J. Chem. Soc., Faraday Trans. 1, 1986, **82**, 767–785

Activity Measurements and Spectroscopic Studies of the Catalytic Oxidation of Toluene over V_2O_5/Al_2O_3-C Catalysts

Bo Jonson, Bernd Rebenstorf and Ragnar Larsson
*Department of Inorganic Chemistry 1, Chemical Center, University of Lund,
P.O. Box 124, S-221 00 Lund, Sweden*

S. Lars T. Andersson* and Sten T. Lundin
*Department of Chemical Technology, Chemical Centre, Lund Institute of Technology,
P.O. Box 124, S-221 00 Lund, Sweden*

Vanadium oxide catalysts based on Al_2O_3-C (γ-Al_2O_3) as support contain at least four different forms of vanadium. The distribution between these depends on the vanadium loading. The activity (per gram of vanadium) of these catalysts for toluene oxidation increases with increasing loading. The selectivity for benzene formation decreases from 2% for the support to 0% for 0.5 wt% V, while the selectivity for benzaldehyde formation first appears at this concentration and rises to 29% for 10 wt% V. It is suggested that benzene is formed at Lewis acid sites on the support, whereas benzaldehyde is formed on vanadium sites. At low loadings (0.1 and 0.2 wt% V) single vanadium species with tetrahedral coordination are formed. The oxidised forms have u.v. bands at 35500 and 42000 cm^{-1} and the reduced forms have i.r. bands of adsorbed CO at 2200 cm^{-1} (room temperature) and at 2190 and 2158 cm^{-1} (133 K). At medium loadings, vanadium surface clusters with varying degrees of agglomeration are formed in addition to the other species. These are suggested to be single chain species with vanadium in tetrahedral coordination, double chain species with vanadium in square pyramidal coordination and aggregates of octahedral vanadium formed by the coupling of double chains. The oxidised forms have u.v. bands at 34500 and 43000 cm^{-1} and the reduced forms have i.r. bands of adsorbed CO at 2178 cm^{-1} (room temperature) and at 2178 and 2158 cm^{-1} (133 K). The agglomerates are more active than the isolated species and show some selectivity for benzaldehyde. Both the activity and the selectivity appear to increase with the degree of agglomeration. At high vanadium loadings (10 wt% V), surface crystallites of vanadium oxide are formed in addition to the other species. The oxidised forms have u.v. bands at 30000 and 43000 cm^{-1} and the reduced forms have i.r. bands of adsorbed CO at 2181 cm^{-1} (room temperature) and at 2181 and 2145 cm^{-1} (133 K). These crystallites are more active and selective than other species with less agglomeration. It is suggested that the increased activity for the larger species is due to the possibility of a transition from corner to edge sharing octahedra at the release of oxygen, which increases the activity of the double-bonded oxygen.

Vanadium catalysts of the monolayer type have aroused considerable attention during the last few years. Excellent catalytic performances have been reported[1] in some cases. Many studies have been concerned with the structure of the catalysts and it appears that the choice of the support and its loading are the most important factors, while the procedure to introduce vanadium is less significant.[2,3] Although considerable efforts have been made to elucidate the structure of monolayer catalysts, the detailed nature of the various surface species, and especially that of vanadium surface compounds, is unknown.

The studies reported herein were begun with the intention of adding some knowledge of the structure of vanadium oxide catalysts, specifically those based on Degussa Al_2O_3-C as the support and with varying loading. We have studied the activities and selectivities shown for the oxidation of toluene. These results were correlated with the features shown by XRD, ESCA, and e.s.r., u.v./vis. and i.r. spectroscopies of adsorbed CO studies. This is a complex reaction, which is probably structure sensitive, and the various products and reaction paths have been discussed in detail elsewhere.[4] With V/Al_2O_3 catalysts, products of side chain oxidation are mainly formed, as well as some derived from oxidative coupling. This reaction is excellent for use as a test reaction in catalytic studies concerning surface structure since it appears that the partitioning between the various routes is very sensitive to the form of the catalyst.

Experimental

Catalyst Preparation

The catalysts were prepared by adding aqueous solutions of NH_4VO_3 to Al_2O_3-C (Degussa) at room temperature. The samples were dried at 393 K in air (which we will call the dried form), and then evacuated and heated in oxygen at 773 K for 1 h (oxidised form) or reduced at 773 K with CO for 1 h (reduced form).

Activity Measurements

A conventional flow apparatus operated at atmospheric pressure was used. It has been described in detail elsewhere.[5] The gas flow was 10–60 $dm^3\ h^{-1}$. Toluene was introduced with saturators giving a toluene concentration of 1.28 vol% in air. The flow entered the fixed bed reactor (15 mm i.d.) which was loaded with 1–4 g of catalyst of 100–200 μm particle size. The isothermal operation of the reactor (400 ± 1 °C) was checked with several thermocouples positioned at the bottom and upper ends of the bed. The 2.0–10% V/Al_2O_3 catalysts were diluted with quartz to avoid adverse thermal effects. The flow was divided into different streams for the analysis of partial oxidation products on one gas chromatograph and carbon oxides on another. The analytical methods have been described in detail elsewhere.[6] The data were extrapolated back to obtain conversions and yields at zero time so as to best represent the initial state of the catalysts. The change in activity with time during the 1–3 h of operation is low and appears to be similar for all catalysts. The reactor was operated with conversions of 0.5–8% and the rates obtained from the differential data by division with W/F (g h $mmol^{-1}$).

Surface Area Measurements

Surface areas were measured by the B.E.T. method[7] with a gravimetric apparatus based on a Cahn 2000 electrobalance. Samples were outgassed at 300 °C for 18 h at a pressure of 4×10^{-5} Torr† prior to N_2 adsorption.

X-Ray Diffraction Measurements

X-Ray diffraction analyses were carried out on the catalysts by use of a Philips X-ray diffraction instrument using a PW 1310/01/01 generator and Cu $K\alpha$ radiation.

Electron Microscopic Studies

Scanning electron microscopic investigations were performed with an ISI-100A instrument.

---

† 1 Torr ≈ 133.3 Pa.

Electron Spin Resonance Measurements

A Varian E-3 spectrometer was used for the e.s.r. studies of the powdered samples. The spectra were recorded in air or vacuum at room temperature as well as in vacuum at 77 K. The spectra were calibrated with DPPH.

I.R. Measurements

Infrared measurements of adsorbed CO were performed with self-supporting discs placed in an i.r. cell as previously described.[8] Spectra were recorded on a Perkin Elmer 580B i.r. spectrophotometer. All handling of spectra was performed on a PE 3600 data station.

Diffuse Reflectance Measurements

Diffuse reflectance spectra were recorded with the samples under nitrogen in a cylindrical quartz tube with a Schlenk attachment. The instrument used was a Hitachi 330 u.v./vis./n.i.r. spectrophotometer with an integrating sphere. The spectra were stored in a PE 3500 data station, transferred to a Tektronix 4051/4662 desk computer and recalculated according to the Kubelka–Munk function.[9] Sharp bands at 4600 and 7100 cm^{-1} are combination vibrations or first overtones from the stretching modes of the O—H and Al—O bonds.

ESCA Measurements

ESCA measurements were performed on an AEI ES 200B electron spectrometer equipped with an Al anode (1486.7 eV). The full width at half maximum (f.w.h.m.) of the Au $4f_{7/2}$ line was 1.8 eV. Sample charging was corrected for with the hydrocarbon contamination C $1s$ line at 285.0 eV. For the quantitative estimations, peak areas above a linear base line were measured with a planimeter. Measuring the V $2p_{3/2}$/Al $2p$ intensity ratio is difficult owing to the overlap between the O $1s$ $K\alpha_{3,4}$ satellite and the V $2p_{3/2}$ line. It was estimated by measuring the V $2p_{3/2}$+O $1s$ $K\alpha_{3,4}$ intensity and subtracting the O $1s$ $K\alpha_{3,4}$ value as estimated from the O $1s$ $K\alpha_{1,2}$ intensity with a weight factor measured on Al_2O_3.

The general principles governing the quantification of XPS data are given in ref. (10). The calculation of $I_{\text{V}\,2p_{3/2}}/I_{\text{Al}\,2p}$ intensity ratios was done for the case of uniform monolayers of vanadium oxide on top of the Al_2O_3 support.

The following equation was applied up to a complete coverage $\phi_1 = 1$ of the first layer:

$$\frac{I_{\text{V}\,2p_{3/2}}}{I_{\text{Al}\,2p}} = \left(\frac{I^{\infty}_{\text{V}\,2p_{3/2}}}{I^{\infty}_{\text{Al}\,2p}}\right)\left(\frac{\phi_1\{1-\exp[-a/\lambda_{\text{V}}(\text{V}_2\text{O}_5)\sin\theta]\}}{1-\phi_1\{1-\exp[-a/\lambda_{\text{Al}}(\text{V}_2\text{O}_5)\sin\theta]\}}\right). \tag{1}$$

After completion of the first layer ($\phi_1 = 1$), a second layer with coverage ϕ_2 was considered using:

$$\frac{I_{\text{V}\,2p_{3/2}}}{I_{\text{Al}\,2p}} = \frac{I^{\infty}_{\text{V}\,2p_{3/2}}\left\{(1-\phi_2)\left[1-\exp\left(\frac{-a}{\lambda_{\text{V}}(\text{V}_2\text{O}_5)\sin\theta}\right)\right]+\phi_2\left[1-\exp\left(\frac{-2a}{\lambda_{\text{V}}(\text{V}_2\text{O}_5)\sin\theta}\right)\right]\right\}}{I^{\infty}_{\text{Al}2p}\left[(1-\phi_2)\exp\left(\frac{-a}{\lambda_{\text{Al}}(\text{V}_2\text{O}_5)\sin\theta}\right)+\phi_2\exp\left(\frac{-2a}{\lambda_{\text{Al}}(\text{V}_2\text{O}_5)\sin\theta}\right)\right]} \tag{2}$$

where θ is the emission angle to the surface plane. The monolayer thickness (a) was calculated as 2.34 Å from the density of V_2O_5 and is close to structure data for the height of $O_4V{=}O$ species.[11] The electron mean free paths for V $2p_{3/2}$ in V_2O_5, $\lambda_V(V_2O_5) = 25.3$ Å; Al $2p$ in V_2O_5, $\lambda_{Al}(V_2O_5) = 30.6$ Å; and $\lambda_{Al}(Al_2O_3) = 24.9$ Å in Al_2O_3, were calculated with the equation for inorganic samples.[12] The intensity ratio for pure samples was calculated to be 6.40 using:

$$\frac{I^{\infty}_{V\,2p_{3/2}}}{I^{\infty}_{Al\,2p}} = \frac{\sigma_{V\,2p_{3/2}}\,\lambda_V(V_2O_5)\,N^{\infty}_V\,T_V(1+0.25\beta_V)}{\sigma_{Al\,2p}\,\lambda_{Al}(Al_2O_3)\,N^{\infty}_{Al}\,T_{Al}(1+0.25\beta_{Al})} \tag{3}$$

where the cross sections $\sigma_{V\,2p_{3/2}} = 6.37$ and $\sigma_{Al\,2p} = 0.537$ were taken from Scofield.[13] The atom density ratio $N^{\infty}_V/N^{\infty}_{Al} = 0.4745$ was calculated from the weight density and molecular weights of V_2O_5 and Al_2O_3. The analyser transmission ratio $T_V/T_{Al} = 0.669$ was calculated from the data of Barbaray *et al.*[14] The angular asymmetry parameters were $\beta_V = 1.42$ and $\beta_{Al} = 0.93$.[15] The coverages ϕ_1 and ϕ_2 at different wt% V were calculated as $\phi_1 = \%$ V/8.6 if less than unity or $\phi_2 = (\%$ V/8.6$) - 1$, where 8.6 is the % V giving a complete monolayer, which corresponds to *ca.* 1.0×10^{19} VO_x species m^{-2}. The same value was also obtained from calculations on the density of the unit-cell volume or from structural data for the $V_2O_5(010)$ crystal plane.

Results and Discussion

Surface Areas

The surface areas of all samples, except that with 10% V, are similar, both as per gram of catalyst (A) and per gram of Al_2O_3 (A_0) (table 1). The surface area of 10% V/Al_2O_3 per gram catalyst is, however, much lower than for the support alone. When comparing areas per gram of support, no differences should occur in the case of a monolayer catalyst. If a separate phase or discrete crystals of vanadium oxides exist on the support, these should contribute some additional area. In the XRD studies, the presence of NH_4VO_3 was indicated by seven weak peaks for the 10% V/Al_2O_3 catalyst (dried form). For 0–2% V/Al_2O_3, only very broad peaks, similar to those measured for Ketjen γ-Al_2O_3, could be observed. The broadening is caused by the small crystallite size. We observed by TEM particle sizes in the range 4–44 nm (mean value 20 nm, *i.e.* slightly larger than the literature value of 8–9 nm).[16] SEM studies revealed no large crystallites on any samples, indicating a size interval of *ca.* 4–100 nm for 10% V/Al_2O_3 and <4 nm for 0.1% V/Al_2O_3.

ESCA Studies

The difficulty in doing ESCA studies with an ordinary X-ray anode on supported vanadium oxide catalysts, is that the V $2p_{3/2}$ peak overlaps with the O $1s$ $K\alpha_{3,4}$ satellite. Only in the case of the 10 and 2% V/Al_2O_3 could the V $2p_{3/2}$ peak be distinguished clearly (fig. 1). The V $2p_{3/2}$ b.e. (binding energy) was 517.1 eV for both of these catalysts as deduced from the difference spectra obtained by subtracting spectra from the pure support, *i.e.* containing only the O $1s$ $K\alpha_{3,4}$ satellite. This V $2p_{3/2}$ b.e. is slightly higher than the 516.6 eV observed for V_2O_5.[17] Vanadium is evidently present dominantly in the pentavalent state and there are considerable interactions with the support. Similar b.e. shifts have been reported for V supported on SiO_2, and may be due to an electron withdrawing effect of the support which increases the positive charge on the V^{5+} ions.[18, 19]

No large effects were observed in the O $1s$ core line-shape. A small shift, *ca.* 0.3 eV, towards a lower b.e. was noted for the catalyst 10% V/Al_2O_3. In vanadium oxides the O $1s$ b.e. is *ca.* 529.6 eV[17] and for γ-Al_2O_3 it is 531.2 eV. The shift is probably due to a contribution to the O $1s$ spectra from vanadium-bonded oxygens in vanadium–oxygen clusters.

The quantitative interpretation of the ESCA studies gives information about the

Table 1. Surface areas of V/Al_2O_3 catalysts

V_2O_5 (wt% V)	$A/m^2\ g^{-1}$	$A_0/\ m^2\ g^{-1}$
0	101.2	101.2
0.5	104.0	104.9
2.0	99.7	103.4
10.0	87.6	106.6

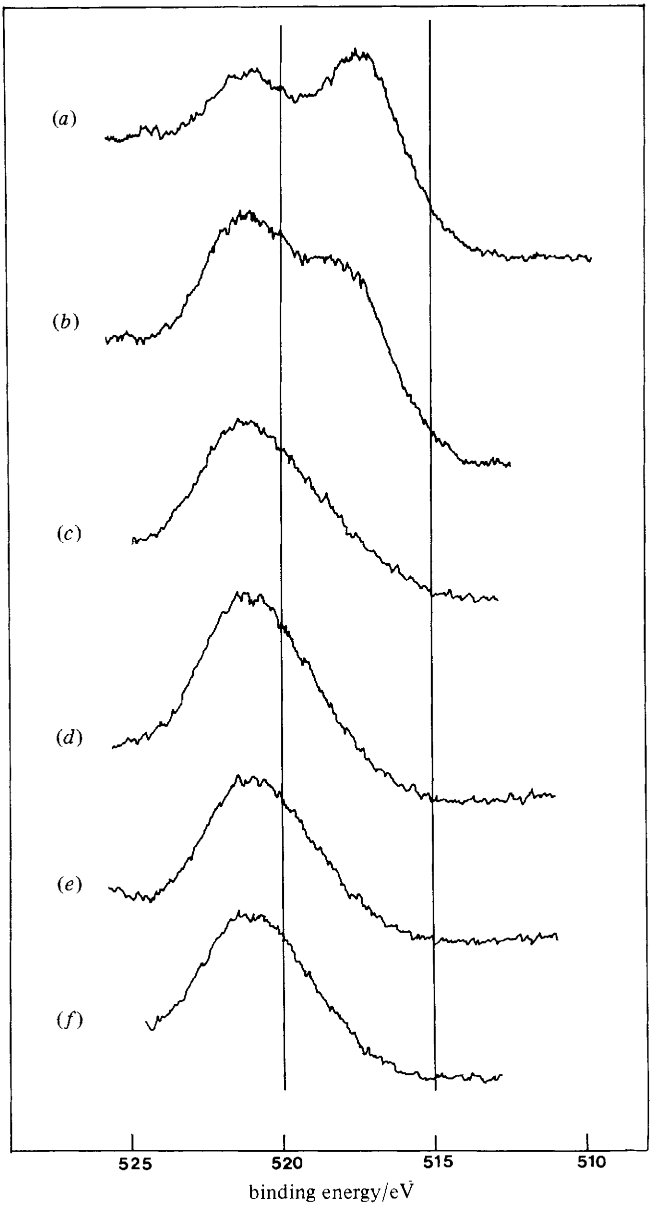


Fig. 1. Electron spectra of the V 2*p* binding energy region for V/Al_2O_3 catalysts: (*a*) 10%, (*b*) 2%, (*c*) 0.5%, (*d*) 0.2%, (*e*) 0.1% V/Al_2O_3 and (*f*) Al_2O_3.

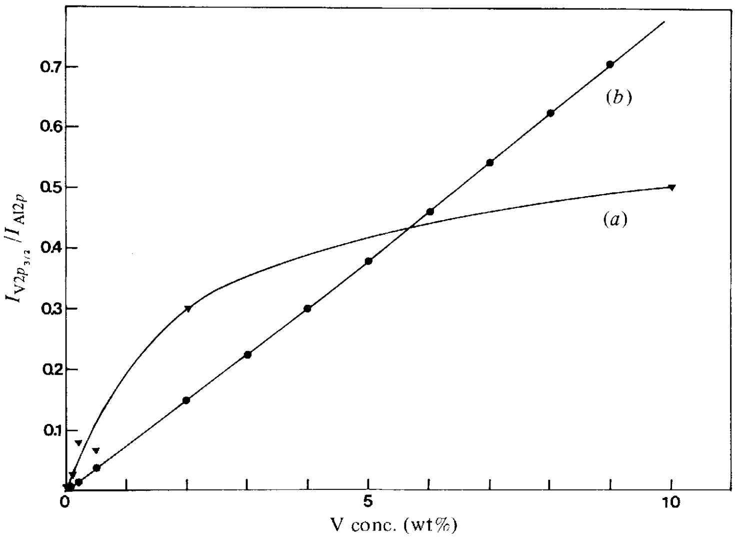


Fig. 2. V $2p_{3/2}$/Al $2p$ intensity ratios from ESCA measurements plotted against vanadium concentration in V/Al_2O_3 catalysts: (*a*) experimental data, (*b*) calculated data.

dispersion of vanadium on the support. The simplest approach is to compare the V $2p_{3/2}$ and Al $2p$ core line-intensities for the V/Al_2O_3 catalysts with varying loadings. Fig. 2 shows the V $2p_{3/2}$/Al $2p$ intensity ratio as a function of wt% V in the V/Al_2O_3 catalysts. It is seen that the experimentally determined V $2p_{3/2}$/Al $2p$ ratio increased with the loading, but levelled off at higher concentrations. The ratios calculated for uniformly distributed VO_x units are shown in fig. 2. Apparently the support particles in 0.1–2% V/Al_2O_3 catalysts are surface-enriched with vanadium of high dispersion. The sample 10% V/Al_2O_3 had an intensity ratio which was too low, probably caused by the partial occurrence of vanadium oxides of low dispersion. The measured V $2p_{3/2}$/Al $2p$ intensity ratio in the latter case actually corresponds to the calculated monolayer ratio at 6.5% V. *Ca.* 3.5% of the total 10% V in that sample was consequently not contributing very much during the ESCA analysis and was probably of low dispersion. Since no crystallites were detected in the SEM studies, one could assume that the size of these particles was smaller than 100 nm. Furthermore, assuming it to be the same phase as that detected in the XRD studies, a particle size interval of 4–100 nm is indicated. As discussed earlier, there was an increase in the surface area per gram of Al_2O_3 owing to this additional phase. Thus, from the surface area and weight of this phase, the mean particle radius and number per square metre can be calculated to be 16 nm and 1.2×10^{13} m^{-2}, respectively. The summed area of these particles covers < 1% of the total area.

E.S.R. Studies

The presence of paramagnetic V species in the V/Al_2O_3 catalysts was confirmed by e.s.r. (table 2). In the catalysts containing 0.1–2% V, e.s.r. spectra with hyperfine structure (h.f.s.) were obtained, while for the 10% V/Al_2O_3 catalyst a broad asymmetric signal was observed with a *g* value of 1.977. The latter was probably due to the separate NH_4VO_3 phase which evidently contained some V^{4+}. Similar spectra were obtained on partially reduced V_2O_5 an lower vanadium oxides. When the spectrum of the sample kept at 77 K was recorded a h.f.s. similar to that observed for the other samples was seen

Table 2. E.s.r. parameters for VO^{2+} on V/Al_2O_3 catalysts[a]

V (wt%)	$g_\parallel$	$g_\perp$	$-A_\parallel/G$	$-A_\perp/G$	relative spin conc.[b]	relative spin conc.[c]
			used catalysts			
0	—	—	—	—	—	1
0.1	1.945	1.999	179	62	1	2
0.2	1.943	1.999	181	63	1.4	2.2
0.5	1.953	1.998	172	62	5.2	6.1
			unused catalysts			
2.0	1.935	1.996	177	60	0.8	—
10.0[d]	1.977		—	—	5.4	—

[a] E.s.r. spectra obtained with samples in air at ambient temperature. [b] Taken as I H/2/gain. [c] Sharp signal at $g = 2.005$, width 8G obtained with samples in vacuum. [d] Only one broad signal at $g = 1.977$.

superimposed on the broad peak. It consisted of $< 5\%$ of the total intensity and indicated the presence of similar paramagnetic species to those in 0.1–2% V/Al_2O_3, but probably with a shorter relaxation time. The effect of sample temperature on the e.s.r. spectra for the 0.1–2% samples showing h.f.s. was also investigated. At 77 K the same h.f.s. as at room temperature was obtained, and there was a 3–4 fold increase in intensity, which follows the normal Curie dependence. The e.s.r. spectra which showed h.f.s. were fairly similar to spectra reported in the literature for vanadium on Al_2O_3,[20–24] and especially VO^{2+} ion-exchanged in various materials[25, 26] as well as the slow-motional spectra of $VO[acac_2(pm)]$ in toluene.[27]

The 0–0.5% V/Al_2O_3 catalyst data (table 2) are for samples used for the catalytic oxidation of toluene, while the 2 and 10 wt% V/Al_2O_3 catalysts were unused. Also shown in table 2 are the relative spin concentrations for the VO^{2+} species. The spin concentration increased with the V concentration in the samples 0.1–0.5% V/Al_2O_3. This corresponds to *ca.* 10–15% of the total vanadium content. The catalysts are apparently reduced when used in the catalytic oxidation of toluene since these gave a higher spin concentration than unused catalysts. The figure given for the 10% V/Al_2O_3 catalyst is for the broad signal. If the h.f.s. detected at 77 K is considered to be *ca.* 5% of the broad signal, a relative spin concentration of 0.3 is obtained.

E.s.r. spectra of the samples in vacuum showed no effect on the h.f.s. of the VO^{2+} species. However, a sharp resonance at $g = 2.005$ and with a half-width of 8 G appeared for the used catalysts 0–0.5% V/Al_2O_3. Evidently, these paramagnetic species are confined to the surface of the alumina and are not seen in air owing to dipole–dipole broadening caused by adsorbed oxygen. Lowering the temperature to 77 K resulted in an increased intensity. During catalytic measurements, the catalysts underwent a colour change. All of the catalysts turned light brown, the darkness of which increased with the vanadium concentration. This colour change is assumed to be due partially to the surface paramagnetic species of $g = 2.005$. A similar singlet was observed after the adsorption of a mixture of toluene and air on 3% V/SiO_2 at 200–300 °C, followed by pumping down to vacuum.[28] The initial presence of O_2^- anions also results in the appearance of the singlet upon adsorption of toluene.[29] Desorption results in the production of carbon oxides.[29] The spin concentration was *ca.* $(0.4–2.5) \times 10^{18}$ spins g^{-1} for the 0–0.5 wt% V/Al_2O_3 catalysts. This magnitude is comparable to that of polynuclear aromatics on, for example, silica–alumina[30] or MoO_3/Al_2O_3.[31] As in these cases, it is reasonable to assume that Lewis acid sites are responsible for the formation of radicals on V/Al_2O_3 in toluene oxidation.

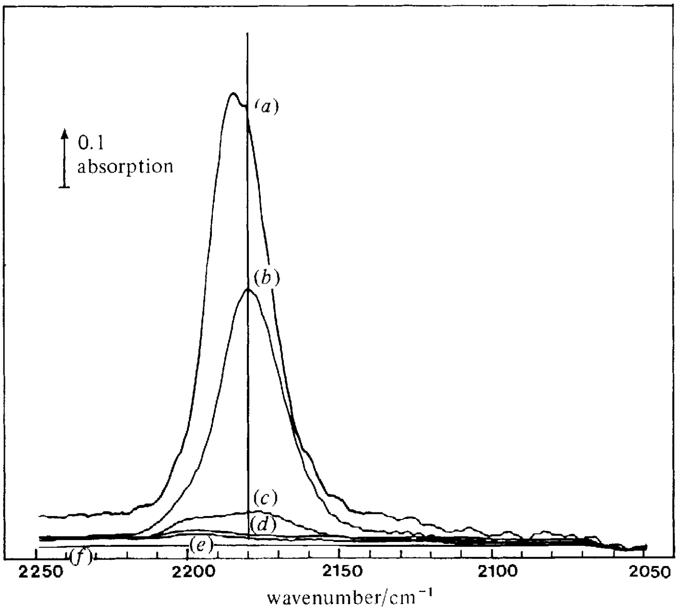


Fig. 3. I.r. spectra of adsorbed CO (10 kPa) at room temperature. The vanadium concentrations of the V/Al_2O_3 samples are: (*a*) 10%, (*b*) 2%, (*c*) 0.5%, (*d*) 0.2%, (*e*) 0.1% and (*f*) 0%.

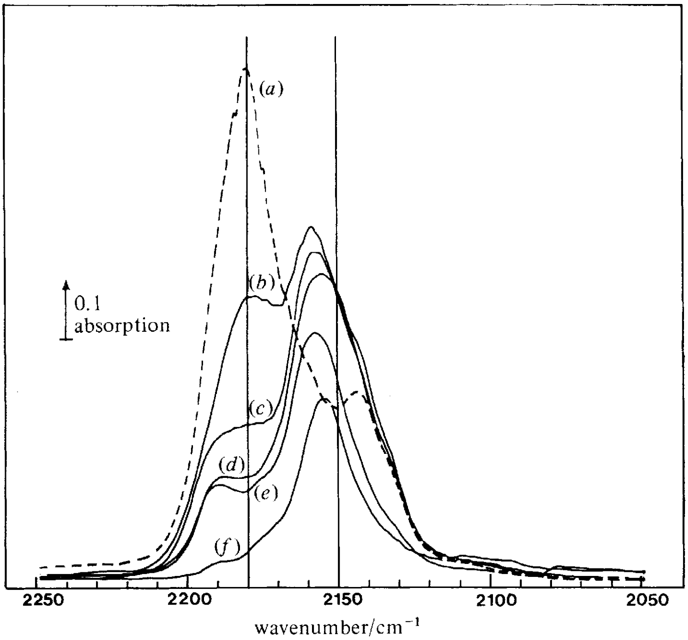


Fig. 4. I.r. spectra of CO adsorbed (10 kPa) at 133 K on the V/Al_2O_3 samples. (*a*)–(*f*) as in fig. 3.

Infrared Spectra of Adsorbed CO

In fig. 3 and 4 the i.r. spectra illustrating CO adsorption on reduced samples at room temperature (fig. 3) and at 133 K (fig. 4) are shown. The peak of the i.r. spectrum in fig. 3 shifts from 2200 cm^{-1} for samples with 0.1 and 0.2% V [spectra (*d*) and (*e*)] to 2178 and 2181 cm^{-1} for 0.5 and 2% V, respectively [spectra (*c*) and (*b*)], and to 2185 cm^{-1} for 10% V/Al_2O_3. Alumina showed no adsorption band under these conditions [spectrum (*f*) in fig. 3]. The i.r. adsorption at 2200 cm^{-1} is most likely due to a vanadium surface compound, possibly V^{3+}, while the band at *ca.* 2180 cm^{-1} can be assigned to CO adsorbed on reduced vanadium oxides on alumina. In a previous study of CO adsorbed on 0.5% V/SiO_2, bands at *ca.* 2187 and 2174 cm^{-1} were observed.[32] In spectra taken at lower temperatures (fig. 4), two i.r. absorption bands of adsorbed CO are observed at *ca.* 2185 and 2155 cm^{-1}. The first band is missing for alumina without vanadium [spectrum (*f*)]. A shift, similar to that in fig. 3, also occurs for the band at *ca.* 2185 cm^{-1}. This band appears at 2190 cm^{-1} for 0.1 and 0.2% V/Al_2O_3 [spectra (*e*) and (*d*)], and 2178 and 2181 cm^{-1} for 2 and 10%, respectively [spectra (*b*) and (*a*)]. In the case of 0.5% V/Al_2O_3, a broad shoulder is observed at these wavenumbers. The assignment of adsorbed CO for room-temperature spectra is also valid here (fig. 3). The peak at *ca.* 2155 cm^{-1}, which is also observed for silica gel, is assigned to CO adsorption on surface hydroxyl groups.[33] It should be noted that the intensity of this band increases with the vanadium concentration and is twice as high for 2% V/Al_2O_3 [spectrum (*b*) in fig. 4] as for the support [spectrum (*f*) in fig. 4]. This i.r. band is shifted to 2145 cm^{-1} in the case of 10% V/Al_2O_3 [spectrum (*a*) in fig. 4], which means that the alumina surface is completely covered by vanadium.

Diffuse Reflectance Spectra

In fig. 5 the diffuse reflectance spectra of the oxidised catalysts are shown. For low concentrations [0.1, 0.2 and 0.5% V; spectra (*e*), (*d*) and (*c*)], two u.v. bands are observed at 35 500 and 42 000 cm^{-1}. With higher vanadium concentrations, the former band shifts to 34 500 cm^{-1} [2%, spectrum (*b*)] or to 30 000 cm^{-1} [10%, spectrum (*a*)]. At these concentrations, additional bands at 12 000 and 10 000 cm^{-1} [spectra (*b*) and (*a*), respectively] appear. The bands near 35 500 and 42 000 cm^{-1} are due to charge transfer absorptions in surface vanadium(v) on alumina. The shift in these bands indicates agglomeration of vanadium species on the surface of alumina and partial formation of vanadium species with lower oxidation number than five [*d–d* bands at 12 000 cm^{-1} in spectrum (*b*) and at 10 000 cm^{-1} in spectrum (*a*)]. In fig. 6 the diffuse reflectance spectra of 0.5% V/Al_2O_3 for the oxidised and reduced forms are shown. In spectrum (*a*) (after reduction of the oxidised form with CO), new *d–d* bands appear at 11 000, 16 000 and 22 000 cm^{-1} [spectrum (*b*)]. Charge transfer bands at 36 500 and 43 000 cm^{-1} arising from V^{3+} and V^{4+}, although there may be some contribution from V^{5+} species still left, also appeared. In contrast to results from studies of vanadium on silica gel,[34, 35] adsorbed CO changed the spectrum very little [spectrum (*c*)]. In spectrum (*d*), which shows the results of adsorption of oxygen at room temperature, strong bands appear at 15 000, 35 000 and 42 000 cm^{-1}. These arise from vanadium(IV)–O_2^- surface complexes.[35] The results from diffuse reflectance spectra (fig. 6) and those from i.r. CO adsorption prove that vanadium surface compounds also exist on Al_2O_3-C. They are, however, less reactive than those on silica gel,[34, 35] for instance in the adsorption of N_2, CO, *etc.*

Catalytic Activity and Correlations with Surface Structure

Fig. 7 shows the reaction rate for the oxidation of toluene on V/Al_2O_3 catalysts *vs.* the concentration of vanadium in the catalysts. The reaction rate clearly increases with the vanadium concentration. This result agrees with the reaction rates for the oxidation

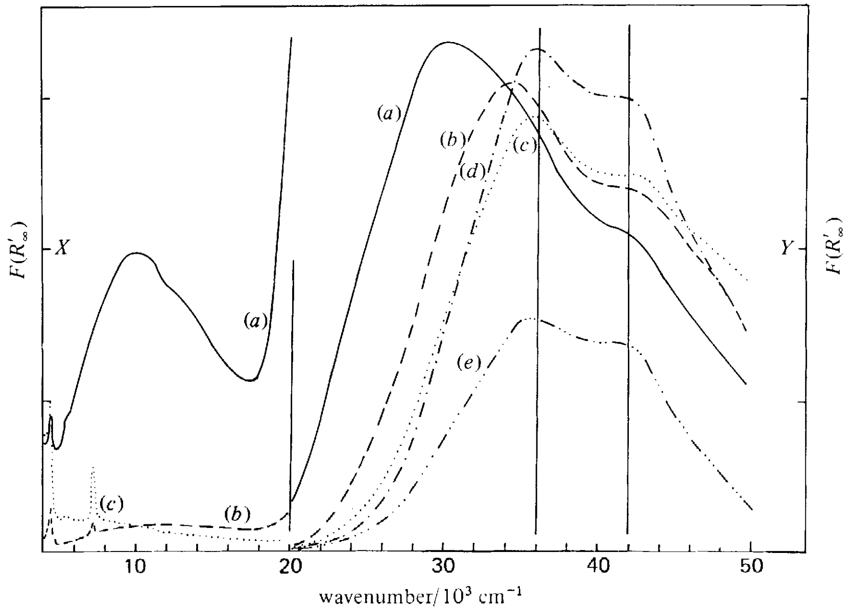


Fig. 5. Diffuse reflectance spectra of oxidised samples. The scale of $F(R'_\infty)$ has been varied in order to show samples with widely different vanadium concentrations. Scales: (*a*) 10% V, $X = 1$, $Y = 10$; (*b*) 2% V, $X = 0.5$, $Y = 5$; (*c*) 0.5% V, $X = 0.5$, $Y = 1.5$; (*d*) 0.2% V, $Y = 0.5$; (*e*) 0.1% V, $Y = 0.5$.

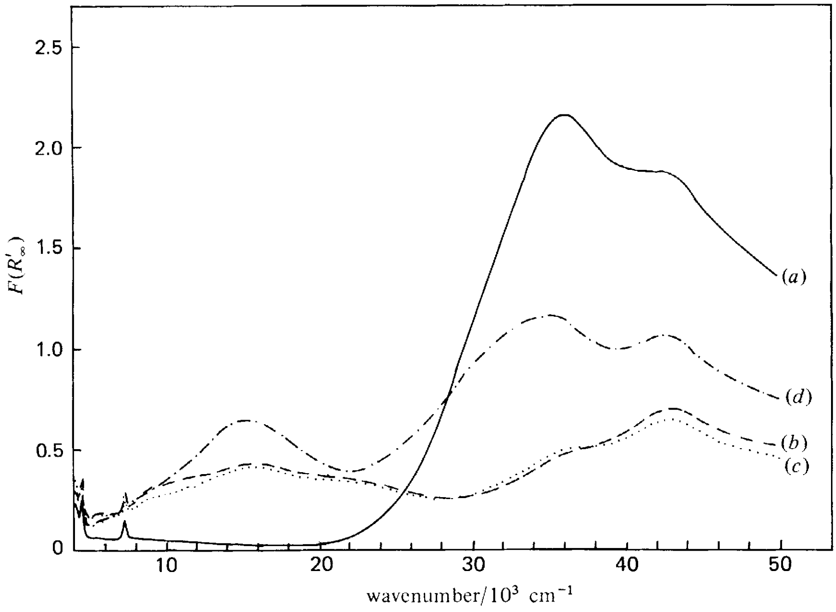


Fig. 6. Diffuse reflectance spectra of 0.5% V/Al_2O_3. (*a*) Oxidised sample under 100 kPa N_2; (*b*) reduced sample under 100 kPa N_2; (*c*) reduced sample under 100 kPa CO; (*d*) reduced sample contacted with 100 kPa O_2 for 12 h.

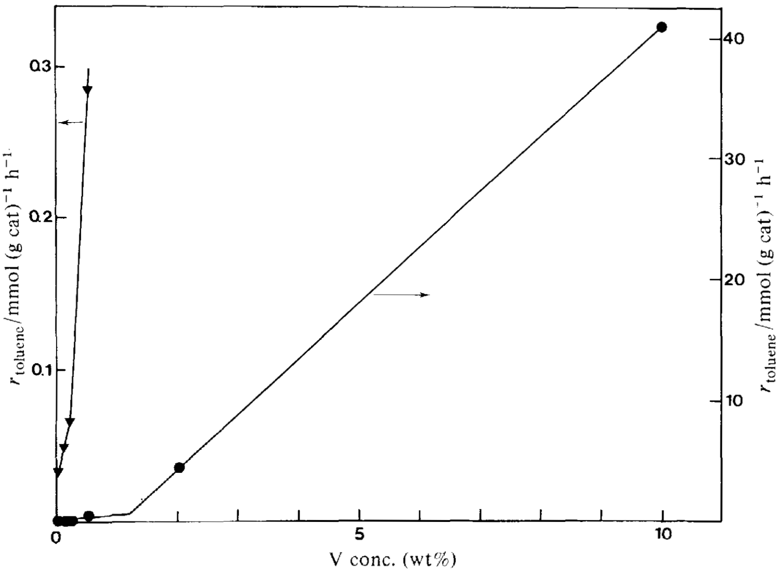


Fig. 7. Reaction rate per gram of catalyst for the oxidation of toluene on V/Al_2O_3 as a function of vanadium loading.

of butadiene[21] and benzene.[36, 37] At higher loadings than we have studied, the reaction rate for these reactions reaches a maximum and thereafter decreases towards the value for pure V_2O_5. In our case, at very low concentrations, the increase was fairly low and accelerated at higher concentrations. There are apparently break points at 0.2 and 1.2 wt% V. The increased activity is not only due to the larger amount of vanadium ions available at higher loadings. Fig. 8 shows the rate of oxidation of toluene per gram of vanadium *vs.* vanadium concentration. Evidently, the activity per gram of vanadium increases with the vanadium loading of the V/Al_2O_3 catalysts. This proves that different vanadium species of different nature and activity exist in these catalysts. The 0.1 and 0.2% V/Al_2O_3 catalysts gave the same activity per gram V, suggesting these two catalysts contain similar species.

In fig. 9 the selectivities for benzene and benzaldehyde are shown *vs.* wt% V in the V/Al_2O_3 catalysts. Pure Al_2O_3, 0.1 and 0.2% V/Al_2O_3 produced only benzene and carbon oxides. The reaction rates for toluene oxidation over these catalysts were very low (fig. 7). The benzene selectivity decreased with increasing loading and was zero for 0.5% V/Al_2O_3. It is reasonable to assume that the vanadium ions are primarily located on the sites otherwise active for benzene production. These are probably Lewis-acid sites of high acid strength, eventually consisting of trigonal aluminium ions. One support for this suggestion is that the skeletal isomerisation of cyclohexene proceeds at a much higher rate on alumina than over V/Al_2O_3 catalysts.[38] This reaction requires sites of high acid strength. By extrapolation one obtains zero selectivity for benzene at *ca.* 0.35 wt% V, which corresponds to 4×10^{19} sites per gram of catalyst. This is a much higher value than the concentration of aromatic radicals detected by e.s.r. and there is no simple relationship evident between the sites responsible for benzene and radical production. The radical concentration also increased with vanadium loading,[38, 39] which could very well explain the increased radical production.

In fig. 10 the ratios of CO_2 to CO production are shown as a function of the vanadium concentration. Clearly, the CO_2/CO ratio increased with the vanadium concentration except for an initial decrease between pure alumina and 0.1% V/Al_2O_3. The initial

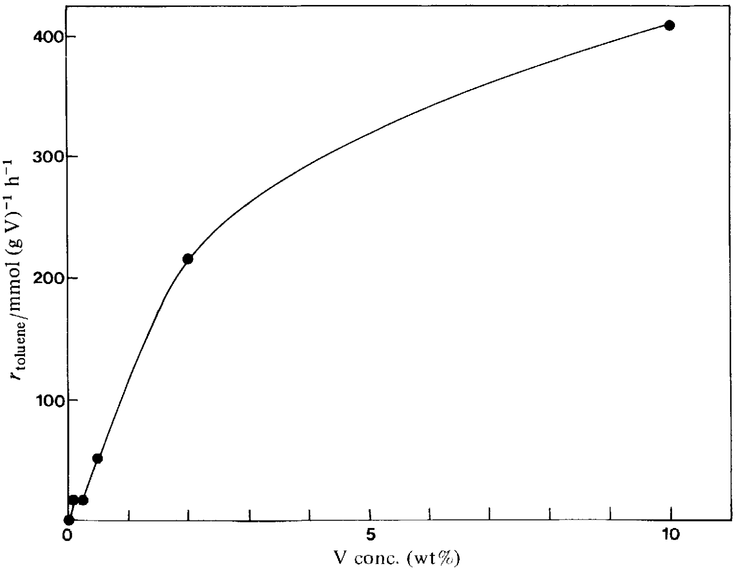


Fig. 8. Reaction rate per gram of vanadium for the oxidation of toluene on V/Al_2O_3 catalysts as a function of vanadium loading. The value r_{toluene} is calculated as $(r_{\text{V/Al}_2\text{O}_3} - r_{\text{Al}_2\text{O}_3})$ $(\%\ \text{V}/100)^{-1}$.

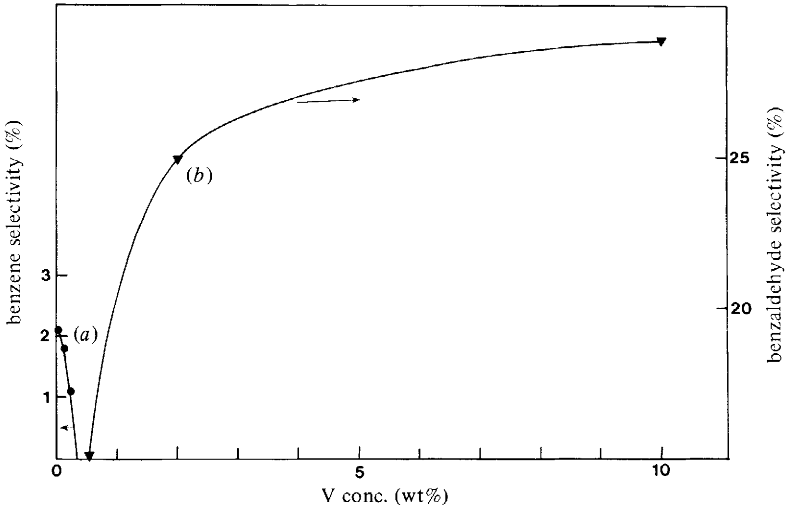


Fig. 9. Selectivity for benzene (*a*) and benzaldehyde (*b*) in oxidation of toluene on V/Al_2O_3 catalysts as a function of vanadium loading.

decrease may possibly be due to the blocking of very strong Lewis-acid sites discussed above by the first few tenths of a percent of vanadium ions, *i.e.* these sites were replaced by sites producing less CO_2. The continuous increase from 0.1 to 10% V/Al_2O_3 is most probably due to the appearance of V species active in oxidising CO as well as toluene.

During efforts to study the adsorption of toluene by i.r. spectroscopy we found adsorbed benzoate species on the 2% V/Al_2O_3 catalyst. It has been suggested that the benzoate species are stabilised on the alumina surface.[40] These species are preferentially adsorbed at Lewis-acid sites. They could yield benzene *via* decarboxylation, which would

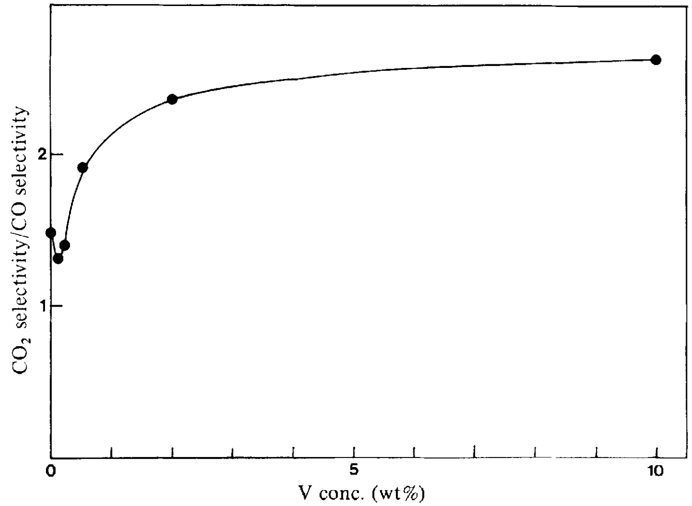


Fig. 10. The ratio of the selectivity for CO_2 to the selectivity for CO in the oxidation of toluene on V/Al_2O_3 catalysts as as function of vanadium loading.

then require OH groups supplying hydrogen atoms. The presence of OH groups in all catalysts, both on alumina and on the vanadium oxide, was determined by the i.r. studies of CO adsorption. Adsorbed carboxylate species are often considered as intermediates in the production of carbon oxides.[41–43]

0.1 and 0.2% V/Al_2O_3 showed the same low activity per gram of catalyst (fig. 8), suggesting both catalysts contain similar species. U.v./vis. studies on oxidised catalysts indicated the presence of isolated V^{5+} species. The i.r. spectra of adsorbed CO on CO reduced catalysts revealed the presence of V^{3+} species. E.s.r. studies revealed the presence of VO^{2+} species in both used catalysts. These results are in agreement with u.v. spectroscopic studies where V^{5+} in tetrahedral coordination was found.[44] This has also been shown by Raman[45] and t.p.r.[3] studies.

The activity for oxidation of toluene on 0.5% V/Al_2O_3 was higher than on 0.1 and 0.2% V/Al_2O_3, although these are also fairly inactive catalysts (fig. 7). The activity taken per gram of vanadium was three times that of 0.1 and 0.2% V/Al_2O_3. Evidently, a second type of vanadium species of higher activity is present in 0.5% V/Al_2O_3. In fig. 9 it is seen that no benzene was produced, but there was a selectivity for benzaldehyde of *ca.* 15%. Apparently, the second type of V species introduced at medium concentrations are responsible for the production of benzaldehyde. VO^{2+} ions were observed by e.s.r. in the 0.1 and 0.2% V/Al_2O_3 catalysts, but small variations in the e.s.r. parameters possibly indicate an increased tendency for agglomeration. According to the u.v./vis. diffuse reflectance spectra of oxidised 0.5% V/Al_2O_3, the appearance of a shoulder at wavenumbers lower than 35500 cm^{-1} [fig. 5, spectrum (*c*)] indicates some agglomeration of V^{5+} species. Reduction of the catalyst produced bands due to V^{3+} and V^{4+}. I.r. spectra of the adsorbed CO on the reduced sample show V^{3+} species as being present in 0.1 and 0.2% V/Al_2O_3, but also show the additional presence of reduced agglomerated V species in about equal amounts. Oxygen adsorption on this sample produced bands typical for V^{4+}–O_2^- species. Raman[45] and t.p.r.[3] studies have shown that isolated tetrahedral vanadium species are accompanied by octahedral vanadate species agglomerated in a two-dimensional structure at medium concentrations. The reaction between NO and NH_3 performed with the rectangular pulse technique is claimed to give both the V=O concentration and the layer thickness.[46] However, the sample of the lowest V concentration studied,[47] 1 mol% V_2O_5, which is higher than our catalyst discussed above, did not give a measurable conversion. For 2 and 5 mol% V_2O_5 it was shown that one or possibly two layers of the polyvanadate structure existed. The catalytic centres on alumina which are responsible for the production of benzene are covered by the vanadium overlayer on this catalyst. The isolated V species of low activity and selectivity corresponded to just less than half of the total vanadium present, whereas the remaining amount was present as agglomerates of vanadate species (oxidised form). These were considerably more active than the isolated V species in the oxidation of toluene and produced benzaldehyde additionally.

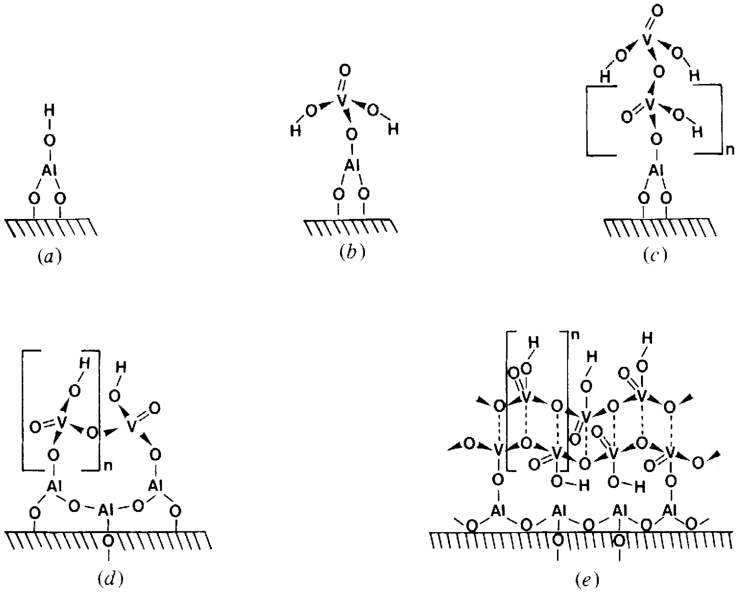
The activity of 2% V/Al_2O_3 is remarkably higher than that of the 0–0.5% V/Al_2O_3 catalysts (fig. 7). As shown in fig. 8, the activity per gram of vanadium is also much higher for this catalyst. Evidently, new species of higher activity are present in 2% V/Al_2O_3, which are also more selective (25%) for benzaldehyde production (fig. 9). Assuming that for 0.5% V/Al_2O_3 catalyst the overall rate is a sum of the rate for isolated and agglomerated species, the activity of the agglomerated species is *ca.* 85 mmol $(gV)^{-1}$ h^{-1} of vanadium, which is much lower than that found for 2% V/Al_2O_3. According to some literature reports,[36, 37, 48] the reaction rate should be determined by the layer area or rather number of V=O species, whereas the layer thickness should determine the selectivity in oxidation of a number of different hydrocarbons. These findings correspond roughly to our results, but do not explain the detailed behaviour. The u.v./vis. diffuse reflectance spectra of oxidised 2% V/Al_2O_3 showed bands due to agglomerated V^{5+} containing some V^{4+}. E.s.r. spectra confirmed the presence of VO^{2+} ions on unused catalysts (dried form). I.r. spectra of CO adsorbed on reduced 2% V/Al_2O_3 showed the presence of reduced agglomerates. Isolated V^{3+} species could not be detected. The shifts in the bands (u.v./vis. and i.r.) suggests the formation of three-dimensional agglomerates to some extent. By the rectangular pulse technique, it was shown that the thickness is 1–2 monolayers at this concentration.[47] Laser Raman studies[45] revealed formation of V_2O_5 crystallites at 3.7% V, but not at 2.1% V, which is supported by the t.p.r. studies.[3] One observation which supports the fact that V_2O_5 crystallites are not present on this catalyst is that the products typical for V_2O_5 are not obtained.

The 10% V/Al_2O_3 showed a very high reaction rate per gram of catalyst (fig. 7) and, calculated per gram of vanadium, it was twice as active as the 2% V/Al_2O_3 catalyst (fig. 8). The rapid increase up to 2% V, levelled off, which is understandable considering the vanadium oxide crystallite formation for 10% V. However, selectivity, *ca.* 29% for benzaldehyde for the 10% V/Al_2O_3 catalyst, has not increased very much. It produces other products also, with selectivities of 4.1% for phthalic anhydride, 2.1% for methyl diphenylmethane, 0.4% for diphenylmethanone, 0.5% for (4-methylphenyl)phenyl methanone and 7.1% for anthraquinone. These products are typical for pure V_2O_5 catalysts,[5] but the activity taken per m^2 is only *ca.* one fifth of that for V_2O_5 prepared by decomposition of NH_4VO_3. The spectroscopic studies revealed the presence of crystallites. E.s.r. showed only one broad asymmetric signal due to V^{4+} ions in a separate vanadium-containing phase. It was identified by XRD as NH_4VO_3 in fresh samples (dried form). The B.E.T. surface area calculated per gram of support indicated an additional area of a few m^2 due to this phase. ESCA studies also revealed particle formation in this sample, with *ca.* 3.5% of the total of 10% V contained in the separate phases of low dispersion. The SEM and XRD results indicated a size interval of 40–1000 Å. E.s.r. spectra at 77 K showed a signal with h.f.s. superposed on the broad signal, which showed the presence of VO^{2+} ions as well in this catalyst. The u.v./vis. diffuse reflectance spectra of the oxidised sample showed bands due to agglomerated V^{5+} and containing V^{4+}. I.r. spectra of adsorbed CO showed bands indicating the presence of reduced vanadium oxides, probably in addition to reduced agglomerates. It was evident from the bands due to CO adsorbed on hydroxyl groups in the 10% V/Al_2O_3 catalyst that all Al—OH groups and the first type of V—OH groups had disappeared. Instead a second type of V—OH group was observed. Apparently the vanadium species almost completely covered the support surface. T.p.r. studies reveal that the crystallite formation had already begun at 3.7 wt% V and that at 17.7 wt% V there were still isolated and agglomerated vanadium species left in considerable quantities.[3]

Structure of Vanadium Surface Compounds

The preparation of the catalysts was done by impregnating the Al_2O_3-C (γ-Al_2O_3) carrier with an ammonium vanadate aqueous solution. In this solution, the vanadate ion can exist in different forms. For example, the metavanadate ion is polymerised to chains of VO_4 tetrahedra sharing corners giving polyanions with OH in the ends. This solution reacts with the alumina surface forming V^{5+} surface compounds bonded to the alumina with V—O—Al bridges. At low loadings, V^{5+} surface compounds with tetrahedral configuration are formed, *e.g.* isolated vanadate ions [fig. 11(*b*)]. At higher vanadium concentrations, single chain polyvanadium surface complexes with V—O—V and V—O—Al bonds are formed [fig. 11(*c*) and (*d*)]. In these species double-bonded oxygen V=O constitutes the active oxygen which has a high activation energy in the oxidation of toluene and thus a low reactivity owing to the low oxidation state V^{3+} in the reduced form. The oxidation of toluene is unselective and the products formed are mostly carbon oxides. These types of surface compounds are present at low loadings corresponding to 0.1 and 0.2% V. The doubled number of OH groups, as observed in the i.r. studies on adsorbed CO, is in agreement with the formation of a mixture of surface species (*b*), (*c*) and (*d*) as shown in fig. 11.

At higher loadings of vanadium, the polymeric chains of vanadium become longer and closer to each other, resulting in a new surface complex formed by linking together two single polyvanadium chains giving a double polyvanadium chain consisting of linked VO_5 polyhedra [fig. 11(*e*)]. The coordination thus changes from tetrahedral to square pyramidal. Each vanadium has a double-bonded oxygen which constitutes the active oxygen. The double-bonded oxygen is in the apex of the pyramid. Adjacent pyramids share edges and the directions of the apices alternate, as shown in fig. 11(*e*). The reactivity is still low owing to a high activation energy.



(*a*) (*b*) (*c*)

(*d*) (*e*)

Fig. 11. Vanadium surface compounds formed with alumina (*a*). For (*b*)–(*e*) see text.

At still higher loadings, the double chains group together in clusters on the surface and the coordination shifts to octahedral through the connection of the V atoms of one chain to the doubly bonded oxygens of the other chain. This change in the oxygen coordination also lowers its activation energy in oxidation reactions. The removal of this oxygen does not change the octahedral coordination of the vanadium ions, but results only in a shift from corner to edge sharing of the octahedra. The oxidation number then decreases from +5 to +4, but this occurs for two adjacent vanadium ions. It is more favourable energetically to form two V^{4+} than one V^{3+}. The transformations in the coordination of the octahedra are analogous to the well known shear structure formation in vanadium oxides. The existence of the larger vanadium clusters where shear transformations are possible explains the increased performance of the catalysts with higher vanadium loading. This type of surface compound is formed at loadings higher than 0.5% V and is responsible for the higher activity and for the formation of benzaldehyde.

We thank the Swedish Board for Technical Development for financial support. The assistance of Mrs B. Svensson in surface area measurements and in microscopic work is gratefully acknowledged.

References

1 See for example G. C. Bond and P. J. König, *J. Catal.*, 1982, **77**, 309.
2 See for example Y. Murakami, M. Inomata, K. Mori, T. Ui, K. Suzuki, A. Miyamoto and T. Hattori, in *Proc. 3rd Int. Symp. Scientific Bases for the Preparation of Heterogeneous Catalysts*, Louvain-La-Neuve, Sept., 1982, ed. G. Poncelet, P. Grange and P. A. Jacobs (*Stud. Surf. Sci. Catal.*, 1983, **16**, 531).
3 F. Roozeboom, M. C. Mittelmeijer-Hazeleger, J. A. Moulijn, J. Medema, V. H. J. de Beer and P. J. Gellings, *J. Phys. Chem.*, 1980, **84**, 2783.
4 S. L. T. Andersson, *J. Catal.*, submitted for publication.
5 S. L. T. Andersson, in preparation.
6 S. L. T. Andersson, *J. Chromatogr. Sci.*, 1985, **23**, 17.
7 S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, 1938, **60**, 309.
8 B. Rebenstorf and R. Larsson, *Z. Anorg. Allg. Chem.*, 1979, **453**, 127.
9 *Surface Properties and Catalysis by Non-metals*, ed. F. S. Stone, J. P. In Bonnelle, B. Delmon and E. Derouane (D. Reidel, Dordrecht, 1983), p. 237.
10 M. P. Seah in *Practical Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy*, ed. D. Briggs and M. P. Seah (John Wiley, Chichester, 1983), p. 181.
11 H. G. Bachmann, F. R. Ahmed and W. H. Barnes, *Z. Kristallogr.*, 1961, **115**, 110.
12 M. P. Seah and W. A. Dench, *Surf. Interface Anal.*, 1979, **1**, 2.
13 J. H. Scofield, *J. Electron Spectrosc. Relat. Phenom.*, 1976, **8**, 129.
14 B. Barbaray, J. P. Contour and G. Mouvier, *Analusis*, 1977, **5**, 413.
15 R. F. Reilman, A. Msezane and S. T. Manson, *J. Electron Spectrosc. Relat. Phenom.*, 1976, **8**, 389.
16 S. Soled, *J. Catal.*, 1983, **81**, 252.
17 S. L. T. Andersson, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 1356.
18 B. Horvath, J. Strutz, J. Geyer-Lippmann and E. G. Horvath, *Z. Anorg. Allg. Chem.*, 1981, **483**, 181.
19 B. Horvath, J. Strutz, J. Geyer-Lippmann and E. G. Horvath, *Z. Anorg. Allg. Chem.*, 1981, **483**, 193.
20 L. L. Van Reijen and P. Cossee, *Discuss. Faraday Soc.*, 1966, **41**, 277.
21 K. Tarama, S. Yoshida, S. Ishida and H. Kakioka, *Bull. Chem. Soc. Jpn*, 1968, **41**, 2840.
22 P. Akimoto, M. Usami and E. Echigoya, *Bull. Chem. Soc. Jpn*, 1978, **51**, 2195.
23 M. Inomata, K. Mori, A. Miyamoto and Y. Murakami, *J. Phys. Chem.*, 1983, **87**, 761.
24 K. V. R. Chary, B. M. Reddy, N. K. Nag, V. S. Subrahmanyam and C. S. Sunandana, *J. Phys. Chem.*, 1984, **88**, 2622.
25 R. J. Faber and M. T. Rogers, *J. Am. Chem. Soc.*, 1959, **81**, 1849.
26 C. Ferragina, A. La Ginestra, M. A. Massuci and A. A. G. Tomlinson, *J. Phys. Chem.*, 1984, **88**, 3134.
27 R. F. Campbell and J. H. Freed, *J. Phys. Chem.*, 1980, **84**, 2668.
28 V. M. Vorotyntsev, Yu. I. Pyatnitskii and G. I. Golodets, *Kinet. Catal.*, 1974, **15**, 1420.
29 A. M. Gasymov, V. A. Shvets and V. B. Kazanskii, *Kinet. Katal.*, 1982, **23**, 951.
30 R. L. Hodgson and J. H. Raley, *J. Catal.*, 1965, **4**, 6.
31 C. Naccache, J. Bandiera and M. Dufaux, *J. Catal.*, 1972, **25**, 334.
32 B. Rebenstorf, M. Berglund, R. Lykvist and R. Larsson, *Z. Phys. Chem. N.F.*, 1981, **126**, 47.
33 G. Ghiotti, E. Garrone, C. Morterra and F. Boccuzzi, *J. Phys. Chem.*, 1979, **83**, 2863.

34 J. Geyer-Lippmann, *Dissertation* (Freie Universitet Berlin, West-Berlin, 1981).
35 B. Horvat, J. Geyer and H. L. Krauss, *Z. Anorg. Allg. Chem.*, 1976, **426**, 141.
36 K. Mori, M. Inomata, A. Miyamoto and Y. Murakami, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 2655.
37 A. Miyamoto, K. Mori, M. Inomata and Y. Murakami, *8th Int. Congr. Catal.*, Berlin, July, 1984 (Verlag Chemie, Weinheim, 1984), vol. iv, p. 285.
38 K. Nowińska, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1980, **28**, 329.
39 Z. Sobalík and V. Pour, *Collect. Czech. Chem. Commun.*, 1984, **49**, 355.
40 M. Niwa, H. Ando, and Y. Murakami, *J. Catal.*, 1977, **49**, 92.
41 R. Delobel, M. Le Bras, M. Traisnel and J-M. Leroy, *Proc. 2nd Int. Conf. Vibr. Surf. 1980, Namur* (Plenum Press, New York, 1982), p. 315.
42 V. G. Mikhal'chenko, V. D. Sokolovskii, A. A. Filippova and A. A. Davydov, *Kinet. Catal.*, 1973, **14**, 1099.
43 A. A. Davydov, *React. Kinet. Catal. Lett.*, 1981, **18**, 25.
44 N. S. Kozlov, G. V. Isaguliants, E. A. Skrigan, I. P. Belomestnykh, G. V. Milorava, G. V. Shakhnovich and L. A. Kupcha, *8th Int. Congr. Catal., Berlin*, 1984, volume IV, 485.
45 F. Roozenboom, J. Medema and P. J. Gellings, *Z. Phys. Chem. N.F.*, 1978, **111**, 215.
46 A. Miyamoto, Y. Yamazaki, M. Inomata and Y. Murakami, *J. Phys. Chem.*, 1981, **85**, 2366.
47 Y. Murakami, M. Inomata, A. Miyamoto and K. Mori, *Proc. 7th Int. Congr. Catal.*, Tokyo, July, 1980, ed. T. Seiyama and K. Tanabe (Elsevier, Amsterdam, 1981) (*Stud. Surf. Sci. Catal.*, 1981, **7B**, 1344).
48 K. Mori, M. Inomata, A. Miyamoto and Y. Murakami, *J. Phys. Chem.*, 1983, **87**, 4560.

Paper 5/594; *Received* 9*th April*, 1985