$H_2SO_4$ , Fe(III)) and photoelectrochemical changes are indicated. The resulting trace shows a large initial photopotential followed by a large reversal of the signal that becomes steady due to a new product. This product gives smaller, more reversible photopotentials during the later on-off cycles. SDS reduces the photopotential by causing an increase in product formation (Table IV), and better reversibility is obtained. The explanation for this behavior is similar to that for  $[Ru(bpy)(dmbpy)_2]^{2+}$ . The different photogalvanic product implied in Figure 7 hints at some unknown modification of the electrochemical reactions in SDS.

Permanent changes do not seem to occur for  $[Ru(bpy)_2(bpd)]$ in water. Yet the photogalvanic trace does indicate an initial chemical change, and a steady-state intermediate subsequently gives negligible photopotentials. However, on stopping the experiment, the reaction is reversed and the emission spectrum before and after the experiment is of the same shape and intensity. Again SDS enhances permanent photoelectrochemical change, and for this reason the photogalvanic trace exhibits a larger slowly reversible signal (than in water).  $[Ru(bpy)(dpp)_2]^{2+}$  (Figure 4) behaves similar to  $[Ru(bpy)_2(bpd)]^{2+}$  except that Table IV shows a permanent photoelectrochemical reaction with an increase in emission intensity in water, while SDS causes a decrease in intensity. This could be taken as an indication of different products being formed in the two media.

#### Conclusion

In water, high reversible photopotentials were obtained for  $[Ru(bpy)(dmbpy)_2]^{2+}$ . The other three complexes are plagued

by unfaborable <sup>3</sup>MLCT redox potentials,<sup>36</sup> photochemical and/or photoelectrochemical changes, and possibly by a less reversible Ru(III)/Ru(II) redox couple than is known for  $[Ru(bpy)_3]^{2+}$ . The previously expected SDS-induced protection against photochemistry, due to less thermal population of the photolabile d-d state, is overcome by protection against quenching of the <sup>3</sup>MLCT state. The enhanced quenching by the micelle-bound Fe(III) and the competition between protons and complex for adherence to the micelle play an important role as well.

The same factors play an equally important role in shaping the outcome of the photogalvanic experiment in SDS. In addition to such factors photoelectrochemical changes and enhanced back electron transfer between micelle-bound Fe(II) and Ru(III) species contribute to the poor phototraces of  $[Ru(bpy)(dmbpy)_2]^{2+}$ . In the three remaining complexes, SDS slightly enhances the photopotential traces due to enhanced formation of products, which seem to be responsible for the improvement.

Acknowledgment. Financial support by the Ministry of Planning, Jordan, the Kuwait Development Fund, and Yarmouk University Research Fund is deeply appreciated. This work is part of N.A.R.'s Master Thesis.

# Valence States of Vanadia-on-Titania/Silica and Molybdena-on-Silica Catalysts after Reduction and Oxidation

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The behavior of vanadia-on-titania/silica and molybdena-on-silica catalysts during reduction by ammonia and oxidation by nitric oxide or oxygen at elevated temperatures was studied. The heat evolved during adsorption, reduction, and oxidation was measured by means of a differential scanning calorimeter. Ammonia reduces the catalysts to a certain extent under the formation of  $N_2$  and  $H_2O$ . On the basis of the heat measured, the amount of reduced species was calculated. The reduced catalysts were oxidized by NO and  $O_2$ , producing an amount of heat that corresponds to the respective reactions. The valence changes of V(V) to V(IV) and Mo(VI) to Mo(IV) were confirmed by means of X-ray photoelectron spectroscopy. The results of the differental scanning calorimetry measurements were used to calculate initial apparent rates of reduction and of oxidation. It was found that the rate of oxidation by  $O_2$  was about 5 times higher than that by NO. Moreover, the initial apparent rate of reduction by NH<sub>3</sub> of the molybdena catalyst was significantly higher than that of the vanadia catalyst; namely, NO does not participate in the reaction over the molybdena catalyst, while it does over the vanadia catalyst.

#### Introduction

The selective catalytic reduction (SCR) of  $NO_x$  is one of the options for postcombustion control of  $NO_x$  emissions. Of the possible reducing agents such as  $NH_3$ ,  $H_2$ , CO, and CH<sub>4</sub>, only ammonia was found to be selective for the reduction of  $NO_x$  in atmospheres containing excess oxygen.<sup>1</sup>

The mechanism of the overall reaction of NO,  $NH_3$ , and  $O_2$  (reaction 1) over vanadia catalysts has been studied by using labeled molecules.<sup>2,3</sup>

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$
 (1)

Two types of active sites were present on the surface of the catalyst. The sites were assigned to vanadium species with valences 4+ and 5+. Two different reactions occurred on these sites. Ammonia reduces the oxidized sites, while reoxidation was brought

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catalyst	compn, wt % of V or Mo by AAS	amt used, µmol of V or Mo	$S_{BET}$ , m <sup>2</sup> g <sup>-1</sup>
V <sub>2</sub> O <sub>5</sub> on TiO <sub>2</sub> /SiO <sub>2</sub>	1.9ª	17.9	235
V,O,	56	549	1
MoO <sub>3</sub> on SiO <sub>2</sub>	7.0	35.3	67
MoO <sub>3</sub>	67	349	

"Vanadia on titania/silica, 19.6 wt % Ti.

about by oxygen from the gas phase. Furthermore, it was found that most of the vanadium present in the catalyst is in the 5+ valence state under SCR conditions.<sup>4</sup> Bjorklund et al. also showed that reduction of V5+ to V4+ and oxidation of V4+ to V5+ occurred during the SCR reaction.<sup>5</sup>

Recently, we reported on the overall reaction of NH<sub>3</sub> and O<sub>2</sub> over an MoO<sub>3</sub>-on-SiO<sub>2</sub> catalyst (reaction 2).<sup>4,6</sup>

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$
 (2)

It was observed that during the reaction of NH<sub>3</sub>, NO, and O<sub>2</sub> over this catalyst, the formation of water occurred according to the same mechanism as that for the reaction of NH<sub>3</sub>, NO, and O<sub>2</sub> over vanadia catalyst.<sup>4</sup> Moreover, it was observed that NO did not participate in the reactions over silica-supported molybdena.6

This paper describes a study carried out to find an explanation for differences in the behavior of gas mixtures of NH<sub>3</sub>, NO, and O<sub>2</sub> over supported vanadia and molybdena catalysts. Differential scanning calorimetry (DSC), X-ray photoelectron spectroscopy (XPS), mass spectrometry, and a fixed-bed plug-flow reactor were used to study the reduction and oxidation behavior of the catalysts separately. This approach is based on the assumption that the reduced and oxidized states of the catalysts occur simultaneously under SCR conditions. The following issues were examined: (i) adsorption and chemisorption of ammonia on previously calcined catalysts, (ii) chemisorption of O<sub>2</sub> or NO or NH<sub>3</sub>-reduced catalysts, and (iii) desorption of water- and nitrogen-containing species during interaction of NH<sub>3</sub> or NO with the catalysts.

#### **Experimental Section**

Catalysts. The catalysts used in the DSC and XPS experiments and some characteristics are summarized in Table I. Samples of unsupported MoO<sub>3</sub> (Cerac, ultrapure) and V<sub>2</sub>O<sub>5</sub> (prepared by decomposition of  $NH_4VO_3$  (Merck) at 675 K in air for 8 h) were used as references in the XPS measurements.

The elemental composition of the catalysts was determined by means of atomic absorption spectrometry (AAS). BET surface areas were measured with a Carlo Erba Sorptomatic 1800.

Both supported catalysts were provided by John Geus's group (University of Utrecht, The Netherlands). The vanadia-on-titania/silica catalyst was prepared by the homogeneous deposition precipitation technique as described elsewhere.<sup>7</sup> The molybdena-on-silica catalyst was prepared by means of impregnation. In order to achieve good interaction between the active material and the silica support, lower valent vanadia, titania, and molybdena precursors were used.<sup>6,8</sup> After preparation, the catalysts were washed, dried, and calcined in air at 675 K for at least 24 h.

Gases. Gas mixtures of NO (2050 ppm), NH<sub>3</sub> (1990 and 1960 ppm), and  $O_2$  (25% and 1030 ppm) all in helium, as well as high-purity helium, were purchased from Air Products and were used without further purification. In the XPS experiments, the

gases were used in undiluted form, with a flow of approximately  $0.2 \text{ cm}^3 \text{ s}^{-1}$ . In the DSC experiments, gas mixtures of NO, NH<sub>3</sub>, and  $O_2$  in helium were made from the various mixtures with the aid of mass flow controllers. The total gas flow in the DSC experiments was 1.0 cm<sup>3</sup> s<sup>-1</sup>.

Apparatus. The system used in the heat measurements and the calibration of the differential scanning calorimeter has been described previously.<sup>9,10</sup> The system consisted of a gas-mixing system and a heat-flow differential scanning calorimeter (Setaram 111-G) coupled to a quadrupole mass spectrometer (Leybolt Q200). The sample cell of the differential scanning calorimeter (5-mm i.d.) contained 48 mg of catalyst (equal to 17.9 µmol of V or 35.3  $\mu$ mol of Mo). The reference cell contained 50 mg of silica. The mass spectrometer was used in the single-ion detection mode to study the production or consumption of compounds as a function of time.

XPS measurements were performed by using a VG-Scientific Escalab MK II spectrometer (resolution 0.1 eV) with a Mg K $\alpha$ source (1253.6 eV). Reductions and oxidations were carried out in a cell that was mounted on the preparation chamber.

Procedures. Catalysts with particle sizes between 0.25 and 0.50 mm were used. The catalysts were calcined in situ in  $25\% O_2$  in He at 675 K for 1 h.

In order to examine the interaction of ammonia with the catalysts, adsorption, chemisorption, and desorption measurements were carried out at temperatures ranging from 330 to 780 K. The measurements were performed as follows: The catalyst was first calcined. Then NH<sub>3</sub> in helium was admitted to the catalyst, which was kept at a fixed temperature. The heat evolved was monitored by the differential scanning calorimeter. The adsorption or reaction was considered completed when the heat signal was constant for at least 5 min and below 0.1 mJ  $s^{-1}$ . Then the entire system was flushed with helium for 15 min to desorb ammonia. The heat consumed was measured.

The reaction of NO or  $O_2$  with the reduced catalysts was examined as follows: The catalyst was reduced by NH<sub>3</sub> at 675 or 725 K and flushed with helium, as described above. Then NO or O<sub>2</sub> in helium was admitted to the reduced catalyst, which was kept at a fixed temperature of 675 or 725 K. The heat evolved was measured by the differential scanning calorimeter.

Flushing of a reduced catalyst with helium resulted in a constant DSC signal of 0.1 mJ s<sup>-1</sup> maximum. This is ascribed to the heat produced by the reaction of traces of inevitable oxygen leakage into the system (<5 ppm, measured by the mass spectrometer) with the reduced catalyst or with ammonia. Since far higher amounts of heat are usually measured, values below 0.1 mJ s<sup>-1</sup> are considered negligible. The area under the peak of the DSC signal vs time is proportional to the heat evolved or consumed. Amounts of heat were calculated by means of graphical integration.

Prior to an XPS measurement, the samples were treated in flowing air or NH<sub>3</sub> at 725 K for 2 h. After reduction or oxidation, the cell was evacuated to 0.5 Pa, after which the samples were transported into the analyzing chamber  $(10^{-7} Pa)$ . Although correction for charging effects in XPS measurements using the position of the peak maximum of the C 1s peak (284.7 eV) has certain drawbacks, this method is considered to be suitable to distinguish between the various valence states of the samples. Full widths at half-maximum (fwhm) of the photoelectron peaks were determined graphically.

#### **Results and Interpretation**

No conversion of ammonia was observed below 550 K. NH<sub>3</sub> was converted into H<sub>2</sub>O and N<sub>2</sub> in the temperature range 600-780 K. Compounds such as N<sub>2</sub>O and NO were not detected. The ratio of the amounts of  $H_2O$  and  $N_2$  is about 3, and the ratio of the amount of ammonia converted and the amount of nitrogen

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Figure 1. Heat evolved during adsorption, desorption (solid lines), and reaction (dotted lines) of NH<sub>3</sub> with the vanadia and molybdena catalysts as a function of temperature.  $\bullet$ , +, and  $\bullet$  represent desorption, adsorption, and reaction with the vanadia catalyst, respectively.  $\Box$ ,  $\nabla$ , and  $\Delta$  represent desorption, adsorption, and reaction with the molybdena catalyst, respectively. Catalyst weight = 48 mg;  $[NH_3]_i = 670$  ppm; flow = 1 cm<sup>3</sup> s<sup>-1</sup>.



Figure 2. Heat flow during reduction of the vanadia catalyst by  $NH_3$  at 675 K.  $[NH_3]_i = 330, 650, 980$  ppm. Other conditions are as in Figure 1.

produced is about 2. This suggests that  $H_2O$  and  $N_2$  were produced by the overall reaction

$$3[O]_{catalyst} + 2NH_3 = N_2 + 3H_2O$$
 (3)

Figure 1 shows the heat during adsorption, desorption, and reaction of NH<sub>3</sub> with the catalysts as a function of temperature from 330 to 780 K. The solid lines indicate adsorption and desorption of ammonia. The dotted lines may be ascribed to the heat produced by the reaction of  $NH_3$  with the catalysts. The lines intersect at about 600 K. The following interesting features were noted: (i) the heat evolved during adsorption or desorption decreases with increasing temperature from 330 to 550 K, but above 600 K, only exothermal effects are observed; (ii) the curves below 550 K are symmetrical, which means that the exothermal heat during interaction of ammonia with the catalysts is equal to the endothermal heat during desorption; (iii) the heat evolved during interaction of ammonia with the vanadia catalyst is higher than that with the molybdena catalyst at temperatures below 550 K (the same trend is observed for the heat during desorption); (iv) the evolution of heat during interaction of NH<sub>3</sub> with the molybdena catalyst starts at a lower temperature than with the vanadia catalyst.

The amount of  $NH_3$  adsorbed could not be measured by using the mass spectrometer. If monolayer coverage of ammonia is assumed, an estimated amount of about  $10^{-3}$  mol of  $NH_3$  is adsorbed/50 mg of catalyst. The heat measured during adsorption is about 250 mJ (Figure 1). This gives an estimated adsorption heat of 0.25 kJ mol<sup>-1</sup>, which is much lower than what is normally found for heats during monolayer adsorption. Presumably the



Figure 3. Heat flow during reduction of the molybdena catalyst by  $NH_3$  at 675 K.  $[NH_3]_i = 330, 650, 980, 1960$  ppm. Other conditions are as in Figure 1.



Figure 4. Heat flow during oxidation of the reduced molybdena catalyst by NO at 675 K.  $[NO]_i = 340, 690, 1030$  ppm. Other conditions are as in Figure 1.



Figure 5. Heat flow during oxidation of the reduced molybdena catalyst by  $O_2$  at 675 K.  $[O_2]_i = 170, 520, 1030$  ppm. Other conditions are as in Figure 1.

surface is not completely covered with NH<sub>3</sub>. The higher amount of heat evolved during the adsorption of NH<sub>3</sub> on the vanadia catalyst in comparison with that on the molybdena catalyst is ascribed to the larger surface area of the vanadia catalyst (Table I).

Both catalysts were oxidized and reduced over 300 times. Each time the same amount of heat of reduction or oxidation was measured, illustrating that the reductions and oxidations are reversible.

Figures 2 and 3 show DSC curves obtained when the vanadia and molybdena catalysts were reduced by ammonia at 675 K respectively. Interesting trends: (i) the reduction of the molybdena catalyst takes less time than that of the vanadia catalyst; (ii) a

TABLE II: Heat Measured during Reduction or Oxidation at 675 and 725 K and Calculated Amounts of V4+ or Mo4+ Present after **Reduction**<sup>4</sup>

	heat produced, mJ		amt of V4+ or Mo4+, µmol		
	675 K	725 K	675 K	725 K	
	V <sub>2</sub> O <sub>3</sub> on TiO <sub>2</sub> /SiO <sub>2</sub>				
$NH_3$	747	805	7.9	8.5	
NO	1640		8.0		
O <sub>2</sub>	783		6.8		
$MoO_3$ on $SiO_2$					
$NH_3$	604	1230	<sup>-</sup> 11.0	22.4	
NO	2327	7400	9.5	30.2	
0 <sub>2</sub>	1528	4125	9.9	26.6	

"The amount of catalyst is 48 mg (equal to 17.9  $\mu$ mol of V or 35.3  $\mu$ mol of Mo). The flow rate is 1 cm<sup>3</sup> s<sup>-1</sup>.

higher NH<sub>3</sub> concentration results in higher and narrower DSC peaks; and (iii) at each NH<sub>3</sub> concentration, the area under the DSC curves is the same. The same trends were found when the reduction was carried out at 725 K.

Figures 4 and 5, respectively, show the influence of the initial NO and O<sub>2</sub> concentrations on the shape of the DSC peaks for the oxidation at 675 K of the reduced molybdena catalyst. No formation of  $N_2O$  or NO occurred during the oxidations. When the reduced catalysts were oxidized by nitric oxide, the formation of N<sub>2</sub> was observed. Similar trends were observed for the vanadia catalyst. Interesting trends: (i) oxidation by NO takes more time than oxidation by  $O_2$ ; (ii) higher initial concentrations of NO and O<sub>2</sub> result in higher and narrower peaks; and (iii) for each concentration, the area under the DSC curve is the same. Oxidations carried out at 725 K showed a similar influence of the NO or O<sub>2</sub> concentrations on the DSC signal.

The amounts of heat produced during reduction or oxidation of the catalysts and the corresponding calculated amounts of vanadia and molybdena that are reduced or oxidized are shown in Table II. The figures in this table are averaged values of 10 measurements.

The positions of the photoelectron peaks of the V  $2p_{3/2}$  and Mo  $3d_{5/2}$  electrons of the supported catalysts are shown as a function of treatment in Figures 6 and 7. Treatment of unsupported and supported V<sub>2</sub>O<sub>5</sub> samples with NH<sub>3</sub> at 725 K broadened the V 2p3/2 peak and shifted the peak maximum to a lower binding energy by about 1 eV. This shift was also observed for untreated reference samples such as  $V_2O_5$  and  $VO_2$ , which makes reduction to the V<sup>4+</sup> valence the most probable outcome. The broadening of the V 2p3/2 peak probably indicates the presence of both V<sup>5</sup> and  $V^{4+}$  in the reduced materials. This gives additional support to the previous model for the SCR where  $V^{5+}$  and  $V^{4+}$  species were assumed as well.<sup>2,3,5</sup>

Treatment of unsupported and supported MoO<sub>3</sub> samples with NH<sub>3</sub> gives an additional photoelectron peak (unsupported MoO<sub>3</sub>) or shoulder (MoO<sub>3</sub> on SiO<sub>2</sub>) at approximately 230 eV. However, the Mo 3d<sub>5/2</sub> peak at 233.1 eV (Mo<sup>6+</sup>) did not disappear. The difference in binding energy between the shoulder or peak at 230 eV and the Mo  $3d_{5/2}$  peak of the untreated samples of about 3.2 eV makes reduction to the Mo<sup>4+</sup> valence the most probable outcome. The same shift of the peak of the 3d electrons of Mo in MoO<sub>3</sub> and MoO<sub>2</sub> materials was reported previously.<sup>11-14</sup> Peak fitting of the Mo 3d spectra of the reduced molybdena materials indicates the presence of two Mo 3d doublets: for Mo<sup>6+</sup> and Mo<sup>4+</sup>.

To be able to calculate rates of reduction or oxidation, the reduced or oxidized amounts of molybdena and vanadia had to be determined. If conversion of  $V^{5+}$  to  $V^{4+}$  and of  $Mo^{6+}$  to  $Mo^{4+}$ is assumed, the amounts of molybdena and vanadia that are reduced or oxidized can be calculated from the measured heats



Figure 6. Position of the V  $2p_{3/2}$  XPS peak of the supported vanadia catalyst as a function of reduction or oxidation treatment. Dotted lines indicate reference values for the position of the V  $2p_{3/2}$  peak of  $V_2O_5$  and VO<sub>2</sub>. Treatments were carried out at 725 K for 2 h.  $[NH_3]_i = 1990$ ppm.



Figure 7. Position of the Mo  $3d_{5/2}$  and Mo  $3d_{3/2}$  XPS peaks of the supported molybdena catalyst as a function of reduction or oxidation treatment. Dotted lines indicate reference values for the positions of the Mo  $3d_{5/2}$  peaks of MoO<sub>3</sub> and MoO<sub>2</sub>. Other conditions are as in Figure 6.

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TABLE III:  $\Delta H$  for Reactions Occurring in the Various Reductions and Oxidations at 675 K<sup>16</sup>



**Figure 8.** Amount of V<sup>5+</sup> present in the DSC cell that is reduced by NH<sub>3</sub> to V<sup>4+</sup> at 675 K and reoxidized by NO or O<sub>2</sub>. [NH<sub>3</sub>] = 330 ppm, [NO] = 690 ppm, and [O<sub>2</sub>] = 170 ppm. [V<sup>5+</sup>]<sub>i</sub> = 17.9  $\mu$ mol. Other conditions are as in Figure 1.

(Table II) and the  $\Delta H$  values given in Table III. From Table II it can be seen that the reduced amounts are about equal to the oxidized amounts, indicating complete oxidation. Moreover, if reduction to other valences such as Mo<sup>5+</sup> or V<sup>3+</sup> was assumed, no correlation was obtained between the reduced and oxidized amounts. The presence of such valences was therefore supposed to be negligible.

At 675 and 725 K the amounts of vanadia that are reduced are about equal. The vanadia catalyst was therefore examined at 675 K only. The average reduced or oxidized amount is 8  $\mu$ mol of V (45%). The average reduced or oxidized amounts for the molybdena catalyst are 11  $\mu$ mol of Mo (30%) at 675 K and 26  $\mu$ mol of Mo (75%) at 725 K. It was suggested in a previous study that different molybdena species such as crystalline MoO<sub>3</sub> and silicomolybdic acid are present in silica-supported molybdena catalysts.<sup>6</sup> Thus, this extra amount (15  $\mu$ mol = 3 wt % Mo) of molybdena can be ascribed to the presence of silicomolybdic acid, which is in agreement with the findings of Barbaux et al.,<sup>15</sup> who found that 5 wt % of the Mo in the catalyst is present as silicomolybdic acid.

Initial apparent rates of reduction and of oxidation can be estimated from the DSC results: the cumulative amount of vanadia or molybdena that was reduced or reoxidized at 675 or 725 K is plotted as a function of time, as shown in Figures 8 and 9. Initial apparent rates are equivalent to the tangents at the curves. These rates are shown in Table IV. Higher gas concentrations resulted in higher initial reaction rates. However, the measurements are not considered to be sufficiently accurate to calculate reaction orders.

### Discussion

In order to enable a comparison of the apparent initial reaction rates shown in Table IV for both catalysts, the figures given for the molybdena catalyst should be multiplied by a factor of 2. This



Figure 9. Amount of Mo<sup>6+</sup> present in the DSC cell that is reduced by NH<sub>3</sub> to Mo<sup>4+</sup> at 675 and 725 K and that is reoxidized by NO or O<sub>2</sub>. [NH<sub>3</sub>] = 980 ppm (675 K), 660 ppm (725 K). [NO] = 1030 ppm (675 K), 340 ppm (725 K). [O<sub>2</sub>] = 520 ppm. [Mo<sup>6+</sup>]<sub>i</sub> = 35.3  $\mu$ mol. Other conditions are as in Figure 1.

TABLE IV	V: Initial	Apparent	t Rates o	of Reduction	with NH <sub>3</sub>	and
Oxidation	with O <sub>2</sub> c	or NO: n	imol s <sup>-1</sup>	(mol of Mo	or V)-1	

amt of reductant	MoO <sub>3</sub> on SiO <sub>2</sub>		V <sub>2</sub> O <sub>5</sub> on TiO <sub>2</sub> /SiO <sub>2</sub>		
or oxidant, ppm <sup>a</sup>	675 K	725 K	675 K		
Reduction by NH <sub>3</sub>					
330	0.3	0.5	0.1		
650	0.4	0.8	0.2		
980	0.9	1.1	0.2		
Oxidation by O <sub>2</sub>					
170	0.3	0.3	0.4		
520	0.3	0.6			
3.3%			1.5		
Oxidation by NO					
340	0.1	0.2	0.2		
690	0.1	0.3	0.2		
1030	0.2	0.7	0.3		

"Unless noted otherwise.

is because twice the number of electrons is involved in the reduction and oxidation of molybdena in comparison with the case of vanadia.

The apparent rates of oxidation of the reduced catalysts by oxygen and by NO are about equal for both catalysts. The rate of oxidation by NO is about 5 times lower than that by  $O_2$ . This means that when a mixture of NH<sub>3</sub>, NO, and  $O_2$  is admitted to the catalyst, little interaction of NO with the catalyst is likely to occur. This is in agreement with previous findings, in which it was observed that over molybdena catalysts little interaction with NO occurs<sup>6</sup> and that over vanadia catalysts NO reacts from the gas phase with chemisorbed NH<sub>x</sub> species.<sup>2,3</sup>

When the temperature is raised from 675 to 725 K, the apparent rate of oxidation of the molybdena catalyst by NO increases more than the apparent rates of the other reactions over this catalyst (Table IV). This explains why the selectivity of this catalyst for the  $NH_3 + O_2$  reaction decreased at higher temperatures from 100% at 625 K to 90% at 675 K while  $N_2$  and  $N_2O$  were produced.<sup>4</sup>

The apparent rate of reduction of the vanadia catalyst by  $NH_3$ is significantly lower than that of the molybdena catalyst. Morever, from Figure 1 it can be seen that reduction of the molybdena catalyst by  $NH_3$  starts at lower temperatures than that of the vanadia catalyst, indicating a higher reducibility of the molybdena catalyst by  $NH_3$ . Since the other rates (oxidation) are about equal

<sup>(15)</sup> Barbaux, Y.; Elamrani, A. R.; Payen E.; Gengembre, L.; Bonelle, J. P.; Grzybowska, B. Appl. Catal. 1988, 44, 117.

<sup>(16)</sup> Barin, I.; Knacke, O.; Kubaschewski, O. Thermochemical Properties of Inorganic Substances; Springer Verlag: New York, 1977.



Figure 10. Production of  $H_2^{18}O$  in  ${}^{18}O_2$  transient experiments at 675 K<sup>4</sup> as a function of time. 50 mg of catalyst was used. NH<sub>3</sub>, NO, and O<sub>2</sub> or  ${}^{18}O_2$  concentrations of 500 ppm were used.

for both catalysts, the different catalytic behavior of the catalysts (reactions 1 and 2 occurring over the vanadia and molybdena catalysts, respectively) is likely caused by the difference in NH<sub>3</sub> reduction rate. Probably, recombination of chemisorbed NH<sub>x</sub> species to produce N<sub>2</sub> competes with reaction of NO from the gas phase with chemisorbed NH<sub>x</sub>. The presence of NH<sub>x</sub> species on NH<sub>3</sub>-reduced catalysts will be dealt with in a forthcoming paper. Since the molybdena catalyst is reduced faster by NH<sub>3</sub> than the vanadia catalyst, it can be assumed that recombination of NH<sub>x</sub> species is fast over the first catalyst, which means that the reaction between NO and chemisorbed NH<sub>x</sub> is unable to compete with the recombination of NH<sub>x</sub> species.

When 500 ppm of NH<sub>3</sub> and 320 ppm of O<sub>2</sub> were passed onto reduced vanadia and molybdena catalysts at 675 K, the catalysts were oxidized.<sup>4</sup> It was concluded that the catalysts were mainly in the highest oxidation state under actual reaction conditions. Supporting evidence for this suggestion is the higher apparent rate of oxidation by O<sub>2</sub> in comparison with the apparent rate of reduction by NH<sub>3</sub> for the vanadia catalyst (Table IV). For the molybdena catalyst the reduction by NH<sub>3</sub> and the oxidation by O<sub>2</sub> are about equally fast (Table IV). Additional information on the interaction of NO with  $NH_x$  species can be obtained by comparison of the rate of reduction by ammonia and the reaction rate of the overall reactions (reaction 1 or 2). The apparent rates of the overall reactions can be estimated from the rate of the production of water under reaction conditions. In previous transient experiments with  ${}^{18}O_2$  the production of  $H_2{}^{18}O$  at 675 K as a function of time was studied.<sup>24</sup> It can be deduced from the stoichiometry shown in reaction 3 that if chemisorbed  $NH_x$  species are recombined to produce  $N_2$  instead of reacting with NO from the gas phase, the apparent rate of  $NH_3$  reduction has to be two-thirds that of the water production.

When the amount of  $H_2^{18}O$  produced is plotted as a function of time (Figure 10), the initial rate of the production of water is equivalent to the tangent at the curves. These rates are 0.7 mmol  $s^{-1}$  (mol Mo)<sup>-1</sup> and 1.8 mmol  $s^{-1}$  (mol V)<sup>-1</sup>. From Table IV it can be seen that for the molybdena catalyst the apparent rate of NH<sub>3</sub> reduction is about two-thirds that of water production, indicating that interaction of NO with chemisorbed NH<sub>3</sub> species is low. For the vanadia catalyst the apparent rate of NH<sub>3</sub> reduction is much lower than that of water production (Table IV). This probably means not only that water is produced via reaction of NH<sub>4</sub> species with oxygen from the vanadia but that oxygen from gas-phase NO is also involved.

## Conclusions

Vanadium in a  $V_2O_5$ -on-Ti $O_2/SiO_2$  catalyst was reduced to the 4+ valence by NH<sub>3</sub> at 675 and 725 K. The percentage of vanadia reduced is 45% at both temperatures. The percentage of molybdenum in an MoO<sub>3</sub>-on-SiO<sub>2</sub> catalyst that was reduced by NH<sub>3</sub> to the 4+ valence is 30% at 675 K and 75% at 725 K.

The reduced catalysts are completely oxidized by  $O_2$  or NO at 675 and 725 K. The rates of oxidation are about equal for both catalysts. Oxidation by  $O_2$  is about 5 times faster than oxidation by NO. The faster oxidation by  $O_2$  of the vanadia catalyst in comparison with oxidation by NO and the observed valence change after reduction from V<sup>5+</sup> to V<sup>4+</sup> give support to a reaction model proposed earlier for the selective catalytic reduction of NO with NH<sub>3</sub>.

Nitric oxide does not participate in the reactions over the molybdena catalyst, while it does take part in the reactions over the vanadia catalyst. This is explained by the observed faster reduction by  $NH_3$  of the molybdena catalyst than of the vanadia catalyst.

Acknowledgment. We thank Jean Paul Kelderman for his contribution to the DSC experiments, Hein Weijers for his practical assistance in the XPS experiments, and John Geus's group of the University of Utrecht (The Netherlands) for kindly providing the catalysts used in this study.

**Registry** No.  $V_2O_5$ , 1314-62-1; TiO<sub>2</sub>, 13463-67-7; MoO<sub>3</sub>, 1313-27-5; NH<sub>3</sub>, 7664-41-7; NO, 10102-43-9; O<sub>2</sub>, 7782-44-7; V, 7440-62-2; Mo, 7439-98-7.