WO_x/TiO₂ Catalysts Prepared by Grafting of Tungsten Alkoxides: Morphological Properties and Catalytic Behavior in the Selective Reduction of NO by NH₃

J. Engweiler, J. Harf, and A. Baiker¹

Department of Chemical Engineering and Industrial Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland

Received September 22, 1994; revised November 25, 1995; accepted November 30, 1995

Tungsten oxide on titania catalysts with loadings of 3.5-11 μ mol(W) m⁻²_{BET} were prepared in a multiple grafting procedure using tungsten (VI)-oxo-methanolate and tungsten(V)-ethanolate as precursors. The efficiency of the deposition depended markedly on the combination of alkoxide precursor and solvent. Calcination at elevated temperature, 1023 K compared to 573 K normally used, resulted in the formation of additional Brønsted acid sites as indicated by TPD measurements. In line with this finding the activity for selective catalytic reduction of NO with NH3 increased by almost 100% upon calcination at 1023 K and nitrogen remained the only product observed. The structural changes induced upon tungsten deposition and calcination in dry O2/Ar at different temperatures were followed using XRD and laser Raman spectroscopy. The formation of a stabilized polytungstate layer, indicated by a prominent Raman band at 985 cm⁻¹, was found to be favored by increasing WO_x loading and calcination temperature. As a minor species, paracrystalline WO₃ was found in samples with loadings higher than 9 μ mol(W) m⁻² after high temperature (1023 K) calcination in moist air. TPR investigations in combination with AAS indicated a stepwise reduction of W(VI), with W(IV) being stable up to ca. 1150 K. © 1996 Academic Press, Inc.

INTRODUCTION

Supported tungsten oxide catalysts are used for hydrotreating and for alkene metathesis reactions because of their solid acid properties (1) and they are active for the selective catalytic reduction (SCR) of nitric oxide with ammonia (2, 3, 4).

Commercial SCR catalysts are mostly based on vanadia/titania and often contain considerable amounts of tungsten oxide and/or molybdenum oxide (5). Chen and Yang (6) described the role of tungsten oxide in vanadia–tungsten oxide/titania catalysts. Tungsten oxide broadens the temperature range for SCR and better resistance toward poisoning by alkali salts and arsenic is observed. Higher temperatures can be used because ammonia oxidation is suppressed. Raman (7, 8) and diffuse reflectance FTIR spectroscopic investigations (9) showed that tungsten oxide did not interact with the vanadia species when both WO_x and VO_x were present together on TiO₂. More profound investigations on the WO_x/TiO_2 system and on its catalytic behavior in SCR are necessary for further understanding its role in composite catalytic systems.

The morphological properties as well as the acidity of WO_x/TiO_2 catalysts have been investigated for submonolayer and monolayer samples. The structure of the supported WO_x species has been described mainly by Raman spectroscopy (8, 10, 11) and EXAFS (12). Tungsten oxide on titania was reported to form isolated tetrahedrally coordinated surface species as well as two-dimensional layers of octahedrally coordinated species at low concentrations (8, 12). Upon dehydration all tungsten oxide species were converted into a distorted octahedrally coordinated structure (8, 12). No crystalline WO₃ was detected with XRD at surface coverages up to $10 \,\mu \text{mol}(W) \,\text{m}^{-2}_{\text{BET}}$ (13), but based on Raman spectroscopy the formation of a paracrystalline WO₃ phase at >6 μ mol(W) m⁻² was stated to occur (8, 11). Recently, the acidic properties of tungsten oxide/titania catalysts have been studied by several authors using vibrational spectroscopy (10, 14–16). It was found that Brønsted acid centers are formed upon deposition of WO_x on TiO_2 and that strong Lewis acid centers are present as well.

Different preparation methods have been reported for WO_x/TiO_2 catalysts. Impregnation methods with aqueous solutions of tungstate salts are widely used (3, 9, 10) and Hilbrig *et al.* (12, 16) reported the formation of WO_x layers on TiO_2 and Al_2O_3 by solid–solid wetting. To our knowledge the preparation of tungsten oxide/titania catalysts by grafting of tungsten alkoxides has not been reported so far. Grafting of vanadium alkoxides on titania and mixed silica–titania support materials resulted in highly dispersed vanadia species active for SCR and allowed good control of the vanadia loading in the submonolayer region (17, 18, 19).

The aim of this work was to gain information on the influence of preparation parameters on both the structural

¹ To whom correspondence should be addressed.

TABLE 1

Morphological Properties of WO_x/TiO₂ Catalysts Calcined at Different Temperatures (O₂/Ar, 7.2%)

Sample	T _{calcination} (K)	$\frac{S_{\rm BET}}{({ m m}^2{ m g}^{-1})^a}$	W loading $(\mu \text{mol g}^{-1})$	W loading $(\mu \text{mol } \text{m}^{-2}_{\text{BET}})$	H ₂ consumed in TPR $(\mu \text{mol } \text{g}^{-1})^b$	XRD: $I_a I_r^{-1c}$
TiO ₂ (573)	573	47	0	0	_	2.28
TiO ₂ (1023)	1023	13	0	0	—	0.00
Wm3.5(573)	573	47	155	3.3	171	_
Wm3.5(1023)	1023	32	155	4.8	—	1.65
Wm7(573)	573	45	314	7.0	323	_
Wm7(1023)	1023	41.5	314	7.6	_	2.00
Wm9(573)	573	42.5	384	9.0	406	_
Wm9(1023)	1023	40	384	9.6	351	2.12
Wm11(573)	573	41.5	453	10.9	484	2.25
Wm11(698)	698	41	453	11.0	_	_
Wm11(823)	823	40.5	453	11.2	_	2.26
Wm11(948)	948	39	453	11.6	_	2.26
Wm11(1023)	1023	38	453	11.9	_	2.25^{d}
We3.5(1023)	1023	29	103	3.6	95	_
We4.5(1023)	1023	38	172	4.5	170	_
We5.5(823)	823	44	229	5.2	220	_
We5.5(948)	948	40.5	229	5.7	_	_
We5.5(1023)	1023	39	229	5.9	210	—

^{*a*} The maximum error is estimated to $\pm 3\%$.

^b Integrated signal from 550 to ca. 1140 K.

^c XRD: $I_a I_r^{-1}$: ratio of peak intensities (areas) of anatase (101) and rutile (110).

^d Crystalline WO₃ was detected by XRD only after calcination at 1023 K for 3 h in moist air (Fig. 2, Trace d).

properties of the grafted WO_x/TiO_2 catalysts and on their behavior in SCR of NO by NH₃. The structural changes induced upon tungsten deposition and calcination at different temperatures were followed by means of XRD, TPR, and laser Raman spectroscopy. Temperature-programmed desorption after exposure of the samples to SCR reaction conditions (SCR-TPD) was used to investigate the changes in the adsorption characteristics of the titania-based catalysts resulting from the tungsten oxide deposition.

EXPERIMENTAL

Catalyst Preparation

The WO_x/TiO₂ catalysts were prepared by a multi-step grafting procedure similar to the one described for VO_x/ TiO₂ (18). Titania (P25, Degussa) was stirred with doubly distilled water, then successively dried in a rotary evaporator for 12 h at 323 K/100 mbar and in an oven for 12 h at 423 K. The TiO₂ agglomerate was crushed and sieved to particles with a diameter of 0.3–0.5 mm to give the desired support material. Two different precursors were used for the grafting procedure. A tungsten (VI)–oxo– methanolate, WO(OCH₃)₄ (*Wm*), was prepared according to the procedure described in Ref. (20), and commercial W(OC₂H₅)₅ (*We*) was obtained from Gelest. *Wm* and *We* were dissolved in tetrahydrofurane and *n*-hexane (both FLUKA, p.a.), respectively. The following grafting procedure was then used. The preconditioned support was transferred into a dried glass reactor and degassed at 398 K for 2 h under vacuum (10 Pa) to obtain a mildly dehydrated surface. Then 0.3 mmol tungsten precursor per gram TiO₂, dissolved in 3 ml solvent, were injected into the reactor at room temperature. The temperature was raised to 323 K for 12 h. Afterward, the solution was removed, the sample was washed three times with fresh solvent, and it was dried in flowing nitrogen at 353 K for 3 h. Subsequently a stream of 200 ml min⁻¹ N₂, saturated with water at room temperature, was passed through the sample bed at 573 K to hydrolyze the anchored alkoxides and to remove the organic ligands from the catalyst. Calcination was performed in pure O₂ at 573 K for 3 h.

The catalysts are referred to as "WpL(T)" where Wp specifies the alkoxide precursor used for the grafting (Wm for WO(OCH₃)₄, We for W(OC₂H₅)₅), L gives the approximate loading of tungsten in μ mol m⁻²_{BET} for the catalysts after standard calcination at 573 K in oxygen, and (T) indicates the calcination temperature in K. Note that upon calcination of one sample (Wm3.5) at 1023 K sintering of the support material occurred leading to lower surface area (Table 1) and consequently to higher tungsten loading per S_{BET} .

Catalyst Characterization

Nitrogen physisorption. The specific surface areas, S_{BET} , and the mean pore diameters, $\langle d_p \rangle$, were determined

from nitrogen physisorption at 77 K using a Micromeritics ASAP 2000 instrument. Prior to the measurements samples were degassed to 0.1 Pa at 423 K. BET surface areas were calculated in a relative pressure range of 0.05-0.2 assuming a cross-sectional area of 0.162 nm^2 for the nitrogen molecule. The pore size distributions were calculated from the desorption branches of the isotherms (21) using the BJH method (22).

X-ray diffraction, XRD. To check the coexistence of different crystal phases X-ray powder diffraction patterns were measured on a Siemens θ/θ D5000 powder X-ray diffractometer. The diffractograms were recorded with CuK α radiation over a 2θ range of 20° to 44° . A scintillation counter with monochromator was used. I_a/I_r , the ratio of the intensities of the {101} reflection of anatase (23) and the {110} reflection of rutile (24), respectively, was used as a measure of the anatase fraction of the TiO₂ phases.

Laser Raman spectroscopy, LRS. For the Raman spectroscopy 0.1 g of calcined catalyst was ground and the samples were kept in a glass cuvette. Spectra were recorded under ambient conditions. The spectra were excited using the 1064 nm line of a NdYAG laser and recorded with a Perkin–Elmer 2000 NIR-FT-Raman spectrometer. The laser power was 50–150 mW.

Temperature-programmed reduction, TPR. For TPR measurements 1.5% H₂ in He at 250 ml_{STP} min⁻¹ was passed through a sample bed containing the equivalent of ca. 0.2 mmol W. Temperature was raised from ambient to 1350 K at 10 K min⁻¹. The H₂ consumption was determined from the concentration measured by mass spectrometry. The apparatus used and further details of the measurements are given in Refs. (25, 26).

Temperature-programmed desorption, TPD. SCR-TPD experiments were performed in situ with the same samples as used for the catalytic tests. SCR feed gas (50 ml min^{-1}) was passed through the catalyst bed at 303 K for 1 h after the complete SCR testing (12 h, see below). After purging for 1 h with argon (99.999%, Pan Gas, 20 ml min⁻¹) the temperature was raised at 10 K min⁻¹ up to 723 K and the concentrations of the evolving species H₂O, NH₃, NO, N₂, and N₂O were monitored by mass spectrometry (MS). To assess the influences of mass transfer and readsorption on the TPD spectra the criteria of Demmin and Gorte were applied (27). For the working conditions used, intraparticle concentration gradients seem to be negligible as the ratio of the carrier-gas flow rate to the rate of diffusion was calculated to be 0.07 (> 0.05 is given as a limit for negligible gradients). In contrast, readsorption phenomena cannot be ruled out in TPD measurements carried out at atmospheric pressure. The diffusion rate of the desorbed species as well as the carrier gas flow rates are much lower than the adsorption rate of, e.g., NH₃, even under optimum flow TPD conditions.

Catalytic Tests

Tests for the selective catalytic reduction (SCR) or NO by NH₃ were carried out in a continuous flow fixed-bed microreactor made of a quartz glass tube with 4 mm inner diameter. Volumes of 0.126 cm³, corresponding to 95–120 mg of catalyst granules, were used for the measurements. Prior to SCR activity tests the catalysts were pretreated in situ in flowing O₂/Ar (7%) at the temperature specified (573–1023 K). The reaction gas mixture consisted of 900 ppm NO, 900 ppm NH₃, and 1.8% O₂ in an argon balance. This gas mixture, which is referred to as the SCR feed, was mixed from argon (99.999%) and single component gases in an argon balance (3600 ppm NO/Ar, NH₃/Ar certified by $\pm 2\%$, Union Carbide). Feed and product concentrations of NO, NO₂, NH₃, H₂O, N₂O, O₂, and N₂ were quantitatively analyzed on line using a computer controlled Balzers quadrupole mass spectrometer QMA 112A.

Conversion measurements as a function of temperature were carried out at a gas hourly space velocity, GHSV, of ca. 24,000 h⁻¹ (flow rate per total bed volume; STP; $\varepsilon_{bed} \approx 0.5$) after steady-state SCR activity had been established at 423 K (typically after 2 h). The activity parameters, k_m and k_s , and the apparent activation energies, E_a , were calculated assuming first order kinetics in NO and zero order in NH₃ and O₂ (3). k_m values were calculated according to the performance equation of an isothermal plug-flow reactor,

$$k_{\rm m} = Fm^{-1} \cdot \ln[(1 - X_{\rm NO})^{-1}],$$

where *F* is the feed flow rate in m³ s⁻¹ and *m* is the catalyst mass in kg. The rate constants of the NO conversion will be presented for specific temperatures as $k_{\rm S}$ on a surface area basis: $k_{\rm S} = k_{\rm m} (S_{\rm BET})^{-1}$.

The criterion of Weisz and Prater (28) was checked for the most active catalyst, Wm11(1023), under the reaction conditions of the SCR tests. Any influence of internal mass transfer could be ruled out for this sample and all the other catalysts showing virtually the same pore size distribution.

For all measurements, a nitrogen balance including feed and product stream concentrations of all N-containing compounds was calculated. Even for high conversions of NO and NH₃, the error in the N-balance did not exceed $\pm 5\%$.

RESULTS AND DISCUSSION

Properties of Calcined Catalysts

The standard preparation procedure included calcination at 573 K for 3 h in a stream of dry oxygen. Prior to the catalytic tests the samples were calcined *in situ* in O₂/Ar (7.2%) at a temperature ranging from 573 to 1023 K. Table 1 summarizes the morphological properties of the *in situ* calcined tungsten oxide on titania catalysts. Temperature-programmed oxidation experiments (conditions: 50 ml min⁻¹ of 7% O₂/Ar, heating rate = 10 K min⁻¹)



FIG. 1. Influence of number of grafting steps on tungsten loading for the two series of WO_x/TiO₂ catalysts prepared by multiple step grafting with different precursors: $\Box WmL$, $\bigcirc WeL$.

performed with samples after preparation (dried and calcined) indicated that the organic ligands had been removed to >99% by the calcination in dry oxygen.

Tungsten deposition. The stepwise deposition of tungsten on the titania support by the multiple grafting procedure is illustrated in Fig. 1. The first and the second grafting steps with the methanolate precursor $(WO(OCH_3)_4, Wm)$ resulted in a deposition of (~160 μ mol(W) g⁻¹ each, whereas the following two grafting steps increased the loading only by $\sim 70 \,\mu$ mol g⁻¹. A slight decrease in total surface area, S_{BET} , occurred with the multiple grafting steps for the samples calcined at 573 K (47 to 41.5 m^2g^{-1}). Using the ethanolate precursor $(W(OC_2H_5)_5, We)$ the first deposition was again the most effective, giving $\sim 105 \,\mu \text{mol}(W) \text{g}^{-1}$. The subsequent two steps both resulted in additional \sim 65 μ mol g^{-1} . The WO_x deposition is obviously more effective when using WO(OCH₃)₄ in THF than W(OC₂H₅)₅ in *n*-hexane. Two effects possibly contribute to the higher efficiency of the Wm grafting procedure: different wetting abilities of the titania support by the solvent and a steric effect due to the different size of the alkoxide ligands. THF results in better wetting of the support material because it is more protic than *n*-hexane.

Note that a saturation effect is observed at a loading corresponding to 7–9 μ mol m⁻²_{BET} for the preparation of the *Wm* catalyst series, which is less hindered by both steric effects and incomplete wetting. A theoretical monolayer coverage, deduced from a virtual spreading of a single layer of the WO₃ structure on the support material, would correspond to 11.2 μ mol(W) m⁻² (11). Bond *et al.* (11) found an experimental monolayer capacity based on XPS measurements at 6.0 μ mol(W) m⁻² for P25-based samples. This is slightly more than a ratio W: Ti₈ of 0.5 (Ti₈ = Ti⁴⁺ ions exposed to the surface; 6.25 nm⁻² for {100} anatase surface (29) and matches double anchoring on surface OH groups on titania (ca. 6 nm⁻² (30)). Hilbrig *et al.* (12, 16) prepared fully dispersed tungsten oxide on titania contain-

ing up to 9 μ mol(W) m⁻²_{BET} by solid–solid wetting. Let us keep in mind for the further discussion of the morphological properties and the activity results that the loading of the catalysts *Wm*11 exceeds the capacity of an experimentally observed monolayer (11, 12) and their W surface concentrations correspond approximately to a theoretical monolayer. Sample *Wm*9 contains ca. the experimentally observed monolayer of WO_x on TiO₂, whereas all the other samples, including the catalysts of the *WeL* series, contain less tungsten than would correspond to a monolayer of WO_x on TiO₂.

Sintering and crystallinity. Calcination of the pure titania support at 1023 K resulted in complete anatase to rutile transformation and in a marked decrease of the BET surface area from 47 to 13 m²g⁻¹ (Table 1). Upon deposition of increasing amounts of tungsten, the extent of phase transformation as well as sintering was suppressed, resulting in a less pronounced loss in surface area for *Wm*11 (8%) and an unchanged ratio of the two titania phases upon *in situ* calcination at 1023 K (cf. I_a/I_r , Table 1). As already stated by Ramis *et al.* (10) tungsten deposition on TiO₂ stabilizes the morphology of the titania. It inhibits sintering as well as the anatase to rutile transformation and therefore leads to a higher thermal stability of the catalysts.

The XRD patterns of the catalyst Wm11, depicted in Fig. 2, show well-developed anatase and rutile crystallites.



FIG. 2. XRD analysis of the WO_x/TiO₂ catalyst with the highest tungsten loading, Wm11, calcined (a) in O₂ at 573 K for 3 h; (b) in O₂/Ar (7.2%) at 1023 K for 3 h; (c) in O₂/Ar (7.2%) at 1023 K for 3 h, followed by exposure to SCR reaction conditions at ca. 600 K for 24 h; (d) in moist air at 1023 K for 3 h. Reflections due to crystalline phases are marked: \blacktriangle anatase, \diamondsuit rutile, \bigstar WO₃.

Crystalline WO₃ was not detected after calcination up to 1023 K with all catalysts. XRD analysis indicated a crystalline tungsten oxide phase only after calcination in moist air at 1023 K (cf. Fig. 2). The same picture emerges from the LRS measurements presented in Fig. 3. The characteristic peaks for WO₃ observed at 807, 715, 324, 293, and 270 cm⁻¹ (31) are clearly present for the *Wm*11 sample only after calcination in moist air. Chan *et al.* (32) have shown that the ratio of the relative Raman intensities of the major band for WO₃ (807 cm⁻¹) and of the surface tungsten oxide compound (at 985 cm⁻¹, cf. discussion of the surface tungsten species, below) is 160:1. An estimation on this basis indicates an amount of ca. 1% paracrystalline WO₃ of the total tungsten content.

Hilbrig *et al.* (12, 16) reported on the spreading of WO₃ on TiO₂ in O₂ at 723 K and found that this process took place only in the presence of moisture, whereas the spreading of vanadia on both TiO₂ and γ -Al₂O₃ took place under dry conditions as well, but was accelerated by the presence of water vapor (33). Although the microscopic mechanism of the solid-solid wetting is still not known in detail, the phenomenon is attributed to a minimization of the surface free energy. The influence of water is related to the possible formation of oxyhydroxides as the mobile phase of the layered oxide (33). The formation of crystalline WO₃ at elevated temperature in the presence of water vapor (under SCR reaction conditions and upon calcination in moist air) is therefore attributed to the inverse process of the spreading phenomenon. Still the minimization of surface free energy is the driving force of the process. Tungsten that is not stabilized in a surface layer agglomerates and forms crystallites of WO₃ as soon as its mobility is increased by elevated temperature and by the presence of water vapor. We conclude that a highly dispersed tungsten oxide overlayer was produced by the multiple grafting procedure which exceeds the monolayer capacity in the case of Wm11. Upon annealing under moist conditions the thermodynamically most stable proportion of surface tungsten oxide species and paracrystalline WO₃ is established.

Raman investigations. To identify structural changes of the supported tungsten oxide upon calcination under different conditions, Raman spectra of the *Wm* catalyst series were recorded. For better visualization of the scattering caused by the grafted tungsten oxide a magnification of the 1100–750 cm⁻¹ region is shown in the figures (original magnification factor of 5) together with normalized spectra in the 1100–220 cm⁻¹ range (most intense peak of anatase at 635 cm⁻¹ was set 100%). Observable peaks attributed to tungsten (surface) species are expected in the 740–1060 cm⁻¹ region for W–O–W modes and W=O stretching modes (34) and crystalline WO₃ shows sharp bands at 807 and 715 cm⁻¹ and in the range 240–350 cm⁻¹ (31). The bands due to the anatase and rutile modifications of the support are detected at 635, 515, and 400 cm⁻¹ and at

FIG. 3. Raman spectra of the grafted WO_x/TiO₂ catalyst with the highest tungsten loading, Wm11, recorded under ambient conditions. Different calcination procedures were applied: (a) in O₂ at 573 K for 3 h; (b) in O₂/Ar (7.2%) at 1023 K for 3 h; (c) in moist air at 1023 K for 3 h. Most intense peak of anatase at 635 cm⁻¹ was set 100%. For better visualization of scattering due to WO_x species the region of 750–1100 cm⁻¹ is enlarged (original magnification factor: 5).

440 and 612 cm⁻¹, respectively, and a second order feature of TiO₂ occurs at 783 cm⁻¹ (35).

The Raman spectra after calcination at 573 K in dry oxygen, after calcination under dry conditions (*in situ*, O_2/Ar 7.2 %) at 1023 K, and after calcination at 1023 K in moist air are presented in Fig. 3. As discussed above (see sintering and crystallinity) the tungsten oxide exceeding the monolayer capacity of the titania support forms crystalline WO₃ in the presence of moisture at elevated temperature. The layered oxide on the sample calcined under moist conditions is therefore regarded as a thermodynamically equilibrated monolayer and its Raman spectrum shows a single maximum at 985 cm⁻¹ with some tailing toward lower wavenumbers. Compared to the spectrum recorded after dry calcination at 1023 K the shoulder at ~930 cm⁻¹ is less prominent.

The Raman spectra after calcination at 573 K are depicted in Fig. 4A for the *Wm* catalyst series. The spectrum of *Wm*3.5(573) shows a band at ~940 cm⁻¹ together with the second order feature of TiO₂ at 783 cm⁻¹ (35). With increased loading the band shifts upward to 985 cm⁻¹ for





FIG. 4. Raman spectra of the WmL catalyst series with different WO_x loading recorded under ambient conditions: (A) samples after calcination at 573 K: (a) TiO₂, (b) Wm3.5, (c) Wm7, (d) Wm9, (e) Wm11; (B) after additional *in situ* calcination for 3 h at 1023 K in O₂/Ar(7.2%): (a) Wm3.5, (b) Wm7, (c) Wm9, (d) Wm11. Assignments as in Fig. 3.

Wm9(573) and it is centred at 970 cm⁻¹ for Wm11(573). The difficulties to assign Raman bands of surface tungsten species between 915 and 980 cm⁻¹ have been discussed by Horsley et al. (34). They suggest a characteristic frequency range of 740–980 cm⁻¹ for octahedrally coordinated WO_x species and bands between 913 and 1060 cm⁻¹ to be indicative for tetrahedral species. It has been reported by Deo and Wachs (36) that the molecular structure of various supported transition metal oxides follows structures observed in aqueous medium and depends on the pH at the point of zero charge of the support. For WO_x on TiO_2 they predicted the presence of species with structures like $WO_{4(aq)}$ $(at \sim 930 \text{ cm}^{-1})$ and $W_{12}O_{39(aq)}$ (at $\sim 960 \text{ cm}^{-1}$), the latter being the major species at monolayer coverage. The band observed in the 930 to 990 cm^{-1} region will therefore be interpreted as an overlap of two characteristic bands. At low tungsten loadings mainly isolated fourfold-coordinated tungsten species are formed (band at ~935 cm⁻¹ dominating the spectrum). With increased loading, polytungstate species with an octahedral environment become predominant (band at 985 cm^{-1}). The formation of a polytungstate layer appears to be complete for Wm9(573) (maximum band wavenumber). Upon a further grafting step surplus tungsten is deposited and the band is shifted downward to 970 cm⁻¹. The shift to higher wavelength observed with

increasing tungsten loading and the above assignments are supported by other authors (8, 11). Note that in the studies cited, the samples were calcined at 723 K.

The changes occurring upon calcination at 1023 K under dry conditions become apparent when the spectra in Figs. 4A and 4B are compared. The band observed at 940 cm⁻¹ for the single loaded catalyst (*Wm*3.5) after calcination at 573 K is shifted to 965 cm^{-1} . A similar shift to higher wavenumbers occurs for the doubly loaded sample (from 960 cm⁻¹ broadened to 960–980 cm⁻¹). The three to fourfold grafted samples show a sharp band at 985 cm⁻¹ after in situ calcination at 1023 K. For Wm9(1023) a superposition with a broad band centred around 900 cm⁻¹ is visible, whereas for Wm11(1023) a shoulder around 930 cm⁻¹ is formed. The presence of the Raman band at 985 cm⁻¹ indicates the formation of a two-dimensional surface layer of polytungstate species, as also observed after the moist calcination of Wm11 at 1023 K (cf. Fig. 3). The position of this band coincides with the one reported for surface tungstate species produced by solid-solid wetting (33).

Temperature-Programmed Reduction, TPR

The TPR profiles of the Wm series are presented in Fig. 5 for samples calcined in O₂ at 573 K. A maximum hydrogen



FIG. 5. Temperature-programmed reduction profiles for the Wm catalyst series. The samples were previously calcined *in situ* for 3 h in O₂ at 573 K. TPR in flowing H₂/He (1.5%), heating rate: 10 K min⁻¹.

consumption is observed at 1050–1065 K and a second peak appears at 750–820 K for all samples, whereas the small peak observed for *Wm*11 at 920 K corresponds to a shoulder for *Wm*9, and is not resolved for the one- and two fold grafted *Wm* samples. It emerges that the reduction is not complete at 1150 K. The hydrogen consumed in the range \sim 500 K $\leq T \leq$ 1150 K corresponds for the samples approximately to the total tungsten content determined by AAS (cf. Table 1), assuming a reduction of W(VI) to W(IV). This is a strong indication that W(IV) species are stable on the titania surface up to ca. 1100 K. Further reduction to lower oxidation states of W occurs at higher temperature, as indicated by the TPR profile. Vermaire and van Berge (37) used TPR ($10\% H_2/Ar$, $10 \text{ K} \text{min}^{-1}$) to investigate the reduction behavior of WO₃/TiO₂ (P25) samples prepared by ion exchange. The stepwise reduction followed the stoichiometry observed in this study. The authors proposed W(IV) to be stabilized on TiO₂ (anatase and rutile) because of the similarity in the ion radius of W⁴⁺ and Ti⁴⁺, the W–O and Ti–O bond lengths, and the crystal structures of WO₂ and titania.

The influence of calcination at 1023 K on the reduction behavior was checked for sample Wm9 (not shown in Fig. 5). The low-temperature peak shifted by ca. 30 K to higher temperature and decreased in intensity, indicating a lower amount of easily reducible WO_x species, which further points to a stabilization of the WO_x surface layer upon calcination at elevated temperature.

Temperature-Programmed Desorption, TPD

Recently we have shown that SCR-TPD is a suitable method to describe the changes in Brønsted and Lewis acidity as well as the oxidizing abilities of vanadia on titania (anatase) (38, 39).

Influence of tungsten loading. For the Wm catalysts the desorption profiles after exposure of SCR feed gas at 303 K are shown in Fig. 6. The samples were calcined at 1023 K and the TPD was run after the complete SCR activity testing. The desorption rates of both water (left) and ammonia (right) are presented on a surface area (S_{BET}) based scale. Neither N₂, O₂, NO, nor N₂O was detected in the argon carrier gas stream during TPD, indicating that no other adsorbed species apart from ammonia and water are present in significant amounts under the conditions applied. On the



FIG. 6. Temperature-programmed desorption of H_2O (left) and NH_3 (right) after exposure to SCR feed at 303 K (SCR-TPD) for the catalysts of the *WmL* series, calcined at 1023 K and used for catalytic tests for 12 h. Numbers on curves indicate tungsten loading. The concentrations are referred to the total surface area (BET) of the samples as given in Table 1. TPD in flowing Ar (20 ml min⁻¹, STP), sample bed volume: 0.126 ml, heating rate: 10 K min⁻¹.



FIG. 7. Profiles of temperature-programmed desorption of H_2O (left) and NH_3 (right) for the triply loaded Wm7 catalysts (SCR-TPD). Same experimental conditions as in Fig. 6, but the catalysts were calcined *in situ* at different temperatures (indicated on curves).

other hand, it shows that no oxidation of adsorbed ammonia species occurred during the TPD experiments, which implies that all water evolved in TPD originates from molecularly adsorbed H_2O or from a recombination of surface hydroxyl groups.

The desorption profile of H₂O shows a peak maximum at 405 K for Wm3.5(1023) and Wm7(1023) with a long tailing to the highest temperature recorded (700 K). The maximum intensity of the signal decreases slightly with higher tungsten loading (Wm7(1023)). Upon further loading of the WO_x/TiO_2 catalysts the peak exhibits a broad maximum at 390-470 K (Wm9(1023)). Only half of the estimated total amount of water desorbing from the pure titania samples TiO₂(573) (ca. 3.6 μ mol m⁻²) or TiO₂(1023) (ca. 3.4 μ mol m⁻²) is calculated for the *Wm* catalysts (1.5– 1.75 μ mol m⁻²; 300–700 K) with Wm9(1023) showing the lowest total amount of evolved water. A high degree of hydroxylation can be expected, because most of the desorbing water is supposed to originate from the recombination of surface OH groups (especially at $T \ge 450$ K). The evolution of ammonia shows a more distinct change with increasing tungsten concentration. A very broad feature is observed at 400-700 K (maximum at ca. 600 K) for Wm3.5(1023). Upon increasing the tungsten loading the high-temperature ammonia evolution decreases in intensity and a steadily increasing maximum NH₃ concentration is observed at ca. 450 K. The estimation of the total amount of ammonia desorbed during the TPD experiments ranges from 2.35 μ mol m⁻² (*Wm*7(1023)) to 3.25 μ mol m⁻² (*Wm*11(1023)). This corresponds to approximately twice the amount of water detected. WO₃/TiO₂ catalysts are known to show both Brønsted and Lewis acidity (10, 16). An increasing density of acidic protons was described for increasing tungsten loading by Hilbrig et al. (16). Ramis et al. (10) found that coordinates ammonia is thermally more stable than protonated ammonia. In line with these findings we assign the ammonia desorbing at 400-500 K to be mainly bound to Brønsted acid centers. Tungsten deposition on titania at half to full monolayer coverage (ca. 5–9 μ mol m⁻²) thus

effects the preferential formation of protonic ammonia coordination sites at the expense of centers showing strong NH₃ coordination and likely to be of Lewis type.

Influence of calcination temperature. Desorption profiles of the threefold loaded catalyst *Wm*9 calcined *in situ* at different temperatures are shown in Fig. 7. After calcination at 573 K the traces of ammonia and water show rather constant desorption rates at ca. 400–700 K. Weak

TABLE 2

Selective Catalytic Reduction of NO by NH₃

Sample	T _{calcination} (K)	$k_{\rm S} \cdot 10^8 (585 \text{ K}) (m^3 \text{s}^{-1} m^{-2}_{\rm BET})$	$E_{\rm a}$ (kJ mol ⁻¹)	Conversion ^{<i>a</i>} $T_{X_{NO}=0.5}$ (K)
Wm3.5(573)	573	1.5	149	647
Wm3.5(1023)	1023	12.9	111	616
Wm7(573)	573	11.3	149	603
Wm7(1023)	1023	26	109	588
Wm9(573)	573	23	143	589
Wm9(1023)	1023	54	121	571
Wm11(573)	573	37	124	575
Wm11(698)	698	37	124	577
Wm11(823)	823	49	121	571
Wm11(948)	948	58	117	567
Wm11(1023)	1023	67	115	563
We3.5(1023)	1023	2.4	120 107	669 619
We5.5(823)	823	9.3	128	613
We5.5(948)	948	10.3	111	615
We5.5(1023)	1023	20.5	104	599
We5.5(1023)	1023	19.7	105	599
$We5.5(1023)^{b}$	1023	12.7	117	608

Note. The kinetic data are given as surface based rate constants, k_s , determined at 585 K from the analysis of integral activity measurements, and as apparent activation energies (E_a). The temperature required for 50% NO conversion ($T_{X_{NO}=0.5}$) reflects a measure of the overall activity.

^a Determined at constant GHSV of 24,000 h⁻¹.

^b Feed containing ca. 3000 ppm H₂O.



FIG. 8. Dependence of the SCR activity on the calcination temperature k_s , the rate constant of NO reaction referred to the surface area (BET), is plotted versus the calcination temperature (calcination *in situ*, O₂/Ar 7.2%) for the two samples with highest tungsten loadings of both preparation series, *Wm*11 and *We*5.5.

maximum desorptions are visible around 400 K for water and at 660 K for the NH_3 evolution. Such broad desorption features are generally the result of a wide distribution of adsorption sites of different strength. Upon *in situ* calcination at 1023 K ammonia desorbs with a distinct maximum at 430–470 K and the amount of more strongly bound NH_3 decreases. A less pronounced change is seen in the desorption behavior of water with a maximum at 390–470 K. The increased low-temperature desorption of NH_3 upon calcination at elevated temperature indicates the formation of additional Brønsted acid sites.

Catalytic Behavior

In Table 2 the results of the SCR activity measurements are summarized. For all measurements the selectivity to N₂ was 100% and a 1:1 stoichiometry was observed for the NH₃–NO reaction. This indicates that no ammonia oxidation occurred in the temperature range investigated (480– 700 K) (3). The overall activity is best represented by the temperature to obtain 50% NO conversion, $T_{\text{XNO}=0.5}$. Catalyst *Wm*11(1023) converts 50% NO at the lowest temperature, 563 K, whereas 575 K is needed after calcination at 573 K (*Wm*11(573)). A similar dependence on the calcination temperature emerges for all catalysts. Comparing all samples calcined at 1023 K, $T_{\text{XNO}=0.5}$ decreases with increasing tungsten loading for both catalyst series prepared (*Wm* and *We*), which indicates the increasing activity with higher tungsten concentration.

NO reaction rates are used to illustrate the above mentioned dependences of the activity on the tungsten loading as well as on the calcination temperature. Because the specific surface areas (BET) of the samples varied between 32 and 47 m²g⁻¹ the NO reaction rate is referred to the total surface area (BET) and represented as $k_{\rm S} = k_{\rm m} S_{\rm BET}^{-1}$, instead of $k_{\rm m}$, the conventional rate constant, which is referred to the catalyst mass.

In Fig. 8, k_s (at 585 K) is plotted versus the calcination temperature for the two samples with highest tungsten loading of both preparation series, Wm11 and We5.5. The NO reaction rate is doubled when Wm11 is calcined at 1023 K instead of 573 K, and the same behavior is observed for We5.5 upon increasing the calcination temperature from 823 to 1023 K. Figure 9 depicts the dependence of k_s on the catalyst loading. In the left panel (A) the Wm samples are represented after calcination at 573 K and the right panel (B) shows the reaction rates for the samples of both



FIG. 9. Dependence of the SCR activity on the tungsten loading of the catalysts. (A) shows k_s values for the *Wm* samples after calcination at 573 K and (B) the reaction rates for the samples of both series, calcined at 1023 K.

series, calcined at 1023 K. After calcination at 573 K very low activity is determined for W loading $<7 \mu \text{mol m}^{-2}$ and moderate activity is found at 7–11 μ mol m⁻². Note that *in situ* calcination at 1023 K on the other hand leads to a linear dependence of the NO reaction rate on the surface concentration of tungsten. At low loadings, however, very low SCR activity is measured. This hints toward uniform intrinsic SCR activity of the tungsten surface species above a basic loading of ca. 3 μ mol m⁻². When 9A and 9B are compared the increase in activity with higher calcination temperature emerges.

Addition of ca. 3000 ppm H_2O to the SCR feed leads to a decrease in activity, as listed in Table 2 for *We5.5* At 585 K the NO reaction rate was lowered to ca. 2/3 of the value determined for reaction under dry conditions. If we consider a reaction mechanism involving the reaction of adsorbed NH₃ with NO, either adsorbed or from the gas phase (3), this would imply a H₂O desorption step. At an increased partial pressure of water the desorption of H₂O may influence the reaction rate because it determines the site density for ammonia activation. Thus we may explain the decrease in activity observed by concurrent adsorption of NH₃ and H₂O on active sites.

Recapitulating the changes in activity and desorption behavior of the grafted WO_x/TiO_2 catalysts, the increase of both Brønsted acidity and SCR activity at increasing tungsten loading and calcination at elevated temperatures has to be stressed. The results illustrate the important role of protonic acid centers in the SCR of NO with NH₃ over WO_x/TiO_2 catalysts.

CONCLUSIONS

Grafting of tungsten alkoxides onto titania allows the immobilization of tungsten oxide species in highly dispersed form at loadings up to a monolayer coverage, which is estimated to be ca. 9 μ mol (W) m⁻²_{BET}. Even higher loadings (11 μ mol m⁻²) are stabilized after calcination at 573 K, but the surplus tungsten content is converted into crystalline WO₃ when the sample is treated under moist conditions at elevated temperature (1023 K). Tungsten deposition on TiO₂ leads to a higher thermal stability of the catalysts due to a concomitant suppression of sintering as well as rutilization of the titania support.

The Raman results indicate the formation of a tungsten oxide layer upon calcination at 1023 K, which is characterized by a band at 985 cm^{-1} under ambient conditions.

SCR-TPD investigations revealed that both calcination at elevated temperature (1023 K) and increasing of the tungsten loading increased the ratio of Brønsted-to-Lewis acid site density of the catalysts. As no N₂, O₂, NO, or N₂O are observed during TPD we conclude that no NO_x or Ocontaining reaction intermediates are adsorbed under the conditions applied and that no oxidation of adsorbed NH₃ occurred during TPD. This reflects the 1:1 stoichiometry for NH₃ and NO observed under SCR reaction conditions (absence of ammonia oxidation).

The SCR activity of the WO_x/TiO_2 catalysts is strongly influenced by the tungsten loading and the calcination temperature. Brønsted acid sites were found to be important for the SCR reaction over WO_x/TiO_2 catalysts. The surface density of protonic acid sites increases with the tungsten loading and with calcination at elevated temperature.

ACKNOWLEDGMENTS

Thanks are due to H. Viebrock for the preparation of the *Wm* precursor. Financial support by the "Nationaler Energie-Forschungs-Fond" (NEFF) and by the Swiss National Science Foundation (NFP 24) is kindly acknowledged.

REFERENCES

- 1. Tanabe, K., Misono, M., Ono, Y., and Hattori, H., *Stud. Surf. Sci. Catal.* **51**, 5 (1989).
- 2. Bosch, H., and Janssen, F., Catal. Today 2, 369 (1988).
- 3. Imanari, M., and Watanabe, Y., Stud. Surf. Sci. Catal. 7, 841 (1981).
- Morikawa, S., Takahashi, K., Mogi, J., and Kurita, S., Bull. Chem. Soc. Jpn. 55, 2254 (1982).
- Sloss, L. L. et al., "Nitrogen Oxide Control Technology Fact Book," Noyes Data Corporation, Park Ridge, 1992.
- 6. Chen, J. P. and Yang, R. T., Appl. Catal. 80, 135 (1992).
- 7. Deo, G., and Wachs, I. E., J. Catal. 146, 335 (1994).
- Vuurman, M. A., Wachs, I. E., and Hirt, A. M., J. Phys. Chem. 95, 9928 (1991).
- 9. Ramis, G., Busca, G., and Bregani, F., Catal. Lett. 18, 299 (1993).
- Ramis, G., Busca, G., Cristiani, C., Lietti, L., Forzatti, P., and Bregani, F., *Langmuir* 8, 1744 (1992).
- 11. Bond, G., Flamerz, S., and van Wijk, L., Catal. Today 1, 229 (1987).
- Hilbrig, F., Göbel, H. E., Knözinger, H., Schmelz, H., and Lengeler, B., J. Phys. Chem. 95, 6973 (1991).
- Cristiani, C., Bellotto, M., Forzatti, P., and Bregani, F., *J. Mater. Res.* 8, 2019 (1993).
- Lietti, L., Svachula, J., Forzatti, P., Busca, G., Ramis, G., and Bregani, F., *Catal. Today* 17, 131 (1993).
- Patrono, P., La Ginestra, A., Ramis, G., and Busca, G., *Appl. Catal. A* 107, 249 (1994).
- Hilbrig, F., Schmelz, H., and Knözinger, H., *Stud. Surf. Sci. Catal. B* 75, 1351 (1993).
- 17. Bond, G. C., and Tahir, S. F., Appl. Catal. 71, 1 (1991).
- Baiker, A., Dollenmeier, P., and Glinski, M., *Appl. Catal.* 35, 351 (1987).
- Handy, B. E., Baiker, A., Schraml-Marth, M., and Wokaun, A., *J. Catal.* 133, 1 (1992).
- Kucheiko, S., Turova, N. Ya., Kozlova, N. I., and Zhadanov, B. V., Sov. J. Coord. Chem. 12, 867 (1986).
- Broekoff, J. P., *In* "Preparation of Catalysts, II" (B. Delmon, P. Grange, P. Jacobs, and G. Poncelet, Eds.), p. 663. Elsevier, Amsterdam, 1979.
- Barrett, E. P., Joyner, L. G., and Halenda, P. P., J. Am. Chem. Soc. 73, 373 (1951).
- JCPDS Mineral Powder Diffraction Data File 21-1272, Park Lane, Pennsylvania.
- 24. JCPDS Mineral Powder Diffraction Data File 21-1276, Park Lane, Pennsylvania.

- 25. Koeppel, R. A., Nickl, J., and Baiker, A., Catal. Today 20, 45 (1994).
- Hurst, N. W., Gentry, S. J., Jones, A., and McNicol, B. D., *Catal. Rev. Sci. Eng.* 24, 233 (1982).
- 27. Demmin, R. A., and Gorte, R. J., J. Catal. 90, 32 (1984).
- 28. Weisz, P. B., and Prater, C. D., Adv. Catal. 6, 143 (1954).
- Bond, G., Zurita, J. P., Flamerz, S., Gellings, P. J., Bosch, H., van Ommen, J., and Kip, B. J., *Appl. Catal.* 22, 361 (1986).
- Iwasawa, Y., *in* "Tailored Metal Catalysts" (D. Reidel Ed.), P.I. Reidel, Dordrecht, 1986.
- Daniel, M. F., Desbat, B., Lassegues, J., Gerand, B., and Figlarz, M., J. Solid State Chem. 67, 235 (1987).

- 32. Chan, S. S., Wachs, I. E., and Murrell, L. L., J. Catal. 90, 150 (1984).
- Leyrer, J., Margraf, R., Taglauer, E., and Knözinger, H., Surf. Sci. 201, 603 (1988).
- Horsley, J. A., Wachs, I. E., Brown, J. M., Via, G. H., and Hardcastle, F. D., J. Phys. Chem. 91, 4014 (1987).
- 35. Beattie, I. R., and Gilson, T. R., J. Chem. Soc. A 2322 (1969).
- 36. Deo, G., and Wachs, I. E., J. Phys. Chem. 95, 5889 (1991).
- 37. Vermaire, D. C., and van Berge, P. C., J. Catal. 116, 309 (1989).
- 38. Schneider, H., Tschudin, S., Schneider, M., Wokaun, A., and Baiker, A., J. Catal. 147, 5 (1994).
- 39. Engweiler, J., and Baiker, A., Appl. Catal. A 120, 187 (1994).