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Formic Acid on Titania: Motional Properties and Desorption of Chemisorbed Species

T. W. ROOT AND T. M. DUNCAN

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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NMR spin-labeling and isotopic labeling have been used to characterize exchange between physisorbed and chemisorbed formic acid and within chemisorbed formic acid adsorbed on TiO_2. Contrary to behavior assumed in earlier studies, the exchange between physisorbed and chemisorbed formic acid has a relatively long time constant, between 2 and 400 s at 298 K. Reorientation occurs within the chemisorbed adlayer with a broad distribution of time constants centered at ~20 ms. A possible interpretation of this reorientation is rotation about the surface–formate bond, hindered by hydrogen bonding to neighboring hydroxyl groups. The application of NMR spin-labeling to the characterization of dynamics at interfaces is discussed.

I. INTRODUCTION

Formic acid decomposition is a simple reaction, and as such has received much attention as a prototypical unimolecular catalytic reaction. The reaction products over titania are usually CO and H_2O (*1*). Active site densities are typically 10^{12} cm^{-2}, a small fraction of the saturation coverage of 4×10^{14} cm^{-2}, and the majority of surface sites are unreactive. Two possible mechanisms for the rapid decomposition rate are: (1) desorption, readsorption, and reaction of formic acid initially adsorbed in unreactive sites or (2) surface diffusion resulting in migration from unreactive to reactive sites. This study considers both possibilities, which require that formic acid migrates from an active site without reacting.

Formic acid dehydration over titania has been the subject of many studies (*1*). From transition state theory, Maatman (*2*) concluded that the active site concentration must be on the rough order of 10^{12} cm^{-1} to prevent the entropy of activation from reaching unreasonably large negative values. Using electron spin resonance, Enriquez and Fraissard (*3*) found the electron-donating site density and reaction rate had the same dependence on sample preparation, and concluded that these were the active sites. The densities of electron-donating sites ranged from 1×10^{12} to 1.2×10^{13} cm^{-2}, consistent with the number predicted by analysis of reaction prefactors. In an accompanying study (*4*), ^1H and ^{13}C NMR spectra for multilayers of adsorbed formic acid were reported. From the observed shift in the physisorbed formic acid peak, Enriquez and Fraissard proposed the existence of a paramagnetically shifted chemisorbed adsorption site based on an assumption of rapid exchange between the physisorbed and chemisorbed species.

In a previous paper (*5*), we directly observed formic acid chemisorbed on the surface in majority sites. The NMR spectrum for chemisorbed formic acid had a homogeneous linewidth of 0.49 kHz, demonstrating that the lower limit for the residence time in this site is 0.3 ms. This paper demonstrates the application of NMR techniques to the study of exchange between chemisorbed and physisorbed phases of formic acid on TiO_2.

II. EXPERIMENTAL PROCEDURES

Sample preparation and details of the NMR techniques have been described in a

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previous paper (5). Both the 90% ^{13}C-enriched (KOR Isotopes) and natural-abundance formic acids (Aldrich) were purified with several freeze–pump–thaw cycles before use. Titania samples, maintained at 77 K during adsorption, were warmed to 290 K between sequential exposures to promote uniform distribution of the formic acid.

We use here two labeling techniques to monitor the dynamics of multilayer adsorption of formic acid on titania. In a generic labeling experiment a species is tagged and the tag is tracked along a reaction pathway. Conventional labeling involves stable isotopes of common elements introduced through the gas phase: here we monitor the exchange between chemisorbed $H^{13}COOH$ and physisorbed $H^{12}COOH$. However, isotopic labeling is limited by its speed: mass transport in porous media requires at least 1s, whereas typical processes at surfaces (e.g., desorption, diffusion, reaction) have time constants ranging from 10^{-8} to 10^{2} s. Spin-labeling with NMR spectroscopy, like isotopic substitution, labels the nuclei of a particular species, but it rapidly does so via the spin states of the nuclear magnetic dipoles. Selective saturation (6) or inversion (7) of nuclear spins in a narrow frequency range labels only that subset of the sample creating a nonequilibrium magnetization. The evolution of this state can then be used to detect chemical exchange (8) or molecular motion (9) within the sample.

The ^{13}C nuclear magnetic dipoles in a chosen fraction of the formic acid were selectively labeled with weak rf pulses in the following manner. During an rf pulse, a nuclear dipole will precess about an axis which is the sum of two vectors: the resonance-offset vector which lies along the z axis, and the rf pulse vector which, in this case, lies along the x axis in the rotating frame. For a spin which resonates at ω_0 in a magnetic field of strength H_0, the z component of its magnetization, M_z, after a rf pulse at frequency ω_{rf} and strength H_1, is given by

$$M_z = M_0\left[1 - \frac{1-\cos(\theta(1+\xi^2)^{1/2})}{1+\xi^2}\right] \quad (1)$$

where

$$\xi = \frac{\omega_{\mathrm{rf}} - \omega_0}{\gamma H_1} \quad (2a)$$

and

$$H_1 = \frac{\theta}{\gamma t_{\mathrm{p}}}. \quad (2b)$$

In the above equations, γ is the gyromagnetic ratio and θ is the angle of rotation caused exactly on resonance by a rf pulse of length t_{p} and strength H_1. Thus, for a spin on resonance ($\omega_{\mathrm{rf}} = \omega_0$), a 180° pulse ($\theta = \pi$) will invert the magnetization by causing a rotation about the x axis. For a spin far off resonance relative to the strength of the weak rf pulse ($|\xi| \gg 1$), the pulse has little effect because the rotation is about an axis almost parallel to the z axis. Pulses with $H_1 = 55$ G were used to excite uniformly across the 150 ppm wide frequency range spanned by the powder pattern of chemisorbed formic acid. Attenuated pulses with $H_1 = 0.29$ or 0.58 G were used to excite only a frequency range with a full width at half maximum of 1000 or 500 Hz (20 or 10 ppm in this study), respectively. The pulse sequence used to collect the NMR spectra in this paper is illustrated in Fig. 1. Varying the delay τ between the selective inversion and the observed pulse allows effects of exchange between spin baths to be determined. The range from 50 μs to 1.0 s was examined here. Including a nonselective 180° pulse at the beginning of alternate scans and accumulating the difference between pairs of scans caused the spectra for long delays to decay to zero rather than to the spectra reported previously (5), thereby simplifying the corrections necessary when $\tau \approx T_1$, the spin-lattice relaxation time.

III. RESULTS

A variety of techniques are necessary to measure rates where may span a wide time

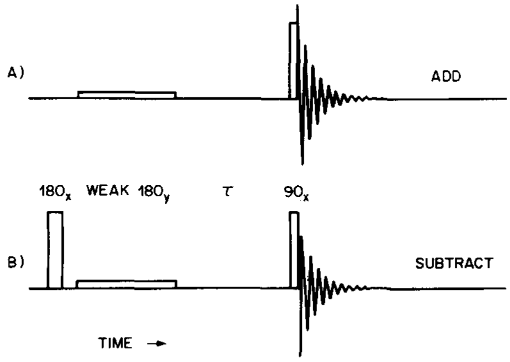


FIG. 1. Pulse sequence for selective-inversion recovery used in the NMR spin-labeling study. Sequences A and B are alternated and the resulting free induction decays are added and subtracted as indicated. The time allowed for exchange to occur is controlled by varying the delay τ. Note that the durations for each event are not drawn to scale.

range. Using sequential dosing of labeled and unlabeled formic acid, exchange between physisorbed and chemisorbed formic acid can be monitored for processes with time constants of 100 s or longer. The isotopic labeling is ineffective for measuring time constants shorter than either the time required for diffusion into the sample pore structure or that needed to collect ^{13}C NMR spectra with adequate signal to noise. We used here the technique of NMR spin-labeling to probe processes on shorter time scales, ranging from the time required to label the system (0.1 to 2 ms) to the lifetime of the label (T_1 = 0.6 s for this system). Results from both techniques are described below.

A. Isotopic Labeling

To detect exchange between the physisorbed and chemisorbed formic acid, a sample was prepared by sequentially adsorbing 0.7 monolayers ^{13}C-enriched formic acid and 2.0 monolayers natural-abundance formic acid on titania. The possible extremes of no exchange and complete exchange are illustrated in spectra (A) and (B) of Fig. 2. If there is no exchange (case A), the ^{13}C-labeled formic acid will remain in the chemisorbed layer and therefore give the powder pattern seen for submonolayer coverages (5). However, if there is complete exchange (case B), the ^{13}C-labeled molecules will be statistically distributed throughout both chemisorbed and physisorbed phases, and the spectrum will show both chemisorbed and physisorbed formic acid. Although the quantitative analysis based on integrated areas will indicate submonolayer coverage, the chemisorbed peak will account for only 1/2.7 of the total peak area.

In the observed spectrum (Fig. 2C), substantial exchange has occurred at 298 K in the 30 min between adsorption of the second formic acid layer and collection of the NMR spectrum. Further NMR spectra obtained after 2 and 12 h gave similar ratios of physisorbed to chemisorbed formic acid, indicating that exchange was essentially complete in less than 30 min. From this data, an upper limit of 400 s may be placed on the characteristic time for exchange.

The relative areas of physisorbed and chemisorbed peaks are consistent with a total coverage of 2.7. This explains the increase in width for the observed physisorbed spectrum over that shown in the

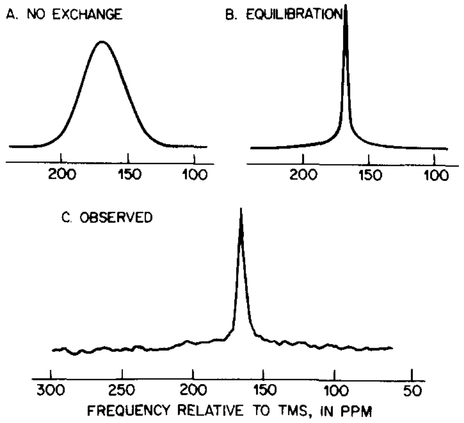


FIG. 2. Upper spectra show the predicted results for (A) no exchange and (B) complete equilibration between chemisorbed and physisorbed adlayers for a sample of TiO_2 dosed with 0.7 monolayers ^{13}C-enriched formic acid, followed by the equivalent of 2.0 monolayers of natural-abundance formic acid. The observed spectrum is (C).

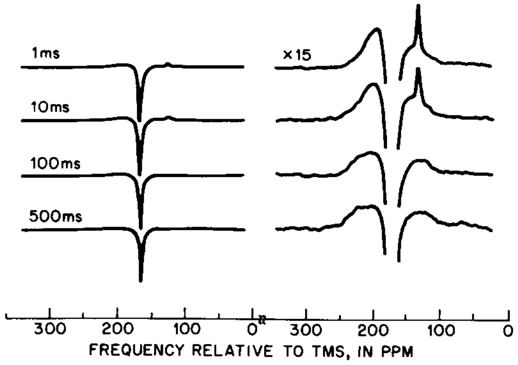


FIG. 3. Selective inversion of physisorbed formic acid nuclear spins. The weak pulse at 168 ppm has an excitation width at half maximum of 10 ppm. The peak at 128 ppm is due to a small (<1%) CO_2 impurity.

theoretical spectrum, which used parameters from the fitted spectrum at 5 monolayers. In the earlier study, it was noted that the physisorbed formic acid lineshape narrowed towards liquid-like behavior only at large multilayer coverages, where surface heterogeneities had little effect on the adsorbed phase.

B. Nuclear Spin-Labeling

Techniques using spin dynamics to selectively label specific adsorbate molecules may also be used to quantify rates. To measure exchange between physisorbed and chemisorbed formic acid, weak pulses were used to invert the magnetization of the physisorbed species. While this also generated a "hole" in the powder pattern due to chemisorbed formic acid at the same frequency, it did not affect the remainder of the chemisorbed peak. Figure 3 shows a series of selective-inversion spectra for 5 monolayers of formic acid adsorbed on titania. Because both physisorbed and chemisorbed formic acid have relaxation times of approximately 0.6 s, in the absence of exchange all spectral features will relax towards zero at the same rate. Consequently, T_1 effects are compensated by rescaling the spectra for long delay times to the initial intensity. These spectra show that at mixing times up to 0.5 s, there is little evidence of transport between the two adsorbed layers. Although the net magnetization in the sample is negative, due to the much larger quantity of physisorbed molecules, the magnetization observed in the chemisorbed powder pattern remains positive and decays only with T_1. As will be seen below, changes in the shape of the chemisorbed spectra can be attributed to processes occurring wholly within the chemisorbed adlayer.

Although there is little exchange between the adlayers, there is mixing within each adlayer. It is apparent from the narrow liquid-like character of the physisorbed formic acid peak that these species are undergoing rapid translational and orientational motion. Transport within the chemisorbed adlayer may be seen by using the selective inversion sequence to invert the magnetization in a small frequency range arbitrarily placed in the powder pattern of a sample with submonolayer coverage. The resonant frequency depends on the molecular orientation relative to the magnetic field (*10*).

$$\omega = \sigma_{11} \sin^2 \theta \cos^2 \phi + \sigma_{22} \sin^2 \theta \sin^2 \phi + \sigma_{33} \cos^2 \theta. \quad (3)$$

Here θ and ϕ are Euler angles of the principal axis system relative to H_0 and σ_{11}, σ_{22}, and σ_{33} are the principal components of the chemical shielding tensor. Therefore, inverting spins in a defined frequency range labels only molecules with certain orientations. Selectively-inverted NMR spectra for 0.6 monolayers of formic acid on titania on the left half of Fig. 4 show that the intensity of the "hole" produced this way does not persist, but decreases as the delay τ increases.

The experimental spectra can be fitted qualitatively with a model which assumes random reorientation upon exchange. For a single exchange rate, τ_e, the evolution of the z component of the magnetization at a given orientation, $n(\theta, \phi, t)$, will be given by

$$\frac{\partial n}{\partial t} = -\frac{n}{T_1} - \frac{1}{\tau_e}(n - \langle n \rangle) \quad (4)$$

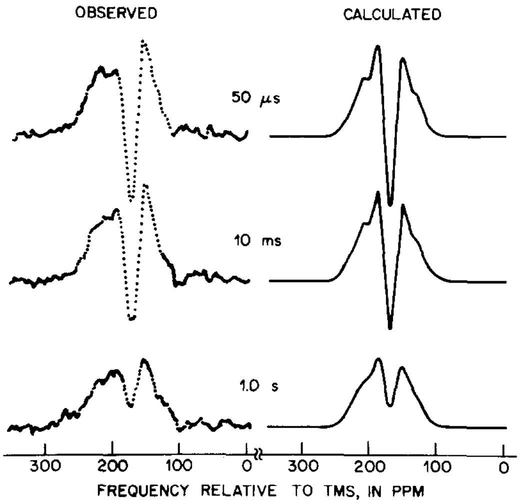


FIG. 4. Selective inversion of a fraction of the chemisorbed formic acid nuclear spins. The weak pulse at 168 ppm has an excitation width at half maximum of 20 ppm. Calculated spectra are computed using the hole profile described in the text.

where

$$\langle n\rangle = \int_\Omega n\, d\Omega \quad \text{and} \quad d\Omega = \sin\theta d\theta d\phi, \qquad (5)$$

and so

$$\frac{d\langle n\rangle}{dt} = -\frac{\langle n\rangle}{T_1}. \qquad (6)$$

Integrating over all orientations gives the T_1 behavior of the unperturbed spectrum, and so relaxation effects are confined to the factor e^{-t/T_1}. The solution for Eq. (4) is

$$n(\theta, \phi, t) = e^{-t/T_1}[\langle n_0\rangle + (n(\theta, \phi, 0) - \langle n_0\rangle)e^{-t/\tau_e}] \qquad (7)$$

with

$$\langle n_0\rangle = \int_\Omega n(\theta, \phi, 0) d\Omega. \qquad (8)$$

To accommodate a distribution of exchange times, the second exponential may be replaced with a weighted of exponentials. The spectra have been simulated, on the right side of Fig. 4, by fitting them to a powder pattern with partially inverted magnetization and constant total area.

For the sample with 5 monolayers, inverting the physisorbed formic acid peak results in a sample with a negative magnetization. Complete exchange would return the spectrum to its original shape but with the same negative area as the initial (no exchange) spectrum. This change would be most visible in the chemisorbed formic acid powder pattern, which would be inverted. With a low coverage multilayer sample, these same considerations indicate that effects of exchange would be most easily observed in the recovery of the physisorbed formic acid peak as it recovered magnetization from the chemisorbed adlayer. Selective inversion applied to samples with 1.4 monolayers of formic acid show that, while the hole in the chemisorbed formic acid powder pattern recovers as described in the preceding paragraph, there is no indication of any recovery in the small physisorbed formic acid peak. Any magnetization transfer into the physisorbed adlayer should be readily observable in this sample, where all of the physisorbed formic acid is adjacent to chemisorbed species. These spectra then are consistent with the earlier observations of motion within the chemisorbed adlayer, but not between chemisorbed and physisorbed species.

IV. DISCUSSION

The evolution of the lineshape in the inverted region for the chemisorbed formic acid contains additional information about the type of process which is occurring. As the inverted spins diffuse throughout the spectrum, the width of the perturbed frequency range remains constant, indicating that the redistribution process is not one involving small angle reorientations. Instead, the reorientations appear to involve large random changes. The motion in the chemisorbed layer, plotted as $(n - \langle n\rangle/n_0 - \langle n_0\rangle)e^{t/T_1}$, is shown in Fig. 5. The nonexponential behavior of this recovery shows that there is a very broad range of exchange times in the sample, which is not unexpected for a powder sample such as this.

Within the chemisorbed formic acid, the

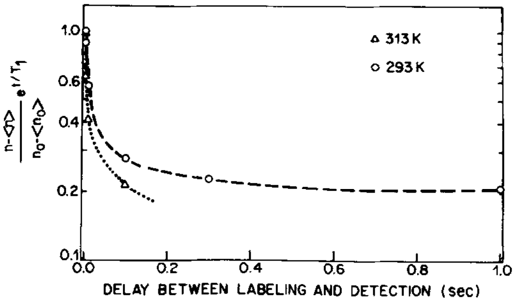
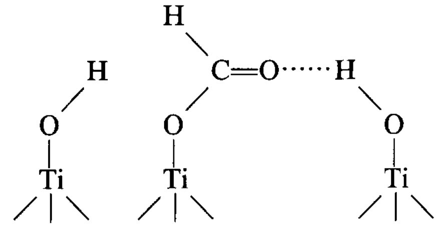


FIG. 5. Decay of hole intensity for chemisorbed formic acid. Hole intensity is determined from fits to calculated spectra similar to those in Fig. 4. Temperatures are as indicated.

time to 50% exchange equilibration is 20 ms at 293 K and 4 ms at 343 K, suggesting that this process has an activation energy of approximately 6 kcal/mole. Among the possible explanations for the observed transport of magnetization through the adsorbate are desorption/readsorption, migration (diffusion), reorientation, and spin diffusion. Desorption and readsorption would involve transport of molecules through the fluid phase in the pore voids. This is not a likely mechanism, because diffusing molecules would be indistinguishable from physisorbed molecules and this exchange has been shown above to be much slower than exchange with the chemisorbed adlayer. Diffusion on the surface would have a much lower activation energy than desorption, and reorientation a yet lower energy barrier to break and reform a hydrogen bond to neighboring surface hydroxyl groups. Spin diffusion, which involves not motion of nuclei but rather exchange of nuclear magnetism, is always a possibility in systems with small distances between neighboring spins such as monolayers. However, spin diffusion rates generally are insensitive to temperature and spin-diffusion is inefficient when diffusion is between states with widely separated frequencies, so this does not appear to be the cause. Therefore, the spectral changes shown in Fig. 4 are probably due to translational or orientational diffusion on the surface, and distinguishing between the two is not possible with this technique. Most models envisioned for translation would also allow exchange with physisorbed species at a comparable rate, but the spectra measured here show no evidence of exchange at such a rate. Hindered or stepwise rotation is a more plausible explanation for these data.

A unidentate formate anion structure with hydrogen bonding between the carbonyl oxygen and neighboring surface hydroxyl groups, as depicted below, best satisfies the data reported here. The rotation of this species between different OH groups will allow reorientation within



the chemisorbed adlayer but not exchange between the chemisorbed and physisorbed species. At typical TiO_2 surface OH densities, between 3 and 6 hydroxyl groups will be present near the adsorption site. Stepwise rotation between these will require complete rupture of one hydrogen bond before formation of the next, resulting in an activation energy comparable to the 5 kcal/mole of a fully developed hydrogen bond. Redistribution of the labeled molecules among a limited number n of alternative orientations would cause the intensity of the selective inversion to decay to $1/n$ rather than zero at long times. The data in Fig. 5 do appear to approach asymptotically ~0.20 and are thus consistent with an average of five possible orientations, although a semilog plot of the approach to this final state does retain some curvature. This is a lower limit for n, because there may exist some orientations which have resonant frequencies within the inversion bandwidth. The curvature may indicate either a distribution of rates or the presence of another exchange process much slower than the stepwise rotation of the hydrogen-bonded formate anion.

Throughout the course of this study, we have been alert for any sign of formic acid adsorbed in sites which are active for the dehydration reaction, but have not seen any. Direct observation of a signal from ~1% of the surface is not practical with current instrumental sensitivity. Indirect observation through the effect on an observable species with which the unobservable moiety is exchanging is possible when the two species have differing magnetic resonance characteristics *and* the exchange is rapid enough that the observable signal reflects an average between the sites available. In this fashion, Enriquez and Fraissard (*4*) interpreted a small shift in physisorbed peak position with coverage as being caused by exchange with a small quantity of chemisorbed active sites paramagnetically shifted to +3934 ppm. In the present study, we have determined that exchange between physisorbed formic acid and inactive chemisorbed formic acid is too slow to have any effect on the lineshape of the physisorbed formic acid. As active sites also appear to involve strong chemisorption forces, it is to be expected that exchange to these sites from the physisorbed adlayer would be similarly slow. Therefore, it appears unlikely that active sites and the physisorbed adlayer are equilibrating with each other on the submillisecond time scale required for the physisorbed formic acid line to show averaging effects. In addition, in this study the physisorbed formic acid peak was always detected at 166 ± 4 ppm and showed no definite coverage dependence, while the work of Enriquez and Fraissard described a definite frequency shift with coverage and predicted physisorbed formic acid peak positions of 177 to 240 ppm for coverages in the range used in this work. We have no explanation which reconciles these disparate results.

V. SUMMARY

The application of selective spin-labeling using NMR to characterize chemical exchange in chemisorption systems is demonstrated. For formic acid on TiO_2, isotopic labeling shows that exchange between chemisorbed and physisorbed adlayers occurs at 298 K with a time constant of less than 400 s. NMR spin-labeling experiments place a lower limit of 2 s on this exchange. This is much slower than the millisecond time scale hypothesized in other investigations of this system. From the slow rate for this exchange, we conclude that characterization of physisorbed formic acid cannot be used to characterize chemisorbed formic acid, and that direct observation of the chemisorbed adlayer as reported in a preceding paper (*5*) is necessary. In the chemisorbed adsorbate, we observed reorientation of the formate species proceeding at 298 K and concluded that this is most likely due to rotation, perhaps as the carbonyl oxygen breaks and reforms hydrogen bonds to surface hydroxyl groups. Consistent with the absence of rapid exchange between various forms of adsorbed formic acid, no evidence of adsites active for the dehydration reaction was observed.

REFERENCES

1. Trillo, J. M., Munuera, G., and Criado, J. M., *Catal. Rev.* **7,** 51 (1972).
2. Maatman, R. W., *Catal. Rev.* **8,** 1 (1974).
3. Enriquez, M. A., and Fraissard, J. P., *J. Catal.* **73,** 77 (1982).
4. Enriquez, M. A., and Fraissard, J. P., *J. Catal.* **73,** 89 (1982).
5. Root, T. W. and Duncan, T. M., *J. Catal.* **101,** 527 (1986).
6. Bloembergen, N., Purcell, E. M., and Pound, R. V., *Phys. Rev.* **73,** 679 (1948).
7. Morris, G. A., and Freeman, R., *J. Magn. Reson.* **29,** 433 (1978).
8. Forsèn, S. and Hoffman, R. A., *J. Chem. Phys.* **39,** 2892 (1963).
9. Kuhns, P. L. and Conradi, M. S., *J. Chem. Phys.* **77,** 1771 (1982).
10. Haeberlen, U., "High Resolution NMR in Solids." Academic Press, New York, 1976.