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PREPARATION AND CHARACTERIZATION OF A MODEL SYSTEM FOR THE STUDY OF MONOLAYERS AND MULTILAYERS OF VANADIA SUPPORTED ON TITANIA

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A model system for the study of structural and chemical properties of monolayers and multilayers of vanadium oxide immobilized on titania is presented. Investigation of the planar oxide-oxide interface by XP, UV and IS spectroscopy indicated that vanadium immobilized by a single impregnation step exists as an incomplete heterogeneous layer containing well dispersed V^{4+} species. Increase of the vanadia loading by multiple impregnations led to vanadia agglomerates with higher apparent oxidation state of the vanadium. TD spectroscopy with O_2 and CO_2 as probe molecules revealed that the chemical reactivity of the vanadia surface species depends on their structure. The surface containing well-dispersed vanadia species exchanged oxygen more easily and showed pronounced interactions with CO_2.

Vanadium oxide, titania, model, oxide-oxide interface

1. Introduction

The use of surface analytical methods for the characterization of oxide-oxide interfaces in technical catalysts frequently causes severe problems due to charging effects, surface roughness (porosity) and contaminants originating from the bulk oxide phase. Here we report the preparation of a model oxide-oxide interface suitable for the investigation by surface analytical methods. The vanadia-titania model interface was prepared to study the chemical and structural properties of monolayers and multilayers of vanadia supported on titania. The corresponding technical catalysts were earlier found to exhibit extremely high activity for the selective catalytic reduction (SCR) of nitric oxide [1].

2. Preparation

Aluminium nitride platelets of 25 × 25 × 0.5 mm size were chosen as mechanical support material due to their good mechanical stability and thermal conductivity. In order to achieve good electrical conductivity a layer of about 200 nm gold was brought onto the aluminium nitride surface by controlled evaporation. On top of the gold layer a titanium layer of about 5 nm was deposited which was then transformed to TiO_2 by oxidation in air at room temperature. The oxidation of the titanium film to TiO_2 was checked by UV-VIS spectroscopy which showed an absorption edge at 355 nm, typical for small TiO_2 particles [3].

Finally, vanadium oxide species were anchored onto the titania surface using the surface reaction of vanadyl triisopropoxide with surface hydroxyl groups of the titania. The immobilization was carried out in n-hexane as described previously [1,2]. After each immobilization step samples were calcined for 20 min in air at 300 ° C. Samples with different vanadium loadings corresponding to single immobilization (referred to as 1V) and four-fold immobilization (4V) were prepared and investigated [4].

Impregnated and calcined samples showed a shift of the UV-VIS absorption edge of titania to ca. 370 nm indicating that some of the small titania particles had transformed to rutile (the thermodynamically more stable phase) during calcination. Similar behavior was observed earlier by XRD with the preparation of the corresponding technical catalysts [1]. Comparative BET surface area measurements of the sample before and after impregnation with vanadia showed that the total surface area of the sample increased by about an order of magnitude upon impregnation. None of the samples showed any detectable Bragg reflections of titania or vanadia in powder XRD, indicating that no bulk oxides were present. The quality of the deposited layers was checked by SEM, ISS and XPS. All sucessful preparations showed only smooth structures in SEM, whereas faulty impregnation led to spherical vanadia particles of about 100 nm size. ISS showed that the impregnated surfaces consist of dense layers of V/Ti oxides. The underlying gold became detectable only after extensive ion etching.

3. Characterization

In order to gain some insight into the chemical structure and reactivity of the vanadia deposited on the TiO_2 surface the two samples (1V and 4V) were investigated using XPS and TDS.

X-RAY PHOTOELECTRON SPECTROSCOPY

Photoemission experiments were carried out in a carbon-free UHV environment of 1×10^{-10} mbar. XPS spectra were obtained with non-monochromated Mg $K\alpha$ radiation and with a LHS 12 hemispherical analyser operating at pass

Table 1
Elemental surface composition of vanadia-titania samples determined by XPS

Samples	Binding energies (eV)		Surface concentration [a] [at%]		
	$V2p_{3/2}$	$V2p_{1/2}$	V	Ti	O
TiO_2	–	–	–	28	72
TiO_2-1V	516.0	523.6	3	22	75
TiO_2-4V	516.4	523.9	15	9	76

[a] Integrals calculated using atomic sensitivity factors of V2p, Ti2p and O1s from ref. [12].

energy 50 eV; no flood gun was used. All annealing was done in the clean UHV of an attached preparation chamber. Preliminary test measurements showed that XPS results gained from samples held under UHV conditions at room temperature were significantly different from those of samples after annealing in UHV at 380 ° C. The annealing caused desorption of atmospheric contaminants and resulted in a more intense and narrow V2p spectrum. All results reported were measured on annealed samples. Table 1 lists the elemental composition of the surface of the samples as determined by XPS. Note that the surface compositions were calculated excluding a significant amount of carbon characterized by a C1s binding energy (b.e.) of 285.3 eV. We refrain from deriving oxide stoichiometries from these data due to the ill-defined escape depth and morphology of the films [5]. The ratio of cationic to anionic species was the same in all samples, indicating that the systems were real interfaces and not thick platelets of oxides on gold. Subsequent impregnation increased both homogeneity and thickness of the vanadium oxide layer as can be seen from the changing V : Ti ratio. We note that the vanadium concentration of the four-fold impregnated sample (4V) appears to be about 5.5 times higher than that of the singly impregnated (1V) sample, which suggests that the vanadia load was not increasing by the same amount with each successive impregnation step. This finding is consistent with earlier results on the technical catalysts [2] which were obtained by measuring the hydroxyl concentration and the vanadium concentration after each impregnation step. These measurements indicated that upon single impregnation only part of the hydroxyl species reacted with the vanadyl alkoxide and that upon calcination new hydroxyl species are formed which in turn may react with other alkoxide species in subsequent impregnations.

Figure 1 shows a typical spectrum of a UHV annealed 1V sample. The raw data were only subjected to a satellite substraction procedure. The shape of the $V2p_{3/2}$ transition permits accurate determination of its binding energy which is not affected by charging effects due to the small and uniform layer thickness. The absence of charging follows from both the $Ti2p_{3/2}$ b.e. of 459.0 eV and the O1s b.e. of 529.7 eV with respect to $Au4f_{7/2}$ (84.0 eV). The shoulder in the O1s spectrum at ca. 531.6 eV is characteristic of hydroxyl groups which are chemisorbed strongly enough to withstand the UHV annealing at 380 ° C. The inset in fig.

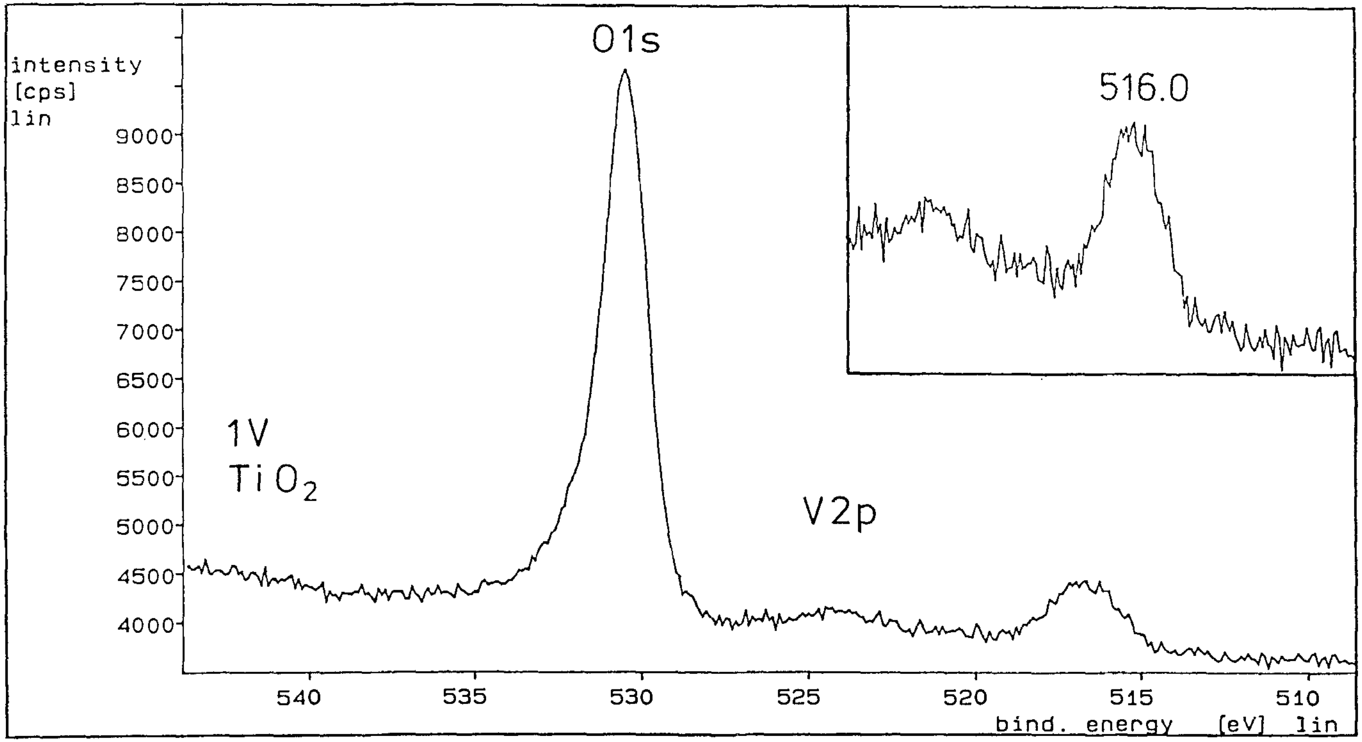

Fig. 1. Raw data scan through the O1s and V2p region of a 1V sample after several annealing cycles of the model interface at 380 ° C for a few minutes. (The binding energy scale is upshifted for 0.86 eV relative to Au4$f_{7/2}$).

1 illustrates that the intensity distribution between the $V2p_{3/2}$ and $V2p_{1/2}$ transition is apparently less than the theoretical value of 3/2. This is due to a wide intensity distribution of the final state satellite spectrum which broadens the total integrated V2p intensity beyond the determination limit given by the background substraction procedure, i.e. the V2p spectrum overlaps partly with the O1s spectrum. It is, therefore, not possible to derive accurate V : O atomic ratios from integration of the $V2p_{3/2}$ and O1s transitions since an unknown fraction of V2p intensity will be lost in the data evaluation.

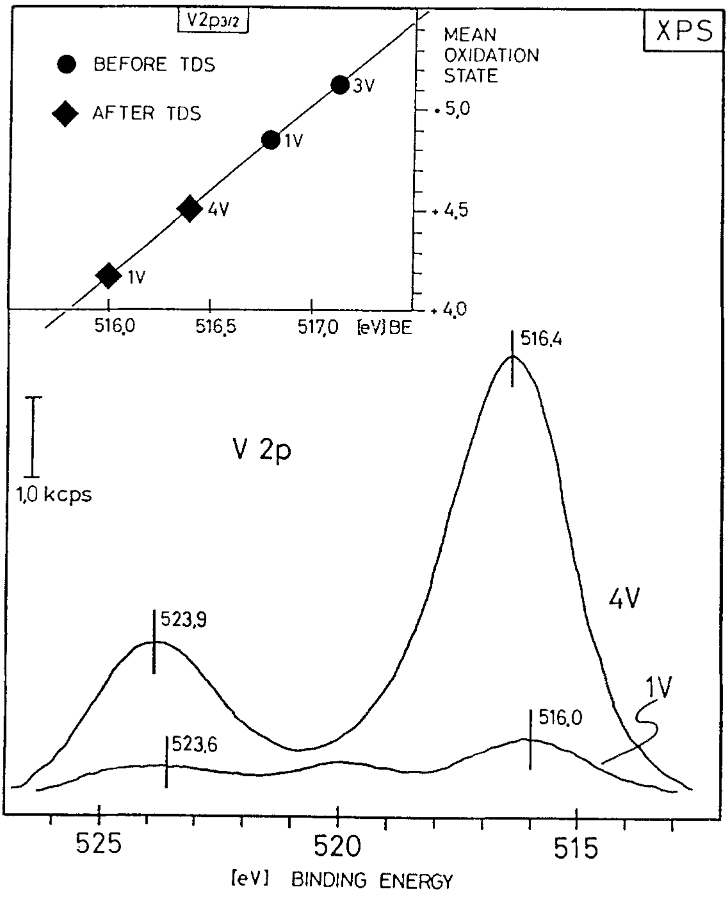

Fig. 2. XPS results of the V2p region of singly impregnated (1V) and fourfold impregnated (4V) samples after corrections for O1s satellites and inelastic background. In the inset, the solid line represents a linear correlation between the binding energies of different vanadium oxides reported in the literature (referred to $Au4f_{7/2} = 84.0$ eV) with their formal oxidation state. The experimental binding energies as measured in the present study are indicated by solid points. Using this correlation the mean oxidation state of vanadia in the samples are estimated to be: (1V) + 4.2; (4V) + 4.5. Note the remarkably higher mean oxidation state of untreated samples, i.e. samples before TDS measurements.

Figure 2 shows the V2p spectra of two samples corrected for inelastic background and X-ray satellites. The binding energy scale which required no correction for charging is referred to Au $4f_{7/2}$ from the substrate. Again, the absence of charging effects was evidenced by the $Ti2p_{3/2}$ (b.e. 459.0 eV) spectrum which was the same in all samples and coincides with the data of reference compounds [6]. Note the chemical shift of 0.4 eV between the two peaks (1V, 516.0 eV; 4V, 516.4 eV) of the vanadium in the two preparations. These data together with binding energies of reference samples and compounds reported in the literature [8] permit a rough estimate of the oxidation state of the vanadium in the two samples. Average oxidation states estimated from this correlation (see inset in fig. 2) were: 4.2 (1V) and 4.5 (4V), respectively. Note that the assumed linear correlation is a rough approximation and does not account for possible influences of Madelung and relaxation effects. However, assuming that the spectroscopic effects are similar for both samples, we can conclude that the formal valency of the vanadium is lower in the 1V sample relative to the 4V sample. This behavior is attributed to the strong interaction of vanadia monolayer with the titania substrate. The interaction is weakened for the vanadia in successive layers as present in the 4V sample. This result is in agreement with the earlier observation by TPR that vanadia in the first layer is more easily reduced than in successive layers [1,7].

The XP spectrum of the 1V sample shows a second maximum for $V2p_{3/2}$ around 520 eV due to charging of some vanadia with relatively loose contact to the surface. A similar shift was also detected in the corresponding O1s spectra. The linewidth (FWHM) of the $V2p_{3/2}$ spectra (3.1 eV) was markedly larger than the linewidths of reference compounds such as V_2O_5 (1.6 eV). In agreement with literature data [8] we may view this as an indication for the formal valency of vanadium being lower than +5 and for unresolved final state effects which broaden the V2p lines.

To sum up, our XPS results indicate that monolayers and multilayers of vanadia supported on titania show distinct spectroscopic differences with regard to their structure and chemistry. The vanadia-support interaction as well as the chemical nature of the vanadium oxide seem to be different for 1V and 4V samples of the model system. Although we cannot exclude an influence from the structure of the titania support and from the impregnation conditions [13], we consider these findings as inherent properties of titania-vanadia layer systems.

THERMAL DESORPTION SPECTROSCOPY

TDS was used to characterize the interaction of oxygen and carbon dioxide with the vanadia layers. The desorption spectra after exposure to oxygen (200 L, 25 ° C) as measured for the two samples (1V and 4V) are shown in fig. 3 (O_2). The major difference between the spectra of sample 1V and 4V is the appearance of three distinct desorption maxima at 80 ° C, 145 ° C and 245 ° C in the spectra of sample 1V. This indicates that the 1V surface exchanges oxygen more easily with

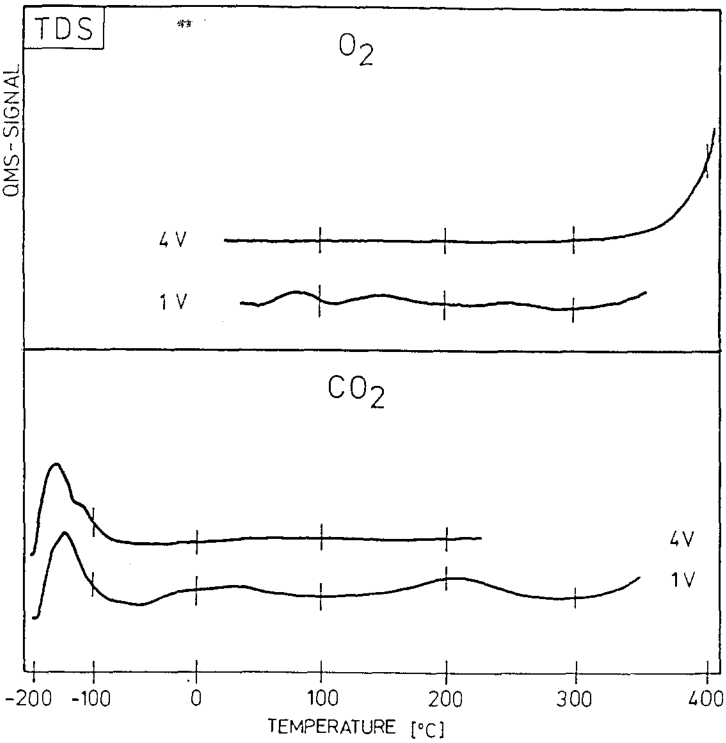

Fig. 3. Thermal desorption spectra of oxygen and carbon dioxide desorption from the singly (1V) and fourfold (4V) impregnated samples. The spectra were recorded after exposure to 200 L O_2 at 25 °C, and after exposure to 1 L (1V) and 2 L (4V) CO_2 at −196 °C (base pressure of the UHV chamber 1×10^{-7} mbar).

the gas phase upon heating than the 4V surface. Thermal reduction of both surfaces set in at about 330 °C leading to strong oxygen desorption from the interface. V_2O_5 has been reported to be stable in vacuum (10^{-2} mbar O_2) up to about 400 °C [9]. Kozlowski et al. [10] have shown that in TiO_2/V_2O_5 systems V^{5+} is reduced to V^{4+} and incorporated into the rutile lattice above 400 °C. At the lower temperatures used in our experiments this behavior was not observed. These results corroborate our conclusion that different XPS data of 1V and 4V samples indicate in fact a chemical difference between the two oxide layers and are not only due to spectroscopic differences. Moreover, the thin layers of vanadia on titania seem to be less stable against thermal degradation than bulk V_2O_5.

The interaction of carbon dioxide with the supported vanadia samples was also tested by TDS. The corresponding spectra measured after CO_2 exposure at −196 °C (4V, 2L; 1V, 1L) are presented in fig. 3 (CO_2). Note that distinct desorption maxima were detected for sample 1V, whereas the 4V sample was virtually non reactive. This result is in line with the conclusion drawn from O_2

adsorption, namely that the chemical properties of the first and subsequent vanadia layers are distinct.

4. Conclusions

We prepared a model interface vanadia-titania which allowed accurate spectroscopic characterisation due to the absence of bulk-support induced lineshifts and line-broadening. Based on earlier investigations [1,7,11] and the results obtained on this present model TiO_2/V_2O_5 interface we propose different structures for the singly impregnated (1V) and the four-fold impregnated (4V) TiO_2/V_2O_5 samples. The singly impregnated sample consists of an incomplete heterogeneous layer of well-dispersed V^{4+} and as a minor phase agglomerates of vanadia in a higher oxidation state, which are loosely bound to the titania surface. Further immobilizations lead to an increase of the titania surface covered with the well-dispersed V^{4+} species and, in particular, to growth of the vanadia agglomerates. It has earlier been shown by high resolution microscopy that these agglomerates are disordered and do not exhibit any long range ordering of the constituents [1]. The studies on the model system show that the valency of the vanadium ions increases from the monolayer to the multilayers. TDS with oxygen revealed that the well-dispersed vanadia of sample 1V exchange oxygen more easily than the larger agglomerates on sample 4V. The TDS results provide further evidence for the structural and chemical difference of monolayers and multilayers of vanadia on titania supports.

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