TEMPERATURE-PROGRAMMED DESORPTION AND FTIR STUDIES OF ADSORBED AMMONIA IN RELATION TO THE SURFACE ACIDITY OF GAMMA ALUMINA

A. McFarlan and J. Galuszka

Energy Research Laboratories

November 1994

DIVISION REPORT ERL 94-42(TR)

ERL 94-042(7R) C.2

SUMMARY

Results of kinetic desorption studies of ammonia and pyridine are used extensively to determine the number and relative strength of acid sites on oxide surfaces. Infrared spectroscopy can also be used to reveal structural and bonding aspects of probe molecules adsorbed at acid sites. This report discusses measurements of ammonia adsorption on γ -alumina in relation to its surface acidity; the data were obtained by using temperature-programmed desorption with mass selective detection (TPD-MS), and simultaneous in situ monitoring of the alumina surface by FTIR.

Ammonia adsorbs at Brönsted and Lewis acid sites of varying strengths and the surface heterogeneity is reflected in the rather broad TPD-MS and TPD-IR profiles. In excess ammonia, adsorption at 300°C or 25°C yields a saturation coverage of about 1.1 μ mols/m² on γ -alumina having a specific surface area of 285 m²/g. Below saturation, the stronger Lewis and Brönsted acid sites are preferentially filled during adsorption at room temperature, and almost all of the acid sites can be exchanged at room temperature using isotopically labelled ammonia.

The 1400-1600 cm⁻¹ region in the spectrum of adsorbed ammonia on alumina is complex and perhaps not totally understood. A better understanding of the acidic properties of alumina may be gleaned from further studies that focus on this spectral region.

i

CONTENTS

INTRODUCTION	1
EXPERIMENTAL	2
RESULTS AND DISCUSSION	3
A) ¹⁴ NH ₃ Adsorption	3
B) TPD/MS/FTIR Studies	5
C) ¹⁴ NH ₃ / ¹⁵ NH ₃ Adsorption	11
CONCLUSIONS	14
REFERENCES	15
TABLE 1 - IR band assignments for NH3 on alumina	3

1 1 1 1 1

.

INTRODUCTION

The characterization of metal oxide surfaces plays an important role in understanding and improving heterogeneous catalysts. A variety of techniques have been developed for determining properties such as surface area, concentration of catalytically active sites, chemical structure at the surface, and acidic or basic properties. For example, temperatureprogrammed desorption (TPD) of adsorbed ammonia and pyridine molecules has been used extensively to determine the number and relative strength of acid sites on oxide surfaces [1,2]. Similar adsorption experiments have been carried out and monitored by infrared spectroscopy in order to reveal structural and bonding aspects, e.g., H-bonding, and Lewis and Brönsted acidity of these probe molecules adsorbed at acid sites [3].

Temperature-programmed desorption using thermal conductivity detectors or ionization gauges, although quantitative, lacks the ability to distinguish components of a mixture in the gas phase. More recently, however, these conventional detection methods have been gradually replaced by mass selective detectors (quadrapole mass analyzers) which can resolve chemical as well as isotopic gas-phase mixtures. The last decade has also seen a revolution in infrared (IR) spectroscopic instrumentation. In particular, the fast scanning capability and high signal-to-noise ratio that can be achieved using modern FTIR spectrometers make it possible to follow changes on the surface of a catalyst during TPD in a time-resolved manner.

This report discusses measurements of ammonia adsorption on γ -alumina in relation to its surface acidity. These measurements were obtained by using temperature-programmed desorption with mass selective detection (TPD-MS), and simultaneous in situ monitoring of the alumina surface by FTIR. Ammonia adsorption on γ -alumina has been studied by TPD [4-7], and by IR spectroscopy [5,8-10], and as such, is a suitable model for demonstrating this combined approach for measuring surface acidity. The advantages of TPD-MS and TPD-IR for probing catalyst surfaces are discussed.

EXPERIMENTAL

The alumina used in this study was a commercial high purity γ -alumina, Versal GL, supplied by LaRoche Chemicals and having a BET specific surface area of 285 m²/g. Anhydrous ammonia (99.99%) and Helium (99.999%) were purchased from Matheson. Ammonia-¹⁵N having an isotopic purity of 99% was purchased from MSD Isotopes. The gases were used without further purification.

Samples containing 7.6-7.8 mg alumina were pressed into thin self-supporting wafers 13 mm in diameter and placed in an evacuable stainless steel transmission infrared cell (Abbspec). The in situ IR cell was connected to a stainless steel gas-handling system and could be evacuated to 10⁻⁵ mbar through a turbomolecular pump and auxillary rotary vane roughing pump. Alternatively, the IR cell could be evacuated through a quadrapole mass analyzer (Balzers) via a variable leak valve, permitting quantitative analysis of gas-phase desorption products during TPD. Isothermal vacuum activation and linear temperature ramps during TPD were controlled using a programmable PID temperature controller.

Prior to adsorbing ammonia, the alumina samples were activated under vacuum at 450°C for 1 h, cooled to room temperature, then a background infrared spectrum was recorded. FTIR spectra were acquired at nominal 4 cm⁻¹ resolution and a rate of about 128 scans per minute using a Nicolet 60SX spectrometer equipped with a broad band MCT detector. Post-processing of interferograms was employed during TPD.

Multiple ion monitoring during TPD-MS was carried out using data acquisition software running on an IBM-compatible PC. The software had the capability to sample 8 different mass channels and an analog input channel for recording the sample temperature. In order to obtain quantitative measurements, the TPD-MS system was calibrated by measuring the pressure drop of ammonia per unit time in the known reactor volume as a function of the parent ion current. During a typical TPD-MS experiment, 400 samples per channel were stored.

RESULTS AND DISCUSSION

(A) ¹⁴NH₃ ADSORPTION

Following vacuum activation at 450°C, an alumina sample was exposed to 1.4 mbar NH_3 at 300°C for 30 min, the temperature was lowered to 25°C, and the IR cell was evacuated for 30 min at 25°C. Figure 1(A) is the resultant infrared difference spectrum showing the total amount of ammonia chemisorbed on the alumina surface at 300°C. The spectrum was virtually identical to that obtained using 10 mbar of ammonia.

Negative peaks at 3790 and 3700 cm⁻¹ indicate the "disappearance" of surface AlO-H stretching modes, while positive peaks at 3395, 3355, 3260, and 3150 cm⁻¹ are due to OH and NH stretching vibrations of various surface species. In the region between 1200 and 1700 cm⁻¹, where N-H deformation modes are expected to absorb, relatively strong bands are observed at 1240 cm⁻¹ and 1620 cm⁻¹. Much weaker bands are also observed at 1450, 1505, and 1560 cm⁻¹, however, these bands varied in position and intensity between experiments.

In their original work, Peri et al. reported the infrared spectrum of ammonia adsorbed on alumina, and assigned infrared bands to ammonia coordinated to Lewis and Brönsted acid sites [8]. Since then, several papers have been published on this subject [5,10, and references therein], and there is general agreement concerning the assignments summarized in Table 1.

Surface Site	Frequencies ¹ (cm ⁻¹)
NH ₃ - Physisorbed	3390, 3350, 3160(br), 1630, 1200
NH ₃ - Brönsted acid	3260, 3165, 1450, 1410
NH ₃ - Lewis acid	3400, 3355, 1625, 1250
Free AlO-H	3795, 3740, 3700

Table 1- Infrared band assignments for NH₃ on alumina

1. Median values. Reported values typically vary by $\pm 5 \text{ cm}^{-1}$.



Fig. 1- A) Infrared difference spectrum showing spectral changes due to ammonia chemisorbed on the alumina surface (see text); B) After heating the sample in A at 200°C under vacuum for 10 min, then cooling to 25°C. The background spectrum of alumina has been subtracted in both cases.

4

CANMET

Based on the above assignments, the spectrum in Fig. 1(A) shows that ammonia adsorbs at Brönsted and Lewis acid sites on alumina at 300°C. Additionally, the broad band having a maximum at about 3150 cm⁻¹ indicates that some physically adsorbed ammonia is also present. The origin of the weak bands at 1505 and 1560 cm⁻¹ is uncertain; similar features were observed by Amenomiya, however, no assignment was made [5].

Subsequent evacuation at 200°C for 10 min removed most of the adsorbed NH_3 , as shown in Fig. 1(B). However, a weak residual band at 1620 cm⁻¹ and a stronger band at 1280 cm⁻¹ (shifted 40 cm⁻¹ to higher frequency) indicated that some NH_3 remained bound to Lewis acid sites on the surface. Evacuation at 450°C completely removed any features attributed to chemisorbed ammonia, thereby allowing several experiments to be carried out using the same alumina sample.

(B) TPD/MS/FTIR STUDIES

In a different experiment, ammonia adsorption was carried out at 300°C using the same conditions as above. Temperature-programmed desorption was subsequently performed and monitored by infrared spectroscopy and mass selective detection of the gas-phase products. Figure 2 shows a series of spectra (having an observation time of about 2 min per spectrum) that was acquired during a linearly programmed temperature ramp between 25°C and 450°C at a rate of 20°C/min. Bands due to adsorbed ammonia dominate the spectrum at near ambient temperatures, but decrease in intensity with increasing temperature during the TPD experiment. The apparent increase in absorbance with increasing temperature below about 1200 cm⁻¹ is due to a combination of emission and temperature broadening of the bulk oxide absorption bands.

Simultaneously, all of the desorbed products were evacuated through a quadrupole mass analyzer and ions having selected mass/charge ratio (m/e) were monitored in the multiple ion detection mode. Ion current versus time for selected masses during the TPD experiment is plotted in Fig. 3. The strong TPD peaks for ions having m/e = 17 and m/e = 16 show that ammonia was the major product desorbed below about 300°C. The m/e = 18 ion trace in Figure 3, and the appearance of a tail in the m/e = 17 and m/e = 16 traces at higher temperatures indicate that in addition to NH₃, a small quantity of water was also desorbed above about 300°C. Desorption of water was observed in all experiments using



Fig. 2 - Series of infrared spectra (256 scans each) acquired during TPD. The mean sample temperature (°C) for each spectral interval is indicated.



Fig. 3 - TPD-MS profile for ions of selected mass/charge ratio during temperatureprogrammed desorption of ammonia on alumina.

·• .

ammonia and a weak peak was also observed in a blank experiment using He. The source of the water, however, remains uncertain; water could have formed via the dissociative chemisorption of NH_3 on the alumina surface, but may also have been present as a trace impurity in the ammonia or as residual water vapour in the stainless steel vacuum line.

In addition to the parent ion and fragment ions, the mass spectrum of NH_3 contained a weak peak at m/e = 28, and this peak was also observed during TPD (Fig. 3). Purification of the NH_3 by repeated freezing and pumping under vacuum did not diminish the m/e = 28 peak relative to m/e = 17 suggesting that N_2 was not present to any extent as an impurity in the ammonia. When ${}^{15}NH_3$ was substituted for ${}^{14}NH_3$, additional weak peaks were observed at m/e = 29 and m/e = 30, confirming that N_2^+ detected in the presence of ammonia was likely due to the decomposition of NH_3 to N_2 and H_2 in the ion source of the mass analyzer.

Figure 4 plots the change in integrated intensity of the deformation bands due to chemisorbed ammonia as a function of temperature during the TPD experiment. The data for a given interval in Fig. 4 were obtained by subtracting and integrating successive spectra shown in Fig. 2. Hence, the kinetic TPD-IR plot in Fig. 4 is of the same form as the TPD-MS plot shown in Fig. 3 and, in agreement with previously reported results, exhibits a maximum at about 100°C then diminishes gradually toward higher temperature [5,7].

In Fig. 4, the temperatures at which the maximum rates of change in intensity occur for the 1620, ~1450, and 1240 cm⁻¹ absorption bands do not coincide, suggesting heterogeneity among the chemisorbed species. However, specific regimes of desorption cannot be easily identified. For example, due to overlapping bands at 1200-1250 cm⁻¹ and 1620-1630 cm⁻¹, the corresponding curves in Fig. 4 probably reflect both the disappearance of weakly bound NH₃ at lower temperatures and that of Lewis acid bound NH₃ at higher temperatures with no clear transition point. Further, accepting that bands near 1400-1510 cm⁻¹ are due to surface bound NH₄⁺, then Fig. 4 suggests that there is a broad range in strength of Brönsted and Lewis acid sites on alumina.

Figure 5 illustrates the effect of reducing the surface coverage of ammonia on alumina in the TPD-MS experiment. Fig. 5(A) plots the m/e = 17 parent ion current during TPD, following adsorption at 300°C using excess ammonia to achieve saturation coverage. (Also see Fig. 2). A similar TPD-MS plot (not shown) was observed following adsorption at 25°C using the same initial pressure (1.4 mbar) of ammonia. Infrared spectra showing the total



Fig. 4 - TPD-IR profile showing the changes in integrated intensity of the IR bands between
1150-135 cm⁻¹ ■, 1600-1700 cm⁻¹ □, 1430-1530 cm⁻¹ O, due to adsorbed ammonia.
Spectra are shown in Fig. 2.



Fig. 5 - TPD-MS profile of m/e = 17 ion during TPD following: (A) adsorption of NH₃ at 300 at a coverage of 1.1 µmols/m²; (B) adsorption of NH₃ at 25°C at a coverage of 0.31 µmols/m²; (C) adsorption of He in a blank experiment.

amount of ammonia adsorbed were almost identical which further suggests that saturation coverage of ammonia had been reached. The total amount of ammonia desorbed was estimated to be $1.1 \ \mu mols/m^2$ from the integrated area under the TPD-MS curve in Fig. 5(A).

In a different experiment, successive small doses of ammonia were admitted to the sample at 25°C until the infrared band at 1240 cm⁻¹ had reached about 40% of its maximum intensity. The TPD-MS plot is shown as Fig. 5(B). In this case, the amount of chemisorbed ammonia measured in the TPD experiment was about 0.31 μ mols/m², the TPD peak was more symmetric, and the maximum rate of desorption was shifted to about 220°C. Therefore, it would appear that at ambient temperature and low surface coverages the stronger adsorption sites were preferentially filled. Finally, Fig. 5(C) shows the contribution to the m/e = 17 ion current due to water that was evolved in a blank experiment using He.

(C) ¹⁴NH₃/¹⁵NH₃ ADSORPTION

Isotopic substitution by ¹⁵NH₃ was studied in order to learn more about the nature of the interaction between ammonia and the various acid sites on alumina. In an experiment like the one above, ¹⁴NH₃ was adsorbed on a 450°C-activated alumina sample at 25°C until about 30% of the maximum surface coverage had been achieved, as estimated from the intensity of the 1200 cm⁻¹ band. The sample was subsequently exposed to additional small doses of ¹⁵NH₃ until about 80% of the adsorption sites had been consumed.

The infrared spectrum of the adsorbed isotopomers exhibited a downward shift in frequency of 4 and 10 cm⁻¹ from 1620 and 1240 cm⁻¹, respectively. Shifts of this magnitude are expected for substitution of N-H vibrations by ¹⁵N. (See Fig. 6 below). However, in the TPD-MS experiment that followed, a peak at higher temperature due mainly to ¹⁴NH₃ was not observed. Rather, the maximum rate of desorption occurred at about 110°C for both ¹⁴NH₃ and ¹⁵NH₃, indicating that scrambling had occurred during TPD. This result was somewhat ambiguous insofar as substitution of ¹⁵NH₃ for ¹⁴NH₃ preadsorbed at the stronger adorption sites may have occurred at room temperature during the ¹⁵NH₃ adsorption step, or may have been facilitated as the temperature increased during the initial stages of TPD. To determine whether temperature was an important factor, the following experiment was carried out.

The 450°C activated alumina sample was exposed to 1.4 mbar $^{15}NH_3$ for 30 min at 25°C and evacuated for 30 min at 25°C. The sample was then exposed to 1.0 mbar $^{14}NH_3$

for 10 min and evacuated for 10 min at 25°C, thereby saturating the alumina surface with $^{15}NH_3$. This exchange step was repeated a second time after which the sample was evacuated for 30 min at 25°C and TPD was carried out.

The infrared spectrum of ¹⁵NH₃ adsorbed on alumina at 25°C, and that recorded after exchange with ¹⁴NH₃ are shown in Fig. 6(A) and (B), respectively. Because of the small isotopic shifts, it is difficult to estimate from the infrared spectra the extent to which the preadsorbed ¹⁵NH₃ underwent exchange on the surface. However, the TPD/MS experiment showed mainly ¹⁴NH₃ being desorbed (1.1 μ mols/m²), thereby confirming that almost all of the preadsorbed ¹⁵NH₃ species had exchanged at room temperature.

The implication of the above result is that at ambient temperature, ammonia is capable of surface mobility among the majority of acid sites on alumina, even though a significant energy barrier exists for desorption to the gas phase. Although the mechanism by which exchange among the sites occurs is not known, the presence of gas-phase NH_3 may play a crucial role. In the case of ammonia adsorbed at Brönsted acid sites, H-bonding interactions between weakly adsorbed NH_3 and chemisorbed NH_4^+ may facilitate the exchange reaction by lowering the activation energy barrier. Alternatively, the energy required to exchange NH_3 molecules bound to Lewis acid sites bay be provided via collisions with gas-phase ammonia molecules.

Weak spectral features have been observed in this work at 1450, 1505, and 1560 cm⁻¹ that are apparently sensitive to the experimental conditions under which ammonia adsorption is carried out (Fig. 6). Similar spectral features have been reported elsewhere in the literature, and although various structures have been proposed, the assignment of these bands seems inconclusive. Further, the band at 1410 cm⁻¹ that has been attributed to Brönsted acidity was not observed here. We cannot speculate as to the structure(s) of chemisorbed species or to the number of surface sites that may be associated with these infrared bands. The present IR results suggest that the 1400-1600 cm⁻¹ spectral region in the spectrum of ammonia adsorbed on alumina is complex and warrants further investigation.



Fig. 6 - (A) Infrared difference spectrum showing bands due to saturation coverage of ${}^{15}NH_3$ adsorbed on alumina at 25°C; (B) following exchange of the sample in A using ${}^{14}NH_3$ and evacuation at 25°C.

CONCLUSIONS

Temperature-programmed desorption employing mass selective detection and in situ monitoring by infrared spectroscopy is a powerful technique for studying acidic properties of catalyst surfaces. Mulitple components in the kinetic TPD profile can be identified and quantified by TPD-MS while TPD-IR offers complementary structural information related to the type of acidity, heterogeneity, and strength of the various acid sites. The technique is, of course, equally applicable to studies of basic catalysts using acidic probe molecules and can be extended further to include mechanistic studies of catalytic processes.

Ammonia adsorbs at Brönsted and Lewis acid sites of varying strengths and the surface heterogeneity is reflected in the rather broad TPD-MS and TPD-IR profiles. Some dissociative chemisorption of NH_3 leading to the liberation of water during TPD may occur, however, other sources of molecularly adsorbed water cannot be ruled out.

In excess ammonia, adsorption at 300°C or 25°C yields a saturation coverage of about $1.1 \ \mu mols/m^2$ on this high surface area (285 m²/g) γ -alumina. Below saturation, the stronger Lewis and Brönsted acid sites are preferentially filled during adsorption at room temperature. However, even though a significant energy barrier exists for ammonia desorption from the stronger acid sites, almost all of the acid sites can be exchanged at room temperature using isotopically labelled ammonia. The presence of gas-phase ammonia may play an important role in facilitating this room-temperature exchange process.

The 1400-1600 cm⁻¹ region in the spectrum of adsorbed ammonia on alumina is complex and perhaps not totally understood. A better understanding of the acidic properties of alumina may be gleaned from further studies focussing on this spectral region.

. . . .

REFERENCES

- 1. A. Baiker, J. Kijenski Catal. Today 5, 2 (1989).
- 2. M. C. Kung, H. H. Kung Catal. Rev. Sci. Eng. 27(3), 425 (1985).
- 3. S. Bhatia, J. Beltramini, D. D. Do Catal. Today 7, 309 (1990).
- 4. Y. Amenomiya, J. H. B. Chenier, R. J. Cvetanovic J. Phys. Chem. 68, 52 (1964).
- 5. Y. Amenomiya, J. Catal. 46, 326 (1977).
- 6. J. Koubek, J. Volf, J. Pasek J. Catal. 38, 385 (1975).
- 7. S. Vásques J. Chem. Soc. Faraday Trans. 86(14), 2051 (1992).
- 8. J. B. Peri, R. B. Hannan J. Phys. Chem. 64, 1526 (1960).
- 9. J. B. Peri, J. Phys. Chem. 69, 231 (1965).
- 10. A. Baiker, E. Jobsen, A. Wokaun J. Chem. Soc. Faraday Trans. 86(7), 1131 (1990).