JOURNAL OF CATALYSIS **101**, 527–531 (1986)

# Formic Acid on Titania: Characterization of Adsorbed Structures with $^{13}C$ NMR Spectroscopy

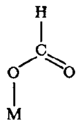
Formic acid decomposition is a convenient model reaction for investigating the effects of surface structure and composition on catalytic reactions. A wide variety of techniques, ranging from analysis of reaction products to *in situ* spectroscopic techniques such as transmission infrared, have been applied to the study of formic acid behavior on metal oxides (*1*). Because titania can contain paramagnetic $Ti^{3+}$ centers which may alter bonding interactions, it is a particularly interesting support for adsorption or reaction. In this note we report the direct observation of chemisorbed formate on $TiO_2$ with $^{13}C$ NMR.

Two reactions may occur on oxide catalysts in varying proportion, with selectivity depending on the particular catalyst and reaction conditions.

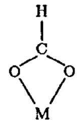
$$HCOOH \rightarrow \begin{cases} H_2O + CO \\ \quad\text{or} \\ H_2 + CO_2 \end{cases}$$

It is reported that formic acid dehydrogenates on MgO and ZnO, dehydrates on $Al_2O_3$ and $SiO_2$, and decomposes via both reactions on the third-period transition-metal oxides. Earlier work has shown $TiO_2$ to be principally a dehydration catalyst at temperatures below 700 K (*2*).

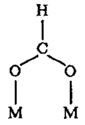
Formic acid adsorbs dissociatively on most surfaces, and the resulting formate anion may be bonded to the surface in one of several possible geometries. Depending on factors such as metal electronegativity, oxide acidity, and surface lattice spacings, the resulting structure may be unidentate (**I**), bidentate (**II**), or bridging (**III**), as illustrated below:



I



II



III

In this study, we have used $^{13}C$ NMR to measure the asymmetry in the electronic environment at the carbon nucleus. This technique can therefore distinguish whether the formate anion has one or two bonds to the surface, but cannot differentiate between the two doubly bonded species (**II** and **III**).

Several studies using nuclear magnetic resonance (NMR) methods have disclosed details of the bonding of adsorbed formate on zeolites and other oxide surfaces. Duncan and Vaughan (*3*) determined that formic acid adsorbs primarily in the bidentate structure on ammonium-Y and ultrastable hydrogen-Y zeolites. Enriquez and Fraissard (*4*) indirectly examined HCOOH chemisorbed on $TiO_2$ in an NMR investigation of multilayer physisorption.

## METHODS

The finely dispersed titanium dioxide (Degussa P25) used in the present study had a surface area of 50 ± 3 $m^2/g$ as measured by nitrogen BET and was primarily in the rutile form. After heating at 250°C (or 400°C for one sample) for 6 h under vacuum to activate the decomposition reaction, the $TiO_2$ samples were exposed to aliquots of formic acid (90% $^{13}C$-enriched) vapor in a stainless-steel gas manifold. The formic acid was subjected to several freeze–

0021-9517/86 $3.00

pump–thaw cycles for purification before dosing.

$^{13}C$ NMR spectra were taken on a Bruker CXP-200 spectrometer at 50.35 MHz. Proton decoupling of 10 to 25 G was used for all spectra reported here. Depending on the sample size, from 64 to 20,000 scans were required to obtain adequate signal to noise. Peak positions are reported relative to tetramethylsilane (TMS) with increasing field (decreasing frequency) plotted to the right. Trace amounts of $CO_2$ also served as internal references, as the temperature-dependent peak shift (5) is less than the 1.2 ppm channel-width used in this work.

## RESULTS

The chemical shift powder pattern of chemisorbed formate was observable at all formic acid coverages studied. As seen in Fig. 1, for submonolayer coverages (i.e., $\theta < 1$) the shape of the spectrum does not change as the coverage increases. The principal components of this spectrum, as obtained with a least-squares fit with 0.89 kHz Gaussian broadening, are at 229, 161, and 122 ppm. At multilayer coverages a narrow peak at 167 ppm appears. We attribute this peak to physisorbed formic acid, which is assumed to be reorienting rapidly and isotropically. The spectrum of the chemisorbed species, still visible in the presence of the physisorbed formic acid, remains intact. In addition, a narrow peak is visible at 124 ppm in the enlarged spectrum which is interpreted as $CO_2$ generated during dosing and accounts for less than 1% of the total peak area.

Because of the quantitative nature of NMR spectra, the number density of a saturated monolayer is readily available from any multilayer spectrum with coverage $\theta > 1$. The saturation density of $4.3 \pm 0.5 \times 10^{14}$ $cm^{-2}$ for formic acid adsorbed on titania corresponds to an area of $23 \pm 3$ Å$^2$ per molecule or adsorption site.

Relaxation times for the adsorbed formate species were measured using both saturation-recovery and inversion-recovery methods. A sample with a submonolayer coverage ($\theta \sim 0.6$) had a distribution of $T_1$'s, with a mean $T_1$ of about 0.7 s. A slightly better fit was obtained with a two-$T_1$ model and relaxation times of 0.5 (80%) and 5.0 s (20%), but there are no indications in the powder pattern that such a distinction is realistic. Both the chemisorbed and physisorbed formate species in the multilayer sample ($\theta \sim 5$) exhibited similar relaxation rates; again there was a distribution of $T_1$'s with a mean $T_1$ of 0.6 s. This similarity in relaxation behavior for physisorbed and chemisorbed formic acid suggests a common relaxation mechanism, either via the substrate paramagnetism, spin diffusion, or

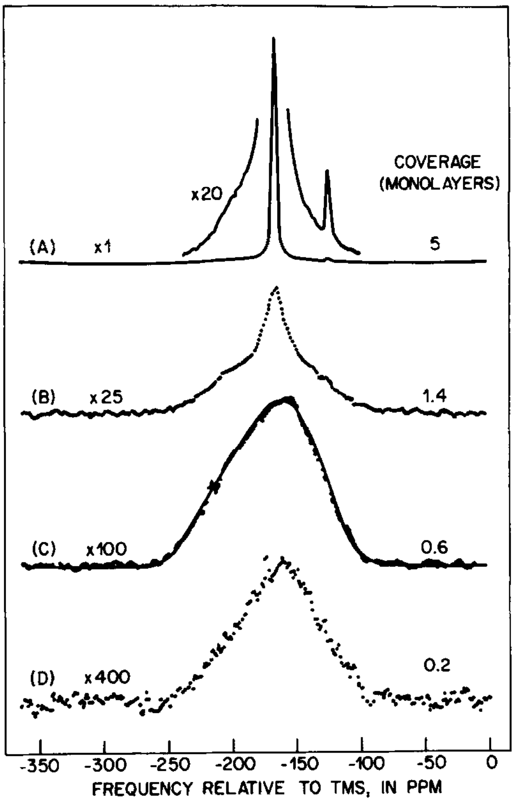


FIG. 1. $^{13}C$ NMR spectra of formic acid adsorbed on $TiO_2$ at 298 K. Approximate coverages are (A) 5, (B) 1.4, (C) 0.6, and (D) 0.2 monolayers. The solid line in spectrum (C) is a least-squares fit to a chemical shift powder pattern convoluted with Gaussian broadening. Spectra are the accumulation of (A) 4000, (B) 2000, (C) 15,000, and (D) 20,000 scans.

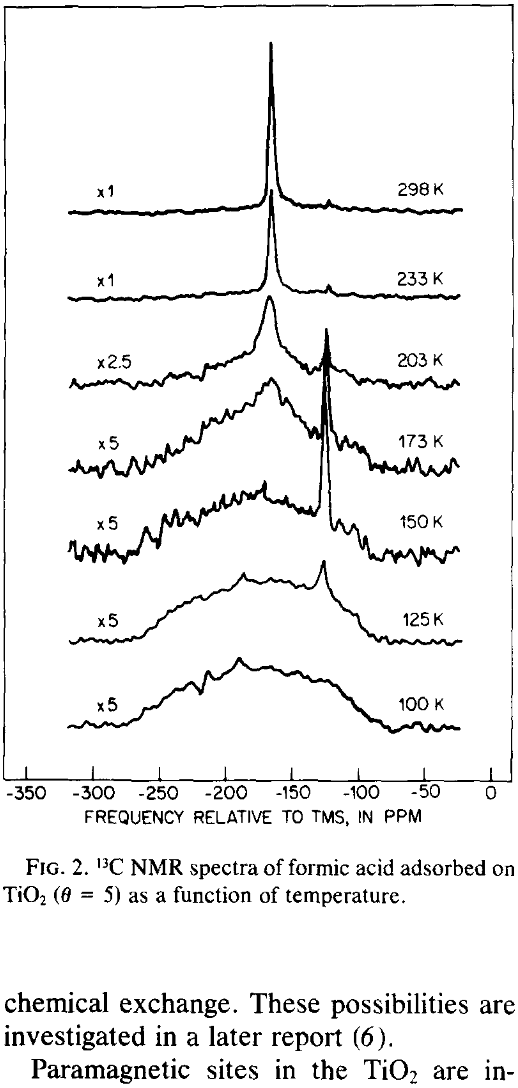


FIG. 2. $^{13}C$ NMR spectra of formic acid adsorbed on $TiO_2$ ($\theta$ = 5) as a function of temperature.

chemical exchange. These possibilities are investigated in a later report (*6*).

Paramagnetic sites in the $TiO_2$ are involved to a degree in the relaxation of the $^{13}C$ spins, as seen from the decrease in relaxation time with increasing processing temperatures. A multilayer ($\theta \sim 3$) sample with $TiO_2$ prepared at 400°C (instead of at 250°C as used for all other samples reported here) had a $T_1$ of 0.29 s. This temperature is reported to give the maximum density of electron-donating sites (*7*), and slightly more than twice the concentration measured at 250°C. However, through-space interaction with paramagnetic centers in the substrate alone are not sufficient to account for the $^{13}C$ relaxation mechanism; the $T_1$ of TMS is the same in a neat liquid as in a physisorbed monolayer on titania prepared as above. The longer $^{13}C$ $T_1$ measured for TMS (approx. 7 s) also shows that the levels of Fe and other magnetic impurities in the $TiO_2$ (<100 ppm) are not high enough to contribute to adsorbate relaxation processes.

Motional averaging in the physisorbed formic acid ceases over a range of temperatures, as may be seen in Fig. 2. While only slight broadening is evident at 233 K, by 203 K the peak widens into two distinct components with widths of ~15 and 70 ppm. On further cooling, more intensity transfers from the narrow to the broad peak. At 125 K, the powder pattern that remains is much broader than the spectrum observed for submonolayer coverage at room temperature. Throughout the temperature range in which the narrower, physisorbed peak is observed, its frequency remains constant at 166 ppm, the same as the neat liquid.

The $CO_2$ peak at 124–128 ppm remains sharp at 173 K, but broadens between 125 and 105 K. The apparent increase in relative area may be caused by the broadening and consequent decrease in peak height of the formate or by $T_1$ effects.[1]

## DISCUSSION

The asymmetry of the powder pattern for chemisorbed formic acid shows that adsorption is principally unidentate. It has been shown earlier (*3*) that the relative position of the center principal shielding component increases monotonically with the ratio of the two C—O bond lengths, and this ratio indicates the amount of unidentate or bidentate character in the adsorbate structure. Here (Table 1), the observed asymmetry shows that the formate on titania is unidentate. Furthermore, the asymmetry indicates that the interaction between the nominally double-bonded oxygen of the chemisorbed formate and its surroundings

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[1] The $CO_2$ relaxation time at room temperature was less than 50 ms, so it is expected that it could be cooled to lower temperatures than formic acid before beginning to lose signal intensity from saturation effects with constant cycle times used here.

TABLE 1

Chemical Shielding Components in Formates

| Compound | Temp. (K) | Principal components | | | | $\frac{\sigma_{22} - \sigma_{33}}{\sigma_{11} - \sigma_{33}}$ | Ref. | $\frac{R_2}{R_1}$[a] |
|---|---|---|---|---|---|---|---|---|
| | | $\sigma_{11}$ | $\sigma_{22}$ | $\sigma_{33}$ | $\langle\sigma\rangle$ | | | |
| $HCOOCH_3$ | 87 | 253 | 136 | 107 | 165 | 0.20 | (8) | 1.12 (9) |
| HCOOH | 125 | 251 | 162 | 92 | 168 | 0.44 | (3) | 1.05 (10) |
| $(NH_4)HCO_2$ | 185 | 225 | 168 | 99 | 164 | 0.55 | (3) | 1.01 (11) |
| $Ca(HCO_2)_2$ | 125 | 235 | 186 | 96 | 172 | 0.65 | (3) | 1.01 /1.00 |
| $Pb(HCO_2)_2$ | 298 | 220 | 183 | 97 | 167 | 0.70 | (13) | 1.04/1.01 (14) |
| $HCOOH/TiO_2$ | 298 | 229 | 161 | 121 | 171 | 0.37 | — | |

[a] Ratio of the two C—O bond lengths.

is weaker than that seen in dimerized solid formic acid and stronger than that observed in solid methyl formate. In addition, the observation of a powder pattern with three distinct shielding components (nonaxially symmetric) at submonolayer coverages shows that the adsorbed molecule is not free to rotate about the O—metal or C—O bonds. This most likely involves coupling between the carbonyl oxygen atom and neighboring O—H groups on the surface. From the amount of asymmetry in the shielding tensor, the strength of the hydrogen bond between the surface and the carbonyl oxygen (i.e., C═O···H—O) is somewhat less than the 7 kcal/bond/mole that occurs in the formic acid dimer (*15*), and only a small fraction of the total adsorption energy of more than 25 kcal/mole, based on the activation energy for decomposition.

Another observation drawn from the variable temperature study is that motion persists in the physisorbed layer well below 281 K, the melting point of neat formic acid. Thus, while multilayers of formic acid are isotropically averaged by tumbling in a liquid-like way, these molecules do not crystallize as bulk liquid does but rather solidify over a broad range of temperatures. This may be caused by the variation of environments provided by the chemisorbed formate monolayer and $TiO_2$ surface. Similar melting-point depressions for physisorbed adlayers have been reported for $CO_2$ on zeolites (*16*) and benzene on charcoal (*17*).

NMR spectra shown here are consistent with the conclusion from infrared studies (*2*) that formic acid adsorbs principally through the loss of the acidic proton, producing a formate anion. However, statistical analysis of observed reaction rates (*18*) indicates that active sites for reaction comprise only a small fraction of the surface, and neither of these spectroscopies is currently capable of directly measuring trace amounts of hypothetical reactive intermediates. Unfortunately, the results of this investigation do not give much information about characteristics of active sites in the dehydration reaction of formic acid. NMR can detect indirectly small amounts of material that are in chemical equilibrium with major components by the effects of such exchange on peak position and lineshape. Estimates of site density from kinetic data range from $1.4 \times 10^{10}$ to $10^{14}$ $cm^{-2}$ (*18*) owing to uncertainty in the amount of entropy loss on adsorption. Using ESR, Enriquez and Fraissard (*7*) measured the density of electron-donating sites between 5 and $10 \times 10^{12}$ $cm^{-2}$ and found that the variation of this density with preparation temperature followed the observed rate for the dehydration reaction. As discussed elsewhere, although there is slow exchange between chemisorbed and physisorbed formic acid (*6*), we have seen no indications of exchange with an active chemisorbed site, as reported by others (*4*). In extending the range examined to lower coverages and temperatures, we have improved the sensitivity of these measurements for the detection of any paramagnetically shifted species, but have not observed any evidence of such a site.

In contrast to the results presented above for titania, on zeolites formic acid adsorbs in a bidentate geometry. Despite this difference in adsorbate structure, both oxides are dehydration catalysts, and therefore it appears that the rate-determining step is independent of the observed structure for chemisorbed formate. Either the active site density is a small fraction of the adsorbate density, if formate is involved in the rate-determining step, or else the rate-determining step does not involve adsorbed formate species. Elimination of water from the surface by condensation of two O—H groups has been proposed by Trillo *et al.* (*1*) for the latter reason.

In conclusion, we have determined that the formate anion bonds to the surface in a unidentate geometry from direct observation with $^{13}C$ NMR of the chemical shift anisotropy powder pattern of formic acid adsorbed on $TiO_2$. There is evidence of hydrogen bonding between the carbonyl oxygen and surface hydroxyl groups which restricts rotation of the adsorbed formate. Physisorbed multilayers are liquid-like both at room temperature and well below the freezing point of neat formic acid. The density of paramagnetic sites does affect the relaxation rate of the adsorbate. However, contrary to results of previous studies, there is no indication of a peak shift induced by paramagnetic $Ti^{3+}$ sites on the surface.

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*Received January 2, 1986*