J. Chem. Soc., Faraday Trans. 1, 1988, 84(10), 3363-3376

# Activity Measurements and Spectroscopic Studies on the Catalytic Oxidation of Toluene over Vanadium Oxides supported on Silica–Alumina COK84

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> We describe a study in which a mixture of silica and alumina (Degussa Aerosil COK84) was impregnated with varying amounts of vanadium. These catalysts were investigated for their activities and selectivities in the oxidation of toluene. The catalytic properties were correlated with the features shown by X.r.d., ESCA and u.v.-visible and i.r. spectroscopies of adsorbed CO. The pure support produces benzene in initial selectivity exceeding 50% on acidic Al-O-Si sites formed during the preparation procedure. The benzene selectivity decreases with time owing to coking effects. Introduction of vanadium decreases the selectivity for benzene and simultaneously selectivity for benzaldehyde appears. The surface area decreases considerably with a loading of 10% V, which is due to a decrease in volume of pores < 80 Å. I.r. spectra revealed that the initially introduced vanadium adsorbs on alumina sites. U.v.-visible data, especially at low vanadium loadings, were similar to those for V/alumina. Comparison between experimental and calculated activities indicated that the first 0.2 % V is adsorbed exclusively on alumina. At 0.5 % V loading, a vanadium species on silica is also detected by i.r. spectroscopy. This loading possesses the most active vanadium, i.e. large agglomerates on alumina. The activity per g V at higher loadings levels off owing to the greater amount of lowactivity vanadium on silica. An increased benzaldehyde selectivity was found for the 2 and 10% V catalysts. On these catalysts V<sub>2</sub>O<sub>5</sub> crystallites are present. This is evident from the X.r.d. results and the product pattern of the 10% V sample.

Supported vanadium oxide catalysts have been extensively studied. A large number of experimental techniques have been applied by different research groups in order to elucidate the structure of the surface species and their catalytic properties. However, it is still not possible to give a detailed description of the surface structure and of the vanadium surface species. To further our knowledge on the structure and catalytic properties of vanadium oxide catalysts, we are presently investigating catalysts based on different supports and with varying loading of the active phase. The catalytic oxidation of toluene is used as a test reaction. Recently we reported results on vanadium oxides supported on alumina<sup>1</sup> and silica.<sup>2</sup> These investigations showed widely different catalytic activities and selectivities of the vanadium species on the respective supports. It is also shown that different types of vanadium species exist on alumina and silica. If a support of mixed silica and alumina is used for vanadium oxides, three possible ways of interaction can be expected. (i) The vanadium species absorbs mainly on alumina and shows properties similar to vanadium surface compounds on alumina. (ii) Vanadium

adsorbs mainly on silica. (iii) New types of vanadium species and catalytic behaviour appear owing to the presence of new surface sites and/or support-support interactions. However, the occurrence of a product pattern different from those found for silica- and alumina-supported catalysts may also be due to spillover effects, *i.e.* further reaction on a second type of site of a molecule initially formed on another site. In this paper the properties and catalytic behaviour of vanadium oxides on a mixed type of support, silica-alumina COK84, are reported.

### Experimental

X-Ray diffraction (X.r.d.), i.r. and diffuse reflectance measurements<sup>1</sup> and surface area, pore size and scanning electron microscopy measurements<sup>2</sup> were performed in the same way as in previous studies.

### **Catalyst Preparation**

The catalysts were prepared by adding aqueous solutions of  $NH_4VO_3$  to an amorphous silica-alumina mixture. The silica-alumina mixture used was the Degussa Aerosil product COK84. It has a surface area of *ca*. 170 m<sup>2</sup> g<sup>-1</sup> and consists of *ca*. 82–86 % SiO<sub>2</sub> (Aerosil 200) and 14–18 %  $Al_2O_3(Al_2O_3-C)$ . The samples were dried at 393 K in air and calcined at 773 K for 6 h in air. For the i.r. and u.v.-visible studies the catalysts were evacuated and heated in oxygen at 773 K for 1 h (oxidized form) or reduced at 773 K with CO for 1 h (reduced form). The concentration of vanadium is given in wt %, defined as (g V per g SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) × 100.

### **ESCA Measurements**

ESCA (electron spectroscopy for chemical analysis) measurements were performed as described earlier,<sup>1</sup> except that for quantitative estimations V  $2p_{3/2}/Si$  2s was used. The intensity ratio for pure samples  $[I^{\infty}(V 2p_{3/2})/I^{\infty}(Si 2s)]$  was calculated to be 1.92. The monolayer thickness, a = 2.34 Å, was calculated for the density of V<sub>2</sub>O<sub>5</sub>. The electron mean free paths for V  $2p_{3/2}$  in V<sub>2</sub>O<sub>5</sub>,  $\lambda_v(V_2O_5) = 25.3$  Å, and for Si 2s in V<sub>2</sub>O<sub>5</sub>,  $\lambda_{si}(V_2O_5) = 29.7$  Å, were calculated by use of the equation for inorganic samples reported by Seah and Dench.<sup>3</sup>

# **Activity Measurements**

A conventional flow apparatus operated at atmospheric pressure was used. The gas flow was  $15-46 \text{ dm}^3 \text{ h}^{-1}$ . Toluene was introduced with saturators, giving a toluene concentration of 1.1-1.3 vol % in an oxygen-nitrogen mixture (20/80). The catalyst bed contained 0.1–2.5 g of catalyst of 200–300  $\mu$ m particle size and was operated isothermally at  $673 \pm 1$  K. The 2 and 10% V/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts were diluted with inert quartz to avoid adverse thermal effects. The analytical methods have been described in detail elsewhere.<sup>4</sup> The catalytic performance changed with time on-stream during the first hour, and for the next 3 h there were only minor changes. This initial change was most apparent for the support and was decreasing in importance with increasing vanadium loading. These effects were most obvious for the benzene formation and for the coking of the catalysts. The catalytic data were therefore taken after 1 h on stream. The reactor was operated with conversions of 1.4-8.2% and the rates were obtained from the differential data by division by W/F (g h mmol<sup>-1</sup>). Experiments with toluene oxidation over the 10% V catalyst at constant W/F and varying gas velocity gave identical results. Measurements on 200–300 and 300–400  $\mu$ m particles also gave identical results. Masstransport effects seem therefore to be of no importance in the present study.



Fig. 1. Surface areas of  $V/SiO_2-Al_2O_3$  catalysts: (a) m<sup>2</sup> per g of catalyst, (b) m<sup>2</sup> per g of SiO\_2-Al\_2O\_3.

# **Results and Discussion**

### Surface Area and Pore Structure

The surface areas of the  $V/SiO_2-Al_2O_3$  catalysts are shown in fig. 1. The surface areas decrease with increasing vanadium concentration. Both surface area per gram of catalyst and per gram of support are shown. If the catalysts had been purely of the 'monolayer' type the surface area per gram of  $SiO_2$ -Al<sub>2</sub>O<sub>3</sub> should have been constant, unaffected by the degree of loading. This is valid for wider pores, but for very narrow pores a decrease in pore radius would have a marked influence on the total surface area. If a separate phase of V<sub>2</sub>O<sub>5</sub> exists without pore blocking, it should contribute some additional area per gram of support. The X.r.d. studies showed that the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> was amorphous in all samples. The presence of  $V_2O_5$  was clearly visible in the diffractogram of the 10% V catalyst, by 7 peaks between  $2\theta = 15$  and 30°, although the highest amplification had to be used. The line broadening indicated an average particle size of ca. 185 A. The  $2\% \text{ V/SiO}_2 - \text{Al}_2\text{O}_3$  catalyst showed only two hardly traceable peaks from  $V_2\text{O}_5$ , and at lower loadings no peaks were found. No  $V_2O_5$  crystallites could be detected in the SEM studies. The V/Si ratio obtained by EDAX analysis were not constant when comparing different areas of a preparation of the 10% V catalyst, which indicates a non-uniform distribution of  $V_2O_5$ .

The pore-size distribution was measured for the COK84 and the 10% V/COK84 catalysts. The distribution is wide for both samples and there is a clear difference between them. The 10% V sample has a larger pore volume compared with the support over 400 Å and between 210 and 340 Å, whereas the COK84 support has a larger volume of pores below 210 Å. This is interpreted as indicating that the vanadium oxide phase fills or blocks the smallest pores considerably. The larger pores are thought to be formed in the vanadium oxide phase and between this phase and the support. The surface area distribution reveals that the support has a much higher surface area of pores <80 Å. The 10% V catalyst has a higher surface area of pores above *ca*. 100 Å.



Fig. 2. Photoelectron spectra of the V 2p binding energy region for  $V/SiO_2-Al_2O_3$  catalysts: (a) 10, (b) 2, (c) 0.5, (d) 0.2 and (e)  $0.1 \% V/SiO_2-Al_2O_3$ ; (f)  $SiO_2-Al_2O_3$ .

### ESCA Studies

Because of overlap between the V  $2p_{3/2}$  core line and the O 1s  $K_{\alpha3,4}$  satellite, no pure V  $2p_{3/2}$  spectra could be obtained. The V  $2p_{3/2}$  peak could be distinguished clearly only in the case of 2 and 10% V/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (fig. 2). The V  $2p_{3/2}$  binding energy was estimated to be 517.2-517.3 eV for both of these catalysts, which indicates the predominance of the pentavalent state. This binding energy is similar to that obtained for both V/Al<sub>2</sub>O<sub>3</sub><sup>1</sup> and V/SiO<sub>2</sub><sup>2</sup> catalysts. It is slightly higher than the 516.6 eV observed for V<sub>2</sub>O<sub>5</sub>,<sup>5</sup> but in addition to the V<sub>2</sub>O<sub>5</sub> crystallites (observed in the X.r.d. studies) there may be also present much smaller aggregates with considerable interaction with the support, thus explaining the shift in binding energy. Other authors have reported similar binding energy shifts for V supported on SiO<sub>2</sub>.<sup>6,7</sup>

Fig. 3 shows the V  $2p_{3/2}/Si$  2s intensity ratio as a function of wt % V in the V/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts. The experimentally determined  $I(V 2p_{3/2})/I(Si 2s)$  ratio increases with

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Fig. 3.  $I(V 2p_{3/2})/I(Si 2s)$  intensity ratios from ESCA measurements vs. vanadium concentration in  $V/SiO_2$ -Al<sub>2</sub>O<sub>3</sub> catalysts: (a) experimental data, (b) calculated data.



Fig. 4. I.r. spectra of adsorbed CO (10 kPa) at ambient temperature  $(SiO_2-Al_2O_3 \text{ spectrum subtracted})$ . The vanadium concentration of the samples are: (a) 10, (b) 2, (c) 0.5, (d) 0.2 and (e) 0.1%.

the loading. Also shown in fig. 3 are the calculated ratios for a uniform distribution of  $VO_x$  units in a monolayer. There are apparently some differences between these two curves. The 2 and 10% V catalysts were shown (*vide supra*) to contain some crystalline  $V_2O_5$  with a crystallite size of *ca*. 185 Å. In such large  $V_2O_5$  crystallites only a part of the



Fig. 5. I.r. spectra of CO adsorption at ambient temperature (gaseous CO spectrum subtracted). The vanadium concentration of the catalysts are: (a) 10, (b) 2, (c) 0.5, (d) 0.2, (e) 0.1 and (f) 0%.

total amount of vanadium will contribute to the ESCA signal. This explains why the intensity ratio levels off at higher loadings, *i.e.* 2 and 10% V/COK84. Assuming monolayer coverage for  $1 \times 10^{19}$  VO<sub>x</sub> units per m<sup>2</sup> one obtains a full monolayer at 15.2 wt % V. The fact that the theoretical curve lies under the experimental one indicates that there is an enrichment of vanadium species on the surface of the silica–alumina particles. In earlier applications to V/Al<sub>2</sub>O<sub>3</sub><sup>1</sup> and V/TiO<sub>2</sub><sup>8</sup> catalysts these correlations worked well.

### I.R. Spectra of Adsorbed CO

The i.r. spectra resulting from the adsorption of 10 kPa CO (80 Torr) on the reduced catalysts are shown in fig. 4, 5 (ambient temperature) and 6 (133 K). The peak arising from CO adsorption on vanadium(III) surface compounds (COK84 spectrum subtracted) at ambient temperature is not evident until the vanadium concentration reaches 0.5% [spectrum (c) of fig. 4] and appears at 2185 cm<sup>-1</sup>. This asymmetric peak shifts to 2187 cm<sup>-1</sup> for 2% V [spectrum (b)] and to 2189 cm<sup>-1</sup> for 10% V/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> [spectrum (a)]. These wavenumbers are higher (4–7 cm<sup>-1</sup>) than those found for V/Al<sub>2</sub>O<sub>3</sub>.<sup>1</sup> CO adsorption of vanadium surface compounds on silica<sup>2</sup> gave rise to asymmetrical bands between 2185 and 2190 cm<sup>-1</sup>, *i.e.* similar spectral features as now found for silica–alumina COK84.

An enlargement of the spectra presented above (without subtracting the spectrum of the support), and the spectrum of CO adsorbed on the support, are displayed in fig. 5. The peak at 2228 cm<sup>-1</sup> in the spectrum of the support [spectrum (f)] is assigned to CO adsorbed on surface aluminium ions.<sup>9</sup> A shoulder at 2226 cm<sup>-1</sup> [spectrum (e)] for the



Fig. 6. I.r. spectra of adsorbed CO at 133 K (SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> spectrum recorded at ambient temperature subtracted). Notation as in fig. 7.



Fig. 7. Diffuse reflectance spectra of oxidized samples in vacuum. The right-hand scale of  $F(R'_{\infty})$  has been varied in order to show samples with widely different vanadium concentrations. Scales: (a) 10% V, X = 10; (b) 2% V, X = 10; (c) 0.5% V, X = 2.5; (d) 0.2% V, X = 1; (e) 0.1% V, X = 0.5.

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Fig. 8. Diffuse reflectance spectra of 0.5 % V/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>: (a) oxidized sample in vacuum, (b) reduced sample in vacuum, (c) reduced sample under 100 kPa CO, (d) reduced sample under 100 kPa O<sub>2</sub> and (e) same as (d) but after 20 h.

sample with a vanadium concentration of 0.1 % indicates that only a few aluminium ions are in this case still accessible for CO. This implies that at low loadings the oxovanadium anions are preferentially located on aluminium ions. Samples with 0.2, 0.5 and 2% V show no absorption bands besides those discussed above. The catalyst with 10% V appears to have two peaks as a consequence of CO adsorption at room temperature [spectrum (a)]. These are, however, due to increased noise in this spectrum (see fig. 6) and are possibly subtraction artefacts.

CO adsorption at 133 K (fig. 6) gives rise to a band at  $2158 \text{ cm}^{-1}$  which can be assigned to CO adsorbed on surface hydroxyl groups.<sup>10</sup> CO cluster formation in pores of the support is indicated by the shoulder around  $2140 \text{ cm}^{-1}$ . The adsorption on vanadium compounds is detectable for 2 and 10% V through bands at 2189 and 2191 cm<sup>-1</sup>, respectively [spectrum (b) and (a)]. CO adsorption arising from V<sup>III</sup> surface compounds were found around 2190 cm<sup>-1</sup> for low vanadium loadings on alumina<sup>1</sup> and around 2180 cm<sup>-1</sup> at high loadings. For V/silica<sup>2</sup> the corresponding bands were found in the region 2185–2190 cm<sup>-1</sup>, which is close to the wavenumbers for vanadium on silica–alumina. Furthermore, these bands around 2190 cm<sup>-1</sup> have the same (asymmetric) shape as observed for V/silica. It seems therefore to be the vanadium species anchored to the silica surface of the silica–alumina that are detected with i.r. spectra of adsorbed CO. Note also that a detectable amount is found first at a loading of 0.5% V.

# **Diffuse Reflectance Spectra**

The diffuse reflectance spectra of the oxidized samples are shown in fig. 7. Charge transfer absorption bands of vanadium(v) surface compounds are observed at 35000 and 42500 cm<sup>-1</sup> for catalysts containing 0.1 and 0.2% V [spectra (e) and (d), respectively). Increasing the vanadium concentration to 0.5% [spectrum (c)] leads to a shift of the charge-transfer bands to 35500 and 42000 cm<sup>-1</sup> and to a reversal in intensity



Fig. 9. Reaction rate per gram of catalyst for oxidation of toluene as a function of vanadium loading on silica-alumina COK84.

of these bands. With a vanadium concentration of 0.5%, an additional band appears at 10000 cm<sup>-1</sup>. This band might be assigned to a d-d transition, probably of  $V^{IV}$ . Absorption bands at these wavenumbers have also been claimed to be due to  $V^{v}-V^{1v}$ intervalance charge transfers.<sup>11, 12</sup> The 2% V sample [spectrum (b)] shows almost the same spectral pattern as the 0.5% V/Si<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> sample. The catalyst with the highest vanadium concentration (10%) differs from those already commented on. The d-d band at 10000 cm<sup>-1</sup> is now more pronounced [spectrum (a)], indicating further formation of vanadium species with an oxidation number < 5. Similar bands were found for V/alumina,<sup>1</sup> but only in the case of 10% V/silica.<sup>2</sup> Note that the intensity of the 10000 cm<sup>-1</sup> band in spectrum (a) is ca. 16% of that found for 10% V/alumina. This intensity ratio corresponds to the composition of the COK84. One also observes broadening and a shift of one charge-transfer band to 34000 cm<sup>-1</sup> and a strong reduction in intensity of the other band. The spectral changes of the charge-transfer bands, *i.e.* shift towards lower wavenumbers and a broadening of the bands, indicate agglomeration of vanadium species on the support surface. The same trend was also observed for V/alumina<sup>1</sup> and V/silica.<sup>2</sup> Spectra of V/alumina showed two charge-transfer bands for all vanadium loadings except 10%. Furthermore, these bands appeared at wavenumbers similar to those just commented on. For V/silica catalysts, only one charge-transfer band could be distinguished.

The diffuse reflectance spectra of the oxidized and reduced forms with a vanadium concentration of 0.5% are shown in fig. 8. Reduction with CO causes the appearance of new d-d bands at 11500 and 17500 cm<sup>-1</sup> [spectrum (b)]. The charge-transfer bands show no shift compared with the oxidized form [fig. 8, spectrum (a) and fig. 7, spectrum (c)], but there is a pronounced decrease in intensity. CO adsorption at ambient temperature gives a shift of the 17500 cm<sup>-1</sup> band to 18500 cm<sup>-1</sup> [spectrum (c)]. The result of oxygen adsorption on 0.5% V/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> is shown in spectrum (d). The band at 15500 cm<sup>-1</sup> is due to V<sup>IV</sup>-O<sub>2</sub><sup>-</sup> complexes.<sup>13</sup> The superoxide was also formed with V/alumina<sup>1</sup> and V/silica.<sup>2</sup> With the latter support, however, only one charge-transfer band of the complex was observed. Prolonged contact with oxygen at room temperature causes oxidation of the sample, as indicated by the increase in intensity of the charge-transfer bands at 35500 and 42000 cm<sup>-1</sup> [spectrum (e)]. The above results are similar to those reported earlier for V/alumina,<sup>1</sup> and differ from those with vanadium on silica gel



**Fig. 10.** Reaction rate per gram of vanadium for oxidation of toluene as a function of vanadium loading on silica-alumina: (a) experimental data and (b) data calculated from support composition and previously found reaction rates.



Fig. 11. Selectivity for benzene as a function of time on stream for V/silica-alumina catalyst of varying loadings: (f) 0, (e) 0.1, (d) 0.2 and (c) 0.5-10% V.

reported by us<sup>2</sup> and other authors.<sup>13, 14</sup> It can therefore be assumed that the vanadium detectable with diffuse reflectance spectroscopy is adsorbed on surface sites consisting of aluminium ions. This statement seems, however, to be in contradiction with the i.r. results. Observations during the experimental work can explain the controversy. Upon working with silica and alumina one observes that V/alumina is more prone to electrostatic interactions with the glass equipment. The u.v.-visible spectra are recorded with the sample (powder) in close contact with the quartz cell, in contrast to the i.r. spectra. This close contact gives the opportunity for quartz-sample electrostatic interactions which are stronger for the alumina primary particles. These are thus closest

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Fig. 12. Selectivity for benzene and benzaldehyde as a function of vanadium loading.

to the window and therefore contribute most to the spectral features at higher loadings when  $(VO_x)$ -silica species are also present.

### Catalytic Performance in the Oxidation of Toluene

Fig. 9 shows the reaction rate for the oxidation of toluene on V/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts as a function of the concentration of vanadium in the catalysts. The reaction rate clearly increases with the vanadium concentration. The increased activity is not only due to the larger amount of vanadium ions per gram of catalyst available at higher loadings. Fig. 10 shows the rate of oxidation of toluene per gram of vanadium as a function of the vanadium concentration. The activity per gram of vanadium increases with the loading up to 0.5% V and thereafter decreases. The increase at low loadings emphasizes the presence of different vanadium species of a different nature and activity in these catalysts. For vanadium supported on alumina<sup>1</sup> and silica<sup>2</sup> there was a continuous increase, in contrast to the present effect. A calculated curve for the activity per gram V is also shown in fig. 10. The calculation was performed assuming an equal distribution of vanadium species on the silica and alumina surfaces of the silica-alumina COK84 of known composition and by use of the previously found activities:  $A_{calcd} = 0.84(A_{silica})$  $+0.16(A_{\text{alumina}})$ . The discrepancy between these two curves indicates that the distribution of vanadium species is different from that assumed of an equal distribution over the whole surface. The fact that the experimental curve lies over the calculated one indicates an accumulation of vanadium compounds on the support surface where a higher activity is achieved, *i.e.* alumina.

In fig. 11 the selectivity for benzene as a function of time on-stream for all catalysts is presented. A strong effect is observed for the pure silica-alumina, and small additions of vanadium are sufficient to severely limit this effect. Above 0.5% V nothing obvious is seen. The stabilized level after 60 min on-stream is plotted in fig. 12, together with the selectivity for benzaldehyde. With increased vanadium loading the selectivity for benzene sharply drops off, whereas the selectivity for benzaldehyde sharply increases instead. It appears as sites responsible for benzene production are replaced by sites beneficial for benzaldehyde production. Pure silica-alumina and 0.1 and 0.2% V catalysts gave very low reaction rates for the oxidation of toluene (fig. 9). Carbon oxides

were the main products for all catalysts. Some minor products were observed in addition to benzene and benzaldehyde. Thus for the silica-alumina, methyldiphenylmethane (MDMP) in 1.5% selectivity was observed. The 0.1 and 0.2% v samples gave traces of maleic anhydride and phenol in addition to benzoic acid, phthalic anhydride and MDMP in selectivities of *ca*. 0.7-2.0%. The 0.5% V catalyst gave the highest reaction rate per gram of vanadium, but the product pattern was similar to that for the 0.1 and 0.2% V catalysts, the difference being higher benzaldehyde and lower benzene selectivities and no phenol. The 2% V gave roughly the same product pattern as the 0.5% V catalyst. The main difference was found for 10% V, with an increased importance for the side products. Thus selectivities of *ca*. 4% for maleic anhydride, 0.4% for benzoquinone, 2% for benzoic acid, phthalic anhydride, MDMP and anthraquinone, and 0.2% for *o*- and *p*-methyldiphenylmethanone and diphenylethanedione. All these latter products are typical for crystalline  $V_2O_5$ , which evidently is present in the 10% V catalyst. The product pattern possible for oxidation of toluene has been described in detail elsewhere.<sup>15</sup>

The time-dependent benzene selectivity, the coking effect and the blocking of benzeneproducing sites at small vanadium loadings is very suggestive. These features are similar to the effects observed in the oxidative dehydrogenation of ethylbenzene.<sup>16,17</sup> These studies suggested that strong acid sites  $(-5.6 > H_0)$  are responsible for the formation of both carbonaceous material and benzene. The activity of these sites declined with time owing to blocking and could be regained by burning off the coke. Furthermore, these sites could be poisoned by the adsorption of pyridine. The strong acid sites on silica-alumina are associated with the Al—O—Si bonds. In the hydroxylated state the strong Brönsted acidity is due to the protonated bridged oxygen, and in the dehydroxylated state the trigonal aluminium ions form strong Lewis sites.

### Surface Conditions of the Catalysts

The investigated support is a mechanical mixture of silica and alumina when received from the manufacturer. During the preparation in aqueous solution, the primary particles become hydroxylated, and the subsequent drying and calcination provide the possibility of the formation of Al--O-Si bonds through condensation reactions. Pores also appear at the interface between the silica and alumina particles, as indicated by the CO cluster formation shown in the i.r. studies. The silica-alumina has a nominal surface area of *ca*. 170 m<sup>2</sup> g<sup>-1</sup>. The constituents of known composition are Aerosil 200 with a nominal surface area of  $200 \pm 10$  m<sup>2</sup> g<sup>-1</sup> and  $Al_2O_3 - C^1$  with a surface area of 101 m<sup>2</sup> g<sup>-1</sup>. Simple arithmetic shows that the surface area of 1 g silica-alumina consists of 16 m<sup>2</sup> alumina surface and 168 m<sup>2</sup> silica. The sum 184 m<sup>2</sup> g<sup>-1</sup> is slightly higher than the nominal 170 m<sup>2</sup> g<sup>-1</sup> and the measured 179 m<sup>2</sup> g<sup>-1</sup> (fig. 1), which implies that some surface area is lost in the formation of the product. We next assume that this loss is equal for the two phases, which gives 16 m<sup>2</sup> Al<sub>2</sub>O<sub>3</sub> and 163 m<sup>2</sup> SiO<sub>2</sub>. Thus 10% of the total surface is Al<sub>2</sub>O<sub>3</sub>.

Benzene is produced on acidic sites on silica-alumina COK84. These sites are most likely associated with the Al—O—Si bonds evolved during the preparation procedure. Selectivity for benzene was also found for low and zero vanadium loadings on alumina.<sup>1</sup> The selectivity shown by that pure support was, however, only one-fifth of that for silica-alumina. The time-dependent effects were also much stronger for silica-alumina and these effects together indicate that different and stronger acidic sites are present on silica-alumina COK84.

I.r. spectra (fig. 5) revealed that the initially introduced vanadium adsorbs on sites in association with surface aluminium ions. Simultaneously the benzene selectivity levels off, whereas benzaldehyde selectivity appears even at the lowest loading, in contrast to V/alumina.<sup>1</sup> This pattern continues with increasing loading up to 0.5% V. This change

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Fig. 13. Calculated distribution of the loaded vanadium between the silica and alumina surfaces of COK84: (a) percentage of loaded vanadium on alumina and (b) percentage of loaded vanadium on silica.

in selectivity can be explained by assuming that the oxovanadate ion reacts exclusively with hydroxyl groups located on alumina. This may be due to the different values of the isoelectric point for silica and alumina. Parks<sup>18</sup> reports *ca.* pH 2 for SiO<sub>2</sub> and *ca.* pH 8 for Al<sub>2</sub>O<sub>3</sub>. The rapid decrease in benzene selectivity caused by the first 0.1 % V indicates that this amount of vanadium adsorbs on the acidic Al—O—Si sites, or at least so close to them that their catalytic properties are affected. This suggestion of a non-uniform distribution of vanadium on the different surfaces is also supported by the curves in fig. 10.

It is now questioned if the vanadium distribution can be calculated from the activity data for the  $V/Al_2O_3^{-1}$  and  $V/SiO_2^{-2}$  series. As shown above, 1 g of silica-alumina consists of 16 m<sup>2</sup>  $Al_2O_3$  and 163 m<sup>2</sup>  $SiO_2$ . From the earlier reported activity data<sup>1, 2</sup> we have derived expressions for the activities per unit area as a function of wt % vanadium. These are:

$$A_{\rm Al}(X) = 4.16 \times 10^{-4} - 1.7 \times 10^{-3} X_{\rm Al} + 1.33 \times 10^{-2} (X_{\rm Al})^2 - 8.41 \times 10^{-4} (X_{\rm Al})^3$$
(1)

$$A_{\rm si}(X) = 1.35 \times 10^{-5} + 6.29 \times 10^{-4} X_{\rm si} + 8.49 \times 10^{-5} (X_{\rm si})^2 \tag{2}$$

where  $A_{A1}$  and  $A_{S1}$  are the activities per unit area for the V/alumina and V/silica series and X wt % V. Next we assume that the activity per unit area for the V/silica-alumina series is the sum of the activities of the respective phases:

$$A_{\rm SiAl}(X_{\rm SiAl}) = [16A_{\rm Al}(X_{\rm Al}) + 163A_{\rm Si}(X_{\rm Si})]/179$$
(3)

with the condition that the vanadium loading  $X_{\text{SiAl}}$  equals the sum of V on SiO<sub>2</sub> plus Al<sub>2</sub>O<sub>3</sub>, *i.e.*  $X_{\text{SiAl}} = 0.16X_{\text{Al}} + 0.84X_{\text{Si}}$  and that  $X_{\text{Al}} \ge 0$  and  $X_{\text{Si}} \ge 0$ . The solution of this equation system gives the distribution of loaded vanadium on the alumina and silica phases, which is plotted against wt % V on silica–alumina in fig. 13. One observes that the first 0.2% vanadium adsorbs only on alumina. The maximum errors (%) in the evaluation of eqn (3) with the solutions for the samples 0.1, 0.2, 0.5, 2 and 10 are 50, 20,

0, 0 and 0, respectively. The errors at the lowest loadings are probably caused by the activity of the support itself, which is higher than that calculated from the pure constituents. At higher loadings this effect is negligible.

The vanadium compounds present on the alumina surface of the support are assumed to have the same structure as previously proposed.<sup>1</sup> The  $(VO_x)$ -Al species probably contribute to a minor part of the total surface area, and consequently no CO adsorption on these can be detected. U.v.-visible spectra, however, revealed the predominance of vanadium species adsorbed on alumina at low loadings. Agglomerates with high activity and selectivity appear at much lower loadings than on Al<sub>2</sub>O<sub>3</sub> owing to the composition of the silica-alumina and the apparently greater affinity for alumina of the oxovanadium species. Yoshida *et al.*<sup>19</sup> have shown that V<sub>2</sub>O<sub>5</sub> crystallites develop better on silica than on alumina, despite the larger surface area of the former support. Their results are in accordance with this study and our previous investigation of silica,<sup>2</sup> where V<sub>2</sub>O<sub>5</sub> crystallites were detected in the SEM studies in contrast to V/alumina.<sup>1</sup>

At vanadium loadings of 0.5% and above,  $(VO_x)$ -Si species are formed, as shown by the i.r. spectra of adsorbed CO. These species possess a much lower activity in the oxidation of toluene<sup>2</sup> than oxovanadium compounds in alumina.<sup>1</sup> Their contribution to the total activity is low, and the initial rapid increase in activity per g catalyst levels off. In addition, the activity per g V decreases by 60% on going from 0.5 to 10% V. Furthermore, the (VO<sub>x</sub>)-Si species might constitute bridges between the primary particles. Such bridging would diminish the surface area, and it can explain the observed decrease in surface area (fig. 1). The volume of small pores would also be reduced. The X.r.d. studies detected V<sub>2</sub>O<sub>5</sub> crystallites on the 2 and 10% V catalysts. These might contribute to the increased benzaldehyde selectivity shown for the highest loadings. Benzaldehyde selectivities >50% have been reported for V<sub>2</sub>O<sub>5</sub>.<sup>8</sup>

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

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Paper 7/1649; Received 11th September, 1987