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Evidence for Production of Surface Formate upon Direct Reaction of CO with Alumina and Magnesia

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The observation of adsorbed formate ion produced by the reaction of CO with MgO or γ-Al_2O_3 surfaces at temperatures between 375 and 575 K is reported. Infrared bands observed near 1590, 1380, 1360, and 1050 are assigned to the fundamentals of adsorbed HCO_2^- ion on the basis of spectra that have been reported for formate ion in solution. The spectral bands and observed isotopic shifts for adsorbed formate produced by reaction of the oxide surface with CO agree with the spectra of formates produced by reaction of methanol or formic acid with the same surfaces. The intensity of IR bands due to formate produced by reaction of the oxide surfaces with CO depends upon the hydroxyl group concentration at the surface. A mechanism for conversion of CO to formate via a surface acylium ion is proposed.

INTRODUCTION

In the course of our investigations of metal carbonyl compounds deposited on a variety of oxide supports, we have discovered that CO reacts directly with appropriately pretreated oxide surfaces above about 375 K to produce adsorbed formate ion. A similar observation for the reaction at 575 K of CO over γ-Al_2O_3 which had been dehydrated at 725 K has been reported in the Russian literature (*1*). The surface formates that are produced may be readily identified by fingerprint ir bands near 1600, 1380, and 1360 cm^{-1} (*2–5*). Formate has often been reported in reactions of CO over these oxide surfaces but it has not been generally recognized that the formate could derive from direct reaction of the surface with CO.

Greenler and Kagel (*3, 5*) have reported that methanol reacts directly with a MgO surface at 440 K to produce adsorbed formate and that preadsorbed methoxide ion, heated to 440 K, also reacts to produce the formate. Their isotopic studies confirmed the identity of the species. Earlier, Kagel (*6*) and Corso (*7*) had shown that methanol, ethanol, *n*-propanol, and *n*-butanol all adsorb on γ-Al_2O_3 at temperatures above 440 K to form the derivative surface carboxylates. The bands for formate, derived from methanol, were identified in those studies.

Formate development on the support surface during catalytic reactions has been reported by several investigators. For example, Dalla Betta and Shelef (*8*) observed the characteristic formate IR bands at 1585, 1397, and 1378 cm^{-1} during the hydrogenation reaction of CO using a Ru/Al_2O_3 catalyst. It was concluded that formate developed directly on the alumina from the reaction of H_2 and CO and that metallic Ru was not required. Amenomiya (*9*) observed formate ion production while studying the water–gas shift (WGS) reaction over alumina; the temperature range was 575–775 K. In trying to establish the intermediate in the water–gas shift reaction on magnesia, Ueno *et al.* (*10*) concluded that a mixture of CO and H_2O and temperatures of 483 to 543 K were required to produce surface formates. We have reported earlier on the appearance of strong bands due to formate on MgO and Al_2O_3 when a supported cobalt catalyst, derived from a cobalt carbonyl, was exposed to CO at temperatures be-

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tween 450 and 550 K. Upon further examination, it was found that the cobalt was not necessary for formate ion development, but that the direct reaction of CO with dehydrated MgO and γ-Al_2O_3 at temperatures above 375 K was sufficient to produce the distinctive IR features of adsorbed formate (*11, 12*).

Solymosi *et al.* (*13*), in their recent study of the reactions of CO_2 and H_2 over a Rh/Al_2O_3 catalyst, reported the observation of formate development at 298 K, while a temperature of 573 K was required for the same reaction over pure alumina. The latter temperature is within the range in which we observe formate development directly from reaction of CO.

These and similar reports in the literature overlooked the possibility that CO may react directly with an oxide surface to yield formate ion, prompting us to report here our observations of the reactions of CO with MgO and γ-Al_2O_3 at elevated temperatures.

EXPERIMENTAL

The experimental technique, including the ir gas cell, was similar to that used previously (*11, 14*). A pressed wafer of either MgO or γ-Al_2O_3 was mounted in a Pyrex or quartz cradle within the cell where it could be positioned between the KBr windows to record ir spectra or moved into the furnace section for thermal treatment. IR spectra were recorded on a Nicolet MX-10 Fourier transform infrared spectrometer. The spectra were, typically, the result of 128 interferograms. Spectral resolution was 2 cm^{-1}.

High purity MgO (A_s = 28 m^2/g BET) was purchased from MK Research and Development Co. Analysis showed 0.58% C, 0.043% N, 0.11% Cl, <0.02% Fe, and <0.002% Co. CK-300 γ-Al_2O_3 (A_s = 160 m^2/g BET) was supplied by Akzo Chemie.

MgO and γ-Al_2O_3 powders were pressed into 5–10 g/cm^3 (≃0.3 mm thickness) wafers at 7000 and 30,000 psi, respectively, in a 1.25-in. stainless-steel die and then cut into 1.25 × 3-mm rectangles for use in the ir gas cell. The MgO and γ-Al_2O_3 were calcined by heating under O_2 to 675 K, then heating *in vacuo* at the desired pretreatment temperature for 2 h.

MgO was deuterated by repeatedly heating in 100 Torr D_2 at 475 K for 2 h. Once deuterated, it was pretreated at the required temperature. Surface OH groups on γ-Al_2O_3 were exchanged by repeated treatments with small doses of D_2O at 475 K; the sample was then vacuum treated at the desired pretreatment temperature.

H_2O and O_2 were removed from the commercially obtained reagent gases by passing them through a dessicant mixture of $MgClO_4/P_2O_5$ and BASF-R3-11 catalyst. The gases also were routinely analyzed by mass spectrometry to check their purity.

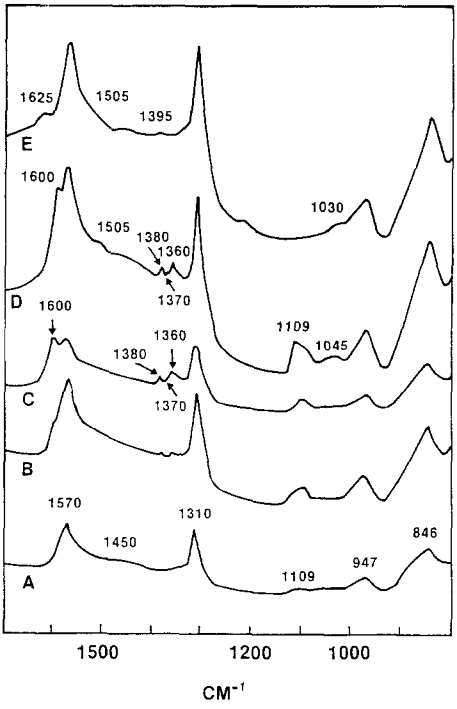


FIG. 1. IR absorbance spectra in the region 800–1700 cm^{-1} for MgO exposed to 30 Torr CO. (A) Background spectrum following pretreatment of MgO at 675 K. (B–E) After heating sample under 30 Torr CO at (B) 375 K for 2 h, (C) 475 K for 2 h, (D) 575 K for 2 h, and (E) 650 K for 2 h.

RESULTS

Figures 1 and 2 and Table 1 present the results of our IR study of CO reacting with MgO and γ-Al_2O_3. The room temperature (RT) exposure of 30 Torr CO to MgO, pretreated at 675 K *in vacuo* for 2 h, does not produce any new IR bands. However, heating the MgO in the presence of CO in the 375–575 K temperature range for 2 h produces bands at 1600, 1380, 1360, and 1045 cm^{-1}. Likewise, no IR bands are produced by the RT exposure of 50 Torr CO to γ-Al_2O_3, pretreated at 525 K for 2 h *in vacuo*, but bands at 1595, 1395, and 1375 cm^{-1} appear when the system is heated at 475 K for 2 h. The frequencies and relative intensities of these bands are virtually identical with those reported previously for formates on magnesia (*5*) and alumina (*3*). The reaction of CO with silicas and zeolites under the

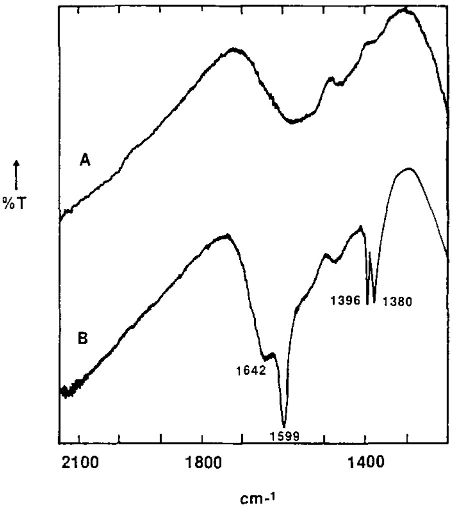


FIG. 2. Infrared transmittance spectra in the region 1200–2200 cm^{-1} for (A) γ-Al_2O_3 following pretreatment and evacuation at 300 K, and (B) heating at 475 K under 50 Torr CO for 2 h.

TABLE 1

Observed Vibrational Bands[a] for Formates on γ-Al_2O_3 and MgO

Formate	Mode					
	$\nu\ (CH)_{stretch}$	$\nu\ (OCO)_{sym\ st}$	$\delta\ (OCO)_{defor}$	$\nu\ (OCO)_{asym\ st}$	$\delta\ (CH)_{in\text{-}plane\ bending}$	$\pi\ (CH)_{out\text{-}of\text{-}plane\ bending}$
	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
Raman[b] HCO_2 aq	2893	1349	762	—	1380	1066
$Na(HCO_2)$[b] salt	2841	1366	772	1567	1337	1073
$Na(HCO_2)$[b] aq	2803	1351	760	1585	1383	1064
$Al(HCO_2)_3$[c] salt		1350		1600	1390	
$Mg(HCO)_2$[d]	2907	1366–1385	761	1603	1404–1391	1081
CH_3OH on Al_2O_3[c]		1377		1597	1396	
$^{13}CH_3OH$ on Al_2O_3[c]		1355		1554	1394	
CD_3OH on Al_2O_3[c]		1347		1595	1034	
CH_3OH on MgO[e]		1370–1340		1600	1382	1088
$^{13}CH_3OH$ on MgO[e]		(1360–1350)[f]		1552	1382	
CD_3OH on MgO[e]		1345–1325		1600	1026	
CO + H_2 on Ru/Al_2O_3[g]		1387		1585	1392	
CO + γ-Al_2O_3		1375		1595	1395	
^{13}CO + γ-Al_2O_3		1347		1554	1396	
CO + deuterated γ-Al_2O_3		1360		1594	—[h]	
CO + MgO		1370–1360		1600	1380	1045
^{13}CO + MgO		1339–1326		1561	1380	
CO + deuterated MgO		1350–1336		1598	1031	

[a] Frequencies in wavenumbers. All spectra except top line are IR spectra.
[b] See Ref. (*2*).
[c] See Ref. (*3*).
[d] See Ref. (*4*).
[e] See Ref. (*5*).
[f] Uncertainty.
[g] See Ref. (*8*).
[h] Not observed.

aforementioned conditions fails to produce any evidence of surface formates.

Although temperatures of at least 375 K are required for the development of surface formates directly from CO on MgO and Al_2O_3, heating above 575 K *in vacuo* results in the release of CO and H_2O as evidenced by temperature-programmed desorption (TPD). Weak bands develop at 1505–1030 cm^{-1} at temperatures above 550 K (Figs. 1D, 1E) as the formate decomposes. Several investigators have assigned a set of bands at these frequencies to unidentate carbonate complexed in solution or bound to an oxide surface (*15*). Even though CO_2 was not observed in the gas phase during the TPD study of decomposition of the surface formate, the presence of new surface carbonate bands suggests some CO_2 formation. Greenler and Kagel (*5, 6*) reported carbonate formation when they heated magnesia adsorbed formate above 600 K.

Because surface pretreatment may affect the nature or degree of the reaction between CO and the oxide, magnesia and alumina pretreated at several different temperatures were studied. Magnesia and alumina dehydrated at high temperatures (>675 K) reacted with CO to produce relatively weak formate bands. When H_2 or H_2O is added to the CO over such a highly dehydroxylated MgO or Al_2O_3, formate production is facilitated, however, confirming the importance of hydroxyl groups for the production of surface formates.

Table 1 compares the IR bands observed in this study with those observed for formate in solution and formate previously reported on Al_2O_3 and MgO. The ν(CH) stretching mode expected near 2800 cm^{-1} and the δ(OCO) deformation mode expected around 760 cm^{-1} are not shown in the table since these regions of the spectrum were not studied.

When ^{13}CO is adsorbed on magnesia and alumina at 475 K, rather large frequency shifts occur for both the 1600- and 1360-cm^{-1} bands, consistent with their assignment as asymmetric and symmetric stretches of the O–C–O group, respectively. The observed isotopic shifts (Table 1) are in agreement with values reported in the literature from other formate studies both in solution and adsorbed on oxide surfaces (*3, 5*).

The band near 1380 cm^{-1}, assigned to C–H in-plane bending motion, is unaffected by ^{13}C substitution because there is little motion of the carbon atom in this vibration. This band should, however, show a major shift upon deuterium substitution. As expected, adsorption of CO on deuterated MgO or γ-Al_2O_3 resulted in a large isotopic shift of the 1380 cm^{-1} band.

The CO stretching modes exhibit much smaller shifts, in the range of 2–20 cm^{-1}, upon deuterium substitution. Again, this is quite consistent with other studies of formate IR spectra.

DISCUSSION

The following generalizations about formate formation on oxide supports can be made from the results obtained in our work.

1. Reactions in the temperature range 375–575 K of CO with the supports MgO and γ-Al_2O_3, pretreated at 525–675 K, result in the development of surface formates. The surface formate then decomposes under vacuum at ca. 565–575 K (TPD) evolving CO and H_2O. The adsorption of CO on other supports such as silicas and zeolites does not result in the formation of surface formate. The oxide pretreatment temperatures are such that the surface was fully dehydrated and probably slightly dehydroxylated in each case.

2. The temperature at which CO reacts with MgO and γ-Al_2O_3 to produce surface formate is dependent upon the hydroxyl concentration on the oxide surface. The greater the degree of dehydroxylation the higher the temperature necessary to produce formates. As a corollary, the intensity of the formate IR bands produced at a given temperature is inversely proportional to the degree of dehydroxylation.

3. The addition of H_2 or H_2O is not neces-

sary for formate development from CO over MgO and γ-Al_2O_3, but the coaddition of H_2/CO or H_2O/CO to magnesia or alumina that has been pretreated above 675 K facilitates formate production. This is due to the rehydroxylation of these oxide surfaces when exposed to H_2 or H_2O.

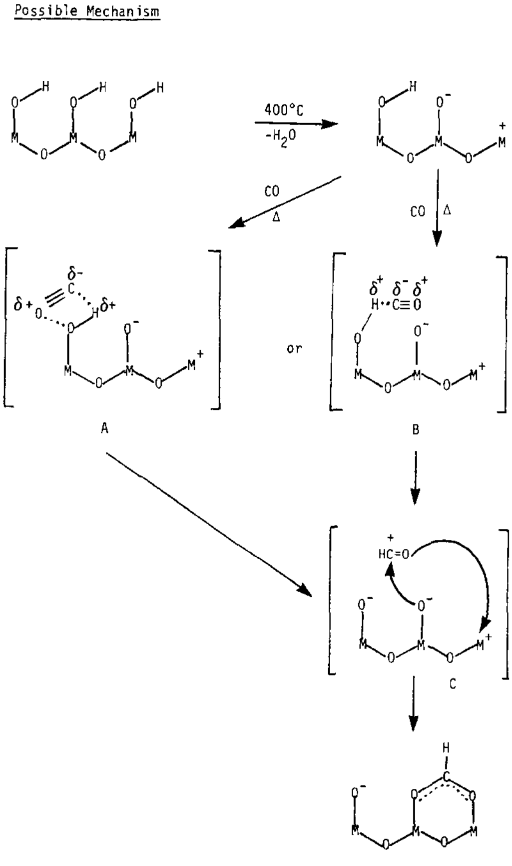
4. The presence of added transition metal ions is not necessary on MgO or γ-Al_2O_3 for formate production.

Structure of the Surface Formate

The formate ion may coordinate to one surface site in a monodentate or bidentate fashion or it may bridge two sites. An empirical approach, using $\nu(CO_2^-)$ modes, has been developed for determining in which of these three forms the acetate ion exists in its various solution complexes (*16–18*). When the difference between the asymmetric and symmetric stretches, $\Delta\nu$, exceeds that in the free ion, the acetate is a monodentate ligand. When $\Delta\nu$ is less than for the free ion, it is bidentate; and when $\Delta\nu$ of the complex is about the same as for the free ion it is acting as a bridging ligand. Applying the same empirical approach to formate on the surfaces suggests the ion bridges two surface metal atoms.

Mechanistic Considerations

It has been proposed that the solution reaction of CO with H_2O to yield formic acid proceeds via an acylium cation (*21*), HCO^+, which has the resonance forms $H{-}C^+{=}O$ and $H{-}C{\equiv}O^+$. The concerted scheme shown below would lead to the acylium intermediate which then could react as a carbonium ion species to form the bridged bidentate product. The initial surface interaction would be as shown due to the fact that the CO dipole for the free molecules is



negative at the carbon (*22*). This orientation is, of course, also consistent with the fact that CO normally coordinates through carbon to Lewis acids such as metal ions.

An alternative mechanism has been proposed by Kleir (*23*) in which CO bonds to the surface through the carbon, reacts with OH, then rearranges to formate.

Decomposition of the surface formate at 575 K presumably occurs via thermolysis of the formic acid formed when the surface formate reacts with H_2O that is liberated by heating the oxide.

Relationship to Previous Studies

The understanding that CO will react directly with supports like alumina and magnesia to produce surface formates might influence interpretations of many catalytic studies. For example, Solymosi *et al.* (*13*), reporting the WGS reaction over a Rh/Al_2O_3 catalyst, discuss the reaction mechanism in terms of formate formation on the Rh particles succeeded by rapid migration of the ions to the Al_2O_3 where they are observed spectroscopically. It seems equally likely that the formate on Al_2O_3 was formed by direct reaction of CO, produced by WGS, with the alumina surface.

The same authors report the complete loss of formate above 673 K and the development of a 2030-cm^{-1} band due to CO on Rh at temperatures above 573 K. Both are consistent with our observation that the adsorbed formate would decompose to CO and H_2O above about 575 K.

Amenomiya reported that formate on alumina decomposed completely to CO and H_2O without observation of either formic acid, CO_2, or H_2 (*9*) and also observed that dry CO reacted with wet Al_2O_3 to yield formate (*24*). Amenoniya also reports that isolated hydroxyls did not appear to be involved in the reactions with CO, consistent with our observation that supports extensively dehydroxylated by heating above 675 K did not react readily with CO. Our study does show, however, that the alumina can be fully dehydrated and even partially dehydroxylated and still react with CO to produce formate.

Finally, Kroeker *et al.*, studying hydrocarbon formation from CO and H_2 over Rh/Al_2O_3 were puzzled by their observation of formate on the alumina surface, even when no H_2 was present (*25*). Again, our results explain these earlier observations.

CONCLUSIONS

IR spectra and isotopic frequency shifts confirm the presence of adsorbed formate on MgO and γ-Al_2O_3 after exposure to dry CO at temperatures between 375 and 575 K. The differences between the symmetric and asymmetric ν(O–C–O) bands suggest the formate ion binds as a bidentate bridge between two metal ions on the surface.

The literature of CO reactions above magnesia- and alumina-supported catalysts is replete with reports of IR bands closely matching those observed in this study. When properly assigned to adsorbed formate, it generally has been assumed that supported metal was essential to the production of the formate or that H_2 or H_2O was required for formate production.

The possible development of surface formates by direct reaction of CO with the oxide surface should be considered in any studies involving reactions of CO at elevated temperatures over alumina or magnesia.

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