CHARACTERIZATION OF SUPPORTED VANADIUM OXIDE CATALYSTS BY LOW TEMPERATURE OXYGEN CHEMISORPTION TECHNIQUE: II. THE V_2O_5/SiO_2 SYSTEM

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ABSTRACT

Low Temperature Oxygen Chemisorption (LTOC) has been applied to characterize a series of silica-supported V-oxide catalysts containing up to 5 μmol V m^{-2}. LTOC data, coupled with ancillary information obtained from ESR, IR, XRD, ESCA and surface area measurements, have thrown light on the nature of the dispersed vanadia which has been found to consist of two distinct highly dispersed V-oxide phases.

Based on the experimental results, a model of the surface structure of the dispersed phases has been proposed. It has been envisioned that a "monolayer" phase containing, in small part, isolated $(VO_4)^{4-}$ species and in great part, a dimeric V^{5+} oxide species, both in tetrahedral coordination, is formed at lower vanadia loading region, while at loadings beyond the so-called "monolayer" coverage a second phase consisting of only V^{5+}-oxide in square pyramidal or octahedral surroundings (i.e., a two dimensional structure akin to that of bulk V_2O_5) is formed preferentially on the top of the "monolayer" phase. The completion of the "monolayer" and the beginning of the formation of the "post monolayer" phases have been clearly identified by a maximum in the oxygen uptake capacity of the samples.

INTRODUCTION

Low temperature oxygen chemisorption (LTOC) at -78°C or below has recently been applied to characterize supported oxide and sulfide catalysts [1,2]. This method offers a means of determining the "active" surface area of supported oxide and sulfide phases. Supported Mo-oxide and -sulfide catalysts have been extensively studied by this technique recently, and attempts have been made to correlate oxygen uptake capacities of the catalysts with their activities for hydrodesulfurization (HDS) reactions [2,3]. From the systematic studies on a series of Al_2O_3-supported Mo-containing sulfided hydroprocessing catalysts, it has been demonstrated that under certain conditions low temperature oxygen uptake capacities of these catalysts can be directly correlated with their HDS and hydrogenation activities [3].

Similar studies on supported V-oxide catalysts are rare and only some fragmentary

information relative to this system is found in the literature [4,5]. Since V-oxide catalysts act as redox systems under oxidation reaction conditions, and since partially reduced oxides of polyvalent transition metals are ideal for oxygen chemisorption at low temperatures, supported V-oxides are suitable candidates for such studies. In view of this, we reported, for the first time, the results of a systematic investigation of the applicability and the merit of this technique in studying the surface structure of V/Al_2O_3 catalysts [6]. Following the work of Weller [1,7] on Mo/Al_2O_3 catalysts, a method was standardized for measuring the amount of chemisorbed oxygen at -78°C on reduced V/Al_2O_3 catalysts. It was demonstrated in our work [6] that specific information on the active surface area, as well as the nature and dispersion of the supported vanadia phase could be obtained from LTOC data. The studies on systems containing the same active phase but dispersed on different supports are important because the surface state of supported metals or metal oxides may be subject to specific interaction with the supports, and this in turn may modify the catalytic activity and selectivity of the supported phase [8-11]. The present work was undertaken in order to verify the applicability of the LTOC technique for structural investigation of SiO_2-supported vanadia catalysts. Additional data were obtained by applying other techniques such as ESR, IR, XRD and surface area measurements in order to better understand the results obtained by the LTOC technique.

EXPERIMENTAL

The details of the experimental procedures for catalyst preparation, and acquisition of oxygen chemisorption data have been given elsewhere [6]. In short, a series of catalysts supported on silica (Ketjen F-5, 672 m^2 g^{-1}, 1.1 ml g^{-1}) containing up to ca. 18% by weight of V_2O_5 were prepared by standard wet impregnation method. Ammonium metavanadate (E. Merck, Analar) was used as the source of vanadia. The V contents of the samples were determined by atomic absorption spectroscopy.

Oxygen chemisorption experiments were performed with a static high vacuum (up to 10^{-6} Torr) system connected to a specially designed cell that permitted *in situ* reduction of the catalysts prior to oxygen chemisorption and subsequent ESR experiments. In a typical experiment, about 0.5 g catalyst was reduced at 500°C for 6 h in a flow of hydrogen (40 ml min^{-1}, and pretreated by Pd "Deoxo", and 4A zeolite molecular sieve maintained at -196°C) and oxygen chemisorption was performed on the reduced sample at -78°C. The amount of chemisorbed oxygen was determined by the double isotherm method standardized by Weller [7]. The same system was used to determine the BET surface area, and the pore size distribution by following the BJH method [12].

The ESR spectra were recorded on a JEOL, X-band (ν = 9.278 GHz) spectrometer with 100 KHz modulation. The XRD and IR spectra were recorded with a Philips PW 1051 diffractometer using Ni-filtered Cu K_α radiation, and a Perkin-Elmer 283B IR spectrometer using the KBr pellet method respectively.
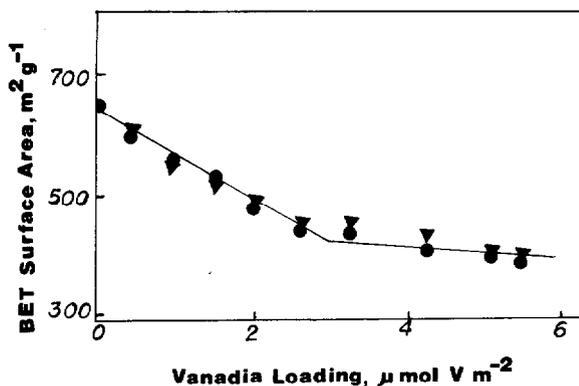
FIGURE 1   BET surface area of V/SiO_2 catalysts as a function of vanadia loading;
● unreduced catalysts; ▼ reduced catalysts.

RESULTS

The BET surface area of the reduced and unreduced catalysts have been plotted
as a function of vanadia loading in Figure 1. Vanadia loading was calculated
from the measured BET surface area of each catalyst. It is noted that the specific
surface area of the catalysts decreases rather sharply as the vanadia loading
increases up to ca. 3 μmol V m^{-2} and then becomes almost independent of V loading.
Reduction does not lead to any change in the specific surface area of the catalysts.
The pore size distribution data (not given here) showed ca. 10% decrease in average
pore diameter when the support was loaded with vanadia, and remained essentially
constant at 2.5 nm for all the samples. This decrease in average pore diameter
is indicative of the filling of larger pores by vanadia, thus leading to a
decrease in the surface area with vanadia loading up to 3.0 μmol V m^{-2}.

ESR spectra of some of the unreduced and reduced catalysts with low and high
vanadia content are given in Figure 2. It is noted that unlike in the case of the
previously reported V/Al_2O_3 system [6], well-resolved spectra with hyperfine
splitting (hfs) due to ^{51}V (I = 7/2) of the unreduced samples could be recorded
at a temperature as high as 25°C, and that the intensity of the spectra increases
but only slightly with increasing vanadia loading. Reduction of the catalysts
does not lead to any change in the hfs pattern; however, the intensity of the
spectra increases appreciably as the loading increases. In contrast to these
observations, V/Al_2O_3 catalysts were found to show ESR spectra with hfs only at
a much lower temperature, namely -164°C [6]. This difference in the temperature
at which well-resolved spectra are obtained is quite significant and will be
dealt with later. The ESR spectra, as depicted in Figure 2, were analyzed by a
method described elsewhere [13-15]. The values of the principal components of
the axially symmetrical spectra, characteristic of $(VO_4)^{4-}$ species in highly
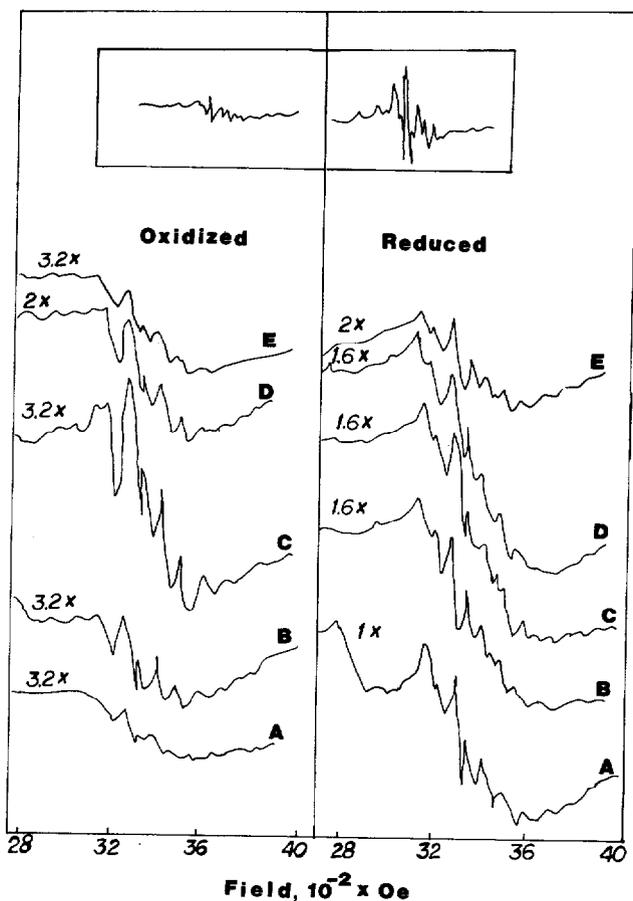distorted tetrahedral ligand field, of the catalysts are given in Table 1.

FIGURE 2 ESR spectra (recorded at 25°C) of unreduced and reduced V/SiO$_2$ catalysts; (A) 2.2% V$_2$O$_5$/SiO$_2$; (B) 8.7% V$_2$O$_5$/SiO$_2$; (C) 13.0% V$_2$O$_5$/SiO$_2$; (D) 15.3% V$_2$O$_5$/SiO$_2$ and (E) 18.1% V$_2$O$_5$/SiO$_2$. Inserts are the spectra (recorded at -164°C) of 10% V$_2$O$_5$/Al$_2$O$_3$ catalysts taken from ref. 6.

None of the supported catalysts, unreduced or reduced, showed any characteristic V=O bond stretching IR band [16] around 1015 cm^{-1}, although a peak around 1015-1020 cm^{-1} was discernible for a sample containing a mechanical mixture of 18% V$_2$O$_5$ in silica. This composition corresponded to the highest vanadia loading in the series of the catalysts studied. The band at 960 cm^{-1} due to assymetric stretching of ←OSi→←O [16] bonds of silica showed a slight shift (from 960 to 970 cm^{-1}) for the unreduced catalysts with low vanadia content, and became broader and broader with vanadia loading greater than 1.5 μmol V m^{-2}. This band became further broadened on reduction, and for the samples containing 2 μmol V m^{-2} or more, the bands of the reduced and unreduced samples looked indistinguishable.

TABLE 1

ESR parameters of V/SiO_2 catalysts determined at 25°C.

	Unreduced	Reduced
g_{11}	1.93 (1.922)[a]	1.93
$g_{\perp}$	2.00 (1.982)[a]	2.00
A_{11}	186.8 ± 1.8 G (182.0)[a]	184.4 ± 1.5 G
$A_{\perp}$	82.8 ± 2.8 G (72.0)[a]	74.4 ± 1.8 G

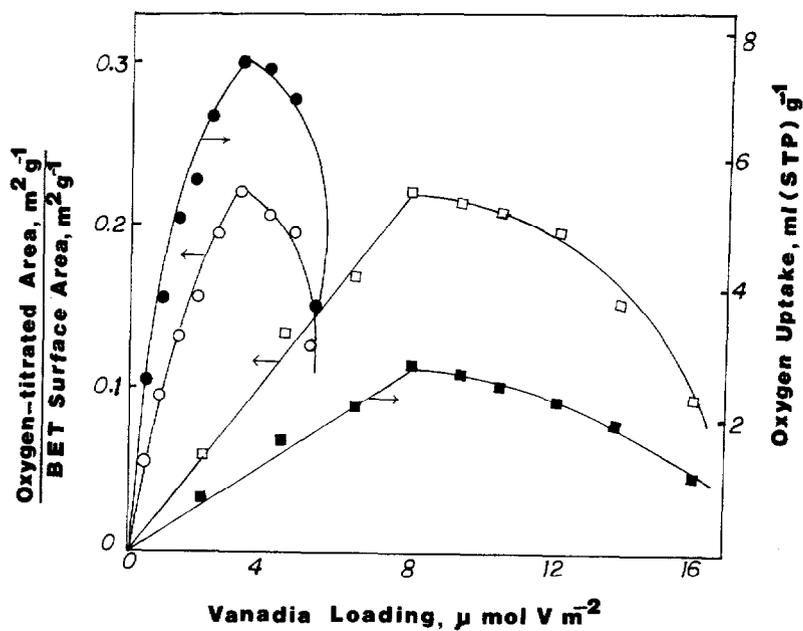[a]The numbers within the brackets are taken from Van Reijn and Cossee's work [26].

FIGURE 3   Oxygen uptake and oxygen-titrated surface area as a function of vanadia loading;○,●,V/SiO_2 catalysts; □ , ■ , V/Al_2O_3 catalysts.

The unreduced catalysts did not show any detectable chemisorption of oxygen at -78°C. Oxygen uptake by the reduced catalysts as a function of vanadia loading is shown in Figure 3. For the purpose of comparison, similar results obtained with the V/Al_2O_3 catalysts (taken from ref. 6) are also shown in Figure 3. Since the specific surface area of silica was much larger (ca. 3.8 times) than that of alumina, the results are reported on the basis of unit surface area for better comparison of the surface properties. It is observed that for both series, oxygen chemisorption capacity increases linearly as a function of vanadia loading up to a certain value and then decreases rapidly with further increase in vanadia loading. The loading at which maximum oxygen uptake occurs is different for different supports, namely 3.5 and 8.5 μmol V m^{-2} for silica- and alumina-supported catalysts, respectively.

DISCUSSION

Surface state of silica-supported vanadia and the nature of the LTOC sites therein

The nature of the surface state of vanadia, supported on silica and alumina, has been investigated by various workers [4,5,17-31]. These studies reveal that the state of the supported vanadia phase, and the distribution of variously coordinated dispersed V-oxide species are very much dictated by the nature of the support as well as the extent of vanadia loading, indicating the specificity of supports in dispersing vanadia. Thus, for instance, it has been reported that when the loading is very low, vanadia on silica remains highly dispersed as isolated $(VO_4)^{4-}$ species with V as V^{4+} in tetrahedral symmetry, and with increased loading, polymeric two-dimensional $(VO_5)_n$ units with V as V^{4+} in distorted square-pyramidal symmetry are formed on the top of the isolated $(VO_4)^{4-}$ species [14]. At still higher loadings, bulky three-dimensional V_2O_5 crystallites are reported to form in addition to the other species just mentioned. Raman spectroscopic investigation with alumina-supported vanadia indicates the presence of three types of V-oxide species differing in the symmetry of V on the support surface [21]. A specific effect of the nature of the supports on the structure of the dispersed vanadia phase has also been noted [18,22].

From the LTOC results, as reported in Figure 3, two types of V-oxide species on the silica surface are discernible. It is observed that the number of oxygen chemisorption sites, as reflected by the oxygen uptake of the samples, increases as a function of vanadia loading, reaches a maximum and then declines sharply. This indicates that in the lower loading region the surface concentration of the oxygen chemisorbing phase increases as a function of vanadia loading up to ca. 3.5 μmol V m^{-2}. In order to get further information on the nature of this phase (to be denoted as the "monolayer" phase) the catalyst samples were isothermally reduced [32] in a Cahn microbalance under the same conditions as used prior to oxygen chemisorption, and the decrease in weight due to reduction was noted as a function of time. It was found that the extent of reduction, following the

stoichiometry: $V_2O_5 \rightarrow V_2O_3$, was between 60 and 70% for all the samples. Detailed ESCA investigation [32] revealed the presence of both V^{3+} and V^{5+} in the reduced samples, in conformity with the reduction results. Additionally, although the reduced samples contained some V^{4+} species, as indicated by strong ESR signals, ESCA did not show any peak due to V^{4+}. This means that the amount of V^{4+} remaining in the reduced samples was very small. Therefore, the net conclusion is that upon reduction most of the supported vanadia was converted to V^{3+}, about 30% remained in the unreduced V^{5+} state and a very small fraction remained stabilized as V^{4+}.

In the light of the above observations, an attempt can now be made to elucidate the surface structure of the "monolayer" phase of silica-supported V-oxides. (The term "monolayer" has not been applied to indicate complete coverage of the support surface; it rather indicates the covering of certain patches of the surface, as discussed further in the text.) It is envisaged that within the "monolayer" region two types of V-oxide species are formed during the preparation step. These species are:
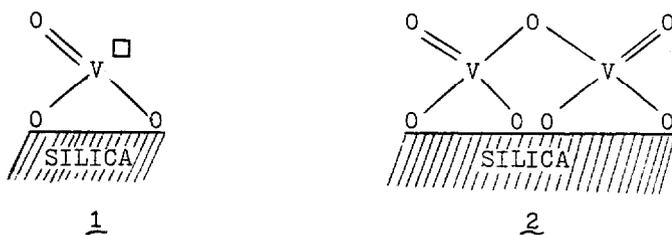
Both the species 1 and 2 have tetrahedral symmetry. Species 1 is responsible for the ESR signal shown by the unreduced as well as the reduced samples. The formation and stabilization of species 1 on silica surface has been repeatedly observed in the past [21,23,26,27]. It is observed from Figure 2 that the ESR signal intensity of the unreduced samples increases by a factor of about 2 upon re-duction. This indicates that a precursor of the species 1, which gives rise to an ESR signal, must have coexisted in the unreduced samples, and this precursor was converted to species 1 upon reduction. In view of these observations, species 2 is tentatively accepted as the precursor of species 1. It is to be noted that species 2 satisfies the valence (i.e., 5^+) as well as symmetry (i.e., Td) require-ments. As mentioned earlier, only a minor fraction of 2 gets reduced to 1, whereas the major fraction is reduced to species 3 containing V^{3+} that serves as the center for oxygen chemisorption at -78°C. The course of reduction is shown in the scheme below:
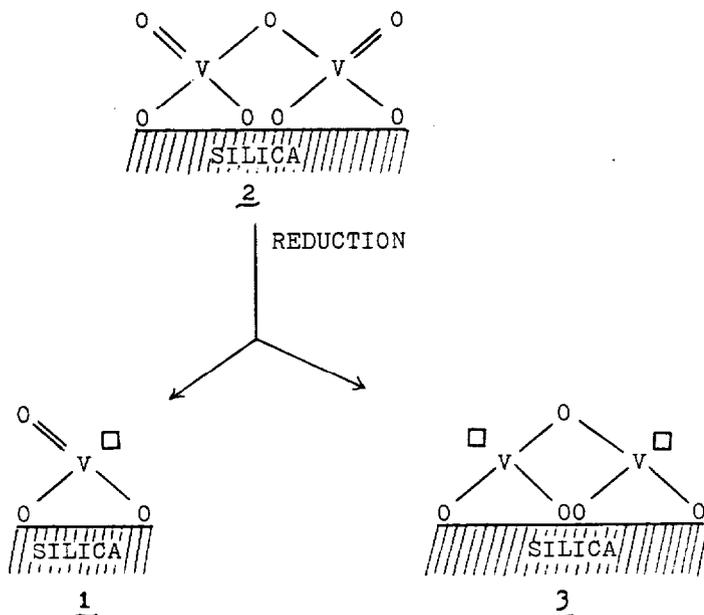
SCHEME 1

In this scheme ☐ denotes a coordinatively unsaturated site (CUS) upon which LTOC occurs. Note that species 2 is one dimensional, and the V ions in it have tetrahedral symmetry. Species 2 maintains its symmetry as well as its registry with the silica surface upon reduction. Results obtained by surface area measurements (Figure 1), ESR and ESCA also indicate that no detectable change of the surface structure of the unreduced "monolayer" phase occurs upon reduction. The absence of any XRD pattern and IR bands characteristic of crystalline V_2O_5 in the samples, both in the reduced and unreduced states, strongly support the highly dispersed and one dimensional structure of the "monolayer" phase as depicted above.

As elaborated below, our ESR results provide further information about the nature of the monolayer phase and the oxygen chemisorption sites. From Figure 2 several important features can be noted: First, unlike in the case of the V/Al_2O_3 system [6] the hyperfine splitting (hfs) pattern due to $^{51}V^{4+}$ (I = 7/2) is observable at higher temperatures, i.e., 25°C for both the unreduced and reduced samples, indicating that a small fraction of vanadium oxide remains stabilized on silica surface as V^{4+} (species 1) in both oxidized and reduced states. Second, the hfs pattern and the axially symmetrical ESR parameters, as given in Table 1, are characteristic of V^{4+} species in tetrahedral symmetry [26,27]. However, because paramagnetic ions (d^1 species in this case) with tetrahedral symmetry have very closely spaced ground and excited energy states [33], the ESR spectra of these ions can be obtained only at very low temperatures and not at 25°C, as observed here, unless the energy gap between the ground and excited states is increased by the influence of some distorting ligand fields. Since in this study

the spectra are obtained at 25°C, it is concluded that the V^{4+} centers are in distorted tetrahedral symmetry. This distortion may have stemmed from the interaction of V with the surface oxygen atoms shared by Si. Indeed the IR spectra, as mentioned earlier in the "Results" section, showed some shift in the assymetric stretching of $O \leftarrow SiO \leftrightarrow O$ bonds. On the contrary, alumina-supported catalysts [6] showed ESR spectra with hfs characteristic of V centers in square pyramidal surroundings and the signals could be obtained only at temperatures as low as -164°C (see the inserts in Figure 2). Third, the ESR spectra of the unreduced silica-supported catalysts are well resolved, and only a slightly increasing trend in the intensity of the spectra is noted as a function of vanadia loading. The spectra of the reduced samples show a similar trend, with the exception that they show a slightly higher intensity as compared with the corresponding unreduced ones. The last two observations indicate that the number of isolated V_{Td}^{4+} sites (i.e., species 1) on the unreduced catalysts increases not drastically, but moderately, with increasing V loading, and that upon reduction, some new V_{Td}^{4+} sites are generated from the precursor (species 2) that coexists with the V_{Td}^{4+} centers in the unreduced samples. These observations support the conclusions reached earlier about the nature of the "monolayer" phase.

The question now arises as to which of the species 1 and 3 is capable of oxygen chemisorption, because both of them have CUS. It is not difficult to perceive that species 3 is definitely capable of oxygen chemisorption because in the reduced catalysts this species constitutes about 70% (as revealed by reduction and ESCA studies) of the "monolayer" phase. However, it is not possible from our results to ascertain whether or not species 1 also can chemisorb oxygen at -78°C. As mentioned earlier, the unreduced catalysts, which contained species 1 as the only potential oxygen chemisorbing centers, did not show any measurable oxygen uptake. This might as well mean that species 1 chemisorbed oxygen, but the amount was too small to be measured by the technique applied for oxygen chemisorption studies.

The next important question concerns the sudden decrease in oxygen uptake capacity beyond the monolayer coverage (i.e., beyond 3.5 μmol V m^{-2}). This behavior provides two valuable pieces of information: First, beyond the monolayer coverage, a different surface vanadia phase is formed, and this phase upon reduction does not chemisorb oxygen; and second, not only does this "post monolayer" phase fail to chemisorb oxygen after reduction, but also it somehow prevents the already existing species 1 and 3 in the "monolayer" phase from chemisorbing oxygen, thus leading to a decrease in the oxygen uptake capacity. The "post monolayer" phase was found not to consist of crystalline V_2O_5 as revealed by XRD results. Following the line of Yoshida et al. [18], it is envisioned that a highly dispersed two dimensional polymeric V-oxide phase containing distorted square pyramidal or octahedral $(VO_5)_n$ species is formed beyond the monolayer region. Obviously, this phase upon reduction does not show any change in the ESR spectra (Figure 2)

because most of it is reduced to V^{3+} state as found by ESCA and reduction studies, nor does it chemisorb oxygen at -78°C. All evidence suggests that the CUS generated on this polymeric phase is not capable of chemisorbing oxygen at -78°C. Indeed there is evidence in the literature that oxygen chemisorption on V centers may or may not be subject to activation energy depending on the symmetry of the V centers having the CUS. Thus, Khalif et al. [34] observed that V centers with tetrahedral symmetry, V_{Td}, chemisorbed oxygen without activation energy, while those with octahedral or square pyramidal symmetry had to overcome a considerable amount of activation energy of chemisorption. Since our oxygen chemisorption experiments were conducted at subambient temperatures (i.e., at -78°C), a temperature which was even lower than that used by Khalif et al. [34], it is quite possible that while the CUS on V_{Td} sites (species 1 and 3) could chemisorb oxygen, those on the polymeric species containing V_{Oh} or V_{C4v} centers, formed by the reduction of polymeric V^{5+} species, failed to do so. If this is so, then the sharp decline in oxygen chemisorption capacity (which is one of the most important experimental observations of this investigation) of the catalysts containing the "post monolayer" phase indicates that this phase is deposited preferentially on top of the already existing monolayer phase, and that the CUS, even if formed on the monolayer phase upon reduction, probably cannot be reached by oxygen due to diffusion restrictions posed by the "post monolayer" phase which covers the "monolayer". The surface area data, as shown in Figure 1, also indicates that as soon as the "monolayer" is completed, no appreciable decrease in the surface area takes place thereafter. This is perfectly in accord with the proposed hypothesis that an additional amount of vanadia beyond the monolayer level does not cover the silica surface, but rather gets deposited on top of the monolayer phase. In none of the samples studied did the vanadia loading reach the level high enough for the formation of three dimensional crystalline V_2O_5 detectable by XRD. Therefore, we have been dealing with two types of vanadia phases, namely, the monolayer phase which contains the species 1 and 2, and the "post monolayer" phase comprised of polymeric two dimensional V-oxide with V^{5+} in square pyramidal or octahedral symmetry.

A surface structural model of V/SiO₂

In view of the above discussion, a model of the surface state of silica-supported vanadia is proposed as follows: Up to a certain surface coverage (3.5 μmol V m^{-2} in this case) vanadia remains on the silica surface partly as isolated species 1 and partly as its precursor species 2. In both these species the central V ion remains in tetrahedral coordination surroundings. Upon reduction, species 2 is partly converted to species 1 which gives the ESR signal, and mostly to species 3 which chemisorbs oxygen at -78°C. The maximum surface coverage by these two species corresponds to what we call the "monolayer" coverage. Thus the "monolayer" coverage in this particular case is ca. 3.5 μmol V m^{-2}. This phase covers

only about one fifth of the total surface area of silica as calculated by taking 0.103 nm^2 as the diameter of one $VO_{2.5}$ unit [20]. Therefore, this is actually a "patchy monolayer", rather than a monolayer. Further addition of vanadia beyond the "monolayer" results in the formation of a second phase containing polymeric two dimensional $(VO_5)_n$ species with V in square pyramidal or octahedral surroundings. This second phase with V in a different symmetry remains on the top of the "monolayer" phase without further occupying the silica surface. Upon reduction, while the "monolayer" phase chemisorbs oxygen at -78°C, the "post monolayer" phase fails to do so, because the latter consists of octahedral or square pyramidal species that do not chemisorb oxygen at low temperatures due to energy of activation requirements [34]. A similar type of picture comprised of a highly dispersed and chemically bound monolayer phase, and crystalline V_2O_5 on the top of it has recently been proposed for vanadia-titania systems by Wachs et al. [31].

Vanadia-silica versus vanadia-alumina

The effect of the nature of support on the dispersion and oxygen chemisorption capacity of the dispersed phase is well demonstrated by the results pertaining to silica- and alumina-supported catalysts. From the results given in Figure 3 it can be concluded that although silica possesses about four times more specific surface area than alumina, the ratio of the active surface area (i.e., the area titrated by LTOC) to the total BET surface area of both the systems at full mono-layer coverage is practically the same. This may be just a coincidence, however, the maximum amount of the dispersed phase at full monolayer coverage is different for the different supports. Thus, ca. 8.5 and 3.5 μmol V m^{-2} are found to be accommodated by alumina and silica respectively at full "monolayer" coverage. This indicates that the alumina surface has higher dispersion capacity than the silica surface. A similar conclusion was reached earlier by Yoshida et al. [18] from reduction and ESR studies. Recalling also the fact that the "monolayer phase" is formed by a strong chemical interaction between the active OH groups on the support surface and the oligomeric vanadate ions present in the impregnating solution [20], it can be concluded that the surface concentration of the active OH groups in alumina is higher than in silica. In other words, the extent of chemical reaction via the condensation of OH groups of alumina and vanadate ions is much higher than that between vanadia and silica. This may well be the reason why vanadia gets more dispersed on alumina than on silica. Selective exposure of certain crystallographic planes (as surface planes) may also play a part in it.

The implications of the above discussed structural models of the surface species are that upon reduction of these species OH groups attached to V and OH groups shared by both V and Si would be expected to form, and that these OH groups should be possible to be detected by infrared spectroscopy. Whether or not this happens will be the subject of future investigation. It would also be interesting to study

the effect of dehydroxylation of the supports (prior to V loading) on the nature of the resulting surface species because they are envisaged to be formed by the interaction of the OH groups of the supports and that of the V salt.

In conclusion, the present work shows that LTOC, in conjunction with other standard techniques, can be a useful tool for studying the surface structure of SiO_2-supported V-oxides. Oxygen chemisorption data are found to provide information on: (a) the "active" surface area of the supported vanadia phase; and (b) the nature i.e., the dispersion, formal oxidation state and the coordination environment of the central V ions of the dispersed species in the "monolayer" as well as the "post monolayer" phases. The LTOC results allow one to clearly identify the vanadia loading where the "patchy monolayer" becomes complete and the "post monolayer" phase starts forming.

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