Characterization of NH₃ Adsorbed on γ-Mo₂N by NMR Spectroscopy

G. W. Haddix, D. H. Jones, J. A. Reimer, and A. T. Bell

Center for Advanced Materials, Lawrence Berkeley Laboratory, and Department of Chemical Engineering, University of California, Berkeley, California 94720

Nuclear magnetic resonance techniques were used to study the structure and dynamics of NH_3 adsorbed on high-surface-area (~100 m²/g) γ-Mo₂N. Proton NMR measurements indicate that NH_3 adsorbs associatively at 298 K, but decomposes on the surface upon heating. The species created by this decomposition are strongly held NH_2, NH, and atomic N and H. Part of the NH_3 adsorbed at 298 K undergoes rapid rotation and translation on the surface, while the species remaining after high-temperature evacuation are locally immobile. Adsorbed NH_2 rotates rapidly about its twofold axis. © 1988 Academic Press, Inc.

INTRODUCTION

The catalytic properties of γ-Mo₂N have been the subject of several recent investigations (*1–4*). Of particular interest has been the observation by Volpe and Boudart (*4*) that γ-Mo₂N exhibits an activity for ammonia synthesis similar to that observed for iron. Their work also shows that ammonia chemisorbs strongly on γ-Mo₂N and thereby inhibits the synthesis reaction. The purpose of this study was to gain an understanding of the structure and motion of ammonia on γ-Mo₂N through the use of proton (¹H) nuclear magnetic resonance (NMR) techniques.

EXPERIMENTAL

The γ-Mo₂N used in this study was prepared by temperature-programmed reduction of MoO₃ in NH₃ (*5, 6*). The reduction temperature was raised from 298 to 638 K over 30 min, ramped linearly from 638 to 738 K over 3 h, ramped linearly from 738 to 973 K over 2 h, and held at 993 K for 30 min before cooling to 298 K in flowing NH₃. The freshly prepared nitride was passivated in a 1% O₂/He mixture to prevent rapid autothermal oxidation of the catalyst upon exposure to air. The BET surface area of the catalyst was determined to be 100 ± 1 m²/g. Transmission electron microscopy and

X-ray diffraction (*6*) indicate that the passivated catalyst is 100% γ-Mo₂N and has a "holey platelet" morphology. From a through-focus series of electron micrographs, the average pore radius was determined to be 2 ± 0.5 nm. A similar value was obtained from an analysis of the hysteresis loop in a complete BET isotherm.

Proton NMR spectra were recorded with a home-built spectrometer. The superconducting magnet for this instrument has a 4-in. bore to accommodate a variable temperature probe containing a quartz microreactor (*7*). The probe circuit used was a single-resonance series LC network tuned for proton resonance (181.2 MHz).

To avoid oxygen contamination, samples of γ-Mo₂N were prepared in the probe and evacuated at 773 K to remove residually adsorbed ammonia. Ammonia was adsorbed on the γ-Mo₂N to achieve saturation coverage. Gas-phase and reversibly held ammonia were then removed by evacuation to $<10^{-6}$ Torr at 298 K. NMR spectra and relaxation times of the adsorbates were recorded after the initial adsorption and following partial desorption of the adsorbate at progressively higher temperatures.

NMR lineshape spectra were obtained by cosubtracting 10,000 free induction decays following phase-alternated 90° pulses. T_1

was measured using the inversion-recovery technique in a cosubtracting manner. To confirm the existence of strong dipolar coupling in the species resulting from ammonia adsorption and subsequent decomposition during high-temperature evacuations, echo techniques were employed. For short delay times ($\tau \ll T_2$), a solid-echo experiment (90_x–τ–90_y) will result in refocusing of the dipolar Hamiltonian to first order (9), while spin-echo (90_x–τ–180_y) and Hahn-echo (90_x–τ–90_x) experiments will only refocus spin interactions linear in the spin variable (10) (i.e., I_z ~ chemical shift, heteronuclear dipolar, field inhomogeneities, etc.) Refocusing is evidenced by an *increase* in the net observable magnetization after the second (refocusing) pulse. Selective inversion techniques ([soft 180_x]–τ–90_y) were also employed to elucidate the interactions experienced by species forming parts of inhomogeneous lineshape spectra. Solid-echo, spin-echo, Hahn-echo, and selective inversion experiments were performed by cosubtraction of free induction decays. Phase alternation for cosubtraction was done either by alternating the phase of the applied radiofrequency pulses or by applying alternately a 180° total spin inversion pulse before the actual pulse experiment. Typical broadband 90° pulses were 4 μs with ~500 W of transmitter power at the probe. Spec-
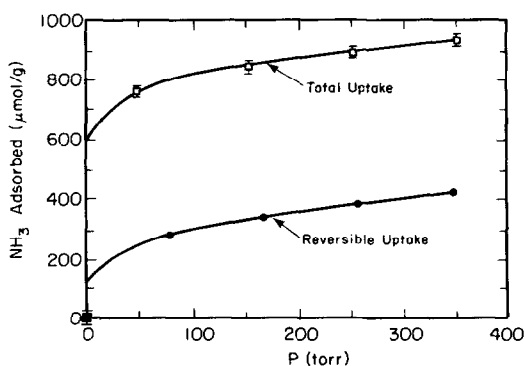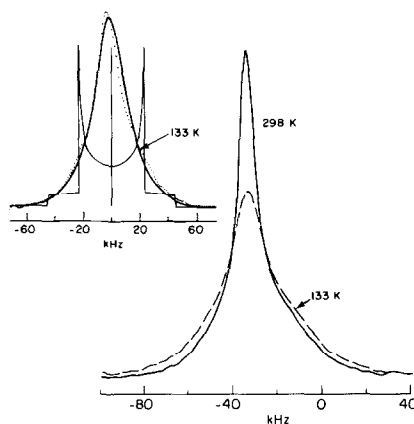

FIG. 2. Proton lineshape of NH₃ irreversibly held on γ-Mo₂N evacuated at 298 K. Spectra taken at 298 and 133 K. Insert shows a theoretical fit to the lineshape at 133 K for a rotating NH₃ molecule broadened by its neighbors. The frequency scale for the fit is set to zero at the center of mass of the spectrum.

FIG. 1. Total and reversible adsorption isotherms for NH₃ on γ-Mo₂N.

trometer and probe were tuned using the signal from adsorbed and gas-phase ammonia (760 Torr). To check for background signal from the probe, 5000 cosubtracted free induction decays were accumulated on an empty coil. No significant proton signal was observed by this means.

RESULTS AND DISCUSSION

Figure 1 shows the total and reversible adsorption isotherms for ammonia on γ-Mo₂N. The maximum uptake of ammonia (reversible plus irreversible) is approximately 768 μmol/g. This corresponds to about 41% of what might be expected based on the BET surface area of the sample, and assuming adsorption at either on-top Mo sites or fourfold hollows on the low-index [(100), (110), (111)] planes of γ-Mo₂N.

The proton NMR spectrum of irreversibly held ammonia on γ-Mo₂N is shown in Fig. 2. At 133 K the entire spectrum can be fit very well by a Gaussian broadened triplet with peaks in a 1:2:1 ratio (three-coupled spin ~ ½ particles). This is the lineshape expected for a translationally immobile NH₃ group rapidly rotating about its threefold axis and interacting with neigh-
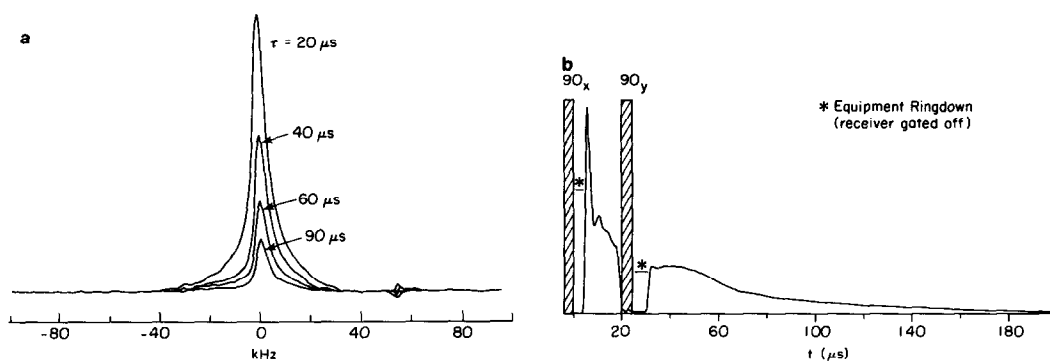
FIG. 3. (a) Fourier transforms of solid echoes performed on NH_3 on γ-Mo_2N evacuated at 298 K. (b) Power ($\{M_x^2 + M_y^2\}^{1/2}$) free induction decay and subsequent solid echo for the $\tau = 20$ μs case.

boring NH_3 groups via dipolar coupling (11). The lineshape at 133 K does not fit well to a single Gaussian lineshape. Also, the heteronuclear dipolar interaction between ^{14}N and ^1H is negligible compared to the homonuclear dipolar interaction between protons.

When the temperature is raised to 298 K, the lineshape changes to one consisting of broad and narrow components. To probe the structure of the lineshape observed at 298 K, a series of solid-echo and spin-echo experiments was carried out. The same delays (τ) between pulses were used for both sets of experiments. Figure 3 shows Fourier transforms of a series of solid

echoes for irreversibly held ammonia on γ-Mo_2N at 298 K. This figure also illustrates a power free-induction decay (Fig. 3b) from the solid-echo sequence to show that there is significant refocusing of the magnetization. The amplitudes of "power" free-induction decays are given by the square root of the sum of the squares of the x and y magnetization. This avoids any phase errors in the data shown. Figure 4 shows a similar set of experiments using a spin-echo sequence. In this case, the power free-induction decay (Fig. 4b) shows no significant refocusing, and Fourier transformation of the "echo" gives little more than a Fourier transform of a truncated free-
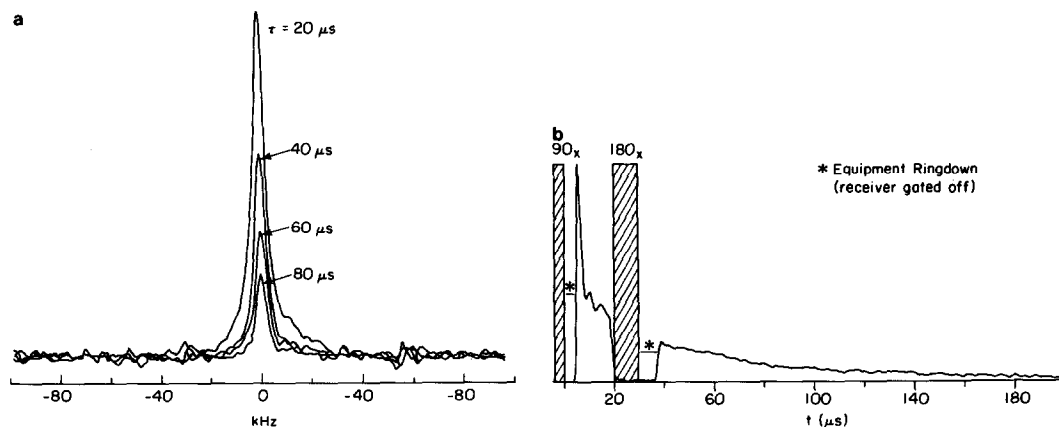

FIG. 4. (a) Fourier transforms of spin echoes performed on NH_3 on γ-Mo_2N evacuated at 298 K. (b) Power ($\{M_x^2 + M_y^2\}^{1/2}$) free induction decay showing the lack of spin echo after the refocusing pulse for the $\tau = 20$ μs case.

induction decay following a 90° pulse (truncated at 2τ, the theoretical echo maximum). For the delay times shown in Fig. 4, little dephasing occurs for the narrow component (long T_2), and thus little refocusing would be expected. The absence of a significant echo for the spin-echo sequence utilizing longer delays (>100 μs) suggests that the relaxation of the narrow component may also be mediated by the dipolar interaction. Taken together, the echo experiments are strong evidence that the broad (short T_2) component of the lineshape for a sample evacuated at 298 K is dominated by the dipolar interaction, while the narrow (long T_2) component is less affected by the dipolar interaction due to rapid motion of the species comprising it. The spectrum obtained at 298 K can then be interpreted as follows. The broad component can be assigned to rotating NH₃ groups that are translationally immobile and the narrow component can be assigned to species undergoing rapid translational motion which results in further averaging of dipolar interactions. We suspect that the narrow component is due to weakly chemisorbed (or strongly physisorbed) ammonia that is rapidly moving across the surface, or rapidly equilibrating with a very dilute gas phase. It should be added that the narrow component cannot arise from an increase in the rotational frequency of translationally immobile surface ammonia at 298 K (11).

The strength of ammonia adsorption was investigated by temperature-programmed desorption (TPD). Ammonia was dosed on
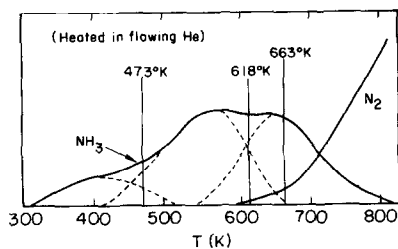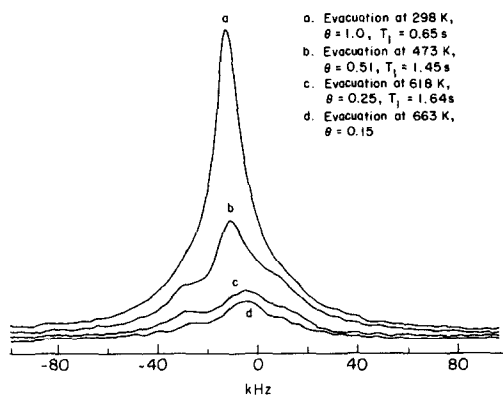
FIG. 6. Time-interrupted TPD NMR showing proton lineshape, T_1, and coverage (θ). (Based on θ = 1 for irreversibly held NH₃ at 298 K.)

a. Evacuation at 298 K, θ = 1.0, T_1 = 0.65 s
b. Evacuation at 473 K, θ = 0.51, T_1 = 1.45 s
c. Evacuation at 618 K, θ = 0.25, T_1 = 1.64 s
d. Evacuation at 663 K, θ = 0.15

clean γ-Mo₂N and the temperature was then ramped to 873 K under flowing He. The rates of ammonia and nitrogen desorption were followed as a function of temperature using a mass spectrometer and the results are shown in Fig. 5. Three overlapping ammonia peaks are evident at 400, 550, and 650 K. Nitrogen desorption is observed above 673 K. These results suggest that ammonia is held in several states, and that above 673 K, desorption is accompanied by ammonia decomposition.

A time-interrupted TPD NMR technique was used (8, 12) to identify the structure of species formed during the decomposition of ammonia. These experiments were performed in the following manner. Ammonia was adsorbed at 298 K. Proton lineshapes and spin–lattice relaxation time (T_1) measurements were then obtained at 298 K after the sample had been evacuated for 2 h at 298, 473, 618, 663, and 773 K. Figure 6 illustrates the resulting spectra and the corresponding values of T_1. The lineshape of the spectra obtained following high-temperature evacuation has the appearance of a triplet. With increasing evacuation temperature, the intensities of the peaks decrease and the value of T_1 increases. After evacuation at 773 K, there was no detectable proton signal. The T_1 observed at 298 K is probably the result of rapidly fluctu-
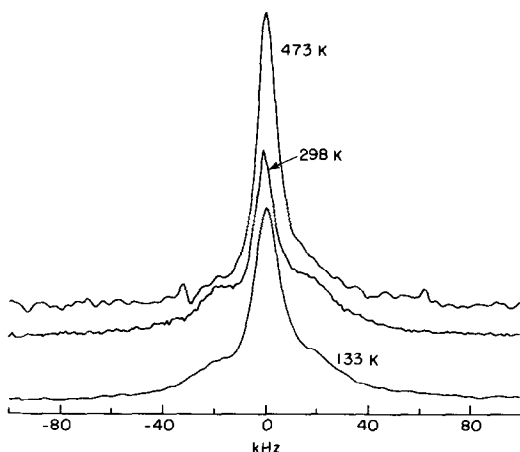
FIG. 5. Temperature-programmed desorption of NH₃ from γ-Mo₂N.

FIG. 7. ¹H lineshape of NH₃ irreversibly held on γ-Mo₂N evacuated at 473 K. Spectra taken at 133, 298, and 473 K.

ating dipolar fields due to the motion of the species contributing to the narrow component.

The spectra presented in Fig. 6 clearly demonstrate that the lineshape changes as the evacuation temperature increases. This suggests that new species (e.g., NH₂, NH, and H) are produced on the catalyst surface as ammonia undergoes thermal decomposition. It was decided to do further NMR lineshape experiments on samples evacuated at 473 K, and 573 K, since they show the triplet character and still afford a reasonable signal-to-noise ratio. To identify the nature of the species present following evacuation at elevated temperatures, lineshape, echo, and selective inversion experiments werre carried out.

After evacuation of the sample at 473 K, lineshapes were recorded at three temperatures and the results are shown in Fig. 7. The lineshapes observed at 133 and 298 K are very similar, in contrast to what is observed after evacuation at 298 K (see Fig. 2). This indicates that the motional frequency of the adsorbates is significantly reduced from the case of evacuation at 298 K. However, as the temperature is raised to the evacuation temperature (473 K), the broad component appears to be motionally

averaged and it fades into the central part of the lineshape. The shoulders reappear upon cooling to 298 K. Details of the motion observed at 473 K will be addressed after a structural assignment has been made for the broad component.

A lineshape with two shoulders around a central peak with the high-frequency shoulder "melting" into the central peak was seen for three different samples at 298 K after evacuation at 473 K. The presence of a local minimum between the low-frequency shoulder and the central peak demonstrates that the broad component cannot be assigned to a single Gaussian component. The high- and low-frequency shoulders (see Fig. 7) in the system under investigation are most likely due to dipolar splitting of the proton resonance by a few neighboring spins. The frequency separation between the central peak and the shoulders ($\sim$22 kHz = 122 ppm) is at the outer limit of observed proton chemical shifts. Large contributions from the Knight shift are ruled out on the basis of both T_1T and shift measurements for hydrogen on γ-Mo₂N (8), and the magnitude of T_1T for the present results.
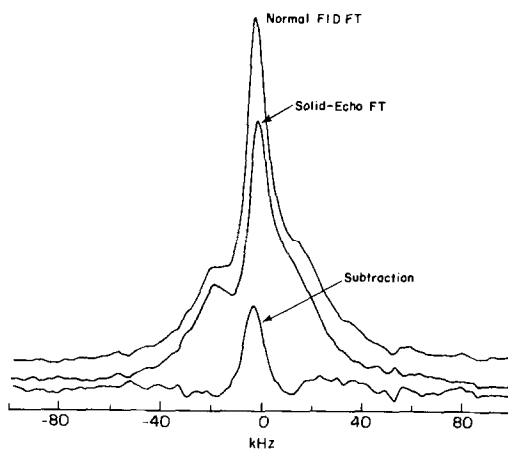
Figure 8 shows the lineshape resulting

FIG. 8. ¹H lineshape of NH₃ irreversibly held on γ-Mo₂N evacuated at 473 K. Fourier transform of FID following a 90° pulse and a solid echo. Bottom spectrum is a subtraction of the solid-echo lineshape from the total ¹H lineshape.
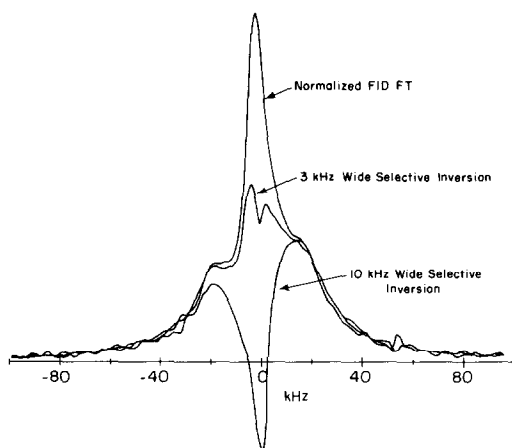
FIG. 9. Selective inversion of central peak for NH₃ on γ-Mo₂N evacuated at 473 K. Indicating the I_z (isolated spin-$\frac{1}{2}$) character of the central peak.

from a solid-echo ($\tau = 20$ μs) experiment compared to the lineshape resulting from a normal free-induction decay. A difference spectrum is also shown. Since the solid echo totally refocuses the dipolar interaction (9), but only partially refocuses interactions linear in I_z (10), the existence of a difference spectrum for the case of evacuation at 473 K suggests that the central peak is *not* the result of strong dipolar coupling between spins. One possibility is that this peak is due to isolated NH groups or atomic H on the surface.

To further confirm the assignment of the central component to isolated spin-$\frac{1}{2}$ particles, selective inversion experiments were performed. The results of these experiments are presented in Fig. 9. A 3-kHz-wide selective inversion pulse (180° pulse set for spin-$\frac{1}{2}$) partially inverts a narrow line in the center of the central peak, indicating that this feature is not dominated by homonuclear dipolar coupling. A 10-kHz-wide selective 180° pulse set for a spin $-\frac{1}{2}$ particle inverts virtually all of the central peak. If the central peak were to represent an $m_I = \frac{1}{2} \Leftrightarrow m_I = -\frac{1}{2}$ central transition of a rotating three-coupled spin $-\frac{1}{2}$ system (e.g., intact NH₃ molecules that are not able to translate) we would have observed a

360° rotation of the central peak magnetization. Thus, the results shown in Fig. 9 provide strong evidence that the central peak is due to isolated spin $-\frac{1}{2}$ particles.

Such isolated spins could arise from either NH groups or atomic H on the surface. Since homonuclear dipolar coupling dominates the lineshape for hydrogen adsorbed on γ-Mo₂N (8), the selective inversion results show that the central component considered here does not arise from clustered atomic hydrogen similar to that observed for hydrogen adsorption. We must therefore conclude that the central component arises from NH groups, or atomic hydrogen adsorbed at sites other than those involved in H₂ adsorption.

Solid-echo and Hahn-echo experiments were used to probe the broad component of the spectrum observed after evacuation of adsorbed ammonia at 473 K. As seen in Fig. 10, the solid-echo experiment strongly refocuses the short T_2 components, while the Hahn-echo experiment seems to result in only a weak echo buried beneath the original FID evolving under the dipolar Hamiltonian. For the 20-μs delay time shown for the Hahn echo, we would expect a weak echo for components linear in I_z (long T_2) compared to the dipolar coupled components (short T_2) that have not yet totally dephased. These observations confirm the spin-$\frac{1}{2}$ nature of the narrow component and indicate that the broad component is a result of strong dipolar coupling between spins.

As shown in Fig. 11, a successful fit of the spectrum of adsorbed NH₃ evacuated at 473 K can be achieved by assuming a Pake doublet (13) with a superimposed Lorentzian. The doublet can be attributed to the existence of NH₂ groups on the γ-Mo₂N surface, while at least part of the central peak is a result of isolated H atoms, probably in the form of NH groups. The best-fit dipolar splitting for the Pake doublet is 45 kHz, while the Gaussian convolution width applied to the doublet is 6 kHz. A doublet width of 42 kHz would be expected for a
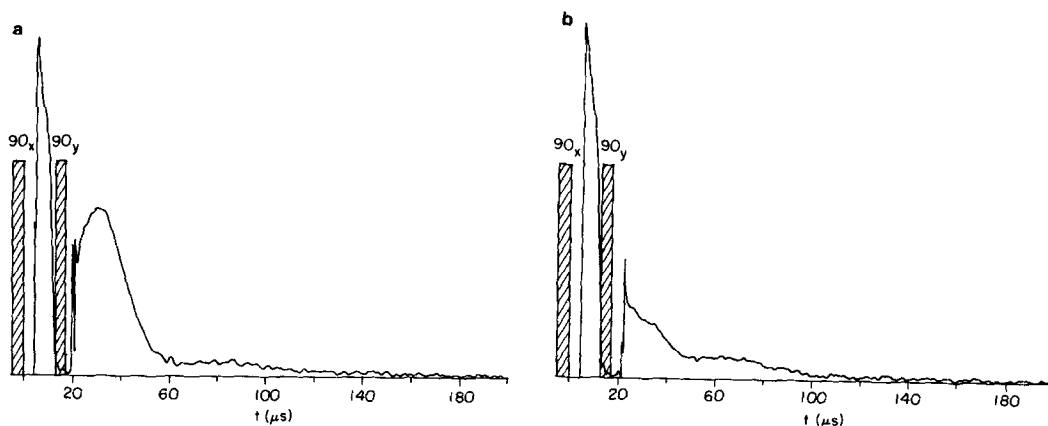
FIG. 10. Power free induction decays for $\tau = 20$ μs echo sequences performed on NH_3 irreversibly held on γ-Mo_2N evacuated at 473 K. (a) Solid-echo sequence. (b) Hahn-echo sequence.

rigid rotor NH_2 group with bond lengths and angles the same as those in methylamine. From the lineshape recorded at 473 K (see Fig. 8), it is clear that the NH_2 groups translate or equilibrate rapidly with other structures at 473 K. The strong dipolar coupling between the two protons of the NH_2 group is averaged due to motion, causing *both* shoulders to disappear simultaneously. It is significant to note that the spectrum shown in Fig. 11 does not fit well to a Gaussian-broaded triplet lineshape for rapidly rotating NH_3 groups (*11*).

The asymmetry observed in the spectrum recorded following the evacuation of adsorbed ammonia at 473 K is difficult to explain. Three possible sources can be considered. The first is that the asymmetry could arise from the chemical-shift anisotropy resulting from the N–H bond. While there appear to be no published values for the principal components of the chemical-shift tensor for NH groups, it is unlikely that the maximum separation between tensor components is greater than 15 ppm (*14*). Anisotropies of this magnitude will have little effect on a lineshape dominated by dipolar splitting (250 ppm for NH_2). A second possibility is that the asymmetry is due to random phasing problems associated with the spectrometer. It is unlikely though

that this is a principal source of the asymmetry, since the lineshape shown in Fig. 11 could be obtained reproducibly. The asymmetry also does not appear to arise from left shifting the free-induction decay, since it is observed in Fourier transforms of echoes as well. A third possibility is that the asymmetry arises from adsorbed hydrogen atoms clustered in a manner similar to that observed upon adsorption of hydrogen on γ-Mo_2N (*8*). As shown in Fig. 11, the addition of a Gaussian component (FWHM = 25 kHz) allows us to achieve a good fit to
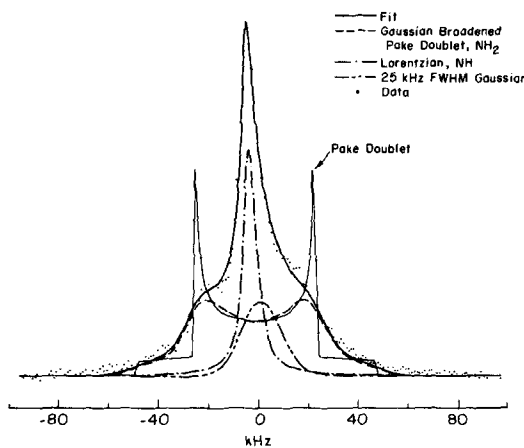

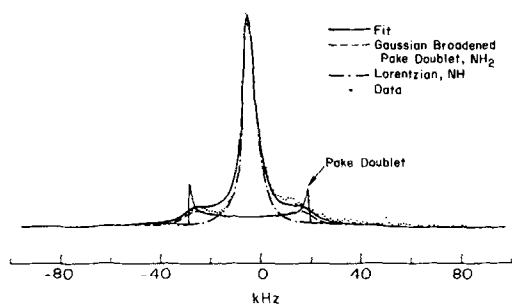FIG. 11. Data after evacuation at 473 K fit to a Pake doublet, Lorentzian, and a 25-kHz FWHM Gaussian.

FIG. 12. Data after evacuation at 573 K fit to a Pake doublet and a Lorentzian.

the experimentally observed lineshape. It should be noted, though, that the position of the Gaussian component is 20 ppm higher than that observed for atomic hydrogen on γ-Mo₂N.

In summary, the data for the case of evacuation at 473 K suggest that molecular NH₃ is no longer the predominant surface species and that stable NH and NH₂ fragments now dominate the lineshape. It is unclear what causes the observed asymmetry in the lineshape spectra.

Evacuation at 573 K results in the lineshape shown in Fig. 12. At this point, the ratio of doublet intensity to central peak intensity is considerably reduced, suggesting an increased ratio of NH to NH₂ groups. Since a component representative of clustered atomic H is not required to achieve a reasonable fit of the lineshape after evacuation at 573 K, it must be concluded that clustered atomic H is not present in this case, although it should be noted that here again the left-hand shoulder of the doublet is slightly exaggerated.

The NMR results provide a means for interpreting the NH₃ TPD spectrum shown in Fig. 5. It seems reasonable to conclude that the first peak arises from the desorption of loosely held molecular NH₃. The second desorption peak may be due to the recombination of NH₂ groups with atomic hydrogen. The third peak may arise from the hydrogenation of NH groups. The hydrogen required for the addition of hydro-

gen atoms to NH₂ and NH groups is provided by NH$_x$ species that undergo total dehydrogenation and eventually desorb as dinitrogen above 673 K.

CONCLUSIONS

At room temperature, ammonia adsorbs molecularly on γ-Mo₂N, the amount of ammonia adsorbed at saturation corresponding to slightly less than one-half of that projected on the basis of the BET surface area. The proton NMR spectrum of adsorbed ammonia indicates that a portion of the adsorbate is strongly bound to the catalyst surface, but undergoes rotation about the threefold axis of the NH₃ molecule; the balance of the adsorbed ammonia appears to be in rapid motion across the catalyst surface, or in rapid exchange with dilute gas-phase NH₃. Upon heating under vacuum, adsorbed NH₃ undergoes progressive dehydrogenation to produce NH₂ and NH groups as well as N and H atoms. The NH₂ groups rotate rapidly about the twofold axis of the group, but neither NH₂ nor NH translates easily across the catalyst surface at room temperature.

REFERENCES

1. Aika, K., and Ozaki, A., "Catalysis, Science and Technology" (Anderson and M. Boudart, Eds.), p. 87. Springer-Verlag, Berlin, 1981.
2. Aika, K., and Ozaki, A., J. Catal. 14, 311 (1969).
3. Hillis, M. R., Kemball, C., and Roberts, M. W., Trans. Faraday Soc. 62, 3570 (1966).
4. Volpe, L., and Boudart, M., J. Phys. Chem. 90, 4874 (1986).
5. Volpe, L., and Boudart, M., J. Solid State Chem. 59, 348 (1985).
6. Ranhotra, G. S., Haddix, G. W., Bell, A. T., and Reimer, J. A., J. Catal. 108, 24 (1987).
7. Haddix, G. W., Reimer, J. A., and Bell, A. T., J. Catal. 106, 115 (1987).

8. Haddix, G. W., Reimer, J. A., and Bell, A. T., *J. Catal.* **108,** 50 (1987).

9. Mansfield, P., *Phys. Rev. A* **137**(3), A961 (1965).

10. Hahn, E. L., *Phys. Rev.* **80**(4), 580 (1950).

11. Andrew, E. R., and Bersohn, R., *J. Chem. Phys.* **18**(2), 159 (1950).

12. Apple, T. M., Gajardo, P., and Dybowski, C., *J. Catal.* **68,** 103 (1981).

13. Pake, G. E., *J. Chem. Phys.* **16,** 327 (1948).

14. Haeberlen, U., "High Resolution NMR in Solids, Selective Averaging," p. 150. Academic Press, New York, 1976.