Vanadium Oxide Monolayer Catalysts

II. A Laser Raman Spectroscopic Study of Oxidic Vanadium/\gamma-\text{Alumina} Catalysts [1]

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Laser Raman spectroscopy is used to study the structure of vanadium ions in V(V)oxide/\gamma-Al\textsubscript{2}O\textsubscript{3} 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 V\textsubscript{2}O\textsubscript{3} 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 VO\textsubscript{4} tetrahedra.


Bei einem Monoschichtkatalysator, der durch Austausch von Oberflächen-Hydroxylgruppen gegen Vanadat-Anionen hergestellt wurde, liegt überwiegend wieder das zweidimensionale Netzwerk von verzerrten Vanadat-Oktaedern vor, zusammen mit einer geringen Menge von isolierten VO\textsubscript{4}-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-Al₂O₃ 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 Al₂(MoO₄)₃ and of ‘free’ MoO₃ 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 (VO₄).species at first, followed by the formation of a (VO₃)₅ network of distorted square pyramidalcoordinated vanadium ions and finally by the formation of massive V₂O₅ 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 pyramidalcoordinated (VO₃)-species (which resembles the (VO₃)-unit in crystalline V₂O₅), a (VO₃)₅ network and massive V₂O₅, 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 SiO₂ (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/SiO₂ of the monolayer type. They found several types of adsorption centers on the surface, viz. \( V^{3+}_{C_1} \) and \( V^{4+}_{T_2} \), which adsorb oxygen without activation energy to form \( V^{5+}_{T_2} \) and \( V^{2+}_{C_1} \) and \( V^{2+}_{T_2} \) which requires a significant activation energy to oxidize to \( V^{5+}_{T_2} \). 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
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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-Al₂O₃ 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 m²·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 analysis.) were used to impregnate the γ-alumina carrier material.

(c) The V₂O₅ used was a Merck A.G. product (purity grade: pro analysis.).

(d) AIVO₄ was prepared according to Burdese [23]: stoichiometric quantities of V₂O₅ and Al(NO₃)₃·9 H₂O (Merck A.G., purity grade: pro analysis) were mixed with 5 wt.% HNO₃. 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 AIVO₄ 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 HNO₃ (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 × 10⁸ N·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—50 cm⁻¹·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/$\gamma$-Al$_2$O$_3$

The Raman spectra of some V(V)oxide/$\gamma$-Al$_2$O$_3$ samples, prepared by wet impregnation and of V$_2$O$_5$ 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 – 1000 cm$^{-1}$, and the other in the range between 800 – 830 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$_4^{2-}$, as present in aqueous solutions, has its most prominent Raman band at 827 cm$^{-1}$, associated with the symmetric stretching mode $v_{VO_4}$ [28]. For solids with isolated VO$_4^{2-}$ units this band lies at 829 – 845 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 $\gamma$-alumina surface.

In the neutral, coloured solutions we used for impregnation, the major solute component is the [V$_{10}$O$_{28}$]$^{6-}$ decavanadate anion (together with tetrahedrally coordinated species with a lower degree of polymerization [29]).
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 \([V_{10}O_{28}]^{6-}\) 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 \([V_{10}O_{28}]^{6-}\) 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 three-dimensional 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 γ-Al\(_2\)O\(_3\), bulk V\(_2\)O\(_5\) 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\(_2\)O\(_5\) as measured by us (see Fig. 1m) and by other authors [33].

It should be mentioned that the relative intensity of the bands due to V\(_2\)O\(_5\) 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\(_2\)O\(_5\).

(4) An interesting phenomenon is that it is seen, on comparing the spectrum of V\(_2\)O\(_5\) with the spectra of the catalyst with 3.7\%, that the intensity ratios of the V\(_2\)O\(_5\) 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. 1e) and increases slowly at higher coverages.

The line at 406 cm\(^{-1}\) also shows a far too low intensity in Fig. 1e. 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\(_2\)O\(_5\) 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.
(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/γ-Al₂O₃

In Fig. 3 two Raman spectra, recorded at different laser output powers,
are given for the monolayer vanadium(V)-oxide/γ-Al₂O₃ 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 VO₆ octahedra on the alumina surface.

(2) Around 830 cm⁻¹ only a very weak, broad band appears, indicating
that isolated VO₄ 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 V₂O₅ lines. This shows that the
liquid phase preparation can be used in order to obtain monolayer coverage
without bulk V₂O₅ formation. The method is far superior to the wet
impregnation method in which V₂O₅ crystallites are formed already at
3.7 wt % V.
(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 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$_2$O$_3$ 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(VO)\(_x\)/Al\(_2\)O\(_3\) 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\(_2\)O\(_3\) crystallites are formed, possibly with an imperfect crystal growth.

The liquid phase preperation 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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