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In Situ Carbon-13 Solid-State NMR Study of the $Cu/ZnO/Al_2O_3$ Methanol Synthesis Catalyst

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Abstract: The reactions of methanol, formic acid, paraformaldehyde, CO_2, and CO were studied on $Cu/ZnO/Al_2O_3$, Cu/Al_2O_3, ZnO/Al_2O_3, ZnO, and Al_2O_3 by in situ ^{13}C solid-state NMR with magic-angle spinning (MAS). These studies relate to the chemistry of methanol synthesis using the standard $Cu/ZnO/Al_2O_3$ catalyst, which produces essentially all of the world's methanol supply. Methanol adsorbs on the alumina phase at 298 K to form a surface-bound terminal methoxy, but it forms a bridging methoxy on the ZnO phase. On catalysts containing Cu, these methoxy groups were oxidized to a surface-bound symmetrical formate at ca. 373 K. Formate is mobile on the surface at 493 K. Heating to ca. 523 K converted formate to carbonate or bicarbonate, but again only on catalysts containing Cu. These carbonates partially decomposed at 523 K to free CO_2. Paraformaldehyde underwent a Cannizzaro-type disproportionation on all catalysts studied to form formate and methoxy groups. This observation is consistent with a transient intermediate role for formaldehyde. Evidence of a surface-bound dioxymethylene was seen on ZnO/Al_2O_3 during this reaction. CO_2 readily adsorbs on $Cu/ZnO/Al_2O_3$ to form carbonate at 298 K. CO adsorbs to form a small amount of carbonate and a weakly bound surface carbonyl. Detailed measurements of relaxation rates and the principal components of the ^{13}C chemical shift tensors are reported for all catalyst/adsorbate systems. All adsorbates showed biexponential ^{13}C T_1 behavior on $Cu/ZnO/Al_2O_3$ only. Our interpretation of this result is that small paramagnetic clusters of Cu are dispersed in an oxide phase. The results of this study are interpreted in terms of several mechanistic controversies.

Introduction

Essentially all of the world's methanol production relies on a ternary catalyst composed of copper, zinc oxide, and alumina (hereafter $Cu/ZnO/Al_2O_3$).[1-5] This catalyst converts synthesis gas to methanol with greater than 99% selectivity, a performance all the more remarkable considering the favorable thermodynamics for the formation of side products such as hydrocarbons, higher alcohols, and ethers. In spite of the near universal use of this catalyst and 25 years of study, there remains widespread disagreement about its structure and function. These issues are customarily introduced in the context of several questions:

1. Is methanol synthesized from CO or CO_2? Synthesis gas (which is obtained by steam reforming of natural gas) is a mixture of CO, CO_2, and H_2, and either carbon oxide can be reduced to methanol.

$$CO + 2H_2 \rightleftarrows CH_3OH$$

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O$$

One reason why this most basic issue has proven difficult to settle is that $Cu/ZnO/Al_2O_3$ also catalyzes the water–gas shift reaction.

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

Furthermore, it is probable that more than one mechanism is operable, at least under certain conditions. Recently, Chinchen and co-workers at ICI have reported radiotracer studies that provide compelling evidence that methanol is synthesized from CO_2 under the conditions used in commercial reactors.[6]

2. What is the state of the copper in the working catalyst? Evidence exists for a variety of copper species, some of them dispersed in the ZnO phase. For example, Solomon and coworkers have used X-ray absorption edge and EXAFS measurements to study Cu/ZnO.[7] A significant amount of Cu(II) was found to be doped into the ZnO lattice in the calcined material. Following reduction, the catalyst contained metallic Cu, small Cu clusters, a Cu_2O phase, and Cu(I) doped into the ZnO lattice. The ICI group has reported that about 30% of the initial copper metal surface is covered with oxygen under working conditions, and that both the bare metal and oxide layer play important roles.[8]

3. What roles are played by ZnO and Al_2O_3? Before the development of $Cu/ZnO/Al_2O_3$, ZnO/Cr_2O_3 was used as the catalyst, but the temperature and pressure requirements were more severe. The current process is typically carried out at 523 K and 50–100 atm, whereas the ZnO/Cr_2O_3 catalyst required 623 K and 250–350 atm. Although a variety of roles have been proposed for ZnO in the current process, some workers assert that copper is the active catalyst (based on correlations between rate and metal surface area) and that the role of the oxides is to prevent sintering.[4,9] One criticism of that conclusion is that important, but not rate-limiting, steps could still occur on ZnO.[10] The ZnO also deactivates the acid sites on Al_2O_3, preventing the synthesis of dimethyl ether.

4. What is the reaction mechanism? A wide variety of mechanisms have been proposed for this process.[1-5] A simplified scheme, favored by the ICI group is shown below.[4]

$$CO_2 \rightleftarrows CO_{2\,ads}$$

$$H_2 \rightleftarrows 2H_{ads}$$

$$CO_{2\,ads} + H_{ads} \rightleftarrows HCOO_{ads}$$

$$HCOO_{ads} + 3H_{ads} \rightleftarrows CH_3OH + O_{ads}$$

$$CO + O_{ads} \rightleftarrows CO_2$$

$$H_2 + O_{ads} \rightleftarrows H_2O$$

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Some of the above steps are probably composites of several elementary reactions. The ICI group proposed that the adsorbed oxygen promotes the adsorption of CO_2. The existence of several intermediates, including formate, has been inferred based on temperature-programmed desorption studies.[11,12] Several infrared investigations of $Cu/ZnO/Al_2O_3$ and related catalysts have also been reported.[13-20] There have been two preliminary NMR studies of adsorbates on $Cu/ZnO/Al_2O_3$, both using low-resolution techniques.[21,22] These studies revealed a Knight-shifted ^1H resonance associated with adsorption on copper metal and broad ^{13}C line shapes for adsorbed methanol.

In this contribution, we report detailed high-resolution ^{13}C NMR studies directed toward an understanding of the chemistry of methanol synthesis. Our approach has been to study the structure, dynamics, and reactivity of the reactants, intermediates, and products obtained by adsorption of CH_3OH, $HCOOH$, H_2CO, CO_2, and CO. In order to further elucidate the roles of the catalyst components, the reactions of some or all of the above species were studied on a variety of catalysts: $Cu/ZnO/Al_2O_3$, ZnO/Al_2O_3, ZnO, Al_2O_3, and Cu/Al_2O_3. The reactions of these catalyst/adsorbate samples were monitored in situ by obtaining ^{13}C magic-angle spinning (MAS) NMR data as the sealed samples were heated in the NMR probe.[23,24]

The primary focus of this investigation is the mechanism of methanol synthesis (question 4 above), but some of the results also bear on the other issues in methanol synthesis catalysis on $Cu/ZnO/Al_2O_3$. Our studies reveal that methanol decomposes to CO_2 on $Cu/ZnO/Al_2O_3$ by way of two forms of surface-bound methoxy, as well as formate and carbonate intermediates. Nonbridging methoxy groups form on the Al_2O_3 component of the catalysts, and bridging methoxy groups form on ZnO or ZnO/Al_2O_3, but these do not oxidize to formate at 523 K without Cu. Relaxation experiments on various catalyst/adsorbate systems provide indirect evidence for two environments on the $Cu/ZnO/Al_2O_3$ surface. One of these environments appears to be ZnO with dispersed paramagnetic Cu, while the other is an oxide phase without paramagnetic sites. Formaldehyde readily disproportionates on all of the catalysts studied to formate and methoxy, possibly via a dioxymethylene intermediate. Formaldehyde was not observed directly during methanol decomposition, presumably due to its high reactivity. Although the pressure requirement (50–100 atm) for running the reaction in the forward direction all the way to methanol was deemed unsafe for MAS NMR experiments with current technology, we did observe that CO_2 is readily taken up by $Cu/ZnO/Al_2O_3$ at modest pressures to form the carbonate species. CO was less reactive on the catalyst but did form a small amount of carbonate and a mobile species believed to be a weakly adsorbed copper or zinc carbonyl.

By analyzing the sideband patterns in slow-speed MAS spectra, it was possible to obtain the principal components of the ^{13}C chemical shift tensors for most of the observed species. This information is useful for making structural assignments and (in conjunction with relaxation measurements) for characterizing the dynamics of several of the surface species over a range of temperatures.

Experimental Section

Catalyst Preparation. All of the catalysts that were studied in this investigation were prepared following the procedure described by Herman and co-workers.[25] Solutions (1 M) of the nitrates of copper, zinc, and aluminum were prepared. Mixtures of the nitrate solutions were made according to the mole percentage of the separate components desired. The catalysts were then coprecipitated from their nitrate solutions by a dropwise addition of 1 M sodium carbonate at 358–363 K until a pH of 6.8–7.0 was reached. After allowing a 1.5-h digestion period, the precipitate was collected and washed thoroughly with distilled water. The catalyst samples were then dried overnight in an oven at 333–373 K. Calcination was carried out in a flow of air (75 mL/min) while heating the catalyst samples in a furnace from room temperature to 623 K in 2.5 h, with the highest temperature maintained for 3 h. Reduction was performed using 2% H_2 in N_2 as reducing gas (50 mL/min) while heating the catalysts from room temperature to 523 K in 30 min and maintaining the temperature at 523 K for 6 h. To avoid reoxidation, the catalysts were stored in a glovebox with a pure nitrogen atmosphere. This procedure was followed in preparing the following catalysts: $Cu/ZnO/Al_2O_3$ (27/53/20), ZnO/Al_2O_3 (80/20), Cu/Al_2O_3 (40/60), ZnO, and Al_2O_3. The numerical designations refer to the mole percentage of the respective components. BET surface areas of the catalysts were determined from nitrogen adsorption isotherms obtained at 77 K and using 0.162 nm^2 for the cross-sectional area of the adsorbed nitrogen molecule. Typical areas obtained were ca. 100 m^2/g for all materials.

Methanol-^{13}*C*, formic acid-^{13}*C*, paraformaldehyde-^{13}*C*, ^{13}CO, and $^{13}CO_2$ were all obtained from Cambridge Isotopes. The isotopic purity of these compounds was 99 atom % ^{13}C. All adsorptions were performed at room temperature. Approximately 0.3–0.5 g of the catalyst was loaded into a zirconia MAS rotor equipped with grooved spacer and cap.[26] The rotor was then loaded into the CAVERN[27] apparatus. These steps were performed in the glovebox. The CAVERN was then attached to the vacuum line and was pumped down to 10^{-5} Torr. The catalyst was then exposed to a predetermined amount of adsorbate. After the adsorption was complete, the rotor was capped and transferred to the NMR probe. Typical loadings were 0.25–0.50 mmol of adsorbate per gram of catalyst.

NMR Spectroscopy. ^{13}C NMR spectra were acquired at 75.5 MHz using a Chemagnetics CMX-300 spectrometer equipped with a variable-temperature accessory which allowed MAS spectra to be obtained over a temperature range 123–523 K. Nitrogen boil-off gas was used for spinning and temperature regulation. Typical parameters were as follows: cross polarization (contact time = 2 ms, pulse delay = 1 s, 400 scans); single-pulse ^{13}C excitation (Bloch decay) with and without proton decoupling (pulse delay = 4 s, 4.0 μs 90° flip, 100 scans); and cross polarization with interrupted decoupling[28] (dephasing time = 50 μs, pulse delay = 1 s, 400 scans). ^{13}C and ^1H relaxation measurements were performed using methods described elsewhere.[29]

To obtain information on the chemical shift anisotropies of the species on the surface of the catalyst, cross polarization (CP) and Bloch decay spectra were acquired at spinning speeds sufficiently slow to provide at least 2 orders of spinning sidebands. Principal components of the ^{13}C chemical shift tensors (δ_{11}, δ_{22}, and δ_{33}) were determined from the intensities of the isotropic peak spinning sidebands using the method of Herzfeld and Berger.[30] The shielding anisotropy ($\Delta\delta$) and the asymmetry parameter (η) were calculated using the most common convention.[31]

Results and Discussion

The structure, dynamics, and reactivity of species formed after the adsorption of methanol-^{13}*C*, formaldehyde-^{13}*C*, and formic acid-^{13}*C* on $Cu/ZnO/Al_2O_3$, ZnO/Al_2O_3, Al_2O_3, and ZnO were studied in detail. Some experiments were also performed on Cu/Al_2O_3, but these were limited due to sintering during preparation or subsequent treatment. Following adsorption at room

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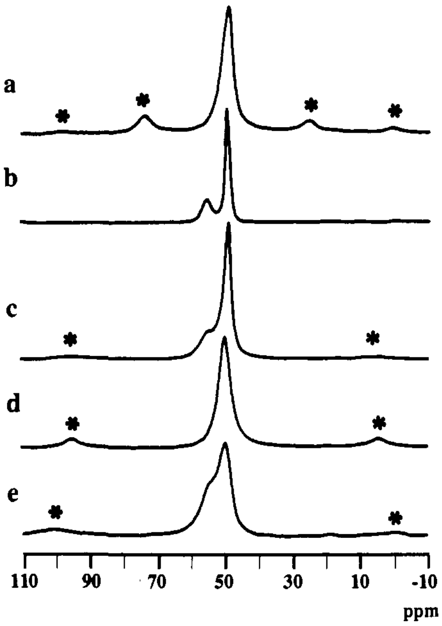

Figure 1. ^{13}C CP/MAS spectra obtained after the adsorption of methanol-^{13}C at room temperature on the following: (a) Al_2O_3; (b) ZnO; (c) ZnO/Al_2O_3; (d) Cu/Al_2O_3; and (e) $Cu/ZnO/Al_2O_3$. Asterisks denote spinning sidebands.

temperature, the principal components of the ^{13}C chemical shift tensor of the adsorbate were measured, and in some cases detailed relaxation measurements were performed. The samples were then heated in the NMR probe. Several general protocols were used. In some cases, the sample temperature was raised incrementally, and spectra were obtained at each temperature and after cooling to ambient. In other cases the sample was heated directly to the maximum temperature of 523 K, and spectra were obtained over a time course and after cooling to room temperature. Some of the catalyst/adsorbate systems were studied several times. The chemical shift assignments made here are plausible but not definitive. However, these assignments are substantially verified by the agreement between the observed chemistry and the expected behavior of the proposed species.

Methanol readily adsorbed on all of the catalysts, and its properties in the adsorbed state were characterized in detail as a probe of surface properties and as a prelude to in situ studies of its decomposition. Figure 1 presents ^{13}C CP/MAS spectra obtained after the adsorption of methanol-^{13}C on the catalysts at room temperature. The appearance of these spectra is summarized as follows: (1) a ^{13}C resonance with an isotropic chemical shift of 49 ppm was observed in spectra of all catalysts; (2) on catalysts which contained ZnO, a second isotropic peak was observed at 54 ppm that was accompanied by spinning sidebands; (3) both the 49- and 54-ppm peaks survived 50 μs of interrupted decoupling; and (4) spinning sidebands from the 49-ppm resonance were observed for all catalysts containing Al_2O_3. The presence of spinning sidebands is characteristic of species bound in such a fashion that they are incapable of isotropic molecular motion on a timescale of ca. 1 ms. Hence, the sideband pattern reflects either the chemical shift anisotropy (CSA) of the nuclear site or the residual CSA after averaging by restricted molecular motion.

From detailed relaxation studies and measurements of the principal components of ^{13}C chemical shift tensors (vide infra) the following picture of the adsorption of methanol on these catalysts emerged: Methanol adsorbs on Al_2O_3 as two distinct species, one tightly bound (chemisorbed) and the other highly mobile and easily removed by evacuation (physisorbed). The 54-ppm peak which forms on catalysts containing ZnO is due to a second species covalently bound to the surface. Intact methanol also adsorbs on ZnO, but it is easily removed. We did not observe Knight shifts in any of the ^{13}C spectra of adsorbates on Cu/Al_2O_3 or $Cu/ZnO/Al_2O_3$; but on the latter catalyst, adsorbed methanol exhibited relaxation behavior consistent with interaction with paramagnetic copper sites (either dispersed Cu(0) or Cu(II)).

Table I. Relaxation Times[a] for the Species Formed after the Adsorption of Methanol-^{13}C on Various Catalysts at 298 K

catalyst	peak[b]	^{13}C T_1	^{13}C $T_{1\rho}$	^1H T_1	^1H $T_{1\rho}$
Al_2O_3[c]	49	418 1389	np	np	np
Al_2O_3[d]	49	2778	27	np	10
ZnO[c]	49	955	19	111	np
	54	1636	31	129	
ZnO/Al_2O_3[c]	49	1390	17	187	5
	54	2190	44	456	7
$Cu/ZnO/Al_2O_3$[c]	49	181 1226	26	15	4
	54	298 1751	46	17	5
$Cu/ZnO/Al_2O_3$[d]	49	331 1832	46	np	np
	54	464 2223	63		
$Cu/ZnO/Al_2O_3$[e]	49	112 1377	np	np	np
	54	284 2206			
Cu/Al_2O_3[c]	49	508	20	15	3

[a] All in ms, when two times are given for a single peak, a biexponential decay of magnetization is implied. [b] In ppm relative to TMS. [c] Sample not evacuated after adsorption of methanol. [d] Sample evacuated after adsorption to remove physisorbed methanol. [e] 20% $^{13}CH_3OH$, 80% $^{12}CH_3OH$ adsorbed followed by evacuation; np denotes measurement not performed.

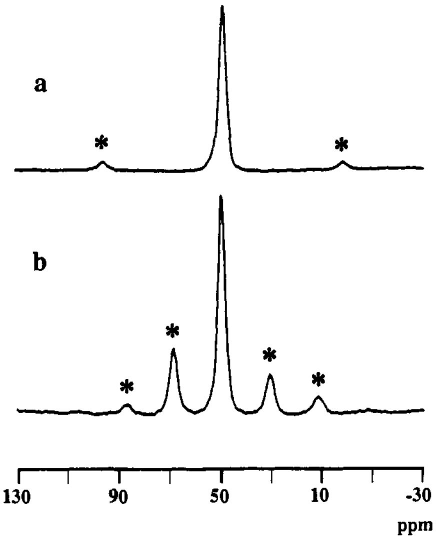

Figure 2. ^{13}C CP/MAS spectra acquired after the adsorption of methanol-^{13}C on Al_2O_3 and evacuation to remove excess methanol at spinning speeds of (a) 3.49 kHz and (b) 1.39 kHz. Asterisks denote spinning sidebands.

Table I shows ^{13}C and ^1H relaxation data for methanol adsorbed on the catalysts. ^1H and ^{13}C $T_{1\rho}$ values do not appear to be diagnostic of either the catalyst surface or the structure of the adsorbate. ^1H T_1 values are approximately 1 order of magnitude lower for catalysts containing copper. The ^{13}C T_1 results are most informative. On Al_2O_3, the 49-ppm methanol peak exhibits biphasic relaxation, and only the long component persists after evacuation to remove physisorbed methanol. The chemisorbed methanol species with a long ^{13}C T_1 also displays significant spinning sidebands in a slow-speed MAS spectrum (Figure 2). Infrared studies have previously shown that methoxy groups form on ZnO.[32] The surface-bound methoxy signal (54 ppm) has a

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Table II. ^{13}C Chemical Shift Parameters[a] for Surface-Bound Methoxy Species and Suitable Model Compounds

sample	T (K)	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	$\Delta\delta$	η	ref
surface-bound methoxy on Al_2O_3	298	49	65	65	17	40	0	this work
surface-bound methoxy on ZnO	298	54	79	79	5	74	0	this work
surface-bound methoxy on ZnO	273	54	79	79	4	75	0	this work
surface-bound methoxy on ZnO	233	53	79	79	2	77	0	this work
surface-bound methoxy on ZnO	193	53	80	80	0	80	0	this work
CH_3OH	177	52	73	73	10	63	0	33
p-dimethoxybenzene	298	56	80	72	16	60	0.12	34
$KOCH_3$	298	58	78	78	18	60	0	33
$Mg(OCH_3)_2$	298	53	74	74	10	64	0	33
$C(OCH_3)_2$	298	55	73	73	20	53	0	33

[a] δ's and $\Delta\delta$'s are in ppm relative to TMS.

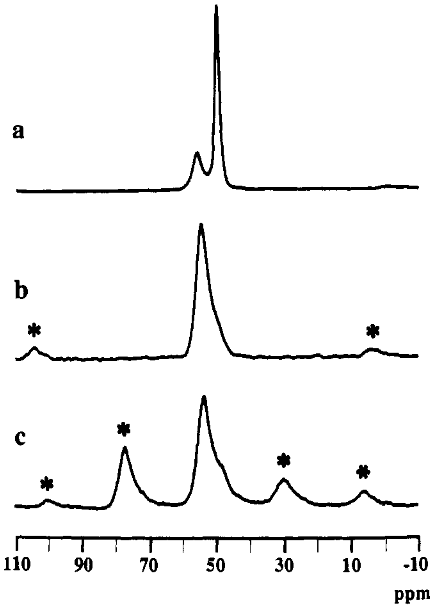
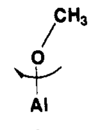


Figure 3. ^{13}C CP/MAS spectra obtained (a) after the adsorption of methanol-^{13}C on ZnO; (b) after the adsorption of methanol-^{13}C on a shallow bed of ZnO and evacuation to remove physisorbed methanol; and (c) for the sample in (b) at a spinning speed of 1.63 kHz. Asterisks denote spinning sidebands.

longer ^{13}C T_1 than the more mobile physisorbed methanol (49 ppm). The latter signal is readily removed by evacuation (Figure 3) to leave almost exclusively the surface-bound methoxy species which displayed the prominent sideband patterns characteristic of restricted reorientation.

All of the $Cu/ZnO/Al_2O_3$ samples studied displayed biphasic ^{13}C T_1 behavior for both the 49- and 54-ppm signals. Although the exact values of the relaxation rates varied from sample to sample, the fast and slow components differed by a factor of 4–10 in all cases. We also studied the relaxation behavior of 20% ^{13}C enriched methanol on $Cu/ZnO/Al_2O_3$ to guard against the possibility that ^{13}C–^{13}C spin diffusion was obscuring even more complicated relaxation behavior, but the biphasic ^{13}C T_1 was also observed with that sample (Table I). The most plausible explanation for the short component is relaxation induced by paramagnetic copper sites dispersed in an oxide phase. Since the catalyst samples were reduced, these are probably Cu(0) sites.

The experiments described above provide evidence for the formation of two chemisorbed species upon exposure to $Cu/ZnO/Al_2O_3$ catalyst to methanol. One is associated with Al_2O_3 and the other with ZnO. The properties of these species were further elucidated using slow-spinning spectra of the type shown in Figures 2 and 3 and calculation of the principal components of the ^{13}C chemical shift tensors using the method of Herzfeld and Berger.[30] Those results are compared with literature data for appropriate model compounds in Table II. The $\Delta\delta$ value for chemisorbed methanol on Al_2O_3 (49 ppm) is slightly smaller than that for the model compounds (53–63 ppm). We were able to account for the observed chemical shift parameters of chemisorbed methanol by operating on the chemical shift tensor of solid methanol with the rotation implied in **1**. Excellent agreement between experiment and calculation was obtained for Al–O–C bond angles of ca. 70°.



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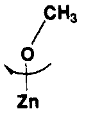
In the case of the surface-bound methoxy species on ZnO, the chemical shift anisotropy ($\Delta\delta$) is significantly *larger* than the values of all of the model compounds. Clearly, the difference in the chemical shift tensor for the surface-bound methoxy group cannot be reconciled with those for the model compounds by invoking motional averaging; an electronic (structural) difference is required. Two structures could be imagined for a surface-bound methoxy species, terminal (**2**) and bridging (**3**). The terminal form would presumably be capable of rotation about the Zn–O axis, and that would lead to a relatively small value for $\Delta\delta$ (cf. species **1**). In contrast, the bridging methoxy would only be capable of motion about the O–C bond axis. In a study of methanol adsorption on zeolite HZSM-5, Dybowski and coworkers[35] characterized a terminal methoxy species analogous to **1**. The ^{13}C T_1 behavior of that species was governed by rotation about the Al–O bond with an activation energy of 11 kcal/mol. We performed variable-temperature ^{13}C T_1 measurements for the methoxy group on ZnO and determined that the motion responsible for T_1 was characterized by an activation energy of 2.2 kcal/mol, exactly what one would expect for unrestricted methyl rotation. The bridging methoxy (**3**) satisfactorily accounts for the dynamics which we observed. Furthermore, it is structurally different from the model compounds, so differences in the principal components of the chemical shift tensor as well as isotropic chemical shift are not unreasonable. One possible explanation for the formation of bridging methoxy species is that methanol reacts with an oxygen vacancy on the ZnO surface.



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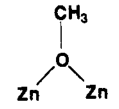

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Having characterized the adsorption of methanol on $Cu/ZnO/Al_2O_3$ and related catalysts in detail, we then studied its decomposition using high-temperature in situ MAS NMR. A typical in situ run involved the acquisition of several dozen to several hundred ^{13}C MAS spectra of the species formed at high temperature probing the structure and the relaxation behavior of those species over a range of temperatures. Several ^{13}C MAS

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(35) Tsiao, C.; Corbin, D. R.; Dybowski, C. *J. Am. Chem. Soc.* **1990**, *112*, 7140.

Table III. ^{13}C Chemical Shift Parameters[a] for Surface-Bound Formates and Suitable Model Compounds

sample	T (K)	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	$\Delta\delta$	η	ref
formic acid on Al_2O_3	298	170	232	173	106	96	0.92	this work
formic acid on ZnO	298	171	234	175	105	99	0.89	this work
formic acid on ZnO/Al_2O_3	298	172	235	177	105	100	0.87	this work
formic acid on ZnO/Al_2O_3	493	172	217	173	127	68	0.98	this work
formic acid on Cu/Al_2O_3	298	172	238	171	108	99	0.95	this work
formic acid on $Cu/ZnO/Al_2O_3$	298	172	235	176	106	99	0.89	this work
methanol decomposition on $Cu/ZnO/Al_2O_3$	298	172	226	164	120	84	0.79	this work
paraformaldehyde disproportionation on $Cu/ZnO/Al_2O_3$	298	172	224	166	125	78	0.79	this work
formic acid	125	168	251	162	92	125	0.84	36
ammonium formate	185	164	225	168	99	98	0.88	36
calcium formate	298	173	231	184	105	102	0.69	37

[a] δ's and $\Delta\delta$'s are in ppm relative to TMS.

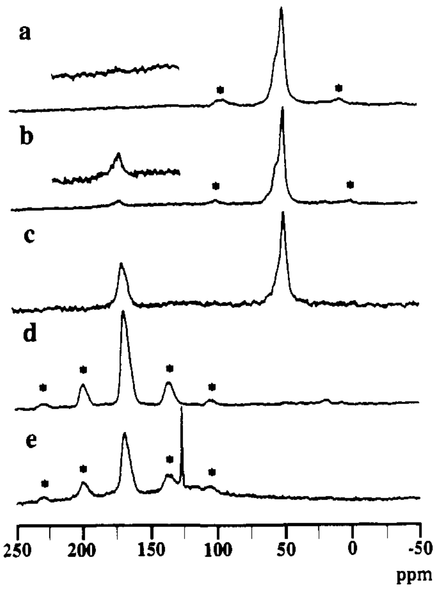


Figure 4. ^{13}C MAS spectra showing in situ decomposition of methanol-^{13}C on $Cu/ZnO/Al_2O_3$: (a) CP spectrum at room temperature; (b) CP spectrum at 353 K; (c) CP spectrum at 453 K; (d) CP spectrum obtained after heating to 523 K and cooling to room temperature; and (e) Bloch decay spectrum obtained after heating to 523 K and cooling to room temperature.

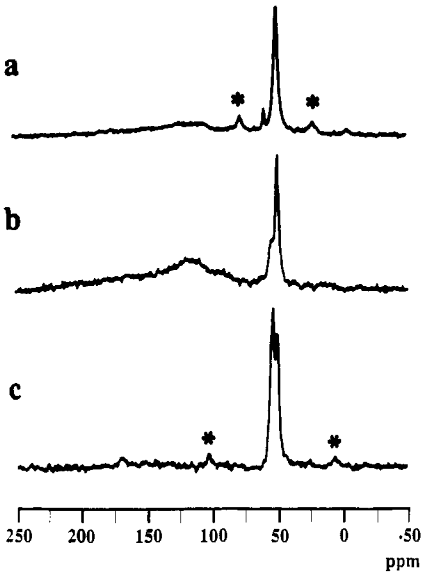


Figure 5. ^{13}C MAS spectra acquired at 493 K after adsorption of methanol at room temperature on the following: (a) Al_2O_3 (Bloch decay); (b) ZnO/Al_2O_3 (Bloch decay); and (c) ZnO (CP). The hump in the Bloch decay spectra is due to probe background. Asterisks denote spinning sidebands.

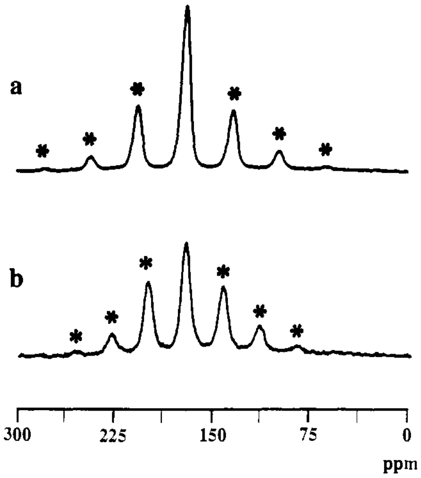


Figure 6. ^{13}C CP/MAS spectra obtained at room temperature after the adsorption of formic acid on (a) ZnO/Al_2O_3 and (b) $Cu/ZnO/Al_2O_3$. Asterisks denote spinning sidebands.

spectra from a representative experiment are shown in Figure 4. Chemisorbed methanol and surface-bound methoxy originally present on $Cu/ZnO/Al_2O_3$ at 298 K (Figure 4a) began forming a formate species immediately after increasing the sample temperature to 353 K (Figure 4b). Considerably more formate formed after the temperature was raised to 453 K (Figure 4c). Upon the sample temperature being raised to 523 K, the formate intermediate was converted into a carbonate (or bicarbonate) intermediate which has spectroscopic properties very distinct from the formate intermediate in spite of similar ^{13}C isotropic chemical shifts (vide infra). Figure 4d and e show two spectra of this sample which were obtained immediately after cycling back to 298 K. The cross polarization spectrum (Figure 4d) shows an intense signal for the carbonate intermediate rigidly bound to the catalyst surface, whereas the Bloch decay spectrum (Figure 4e) not only shows the carbonate but also reveals that approximately 15% of the carbonate had decomposed to gas-phase or physisorbed CO_2. The above experiment then shows the decomposition of chemisorbed methanol and surface-bound methoxy to CO_2, by way of surface-bound formate and carbonate.

Analogous in situ experiments were also performed on Al_2O_3, ZnO/Al_2O_3, and ZnO in order to further elucidate the roles of the catalyst components. Representative high-temperature ^{13}C MAS spectra are shown in Figure 5. None of these catalysts were active for methanol oxidation at the temperature studied, and we conclude that the copper catalyzes the conversion of methoxy to formate. Dimethyl ether (60 ppm) formed on the Al_2O_3 catalyst but not on the ZnO/Al_2O_3 catalyst. Indeed, one of the known roles of ZnO is to deactivate the acidic sites on Al_2O_3 and prevent dimethyl ether formation.

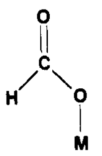
All of the catalysts readily adsorbed formic acid at room temperature to form a surface-bound formate species; representative spectra are shown in Figure 6. ^{13}C chemical shift data for formate species were obtained by Herzfeld–Berger analysis for all of the samples studied. These data are summarized in Table III. The formate species obtained by adsorption of formic acid had essentially identical chemical shift parameters on all of the catalysts.

Table IV. ^{13}C Chemical Shift Parameters[a] for Surface-Bound Carbonates and Suitable Model Compounds

sample	T (K)	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	$\Delta\delta$	η	ref
CO_2 on Cu/ZnO/Al$_2$O$_3$	298	166	225	155	115	89	0.68	this work
decomposition of formic acid on Cu/ZnO/Al$_2$O$_3$	298	166	229	161	114	95	0.75	this work
decomposition of methanol on Cu/ZnO/Al$_2$O$_3$	298	166	235	177	114	104	0.91	this work
calcium carbonate	493	169	217	173	119	75	0.88	38
barium carbonate	298	170	238	171	118	102	0.78	39
potassium bicarbonate	298	162	218	155	113	84	0.75	39
ammonium bicarbonate	298	163	223	152	119	90	0.55	39

[a] δ's and $\Delta\delta$'s are in ppm relative to TMS.

Three bonding modes are possible for formate species on surfaces, monodentate **4**, bidentate **5**, and bridging **6**. Examination



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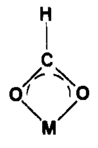

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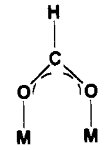

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of the shielding tensor data in Table III suggests that the formates formed from direct adsorption of formic acid at room temperature are not capable of large-amplitude motion; hence the bidentate or bridging species seem most probable. This conclusion is supported by an independent line of reasoning. In a ^{13}C solid-state NMR study of formic acid adsorbed in Y zeolites,[36] Duncan and Vaughan noted that there is a good correlation between δ_{22} and the ratio of the C–O bond lengths of formate species, i.e., δ_{22} shifts from the upfield part of the powder pattern to the downfield part as the C–O bond lengths become more symmetric. This correlation is exhibited by the ratio of the disparity between the upfield and central components ($\delta_{22} - \delta_{33}$) to the overall anisotropy ($\delta_{11} - \delta_{33}$). For methyl formate, where the C–O bond lengths are not the same, this ratio is equal to 0.2. For calcium formate, where the formate ion is chelated to two calcium ions and the C–O bond lengths are the same, the ratio is equal to 0.6. Duncan and Vaughan suggested that, in general, $(\delta_{22} - \delta_{33})/(\delta_{11} - \delta_{33})$ is on the order of 0.6 for symmetrical species, and 0.2 for ester-like formate species. For the surface-bound formate species formed from the adsorption of formic acid on Cu/ZnO/Al$_2$O$_3$ and related catalysts (see Table III), $(\delta_{22} - \delta_{33})/(\delta_{11} - \delta_{33})$ ranged from 0.48 to 0.55, and we conclude that these species are best described as bidentate or bridging.

The formate species formed by the decomposition of methanol on Cu/ZnO/Al$_2$O$_3$ had chemical shift parameters that were slightly different from those measured for species formed from the direct adsorption of formic acid. The $\Delta\delta$ value was approximately 15% lower, but the value of the asymmetry parameter η and the ratio $(\delta_{22} - \delta_{33})/(\delta_{11} - \delta_{33})$ were consistent with the values for the other species. It is not clear whether the slightly smaller value of $\Delta\delta$ reflects an electronic difference or restricted molecular motion. In FT-IR studies of formate species on a variety of metal oxides, Busca and co-workers[18] noted that the infrared frequencies of surface formates were different depending on whether the formate was obtained by adsorption of formic acid or oxidation of methanol.

When the formic acid/Cu/ZnO/Al$_2$O$_3$ sample was heated to 523 K, formation of carbonate and CO$_2$ was observed as noted previously for the methanol/Cu/ZnO/Al$_2$O$_3$ system. The formic acid/ZnO/Al$_2$O$_3$ sample was much less reactive, and only a trace of carbonate was obtained after heating the MAS rotor to 523 K. This result again underscores the role of copper in redox reactions on the catalyst. The low reactivity of formate on ZnO/Al$_2$O$_3$ did allow us to determine that formate is mobile on the catalyst at elevated temperatures. Upon heating from 298 to 493 K (Table III), the $\Delta\delta$ decreased from 102 to 68 ppm, a result consistent with large-amplitude molecular motion. We conclude that formate is mobile on the catalyst surface at reaction temperature.

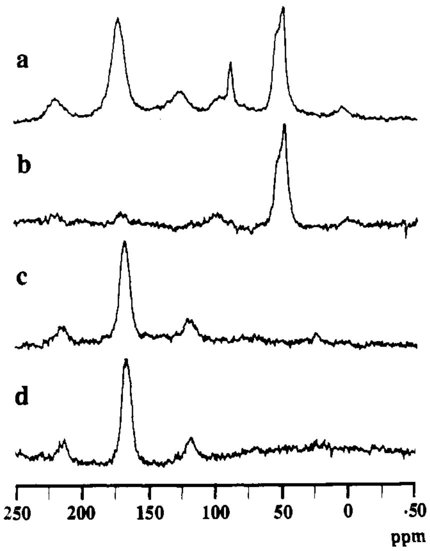

Figure 7. Illustration of the use of interrupted decoupling to distinguish between surface-bound formate and surface-bound carbonate. The sample was prepared by decomposition of paraformaldehyde on Cu/ZnO/Al$_2$O$_3$ (see text): (a) CP/MAS at 298 K after heating to 373 K; (b) same as above except with interrupted decoupling; (c) CP/MAS at 298 K after heating to 523 K; (d) same as above except with interrupted decoupling.

In spite of their similar isotropic ^{13}C chemical shifts, formate and carbonate could always be distinguished based on their response to interrupted decoupling. The formate signals formed by adsorption of formic acid or the decomposition of methanol or paraformaldehyde at ca. 373 K gave ^{13}C signals that did not survive interrupted decoupling, as expected for a protonated carbon in a relatively rigid species. Signals due to carbonate species were not significantly attenuated by interrupted decoupling. As illustrated in Figure 7, the distinction between formate and carbonate was unambiguous.

The principal components of the ^{13}C chemical shift tensors were also characterized for carbonate species formed on some of the catalysts studied; these data are reported in Table IV. Inspecting that table, one notes reasonable agreements between principal component data of surface species and carbonate or bicarbonate model compounds.

Several investigations have suggested an intermediary role of formaldehyde in methanol synthesis.[13,14,17,18,37] For example, Madix and co-workers have proposed that methanol decomposition proceeds by the copper dehydrogenating a methoxy group to formaldehyde which is then oxidized to formate.[37] We have never observed an NMR signal attributable to formaldehyde, or formaldehyde complexes, in in situ studies of methanol decomposition. This does not rule out a role for formaldehyde if one assumes that the formaldehyde is short-lived under the reaction conditions used in this investigation. We investigated the chemistry of formaldehyde on Cu/ZnO/Al$_2$O$_3$ and the other catalysts by decomposing paraformaldehyde-^{13}*C* on the samples in in situ NMR experiments at 373 K. Paraformaldehyde decomposed on all of the catalysts, including pure Al$_2$O$_3$ and pure ZnO, to give equal

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(36) Duncan, T. M.; Vaughan, R. W. *J. Catal.* **1981**, *67*, 49.

(37) Wachs, I. E.; Madix, R. J. *J. Catal.* **1978**, *53*, 208.

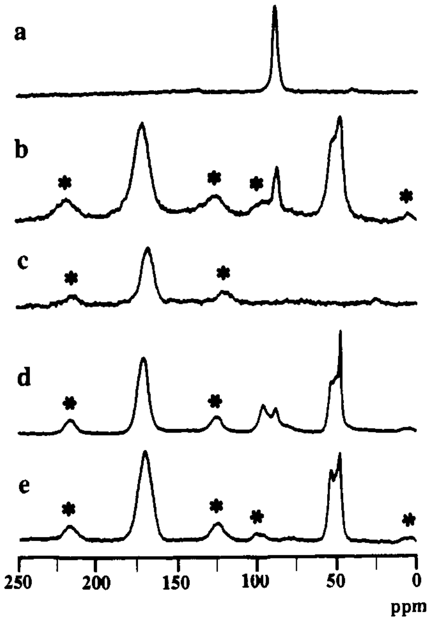
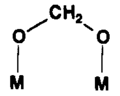


Figure 8. ^{13}C CP/MAS spectra showing the decomposition of paraformaldehyde-^{13}C on $Cu/ZnO/Al_2O_3$ (a) at 298 K; (b) after heating to 373 K and cooling to 298 K; (c) after heating to 523 K and cooling to 298 K; and on ZnO/Al_2O_3 (d) the same as in b; and (e) the same as in c. Asterisks denote spinning sidebands.

moles of surface-bound methoxy groups and formate. This result is reminiscent of the Cannizzaro disproportionation of formaldehyde.[14,20] Representative spectra are reported in Figure 8. Free formaldehyde was not observed in any of the reactions. Formate and methoxy were converted to carbonate (e.g., Figure 8c) upon heating the copper-containing catalyst to high temperature, but catalysts without copper were unreactive.

Figure 8d shows the ^{13}C spectrum of paraformaldehyde-^{13}C on ZnO/Al_2O_3 at room temperature after heating to 373 K. In addition to the signals for formate and methoxy groups and/or methanol, there are two smaller isotropic resonances: a signal at 89 ppm due to unreacted paraformaldehyde and a large signal at 96 ppm. Neither signal survives interrupted decoupling. One mode in which formaldehyde bonds to surfaces is by the formation of the dioxomethylene species 7.[18-20] We are unable to unambiguously assign the 96-ppm signal, but species 7 is a plausible assignment. Further heating of the ZnO/Al_2O_3 resulted in a decrease in both paraformaldehyde and the 96-ppm resonance (Figure 8e).



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The paraformaldehyde decomposition studies are consistent with an intermediary role for formaldehyde in methanol decomposition. We did not observe free formaldehyde in the methanol decomposition studies, but it was not observed in the paraformaldehyde decomposition reactions either. Formaldehyde is very reactive at 373 K for all of the catalysts studied and immediately undergoes oxidation or disproportionation, possibly through a dioxymethylene intermediate.

Detailed relaxation measurements were performed on the paraformaldehyde-^{13}C catalyst samples at room temperature after heating to 373 K. The results of the investigation are summarized in Table V. The relaxation times for the methoxy carbon signals at 49 and 54 ppm followed the same trends as those seen previously for these signals in samples prepared by direct adsorption of methanol. Analogous trends were exhibited by the relaxation data for the formate signals. Very similar formate relaxation data were measured for samples prepared by direct adsorption of formic acid (not shown). As seen previously in Table I, the ^{13}C T_1 values were most diagnostic of catalyst composition. Biexponential relaxation was observed for all three species of the $Cu/ZnO/Al_2O_3$ catalyst, again suggestive of paramagnetic Cu(0) dispersed into the oxide phase. The similarities in relaxation times observed for direct adsorption vs in situ synthesis suggests that these are in fact the same species.

Table V. Relaxation Times[a] for the Species Formed after the Disproportionation of Paraformaldehyde-^{13}C on Various Catalysts[b]

catalyst	peak[c]	^{13}C T_1	^{13}C $T_{1\rho}$	^1H T_1	^1H $T_{1\rho}$
Al_2O_3	49	2820	38	536	12
	172	3740	34	598	16
ZnO	49	1320	77	503	8
	54	2560	100	387	41
	172	2930	171	418	30
ZnO/Al_2O_3	49	1830	27	370	np
	54	2360	67	378	
	172	4620	33	418	
$Cu/ZnO/Al_2O_3$	49	244 2320	34	40	7
	54	317 2600	53	45	9
	172	332 1710	18	38	6
Cu/Al_2O_3	49	1010	32	53	6
	172	1600	16	77	7

[a] All in ms, when two times are given for a single peak, a biexponential decay of magnetization is implied. [b] All measurements performed at room temperature. [c] In ppm relative to TMS; np denotes measurement not performed.

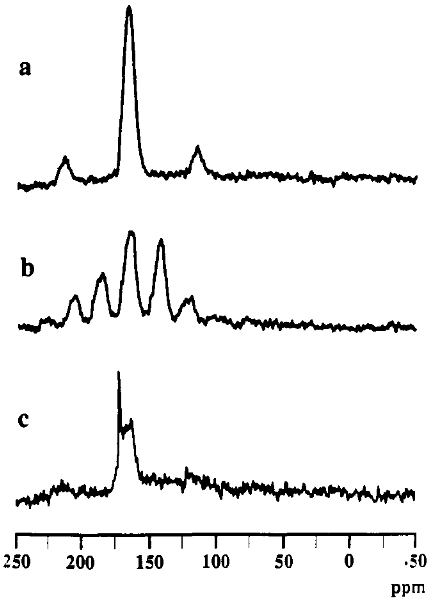

Figure 9. ^{13}C CP/MAS spectra probing the adsorption of $^{13}CO_2$ and ^{13}CO on $Cu/ZnO/Al_2O_3$ at 298 K: (a) after adsorption of $^{13}CO_2$, spinning speed 3.77 kHz; (b) same as above except spinning speed 1.60 kHz; (c) after adsorption of ^{13}CO, spinning speed ca. 3.8 kHz.

As stated earlier, the requirement of 50–100 atm for converting CO_2 or CO and H_2 to methanol precludes the study of the forward reaction by magic-angle spinning NMR with currently available rotor technology. Nevertheless, some results were obtainable for the first step of the reactions of CO_2 and CO on $Cu/ZnO/Al_2O_3$ at low pressure. CO_2 was easily taken up by the catalyst to form a carbonate (Figure 9a and b) with ^{13}C chemical shift data similar to those for carbonates formed from methanol or formic acid decomposition (Table IV). Two signals were observed when ^{13}CO was adsorbed on $Cu/ZnO/Al_2O_3$ at low pressure (Figure 9c). The broad signal at 166 ppm is due to carbonate, but the assignment of the very narrow resonance at 172 ppm is more speculative. Although that chemical shift is identical to that of the formate species observed in this contribution, the signal survived interrupted decoupling and otherwise appeared to be a mobile species.

Gas-phase CO has a ^{13}C chemical shift of 184 ppm, and it usually shifts downfield upon forming strong metal carbonyl complexes. In the case of weak complexes, however, upfield shifts are more common. Cu(I) carbonyl compounds[38–40] are among the weakest carbonyl complexes ever isolated, and the ^{13}C chemical shifts are in the vicinity of 172 ppm.[41] Zn carbonyls have not been investigated by NMR, but they are also expected to involve weak bonding.[42–44] We speculate that the 172-ppm resonance in Figure 9c is a mobile CO on the surface weakly interacting with either copper or zinc.

Summary

The in situ NMR studies presented here enable us to comment on the questions posed in the introduction.

1. Both CO_2 and CO interact with the catalyst surface at low pressure, but CO_2 is taken up more readily to form the carbonate species observed during methanol decomposition on $Cu/ZnO/Al_2O_3$. CO_2 is also formed when the carbonate species formed from methanol is heated to 523 K.

2. ^{13}C T_1 relaxation time measurements provide indirect evidence that paramagnetic Cu(0) atoms or clusters are dispersed into the oxide phase(s) in $Cu/ZnO/Al_2O_3$. This result does not disprove the claim that only the metal surface is important, but the possibility of a role for dispersed clusters and/or a synergistic effect between the metal and oxide phases should not be overlooked.

3. Pure ZnO, pure Al_2O_3, and ZnO/Al_2O_3 were shown to be fairly reactive in this contribution. A terminal methoxy group forms on Al_2O_3, and a bridging methoxy forms on ZnO. Formaldehyde readily disproportionated to formate and methoxy on any of the above catalysts. Copper was essential for the oxidation of formate to carbonate and the oxidation of methoxy to formaldehyde and/or formate at 523 K. Methanol synthesis clearly cannot proceed at 523 K without a metal component, but the oxide phases appear to be more reactive than necessary for a mere support role. Copper alone may be capable of catalyzing all of the steps in methanol synthesis; but under the in situ conditions used in this investigation, several adsorbed species are present on the ZnO and Al_2O_3 components.

4. The most significant results of the present study pertain to the reaction mechanism. The terminal bridging methoxy on Al_2O_3 and the bridging methoxy on ZnO form from either formaldehyde decomposition or methanol adsorption. Formaldehyde is too reactive to be detected as a free species using our in situ protocol, but the paraformaldehyde decomposition studies are consistent with formaldehyde having an intermediary role, possibly as a surface-bound dioxymethylene species. Formate is a ubiquitous intermediate in many catalysis reactions, and it was easily generated and thoroughly characterized in the present investigation. The formate on $Cu/ZnO/Al_2O_3$ and related catalysts is best described as a symmetrical bidentate or bridging species which is rigid at 298 K but exhibits anisotropic motion on the surface on a time scale of ca. 1 ms at 493 K. Surface carbonate is produced readily by oxidation of formate on $Cu/Zn/Al_2O_3$, and the carbonate is in equilibrium with free CO_2.

This study has also reported extensive data on the principal components of the ^{13}C chemical shift tensors of various species on the catalysts studied.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8919741) for support of this work and the Department of Defense for assistance in the purchase of the NMR spectrometer. D.K.M. is a Robert A. Welch Foundation Predoctoral Fellow.

Registry No. Al_2O_3, 1344-28-1; ZnO, 1314-13-2; Cu, 7440-50-8; MeO, 2143-68-2; HCO_2H, 64-18-6; CH_3OH, 67-56-1; $(CH_2O)_x$, 30525-89-4; HCHO, 50-00-0; CO_2, 124-38-9; CO, 630-08-0.

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Symmetries of Hydrogen Bonds in Monoanions of Dicarboxylic Acids

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Abstract: The NMR method of isotopic perturbation of degenerate equilibrium was used to distinguish between single- and double-well potentials in intramolecularly hydrogen-bonded monoanions of ^{18}O-labeled succinic, maleic, and phthalic acids. The observed isotope shift on the ^{13}C spectra demonstrates that these monoanions exist as two equilibrating tautomers in aqueous solution but as a single symmetric structure in a nonpolar solvent. This difference is attributed to the disorder of the aqueous environment.

In the study of hydrogen bonds one of the fundamental questions is whether the potential energy for motion of the hydrogen has a single minimum ("well") or two. If single, the hydrogen is fixed between the two donor atoms (**1**). If there are two minima, the hydrogen will be found closer to one donor than to the other. There are then two tautomeric forms, in rapid equilibrium (**2**), and the symmetric structure is the transition state for interconversion of the tautomers. Both situations have been observed, by a variety of experimental methods.[1] Often there are two forms, even if the donor atoms are identical, as in $CH_3C(OH){=}CH{-}COCH_3$, the enol of acetylacetone. The single, symmetric form is seen in hydrogen maleate (**3**) and hydrogen phthalate (**4**)

$$-O\cdots H\cdots O- \qquad -O{-}H\cdots\cdots O- \rightleftharpoons -O\cdots\cdots H{-}O-$$

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