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Vanadia/silica model catalyst: AFM and XPS investigation of morphological and chemical changes occurring upon exposure to different gas atmospheres

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A model vanadia/silica interface has been prepared by vapour deposition of vanadium-oxy-triisopropoxide onto the native oxide layer of a silicon wafer. The $VO_x/SiO_2/Si$ model system has been used to investigate the morphological and chemical changes occurring with vanadia/silica catalysts when they are exposed to different gas atmospheres. Atomic force microscopy and X-ray photoelectron spectroscopy have been used to follow these changes. The studies show that exposure of the vanadia/silica interface to conditions prevailing during the selective reduction of NO by NH_3 results in temperature dependent morphological changes, while the oxidation states of the vanadia species reflected by the ratio V(III)/V(V) change only little during the surface reconstruction.

Keywords: vanadia/silica; atomic force microscopy; X-ray photoelectron spectroscopy; model catalyst; surface reconstruction; chemical changes

1. Introduction

Mixed oxides and supported oxides are important catalysts for various industrial processes such as the oxidation of hydrocarbons [1] or the selective reduction of nitrogen oxides [2]. It is known that the oxide–oxide interfaces in these catalysts are frequently decisive for the catalytic performance and consequently their structural and chemical characterization is most desirable. Unfortunately, for technical catalysts the use of surface analytical methods for the characterization of oxide–

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oxide interfaces causes severe problems due to charging effects, surface roughness (porosity) and contaminants originating from the bulk oxide phase. To overcome these difficulties, a promising approach is the use of specifically designed multilayer model systems of the catalyst surface [3–7]. In an earlier study of the selective catalytic reduction (SCR) of NO by NH_3 over vanadia on titania [8], we observed an unusual temperature dependence of the rate of nitric oxide reduction. The reaction rate referred to the vanadia surface sites passed through a maximum between 400 and 500 K. This behavior was attributed to changes in the vanadia dispersion caused by the interplay between thermally induced agglomeration and the redox processes occurring during SCR. A similar activity behavior was not observed for alumina-, zirconia- and titania-supported vanadia [9], which indicates the relatively weak interaction and structural instability of the vanadia–silica interface.

These observations have prompted us to investigate the structural and chemical stability of vanadia species supported on silica, when they are exposed to oxygen and hydrogen atmospheres, and to SCR conditions. A model vanadia/silica system has been prepared which allowed to follow the morphological and chemical changes of the supported vanadia by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. SAMPLE PREPARATION

Commercially available, polished Si(100) wafers (Wacker, Germany) were cut into 25 × 25 mm pieces and pretreated in vacuum (1×10^{-2} mbar) for 1 h at 423 K.

Table 1
Quantification of AFM images

AFM figure [a]	Treatment	Surface roughness statistics (nm)		
		(area R_a) [b]	RMS [c]	$(Z_{max} - Z_{avg})$ [d]
1a	1 h O_2, 523 K	1.1	1.5	74
1b	1a [e] + 1 h O_2, 573 K	1.2	1.8	100
1c	1b + 1 h O_2, 723 K	1.6	2.0	131
2a	1b + 1 h H_2, 573 K	0.90	1.2	50
2b	2a + 1 h H_2, 723 K	0.65	0.9	48
3a	1b + 1 h SCR, 423 K	0.9	1.3	77
3b	1b + 1 h SCR, 473 K	1.6	2.1	82
3c	1b + 1 h SCR, 573 K	0.8	1.2	98

[a] Corresponding AFM picture.
[b] Area average of $|\Delta Z|$.
[c] Square root of area average of ΔZ^2.
[d] Difference between highest excursion Z_{max} and average, Z_{avg}.
[e] Exposed sample (starting material).

Inspection of the surface of the pretreated wafer by AFM indicated perfect smoothness on the imaging scale of the presented picture. The presence of surface hydroxyl groups on the native oxide layer of the wafer was evidenced by means of diffuse reflectance FTIR which showed weak OH-stretching bands (low surface area). After cooling to ambient, the sample was exposed at 300 K for 3 h to flowing nitrogen containing a partial pressure of 0.144 mbar vanadium-oxy-triisopropoxide (gas flow 50 ml min^{-1}, 1 bar). After purging with pure nitrogen for some minutes, the gas flow was changed to oxygen, and the sample was heated to 523 K for 1 h.

Survey XP spectra of the samples after impregnation generally showed a substantial C 1s signal. The concentration of Na impurities was found to be very low and no traces of chlorine were indicated in the spectrum. For all samples a weak N 1s signal was detected; the intensity of this signal was highest for the sample exposed to the SCR gas mixture under the most rigorous conditions studied (i.e., 1 h at 573 K).

2.2. ATOMIC FORCE MICROSCOPY

Before the microscopic investigations, samples were exposed for 1 h at the specified temperatures to different gas atmospheres in a specially designed quartz reactor. Pretreatments were carried out in: (i) pure oxygen, (ii) 5% hydrogen/argon, and (iii) SCR reaction mixture, containing 900 ppm NO, 900 ppm NH_3 and 1.8% oxygen in argon (see table 1). After exposure, the samples were cooled rapidly and then exposed to ambient conditions. AFM pictures have been recorded within 5 min after cooling using a Topometrix TMX 2000 instrument equipped with a 1 micron scanner. The scans were performed in the constant force mode using commercially available AFM tips made of silicon nitride. Each sample was investigated at five randomly chosen locations in order to check its homogeneity. This

Table 2
XPS investigation of the changes in the oxidation states of the vanadia resulting from the exposure to different gas atmospheres

AFM figure[a]	Pretreatment	Binding energies (eV) and intensity ratios		
		V(V)	V(III)	V(III)/V(V)
1a	1 h O_2, 523 K	517.1	516.1	2.1
1b	1a[b] + 1 h O_2, 573 K	516.9	–	0
1c	1b + 1 h O_2, 723 K	516.7	–	0
2a	1b + 1 h H_2, 573 K	517.0	515.9	1.4
2b	2a + 1 h H_2, 723 K	517.3	516.3	5.2
3a	1 b + 1 h SCR, 423 K	517.2	516.2	0.7
3b	1 b + 1 h SCR, 473 K	517.1	516.1	0.7
3c	1 b + 1 h SCR, 573 K	517.1	516.1	0.5

[a] Corresponding AFM picture.
[b] Exposed sample (starting material).

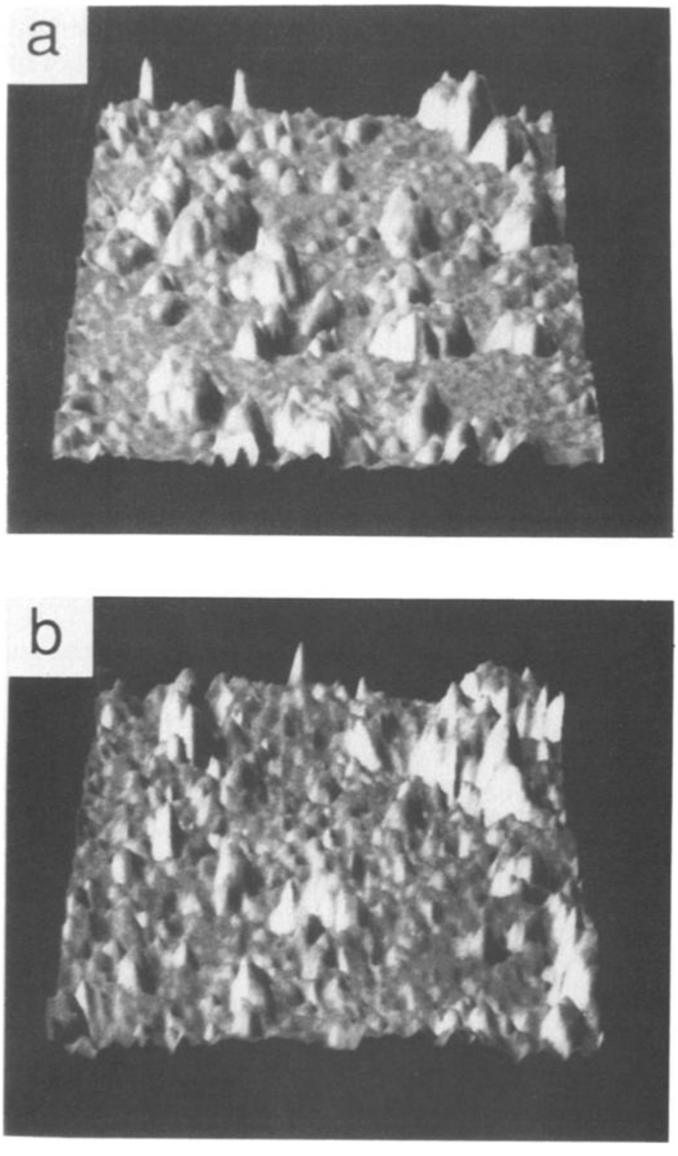

Fig. 1. AFM pictures of $VO_x/SiO_2/Si$ model catalyst surfaces after exposures to oxygen. Scale of all images: $x, y = 1000$ nm, $z = 16$ nm. (a) As-prepared sample after final preparation step (exposure to oxygen for 1 h at 523 K; (b) sample 1a after further exposure to oxygen for 1 h at 573 K; (c) sample 1b after further exposure to oxygen for 1 h at 723 K.

procedure guarantees that the pictures shown are representative for the respective sample morphologies. For better presentation and direct comparison, all topographs have been treated the same way: smoothed (1×, factor 1) and plotted in the 3D mode (shaded) using an x–y range of 1 micron, and a z range of 16 nm. Statistical roughness features of the untreated images are listed in table 1.

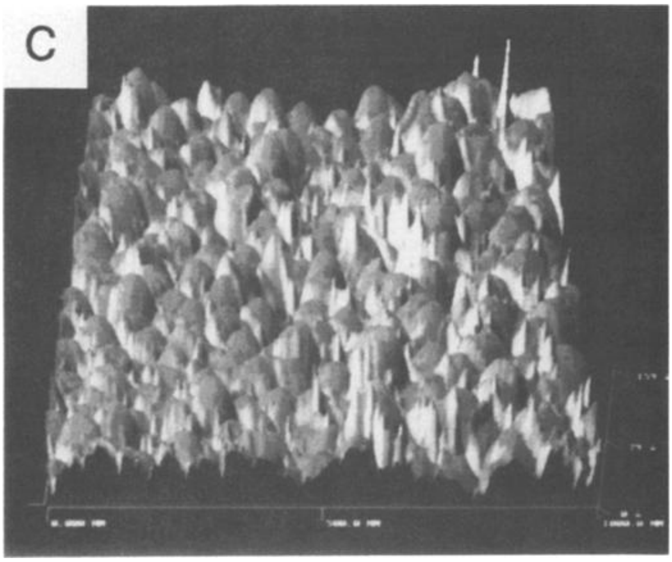

Fig. 1. (continued).

2.3. X-RAY PHOTOELECTRON SPECTROSCOPY

XPS measurements were performed on a UHV surface analysis system (Leybold), equipped with a data acquisition and processing unit (HP 1000, model A 400). The samples were treated in defined hydrogen and oxygen atmospheres (conditions: see table 1) in a high pressure chamber flanged next to the UHV system. Thus, a sample transfer to the analysis position without exposure to ambient conditions was possible. The pretreatments under SCR reaction conditions were performed in a separate reaction chamber, under the conditions specified. In these cases, the sample transfer to the UHV system was managed by sample transport under Ar in special containers.

Mg Kα radiation from an X-ray source (Leybold, model RQ 10/38, operated at 10 kV voltage and 10 mA current) was used for excitation. The 200 mm hemispherical energy analyzer (Leybold, model EA 11/100) was set to a pass energy of 50 eV. For each spectrum, ten scans were recorded with an energy step of 100 meV and a step time of 100 ms. The binding energy scale was calibrated with respect to the Si 2p reference signal at 99.15 eV [10]. The vanadium 2p doublet exhibited a superposition of at least two oxidation states for several samples. After satellite subtraction and suitable smoothing, the spectra were deconvoluted into contributions of V(V) and V(III), using the binding energies given in the literature [11]. The procedure used is described in more detail in ref. [7]. In view of the very similar chemical shifts of V^{5+} and V^{4+} [12], no attempt was made to separate a possible contribution of the V(IV) oxidation state.

The integrated intensities of the respective doublet components were used to cal-

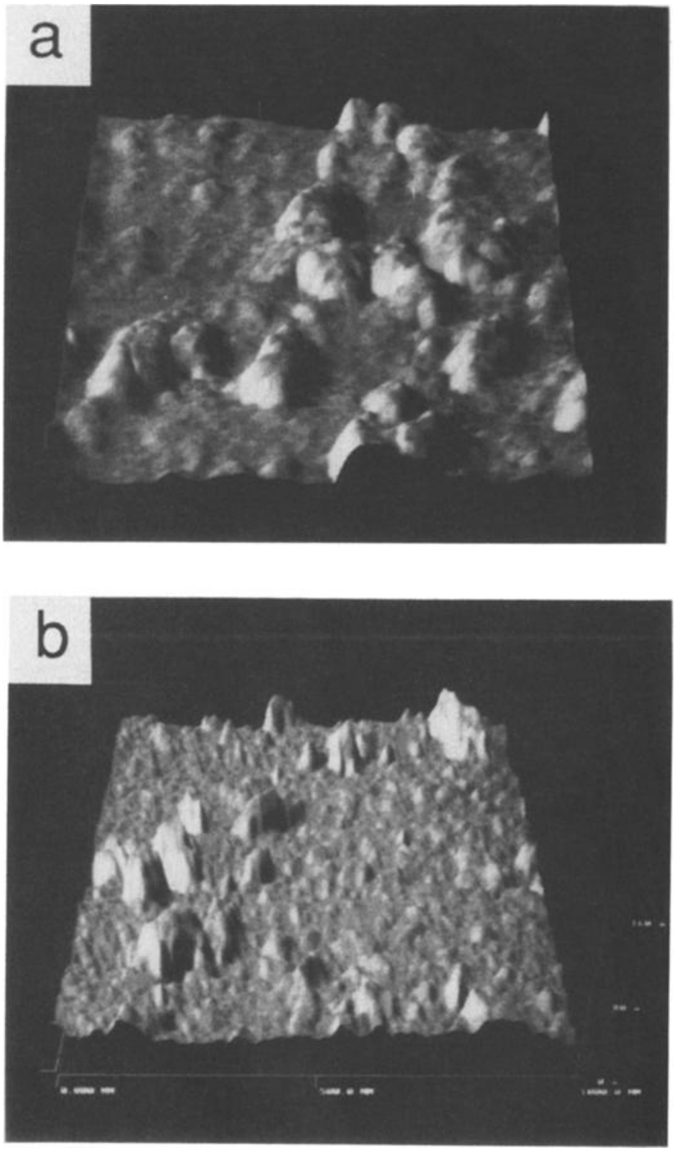

Fig. 2. AFM pictures of $VO_x/SiO_2/Si$ model catalyst surfaces after exposures to hydrogen containing atmosphere (5% H_2 in argon). Scale of both images: $x, y = 1000$ nm, $z = 16$ nm. (a) Sample shown in fig. 1b after exposure to hydrogen containing atmosphere for 1 h at 573 K; (b) sample 2a after further exposure to hydrogen for 1 h at 723 k.

culate V(III)/V(V) intensity ratios. No correction factor was applied as the relevant sensitivity factors are not known for the present samples. Thus the resulting V(III)/V(V) ratios, which are compiled in table 2 together with the binding energies resulting from the fit, should only be considered as a relative measure of the V(III) content.

3. Results and discussion

The changes in the surface morphology of the $VO_x/SiO_2/Si$ model system, which occurred as a result of its exposure to different reactive gas atmospheres at the specified temperatures, are presented in figs. 1–3, and corresponding roughness parameters are listed in table 1. Fig. 1a depicts the surface morphology of the vanadia after deposition and final treatment in oxygen (523 K, 1 h) as used in the standard preparation procedure. In this final preparation step, the deposited vanadium alkoxide precursor was transformed into a mixture of V(III) and V(V) oxides, as indicated by the XP spectrum shown in fig. 4a. A V(III)/V(V) ratio of 2.1 was deduced by deconvolution of the V $2p_{3/2}$ signal centered at 516.5 eV. The peak positions and intensity ratios derived from the XPS measurements are listed in table 2.

Further exposure of the above sample to oxygen at a slightly higher temperature (573 K) did not cause any significant surface morphological changes, as emerges from a comparison of the AFM pictures shown in figs. 1a and 1b. However, the oxidation state of the surface vanadia species changed markedly upon oxygen exposure at 573 K. Only V(V) could be detected by XPS (fig. 4b, table 2), indicating complete oxidation of V(III) to V(V) during exposure at 573 K. Significant changes in the surface morphology were, however, observed after further oxygen exposure at 723 K. The corresponding AFM picture (fig. 1c) shows the formation of relatively large, voluminous tower-like features built up of vanadia (V) species as evidenced by XPS (table 2).

Due to its well defined chemical state (V(V)), the sample conditioned by oxygen exposure at 573 (fig. 1b) was used as the starting material for the study of the morphological and chemical changes induced by exposure to the hydrogen containing (5% H_2 in argon) atmosphere. Fig. 2a depicts the morphology of this sample after exposure to hydrogen at 573 K for 1 h, the corresponding XP spectrum is shown in fig. 4c. The results indicate that exposure of the pre-oxidized surface to a hydrogen atmosphere leads to drastic changes in both morphology (fig. 2a) and oxidation state (fig. 4c, table 2) of the surface. The morphological changes are characterized by a significant decrease in both size and roughness of the VO_x species (table 1). The oxidation state, characterized by the ratio V(III)/V(V), increases from 0 to 1.4 after the hydrogen exposure at 573 K.

Further exposure of the sample to the hydrogen containing atmosphere at 723 K resulted in an annealing (fig. 2b) of the relatively coarse grained surface contours (fig. 2a) and in further reduction of the initially present V(V) species to V(III). The V(III)/V(V) ratio of the surface vanadia species increased from 1.4 to 5.2 (table 2).

The surface morphological changes which occurred upon exposure of the reference sample (fig. 1b) to SCR reaction conditions at different temperatures are presented in figs. 3a–3c. After exposure to the SCR gas mixture for 1 h at 423 K, this sample showed the morphology depicted in fig. 3a, which exhibits characteristic

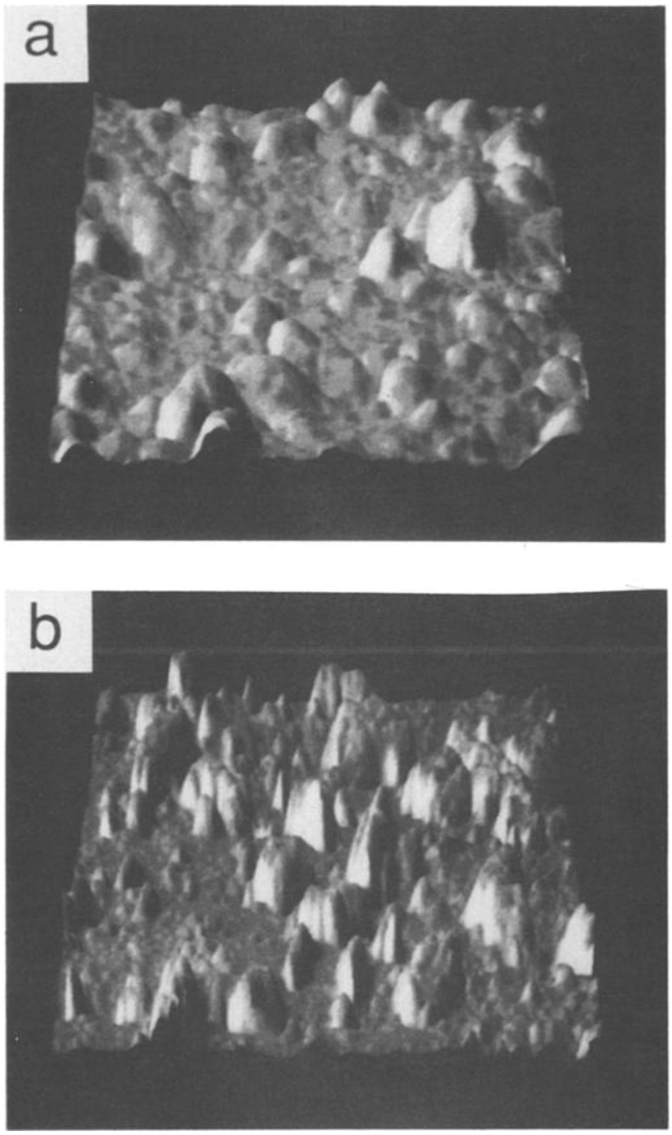

Fig. 3. AFM pictures of $VO_x/SiO_2/Si$ model catalyst surfaces after exposures to SCR reaction gas mixture (900 ppm NO, 900 ppm NH_3 and 1.8% oxygen in argon). Scale of all images: $x, y = 1000$ nm, $z = 16$ nm. (a) Sample shown in fig. 1b after exposure to SCR reaction conditions for 1 h at 423 K; (b) sample shown in fig. 1b after exposure to SCR reaction conditions for 1 h at 473 K; (c) sample shown in fig. 1b after exposure to SCR reaction conditions for 1 h at 573 K.

features similar to those observed after exposure of the same sample to the hydrogen containing atmosphere at 573 K (fig. 2a). The similarity of the effect of these two different pretreatments is also corroborated by the XP spectra shown in figs. 4c and 4d, respectively. However, the exposure to SCR gas resulted in a slightly lower V(III) / V(V) ratio (table 2). Consequently, similar effects to those caused by hydro-

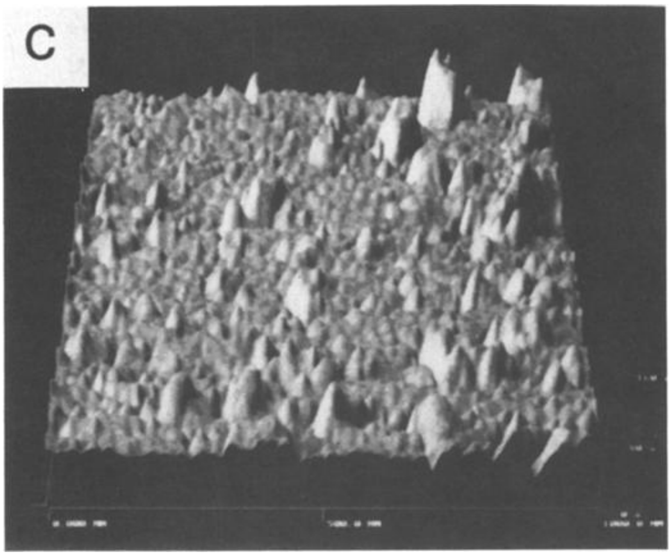

Fig. 3 (continued).

gen exposure are reached at a significantly lower temperature under SCR reaction conditions.

Upon exposure of the sample to the SCR reaction mixture at 473 (fig. 3b) and 573 K (fig. 3c) the surface morphology undergoes significant changes, whereas the oxidation state of the surface species remains almost constant (cf. table 2). These observations corroborate the earlier made suggestion [8] that vanadia species deposited on silica undergo restructuring (redispersion) accompanied with a loss of activity when exposed to SCR conditions in the temperature range 420–570 K, and provide some evidence that the oxidation state of the vanadia species does not change drastically during this reconstruction. Thus it seems that the unusual temperature dependence (non-linear Arrhenius plot [8]) of the reduction rate of NO is predominantly to be attributed to surface reconstruction phenomena. A further study of the observed surface reconstruction on atomic scale is presently being undertaken in our laboratory.

A quantitative view on the morphological changes depicted in figs. 1–3, which have been discussed qualitatively, is provided by the roughness parameters listed in table 1. Oxygen exposure at increasing temperatures gives rise to a significant increase of all three relevant surface roughness measures. On the surfaces reduced in hydrogen, both the RMS deviations and, particularly, the maximum excursions are significantly lower. Reduction at the higher temperature of 623 K has a stronger effect, as expected. The surface reconstruction phenomena occurring under SCR conditions are more complex, as indicated by the AFM images (figs. 3a–3c) and the corresponding surface roughness data (table 1). This behaviour is probably to be attributed to the simultaneous action of oxidizing and reducing species pres-

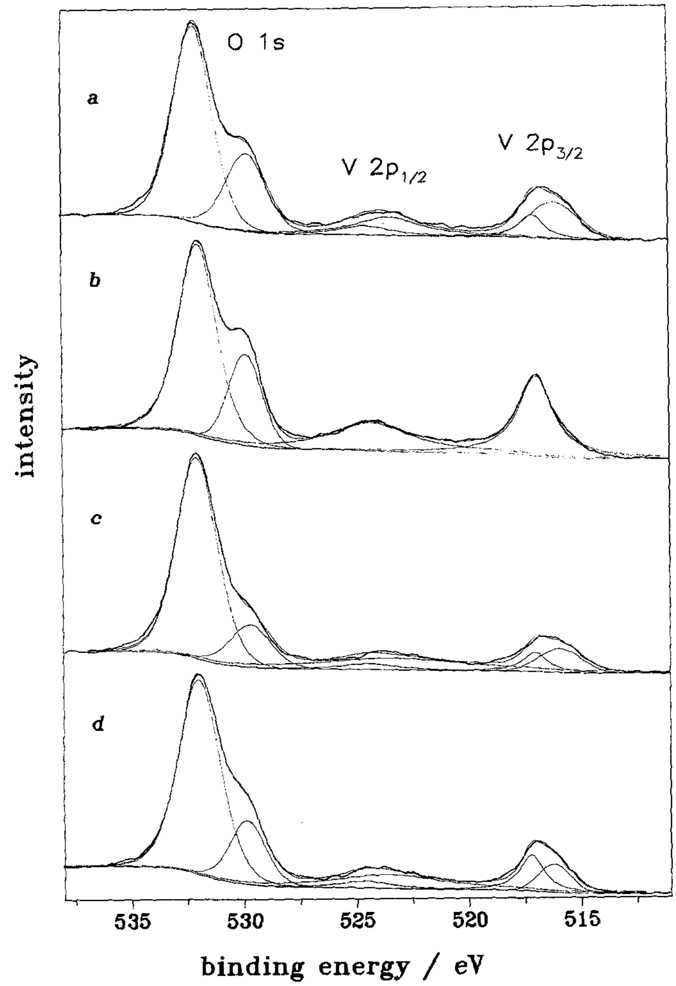

Fig. 4. XP spectra of the $VO_x/SiO_2/Si$ model systems described in figs. 1a (trace a), 1b (trace b), 2a (trace c), and 3a (trace d).

ent in the SCR feed gas. The role of this complex interplay of oxidizing and reducing species in the surface reconstruction is not understood yet.

4. Conclusions

The used $VO_x/SiO_2/Si$ model system is well suitable for AFM and XPS studies of morphological and chemical changes occurring upon exposure of the vanadia/silica interface to different gas atmospheres. The studies provide direct evidence for the structural instability of this interface. When exposed to SCR reaction conditions, the vanadia undergoes drastic temperature-dependent morphological changes leading to redispersion, while the oxidation state of the surface characterized by the ratio V(III)/V(V) changes only little (0.5–0.7) in the temperature range from 420 to 570 K. These results suggest that the earlier observed unusual temperature dependence of the reaction rate of the selective catalytic reduction of NO by NH_3 over vanadia on silica [8] is mainly caused by changes in the surface morphology (redispersion of the vanadia species) and that the oxidation state of the vanadia surface is relatively little affected by the morphological changes.

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