MOLYBDENA ON SILICA CATALYSTS: SELECTIVE CATALYTIC OXIDATION OF AMMONIA TO NITROGEN OVER MoO₃ ON SiO₂ CATALYSTS

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Summary

 MoO_3 on SiO₂ catalysts are suitable for the selective oxidation of ammonia into nitrogen (N₂) and water. The catalysts were prepared by homogeneous deposition precipitation using electrochemically reduced precursors. The experiments were carried out at atmospheric pressure and at temperatures ranging from 200 to 400 °C. Nitrogen and water yields of up to 100% at temperatures over 375 °C were obtained when ammonia and excess oxygen in helium were passed over a MoO_3 on SiO₂ catalyst.

Catalysts containing less than 15 wt.% MoO_3 gave rise to no conversion of ammonia. The presence of small amounts of lead in the catalyst appeared to influence the conversion of NH_3 in a positive way. However, the presence of nitric oxide in the feed did not influence either the conversion of ammonia or the selectivity to nitrogen. The nitric oxide concentration remained constant during the conversion of ammonia. The results indicate that species reducible by hydrogen at 540 °C are related to the activity of the catalysts.

Introduction

Emission of ammonia causes air pollution. Removal of ammonia can be carried out using selective oxidation to nitrogen and water. Since formation of nitrogen oxides must be prevented and at temperatures up to 500 °C no homogeneous reaction takes place, a selective catalyst is needed to perform the oxidation of ammonia.

Selective oxidation of ammonia in car exhaust gases may also be interesting. To deal with nitrogen oxides, very expensive rhodium is required, over which nitrogen oxides can be easily reduced to nitrogen and ammonia. Subsequent oxidation of ammonia must lead selectively to molecular nitrogen.

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Janssen and Van den Kerkhof [1] have described the oxidation of ammonia over V_2O_5/WO_3 on TiO₂, WO_3 on TiO₂ and Fe₂O₃ on SiO₂ catalysts. Though the WO₃ on TiO₂ and Fe₂O₃ on SiO₂ catalysts were highly selective in the oxidation of ammonia to nitrogen and water, the activities were low. The activity of the V_2O_5/WO_3 on TiO₂ catalyst was higher, but the selectivity to nitrogen was low. Moreover, the presence of nitric oxide appeared to suppress the oxidation of ammonia.

This paper describes the performance of PbO/MoO₃ on SiO₂ catalysts which exhibit higher selectivities and activities in the oxidation of ammonia to nitrogen and water than the catalysts described earlier. The effect of NO on the oxidation has also been investigated. The catalysts have been prepared by means of homogeneous precipitation from homogeneous solution onto silica. To establish a sufficiently strong interaction of the precipitating molybdenum species with the silica support, Mo(III) was precipitated instead of the more stable Mo(VI).

For comparison purposes, two Mo(III) solutions were prepared using a Pt or a Pb electrode. Non-supported MoO_3 was also investigated. Both a commercially available ultrapure MoO_3 sample (Cerac) and a MoO_3 sample prepared by precipitation of Mo(III), filtration, drying and calcination were studied. The MoO_3 prepared by precipitation of Mo(III) contained many more lattice defects than the commercially available MoO_3 .

Earlier it was shown that ammonia reacts with the surface of suitable metal oxides to give surface hydroxyl groups and, presumably, adsorbed nitrogen atoms. Adjacent surface hydroxyl groups which are present on reduced metal ions desorb as water, leaving an oxygen vacancy behind. This vacancy is subsequently filled by oxygen from the gas phase. Filling of the surface vacancy brings with it reoxidation of the reduced metal ions. Nitrogen species adsorbed on neighboring sites react to desorb molecular nitrogen.

The above mechanism implies that reduction of the catalytically active metal oxide is an important step in the catalytic oxidation of ammonia. Since the deposited molybdenum species which strongly interact with the silica surface may be difficult to reduce, the activity of these species may be low. Therefore temperature-programmed reduction (TPR) was used to assess the reducibility of the molybdenum species present on the catalysts.

The dispersion of the molybdenum moieties in the different catalysts was established in the transmission electron microscope (TEM). In the catalytic experiments, the concentration of the different gaseous components was determined mass spectrometrically.

Experimental

Catalyst preparation

The catalysts used are listed in Table 1, together with their main characteristics. In all catalysts the same silica support was used. The

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Catalysts used

Catalyst	Composition (wt.%) (by AAS)		
	MoO3	Pb	
Mo (4)	4	1.6	
Mo (5)	5	0.0	
Mo (10)	10	3.2	
Mo (12)	12	0.5	
Mo (15)	15	2.6	
Mo (18) ^a	18	0.2	
Mo (19)	19	0.0	
Mo (25)	25	1.4	
Mo (Cerac) ^b	100	0.0	
Mo (prec) ^c	100	present	

^a 2.5 wt.% Fe₂O₃ present in the catalyst.

^b Commercially available ultrapure MoO₃ (Cerac).

^c Unsupported MoO₃ obtained by precipitation of reduced precursor.

catalysts were prepared by the homogeneous deposition precipitation (HDP) method described by Geus [2]. A reduced molybdenum precursor was used because such precursors give better interaction between the active material and the silica support [3]. The reduced precursors were prepared by electrochemical reduction of Mo⁶⁺ ('molybdic acid', H₂MoO₄:xH₂O, Merck 'zur Synthese') to Mo³⁺ in 8 M HCl. A very low pH level is required to dissolve the Mo⁶⁺ and to stabilize the Mo³⁺ as the hexachloride ion MoCl₆³⁻. Either Pb or Pt electrodes were used. Pb electrodes have the advantage of showing a relatively high overpotential for the production of H₂. However, catalysts prepared using the precursor obtained with the lead electrode were contaminated with lead. The 'platinum' prepared catalysts however, contained no platinum. In this paper catalysts containing lead will be indicated as Mo(Pb).

The precipitation of MoO_3 on silica was performed in a precipitation vessel as described previously in the preparation of V_2O_5 on SiO_2 [4]. The valence of the Mo-species was analyzed spectrophotometrically before precipitation. A suspension of the support $(SiO_2$, Degussa Aerosil 200V, specific surface area $186 \text{ m}^2 \text{ g}^{-1}$) in demineralized water was acidified to a pH of about 0.5 using hydrochloric acid. The suspension was stirred under nitrogen for several minutes in the precipitation vessel, after which a given amount of the Mo^{3+} solution was added. Precipitation of the molybdenum species onto the support was brought about by the slow injection of a dilute solution of sodium hydroxide or ammonia at a rate of 0.1 mmol $OH^- \min^{-1}$. Injection was generally stopped when the pH had reached a level of 8-9. After precipitation the catalyst was filtered, washed and dried in air at $120 \,^\circ$ C for ~ 20 h and then calcined in air at $350 - 400 \,^\circ$ C for ~ 72 h.

Catalytic experiments

The apparatus used in the ammonia oxidation experiments is described elsewhere [1]. The experiments were carried out in a fixed-bed reactor with an i.d. of 3.8 mm. The detection of the reactants and products was performed using a sector mass spectrometer (Varian MAT 112). Both the Pyrex reactor and the stainless steel tubing of the system showed no activity during the experiments. Ammonia in helium, oxygen in helium, nitric oxide in helium and high purity helium were used. All gases were used without further purification. The initial composition of the gas mixture was 500 ppm NH₃ and 2% O₂, with helium as balance. The overall gas flow was 100 cm³ min⁻¹ and the catalyst weight was 50 mg. Before use, the catalysts were pressed at 4 atm for 2 min and then crushed and sieved to particle diameters ranging from 0.25 mm to 0.50 mm. The catalysts were calcined *in situ*, using helium containing 25% oxygen at 400 °C for 1 h. All experiments were reproducible and mass balances were accurate to within 5%.

Temperature-programmed reduction

TPR measurements were carried out using hydrogen in a standard TPR setup. Commercially available hydrogen (5%) in argon was used without further purification. The gas flow was about $50 \text{ cm}^3 \text{min}^{-1}$ and the catalyst weight was about 80 mg. The heating rate was $10 \text{ }^{\circ}\text{C} \text{min}^{-1}$ and the temperature varied from 200 to $850 \text{ }^{\circ}\text{C}$.

Results

Unsupported materials

Activity measurements using unsupported materials show that the oxidation behaviours of MoO_3 (Cerac) and MoO_3 prepared by the HDP technique differ. Figure 1 shows the concentrations of reactants and products over MoO_3 (Cerac) as a function of the temperature. Significant features are: (i) low ammonia conversion; (ii) N_2O is produced; (iii) the N_2 concentration profile shows a maximum at about 375 °C; and (iv) a decrease in nitric oxide concentration. In contrast to the results of the experiments with MoO_3 (Cerac), the MoO_3 (HDP) does not produce N_2O and behaves in a manner similar to the supported catalysts (see Fig. 2).

Supported materials

Catalysts containing less than 15 wt% MoO_3 show no activity in the ammonia oxidation. Ammonia oxidation measurements with the Mo(Pb) catalysts containing more than 15 wt.% MoO_3 show high activity and selectivity. Figure 3 shows the concentration levels of the reactants and products as a function of temperature. Significant features are: (i) high selectivity to N_2 ; (ii) the presence of nitric oxide in the feed does not affect the oxidation of ammonia to N_2 ; (iii) no formation of nitrous oxide or nitric oxide occurs; and (iv) at temperatures higher than ~375 °C the conversion of



Fig. 1. Concentration levels of the reactants and products as a function of temperature for unsupported MoO₃ (Cerac). Catalysts were calcined at 400 °C in a 25% O₂/He flow for 1 h; flowrate 100 cm³ min⁻¹, $[NO]_i = [NH_3]_i = 500$ ppm; $[O_2]_i = 2\%$; balance helium.

Fig. 2. Concentration levels of the reactants and products as a function of temperature for unsupported MoO_3 prepared using the HDP technique. Other experimental conditions as in Fig. 1.



Fig. 3. Concentration levels of the reactants and products as a function of temperature for Mo(Pb) catalysts containing more than 15 wt.% MoO_3 . Other experimental conditions as in Fig. 1.

Fig. 4. Concentration of N_2 in the exhaust gas at 400 °C as a function of the MoO_3 content of the Mo(Pb) (\blacklozenge) and Mo catalysts (\diamondsuit). The lead content varied from 0.2 to 3.2 wt.%. Other experimental conditions as in Fig. 1.

ammonia is complete. The conversion of ammonia and the selectivity towards N_2 and H_2O remain unchanged in the absence of nitric oxide. No relationship exists between the lead content of the Mo(Pb) catalysts and the ammonia conversion (lead contents between 0.2 and 3.5 wt.%).

In Fig. 4 the concentration of N_2 in the exhaust gas at 400 °C is shown as a function of the MoO_3 content of the Mo(Pb) and Mo catalysts. Remarkable features are the rapid increase in the amount of N_2 produced over the catalysts for loadings from 12 to 17 wt.% MoO_3 and the lower amount of N_2 produced over the Mo catalyst compared to the Mo(Pb)catalysts. Again, the selectivity to N_2 and H_2O is high using the Mo and the Mo(Pb) catalysts, and no influence of the presence of nitric oxide in the feed on the oxidation of ammonia was observed. The presence of Fe₂O₃ has no effect on the activity or the selectivity of the catalyst (catalyst Mo(18)).

Transmission electron micrographs of a representative sample are shown in Fig. 5. An extensive investigation of the samples revealed a homogeneous distribution of the molybdenum oxide particles over the support to be present. At higher loadings (more than about 20 wt.% MoO_3), some larger particles were observed. From the electron diffraction patterns, it was concluded that these larger platelike crystallites, which were on the order of 4 nm, were crystalline MoO_3 .

TPR measurements

Figure 6 shows typical TPR profiles, and in Table 2 the temperatures at which the peak maxima appear are presented. For the onset temperature of the peaks, the same trend was found as for the temperature of the peak maxima. For the supported Mo catalysts two peaks were observed, at 540 and 590 °C. At MoO_3 loadings higher than 17 wt.%, the first peak is stronger



(a)

(b)

Fig. 5. Transmission electron micrographs of catalyst Mo(25). Magnification $170\,000 \times$. Bar indicates 100 nm.



Fig. 6. TPR profiles for various catalysts. The catalysts were calcined at 400 °C in a 25% O_2/He flow for 1 h. $[H_2]_i = 5\%$, balance argon; heating rate 10 °C min⁻¹.

than the second, whereas at loadings lower than 17 wt.% the sequence is reversed. For the Mo(Pb) catalysts only one peak is observed. The position of the highest peak in the TPR spectra of both the Mo(Pb) and Mo catalysts is dependent on the MoO_3 loading. Catalyst Mo(18) which contains Fe_2O_3 does not show extra peaks. The unsupported MoO_3 (HDP) shows two peaks, at 520 and at 650 °C. For MoO_3 (Cerac), no peaks below 870 °C were detected. The temperature values at the highest peak of the TPR spectra are plotted against the MoO_3 content in the Mo(Pb) and the Mo catalysts (Fig. 7).

TABLE 2

Temperature (°C) at peak maximum of the TPR profiles from Fig. 6

SiO ₂ -supported catalysts		
Mo < 12 wt.%	540ª	590
Mo $(Pb) < 12$ wt.%	nd	590
Mo > 17 wt.%	540	590ª
Mo(Pb) > 17 wt.%	540	nd
Unsupported catalysts		
Mo (Pb)	520	650 ^b
Mo (Cerac)	nd	$\mathbf{nd^{c}}$

^a Weak peak.

^b Not shown in Fig. 6.

° No peaks observed below 870 °C.



Fig. 7. Temperature of the highest peak in the TPR spectra as a function of the molybdena content present in the Mo(Pb) catalysts (\blacksquare) and Mo catalysts (\blacklozenge). The dotted line shows the ammonia concentration in the exhaust gas as a function of the Mo content at 400 °C for the Mo(Pb) (\bigcirc) and Mo catalysts (\diamondsuit). Experimental conditions as in Fig. 1.

Additionally, the ammonia concentration in the exhaust gas at 400 °C is shown. A distinct decrease in the temperature of the highest TPR peak appears at MoO_3 loadings varying between 12 and 17 wt.%.

Discussion

Previously, we described the mechanism of nitric oxide reduction with ammonia to form N_2 , H_2O and N_2O , both in the presence and in the absence of O_2 , over the catalysts V_2O_5 , V_2O_5 on TiO₂, V_2O_5 on SiO₂/Al₂O₃ and V_2O_5 on Al₂O₃ [5, 6]. Evidence was given that NH₃ does not react with O_2 or O from any source during the reaction, but that N_2 , H_2O and N_2O were produced by a reaction involving all three species, NO, NH₃ and O_2 . In the mechanism proposed, NH₃ chemisorbs on the surface of the catalyst, resulting in a nitrogen-containing species and an OH group. Subsequent reaction of the dissociated ammonia species in the presence of NO leads to the formation of N₂, H₂O and N₂O. Another step in the mechanism is the dehydration of the surface, creating an oxygen vacancy. This vacancy is immediately occupied by one oxygen molecule. When a vacancy arises next to the adsorbed oxygen molecule, O₂ dissociates and one of the atoms becomes adsorbed on the vacancy, with the other remaining on the original site.

In a previous paper [7], it was suggested that for the molybdena catalyst the mechanism of the insertion of molecular oxygen is identical to that for the vanadia system. However, the behaviour of nitric oxide over the molybdena catalyst is different from its behaviour over the vanadia catalyst. From the results shown in Figs. 2 and 3 it may be concluded that nitric oxide does not react with the chemisorbed NH_x species, which implies that these species are bonded to the MoO_3 surface in a manner different than those on the V_2O_5 surface. This explanation does not hold for the MoO_3 (Cerac) material. NO is consumed when the temperature of the catalyst is in the temperature range 300–390 °C, and NO is produced above 390 °C.

The unsupported catalyst (HDP) shows a peak at 520 °C in the TPR spectrum (Fig. 6) and fairly considerable activity and selectivity in the oxidation of ammonia. The MoO_3 (Cerac) shows no TPR peaks below 870 °C but is still active in the oxidation of NH_3 (Fig. 1). However, the selectivity to N_2 is different. This may be attributed to a difference in surface structure. The MoO_3 (Cerac) contains far fewer lattice defects (oxygen ion vacancies) at the surface of the oxide than the precipitated MoO_3 [8]. The number of defects is probably associated with the catalytic activity.

The MoO₃ on SiO₂ system becomes catalytically active at loadings of 15 wt.% and above (Fig. 4). That is, ammonia is selectively oxidised to molecular nitrogen and water (Fig. 3). The TPR spectra of these high-loaded molybdena catalysts show two peaks, at 540 and 590 °C (Table 2). However, the catalysts with lead give rise to only one peak at 540 °C in the TPR spectrum. Both types of catalysts are active, which implies that the species reducible at 540 °C is concerned in the activity of the catalyst. This statement (hypothesis) is supported by the negative results obtained from the use of low-load materials. Amounts of molybdena lower than 15 wt.% on silica do not behave as a catalyst and show no reducible species at 540 °C (Table 2). Moreover, from Fig. 7 it is evident that the activity is related to the reducible species which is attributable to the peak at 540 °C in the TPR spectrum.

The high activity of catalysts with amounts of 15 wt.% of MoO₃ and more may be explained from the following considerations. It is assumed here that at loadings of MoO₃ of about 17 wt.% a monolayer of molybdena is present, which ensures complete coverage of the silica support. A complete monolayer on the SiO_2 used requires an amount of about 20% MoO₃, using the most likely crystal plane of the unit cell of MoO₃ in the calculations $(50 \text{ Å}^2 \text{ per molybdena site})$. The specific surface area of $(20 \text{ wt.}\%) \text{ MoO}_3$ on SiO_2 was 140 m² g⁻¹. The monolayer and complete cover of MoO_3 on SiO_2 give rise to a reducible species at 540 °C in the TPR spectrum. The presence of different reducible sites such as silicomolybdic acid, polymolybdate and MoO_3 at sub-monolayer loadings of MoO_3 have already been described [9-12]. Barbaux et al. [11] suggest that for a MoO_3 content between 1.5 and 7.5 wt.% silicomolybdic acid is the main Mo species. Above 7.5 wt.% and below 15 wt.% MoO₃, a polymolybdate phase appears, whereas at loadings of ≥ 22.5 wt.% crystalline MoO₃ was found. The specific surface area of the SiO₂ support used in their study was $130 \text{ m}^2 \text{g}^{-1}$. Indeed, at molybdena loadings higher than about 17 wt.% MoO₃ we observed a crystalline MoO₃ phase from the transmission electron micrographs, which is in agreement with the work of Barbaux *et al.* [11] and of Muzalidhar *et al.* [12]. Since at these higher molybdena loadings both increased NH_3 oxidation activity and H_2 reducibility (at 540 °C) can be observed, it is suggested that a MoO₃ phase in the catalyst is responsible for the activity of the catalyst. Moreover, it is supposed that this MoO₃ phase is present at MoO₃ concentrations close to the monolayer concentration.

The role of lead in the catalyst is unclear. Evidence for the presence of obvious species such as basic lead molybdate $PbO \cdot PbMoO_4$, was not found.

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