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Infrared Studies on the Interaction of Ammonia and Water on MoO_3/SiO_2 Catalysts

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Highly dispersed MoO_3/SiO_2 catalysts were prepared using the reaction of $MoCl_5$ with surface SiOH in CCl_4. The interaction of ammonia and water on the catalysts has been studied by means of a McBain balance and an IR vacuum cell. Specific absorption coefficients of the 1435- and 1620-cm^{-1} IR bands were determined by calibration with samples containing pure $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. The investigation of ammonia adsorption in relation to pretreatment temperature, H_2O adsorption, and molybdenum contents shows that ammonia adsorption is both reversible and irreversible. The irreversible adsorption of NH_3 and H_2O takes place in a competing manner on molybdenum Lewis sites, whereas water adsorption probably causes the formation of molybdate ions and protons.

INTRODUCTION

Bianchi *et al.* (*1*) investigated the adsorption of ammonia on a highly dispersed MoO_3 prepared via flame hydrolysis. Although they found IR bands assigned to NH_4^+ at 1435 cm^{-1} they concluded that MoO_3 exhibits no Brønsted acidity because they could not find OH groups. On the other hand, both Brønsted and Lewis acidity was found by Belokopytov *et al.* (*2*) on MoO_3 calcined at 500°C as well as by Janowski *et al.* (*3*) on MoO_3/SiO_2. The SiO_2 carrier increases the acidity of MoO_3. Matuyama *et al.* (*4*) observed no acidity in the case of MoO_3, while in the case of MoO_3/SiO_2 they found a strong acidity.

In view of the important role of ammonia in ammoxidation processes we examined the interaction of ammonia with MoO_3/SiO_2 catalysts in order to obtain more detailed information about acidity.

EXPERIMENTAL

The MoO_3/SiO_2 catalysts have been prepared under protection of argon by reaction of granulated SiO_2 (Degussa Aerosil-200, $S = 200\ m^2/g$) with $MoCl_5$ dissolved in CCl_4, according to the method already published (*5*). After reaction the catalysts have been hydrolysed in a wet argon stream (8 h), in a wet air stream (24 h) and then dried in an air stream at 378 K (12 h). The dried catalysts then contain no Cl^- (*5*).

IR investigations were carried out after thermal pretreatment of the catalyst pellets at 623 K in oxygen (2.7 kPa) (*6*). Water formed was removed in a trap by cooling in liquid nitrogen. After evacuation to 0.01 Pa dry ammonia was adsorbed at room temperature. IR spectra were recorded compensating the absorption of SiO_2 by introducing into the reference beam a SiO_2 disk equal in weight to the catalyst disk. Absorbances were determined according to

$$A = -\log \frac{I}{I_0}. \qquad (1)$$

Specific absorption coefficients were determined according to

$$a = \frac{A}{l \cdot c}, \qquad (2)$$

where l represents the sample path length in centimeters and c the concentration of the absorbing substance in mol · g^{-1}. Adsorption of ammonia and water was investigated with a McBain balance under conditions

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similar to those of the IR measurements. After inlet of 2.7 kPa NH_3 or 2.0 kPa H_2O, respectively, adsorption and evacuation were carried out until the weight was constant. Each operation was finished after 15–20 min.

Measurement of the specific absorption coefficients of the 1435- and 1620-cm^{-1} IR bands was made as follows. For the specific absorption coefficient of the NH_4^+ 1435-cm^{-1} band we prepared samples using a solution of pure recrystallized $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (8.32 ± 0.02 wt% NH_3, theor. 8.27 wt%) in water and Aerosil with NH_3 contents between 0.19 and 0.65 wt%). The subtracted spectra were recorded using a disk of about 20 mg weight and a SiO_2 disk of nearly the same weight in the reference beam.

Table 1 gives the values of absorbance measured in dependence on the NH_3 contents. A direct correlation, the correlation coefficient being 0.9955, was observed. The specific absorption coefficient resulting from this correlation is 58.18 g · mol^{-1} · mg^{-1}, where the concentration of NH_3 is given in mol · g^{-1}, and the sample path length is expressed by the weight of the pellet with a diameter of 16 mm. Using the thickness of the sample (about 10^{-2} cm) we obtain the value of 1.1635×10^5 g · mol^{-1} · cm^{-1} for this coefficient. By means of the specific absorption coefficient obtained in this way we can determine the amount of NH_4^+ in the catalyst. The difference between the amount of adsorbed NH_3 determined by means of the McBain balance and the amount of NH_4^+ from the IR measurement equals the amount of NH_3 corresponding to the 1620-cm^{-1} band, assuming that only these two species are present. In this way we can also obtain the specific absorption coefficient of the 1620-cm^{-1} band. Having investigated eight catalysts, we found in this way the value of $0.33 \pm 0.09 \times 10^5$ g · mol^{-1} · cm^{-1}. Thus the 1435-cm^{-1} band is nearly 3.5 times more intense than the 1620-cm^{-1} band.

TABLE 1

Absorbance of the 1435-cm^{-1} IR Band in Dependence on NH_3 Contents in $(NH_4)_6Mo_7O_{24}/SiO_2$ Samples

$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ contents (wt %)	NH_3 contents		Absorbance related to 20 mg
	(wt %)	(mmol/g)	
7.82	0.651	0.382	0.453
6.29	0.523	0.307	0.324
3.85	0.320	0.188	0.205
2.29	0.191	0.112	0.108

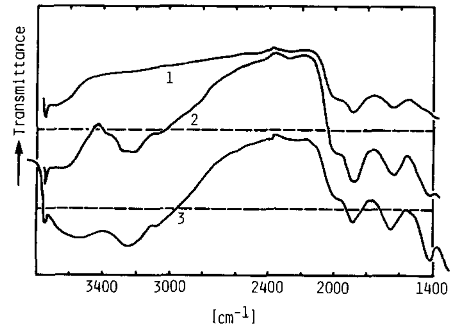

FIG. 1. IR spectra of a catalyst containing 4% Mo. (1) After pretreatment with O_2 at 6.7 kPa and 350°C followed by evacuation; (2) adsorption of 2.7 kPa NH_3 after procedure (1) followed by evacuation at room temperature; (3) Aerosil containing 8% $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$.

The relation between the specific absorption coefficients of both the 1435- and 1620-cm^{-1} bands was determined also in another way. On a catalyst calcined at 350°C NH_3 was adsorbed and the IR spectra were recorded. Adsorption of water then transforms the greater part of NH_3 into NH_4^+. Assuming that no NH_3 desorbs during water adsorption the relation between the increase of the absorbance in the 1435-cm^{-1} band and the decrease of the absorbance in the 1620-cm^{-1} band corresponds to the relation between the specific absorption coefficients. From eight experiments, we found the average value of 3.7, corresponding very well to the value obtained by the method described above.

RESULTS

Figure 1 shows spectra of a catalyst containing 4% Mo before and after NH_3 ad-

TABLE 2

Ammonia Adsorption on a MoO_3/SiO_2 Catalyst Containing 4.65% Mo in Dependence on the Temperature of Pretreatment with O_2 at 6.7 kPa

Temperature (°C)	NH_3 adsorption ($mmol/g_{cat}$)						NH_3 adsorption (mol/mol Mo) after evacuation at 50°C		
	2.7 kPa NH_3		NH_4^+	NH_3	After evacuation at				
	$NH_{3_{tot}}$	$NH_{3_{rev\,at\,50°C}}$			50°C $NH_{3_{tot}}$	100°C $NH_{3_{tot}}$	$NH_{3_{tot}}$	NH_4^+	NH_3
200	0.73	0.44	0.24	0.49	0.29	0.07	0.60	0.44	0.16
300	0.79	0.51	0.15	0.64	0.28	0.05	0.58	0.31	0.27
350	0.78	0.49	0.13	0.65	0.27	0.00	0.56	0.31	0.25
400	0.86	0.51	0.13	0.73	0.35	0.04	0.72	0.31	0.41
500	0.38[a]	0.12	0.06	0.32	0.26[a]	0.06[a]	0.54[a]	0.17	0.37
600	0.35[a]	0.09	0.06	0.29	0.26[a]	0.02[a]	0.54[a]	0.17	0.34

[a] Calculated from IR spectra.

sorption and for comparison the spectrum of a sample containing 8% $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. After NH_3 adsorption and evacuation the IR spectra of the catalysts exhibit bands at 1435, 1620, 3060, 3225, 3285, and 3380 cm^{-1} to be related to adsorbed forms of NH_3 or NH_4^+.

The results of NH_3 adsorption and IR investigations in dependence on the thermal pretreatment obtained with a catalyst sample containing 4.65% Mo are given in Table 2.

The influence of water adsorption before and after NH_3 adsorption can be seen from Table 3.

TABLE 3

Irreversible Adsorption of Ammonia and Water on a Catalyst Containing 4% Mo

Treatment	Amounts of adsorbed species (mol/mol Mo)			
	H_2O	$NH_{3_{tot}}$	NH_4^+	NH_3
350°C, 6.7 kPa O_2, RT, 0.1–0.01 Pa				
(1) 2.7 kPa NH_3, 0.1–0.01 Pa	—	0.55	0.13	0.42
2.0 kPa H_2O, 0.1–0.01 Pa	0.86	0.55	0.27	0.28
(2) 2.0 kPa H_2O, 0.1–0.01 Pa	0.78	—	—	—
2.7 kPa NH_3, 0.1–0.01 Pa	0.78	0.57	0.18	0.39
2.0 kPa H_2O, 0.1–0.01 Pa	0.84	0.57	0.50	0.07

Table 4 shows the relation between absorbances in both the 1435- and 1620-cm^{-1} band after evacuation as a function of evacuation time and temperature.

Table 5 shows the irreversible adsorption of NH_3 and H_2O in dependence on molybdenum contents. Figure 2 illustrates the thermal stability of irreversible adsorbed ammonia on catalysts with various molybdenum contents.

Figure 3 shows the total irreversible ammonia adsorption, and the amount of NH_4^+

TABLE 4

Ratio of Absorbances of the NH_4^+ (1435 cm^{-1}) and the NH_3 (1620 cm^{-1}) IR Bands after Evacuation as a Function of Evacuation Time and Temperature

Pretreatment temperature (°C)	Absorbance ratio $\frac{A_{1435\,cm^{-1}}}{A_{1620\,cm^{-1}}}$		
	Immediately after evacuation	30 min at beam temperature	10 min at 100°C
200	7.0	5.3	8.5
300	2.1	5.0	4.0
350	2.1	3.3	5.0
400	1.9	3.3	3.0
500	1.6	3.0	5.7
600	1.6	3.0	[a]

[a] Only the 1435-cm^{-1} band was obtained.

TABLE 5

Irreversible Adsorption of Ammonia and Water on Catalysts Containing 0.5–10.8% Mo

Molybdenum contents (wt %)	surface area (m^2/g)	quantity of adsorbed NH_3 ($mmol/g_{cat}$)	Amounts of adsorbed species (mol/mol Mo)							H_2O conversion (%)
			Before H_2O adsorption			After H_2O adsorption				
			$NH_{3_{tot}}$	NH_4^+	NH_3	H_2O	NH_4^+	NH_3	ΔNH_4^+	
0.5	225	0.115	2.21	0.19	2.02	1.08	0.50	1.71	0.31	29
2.0	217	0.204	0.98	0.15	0.83	0.41	0.28	0.70	0.13	32
4.2	182	0.213	0.49	0.03	0.46	0.30	0.12	0.37	0.09	30
10.8	177	0.247	0.22	0.11	0.11	0.25	0.17	0.05	0.06	24
4.0[a]	196	0.229	0.55	0.12	0.43	0.86	0.23	0.32	0.11	13

[a] Prepared by impregnation.

and NH_3 in dependence on molybdenum contents.

DISCUSSION

The results show that NH_3 on MoO_3/SiO_2 catalysts was adsorbed both reversibly and irreversibly (Table 2). The quantity of the reversible part desorbed via evacuation at 50°C (beam temperature) is approximately constant up to pretreatment temperature of 400°C and corresponds to a fraction of the surface of about 42 m^2/g (calculated with the ammonia cross-sectional area of 0.14 nm^2 (*7*)).

At pretreatment temperatures of 500 and 600°C the amount of reversibly adsorbed ammonia decreases. Jerschkewitz and Ehrhardt (*8*) showed that in this region of temperature the geometrical arrangement of silanol groups changes significantly: the quantity of paired silanol groups decreases whereas the quantity of isolated silanol groups strongly increases. Therefore we conclude that the reversible ammonia adsorption can be correlated with the existence of paired silanol groups.

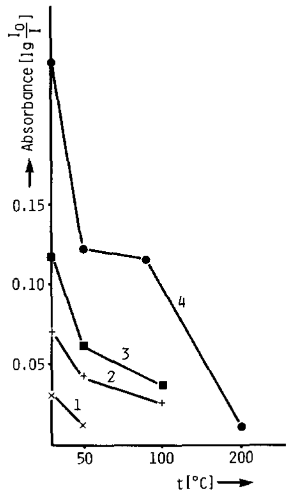

FIG. 2. Absorbance of the 1435-cm^{-1} band in dependence on thermal treatment. (1) 0.5% Mo; (2) 2.0% Mo; (3) 4.0% Mo; (4) 10.8% Mo.

The irreversible ammonia adsorption takes place on molybdenum centers. This follows from the fact that ammonia adsorption on Aerosil was not detected either by means of the McBain balance or by means of IR spectroscopy. Moreover, the observed bands at 1435, 3060, and 3225 cm^{-1} after ammonia adsorption correspond to those obtained from 8% ammonium molybdate on Aerosil.

Table 4 shows that the $NH_4^+ : NH_3$ ratio is greater after 30 min evacuation than after 0 min and decreases further after evacuation 10 min at 100°C. So NH_4^+ desorbs less readily than NH_3.

Adsorption of water before and after ammonia adsorption strongly influences the $NH_4^+ : NH_3$ ratio (Table 3). When the sample was calcined at 350°C in O_2 the NH_3 species predominate, i.e., the adsorption takes place on Lewis sites or via hydrogen bonds: for instance, on a catalyst containing 4% Mo only 24% of the total adsorbed ammonia was in the form of NH_4^+. It can be seen also from Table 3 that adsorption of water before ammonia adsorption gives a smaller effect than after ammonia adsorption. Preadsorption of water gave 32% NH_4^+, adsorption of water after ammonia adsorption increased the amount of NH_4^+ up to nearly 50% of the total adsorbed NH_3. The greatest amount of NH_4^+ (almost 90%) was found when water was added before and after ammonia adsorption. The variation of the thermal pretreatment of the catalysts shows a maximum ammonia adsorption at the calcination temperature of 400°C (Table 2). Further rise of temperature diminishes both reversible and irreversible ammonia adsorption. At the same time thermal pretreatment strongly influences the ratio of the two forms of ammonia. Whereas at the calcination temperature of 200°C NH_4^+ ions prevail, after calcination at 500°C NH_3 forms predominate (Table 2, columns 9 and 10).

With increasing temperature of evacuation the irreversibly adsorbed forms of ammonia became unstable. The decrease of intensity of the 1435- and 1620-cm^{-1} bands is nearly the same, but it seems that the first one is slightly more stable (Table 4).

Figure 2 shows the thermal stability of the 1435-cm^{-1} band in the case of four catalysts. After evacuation at 200°C under our conditions only in the spectra of the catalyst containing 10.8% Mo and the catalyst containing 4.65% Mo pretreated at 200°C do bands related to NH_4^+ ions remain. The quantity of irreversibly adsorbed ammonia increased with rising molybdenum contents; however, no linear correlation was observed (Table 5, Fig. 3) and we found a strong decrease of ammonia adsorption related to 1 mol Mo (Table 5, column 4). We assume that the decrease of the quantity of irreversibly adsorbed ammonia related to 1 mol Mo is connected with the increase of cluster or crystallite size. Simultaneously the ratio between NH_3 species and NH_4^+ ions decreases with rising molybdenum contents (Fig. 3).

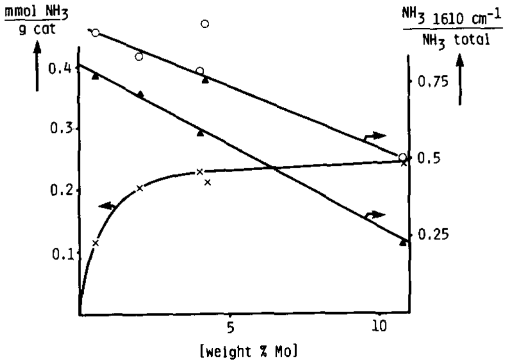

FIG. 3. Total adsorption of ammonia and $NH_{3_{1610\,cm^{-1}}} : NH_{3_{tot}}$ ratio in dependence on molybdenum contents. (×) Total adsorption; (○) $NH_{3_{1610\,cm^{-1}}} : NH_{3_{tot}}$ ratio before water adsorption: (▲) $NH_{3_{1610\,cm^{-1}}} : NH_{3_{tot}}$ ratio after water adsorption.

Thus our results clearly demonstrate that ammonia on dehydrated MoO_3/SiO_2 catalysts irreversibly adsorbs predominantly on Lewis sites or on O^{2-} ions by means of hydrogen bonds. Bianchi *et al.* (*1*) were able to show that H_2O on highly dispersed MoO_3 does not adsorb dissociatively. In the IR spectra they observed no bands related to OH. They explained the 1435-cm^{-1} band obtained after ammonia adsorption by a content of water in the used ammonia. In our case this explanation is improbable: the ammonia was dried with zeolite and the residual quantities of water are not sufficient to explain the amount of NH_4^+ obtained in our experiments. However, in our experiments we also could not find any evidence for the formation of additional hydroxyls after adsorption of water on dehydrated MoO_3/SiO_2 catalysts.

Therefore, we assume that both H_2O and NH_3 compete for Lewis sites. Protons may be obtained via formation of molybdate, polymolybdate or silicomolybdate clusters (*8*) when water was adsorbed

$$MoO_3 + H_2O \rightarrow MoO_4^{2-} + 2H^+. \quad (3)$$

At room temperature Reaction (3) proceeds only incompletely (Table 3, and Table 5, column 11).

According to Castellan *et al.* (*9*) MoO_3/SiO_2 catalysts with total Mo concentration which does not exceed about 10% are containing silicomolybdate clusters. With rising Mo contents the concentration of silicomolybdate anions decreases but that of polymolybdate anions increases. Our investigations allow us to conclude that silicomolybdate species are able to adsorb ammonia in the form of NH_3 species on Lewis sites or on O^{2-} ions by means of hydrogen bonds whereas polymolybdate clusters at higher Mo concentration form NH_4^+ by means of the protons contained in the structure of these clusters.

Summarizing our results we can conclude that ammonia adsorbs in three forms:

—reversibly on paired silanol groups;

—irreversibly on dehydrated catalysts predominantly on Lewis sites or on O^{2-} ions by means of hydrogen bonds;

—irreversibly on hydrated catalysts or on catalysts containing large polymolybdate clusters as NH_4^+ ions.

REFERENCES

1. Bianchi, D., Bernard, J.-L., Camelot, M., Benali-Chaoup, R., and Teichner, S. J., *Bull. Soc. Chim. Fr.*, 275 (1980).
2. Belokopytov, Y. V., Kholyavenko, Kh. M., and Gerei, S. V., *J. Catal.* **60,** 1 (1979).
3. Janowski, F., Sofianos, A., and Wolf, F., *React. Kinet. Catal. Lett.* **12,** 157 (1979).
4. Matuyama, K., Hattori, H., and Tanabe, K., *Bull. Soc. Chem. Jpn.* **50,** 86 (1977).
5. Fricke, R., Hanke, W., and Öhlmann, G., *J. Catal.* **79,** 1 (1983).
6. Hanke, W., Kaduschin, A. A., Kutyreva, N. A., Schnabel, K.-H., and Walkov, V., *Oxid. Commun.* **1,** 373 (1980).
7. McClellan, A. L., and Harnsberger, H. F., *J. Colloid Interface Sci.* **23,** 577 (1967).
8. Jerschkewitz, H.-G., and Ehrhardt, K., *Z. Anorg. Allg. Chem.* **502,** 102 (1983).
9. Castellan, A., Bart, J. C. J., Vaghi, A., and Giordano, N., *J. Catal.* **42,** 162 (1976).