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AN XPS STUDY OF DISPERSION AND VALENCE STATE OF TiO_2 SUPPORTED VANADIUM OXIDE CATALYSTS

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"Monolayer" vanadium species are mainly in the V(V) valence state, but with XPS a small fraction of V^{4+} species are identified. Prolonged analysis treatment increases the V^{4+} concentration. With increasing vanadium concentration, a monolayer coverage corresponding to 1 mg V_2O_5 per m^2 develops, and it contains additional layers with a thickness of about 250 Å at 4 mg V_2O_5 per m^2, covering 3% of its surface area.

1. Introduction

V_2O_5 supported on TiO_2 is an important catalytic system that has received much attention and finds applications especially for oxidation [1–6] and ammoxidation [7–9] reactions. The beneficial influence of the support, TiO_2, appears to be connected to its chemical and structural properties suitable for producing a high dispersion of the supported phase. Surface vanadium oxide species on titania shows a complex nature, but it appears as a preferential exposure of agglomerates is advantageous or amorphous structures is advantageous over pure monolayer exposure [6,9,10]. The monolayer phase, acting as anchoring site for the other phases, has been considered, from measurements with EXAFS [11], XPS [4,6] and TPR [12,13], as containing V(V) species mainly. However, results from chemical titration points at a high content of V(IV) in the monolayer [8–10,14–17]. Since earlier XPS studies [4,6,18,19] were performed with standard X-ray radiation, with the presence of satellites producing peaks interfering with the V 2p peaks, it is considered important to re-investigate the V_2O_5/TiO_2 monolayer catalysts with monochromatic X-ray radiation. It is also of interest to compare models for monolayer coverage and dispersion of the external phases from intensity data of these pure spectra.

2. Experimental

The catalysts were prepared by adding aqueous solutions of NH_4VO_3 (Merck, P.A.) to TiO_2 (Degussa, P25). The surface area of the TiO_2 batch used is 45 m^2/g. The samples were dried at 393 K in air and calcined at 773 K for 6 h in air. Some samples were also prepared from solutions of NH_4VO_3 and oxalic acid, containing VO_2^+ species, by impregnation followed by calcination at 673 K for 4 h.

XPS measurements were performed with a Kratos XSAM 800 instrument equipped with a X-ray monochromator. The slit width was set at 40° and the analyzer was operated at 40 eV pass energy and at low magnification. Measurements were also performed with standard Al and Mg $K\alpha$ X-ray radiation and then the analyzer was operated at 20 eV pass energy and at high magnification. As peak intensities the area above a linear base line were taken. Charging effects were corrected for by adjusting the Au $4f_{7/2}$ peak, of gold deposited on the samples, to a position at 83.8 eV. For this purpose, several samples were prepared, in a vacuum evaporator, with gold deposited as small islands.

3. Results and discussion

3.1. VANADIUM VALENCE STATE

Fig. 1 shows V $2p_{3/2}$ photoelectron spectra, excited with both standard and monochromatic Al $K\alpha$ X-ray radiation, for various V_2O_5/TiO_2 catalysts. Spectrum C for TiO_2 obtained with standard X-ray radiation shows the O 1s $K\alpha_{3,4}$ satellite, clearly interfering with the V $2p_{3/2}$ peak at about 517 eV. At low V-concentration, spectrum A, the V $2p_{3/2}$ line is just barely visible as a shoulder, meaning that its B.E. is not easily measured. Although subtraction of a pure O 1s $K\alpha_{3,4}$ satellite spectrum or curve resolution could reveal its features, it will not produce as accurate data as a pure spectrum obtained with monochromatic X-ray radiation. Therefore, some earlier studied [6] V_2O_5/TiO_2 catalysts, and some new preparations, were measured with monochromatic X-ray radiation. Fig. 1, spectra D–G shows the V 2p spectra obtained. Clearly, the spectra show that for 10 wt% V/TiO_2 and 2 wt% V/TiO_2 only one component is present and the V $2p_{3/2}$ B.E. of 517.3 eV identifies it as V(V) (see table 1 that summarizes all B.E. data). The small positive shift compared with V_2O_5 could be an effect of the high dispersion. For the catalysts 0.5 wt% V/TiO_2, however, a slightly shifted position and asymmetry towards lower B.E. is obtained. See spectrum F, fig. 1. This difference is explained by the presence of a small amount of V(IV), that should have a B.E. about 1 eV lower than V(V), as deduced from the difference between V(V) in V_2O_5 or NH_4VO_3 and V(IV) in $C_{10}H_{14}O_5V$ (see table 1). The amount of V(IV) in this sample can be estimated as less than 20%, but to be on the conservative side 40% is assumed. The spectrum for 0.2 wt% V/TiO_2, G in fig. 1, is further shifted

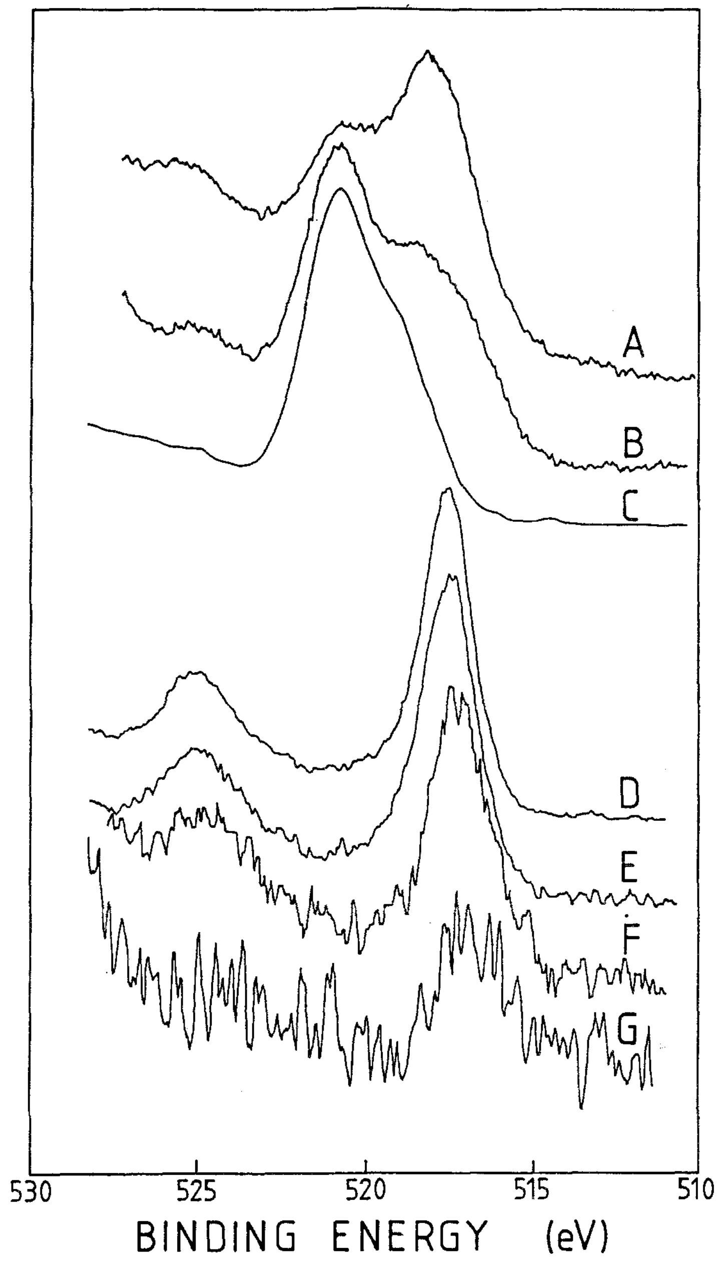

Fig. 1. V 2p XPS spectra of V_2O_5/TiO_2 catalysts. Standard Al Kα radiation: (A) 2 wt% V/TiO_2, (B) 0.5 wt% V/TiO_2, (C) TiO_2. Monochromatic radiation: (D) 10 wt% V/TiO_2, (E) 2 wt% V/TiO_2, (F) 0.5 wt% V/TiO_2, (G) 0.2 wt% V/TiO_2.

indicating a higher amount of V(IV). Thus, it is possible with XPS to identify small amounts of V(IV) on the surface of these monolayer type catalysts. The amount can be estimated to about 0.1–0.2 wt% V, at the most which is very little

Table 1
Binding energies [a] (eV) for V_2O_5/TiO_2 catalysts

wt% V	O 1s	V $2p_{3/2}$	Ti $2p_{3/2}$	After 50 h exp. V $2p_{3/2}$
0	530.2	–	458.9	–
0.2	530.2	516.7	458.9	516.0
0.5	530.1	517.0	458.9	516.3
2.0	530.1	517.3	458.9	516.8
4.0	530.2	517.1	458.9	–
7.0	530.2	517.2	458.9	517.1
10.0	530.0	517.3	458.9	517.2
1.5 [b]	530.2	517.3	458.9	516.7
3.0 [b]	530.3	517.2	458.9	516.8
4.5 [b]	530.2	517.2	458.9	516.9
V_2O_5	529.7	516.8		
NH_4VO_3	529.9	516.7		
$C_{10}H_{14}O_5V$	530.7	515.7		

[a] Charging effects corrected for with Au $4f_{7/2} = 83.8$ eV on separate samples. Data obtained with monochromator.
[b] Prepared by oxalic acid method (VO^{2+}).

compared to the about 2 wt% V required for a monolayer (vide infra). The earlier results indicating a V(V) monolayer [4,6,11–13] can thus be understood on the basis of the low concentration of V(IV), being that V(V) dominates. There is no evidence for the presence of an exclusively almost V(IV) layer at these concentrations in contradiction to chemical titrations [8–10,14–17]. The difference could possibly be connected to the various preparation methods, but also to the procedures for chemical titration. In all these cases the initial vanadium solution was reduced with oxalic acid and thus impregnation performed with a solution containing mainly VO^{2+} species, whereas in our case an aqueous solution of NH_4VO_3, probably containing various vanadate species, were used. The initial dried catalyst could thus be different, considering V(IV) and V(V) species, which must persist calcination at 400°C for 3 hours as applied [8–10,14,16,17,20]. For this purpose we also prepared some catalysts by the oxalic acid method, data included in table 1. The V $2p_{3/2}$ B.E. and spectra are similar to those presented in fig. 1 for 2 wt% V/TiO_2. One difficulty encountered with the XPS analysis was that prolonged treatment of catalysts in vacuum, but also X-ray exposure, resulted in reduction of the materials. Evidently the V species are quite reactive, giving off oxygen in vacuum which results in formation of V^{4+}. Although the large transformations were observed over several days of treatment, it is a little uncertain to what extent the quite small fraction of V^{4+} observed on 0.2 wt% V/TiO_2 and 0.5 wt% V/TiO_2 are genuine or formed in the analysis treatment.

As shown above, the different preparation methods seems to give similar results, wherefore the difference possibly could be caused by some elements in the titration procedures. The titration is generally performed by first extracting "soluble" VO_x species by an aqueous NH_3 solution, and the solid fraction is dissolved in strong H_2SO_4. It is, however, well known that V(IV) in alkaline solutions at room temperature is rapidly oxidized by air to V(V) [21]. This explains why extraction with an aqueous solution of NH_3 always give exclusively dissolution of V(V) [8,9,14–18] since V(IV) is rapidly oxidized. At high vanadium concentrations the re-oxidation rate is determined by oxygen diffusion [21]. The time of extraction is also important for the re-oxidation but also for the amount extracted. The redox potential for the V(IV)/V(V) couple is considerably dependent on the temperature and acidity of the solution. In acidic media, VO_2^+ is a powerful oxidizing agent. The dissolution of the solid fraction in strong H_2SO_4 gives a solution containing the amount of Ti^{3+} originally present in the solid, which may depend on the preparation of TiO_2. It is conceivable that it, in solution, is oxidized, producing V(IV) independent of initial V-concentration. Possibly, this could correspond to the difference in V(IV) concentration obtained by both methods. Non-extractable vanadium species may, except for surface bonded, also be present as inclusions or dissolved in the structure. Rutile may hold quite high amounts of V(IV) [7], and recent data has shown that a small amount of V(IV) may be dissolved in anatase [22].

3.2. MONOLAYER COVERAGE AND DISPERSION

Fig. 2 shows the $I_{\mathrm{V}\,2p_{3/2}}/I_{\mathrm{Ti}\,2p_{3/2}}$ intensity ratios measured here with monochromatic radiation as well as with standard Mg Kα and Al Kα radiation. The area measurements of the monochromatic spectra are quite straight forward, while the standard Al Kα spectra were fitted with two components, one Gaussian for V $2p_{3/2}$ while for the O 1s Al K$\alpha_{3,4}$ component the natural curve form measured for TiO_2 was taken. For the Mg Kα spectra satellite subtraction was applied. The intensity for the Ti $2p_{3/2}$ peak was taken as 0.67 times the area above a linear base line of both Ti 2p components. Attempts to include satellites failed due to difficulties in defining the base line. Not much chemical difference occur between the samples, the support being the same for all and the surface phase being similar vanadium oxide species, so it is expected that very little differences in intrinsic multielectron excitations do occur. The deviation of the points obtained with Mg Kα radiation is considered to depend on the satellite subtraction procedure.

The theoretical model to explain the decline of the initial rapid increase in the intensity ratio seen in fig. 2, is based on that presented for V/Al_2O_3 [23] and V/TiO_2 [6] catalysts, but extended to incorporate multilayer formation. As a first approximation, the model assumes that initially a monolayer of VO_x species are formed. The coverage of this monolayer, X_1, is a function of the vanadium loading as;

$$X_1 = \mathrm{wtV}/M \tag{1}$$

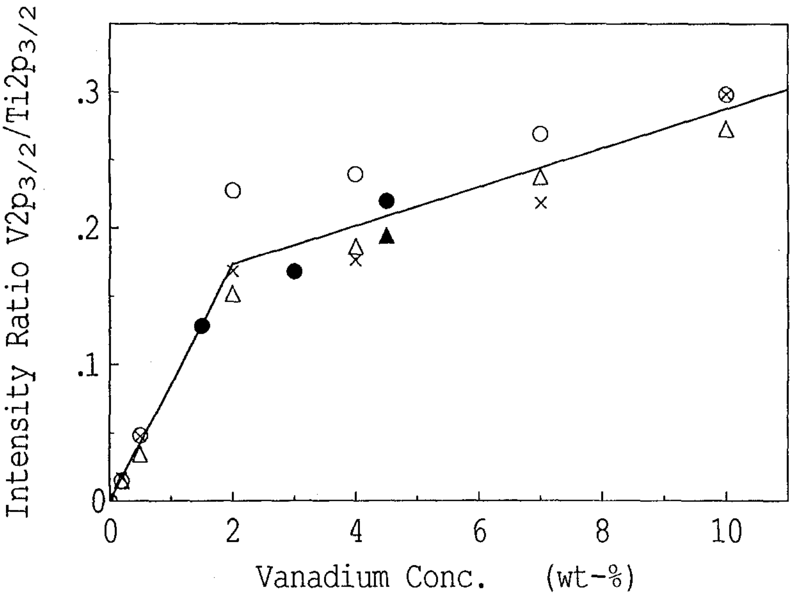

Fig. 2. $I_{V\,2p_{3/2}}/I_{Ti\,2p_{3/2}}$ intensity ratio as a function of nominal vanadium loading. (△) data by monochromator; (x) data by standard Al Kα radiation. (Curve resolved); (○) data by standard Mg Kα radiation (satellite subtracted); Filled symbols represent catalysts prepared by oxalic acid method. The solid line represents calculated data.

where wtV is wt% V and M the theoretical monolayer capacity. Calculation of the latter is a bit arbitrary, but is here taken as earlier [6] as a sheet of VO_x units as partly appearing in the V_2O_5 structure, and this value, 4.09 wt% V, should be considered as an upper limit for M. Relation (1) is valid up to completion of the real monolayer formed on the catalyst. Within this concentration range the XPS intensity ratio is given by;

$$I_{V\,2p_{3/2}}/I_{Ti\,2p_{3/2}} = C \cdot \frac{X_1 \cdot (1 - e^{-a})}{1 - X_1 \cdot (1 - e^{-b})} \tag{2}$$

where a, b and c contain the usual terms which are given earlier [6,21]. This almost linear relation was fitted to the data for catalysts of 0 < = wt% V < = 1.5, and gave a value for C of 3.48. As seen in fig. 2, this relation fits to the data up to about 2 wt% V, which is the real monolayer coverage. It should be realized, however, that this is not a unique solution, since not a large deviation is obtained by growing partly a layer of doubled thickness with the total coverage then decreased proportionally. Perhaps, the most realistic model is to allow for smaller areas of two or three layers thickness already at this loading. Due to the relatively sharp leveling off from relation (2) above 2 wt% V, it seems however definite that the so called monolayer coverage only increases little thereafter.

At vanadium loadings between 2 and 10 wt% a different expression than relation (2) is needed to explain the data. As a first approximation, it is assumed that in this region additional vanadium is deposited on top of the already formed monolayer, with a thickness n, in number of monolayers taken as 2.4 Å [6,21], and with a coverage X_2. It was found not possible to fit such a model, but necessary to allow X_2 to grow with the vanadium loading. Also it was necessary that the monolayer could continue to grow with a coverage X_3 at higher loading. To approximately allow for these variables, the following relations were assumed:

$$X_2 = (\mathrm{wtV} - 2)/H \tag{3}$$

$$X_3 = (\mathrm{wtV} - 2)/G \tag{4}$$

where G and H are constants. The thickness of the overlayer in this concentration interval is given by:

$$n = (\mathrm{wtV}/M - X_1 - X_3)/X_2 + 1. \tag{5}$$

The free exposed monolayer coverage is changing to $X_1 - X_2 + X_3$ and the exposed TiO_2 surface is $(1 - X_1 - X_3)$. The expression for the XPS intensity ratio in this interval is given by;

$$\frac{I_{\mathrm{V}\,2\mathrm{p}_{3/2}}}{I_{\mathrm{Ti}\,2\mathrm{p}_{3/2}}} = C \cdot \frac{(X_1 - X_2)\cdot(1 - \mathrm{e}^{-a}) + X_2\cdot(1 - \mathrm{e}^{-an}) + X_3\cdot(1 - \mathrm{e}^{-a})}{1 - X_1\cdot(1 - \mathrm{e}^{-b}) - X_2\cdot(\mathrm{e}^{-b} - \mathrm{e}^{-bn}) - X_3\cdot(1 - \mathrm{e}^{-b})} \tag{6}$$

where a, b and C are as given for relation (2). By fitting this expression to the data for $2 < = \mathrm{wt\%\ V} < = 10$, and with $C = 3.48$ as derived from relation (2), values for X_1, G and H were obtained. These are $X_1 = 0.49$, $G = 54$ and $H = 501$. The fraction of the monolayer where continued growth is obtained is given by relation (3) and it increases up to 0.016. . The thickness, n, is increasing up to about 110 corresponding to over 250 Å. The continued growth of the monolayer X_3, increasing up to 0.15, is given by relation (4). It is for the quantification model (4) not necessary that the additional layer is continuous, but could almost equally well be broken up in particles or patches. However, as a sort of "average model" the data suggests a monolayer coverage of 0.5 + 0.15 and a continued growth over about 3% of its area with additional layers with a thickness up to about 250 Å at a vanadium loading of 10 wt% V. The total monolayer coverage corresponds to 1.04 mg V_2O_5 per m^2. The line in fig. 2 shows the data calculated by relations (2) and (6). It should be considered that the model is sort of an "average" model and could be refined, allowing for a distribution of patches of different coverages and heights.

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