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Selective oxidation of ammonia to nitrogen over silica supported molybdena catalysts

A structure-selectivity relationship

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Abstract

The selective catalytic oxidation of NH_3 to N_2 over unsupported and silica-supported MoO_3 catalysts has been investigated. The defect structure of the catalysts greatly affects the selectivity towards N_2O. The performance of the silica supported catalysts is controlled by the thermal pretreatment and the structure, which is installed by the preparation procedure. Water dramatically decreases the selectivity to N_2 of MoO_3-on-SiO_2 catalysts with low loadings. The selectivity to N_2 highly depends on the ability of the catalyst to decompose released N_2O, which proceeds on oxygen vacancies.

1. INTRODUCTION

The emission of ammonia substantially contributes to the present air pollution. About 94 % of the ammonia emitted in, e.g., the Netherlands originates from agricultural sources [1]. In areas with intensive stock breeding emission of ammonia leads to acidification of the atmosphere. Large volumes of ammonia are additionally produced in coal gasification and hydrotreating plants. If the NH_3 produced is subsequently converted to nitrogen oxides, the environments will be comparably adversely affected.

Many studies have been dedicated to the Selective Catalytic Reduction (SCR) of NO_x with NH_3. Silica- and titania-supported V_2O_5 catalysts have proven to perform adequately in the abatement of NO_x [2,3]. A severe difficulty of the SCR is the stoichiometric amount of NH_3 with respect to NO_x that must be injected and thoroughly mixed into the gas stream to avoid slip of either NH_3 or NO_x.

The Selective Catalytic Oxidation (SCO) of NH_3 can meet with the removal of NH_3 from stack gases. Molecular oxygen is used for the selective oxidation of NH_3 to N_2 and H_2O

(reaction 1). However, besides the desired products, i.e., N_2 and H_2O, also N_2O and NO can result (reactions 2-3). A number of catalysts can be used for the SCO [4]. Some -unsupported- transition metal oxides, such as, MoO_3, V_2O_5, Bi_2O_3 and PbO, exhibit a sufficient selectivity towards N_2.

Thermodynamically, molecular nitrogen is the most stable reaction product [5]. A sequential oxidation path to the deepest oxidation product with N_2 and N_2O as intermediate products (reaction 4) can therefore be excluded at the temperatures of interest (below 700 K).

$$4\,NH_3 + 3\,O_2 \rightarrow 2\,N_2 + 6\,H_2O \qquad \Delta G^0(298\ K) = -156.1\ kJ/mol \qquad (1)$$

$$2\,NH_3 + 2\,O_2 \rightarrow N_2O + 3\,H_2O \qquad \Delta G^0(298\ K) = -131.2\ kJ/mol \qquad (2)$$

$$4\,NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O \qquad \Delta G^0(298\ K) = -144.7\ kJ/mol \qquad (3)$$

The catalytic oxidation of NH_3 is presumed to proceed by a reduction-oxidation mechanism [6], in which the reduction-oxidation behaviour of the catalyst affects the catalytic performance. According to Golodets [4], the bond energy of lattice oxygen within the bulk oxides determines mainly the selectivity ratio (N_2/N_2O+NO), if a parallel reaction scheme is assumed (reaction 1-3).

$$NH_3 \xrightarrow{\text{catalyst}} N_2 \xrightarrow{\text{catalyst}\ \times} N_2O \xrightarrow{\text{catalyst}\ \times} NO \qquad (4)$$

Baiker *et al.* [7] found that the selectivity of the SCR reaction over annealed MoO_3 samples highly depends on the grain morphology and the exposed lattice planes. Depending on the preparation procedure, samples with different distributions of exposed lattice planes can be produced. A sample with predominantly exposed (010) planes appeared to be less selective for the formation of N_2O in the SCR reaction than a sample exposing more (100), (001) and (101) faces. Gandhi *et al.* [8] investigated the influence of H_2O on the performance of copper(II) molybdate catalysts in the selective oxidation of NH_3 to N_2. Addition of H_2O reduces the activity of these catalysts due to competitive adsorption of H_2O on sites active for NH_3 adsorption. The selectivity for N_2 decreases as well. Thus, Baiker proved that, in addition to its chemical characteristics, the catalytic properties of a compound strongly depend on its surface texture. This simply explains why the preparation conditions affect the catalytic performance. It may be expected that with supported catalysts this effect is even more pronounced, because the texture of the supported particles of the catalytically active component strongly depends on the preparation conditions. A number of additional features controls on the performance in the selective oxidation of NH_3 to N_2 as well. The structure of the catalyst particles, the reduction behaviour, and thermal pretreatment are important parameters.

Supported catalysts, such as, WO_3/TiO_2 and Fe_2O_3/SiO_2, have appeared to be fairly selective in the oxidation of NH_3 to N_2, but exhibit a poor activity. In this paper, the catalytic performance of a number of silica-supported MoO_3 catalysts will be dealt with. The influence on the selectivity of the structure of the catalysts as determined with various characterisation techniques, will be discussed and compared with that of some unsupported MoO_3 catalysts.

2. EXPERIMENTAL

2.1. Preparation of the Catalysts

The MoO_3-on-SiO_2 catalysts were prepared by deposition of a molybdenum precursor from homogeneous solution onto SiO_2 (aerosil 200V, Degussa) as described by Geus [9]. To establish a sufficiently high positive interaction between the active phase and the support a precursor of a lower valence was used ($Mo^{III}Cl_6^{3-}$), prepared by electrochemical reduction of H_2MoO_4 in concentrated HCl. It has been well documented that the preparation of MoO_3/SiO_2 catalysts from a hexavalent ammonium heptamolybdate (AHM) precursor leads to the formation of fairly large MoO_3 crystallites [10-14] due to its poor interaction with silica. The merely anionic, dissolved (hexavalent) molybdenum species ($Mo_7O_{24}^{6-}$ and $Mo_8O_{26}^{4-}$ [15]) have no interaction with the SiO^- groups on the surface of the support. Therefore, thus prepared catalysts usually exhibit the catalytic features of bulk MoO_3. The interaction of trivalent molybdenum with SiO_2 is much better, because of the lower acidity of this precursor.

Precipitation of the active phase was brought about by slow injection of a 5% NH_3-solution into a vessel containing $Mo^{III}Cl_6^{3-}$ in an aqueous SiO_2 suspension. Homogeneity was ensured by vigorous stirring and the presence of baffles in the vessel. When the pH had reached the level of 7.0, the injection was stopped, the slurry was filtered off, and washed with demineralised water. The catalysts were dried in air at 393 K for 16 hours, and calcined in air at 723 K for 72 hours.

Unsupported MoO_3 catalysts were obtained by precipitation of $Mo^{III}Cl_6^{3-}$ from a homogeneous solution without suspended SiO_2 (*type 1*:precipitated) or purchased from Cerac (ultrapure quality) (*type 2*: annealed). Both unsupported catalysts were calcined at 723 K.

2.2. Characterisation of the catalysts

The catalysts were characterised by various techniques: Thermal Analysis (TA), X-ray Photoelectron Spectroscopy (XPS), Raman Spectroscopy, and Extended X-ray Absorption Fine Structure (EXAFS). A short description of the experimental procedures is given.

Thermal Analysis experiments were performed within a Mettler TA-2 balance in a 10% H_2/Ar flow (100 ml/min.). A sample of typically 50 mg of the powder was subjected to a temperature program (rate: 5 K/min.). The weight loss between 673 and 1073 K was used to calculate the degree of reduction of the samples.

Raman experiments were executed in a triplemate Spex (1877 model) spectrometer, coupled to an optical multichannel analyzer (Princeton Applied Research, model 1463) equipped with a intensified photodiode array detector. The 514.5 nm line of an Argon laser (Spectra Physics) was used as an excitation source. The sample was pressed into KBr and spun at 2000 rpm. The experiments were done under ambient conditions at a laser power of 10-50 mW.

The XPS-experiments were accomplished in a VG-Scientific Escalab MK II with a Mg K_a source (1253.6 eV). The position of the peak maxima could be determined with an accuracy of $\pm$ 0.1 eV. The spectra were corrected for static charging effects with the C (*1s*) peak as an internal reference.

The X-ray absorption spectra in the EXAFS region (Mo K-edge at 19,999 eV) were measured at station 9.2 of the S.R.S. laboratory in Daresbury (U.K.). The storage ring was handled at 2.0 GeV with a ring current of 150-200 mA. A Si(220) crystal was used as the monochromator. Samples were crushed and pressed into a sample holder. Spectra were recorded at 290 K in helium atmosphere.

2.3. Kinetic Measurements

After calcination the catalysts were pelleted at 400 MPa for two minutes and subsequently crushed and sieved into the fraction range of 0.25-0.50 mm. The amount of catalyst was typically 100 mg. The catalysts were treated *in situ* at 673 K in a flow of 25 % O_2 in helium for two hours prior to the kinetic measurements. Mixtures of NH_3/He, NO/He, O_2/He, and high-purity helium were purchased from Air Products and used without further purification. The experiments were carried out at atmospheric pressure in a fixed bed reactor made of quartz. A Leybolt Q 200 mass spectrometer was used for detection of the reactants and products. The detection limit for the various products was 1 ppm. In some experiments NO was added to the feed to investigate the interference of this compound with the SCO reaction.

The performance of the MoO_3/SiO_2 catalysts was also tested under non-stationary conditions. The catalysts, after prolonged exposure to ambient atmosphere (i.e., hydrated conditions), were submitted to a temperature program of 10 K/min in a flow of 5000 ppm NH_3, 2 % O_2 and 97.5 % He. The LHSV was 12,000 hr^{-1}.

3. RESULTS

3.1. Preparation and characterisation of the catalysts

A number of unsupported and silica-supported MoO_3 catalysts was prepared according to the procedures described in the experimental section. Table 1 presents the codes and the metal oxide loadings (defined as $\frac{wt\ MoO_3}{wt\ MoO_3 + SiO_2} \cdot 100\%$) of the samples, as determined by Inductively Coupled Plasma analysis (ICP).

Table 1
Properties of the catalysts

code	catalyst	preparation	loading (%)
Mo (prec.)	MoO_3	HDP[1]	-
Mo (ann.)	MoO_3	MoO_3 annealed	-
Mo6	MoO_3/SiO_2	HDP[1]	5.6
Mo11	MoO_3/SiO_2	HDP[1]	11.3
Mo26	MoO_3/SiO_2	HDP[1]	26.0

[1] Homogeneous Deposition Precipitation

The reduction profiles as obtained from TA-experiments are shown in figure 1. A significant difference in onset temperature of reduction of the two bulk-MoO_3 samples (*d* and *e*) is observed. Although these samples are chemically identical, their reduction behaviour is quite different. X.R.D.-analysis gave no elucidation of a possible difference in exposed lattice planes in the bulk samples. The explanation of the different reduction characteristic can be found in the

heterogeneity of the surface of the MoO_3 samples. Van den Berg *et al.* [16] have shown that the activity for CO- and H_2-oxidation on V_2O_5 catalysts and vanadium bronzes strongly depends on the concentration of defects in the V_2O_5-lattice (usually oxygen-vacancies). The catalytic reaction at high temperature proceeds via a reduction-oxidation mechanism, in which oxygen vacancies are the active species. Thus, it is feasible that a high concentration of defects in an oxidic lattice like V_2O_5 or MoO_3 locally destabilises the lattice and thus enhances the activity for an oxidation reaction. Since the TA-experiment in H_2-atmosphere can be envisioned to be an oxidation of H_2 by the catalyst, the concentration of surface defects will control the onset temperature of the reduction of the catalyst. The lower onset temperature of Mo(prec.) can thus be explained by its higher content of defects due to the preparation procedure: precipitation of molybdenum (hydr)oxide from an aqueous solution yields a porous, badly crystallised solid even after calcination. The heterogeneity of Mo(prec.) is considerably higher than that of Mo(ann.), which contains annealed, well crystallised, stoichiometric MoO_3 particles.

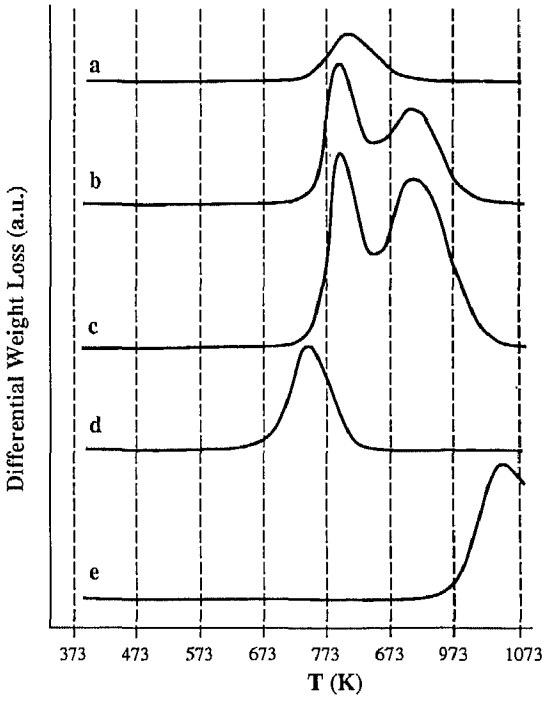

Figure 1 Thermogravimetric analysis of a) Mo6, b) Mo11, c) Mo26, d) Mo (prec.), and e) Mo (ann.) in a 10 % H_2/Ar flow.

The onset temperatures of Mo6, Mo11, and Mo26 (*a-c*) are equal, but the shape of the peaks and the integrated weight loss deviate strongly. Mo11 and Mo26 both exhibit a second peak at high temperature, which corresponds to deep reduction to metallic molybdenum, as evidenced by High Temperature XRD experiments. Mo6, however, has no peak at high temperatures and can be reduced less profoundly. with XPS, it was checked , that in all samples molybdenum is initially present in 6+ oxidation state. The Mo ($3d_{5/2}$) peak is located at 232.8 eV. The reference values of the binding energy of the photoelectrons in MoO_3 and MoO_2 are 232.5 and 229.2 eV respectively. From the TG and XPS results we have calculated that Mo6 can be reduced only for 35%, whereas Mo11 and Mo26 can almost completely be reduced.

The Raman spectra of Mo6, Mo11, Mo26, and Mo (ann.) are represented in figure 2. The main bands of Mo (ann.) are positioned at $\tilde{\nu}$= 996, 821, 668, 285 and 159 cm^{-1}; This corresponds with the literature values of bulk MoO_3 [17]. Obviously Mo11 and Mo26 contain crystalline MoO_3. Mo6, however, has a distinctly different structure: the bands at $\tilde{\nu}$= 944 , 880 and 220 cm^{-1} indicate the presence of oligomeric molybdenum oxide clusters (comparable to aqueous hepta/ octamolybdate) [18]. The Raman bands at 480 and 370 cm^{-1} are due to SiO_2 and a surface molybdenum oxide respectively.

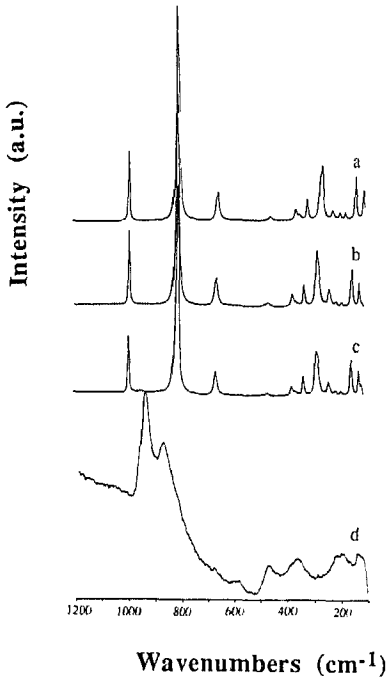

Figure 2 Raman spectra of a) Mo (ann.), b) Mo26, c) Mo11, and d) Mo6, recorded at ambient conditions

The results of a preliminary EXAFS study reveal analogous results. The amplitude of a k^1 fourier transform of the $\chi(k)$ is shown in figure 3. The Mo-Mo shell in Mo(ann.) is positioned at approx. 3.5 Å and originates from a strong Mo-Mo contribution, diagnostic for the existence of larger molybdenum oxide particles with long range order. The Mo-O peak at 1.5 - 2.2 Å is ascribed to more than one Mo-O distance due to distortion of the octahedral environment of the absorber. The same pattern is observed for Mo11 and Mo26: The Fourier transform of Mo6, however, deviates dramatically from the bulk reference. It reveals hardly any long range order, as evidenced by the decrease of the Mo-Mo contribution at ~3.5 Å.

The combined results of the characterisation of the catalysts show that Mo11 and Mo26 contain crystalline molybdenum(VI) oxide particles, highly dispersed onto the SiO_2 support, whereas Mo6 consists of very small molybdenum oxide clusters strongly interacting with the support. The different reduction behaviour of Mo6 is presumably caused by the strong interaction with the support: the tiny molybdenum oxide particle cannot be reduced to metallic molybdenum. Consequently, the reduction behaviour, i.e., the onset temperature and the maximum degree of reduction depend on the structure of the catalyst.

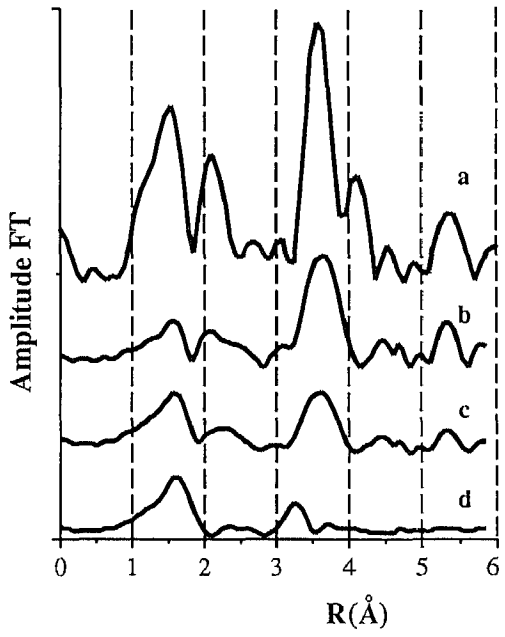

Figure 3 EXAFS k^1 fourier transforms of $\chi(k)$ (3.45 $Å^{-1} < k <$ 12.9 $Å^{-1}$) of a) Mo (ann.), b) Mo26, c) Mo11, and d) Mo6

3.2. Kinetic experiments

Ammonia oxidation experiments were performed over Mo (ann.) and Mo (prec.) in the presence of NO. The concentration profiles as a function of the temperature are shown in figure 4.

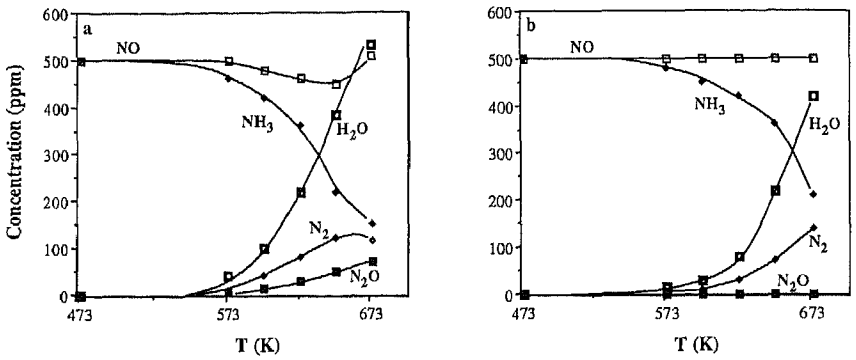

Figure 4 Concentration profiles of NH_3, NO, N_2, N_2O and H_2O in the NH_3-oxidation over a) Mo (ann.), and b) Mo (prec.)

Despite the chemical equivalence of the two samples, their catalytic performance is quite different. The NH_3-conversion at 673 K of Mo (ann.) is somewhat higher than Mo (prec.). The selectivity towards N_2, however, is almost 100% up to 673 K for Mo (prec.), whereas Mo (ann.) produces a considerable amount of N_2O. Moreover, NO is reactive with Mo (ann.) and remains unaffected with Mo (prec.). It is interesting to note that the minimum for NO in Mo(ann.) is associated with a maximum in N_2. Apparently the formation of NO and N_2 from NH_3 is non-independent.

The results of the catalytic performance tests of the MoO_3/SiO_2 catalysts are presented in figure 5. The selectivity of Mo6 strongly deviates from Mo11 and Mo26. Mo6 produces a substantial amount of nitrous oxide (33% of the amount of NH_3 converted), whereas Mo11 and Mo26 produce only 8 and 5% N_2O respectively. With Mo6 formation of NO proceeds at temperatures above 773 K, which is accompanied by a decrease of the selectivity for N_2O. This observation suggests that the formation of N_2, N_2O, and N_2 is interdependent, and that the reaction mechanisms for the formation of these products do not run completely parallel.

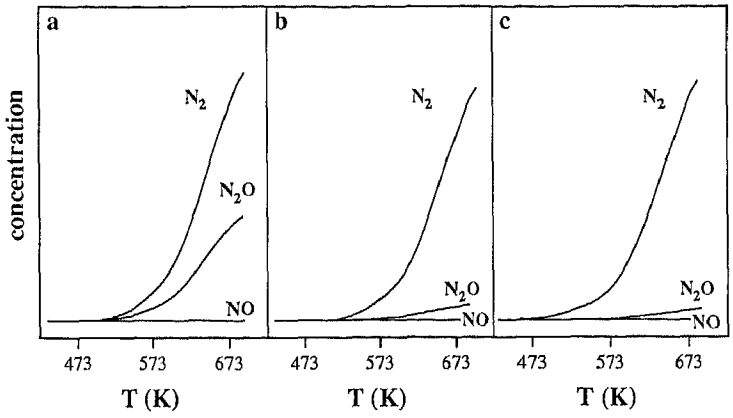

Fig. 5 formation of N_2, N_2O and NO over a) Mo6, b) Mo11, and c) Mo26

These measurements were performed on fresh, calcined samples and, thus, contain adsorbed H_2O due to prolonged exposure to the ambient atmosphere. The selectivity of the catalysts drastically increases after a thermal pretreatment in O_2 at 673 K. Table 2 shows the selectivities of the catalysts for the production of N_2 at 673 K before and after thermal treatment.

Table 2
Selectivities to N2 at 673 K

catalyst	selectivity	
	fresh	after pretreatment
Mo6	67	>98
Mo11	92	>98
Mo26	95	>98

The origin of the low selectivity of the fresh samples will next be discussed.

4. DISCUSSION

The reduction behaviour of Mo (ann.) and Mo (prec.) exhibits large differences. It has been mentioned that the onset temperature for the reduction of the samples strongly depends on the

concentration of lattice defects present at the surface of catalyst particles and the ability of the oxide to accommodate vacancies. The different catalytic performance of the samples in the oxidation of NH_3 can be explained along the same lines. The formation of each N_2-molecule requires two nitrogen atoms from different NH_3-molecules, which implies that a NH_3-molecule has to adsorb dissociatively in close proximity of another NH_3. The mobility of adsorbed N-species is low, as reported for V_2O_5/TiO_2 catalysts [19]. The recombination probability of two adsorbed nitrogen atoms to form an N≡N bond is thus determined by the surface density of active sites. Active sites for this reaction are oxygen atoms capable of accepting the hydrogen atoms from NH_3, i.e., reducible under the conditions of the reaction. Mo (prec.) contains a high number of active sites for the SCO reaction, as evidenced by the low onset temperature of reduction in the TA-profile (figure 1). The selectivity to N_2 is optimal, because of the high probability of recombination of two nitrogen atoms to form N_2.

The formation of nitrous oxide in Mo (ann.) is not caused by the sequential oxidation of evolved N_2 to N_2O as discussed before (reaction 4). Golodets *et al.* [4] explain the formation of N_2O by assuming the reaction between two HNO species to form N_2O and H_2O. A number of species is schematically postulated in the model in figure 6.

Each unit on the surface ('cube') represents a surface oxygen atom, without taking specific lattice planes into account. An oxygen vacancy is symbolised by a pit. The adsorption of a NH_3-molecule in (*1*), or remote (*2*) from an oxygen vacancy is depicted in this model. We assume that an NH_3-molecule is adsorbed dissociatively on the MoO_3 surface ('stripped') and tends to occupy an oxygen vacancy, if present. Adjacent surface oxygen atoms are transformed into OH-groups. Two vicinal OH groups (*3*) can form an oxygen vacancy under evolution of H_2O (*4*). The lattice oxygen can be replenished by gas phase O_2. Species *5* visualises the situation of Mo (prec.): two NH_3-molecules are adsorbed and stripped in proximity (hydrogen atoms not shown) and are evolved as N_2 (*6*). When the concentration of active sites is low, then the nitrogen atoms remain isolated, either on the surface of MoO_3 (*2*) or in a vacancy (*1*). In this case the recombination probability of nitrogen atoms is low and development of NO becomes likely (*7*). Two pathways for evolved NO are conceivable. It can react with another nitrogen species to form N_2O (*7-8*) or it is swept out of the reactor (at high temperatures). The high selectivity for N_2O of Mo (ann.) can thus be explained, because Mo (ann.) contains few, remote vacancies.

Implicitly, we have postulated a reaction path opposite to reaction 4, as presented in reaction 5.

$$NH_3 \xrightarrow{(O)} NO \xrightarrow{(N)} N_2O \xrightarrow{(\ )} N_2 + (O) \qquad (5)$$

The last step of reaction 5 is the subsequent decomposition of N_2O occurring preferentially on oxygen vacancies. The oxygen atom from N_2O can be conveniently accommodated in the MoO_3-lattice, while the energy-favourable N≡N bond can be formed. Shelef *et al.* [20] report on the formation and decomposition of N_2O on chromia catalysts. At high space velocities the evolved N_2O cannot decompose and is swept out of the reactor. Keenan *et al.* [21] and Vorotyntsev *et al.* [22] confirm that the decomposition of N_2O takes place on surface vacancies.

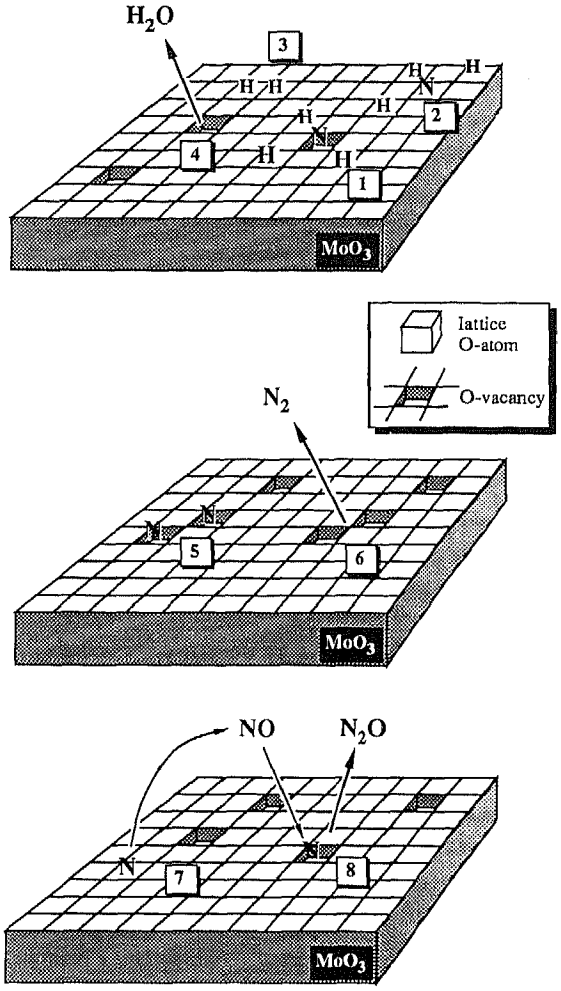

Figure 6 Schematic representation of surface species

The performance of the MoO_3/SiO_2 catalysts is strongly affected by the presence of adsorbed H_2O. The molybdenum oxide phase and the silica are both hydroxylated. Since H_2O is competes with NH_3 for the adsorption on active sites [8], a smaller number NH_3 molecules can be adsorbed and stripped in the presence of H_2O. Water leading to adsorbed hydroxyl

groups thus diminishes the concentration of adsorbed nitrogen species, which decreases the recombination probability of nitrogen atoms and enhances the selectivity towards N_2O.

This effect is far more pronounced with Mo6 than with Mo11 and Mo26, because of the different structure of the catalysts. The oligomeric molybdenum oxide clusters in Mo6 can only be reduced for approx. 35%. Only a limited number of NH_3-molecules can therefore be stripped, since the adsorption of each NH_3 molecule requires the reduction of at least three oxygen atoms (formation of OH-groups). The recombination probability of nitrogen atoms and the rate of decomposition of N_2O are much higher on Mo11 and Mo26 under hydrated conditions as compared to Mo6. The larger MoO_3 crystallites in Mo11 and Mo26 can more easily accommodate oxygen vacancies, because of their higher reducibility.

5. CONCLUSIONS

The activity and, more importantly, the selectivity of (un)supported MoO_3 in the selective oxidation of NH_3 to N_2 appears to depend on the defect structure of the catalysts. The catalytic performance of the two unsupported MoO_3 samples is controlled by the preparation procedure, which installs the reduction-oxidation properties and the selectivity to N_2. It is postulated that the selectivity for N_2 is influenced by the recombination probability of adsorbed nitrogen atoms. The probability is high for catalyst particles with a high surface density of active sites. An active site for the selective oxidation of NH_3 is an ensemble of reducible surface oxygen atoms in the vicinity of an oxygen vacancy. The oxygen atoms must strip the hydrogen atoms from NH_3 to form OH groups. A vacancy is created when two vicinal OH groups desorb under release of H_2O. Surface oxygen is replenished by gas phase O_2. An adsorbed and stripped NH_3-molecule can react with another stripped nitrogen atom or immediately with a gas phase NH_3-molecule. Formation of the energetically favourable $N{\equiv}N$ bond is the driving force for the recombination of two adsorbed nitrogen species. When no other nitrogen atom is in close proximity, NO can desorb.

N_2O results when a NO molecule reacts with another isolated nitrogen atom. The participation of NO is demonstrated by addition of NO to the feed. The Mo (ann.) sample exhibits SCR behaviour. With isotopic experiments Janssen [19] proved that in the SRC reaction over vanadia catalysts the nitrogen atoms in N_2O originate from NO and NH_3. Formation of the undesired N_2O does not present problems, provided it consecutively decomposes under formation of N_2 and an adsorbed oxygen atom. We believe that the selectivity of these catalysts is partly due to the capability to decompose undesired N_2O, which proceeds preferably at oxygen vacancies.

Since NH_3 competes with H_2O for the active sites [8], the catalytic performance of hydrated samples is worse than that of thermally pretreated samples. The selectivity is significantly enhanced by a thermal pretreatment. The increase is most prominent for Mo6. Due to the small dimensions and poor reducibility of the oligomeric molybdenum oxide clusters only a limited number of NH_3-molecules can be stripped at the surface, thus decreasing the recombination probability. Decomposition of evolved N_2O cannot proceed because the required vacancies are occupied by water. The larger MoO_3 crystallites in Mo11 and Mo26 can adsorb and strip more NH_3 molecules and accommodate more vacancies for the decomposition of released N_2O.

6. ACKNOWLEDGEMENT

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