also.

Experimental

Materials

(a) The γ -alumina support was from Degussa, type C, with a specific surface area of about $80 \text{ m}^2 \cdot \text{g}^{-1}$. Because of its rather low fluorescence it has favourable properties for recording Raman spectra.

(b) Aqueous solutions of ammonium metavanadate (Merck A.G., Germany, purity grade: pro analysi.) were used to impregnate the γ -alumina carrier material.

(c) The V_2O_5 used was a Merck A.G. product (purity grade: pro analysi.).

(d) AlVO_4 was prepared according to Burdese [23]: stoichiometric quantities of V_2O_5 and $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ (Merck A.G., purity grade: pro analysi) were mixed with 5 wt % HNO_3 . The slurry was then dried on a steam bath, next slowly heated up to 773°K and kept at this temperature for 40 h. Finally the sample was heated for 80 h at 893°K (Burdese used 873°K , on the basis of our previous work [1] we chose 893°K). A tubular furnace was used, with a special construction in order to avoid temperature gradients. The heating of the reaction mixture was interrupted several times for mixing in a ball mill.

X-ray diffraction revealed that no other compounds than AlVO_4 were present, the composition was checked by X-ray fluorescence.

Catalyst preparation

Two preparation methods were used. The first one was a standard wet impregnation of the support with aqueous solutions with various ammonium metavanadate concentrations.

In the second one a freshly prepared 1 wt % solution of ammonium vanadate in HNO_3 (pH = 4) was passed through a bed of alumina particles. For further details see ref. [1]. Both methods were followed by drying at 383°K for 17 h and calcining in air at 723°K for 2 h.

The vanadium content of the catalyst samples was determined by X-ray fluorescence [24].

Methods

All samples were pelletized at a pressure of $1.5 \times 10^8 \text{ N} \cdot \text{m}^{-2}$ before being mounted in a rotating sample holder. The laser Raman spectra of the samples were recorded with a Jeol JRS-S1 spectrometer. The blue (488.0 nm) emission line from a Coherent Radiation Model Ar^+ laser was used for excitation. The output power of the laser was reduced to 10–120 mW, the spectral slit width was usually 14 cm^{-1} , the scanning speed ranged from $10\text{--}50 \text{ cm}^{-1} \cdot \text{min}^{-1}$. The

sensitivity was adjusted to the intensity of the Raman scattering. All samples were rotated at a frequency of approximately 30 Hz. The wavenumbers obtained from the spectra are accurate to within about 2 cm^{-1} .

Results and discussion

The work, presented by Griffith [25, 26] shows that vibrational spectra of vanadates can be classified according to their crystal structure and symmetry. Compounds (or solute components) with equal symmetry will have similar vibrational spectra. This holds for the overall spectrum, for the approximate position of absorption bands as well as for their relative intensities. The exact position of each band is related to the vanadium-oxygen distance and to the V–O bond order, as demonstrated by Cotton and Wing [27]. Thus the determination of the nature of vanadium species is based on the comparison of overall spectra and on relating these spectra to spectra of vanadium species (solid or solute) with known molecular structure.

Wet impregnated vanadium (V)-oxide/ γ - Al_2O_3

The Raman spectra of some V(V)oxide/ γ - Al_2O_3 samples, prepared by wet impregnation and of V_2O_5 are shown in Fig. 1. The most important features can be summarized as follows:

(1) At low coverages, i.e. up to 5.2 wt % V two broad bands are observed, one centered around 970 cm^{-1} , accompanied by a minor band or shoulder around $995\text{--}1000\text{ cm}^{-1}$, and the other in the range between $800\text{--}830\text{ cm}^{-1}$. The broadness of the bands indicates the presence of crystallographically ill defined vanadium species at the surface, as was confirmed by X-ray diffraction.

(2) The bands behave rather independently. On increasing the V-content from 0.5–2.1 wt % V the intensities of the 970 cm^{-1} band and the 830 cm^{-1} band are reversed. At 0.5 wt % V the latter is hardly present, whereas from 1.7 wt % it has a higher intensity than the former. This independent behaviour indicates that the spectra are composed of signals which probably arise from different species.

Pure tetrahedral VO_4^{3-} , as present in aqueous solutions, has its most prominent Raman band at 827 cm^{-1} , associated with the symmetric stretching mode ν_{VO_2} [28]. For solids with isolated VO_4^{3-} units this band lies at $829\text{--}845\text{ cm}^{-1}$ [25]. We therefore conclude that the 830 cm^{-1} band, present at low coverages, may be ascribed to isolated VO_4 tetrahedra on the γ -alumina surface.

In the neutral, coloured solutions we used for impregnation, the major solute component is the $[\text{V}_{10}\text{O}_{28}]^{6-}$ decavanadate anion (together with tetrahedrally coordinated species with a lower degree of polymerization [29]).

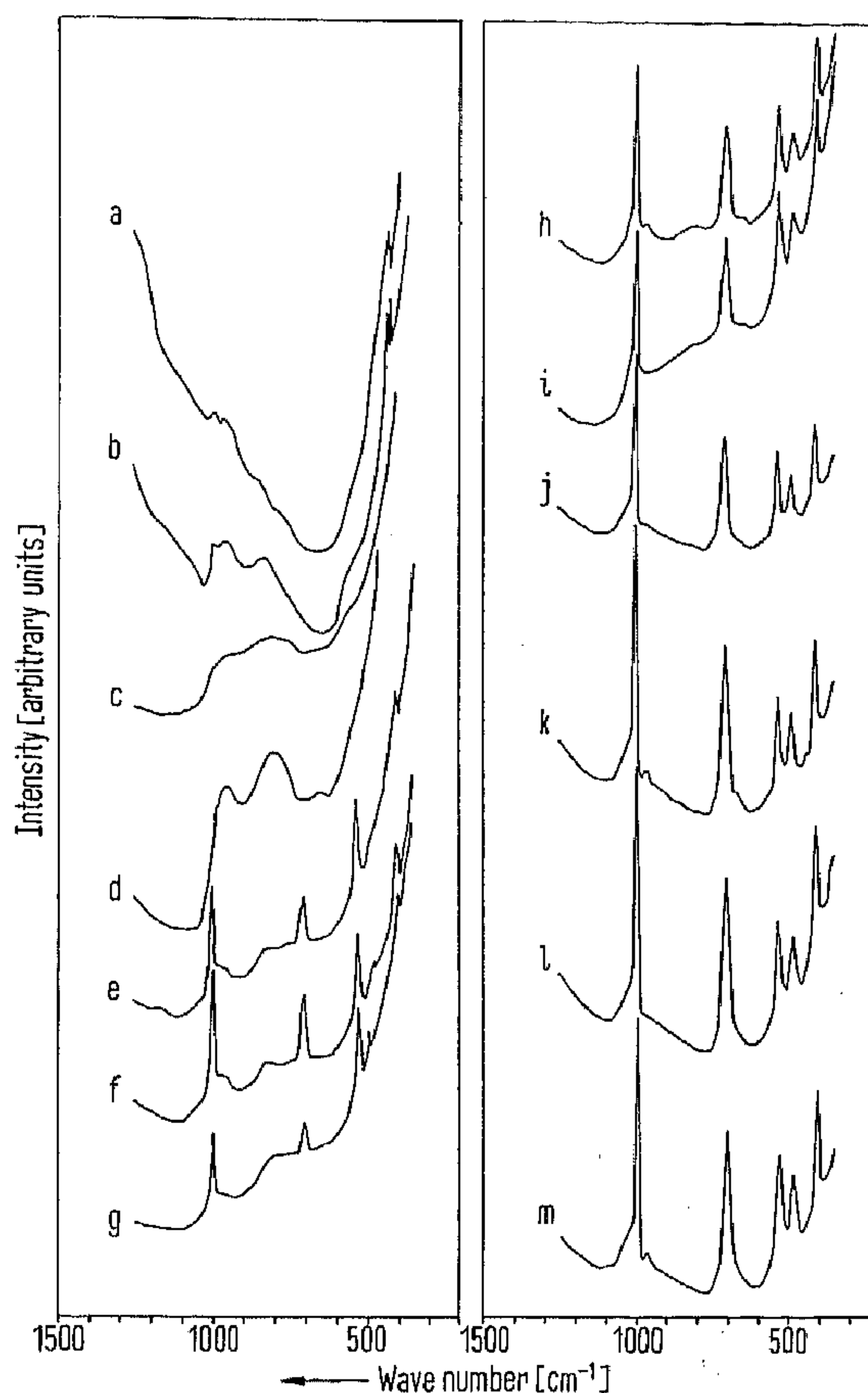


Fig. 1. Raman spectra of impregnated vanadium(V)-oxide/ γ - Al_2O_3 catalysts and V_2O_5 . (a) 0.5% V (by weight); (b) 1.1% V; (c) 1.7% V; (d) 2.1% V; (e) 3.7% V; (f) 4.0% V; (g) 4.7% V; (h) 5.2% V; (i) 7.0% V; (j) 15.0% V; (k) 33.3% V; (l) 35.6% V; (m) V_2O_5 . (All percentages are percentages by weight. For clarity, in Figs. 1–3 the spectra have been translated in vertical direction)

Thus, it is to be expected that the band at 970 cm^{-1} , accompanied by some signal around 995 cm^{-1} can be ascribed to this decamer.

The laser Raman spectra of $[\text{V}_{10}\text{O}_{28}]^{6-}$ in aqueous solutions as well as in some solids have been recorded by Griffith and Lesniak [25]. They found the two most prominent signals exactly at 994 and 970 cm^{-1} .

As these values are exactly equal to the ones observed for our catalysts, this confirms the idea that a polymeric structure is present. The idealized overall symmetry of $[\text{V}_{10}\text{O}_{28}]^{6-}$ is C_{2h} , the structure is centrosymmetric and is based on a 2–3–3–2 array of VO_6 octahedra [30]. The octahedra are bridged by edge-sharing [30] and are strongly distorted [31, 32].

In view of the band position at 970 cm^{-1} (and 995 cm^{-1}) it is extremely likely that the broad band at 970 cm^{-1} represents a vanadium species, built up of distorted vanadate octahedra in a twodimensional polymeric structure sharing corners and/or edges. It cannot be concluded definitely whether all VO_6 octahedra of the polymeric surface species are directly bound to the surface or whether some threedimensional character, as in the original isopolyanion, is maintained. However, on the basis of stability considerations it is to be expected that most of the polyhedra are bound to the alumina surface.

It should be remarked that also for Mo- and W-oxide supported catalysts broad Raman bands are found around 970 cm^{-1} . These are also assigned to a twodimensional polymeric form of distorted MoO_6 - or WO_6 -octahedra [7, 20–22]. It therefore seems probable that similar structures are being formed on alumina surfaces for different metal-oxygen octahedra.

(3) On the catalyst containing 3.7 wt% V on $\gamma\text{-Al}_2\text{O}_3$, bulk V_2O_5 is formed, as shown by the appearance of a series of sharp lines, superposed on the background spectrum with the broad bands.

These lines correspond exactly with the Raman spectrum of V_2O_5 as measured by us (see Fig. 1*m*) and by other authors [33].

It should be mentioned that the relative intensity of the bands due to V_2O_5 and those due to the vanadium surface species may be misleading.

Kerkhof et al. [34] found for tungsten oxide metathesis catalysts that the Raman activity of bulk WO_3 is much higher than that of the W(VI)oxide surface species. Thus it may be that at 3.7 wt% V the vanadium surface species are at least as abundant as “free” V_2O_5 .

(4) An interesting phenomenon is that it is seen, on comparing the spectrum of V_2O_5 with the spectra of the catalyst with 3.7%, that the intensity ratios of the V_2O_5 lines are different, whereas a shift of the line positions is not observed. The line at 483 cm^{-1} is hardly present at 3.7 wt% V (Fig. 1*e*) and increases slowly at higher coverages.

The line at 406 cm^{-1} also shows a far too low intensity in Fig. 1*e*. Similar effects were found for Mo- and W-containing catalysts [7, 20]. This can be ascribed tentatively to a polarization effect of small, probably imperfect crystals of V_2O_5 by the carrier surface.

(5) As one might also expect the formation of bulk AlVO_4 , the Raman spectrum of this salt was recorded as given in Fig. 2. Baran and Botto [35] recorded the IR-spectrum of this compound and argued that a simple assignment of some bands is hindered by the presence of mixed vibrations of complex nature. Nevertheless, from a comparison with the Raman spectrum of AlVO_4 it is clear that, if this compound is formed at all, its concentration must be extremely low. This is in agreement with the limited possibility for the formation of bulk AlVO_4 [36], and supports the idea that the V–O polyhedra are not inside, but *on top of* the alumina surface.

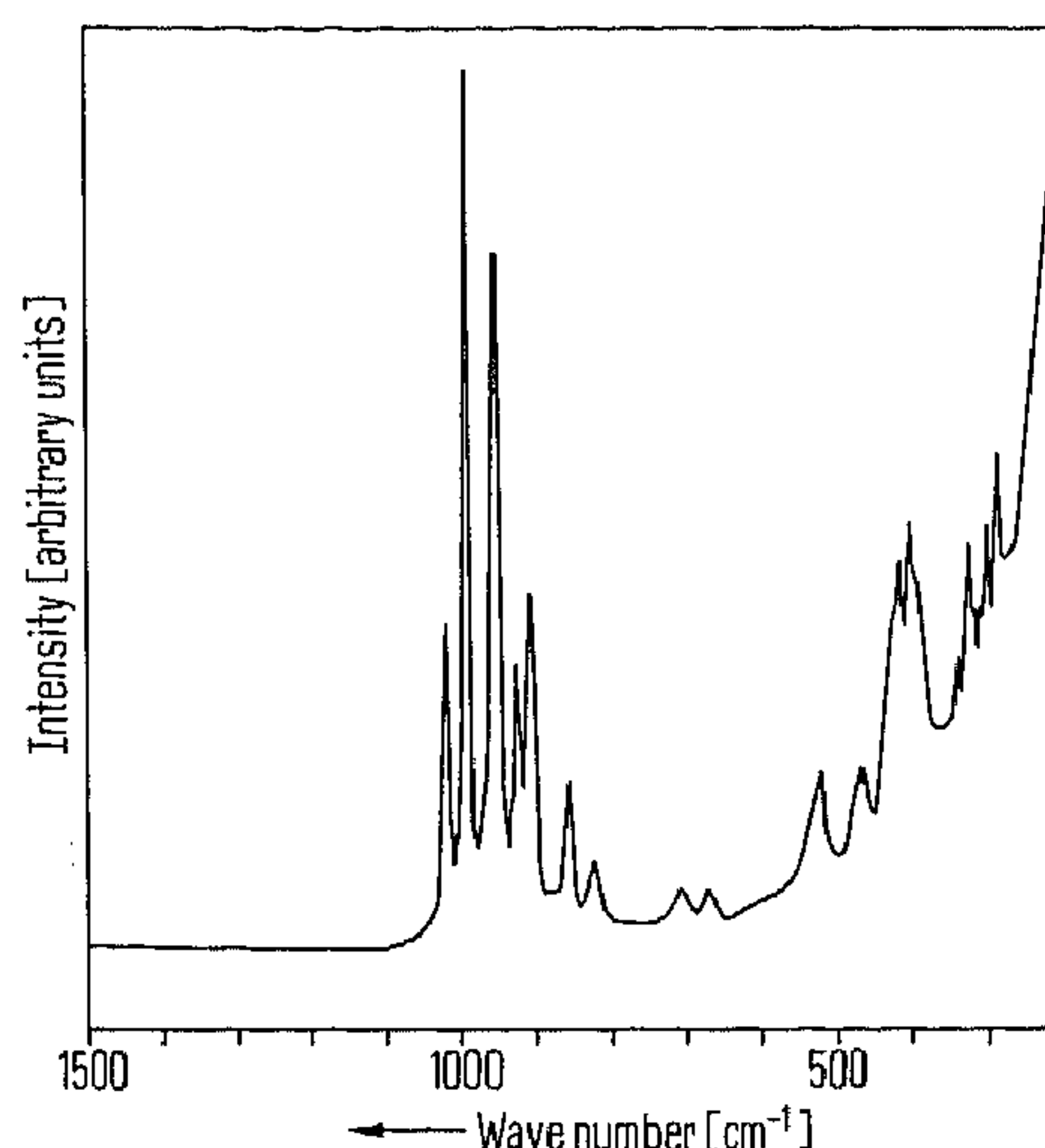


Fig. 2. Raman spectrum of AlVO_4

(6) It is noteworthy that, especially at low coverages up to 2.1 wt % V, the colour of the samples turned from light-yellow to dark brown immediately after exposure to the laser beam. Even when the samples were rotated a dark ring was formed. Thus, especially the surface species seem rather sensitive to the laser radiation, as discussed later.

Liquid-phase prepared vanadium(V)-oxide/ $\gamma\text{-Al}_2\text{O}_3$

In Fig. 3 two Raman spectra, recorded at different laser output powers, are given for the monolayer vanadium(V)-oxide/ $\gamma\text{-Al}_2\text{O}_3$ catalyst, prepared as described earlier [1]. The most significant observations are:

(1) At low power output the most important band is the broad band around 970 cm^{-1} , which appears jointly with a weak signal around 995 to 1000 cm^{-1} . Again, this band is assigned to a two-dimensional polymeric form of distorted VO_6 octahedra on the alumina surface.

(2) Around 830 cm^{-1} only a very weak, broad band appears, indicating that isolated VO_4 tetrahedra are hardly present on this catalyst (Fig. 3a). The fraction of vanadium in tetrahedral coordination is so small that it cannot be estimated quantitatively.

(3) At surface loadings as high as 6.8 wt % V the spectra of the monolayer catalyst still show a complete absence of V_2O_5 lines. This shows that the liquid phase preparation can be used in order to obtain monolayer coverage without bulk V_2O_5 formation. The method is far superior to the wet impregnation method in which V_2O_5 crystallites are formed already at 3.7 wt % V.

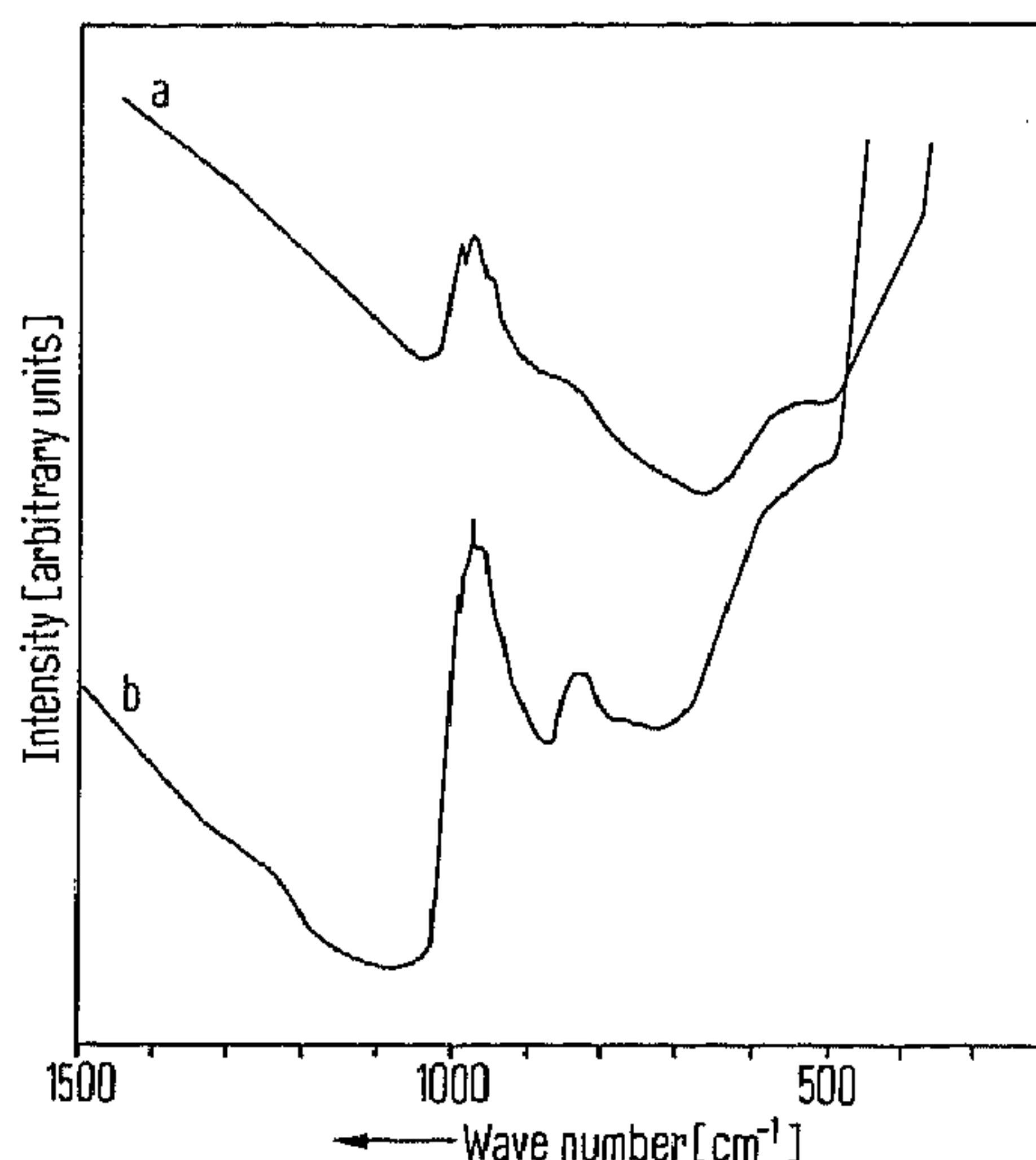


Fig. 3. Raman spectrum of the liquid-phase prepared vanadium(V)-oxide/ γ - Al_2O_3 monolayer catalyst, (6.8 wt% V), recorded at different laser power outputs. (a) Laser power 20 mW; (b) laser power 75 mW

(4) In this case also, no indications for the presence of AlVO_4 were found.

(5) As already mentioned above, it seems that especially the surface species become dark colored as soon as they are exposed to the laser beam. This sensitivity for laser radiation is also observed for the monolayer catalyst.

Undoubtedly, the heat and/or the electromagnetic component of the laser radiation play some role in the coloration of the surface phase. However, an unambiguous explanation is not yet possible. Two possibilities are:

(a) Vanadates are more deeply colored with increasing degree of polymerization. Also the tendency of a decavanadate solution of $\text{pH} \approx 1.5$ to produce a precipitate is increased by laser irradiation [25]. Thus during recording under the influence of the laser radiation the degree of *polymerization* of the surface vanadate species might be increased. However, this is not in complete agreement with the intensity changes in the spectra of Fig. 3.

(b) Another explanation might be a change in coordination of vanadium, perhaps accompanied by some *reduction*. Recently, Medema *et al.* [37] studied the influence of reduction and of temperature on the Raman spectra of, non-rotating, Mo(VI)-oxide/ γ - Al_2O_3 samples. The reduced samples gave spectra which were very similar to those of the laser-heated, non-rotating, samples. The effect in their measurements will be far more pronounced than in ours, as our samples were being rotated. Furthermore, our vanadium oxide samples seem to be more sensitive for structural transformations under the influence of laser radiation. For instance, Fig. 3 shows that, on increasing the laser power, the band at 970 cm^{-1} (octahedral polyvanadate) decreases in

favour of a band around 830 cm^{-1} . This band may be ascribed to a change in coordination together with some reduction, in accordance with the findings of Medema et al. [37]. In the near future it is planned to record spectra with a He-Ne-laser in order to investigate any photochromic effects.

Concluding remarks

At least three vanadium species are present on wet impregnated V(V)oxide/ Al_2O_3 catalysts. At low coverage isolated VO_4 tetrahedra are present on the alumina surface, as well as a twodimensional polymeric aggregate of distorted vanadate octahedra sharing corners and/or edges. At higher coverage V_2O_5 crystallites are formed, possibly with an imperfect crystal growth.

The liquid phase preparation results in a far more uniform coverage of the monolayer type. The dominant species formed is again the twodimensional network of distorted octahedral polyvanadate, together with a minor amount of isolated monomeric VO_4 tetrahedra.

In our laboratories additional vanadium catalysts on other carrier oxides are being studied. The results will be published in the near future.

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