JOURNAL OF CATALYSIS **124**, 127–132 (1990)

ESCA and Gravimetric Reduction Studies on V/Al_2O_3 and V/SiO_2 Catalysts

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Received February 15, 1989; revised October 31, 1989

Two series of supported vanadia catalysts, namely V/Al_2O_3 and V/SiO_2, with V_2O_5 loadings up to 20%, have been studied in their oxidized state by ESCA, and their reducibility has been studied by gravimetry. The vanadium was found to be highly, possibly monomolecularly, dispersed in the oxidized catalysts. Upon reduction in hydrogen at 500°C, the V/Al_2O_3 catalysts showed stable V^{4+} state as inferred by gravimetric measurements. Hydrogen-reduced V/SiO_2 catalysts showed about 70% reduction of V^{5+} to V^{3+}. The results are discussed in terms of possible surface species present on these catalysts.

INTRODUCTION

The surface structure of catalytically active oxides, such as vanadia and molybdena, dispersed on supports like alumina, titania, and silica, may be considerably different from that of their bulk phases. The surface phases are, to a major extent, responsible for unique catalytic activity and selectivity acquired by the active phase–support combination. For example, vanadia supported on titania shows excellent catalytic activity and selectivity for the oxidation of benzene to maleic anhydride, naphthalene, and *o*-xylene to phthalic anhydride, whereas bulk V_2O_5 leads to high combustion of the organic molecules to carbon dioxide (*1*). It is important, therefore, to study the surface structure of the active phase in order to understand the relationship between catalytic functionality and activity/selectivity. To this end, a considerable research effort has been made by applying techniques such as ESR (*2–16*), XRD (*5–7, 10–12, 15, 17*), IR/Raman spectroscopy (*3, 6, 11, 12, 17–19*), oxygen chemisorption (*13, 15–17*), and ESCA (*11, 13, 17, 20–23*). On the basis of the results of these investigations, it is now generally accepted that at low vanadia loadings, V-oxide remains as a highly dispersed amorphous "monolayer" phase containing isolated V-oxide species anchored to the support surface by strong carrier–catalyst interactive forces. At higher loadings of vanadia, a bulk V_2O_5 phase also coexists with the "monolayer" phase.

Gil-Llambias *et al.* (*21*) have reported a linear correlation between ESCA intensity ratio of V2*p* to Al2*p* or Ti2*p* peaks as a function of V_2O_5 loading up to a certain level. A similar observation has been made by Meunier *et al.* (*22*). Both of these groups noted a positive shift, relative to bulk V_2O_5, in the BE corresponding to V2*p* state in V/SiO_2, in agreement with a similar observation made earlier by Horvath *et al.* (*20*). Also, Roozeboom *et al.* (*23*) found a positive shift in the BE of V2*p* state for a specially prepared V/Al_2O_3 monolayer catalyst.

For any redox system, as V_2O_5 is, the changes, if any, in the surface structure and dispersion brought about by reduction is of considerable importance because under actual reaction conditions, these catalysts undergo cycles of reduction and oxidation (*24*). Roozeboom *et al.* (*19*) used tempera-

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0021-9517/90 $3.00

ture-programmed reduction to characterize supported vanadia catalysts, and Haber *et al.* (*25*) studied their reducibility by a gravimetric technique. The purpose of the present investigation was to compare the effect of alumina vs silica support on vanadia dispersion and reducibility.

EXPERIMENTAL

Details of catalyst preparation have been given elsewhere (*15*). The supports, Al_2O_3 (180 m^2/g, ACC, India) and SiO_2 (672 m^2/g, Ketjen), were first calcined overnight at 500°C and then impregnated with aqueous solutions containing stoichiometric amounts of ammonium metavanadate (E. Merck, Analar) with constant stirring. Excess water was evaporated by drying at 120°C for 16 h followed by calcining at 500°C for 4 h in air. The V contents of the finished catalysts were determined by atomic absorption spectroscopy. Pure V_2O_5 was prepared by heating ammonium metavanadate in air at 450°C for 4 h. Bulk VO_2 and V_2O_3 were purchased from Aldrich.

A flow microbalance system (Cahn Model 2000) was used to study the hydrogen reduction of the samples gravimetrically. A hydrogen flow of about 40 ml/min was used to reduce the samples at 500°C, and the reduction was continued up to 6 h.

A Hewlett–Packard (Model 5930) ESCA spectrometer, using Al*Kα* monochromatic X-rays (1487 eV) and equipped with a charge-compensating electron gun, was used for the investigation. Samples were finely ground and dusted on double-stick Scotch tape on a copper sample holder (12 × 10 × 1 mm). The sample was evenly spread on the tape and covered by a gold mask with an opening of 7 × 3 mm at the center where the X-ray beam could be focused. The sample holder was then mounted on the ESCA probe. The scanning of the spectra was done at pressures less than 10^{-8} Torr, and the information gathered was stored in a computer for subsequent data processing. Binding energies were measured for $V2p_{3/2}$, $Al2s$, $Si2s$, and $C1s$. The $C1s$ binding energy of 284.6 eV due to hydrocarbon C present was taken as the standard for correction of experimental binding energies pertaining to V states.

RESULTS

Several bulk V-oxides were used to determine the $V2p_{3/2}$ binding energies (BE) corresponding to V^{5+}, V^{4+}, and V^{3+} states in the bulk. The spectra of these oxides are shown in Fig. 1 and the BEs are given in Table 1. It is observed from Fig. 1 that the $V2p_{3/2}$ peaks become broader with decreasing formal oxidation state of the V ion. It is also observed that the VO_2 sample (as supplied by Aldrich) apparently contained some V_2O_3. On the basis of these results, the following binding energy assignments are made: V^{5+}: 518.1, V^{4+}: 517.4, and V^{3+}: 516.6 eV.

Typical spectra of oxidized V/Al_2O_3 and V/SiO_2 samples are shown in Fig. 2. The spectrum of bulk V_2O_5 is also given for comparison. Considerable broadening of the

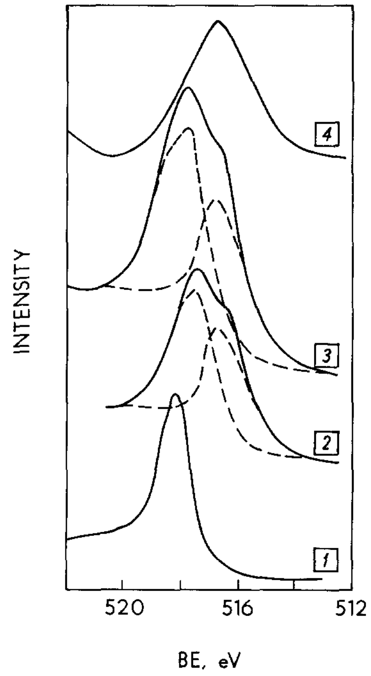


FIG. 1. ESCA spectra of bulk V-oxides. (1) V_2O_5, (2) reduced V_2O_5, (3) VO_2, (4) V_2O_3.

TABLE 1

Binding Energies of Vanadium Oxide Samples[a]

Catalyst	BE (eV)
V_2O_5 (lab)	518.1
V_2O_4 (comm.)	517.6, 516.4
V_2O_3 (comm.)	516.6
13.7% V_2O_5/Al_2O_3	517.9
13.5% V_2O_5/SiO_2	518.6

[a] BE values of $V2p_{3/2}$ referenced to $C1s$ of 284.6 eV.

$V2p_{3/2}$ peaks of the supported vanadia compared with those of bulk V_2O_5 is evident, as are shifts in the peak positions, the V/SiO_2 sample showing a higher and the V/Al_2O_3 sample a lower BE compared to that of pure V_2O_5 (Table 1). Binding energies in both series of catalysts were independent of V loading. Experimental ESCA peak area intensity ratios (V/Al and V/Si) as a function of the bulk atomic ratios are given in Fig. 3. The linear nature of these plots, coupled with the peak broadening noted in Fig. 2, indicates a high state of dispersion of V in both series of catalysts.

Time courses of reduction of some typical samples obtained in the flow microbalance are shown in Fig. 4. Lined-out states of reduction were attained in about 4 to 6 h. Extents of reduction of a number of samples, assuming the presence of only V_2O_5 state in the oxidized samples, are given in Table 2. Reduction of bulk V_2O_5 resulted in about 90% conversion to V_2O_3. For the supported catalysts, account was taken of the weight

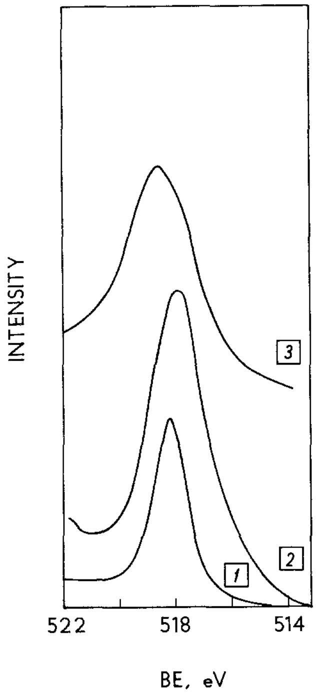


FIG. 2. ESCA spectra of oxidized samples. (1) V_2O_5, (2) 13.7% V_2O_5/Al_2O_3, (3) 13.5% V_2O_5/SiO_2.

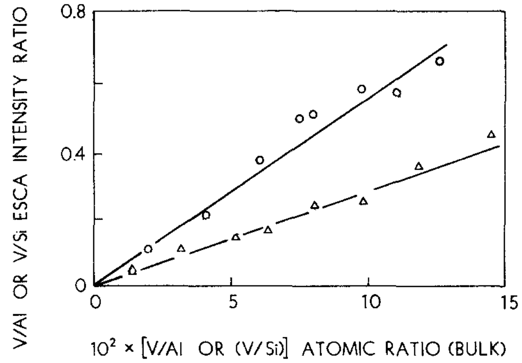


FIG. 3. V/Support ESCA intensity ratios vs V loading. (○) V/Al_2O_3; (△) V/SiO_2.

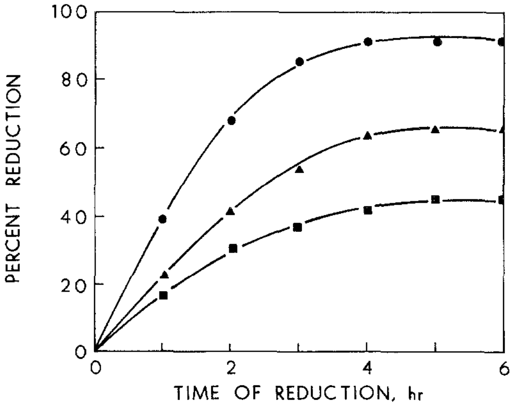


FIG. 4. Time course of reduction of typical V-samples. (●) V_2O_5; (■) 11.9% V_2O_5/Al_2O_3; (▲) 15.2% V_2O_5/SiO_2.

loss due to desorption of absorbed water during heatup in N_2. The V/Al_2O_3 samples gave an average degree of reduction closely corresponding to VO_2. The V/SiO_2 catalysts showed an average reduction to V_2O_3 of 70%. It is noteworthy that the same degree of reduction was obtained for all catalysts, irrespective of the V loading.

DISCUSSION

V/SiO_2 Catalysts

The oxidic V/SiO_2 catalysts exhibited an appreciably higher BE than the bulk V_2O_3 sample (Table 1), in agreement with other reported results (*13, 17, 20, 21*). The V/Si ESCA results of Fig. 3 show good linearity with V content, implying a monomolecular dispersion of the vanadia up to the maximum level studied. This is supported by the broadening of the peaks, another indication of high dispersion. We cannot rule out the possibility of double or even multilayers being present; however, in such a case, they would have to be the same number at all vanadia loadings. Referring to the data of Haber *et al.* (*25*) and assuming monomolecular dispersion of the vanadia, our maximum-loaded catalyst would have about 30% of monolayer coverage.

In a previous paper (*16*), the structure of the vanadia phase at low loading was envisaged to consist of a predominant one-dimensional, dimeric V–O species attached to the silica surface, together with a small number of isolated $V^{4+}O_3$ units also bonded to the surface. At higher loadings, an undefined "postmonolayer" phase, which partly covered the dimer species, was proposed. If this postmonolayer phase is only one layer thick, it would hardly be expected to affect the ESCA V/Si ratio, as observed in the present investigation; multilayer growth, on

TABLE 2

Reduction Results on Vanadium Catalysts

Catalyst[a]	Wt loss (mg)		% Wt loss[e]	% Reduction[d]	
	N_2[b]	H_2[c]		To VO_2	To V_2O_3
V_2O_5 (bulk)	0	8.0	16.0	—	91
% V_2O_5/Al_2O_3					
3.4	2.2	0.13	8.0	91	
7.0	2.5	0.28	8.4	95	
11.9	2.0	0.46	8.1	92	
16.4	3.1	0.65	8.5	97	
18.5	2.9	0.70	8.0	91	
				Avg. 93 ± 3	
% V_2O_5/SiO_2					
4.6	2.5	0.30	13.7		78
7.2	3.2	0.40	11.9		68
8.4	3.5	0.50	12.8		73
13.0	2.8	0.70	11.4		65
15.2	3.0	0.83	11.6		66
					Avg. 70 ± 5

[a] Sample charge of 50.0 mg.

[b] Weight loss during heatup to 500°C in N_2.

[c] Weight loss during reduction in H_2 at 500°C for 6 h.

[d] Percentage reduction calculated on equivalent V_2O_5 basis in oxidized sample, corrected for sample weight loss during heatup.

[e] Theoretical weight loss due to oxygen removal: $V_2O_5 \rightarrow 2VO_2$: 8.8%; $V_2O_5 \rightarrow V_2O_3$: 17.6%.

the contrary, would result in lower ratios at higher V loadings. Roozeboom *et al.* (*19*) observed the presence of both a dispersed and a crystalline V_2O_5 phase on V/SiO_2, the latter appearing by XRD at a concentration of 1.8 V/nm^2, above our maximum loading of 1.5 V/nm^2.

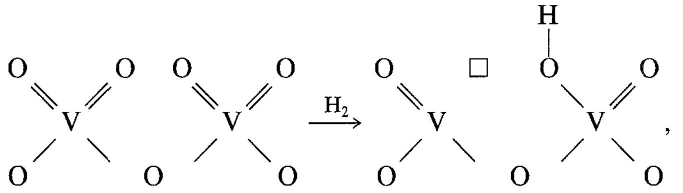
The V/SiO_2 catalysts are not completely reduced to V_2O_3 at 500°C. Gravimetric results indicate about 70% reduction to V_2O_3. Programmed temperature reduction studies of Bosch *et al.* (*26*) indicated that reduction proceeds through several stages, viz, $V_2O_5 \rightarrow V_6O_{13} \rightarrow VO_2 \rightarrow V_2O_3$. Our results are in agreement, showing incomplete reduction to V_2O_3 at 500°C in 6 h. That the extent of reduction was independent of the V content is further evidence for the absence of bulk V_2O_5 in the samples. Roozeboom *et al.* (*19*) reported complete reduction of V/SiO_2 to take place above 525°C.

V/Al_2O_3 Catalysts

The ESCA data on the V/Al_2O_3 catalysts show a consistent, but slightly lower V^{5+} binding energy compared with that of bulk V_2O_5 (Table 1). This is at variance with other studies (*11, 21*), which report a positive shift. We have no explanation for this difference. However, in view of our results on the V/SiO_2 catalysts, which showed an opposite effect (see above), we believe the BE shift to be real for our samples.

The linearity of the ESCA data (Fig. 3) and the broadening of the peaks (Fig. 2) indicate a monomolecular dispersion of the vanadia, even at the highest V level studied. From the data of Haber *et al.* (*25*), our highest-loaded catalyst would have close to 90% of monolayer coverage.

The gravimetric results gave 93 ± 3% reduction to VO_2, the balance presumably being due to unreduced V_2O_5. Apparently, the alumina support stabilizes V^{4+} in the reduced state. However, another explanation may be offered, based on a proposed model of Haber *et al.* (*25*). These authors envision a dimeric V – O structure bonded to the alumina surface for the oxide catalyst, which when reduced consumes $\frac{3}{2}$ mol of H_2 (instead of 2 mol for $V_2O_5 \rightarrow V_2O_3$), viz,



where □ represents an anion vacancy. Correcting our gravimetric data for one H retained per two V in the reduced state, gives an average reduction of 99 ± 3%, in excellent agreement with the proposed reaction sequence above.

SUMMARY

The results of the present investigation show vanadia to be highly, possibly monomolecularly, dispersed on Al_2O_3 and SiO_2 for loadings up to at least 8.3 and 1.5 atoms V/nm^2, respectively. The dispersed vanadia is reducible to different oxidation states, namely to 4+ for V_2O_5/Al_2O_3 and 3+ for V_2O_5/SiO_2 catalysts. The V^{4+} state apparently is stabilized on the Al_2O_3 but not on the SiO_2 surface.

ACKNOWLEDGMENTS

The authors thank the University of Utah for an internal research grant to carry out this work and the Regional Research Laboratory, Hyderabad, India, for supplying the catalysts.

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