Nitrogen containing species as intermediates in the oxidation of ammonia over silica supported molybdena catalysts

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Abstract

The behaviour of ammonia and oxygen over silica supported molybdena catalysts has been studied by means of thermal analysis techniques, such as thermo-gravimetry and heat-flow calorimetry. The composition of the reactants and products was determined by means of mass spectrometric analysis. Nitrogen- and hydrogen-containing species were observed to be present on the catalyst surface after reduction of the catalysts by ammonia and subsequent flushing in helium. Additional evidence for the presence of these species was provided by experiments in which labelled molecules were used as well as by means of X-ray photo-electron spectroscopy. The nitrogen- and hydrogen-containing species could be removed from the surface by O₂ or NO. The reaction products were found to be N₂ and H₂O.

In the light of these results, a working model is proposed that describes the adsorption of ammonia on; and the oxidative production of nitrogen and water from ammonia over, silica-supported molybdena catalysts.

Keywords: adsorption, ammonia oxidation, molybdena/silica.

INTRODUCTION

The reaction of NH₃ and O₂ over MoO₃ on SiO₂ catalysts has been studied previously [1]. High activities and selectivities for the oxidation of NH₃ with...
O₂ to give N₂ and water were observed over catalysts with molybdenum loadings higher than 7 wt%. It was assumed that a crystalline MoO₃ phase is responsible for the catalytic activity. The conversion of NH₃ and the selectivity for N₂ were not influenced when NO was introduced to the reaction gas, as was also observed in several other studies [2,3]. Negligible reduction of the catalyst by NH₃ was observed at temperatures below 550 K; above 625 K, negligible adsorption of NH₃ occurred while the molybdenum was reduced to Mo⁴⁺ [2,3]. Both O₂ and NO completely oxidised the reduced catalyst. The high selectivity of the molybdena catalyst for the oxidation of NH₃ to give N₂ and water was suggested to be caused by the faster recombination of chemisorbed NHₓ species to produce N₂ in comparison to the reaction of such species with NO from the gas-phase.

This paper describes the role of N-containing species as intermediates in the oxidation of NH₃ over MoO₃ on SiO₂ catalysts in more detail. N- and H-containing species were observed to be present on the catalyst surface after reduction by NH₃. It was found that these N- and H-containing species could be removed during oxidation. Differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TG) were used to study the degree of reduction and oxidation of the catalysts. TG was also used to study the adsorption behaviour of NH₃ at 395 K. Reduction and oxidation experiments with labelled components such as ¹⁵NH₃, ND₃ and ¹⁵NO were used to establish the origin of the N- and H-containing species found on the catalyst surface. Measurements by means of X-ray photoelectron spectroscopy (XPS) were used to give additional support for the presence of nitrogen-containing species on the surface of the catalyst after reduction by NH₃.

In the light of these results a working model is developed, that describes the reaction of ammonia with oxygen over silica-supported molybdena catalysts. This model is used to explain the results of not only the experiments described in this paper, but also those of previous studies [1-3] (such as the influence of different structures of molybdena present in the catalysts on the catalytic activity), as well as relevant data from the literature.

**EXPERIMENTAL**

**Catalysts and gases**

The catalysts and some characteristics are summarised in Table 1. Details on the catalyst preparation procedures applied are given elsewhere [1]. The catalysts were provided by John Geus's group (University of Utrecht, the Netherlands). Catalysts Mo10 and Mo3, which are used in the TG experiments, were prepared using the homogeneous deposition-precipitation technique as described elsewhere [1]. In order to obtain good interaction between the active material and the silica support an electrochemically prepared lower
TABLE 1

Catalysts used in this study.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Composition (AAS)</th>
<th>Preparation method</th>
<th>( S_{\text{BET}} ) (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo3</td>
<td>3 wt% Mo, 1.6 wt% Pb</td>
<td>HDP¹⁾</td>
<td>140</td>
</tr>
<tr>
<td>Mo7</td>
<td>7 wt% Mo, 0 wt% Pb</td>
<td>imp²⁾</td>
<td>67</td>
</tr>
<tr>
<td>Mo10</td>
<td>10 wt% Mo, 2.6 wt% Pb</td>
<td>HDP¹⁾</td>
<td>140</td>
</tr>
</tbody>
</table>

1) Homogeneous deposition precipitation of a Mo³⁺ precursor [1]
2) Incipient wetness impregnation of a Mo³⁺ precursor.

valent Mo³⁺ solution was used for the precipitation. Lead was introduced into the catalyst by using lead electrodes for the electrolysis of the precursor. The presence of lead in the catalysts appeared to improve the activity, while the selectivity was not influenced.

Catalyst Mo7, which is used in the DSC and XPS experiments, was prepared by means of incipient wetness impregnation of an electrochemically prepared Mo³⁺ precursor (which contained no lead) onto silica [1].

Gas mixtures of NO (2050 ppm), NH₃ (1960 ppm) and O₂ (1030 ppm) all in helium as well as high purity helium, were purchased from Air Products and were used without further purification. \(^{15}\)NH₃, ND₃ and \(^{15}\)NO (isotopic purity 99 atom %) were obtained from MSD isotopes (Canada) and were used in the DSC apparatus without further purification. Gas mixtures of these labelled compounds in helium with concentrations of about 1000–2000 ppm and pressures of up to 10 MPa were prepared by conventional static gravimetric methods in our laboratory. The ND₃-containing mixture appeared to contain ND₃, ND₂H, NDH₂ and NH₃. The molar ratio of D/H in this mixture was 2.4.

APPARATUSS

The DSC apparatus system used for the heat measurements and the calibration of this system has been described elsewhere [4,5]; the DSC (Setaram 111-G) was coupled to a quadrupole mass spectrometer (Leybolt Q200). In a typical experiment, the sample cell of the DSC apparatus contained 48 mg of Catalyst Mo7 and the reference cell contained 50 mg of silica. The mass spectrometer was used in the single ion detection mode to measure the production or consumption of compounds, as a function of time. The gas-flow in the DSC experiments was 1.0 cm³ s⁻¹.

TG measurements were performed using a Perkin Elmer TGA 7. Samples of Catalysts Mo3 and Mo10 of about 10 mg were examined. The apparatus was calibrated prior to the experiments. The balance was kept under helium (40
cm$^3$ min$^{-1}$) and the samples were treated in flowing air or NH$_3$ in He. The gas-flow over the sample was 20 cm$^3$ min$^{-1}$.

XPS measurements were performed using a VG-Scientific Escalab MK II with a Mg K$_\alpha$ source (1253.6 eV). Reduction and oxidation were carried out at atmospheric pressure in a gas-cell which was mounted to the preparation chamber. The position of the peak maximum of the photo-electron peaks could be determined with an accuracy of ±0.1 eV [2].

**PROCEDURES**

Catalysts with particle sizes ranging from 0.25 to 0.50 mm were used.

The Mo7 Catalyst was reduced by NH$_3$ in the DSC apparatus at 725 K. The reduction was considered to be completed when the heat signal remained constant and below 0.1 mJ s$^{-1}$, as has been discussed previously [2]. The system was then flushed with helium for 20 minutes, after which NO or O$_2$ was admitted to the reduced catalyst, which was kept at a fixed temperature of 725 K. The area under the peak of the DSC signal, which was determined graphically, is proportional to the heat evolved. The amount of molybdenum reduced was calculated from the measured heat by means of a method described previously [2].

Mo3 and Mo10 samples were calcined in the TG apparatus in flowing air at 775 K for 1 hour. The sample was then cooled to 395 K and kept under helium until the TG signal was constant, after which NH$_3$ was admitted to the sample. After 15 minutes, the temperature was raised at a rate of 10 K min$^{-1}$ to 775 K. The sample was subsequently kept under flowing NH$_3$ for 160 minutes at 775 K, after which the NH$_3$ feed to the sample was changed to air.

Prior to an XPS measurement, the Mo7 Catalyst was treated for 2 hours at 775 K in a flow of NH$_3$ or air. The gas-flow was approximately 0.2 cm$^3$ s$^{-1}$. After reduction or oxidation the gas-cell was evacuated to 0.5 Pa after which the sample was transported into the analysing chamber (10$^{-7}$ Pa). The positions of the XPS peaks were corrected for charging effects using the position of the peak maximum of the C 1s photo-electron peak (284.7 eV).

**RESULTS AND INTERPRETATION**

**DSC experiments**

Nitrogen and water were produced when the NH$_3$-reduced and subsequently helium flushed Mo7 Catalyst was oxidised by NO or O$_2$. This experiment was repeated more than 15 times; each time, it was found that equal amounts of nitrogen and water were produced during oxidation, indicating that nitrogen- and hydrogen-containing species were present on the reduced catalyst and that...
adsorption and desorption of these species were reproducible. Production of compounds such as N₂O or NO was not observed.

It was found previously that the concentration of oxygen leakage into the system was lower than 5 ppm [2]. Oxidation of reduced catalysts or reaction of traces of NH₃ that were left after reduction of the catalyst with this amount of oxygen has been found to give a calculated heat effect of maximally 0.1 mJ s⁻¹. The influence of the flushing-time on the heat evolved during oxidation and on the amounts of nitrogen and water produced was investigated, to be sure that the observed production of nitrogen and water during oxidation was not caused by oxidation of traces of physisorbed ammonia. It was found that both the heat during oxidation of the reduced catalyst and the amounts of nitrogen and water produced, decreased with longer flushing periods, indicating that oxidation had occurred. If oxidation of physisorbed ammonia had occurred the amount of water produced would have been threefold the amount of nitrogen produced. However, the amounts of N₂ and water that were produced during the oxidation by O₂ for flushing periods between 20 and 160 minutes were equal to one another at each period, indicating that oxidation of physisorbed ammonia was negligible at each flushing period. A flushing period of 20 minutes was therefore considered to be sufficient to remove traces of physisorbed ammonia.

Figure 1 shows the production of N₂ and H₂O and the heat evolved during oxidation by O₂ of the NH₃-reduced catalyst, as a function of time. Differences in the peak shapes for the production of N₂ and H₂O are due to different re-

Fig. 1. The heat flow and the production of N₂ and water, as a function of time during oxidation of a NH₃-reduced Mo7 Catalyst by O₂. Temperature = 725 K; Catalyst weight = 48 mg; Flow = 1 cm³ s⁻¹; [O₂] = 520 ppm.
Response times of the mass spectrometer. The production of water and of nitrogen decreased to zero after about 30 minutes. The profiles of the evolution of heat (DSC) and of $N_2$ concentration (MS) are similar. This means that both the reduced molybdenum and the nitrogen-containing species on the catalyst are oxidised equally rapidly, assuming that the influence of both different detection techniques on the shape of these profiles is negligible. The areas under the curves are equivalent to 4.8 J, 3 $\mu$mol $N_2$ and 3 $\mu$mol $H_2O$ respectively. The experiment was repeated several times and these amounts of 3 $\mu$mol of $N_2$ and water were observed each time, indicating good reproducibility and reversibility of the process of production and removal of N- and H-containing species. Since the amount of molybdenum in the DSC was equivalent to 35.3 $\mu$mol, the percentage of nitrogen- and hydrogen-containing species on the molybdenum was 9%. The formation of $N_2$ and $H_2O$ from the N- and H-containing species requires about 0.7 J, assuming that formation of $H_2O$ ($\Delta H_{298 K} = 228.6$ kJ mol$^{-1}$) gives the major contribution to this effect. About 4.1 J was thus evolved during oxidation of the catalyst. From this heat it is calculated that the amount of molybdenum that is reduced prior to oxidation with oxygen is 26 $\mu$mol (equal to 74% of the molybdenum present in the DSC). The enthalpy change of the following reaction is used in this calculation, which has been described in more detail earlier [2]:

$$2 \text{MoO}_2 + O_2 \rightarrow 2 \text{MoO}_3 \quad \Delta H_{298K} = -310 \text{kJ}$$

TG experiments

Figure 2 shows the weight of a sample of the Mo10 Catalyst, as a function of time. Interesting features are as follows: (i) the sample weight decreased during the pretreatment in air at 775 K, indicating that probably water was desorbed; (ii) the weight of the sample increased when ammonia was admitted to it at a temperature of 395 K. This increase in weight may be attributed to adsorption of $NH_3$; (iii) the weight of the sample which was kept under ammonia, decreased when the temperature was increased from 395 K to 775 K, with a shoulder occurring at a temperature of about 550 K. The first part of this decreasing curve (until the shoulder at about 550 K) may be attributed to desorption of the adsorbed ammonia, while the second part may be attributed to reduction of the sample by $NH_3$; and (iv) the sample weight increased when the feed was changed from ammonia to air at 775 K, indicating oxidation of the sample.

The increase of the sample weight during treatment with $NH_3$ at 395 K is equivalent to 5.7 $\mu$mol $NH_3$. Since the Mo amount in the sample cell of the TG was 14 $\mu$mol, the calculated molar ratio of $NH_3_{adsorbed}/Mo$ is equal to 1/2.4.

The decrease of the sample weight during reduction at 775 K was 0.15 mg.
The DSC experiments showed that about 9% N- and H-containing species was present on the reduced catalyst. This percentage corresponds to a weight of 0.02 mg. The decrease caused by reduction of the sample weight itself is thus equal to 0.17 mg, which is equivalent to an amount of oxygen (O) removed during reduction of 10.6 μmol. A reduction percentage of 76% is thus calculated, assuming reduction of MoO$_3$ to MoO$_2$. The percentage of reduced molybdenum, calculated from the results of the TG experiments is thus in good agreement with that calculated from the DSC results (74%). However, different assumptions were made in these two sets of calculations: (i) in the interpretation of the DSC results, the enthalpy change during reduction is estimated from thermodynamic data, valid for unsupported materials; and (ii) in the interpretation of the TG results, the reduction of MoO$_3$ to MoO$_2$ and the percentage of N- and H-containing species on the reduced catalyst are assumed. However, similar reduced fractions are calculated, using both techniques indicating that the assumptions made in both techniques are correct.

The increase of the sample weight during oxidation at 775 K was 0.11 mg, which is equivalent to 7 μmol oxygen (O). This could indicate that the oxidation was not complete. However, it was concluded from results shown earlier [2,3] that oxidation was complete.

Since the oxidation was carried out using air while the TG apparatus had been calibrated using helium, the sample weight measured during oxidation is considered to be less accurate; this may account for the discrepancy between the observed degrees of re-oxidation and reduction. No changes of weight of the Mo3 sample during adsorption or during reduction by NH$_3$ were observed.
The detection limit of the TG is 0.01 mg, which means that for this sample, the percentages of ammonia that was adsorbed and of molybdenum that was reduced are below 20% and 10% respectively using the calculation shown above.

**Experiments with labelled molecules**

Labelled components such as $^{15}$NH$_3$, ND$_3$ and $^{15}$NO were used to demonstrate that the N- and H-containing species found on the catalyst after reduction by NH$_3$ originate from NH$_3$ and not from other sources such as reaction of hydroxyl groups with nitrogen from gaseous compounds; or from nitrogen that might be left in the catalyst after the preparation procedure $[1]$. Oxidation of the NH$_3$-reduced Mo$_7$ Catalyst by $^{15}$NO at 725 K resulted in production of $^{15}$NN, $^{15}$N$_2$ and H$_2$O. $^{15}$NN was produced during the oxidation of N-containing species, while $^{15}$N$_2$ was produced during the oxidation of the reduced catalyst. The experiment was repeated using $^{15}$NH$_3$ as a reducing agent at 725 K. 3 pmol $^{15}$N$_2$ and H$_2$O were then produced during oxidation by O$_2$. No production of $^{15}$N-containing species, such as $^{15}$N$_2$ or $^{15}$NN, was observed when the oxidised catalyst again was reduced in $^{14}$NH$_3$ and then oxidised with O$_2$, indicating that all $^{15}$N-containing species were removed during oxidation. $^{15}$NN, N$_2$ and H$_2$O were produced during oxidation of the $^{15}$NH$_3$-reduced catalyst by NO. Both the evolution of heat and the production of $^{15}$N-containing species during the oxidation by NO lasted about 5 times longer in comparison with that of oxidation by O$_2$, indicating that the oxidation by NO of the reduced catalyst and of the N-containing species is slower than that by O$_2$.

Production of N$_2$, D$_2$O, DHO and H$_2$O was observed when the catalyst was reduced by ND$_3$ and then oxidised by O$_2$. The total amount of D$_2$O, DHO and H$_2$O was 3.1 µmol. The ratio of D/H of the products was 2.1, which is in agreement with the ratio of D/H in the ND$_3$-containing gas of 2.4 (see experimental section).

It is concluded from the results of these experiments, that nitrogen and hydrogen present after reduction of the Mo$_7$ Catalyst are derived from ammonia and that the amounts of nitrogen and hydrogen in these species are equal. Furthermore, the amounts of nitrogen and water produced during removal of the N- and H-containing species were equal to those observed in the experiments that were carried out with unlabelled compounds, indicating good reproducibility.

**XPS experiments**

Only weak signals were observed in the XPS experiments. The reduction and oxidation experiments were therefore repeated several times; similar results were obtained each time, indicating that the weak signals were reproducible. The position of the N 1s photo-electron peak of the Mo$_7$ Catalyst is shown,
Fig. 3. The position of the N 1s photo-electron peak of the Mo7 Catalyst, as a function of ammonia and heat treatment. The untreated sample was measured as received. Ammonia was admitted to the catalyst at 395 K and 775 K. [NH₃] = 1990 ppm.

as a function of ammonia treatment and temperature in Figure 3. Untreated samples showed an N 1s photo-electron peak at about 398 eV. A similar peak was observed for samples that had been treated with ammonia at 395 K. Measurements with untreated Mo3 and Mo10 samples also showed this N 1s photo-electron peak. The shape and intensity of the peak did not change after oxidation of the sample in air. Treatment of the Mo7 Catalyst with NH₃ at 775 K resulted in a broadening of the N 1s photo-electron peak. A peak was found at 395 eV when the N 1s photoelectron peak of the untreated sample was subtracted from this broadened N 1s peak. This peak was also observed when a mathematical peak fitting procedure was applied on the broadened N 1s photo-electron peak. The peak at 395 eV is probably related to the N-containing species present on the catalyst after treatment with NH₃ at 775 K.

DISCUSSION

It has been shown that Catalysts Mo7 and Mo10 are equally active and selective for the oxidation of NH₃ to give N₂ and water [1,2]. Moreover, the times needed for the reoxidation of both catalysts were about the same indicating these processes occurred simultaneously, see Figures 1 and 2. The same remarks hold for the Mo⁴⁺ fraction in both catalysts after reduction with NH₃. The results of the DSC and XPS measurements with Catalyst Mo7 and of the TG measurements with catalyst Mo10 are therefore considered to be comparable.
Fig. 4. Proposed reaction sequence for the oxidation of ammonia over MoO₃ on SiO₂ catalysts.
A working model that describes the formation of water and nitrogen from ammonia over silica-supported molybdena catalysts is shown in Figure 4. It must be stressed that the structures shown in this figure are useful as a working model. At least two different surface structures of molybdena are assumed to be present on MoO₃ on SiO₂ catalysts: (i) so-called 'combined' molybdena species (Species A); and (ii) 'isolated' molybdena species (Species F). The 'combined' molybdena species are supposed to be active for the selective oxidation of ammonia to give nitrogen and water, while the 'isolated' molybdena species are responsible for the presence of N- and H-containing species after reduction of the catalyst by NH₃.

The chemisorption of ammonia on 'combined' molybdena is shown schematically in Reaction 1 of Figure 4. A 'combined' Species A is reduced by one ammonia molecule to form Species B and C. In this reaction the valency of each molybdenum ion is decreased from 6+ to 5+. Two chemisorbed Species C are then assumed to react according to Reaction 2 to produce a bridged -HN-NH- Species D. Two more Mo=O groups (Species A) are converted into hydroxyl groups (Species B) in this reaction. The valency of the molybdenum remains 5+. Nitrogen is assumed to be produced via recombination of -HN-NH- Species D according to Reaction 3. Two hydroxyl groups (Species B) are produced in this reaction. The valency of the molybdenum remains 5+. The production of water is assumed to occur via recombination of hydroxyl groups (Species B), as is shown in Reaction 4. The valency of one molybdenum atom is decreased from 5+ to 4+, while the other molybdenum atom is oxidised to Mo⁶+. The reduced Mo⁴⁺ atoms (Species E) are oxidised by oxygen, as is shown in Reaction 5.

Ammonia chemisorbs on 'isolated' molybdena species, as is shown in Reaction 6 of Figure 4. An 'isolated' Species F is reduced by one ammonia molecule to form Species G. The valency of the molybdenum is decreased from 6+ to 5+ in this reaction. Species G is then assumed to react further according to Reaction 7 to produce Species H and water. The valency of the molybdenum remains 5+.

The nitrogen and hydrogen atoms in Species H are 'isolated'; this means that recombination of these species to produce nitrogen and water is not likely. It is therefore assumed that these species are inactive for the oxidation of ammonia to give nitrogen and water and that the N- and H-containing species that were observed to be present after NH₃-reduction of the Mo7 Catalyst presumably represent species H. It is assumed that the molybdenum of the 'isolated' species is not further reduced than to Mo⁵⁺ (see Figure 4). Only reduction of Mo⁶⁺ to Mo⁴⁺ was inferred from the results of the DSC and the TG experiments. Furthermore, it was assumed from XPS experiments described previously [2] that the percentage of Mo⁵⁺ present in the Mo7 sample after NH₃-reduction was below 10%. This implies that the percentage of species H in Catalyst Mo7 is below 10%; which is in agreement with the observed
percentage of N- and H-containing species after NH₃-reduction of the Mo₇ Catalyst of 9%. The amount of 'isolated' molybdena species is thus low on relatively high-loaded catalysts such as Mo₇ and Mo₁₀.

Low-loaded MoO₃ on SiO₂ catalysts such as Mo₈ show high dispersion of the molybdena, as was observed in previous TEM measurements [1]; this probably means that mainly 'isolated' molybdena species are present and this implies that these low-loaded catalysts are not active for the oxidation of ammonia. This in turn is in agreement with results of activity measurements [1], where it was found that molybdenum loadings of more than 7 wt% are needed to obtain high conversions of ammonia to give N₂ and water.

The assumption that mainly 'combined' molybdena species are present on high-loaded MoO₃ on SiO₂ catalysts is in agreement with the work of Barbaux et al., who found that mainly crystalline molybdena is present in MoO₃ on SiO₂ catalysts at Mo loadings of 10 wt% and above, while silicomolybdic acid and polymolybdate are the main molybdena species at lower loadings [6]. It is therefore assumed here that the 'combined' molybdena species are associated with MoO₃ crystallites. Of this crystalline MoO₃, 75% of the crystal planes that are exposed to gaseous reactants are (010) planes, as shown by Volta and Portefaix [7]. Baiker et al. also found that 50–90% of the crystal planes of MoO₃ on SiO₂ catalysts that are exposed to gaseous reactants are (010) planes, the value being dependent on the preparation technique used [8]. When it is assumed that reduction of the molybdenum by NH₃ occurs only on the (010) planes, the observed reduction percentages of 75% may be explained by the percentage of these crystal planes exposed for gaseous reactants.

The structure for the 'combined' molybdena species is assumed to be similar to that of the (010) plane of crystalline MoO₃. It is shown in Figure 5 that a good fit of the -HN-NH- species (Species D) on this plane of MoO₃, and thus on the 'combined' molybdena species, is possible. The distances between the atoms shown in this figure are obtained from the literature [7,9,10].

Nitrogen is assumed to be produced via recombination of Species Dₗ as is shown in Reaction 3 of Figure 4. The high selectivity for the oxidation of ammonia to give N₂ and water, as observed in catalytic experiments [1], indicates that formation of N=N bonds is preferred over the formation of N=O bonds, as has also been found by Shelef and Gandhi [11–13]. Tsuchiya and Kozaki also observed in infrared experiments the presence of N-containing species on NH₃-reduced unsupported MoO₃ samples [14]. They also suggested that MoO₂N species were formed during reduction of MoO₃ by ammonia at 775 K, which may be in agreement with the formation of Species H according to Reaction 7.

A molar ratio of NH₃ adsorbed/Mo of 1/2.4 was observed in the TG experiments with the Mo₁₀ sample. NH₃ chemisorption occurs on molybdena, accessible to reduction according to Reaction 1 of Figure 4. It was found in the TG and DSC experiments that about 75% of the molybdena is reduced. This means that the calculated ratio of NH₃ that is adsorbed per reducible molyb-
denum atom is 1/1.8. Chemisorption of ammonia on 'combined' molybdena species according to Reaction 1 would result in a N/Mo ratio of 1/2. However, due to chemisorption of ammonia on 'isolated' molybdena species according to Reaction 6, a higher N/Mo ratio than 1/2 is obtained. From the observed percentage of N- and H-containing species, it is assumed that 9% of the molybdenum atoms are 'isolated', and this results in a calculated N/Mo ratio of 1/1.9, in good agreement with the observed ratio (1/1.8). Alsdorff et al. observed a molar ratio of adsorbed NH₃ on molybdena of 1/2.1 from infrared experiments [15].

No gas-phase oxidation of ammonia was observed at temperatures below 775 K, which indicates that the main function of O₂ is to oxidise the reduced catalysts (Species E and H of Figure 4). It was found in previous ¹⁸O₂ transient experiments that 75% of the oxygen atoms in MoO₃ can be exchanged [3]. Since 75% of the molybdenum atoms can also be reduced, it is assumed that oxygen exchange occurs on reducible molybdenum atoms during the re-oxidation of the catalysts. An oxidising agent such as O₂ or NO was observed to be needed to remove nitrogen and hydrogen from Species H. The ratio of N/H in Species H is in agreement with the observed ratio of N₂ and H₂O produced during oxidation of the reduced Mo7 sample. Since the nitrogen and hydrogen atoms in Species H are isolated, it is assumed that oxidation improves the mobility of these atoms. Due to this increased mobility, recombination to produce nitrogen and water must have become possible.
It was observed from the TG experiments that chemisorption of ammonia occurred within 10 minutes at 395 K (Figure 2). The time needed to reduce the catalyst to a valency of 4+ at 775 K was significantly longer (about 30 minutes). This indicates that the rate of reduction to a valency of 4+ (Reactions 1 to 4 of Figure 4) is lower than the rate of chemisorption of ammonia (Reaction 1); this in turn means that Reaction 1 is not rate determining.

It was found that a sample of the Mo7 Catalyst that had been reduced to Mo4+ was oxidised to Mo6+ during the reaction of NH3 with O2 to give N2 and water [3]. This indicates that the rate of oxidation of the molybdena catalyst during the NH3 + O2 reaction is higher than that of reduction by ammonia; this in turn implies that Reaction 5 is not rate determining.

It was proposed previously that the concentration of NH2 species present on molybdena-on-silica catalysts after reduction by NH3 is low, which implies that the rate of Reaction 2 has to be higher than those of Reactions 3 and 4 [2].

From these considerations, it can be proposed that either Reaction 3 or Reaction 4 or a combination of these two reactions is rate determining in the oxidation of ammonia to give nitrogen and water.

It has been found previously that dehydration of the catalyst surface was rate determining for vanadia catalysts used in the selective catalytic reduction of NOx [16,17]. Furthermore, it was found that the mechanisms of dehydration of the catalyst surface during the oxidation of ammonia over molybdena and vanadia catalysts are similar [3]. It is therefore proposed that dehydration of the catalyst surface according to Reaction 4 of Figure 4 is also rate determining in the oxidation of ammonia over molybdena catalysts.

CONCLUSIONS

Equal amounts of N2 and water were produced when NH3 reduced MoO3 on SiO2 catalysts were oxidised by O2. No other reaction products were observed. A percentage of 9% of the molybdenum was covered with N- and H-containing species, after reduction of the catalyst by NH3. These species were removed during oxidation by O2 or NO. The oxidation of both the reduced catalyst and the N- and II-containing species with O2 is considerably faster than that with NO.

An N 1s photo-electron peak at 395 eV observed in XPS experiments is related to -HN-NH- entities present on the surface of NH3-reduced molybdenum.

The amount of ammonia that is adsorbed on a low-loaded molybdena catalyst (3 wt% Mo) is low. On a higher-loaded molybdena catalyst (10 wt% Mo), adsorption of one ammonia molecule per two molybdenum atoms is observed.

Molybdenum in MoO3 on SiO2 catalysts with a molybdenum content of 7 and 10 wt% are reduced by ammonia at 725 K and 775 K from Mo6+ to Mo4+. 
The reduced molybdenum percentage is 75% for both catalysts. Reduced fractions calculated from DSC and TG results are in good agreement with one another, indicating that assumptions made in both calculations are correct.

A working model is presented for the reduction of molybdena-on-silica catalysts by NH₃ and for the oxidation of ammonia over this type of catalyst.

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