CHARACTERIZATION OF CO ADSORBED ON γ-Mo_2N BY NMR SPECTROSCOPY

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Solid-state nuclear magnetic resonance techniques have been used to show that CO adsorbs in a molecular state on γ-Mo_2N (fcc). An axially symmetric chemical shift powder pattern is observed for ^{13}CO adsorbed at 298 K. The observed lineshape is very similar to that observed for $Mo(CO)_6$. Lineshapes for the α (hcp) and β (fcc) phases of Mo_2C were also recorded for comparison.

1. Introduction

Several recent studies have shown that Mo_2C and Mo_2N are active catalysts for CO hydrogenation to form hydrocarbons [1–7]. An interest arises, therefore, in knowing the state of adsorbed CO on such catalysts. In particular, it is desirable to determine whether CO adsorbs molecularly or undergoes dissociation. Since unsupported transition metal nitrides and carbides are metallic in nature, it is difficult to observe adsorbates on the surface with optical spectroscopies. Structural identification of adsorbed species can be performed, however, using NMR spectroscopy [8,9]. This note reports on the results of a ^{13}C NMR study of CO adsorbed on unsupported γ-Mo_2N.

2. Experimental

Unsupported γ-Mo_2N (100 m^2/g) was prepared by temperature programmed reduction of MoO_3 in NH_3 [10,11]. This reaction was carried out in a flow-through quartz microreactor contained in a variable temperature NMR probe [12]. Ammonia held on the catalyst after synthesis was removed by evacuation to 10^{-6} torr at 773 K. 99% ^{13}CO (Isotec) was then adsorbed on the catalyst surface at 298 K, after which the sample was evacuated to $< 10^{-6}$ torr to remove any physisorbed material. The sample was isolated in 900 torr He prior to the NMR experiments.

Natural abundance samples of α-Mo_2C (hcp phase) were obtained from Alfa Chemical, and were not treated further. The sample of β-Mo_2C (fcc phase) was prepared by temperature programmed reduction of γ-Mo_2N in a 3 : 1 H_2/CH_4 mixture flowing at 150 cm^3/min [10, 11].

^{13}C NMR measurements were carried out with a home-built spectrometer operating at 45.6 MHz. The probe circuit used was the ^{13}C side of a ^{13}C-^1H double resonance circuit similar to that discussed in ref. [13]. Typical 90° pulse durations were 6 μs at ~ 500 W of transmitter power. Probe ringdown following rf pulses was ~ 5 μs. Lineshapes were obtained by Fourier transformation of several thousand cosubtracted [14a] free induction decays. The actual number of signal averages varied for measurements taken at 298 K and at 77 K. No significant change was observed between any of the lineshapes recorded at 298 K and 77 K. Cosubtraction [14a] was implemented by alternately applying a 180° total inversion prepulse and dephasing delay to the spin system. In order to probe the motion and dipolar coupling of the ^{13}C in adsorbed ^{13}CO, spin-echo measurements were performed at 298 K and 77 K. 5000 signal averages were employed for each echo delay. Relaxation times (T_1) for CO on γ-Mo_2N were 4 ± 1 s at 298 K and 8 ± 1 s at 77 K as measured by the saturation-recovery technique. Exact T_1 values were difficult to obtain due to signal noise limitations and the fact that there appears to be a distribution of T_1's across the lineshape (i.e., different relaxation times for different orientations of the chemical shift tensor with respect to the applied magnetic field). Recycle delays for the Mo_2C lineshape experiments were set at 10 s, although only very rough estimates of T_1 were made on these materials.

3. Results and discussion

Figure 1 shows the total and reversible adsorption isotherms for CO on γ-Mo_2N. The maximum uptake (irreversible plus reversible) is approximately 620 μmol/g. This corresponds to 35% of what might be expected based on the BET surface area of the sample, and the assumption of CO adsorption in either four-folds hollows or on available metal atoms in low index ([100], [110], [111]) planes of γ-Mo_2N.

Figure 2 shows the NMR lineshape for ^{13}CO on γ-Mo_2N recorded at 77 K and at 298 K. The lineshape observed is an axially symmetric chemical shift powder pattern [14b] similar that observed for transition metal carbonyls [15,16]. As can be seen in table 1, the principal components of the chemical shift tensor for CO on γ-Mo_2N agree with the principal components observed for $Mo(CO)_6$. This suggests that CO adsorbs on γ-Mo_2N molecularly and that the Mo-C bond is similar to that of $Mo(CO)_6$. However, the similarity of the principal components

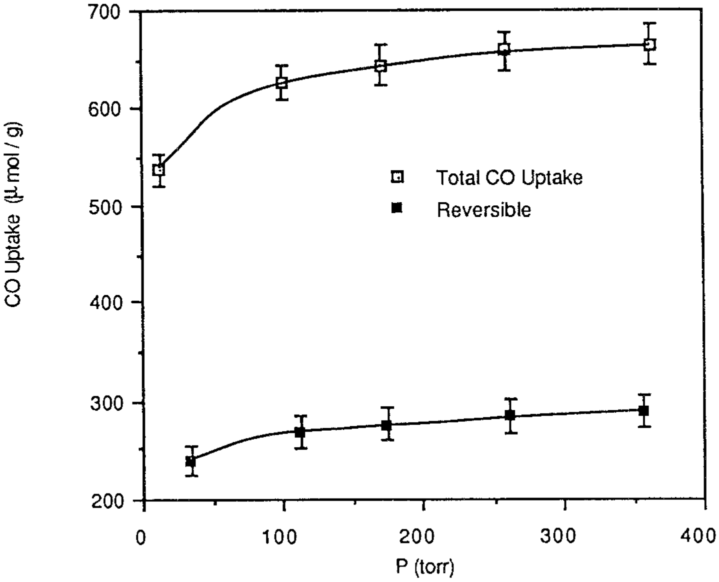

Fig. 1. Total and reversible CO uptake on 100 m^2/g γ-Mo_2N.

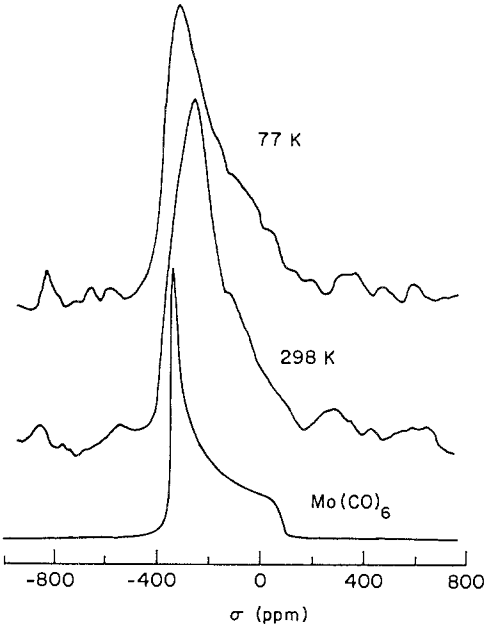

Fig. 2. ^{13}C NMR lineshape for ^{13}CO adsorbed on γ-Mo_2N at 298 K, spectra recorded at 298 K and 77 K. The spectrum at 298 K is the result of 80,000 signal averages. The spectra at 77 K is the result of 20,000 signal averages. Also shown is a chemical shift powder pattern with the same principal components as $Mo(CO)_6$.

Table 1
Chemical shift data

Compound	$\langle\sigma\rangle$ [1]	σ_{11}	σ_{22}	σ_{33}	Reference
CO on γ-Mo_2N	−198	−330 [2]	−330	65	This work
$Mo(CO)_6$	−204	−343	−343	71	[15]
	−202	−338	−332	65	[16]
β-Mo_2C (fcc)	−290 [3]	–	–	–	This work
α-Mo_2C (hcp)	−275	–	–	–	This work; [22]

[1] All values are given in ppm from the ^{13}C resonance in tetramethylsilane using the σ scale. Downfield is negative.

[2] The principal components were determined by fitting the spectra to a symmetric chemical shift powder pattern using a 2.5 kHz Gaussian broadening function.

[3] The NMR spectra of the α and β phases of Mo_2C showed no apparent chemical shift anisotropy and were not fit to powder patterns.

of the chemical shift tensor for adsorbed CO and $Mo(CO)_6$ does not necessarily imply multiple adsorption of CO molecules at individual Mo sites on the surface of γ-Mo_2N.

Spin echo experiments were carried out at 298 K and 77 K to characterize the mobility of adsorbed CO. The results of these experiments indicate little change in the motional state of adsorbed CO upon increasing the temperature from 77 K to 298 K. The T_2 of the echo decay envelope for ^{13}CO adsorbed on γ-Mo_2N is 1150 μs.

Assuming the spin-echo decay is solely due to homonuclear dipolar coupling, the average distance between spins can be calculated using the Van Vleck equation [17]. For a T_2 of 1150 μs, the ^{13}C-^{13}C distance is estimated to be 2.3 Å for four nearest neighbor ^{13}CO species. This distance is significantly smaller than the average distance between four-fold sites on the surface of γ-Mo_2N, which is 3.1 Å for the (100), (110) and (111) planes. The unusually short distances between spins estimated on the assumption that only homonuclear dipolar fluctuations mediate the dephasing of the ^{13}C magnetization suggests that the ^{13}C spins experience additional time-dependent field fluctuations. One possibility is that the spin echoes are affected by heteronuclear dipolar interactions between the observed spins and a rapidly dephasing spin bath [18]. For CO adsorbed on γ-Mo_2N, it is conceivable that relatively weak dipolar coupling between ^{13}C and surface ^{14}N could result in rapid dephasing of the ^{13}C spin due to very rapid dephasing of surface ^{14}N in a non-Zeeman state. Quadrupolar ^{14}N is likely to interact with strong electric field gradients at the catalyst surface, which would result in a very short T_2 for ^{14}N at the surface. Another possibility is that adsorbed CO experiences some non-activated low frequency motion at 77 K, as well as 298 K. Such low frequency motion could be the dominant relaxation mechanism and would invalidate the assumption that homonuclear dipolar coupling regulates the dephasing of the ^{13}C magnetization. It is worth noting that our

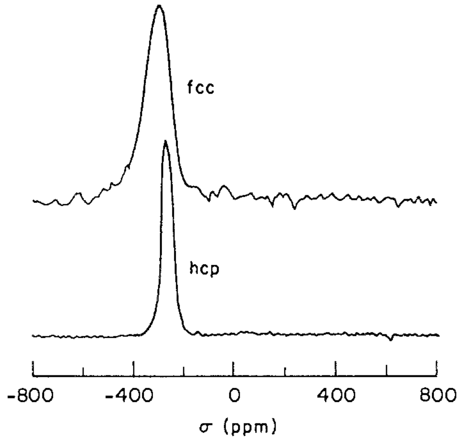

Fig. 3. ^{13}C NMR lineshapes for carbon in fcc Mo_2C and hcp Mo_2C at 298 K. Both spectra are the result of 20,000 signal averages.

NMR studies of hydrogen, ammonia, and acetonitrile on γ-Mo_2N all exhibit relaxation behavior that is attributable to low frequency motions.

To confirm that the observed ^{13}C NMR spectrum is due to adsorbed CO and not to carbon atoms in the lattice of γ-Mo_2N, spectra were recorded for the fcc and hcp phases of Mo_2C. The structure of the fcc phase of Mo_2C is nearly identical to that of γ-Mo_2N, and it is known that carbon can occupy vacant octahedral sites in the γ-Mo_2N [10]. Shown in fig. 3 are the lineshapes for α-Mo_2C (hcp) and β-Mo_2C (fcc). In neither case is a powder pattern observed, consistent with what would be expected for carbon atoms occupying lattice sites with greater than tetrahedral symmetry [14b]. It is also noted that the isotropic chemical shift for carbon in both phases of Mo_2C is significantly different from that for carbon in adsorbed CO. It would therefore appear that very little of the carbon from adsorbed CO enters into the lattice of γ-Mo_2N. This conclusion is in agreement with the observation that CO dissociation does not occur at room temperature on a nitrided Mo(110) surface, the structure of which is very similar to the (100) surface of γ-Mo_2N [19]. Similar observations have been made for carbided Mo(110) surfaces [20,21]. This is in distinct contrast to the neat Mo surface, which readily dissociates CO. Indeed, the ameliorating effects of carbon or nitrogen alloying atoms is a significant factor in nitride and carbide catalysis [7,8,19–21].

4. Conclusions

^{13}C NMR measurements clearly show that CO bonds in a molecular state on γ-Mo_2N. The observed principal components of the chemical shift tensor are very similar to those for $Mo(CO)_6$.

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