Selective catalytic reduction of nitric oxide over vanadia grafted on titania. Influence of vanadia loading on structural and catalytic properties of catalysts

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The selective catalytic reduction (SCR) of NO by NH_3 has been studied over vanadia/titania catalysts prepared by selective immobilization of vanadyl alkoxide species on two structurally different titania supports. The loading of vanadia was varied from 1.8 to 7.5 μmol V^{5+} per m^2 surface area. Comparative kinetic measurements at 150°C show that the NO turnover frequencies increase by more than an order of magnitude when the vanadia loading is increased from 1.8 to ≈ 3 μmol V^{5+}/m^2. In the region of lower SCR activity, i.e. at lower coverages (≈ 2 μmol V^{5+}/m^2), small clusters and ribbons of vanadia are detected in the Raman spectra, whereas at loadings where maximum NO turnovers are achieved (≈ 3 μmol V^{5+}/m^2) the prevalent vanadia species are well-developed two-dimensional vanadia layers bound to titania.

Keywords: Reduction of nitric oxide; ammonia; vanadia/titania; vanadyl alkoxides; selective immobilization; structure sensitivity; structure of vanadia; Raman spectroscopy

1. Introduction

Among the various catalysts [1] which have been tested for the selective catalytic reduction (SCR) of NO by NH_3, vanadia supported on titania has gained wide technical application. At low vanadia coverage, i.e. in the sub-monolayer region, the catalytic activity of these catalysts was found to depend on the vanadia loading [2–4]. In a previous study [4] carried out on vanadia/titania catalysts prepared by selective grafting of vanadyl triisobutoxide onto titania, the dependence of the NO turnover frequency (TOF) on the vanadia surface concentration was investigated. The turnover frequency was found to increase strongly with increasing vanadia content reaching the highest value at about 1.8 wt% vanadia. Further increase of the vanadia loading did not result in

higher TOFs. The studies indicated that the highly dispersed vanadia species, as obtained upon first grafting, have much lower intrinsic SCR activity than the vanadia species of lower dispersion resulting from successive graftings.

Information concerning the structure of vanadia supported on titania originates from spectroscopic investigations [5–10]. These studies revealed that in the sub-monolayer region vanadia is present on titania as monomeric vanadyl and polymeric vanadate species, and that the distribution of these species depends on the vanadia coverage.

The objective of the present study is to correlate the SCR activity behavior of the vanadia titania catalysts with the changes in the structural properties of the immobilized vanadia induced by increasing the loading of V_2O_5. For that purpose we have prepared a series of vanadia/titania catalysts with different loadings, and have investigated them with regard to their catalytic and structural properties using kinetic measurements and laser Raman spectroscopy.

2. Experimental

Titania supported vanadia catalysts were prepared by grafting using the selective reaction of vanadyl alkoxides with support surface hydroxyl groups described in earlier investigations [4,11]. Two morphologically different titania supports were used, a commercial titania P25 (Degussa) and a high surface area titania gel (BET surface area 92 m^2 g). The titania gel (Tigel) was prepared by the addition of 1 N HCl to $Ti(O\text{-}iC_3H_7)_4$ until a $H_2O/Ti(O\text{-}iC_3H_7)_4$ ratio of ≈ 10 was reached and a thick white translucent gel formed. The gel was dried at 120°C and crushed to the 0.3–0.5 sieve fraction. This support is hereafter referred to as "Tigel".

Two different vanadyl alkoxides were used for grafting: vanadyl triisopropoxide (VTIP) from Alfa Inc. (> 98% purity) and vanadyl triisobutoxide (VTIB) synthesized according to the procedure described by Prandl and Hess [12].

Prior to the grafting, P25 and Tigel were conditioned as follows. In a quartz tube, several grams of 0.3–0.5 mm support granules were calcined at 600°C for P25 and 450°C for the Tigel first for 1 h in flowing oxygen, followed by 2 h in nitrogen before cooling under flow to ambient. Catalysts designated P25(150°C, vac) were prepared using P25 pre-conditioned in vacuum (≈ 10 mbar) at 150°C for 30 min prior to the grafting.

The following "standard" grafting procedure was used: the pre-conditioned support was transferred under nitrogen purge to a purged and dried glass reaction flask immersed in an oil bath. A precursor solution of 0.5 ml VTIP in 20 ml hexane was injected into the flask, and the contents maintained at 50°C for 12 h. The solution was then decanted, the sample washed three times with fresh hexane, and dried under nitrogen flow at 50°C. The sample was transferred back to the quartz tube, and activated by first heating in nitrogen to

300°C to degas the surface, then cooling back to ambient, switching to oxygen flow, and re-heating to 300°C and maintaining temperature for 3 h.

Titania supports and catalysts were characterized using powder X-ray diffraction (XRD), temperature programmed reduction (TPR), nitrogen adsorption (BET), X-ray fluorescence (XRF), inductive coupled plasma (ICP), and neutron activation analysis (NAA).

TPR measurements were run on an apparatus which has been described in detail in ref. [13]. The conditions were: sample weight, 0.1–0.4 g, 5% H_2/Ar at 75 ml/min; heating rate, 10 K/min; temperature range, 25–700°C. Prior to each TPR run, the samples were oxidized in situ at 300°C.

Raman spectra were excited with the 488 nm line of an argon ion laser (Spectra Physics, model 2025-05). Plasma lines from the laser were eliminated with a filter monochromator (Applied Photophysics, model 2300). The scattered radiation was dispersed in a triple monochromator (SPEX, model 1877A), and detected using a cooled intensified diode array. This multichannel detection system has previously been described and characterized [14]. Typically, 5 or 100 mW of power were focussed onto a 10×0.1 mm line on the sample. The slit width of the monochromator was adjusted to correspond to a spectral resolution of ≈ 5 cm^{-1}.

Catalyst testing for the selective catalytic reduction of NO with NH_3 was performed in a 6 mm o.d. quartz tube reactor with on-line MS analysis of reactant and product gases. The reactor set-up, experimental procedure and MS analysis methods are described in detail elsewhere [15]. Feed gas was 900 ppm NO and NH_3, 18000 ppm O_2, in a balance of argon at a gas hourly space velocity (GHSV) of 24000 h^{-1}. The reactor bed consisted of 0.1 g of 0.3–0.5 mm granules.

3. Results

3.1. MORPHOLOGICAL PROPERTIES OF SUPPORTS AND GRAFTING PROCEDURE

The bulk structure of the titania supports before and after the grafting procedure has been characterized by powder X-ray diffraction. Fig. 1 depicts the X-ray diffraction pattern of the P25 and Tigel supports after pretreatment prior to grafting. P25 contained about 60% anatase after pretreatment at 600°C compared to about 68% of the original P25, which indicates that partial rutilization took place during pretreatment. Although Tigel was pretreated at lower temperature (450°C) the degree of rutilization was higher. After pretreatment Tigel was made up of about 55% rutile, the rest was anatase with a little brookite.

BET surface area measurements before and after grafting showed only relatively small changes in the surface area due to the grafting. However, with

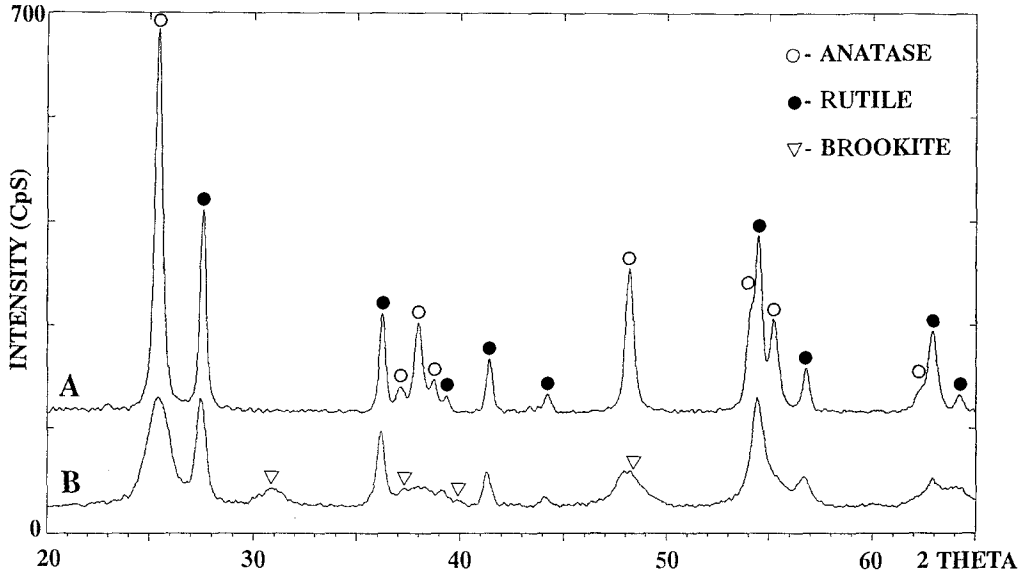

Fig. 1. X-ray diffraction patterns (CuK_α) of titania supports P25 (A) and Tigel (B). The diffraction patterns were measured after the pretreatments at 600°C (P25) and 450°C (Tigel) prior to the grafting with the vanadyl alkoxides.

subsequent graftings, there was a significant loss in surface area due to the thermal treatment between the grafting steps. For P25 samples pretreated at 600°C, the BET surface area decreased steadily from initially 51 m^2/g to about 34 m^2/g after five subsequent grafts. With the Tigel pretreated at 450°C, the BET surface area dropped from initially 92 to 86 m^2/g after two successive grafts. In contrast, no changes in the XRD patterns of the titania and no significant loss in the BET surface area were observed with the P25 samples pretreated in vacuum at 150°C (P25, 150°C, vac, VTIP).

Fig. 2 shows the amount of vanadia immobilized per unit surface area of P25 when successive graftings were made. The vanadia loadings were determined from hydrogen consumption measurements of the grafted samples using TPR. The quantification was based on the previously used assumption that the reduction proceeds according to $V^{5+}{=}O + H_2 \rightarrow V^{3+} + H_2O$ [4,16,17]. The reliability of the hydrogen consumption measurements for the determination of the vanadia loading was checked by means of independent measurements with X-ray fluorescence (XRF), inductive coupled plasma (ICP) and neutron activation analysis (NAA) as described elsewhere [18]. The comparative analytical measurements revealed that for the type of catalysts used in this study agreement within $\pm 6\%$ is obtained between the vanadia contents estimated from the hydrogen consumption and the corresponding values determined by the other methods.

The results shown in fig. 2 indicate that with the same thermal pretreatment, the grafting leads to similar specific vanadia uptakes, regardless whether vanadyl

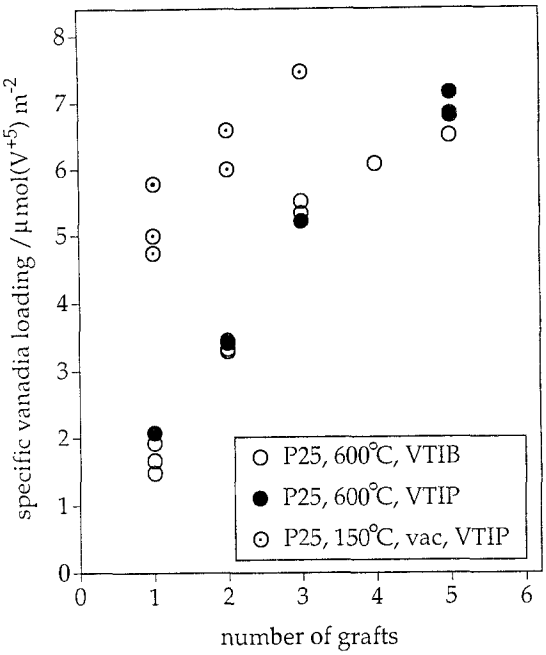

Fig. 2. Amount of vanadia immobilized per grafting step per unit surface area of titania (P25) carrier. Catalysts (P25,600°C, VTIB) were prepared by grafting of carrier pretreated at 600°C with vanadyl triisobutoxide (VTIB). Catalysts P25(600°C, VTIP) were similarly prepared but with vanadyl triisopropoxide (VTIP). Catalysts P25(150°C, vac, VTIP) were prepared using P25 preconditioned in vacuum ≈ 10 mbar at 150°C for 30 min prior to grafting with VTIP.

triisopropoxide (VTIP) or vanadyl triisobutoxide (VTIB) is used as vanadia precursor. The vanadia uptakes resulting from a specific grafting step could be significantly increased when P25 was pretreated at milder conditions, i.e. in vacuum at 150°C, prior to the grafting.

3.2. STRUCTURE OF THE GRAFTED VANADIA

The structure of the grafted vanadia has been investigated by means of laser Raman spectroscopy. The catalysts have been stored under ambient conditions, and the surfaces are consequently equilibrated with atmospheric water. This state of the surface is monitored when recording Raman spectra of self-supporting pressed catalyst disks at low laser powers, to avoid heating of the sample.

To dehydrate the surface, the laser power was raised to 100 mW focussed onto a point of 100 μm radius. Under dehydrated conditions comparatively narrow and characteristic vibrational bands are recorded, from which the various surface species are more easily distinguished. We therefore find it convenient to compare, for each sample, the spectrum of the unmodified hydrated surface and the corresponding dehydrated sample.

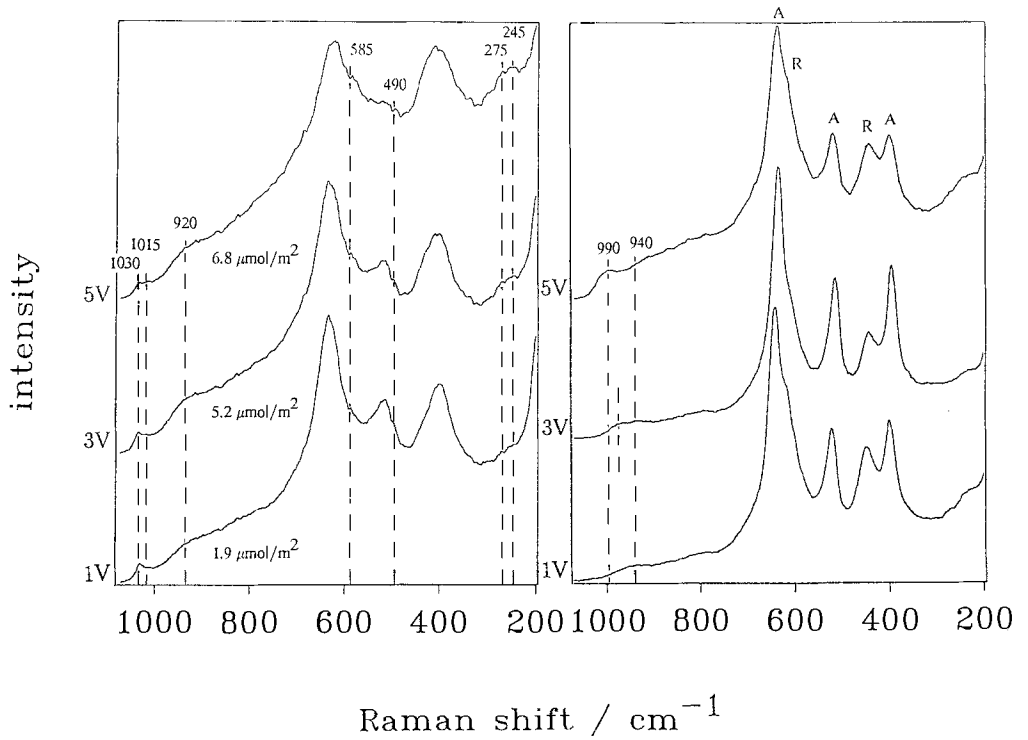

Fig. 3. Raman spectra of vanadia layers immobilized on P25 pretreated at 600°C, P25(600°C, VTIP). Samples prepared by 1, 3, and 5 grafts are shown. The right panel was recorded using a laser power of 5 mW, and corresponds to the hydrated state of the surface. The left panel represents spectra excited with 100 mW laser power, which results in dehydration of the surface species. Details are indicated in section 2.

Comparison of the left- and right-hand panels shows that the bands of the support are broadened by the temperature rise induced by high laser power excitation. On the other hand, the vibrational bands of the dehydrated surface vanadia species are narrower as compared to the low power spectra, in which the bands are inhomogeneously broadened as a consequence of structural heterogeneity in the hydration.

The hydrated spectrum of the singly grafted catalyst (fig. 3) supported on P25(600°C, VTIP) shows dominant bands of anatase (400, 515, and 640 cm^{-1}). Rutile signals (424 cm^{-1}, and shoulders at 611 cm^{-1}) are comparatively intense as a consequence of the 600°C pretreatment. A broad band at 940 cm^{-1} is the only indication of the supported vanadia; the frequency observed corresponds to hydrated polymeric species, such as metavanadates [7,19–21].

After three impregnations an additional broad band appears at 980 cm^{-1} on the hydrated catalyst (fig. 3, second trace on right). This feature becomes prominent after five impregnations, and further shifts to 990 cm^{-1}. The latter frequency matches the one observed earlier on P25 pretreated by a similar

procedure [22], and has been assigned [9,19,21] to two-dimensional surface bound layers of vanadia, in which the central vanadium ion is surrounded by six oxygen ligands in a distorted octahedral environment.

It is interesting to compare these spectra to the corresponding ones recorded under dehydrated conditions (fig. 3, left panel). The singly grafted catalyst exhibits a well-developed band at 1030 cm^{-1} which is assigned [19] to small vanadia clusters. A broad feature centered around 920 cm^{-1}, which is more pronounced after threefold impregnation, corresponds to vanadia ribbons of limited lateral extent [19]. In addition, we observe the development of a second high frequency feature at 1015 cm^{-1} which is present as a shoulder after single impregnation, more intense in the 3V sample, and strongest in the fivefold impregnated catalyst. The latter vibration corresponds to V=O stretching motions in the two-dimensional vanadia layers [9,19,21]. The assignment is confirmed by the matching bands at 270 cm^{-1} (V=O deformational motion), 490 cm^{-1} (V_2O stretching) and 585 cm^{-1} (V_3O stretching). In particular, the latter two bands are characteristic indicators of the vanadia layer structure [23].

In the vacuum-pretreated P25 support, the fraction of rutile is significantly lower, as seen from the reduced intensity of the 444 cm^{-1} vibration, and the absence of the 611 cm^{-1} shoulder (fig. 4, bottom trace on right-hand side). Comparison with fig. 3 is a convincing demonstration of the fact that on a given support (titania), the relative concentrations of vanadia surface species are mainly determined by the vanadia loading. In the first grafting step, 5.1 μmol V^{5+}/m^2 of V_2O_5 are immobilized on vacuum-dried P25. This coverage is similar to the one achieved on P25(600°C) after three graftings, i.e. 5.2 μmol V^{5+}/m^2. The corresponding spectra of dehydrated catalysts in figs. 4 and 3, respectively, are in fact very similar with regard to the vanadia-related band.

Twofold impregnation of vacuum-pretreated P25 results in a modest increase in V_2O_5 coverage to 6.0 μmol V^{5+}/m^2. The 1015 cm^{-1} band corresponding to well-developed two-dimensional vanadia layers is pronounced in the spectra both under ambient and dehydrated conditions (fig. 4, middle traces). Apparently, the high density of surface hydroxyl groups available on this mildly pretreated support provides favorable conditions for the development of this structure. The coverage achieved after the third impregnation of P25(150°C, vac), 7.5 μmol V^{5+}/m^2, is somewhat higher than the loading realized on P25(600°C) by five impregnation cycles (6.8 μmol V^{5+}/m^2). Again, the similarity of the corresponding spectra is apparent from a comparison of figs. 4 and 3. Ribbons (920 cm^{-1}) and two-dimensional vanadia layers (1015 cm^{-1}) are identified by intense and broad bands in the spectrum of *hydrated* 3V-P25(150°C, vac). In the matching spectrum recorded under *dehydrated* conditions, the additional bands which are indicative for the two-dimensional layer structure, as mentioned above, are clearly recognized.

Similar tendencies as observed for the catalysts prepared by grafting vanadia onto P25 have also been observed for the catalyst prepared from Tigel [18],

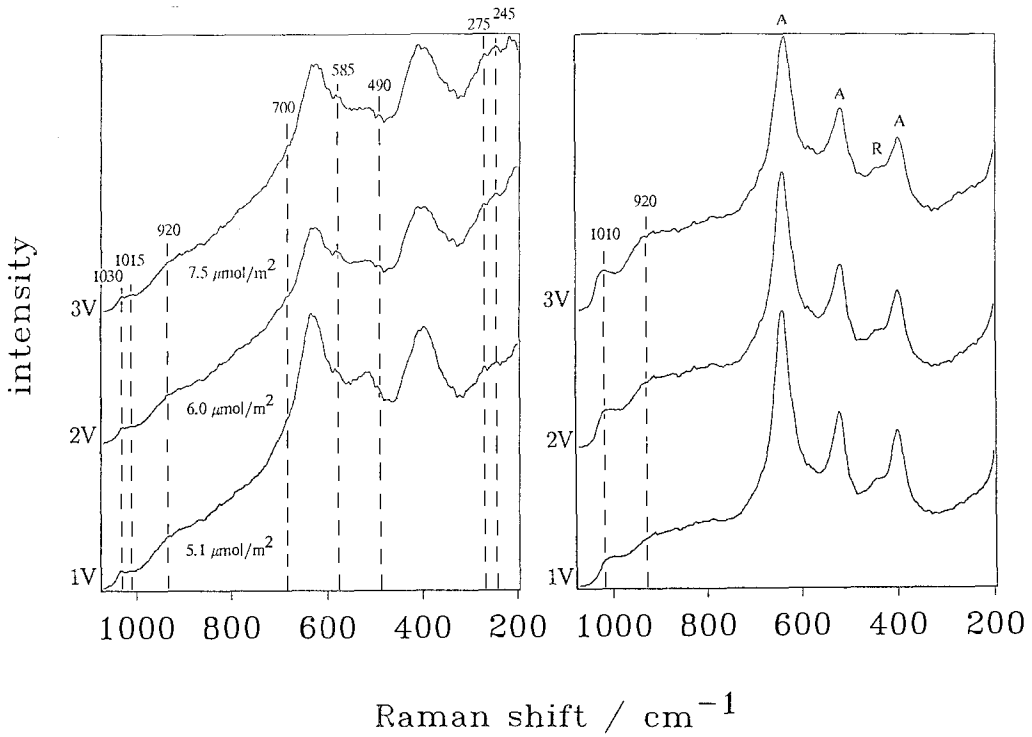

Fig. 4. Raman spectra of vanadia layers immobilized on vacuum pretreated P25, P25(150°C, vac, VTIP). Samples prepared by 1, 2, and 3 grafts are shown. The right panel was recorded using a laser power of 5 mW, and corresponds to the hydrated state of the surface. The left panel represents spectra excited with 100 mW laser power, which results in dehydration of the surface species. Details are indicated in section 2.

which was predominantly made up of rutile as XRD and Raman spectroscopy indicated. Thus it appears that the specific vanadia loading and the degree of surface hydroxylation [6,24] are the decisive factor determining the structure of the immobilized vanadia, whereas the phase composition (anatase or rutile) seems to be of minor importance.

3.3. CATALYTIC PROPERTIES

Over the temperature range investigated (100–300°C), products of the SCR reaction were essentially N_2 and H_2O, with small amounts of N_2O appearing only for $T \gtrsim 250$°C. The results of the kinetic studies are described in detail elsewhere [18]. Here we only address the structure sensitivity of the selective catalytic reduction of NO. Fig. 5 depicts the influence of the specific loading of vanadia on its intrinsic catalytic activity. Turnover frequencies (TOFs) measured at 150°C are plotted versus specific loadings of vanadia as determined by TPR, and checked by ICP, XRF and NAA.

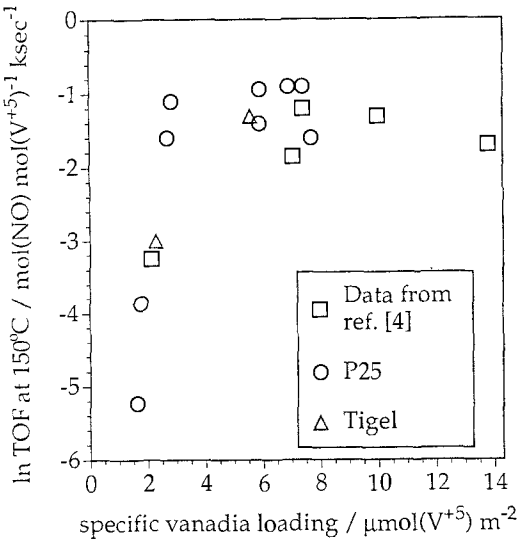

Fig. 5. Influence of the specific loading of vanadia on its intrinsic catalytic activity in SCR. Turnover frequencies measured at 150°C are plotted versus specific vanadia loading. Conditions of experiments are given in section 2. Note that the data represented from ref. [4] (squares) were measured under the same experimental conditions, except that GHSV was 9000 h^{-1}, compared to 24000 h^{-1} used in this work.

Note that the calculation of the NO turnover frequencies has been based on the assumption that all V^{5+} sites determined by TPR are also accessible and active for the selective reduction of NO. This assumption is reasonable for catalysts with low loadings and high dispersion of the vanadia, as those used in this study (all catalysts have vanadia loadings in the submonolayer region). With higher vanadia loadings the number of V^{5+} sites accessible for the reactants (NO, NH_3) will probably be overestimated, since TPR does not differentiate between surface and "bulk" V^{5+} sites. Thus the rise in TOF with increasing vanadia loading plotted in fig. 5 is certainly based on a conservative calculation and may in reality be even larger. At any rate, this phenomenon does not affect the major conclusion emerging from the catalytic studies (fig. 5) that TOF is low for low specific loadings of vanadia and steeply rises between 1.8 and ≈ 3 μmol V^{5+}/m^2, reaching highest values at V^{5+} coverages exceeding 3 μmol V^{5+}/m^2. Higher loadings than about 7 μmol V^{5+}/m^2 do not result in significantly higher intrinsic activity (TOF); there is even some indication that TOF declines when the vanadia loading is increased further, probably due to the increase of the number of bulk V^{5+} species which are determined by TPR, but do not necessarily contribute to the activity for SCR [4]. Finally, it should also be mentioned that a similar tendency, as shown in fig. 5 for 150°C, was also observed for kinetic measurements performed at other reaction temperatures [18].

4. Discussion

The present study provides further evidence for the earlier findings that the intrinsic SCR activity of titania supported vanadia catalysts depends on the specific loading of the immobilized vanadia [2–4]. In the coverage range from 1.8 to ≈ 3 μmol V^{5+}/m^2, the NO turnover frequency based on V^{5+} sites rises steeply by more than an order of magnitude. A similar rise of the activity was observed in the earlier investigations [4]. However, in ref. [4] only catalysts with vanadia loadings of 2.1, 7.0, 7.4, 10.0, and 13.8 μmol V^{5+}/m^2 were compared with regard to their activity, and no specific assignments of the structure of the vanadia in this coverage range could be made.

In the region of lower SCR activity, i.e. at lower coverages (≈ 2 μmol V^{5+}/m^2), small clusters and ribbons of vanadia are detected in the Raman spectra of hydrated and dehydrated surfaces. Maximum NO turnovers (TOF) are achieved when the vanadia surface concentration exceeds about 3 μmol/m^2. This level of activity is only weakly influenced upon further grafts up to a coverage of about 7.5 μmol V^{5+}/m^2. In this coverage range, the prevalent vanadia species are well-developed two-dimensional vanadia layers bound to titania, as identified by a prominent vibration at 1015 cm^{-1} on the dehydrated surfaces.

Compared to the specific loading of the grafted vanadia, the morphological properties (BET surface area, phase composition) of the titania support appear to be less important. This behavior emerges from the comparison of the intrinsic activities of the catalysts prepared by grafting vanadia onto the morphologically different titania supports (fig. 5). The results of the present work indicate that the decisive factor determining the intrinsic SCR activity of vanadia on titania catalysts is the structure of the vanadia which is predominantly influenced by the surface specific vanadia loading and the degree of surface hydroxylation. Decisive for the latter property are the method of catalyst preparation and the reaction conditions under which the catalyst is used.

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