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Characterization of H_2 Adsorbed on γ-Mo_2N by NMR Spectroscopy

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Nuclear magnetic resonance (NMR) techniques were used to study hydrogen dissociatively adsorbed on high-surface-area (~120 m^2/g) γ-Mo_2N. Based upon proton NMR measurements, we conclude that hydrogen adsorbs on the surface of γ-Mo_2N in the form of rafts of localized hydrogen atoms which occupy only 10% of the total BET surface area. Furthermore, we conclude that the surface hydrogen is strongly bound to the catalyst. The implications of these conclusions for the details of hydrogen adsorption sites and ammonia synthesis are discussed. © 1987 Academic Press, Inc.

INTRODUCTION

The catalytic properties of γ-Mo_2N have been the subject of several recent investigations. These studies have shown that γ-Mo_2N exhibits activity for the formation of methane from both CO and CO_2, and ammonia from N_2 (*1–6*). Since both chemical processes involve adsorbed H_2, there is an interest in understanding the ordering and mobility of adsorbed H_2 on γ-Mo_2N. The application of proton nuclear magnetic resonance (NMR) for this purpose is described here.

EXPERIMENTAL

The catalyst used in this study was prepared by NH_3 reduction of MoO_3 (*7, 8*). To achieve high surface area, the reduction temperature was raised from 298 to 973 K over 9 h. At the end of the reduction, the γ-Mo_2N was cooled to 298 K in flowing NH_3. The freshly prepared nitride was passivated in a 1% O_2/He mixture to prevent possible rapid oxidation of the catalyst upon exposure to air.

The passivated nitride was characterized to determine its structure, surface area, and pore size. Both X-ray and electron diffraction established that the passivated material was 100% γ-Mo_2N. The BET surface area was ~120 m^2/g. TEM observations confirmed the "holey platelet" morphology reported previously (*7, 8*). From a through-focus series of electron micrographs, the average pore radius was determined to be 2 nm. A similar value was also obtained from an analysis of the hysteresis loop in the complete BET isotherm.

Proton (^1H) NMR spectra were recorded with home-built 180- and 270-MHz spectrometers. The probe of the 180-MHz spectrometer was designed to include a small quartz microreactor which could be cooled or heated (*9*). To avoid air exposure of the nitride samples used to study H_2 adsorption, γ-Mo_2N was prepared in the microreactor and freed of residually adsorbed NH_3 by evacuation at 773 K. (This temperature was established to be sufficient by a NH_3 TPD experiment.) H_2 was then adsorbed onto the sample to achieve saturation coverage, and then gas-phase H_2 and any reversibly adsorbed H_2 was removed by evacuation at 298 K. Air-exposed samples can be renitrided by simply heating in flowing NH_3 at 973 K for 1 h. This does not affect the BET surface area, the crystal structure, or the H_2 uptake characteristics.

NMR spectra were obtained by cosubtracting 10,000 free induction decays, following phase-alternated 90° pulses. The spin–lattice relaxation time, T_1, was measured using the inversion recovery tech-

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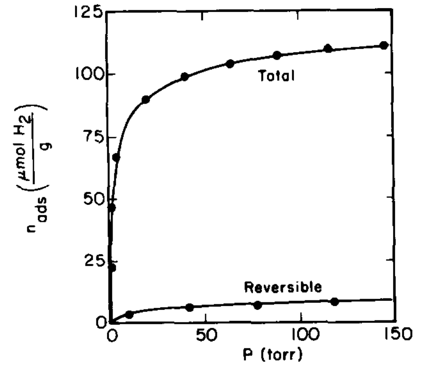

FIG. 1. Total and reversible adsorption isotherms for H_2 on γ-Mo_2N measured at 298 K.

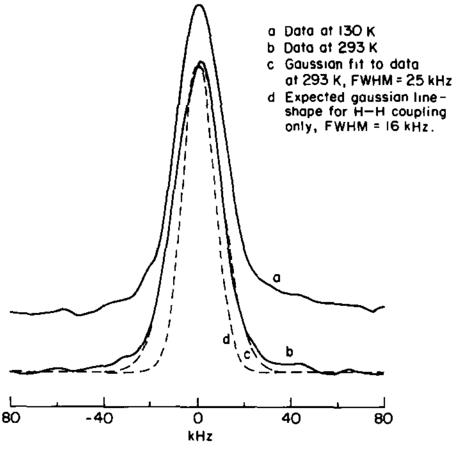

FIG. 2. ^1H NMR spectra of H_2 adsorbed on γ-Mo_2N at 130 and 298 K.

nique in a cosubtraction mode. Spin echoes were also measured in a cosubtraction mode using a 90°–τ–180° pulse sequence. Each point in the spin echo and inversion–recovery decays represents 2000 signal averages. Tune-up of the probe was performed on air-exposed samples of Mo_2N (adsorbed H_2O from the air provides a strong ^1H signal). Samples were then renitrided in the probe, H_2 was adsorbed, and the NMR data recorded. Typical 90° pulse lengths for the probe were 3.5 μs. Probe ringdown was typically 4 μs (*9*).

RESULTS AND DISCUSSION

Figure 1 shows the total and reversible adsorption isotherms for H_2. The maximum total uptake of H atoms is approximately 200 μmol/g. This corresponds to about 10% of what might be expected based on the BET area of the sample.

Proton spectra for the irreversibly adsorbed H_2 at maximum coverage are presented in Fig. 2. At 293 and 130 K only a single Gaussian line is observed with a full width at half-maximum intensity (FWHM) of 25 kHz. Both the Gaussian character of the ^1H lineshape and the absence of change in the FWHM with temperature indicate that the adsorbed H atoms are immobile on a time scale of 100 μs (*10*).

The temperature and frequency dependence of the spin–lattice relaxation time constant (T_1) were examined for the case of maximum adsorbate coverage. Measurements were made for 180 MHz at 120 and 293 K, and for 270 MHz at 293 K. The results of these measurements are shown in Fig. 3. At 120 K, relaxation measurements were made only for pulse delays (between the 180° pulse and the 90° pulse) greater than 0.1 s. From the slope of the line representing the 120 K data, T_1 is deter-

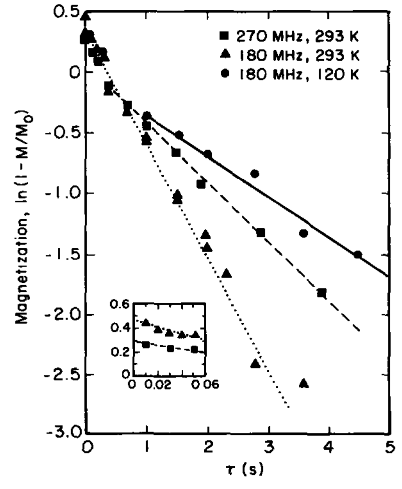

FIG. 3. Results of inversion recovery experiments. Each point represents 2000 signal averages. A 180°–τ–90° inversion–recovery sequence was used. Slopes of the decays shown are proportional to $1/T_1$.

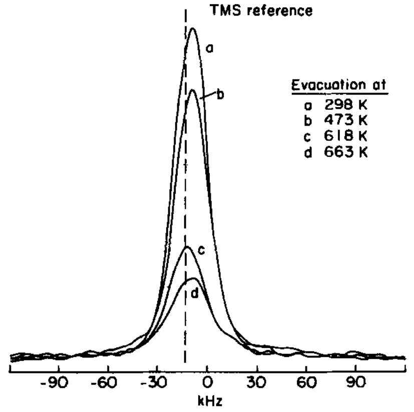

FIG. 4. ^1H NMR spectra taken at 293 K following desorption of H_2 *in vacuo* at progressively elevated temperatures.

mined to be 2.9 s. The data in Fig. 3 clearly show that at 180 MHz and 293 K the relaxation can be fit roughly to the sum of two exponentials with time constants of 0.5 (see inset) and 1.2 s. For the longer T_1 data at 180 MHz, the product T_1T is 346 K · s at 120 K and 340 K · s at 293 K. The fact that T_1T is nearly independent of temperature at 180 MHz suggests that the spin of the proton couples to the spin of electrons in the conduction band of γ-Mo_2N, but is insufficient to discount relaxation by localized motion of the spins. The fact that the long T_1 at 270 MHz (2.1 s) is approximately a factor of 2 greater than T_1 at 180 MHz (1.2 s) suggests that the relaxation is primarily a result of localized low-frequency motion that is unobservable in the linewidth experiments. We conclude that spin–lattice relaxation most likely results from a combination of motions at various low frequencies (a result of site inhomogeneity) and coupling to conduction electrons of the γ-Mo_2N.

The effect of adsorbate coverage on the NMR spectrum FWHM was investigated in two ways. The first approach was to lower the coverage to one-half of the maximum level by simply adsorbing only half of the expected uptake. The ^1H spectrum FWHM and spin-echo decay observed in this case were identical to those found for maximum adsorbate coverage. Completion of the isotherm after the NMR experiments confirmed the existence of half-maximum coverage, as did NMR spin counts for both cases. The second approach involved the stepwise desorption of H_2 at progressively higher temperatures from a nitride sample initially saturated with adsorbed H_2. The spectrum observed after each period of desorption is given in Fig. 4. Here again, it is evident that neither the lineshape nor the FWHM change with H atom coverage. Surface coverages after desorption can be attained by simply integrating the NMR spectrum and comparing to the known initial maximum coverage. T_1 measurements at maximum and half-maximum coverage indicated no T_1 dependence on coverage.

Spin-echo experiments were conducted to identify the extent to which H–H dipolar coupling contributes to the observed linewidth of the ^1H spectrum. The variation in magnetization with delay time (τ) is given in Fig. 5 for maximum and one-half maximum H-atom coverage. The data for both coverages are identical and decay exponentially. The relaxation time constant for H–H dipolar coupling (i.e., the dipolar T_2) was determined to be 150 μs, which corresponds to a

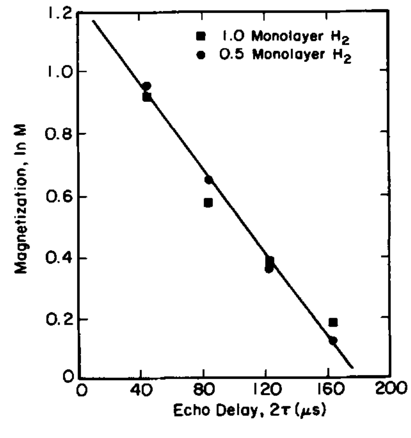

FIG. 5. Spin-echo decay measurement. Each point represents 2000 signal averages. A 90°–τ–180° Hahn spin-echo sequence was used. Slope of the decay shown is proportional to the local density of H atoms.

Gaussian FWHM of 16 kHz. This value of the FWHM is approximately a factor of 1.5 smaller than that observed in the spectra presented in Figs. 2 and 4 (approximately 25 kHz). The remaining broadening results from a distribution of isotropic chemical shifts (from site inhomogeneity, see T_1 dispersion in Fig. 3). The chemical-shift anisotropy for ^1H is small compared to the observed linewidth as are also heteronuclear dipolar interactions (i.e., with molybdenum and nitrogen). Susceptibility broadening was checked also and cannot account for the extra broadening.

The interatomic spacing between hydrogen atoms needed to achieve a FWHM of 16 kHz was calculated by the method of moments (*10*). Assuming that there are four nearest-neighbor H atoms gives a spacing of 0.27 nm, whereas assuming that there are six nearest-neighbor H atoms gives a spacing of 0.28 nm. These spacings are close to that for nearest-neighbor adsorption sites (0.31 nm) calculated on the basis of the known structure of the low-index surfaces of γ-Mo_2N, but are considerably smaller than the spacings calculated on the assumption that the total irreversible uptake is distributed over the available surface area. For saturation coverage, the latter method leads to an H–H nearest-neighbor distance of 1.0 nm, and for one-half saturation, to an interatomic distance of 1.4 nm. It is apparent, therefore, from the spin-echo experiments that H_2 adsorbs in the form of rafts and that the spacing between H atoms in the rafts is independent of the H-atom coverage.

Two important conclusions emerge from the results of this study. The first is that H_2 adsorbs on the surface of γ-Mo_2N in the form of rafts of localized H atoms, which occupy at most only 10% of the total BET surface area. The second conclusion is that the irreversibly held H_2 is strongly bound to the nitride surface since significant H_2 desorption does not occur below 473 K and measurable quantities of adsorbed H are retained up to temperatures as high as 663 K. The occurrence of H_2 in the form of rafts of strongly bound H atoms suggests that H_2 adsorption occurs at nitrogen-deficient patches of Mo present on the nitride surface. This interpretation is supported by the knowledge that the heat of adsorption for H_2 on polycrystalline Mo is ~40 kcal/mol (*11*). Moreover, it is known that C atoms in the fourfold hollows of Mo(100) strongly suppress the adsorption of H_2 (*12*), and it is therefore expected that the presence of N atoms on the surface of Mo should play a similar role. While the presence of metallic Mo was never observed directly in the present study, it is still possible that during desorption of NH_3 from the surface of γ-Mo_2N, small patches of Mo devoid of interstitial nitrogen are formed. Such an interpretation might also explain why the saturation uptake of H_2 is so much smaller than that predicted from the BET surface area.

Finally, it is worth speculating on the implications of these conclusions for the synthesis of ammonia over γ-Mo_2N. The nitride has activity comparable to that of promoted iron catalysts (*13*), and there is some controversy concerning the rate-limiting step of the reaction (*14, 15*). On iron catalysts, it is well known that the dissociative adsorption of N_2 is rate limiting (*13*), but for γ-Mo_2N some evidence exists which supports the view that surface hydrogenation steps are rate limiting (*14*). Our conclusions strongly suggest that the adsorption of strongly bound H atoms in small rafts could limit the availability of hydrogen in surface reactions. We are continuing proton and nitrogen NMR experiments of hydrogen, nitrogen, and ammonia adsorbed on γ-Mo_2N in an effort to elucidate the mechanism of ammonia synthesis.

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