

## *In Situ* Fourier Transform Infrared Study of Methanol Synthesis on Mixed Metal Oxide Catalysts

JAMES F. EDWARDS AND G. L. SCHRADER<sup>1</sup>

*Department of Chemical Engineering and Ames Laboratory—U.S. Department of Energy,  
Iowa State University, Ames, Iowa 50011*

Received August 10, 1984; revised January 11, 1985

Transmission infrared spectroscopy was used to characterize adsorbed species on methanol synthesis catalysts under reaction conditions. A copper carbonyl, bidentate formate, and methoxy species were identified as stable surface species. An adsorbed formaldehyde species was unstable at the reaction temperature, but could be observed on the catalyst surface at the beginning of the reaction. Surface species were very similar for feed mixtures of (1) carbon monoxide and hydrogen, (2) carbon monoxide, carbon dioxide, and hydrogen, and (3) formic acid and hydrogen. Carbon monoxide was adsorbed on copper sites to form a linearly bonded carbonyl species. The formate species was adsorbed on a zinc site different from the zinc site on which formaldehyde and methoxy groups were adsorbed. The rate-determining step in methanol synthesis was determined to be the reaction of hydrogen from a hydroxyl species with a methoxy group to yield methanol. It was established that at the experimental conditions used in this study, the methanol synthesis reaction was far from equilibrium while the water-gas shift reaction was near equilibrium. © 1985 Academic Press, Inc.

### INTRODUCTION

The development of a catalyst for the synthesis of methanol from carbon monoxide and hydrogen occurred during the early part of this century when catalysis was just beginning to play an important role in the chemical industry. Although there have been many improvements in the preparation of methanol catalysts during the succeeding years, the basic components—zinc oxide, copper oxide, and a promoter such as chromia or alumina—have remained unchanged. Methanol synthesis has become a fully developed commercial process, but very little is known about how this catalyst functions to selectively produce methanol. Recent physical and kinetic measurements of methanol catalysts and their precursors have established the relationship between catalytic activity and such variables as crystalline morphology, crystalline phase, electronic structure, and surface composi-

tion (1-4). These investigators concluded that the active component of copper-containing methanol catalysts was a solid solution of Cu(I) ions in the zinc oxide phase. XPS-Auger spectroscopies of methanol catalysts (5, 6) have identified a stable cuprous ion in the surface monolayer of reduced coprecipitated catalysts.

In spite of these advances in the characterization of methanol catalysts, the nature of adsorbed species and of the elementary surface reactions continues to be uncertain. Several mechanisms for methanol synthesis have been proposed in recent years. A chemical trapping technique has identified formate and methoxy species on a used methanol catalyst (7); the proposed methanol synthesis mechanism postulates that formate, methoxy, and methoxy groups are reaction intermediates bonded through oxygen to a metal ion site. A much different mechanistic proposal was suggested by Herman and co-workers (1) involving carbonyl, formyl, hydroxycarbene, and hydroxymethyl intermediates bonded through

<sup>1</sup> To whom correspondence should be addressed.

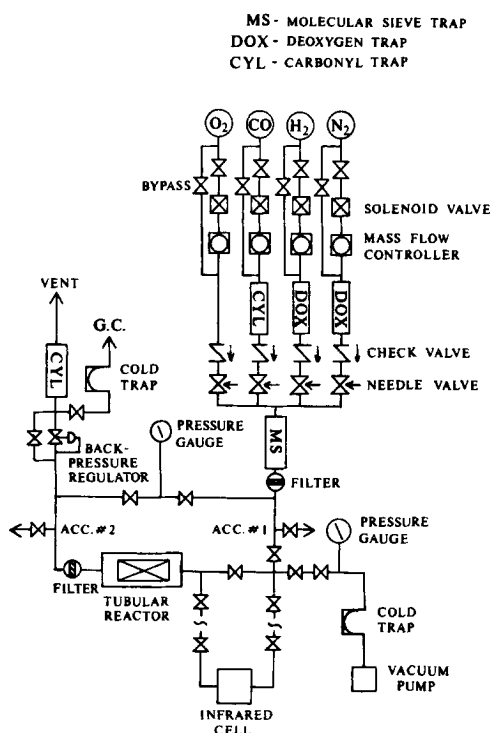


FIG. 1. High-pressure system.

carbon to a Cu(I) ion in the zinc oxide phase. Adjacent zinc ions were the centers for hydrogen adsorption. A recent revision of this mechanism has incorporated hydroxyl, formate, formyl, and methoxy species bonded to a Cu(I) ion in the reaction pathway (8). Other mechanisms have been proposed incorporating both carbon-bonded and oxygen-bonded intermediates in methanol synthesis. A reaction scheme with carbonyl, formyl, formaldehyde, and methoxy intermediates adsorbed on Cu(I) active sites within the zinc oxide lattice was developed from a review of the literature (9). This mechanism was analogous to methanol synthesis by homogeneous catalysis. Another mechanism has proposed that an oxygen vacancy acts as an active site in methanol synthesis (10). After a carbonyl species is hydrogenated to a formyl species, the oxygen on the formyl interacts with an adjacent electron-deficient vacancy. As further hydrogenation occurs, a

methoxy species is formed as the bonding between the oxygen and vacancy is strengthened while the bonding between the carbon and metal ion weakens. The variation in catalytic activity with specific crystal planes of zinc oxide has been ascribed to the relative number of defects (vacancies) in each type of plane (11, 12).

The study reported here has focused on the use of Fourier transform infrared (FT-IR) spectroscopy to characterize adsorbed surface species under methanol synthesis conditions: the objective has been to obtain a better understanding of the molecular interactions occurring on the catalyst surface. In the first aspect of this work, the activity and selectivity of several methanol catalysts were measured under the same conditions used for infrared experiments. Then the identification and transient behavior of adsorbed species were determined *in situ* by FT-IR spectroscopy. This information has been incorporated into a proposed methanol synthesis mechanism.

## METHODS

*Experimental apparatus.* A flow reactor system, shown in Fig. 1, was designed for catalytic studies at pressures from  $10^{-4}$  Torr (1 Torr =  $133.3 \text{ N m}^{-2}$ ) to 100 atm (1 atm =  $1.013 \times 10^5 \text{ N m}^{-2}$ ). There were three major sections in this system: (1) a high-pressure section constructed with stainless-steel components for optimum safety, (2) an atmospheric section to handle the effluent from the system for venting or sampling, and (3) a vacuum section composed of glass and stainless steel to desorb impurities in the system or on the catalyst surface. The entire system was built on a mobile frame permitting the system to be connected with other analytical instruments (i.e., a gas chromatograph or infrared spectrometer).

Cylinders of high-purity gases were used as the pressure source for the system. Each gas flow line had a solenoid valve (Atkomatic, Type SBTD) and a thermal mass

flow controller (Brooks, Model 5810/5835A). The solenoid valves were wired via the alarm relay of a CO detector system (MSA, Model 571) to provide an automatic shut-down feature if a major gas leak (CO or H<sub>2</sub>) should develop downstream. Elevated pressures were set with a Tescom back-pressure regulator and measured with a Heise CMM pressure gauge. The tubing configuration permitted both the prereactor and postreactor pressures to be recorded, from which the pressure drop through the reactor could be determined. The reactor was a 12-in. length of stainless-steel tubing fitted with a sheathed thermocouple (Omega, Sub-Miniature) that passed axially through the reactor inlet to the catalyst bed. The reactor temperature was measured with an Omega 199 indicator and regulated with an Omega 49 proportional controller. The binary oxides were evaluated at a flow rate of 1800 GHSV and the ternary oxides were evaluated at a flow rate of 3600 GHSV. Two ports upstream of the reactor were used as inlet and outlet connections to a high-pressure infrared cell which has been described previously (13). The vacuum section utilized a liquid-nitrogen trap and diffusion pump (Edwards, Model E02).

Reaction products were quantitatively analyzed with a gas chromatograph (Antek, Model 310/40-ALP) using thermal conductivity detectors and a HP 3390A reporting integrator. All species were separated with Porapak N and Porapak T columns in series. Relative molar response factors were determined experimentally using injections from mixtures prepared in a gas-sampling bulb. The relative molar response factors (CO = 1.00) were found to be 1.15 for CH<sub>3</sub>OH, 0.91 for H<sub>2</sub>O, and 0.98 for CO<sub>2</sub>.

Infrared spectra were recorded with a Bruker-Physik AG Model IFS 113 spectrometer using single-beam optics. Each spectrum was produced by accumulating 100 scans at 2 cm<sup>-1</sup> resolution. Only the absorption by the infrared windows (CaF<sub>2</sub>) was subtracted from the spectra. The catalyst and gaseous species, in addition to ad-

sorbed species, contributed infrared bands to the spectra. Attempts to subtract these bands generally resulted in distortion of important spectral regions.

*Catalyst preparation.* The catalysts were prepared by coprecipitating a mixture of metal nitrates with ammonium bicarbonate at 60°C according to the method described by Stiles (14). After filtering and washing with distilled water, the precipitates were dried in air at 115°C for 12 h and then calcined in a stream of oxygen at 400°C for 8 h. The amount of cupric oxide in these catalysts was restricted to no greater than 10% CuO due to the strong infrared absorption by cupric oxide.

The oxidic form of the catalyst was prepared for transmission infrared studies by pressing powder under a load of 4500 kg into a wafer approximately 0.10 mm thick and placing the wafer into the infrared cell. Catalyst activity and selectivity evaluations were conducted in a fixed-bed tubular reactor containing a bed of broken catalyst wafers surrounded by SiC particles. Dry nitrogen gas was flowed through the infrared cell or reactor for approximately 12 h at atmospheric pressure and 200°C to desorb water on the catalyst surface. Under these conditions there was no significant dehydroxylation of the catalyst surface. All experiments were conducted in a continuous flow mode at 60 cm<sup>3</sup>/min (STP) using high-purity gases. Water or formic acid solution could be introduced into the feed system at low concentrations by bubbling the gaseous flow through the liquid which was contained within an enclosed stainless-steel vessel (saturator). Catalysts were reduced by exposing the oxide to a 95/5 N<sub>2</sub>/H<sub>2</sub> stream for 1 h at 200°C and 1 atm (pretreatment 1).

## RESULTS

### *Catalytic Activities*

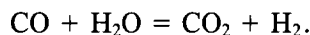
Because the catalysts developed for infrared studies had copper contents considerably lower than industrial catalysts, it

TABLE 1  
Reactivity of Coprecipitated Catalysts at 50 atm

| Catalyst composition<br>(mol%) | Feed composition<br>(vol%)<br>H <sub>2</sub> /CO/CO <sub>2</sub> /H <sub>2</sub> O | CO conversion<br>(%) to CH <sub>3</sub> OH |       | Methanol yield<br>(× 10 <sup>-5</sup> mol/m <sup>2</sup> /h) |       |
|--------------------------------|--|--|-------|--|-------|
|                                |  | 200°C                                      | 250°C | 200°C  | 250°C |
| <b>Zn/Cu oxide</b>             |  |  |       |  |       |
| 95/5                           | 67/33/0/0  | 1.6  | 6.3   | 1.1  | 4.5   |
| 90/10                          | 67/33/0/0  | 1.3  | 5.2   | 0.9  | 3.7   |
| 95/5                           | 66/28/6.6/0  | 0.7  | 11.4  | 0.5  | 8.2   |
| 90/10                          | 66/28/6.6/0  | 1.1  | 15.6  | 0.8  | 11.2  |
| 95/5                           | 67/33/0/0.5  | 1.9  | 8.8   | 1.4  | 6.3   |
| 90/10                          | 67/33/0/0.5  | 1.1  | 12.6  | 0.8  | 9.0   |
| <b>Zn/Cu/Cr oxide</b>          |  |  |       |  |       |
| 90/5/5                         | 66/28/6.6/0  | 0.9  | 10.7  | 0.5  | 6.4   |
| 80/10/10                       | 67/33/0/0  | 7.8  | 13.8  | 4.8  | 8.4   |
| 80/10/10                       | 67/33/0/0.1  | 1.8  | 11.0  | 1.1  | 6.7   |

was important to verify that these coprecipitated oxides were active and selective for methanol synthesis. The effects of catalyst composition, reactor temperature, and feed composition on CO conversion were examined and the results are summarized in Table 1. All binary (CuO/ZnO) and ternary (CuO/ZnO/Cr<sub>2</sub>O<sub>3</sub>) compositions were active for carbon monoxide hydrogenation to methanol at 50 atm and temperatures of 200 and 250°C. The selectivity for methanol was 100% for binary and ternary catalysts at 200°C, while at 250°C the ternary catalysts produced some dimethyl ether (<2%) in addition to methanol. In general, the methanol yield per unit surface area was comparable between binary and ternary catalysts. These results supported the observation (1) that the primary effect of the addition of Cr<sub>2</sub>O<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub> to the composition of a binary oxide was to enhance activity by increasing the surface area. An exception was the 80/10/10 Zn/Cu/Cr oxide which exhibited relatively high activity at 200°C. The addition of an oxidizing agent (CO<sub>2</sub> or H<sub>2</sub>O) to the H<sub>2</sub>/CO feed mixture had little effect on yields at 200°C but significantly improved conversions at 250°C. Carbon dioxide was added as a gas premixed with hydrogen (10% CO<sub>2</sub> in H<sub>2</sub>), while wa-

ter was added by bubbling the H<sub>2</sub>/CO mixture through water at high pressure. The reactor effluent from experiments with water in the feed had no water but did contain some carbon dioxide, indicating that these catalysts had good activity for the water-gas shift reaction:



The thermodynamics of the water-gas shift reaction strongly favors the formation of carbon dioxide and hydrogen at the reaction conditions.

The initial yield of methanol was generally higher than the steady-state yield (value after 8 h). This loss of activity could arise from several causes, and was examined by considering the transient behavior of the 90/10 Zn/Cu catalyst. The concentrations of CO<sub>2</sub>, CH<sub>3</sub>OH, and H<sub>2</sub>O were measured periodically during the first 8 h of a reaction run at 200°C and 50 atm for each of the feed mixtures utilized in this study. The results of these transients are shown in Fig. 2. When a feed of H<sub>2</sub> and CO was used, the initial methanol yield was 50% higher than the steady-state yield. The catalytic activity gradually decreased during the transient, but was still relatively high after 8 h. The small amount of CO<sub>2</sub> in the initial effluent

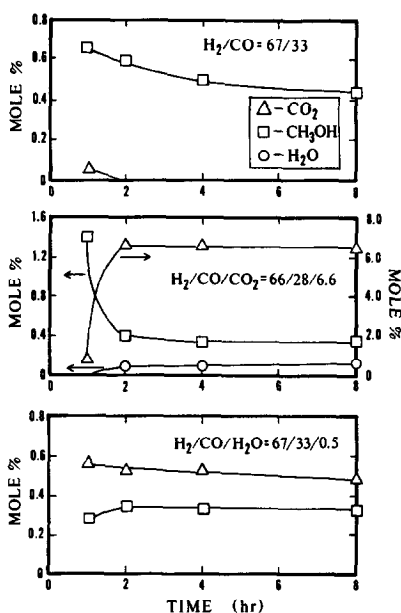


FIG. 2. Reactor effluent concentrations at 200°C and 50 atm (transient behavior).

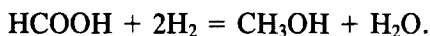
sample most likely arose from the water-gas shift reaction between CO and some residual water formed earlier from catalyst reduction (pretreatment 1).

The transient behavior of the effluent from a reaction run using a feed of CO, H<sub>2</sub>, and CO<sub>2</sub> had some significant differences compared to the reaction run without CO<sub>2</sub>. The initial methanol yield was twice the amount obtained without any CO<sub>2</sub> present, while the amount of CO<sub>2</sub> was approximately one-tenth the feed concentration. Within 4 h the CO<sub>2</sub> concentration had returned to the feed value, and a steady-state methanol yield was established at a level less than the CO/H<sub>2</sub> reaction. Water was also a product in the effluent. Because relatively high CO<sub>2</sub> concentrations were found in the effluent following the pressure drop at the end of an experiment, the initial low level of CO<sub>2</sub> probably resulted from absorption by the catalyst. At steady state the methanol yield could arise from either CO hydrogenation or CO<sub>2</sub> hydrogenation. The water concentration could not be used to determine the hydrogenation rates because

water was also involved in the water-gas shift reaction. Because the methanol yield was less with a feed containing CO<sub>2</sub> at 200°C, the diffusive restrictions caused by CO<sub>2</sub> in the catalyst pores overrode any advantages that CO<sub>2</sub> provided as a reactant or in preventing deactivation (strong reduction) of active sites.

A feed mixture of CO, H<sub>2</sub>, and H<sub>2</sub>O produced effluent concentrations essentially constant over the 8-h period. The methanol yield was approximately the same as the yield obtained from the feed mixture containing CO<sub>2</sub>. The water in this feed mixture was converted to CO<sub>2</sub> by the water-gas shift reaction. A pressure drop at the end of this experiment resulted in relatively high levels of CO<sub>2</sub> and H<sub>2</sub>O in the effluent, indicating some adsorption of these two species.

An adsorbed formate species is a possible reaction intermediate in methanol synthesis from hydrogen and carbon monoxide. Thus a feed mixture containing hydrogen and formic acid might produce methanol:



Reaction runs were conducted using a gaseous mixture of 50/50 H<sub>2</sub>/N<sub>2</sub> bubbled through a formic acid solution (73% HCOOH, 27% H<sub>2</sub>O) at 50 atm. Complete conversion of HCOOH to CH<sub>3</sub>OH occurred over a binary 95/5 Zn/Cu catalyst at 200°C. A ternary 80/10/10 Zn/Cu/Cr catalyst had no activity for methanol synthesis at 200 and 250°C.

#### *Infrared Spectra of Binary Catalysts*

Binary catalysts with low copper contents (Cu/Zn ≤ 0.15) were satisfactory for transmission infrared studies in both oxidized and reduced states. During high-pressure *in situ* studies these catalysts had a significant transmittance loss at lower wavenumbers, requiring that the identification of adsorbed species be based on infrared bands above 2000 cm<sup>-1</sup>.

The adsorption of carbon monoxide on a 95/5 Zn/Cu catalyst at 200°C and 50 atm is shown in Fig. 3. The initial oxidized surface

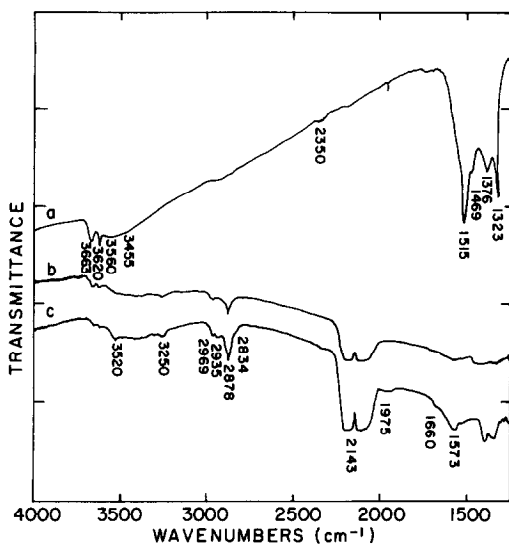


Fig. 3. Carbon monoxide adsorption on 95/5 Zn/Cu oxide at 50 atm and 200°C. (a) Oxidized surface (without pretreatment 1), (b) exposure for 8 h, and (c) exposure for 24 h.

(Fig. 3a) (without pretreatment 1) had residual hydroxyls (bands at 3663, 3620, 3560, and 3455  $\text{cm}^{-1}$ ) and carbonates (bands at 1515, 1469, 1376, and 1323  $\text{cm}^{-1}$ ). Prolonged exposure to CO reduced the catalyst (Fig. 3b), indicated by the formation of the hydroxyl band at 3250  $\text{cm}^{-1}$ . Formate groups (bands at 2969, 2878, 2731, and 1573  $\text{cm}^{-1}$ ), a zinc hydroxyl (band at 3520  $\text{cm}^{-1}$ ), and a zinc hydride (band at 1660  $\text{cm}^{-1}$ ) gradually developed. After 24 h (Fig. 3c) an adsorbed formaldehyde species (bands at 2935, 2834, and 2731  $\text{cm}^{-1}$ ) had formed and the carbonyl band had shifted to 1975  $\text{cm}^{-1}$ . (The band of gaseous CO at 2143  $\text{cm}^{-1}$  masked the carbonyl band in the earlier spectra.)

The hydrogenation of surface species was accelerated by incorporating hydrogen into the carbon monoxide feed. Figure 4 shows the adsorption of a mixture of carbon monoxide and hydrogen ( $\text{CO}/\text{H}_2 = 9/1$ ) on a 95/5 Zn/Cu catalyst at 200°C and 50 atm. Formate groups (band at 2879  $\text{cm}^{-1}$ ) and hydroxyls associated with reduction (band at 3252  $\text{cm}^{-1}$ ) were quickly formed (Fig. 4b). The development of methoxy

groups (bands at 2934 and 2822  $\text{cm}^{-1}$ ) (Fig. 4c) was accompanied by the disappearance of the isolated hydroxyls (bands at 3660 and 3612  $\text{cm}^{-1}$ ). The formate band shifted significantly from 2879 to 2868  $\text{cm}^{-1}$ , due to the development of the methoxy groups.

The adsorption of a stoichiometric 2/1  $\text{H}_2/\text{CO}$  mixture on 95/5, 90/10, and 85/15 Zn/Cu catalysts at 200°C and 50 atm after an hour of exposure is shown in Fig. 5. Very little detail could be observed at lower wavenumbers because of low transmittance. This surface condition would be representative of the adsorbed species during methanol synthesis. The spectra showed the hydroxyl of reduction (band at 3252  $\text{cm}^{-1}$ ), methoxy groups (bands at 2933 and 2822  $\text{cm}^{-1}$ ), and formate groups (bands at 2865 and 1575  $\text{cm}^{-1}$ ) in addition to the band for gaseous carbon monoxide at 2143  $\text{cm}^{-1}$ . The spectra of the 85/15 Zn/Cu catalyst was noisier than the other spectra because its transmittance was an order of magnitude lower than the others.

Methanol synthesis from a stoichiometric feed of carbon monoxide and hydrogen was compared with other feed mixtures. Figure 6 shows the nature of surface species on a

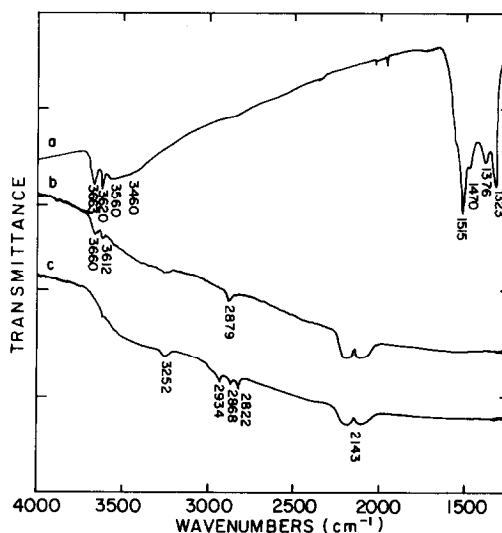


Fig. 4. Adsorption of  $\text{CO}-\text{H}_2$  mixture on 95/5 Zn/Cu oxide at 50 atm and 200°C. (a) Oxidized surface, (b) exposure for 15 min, and (c) exposure for 1 h.

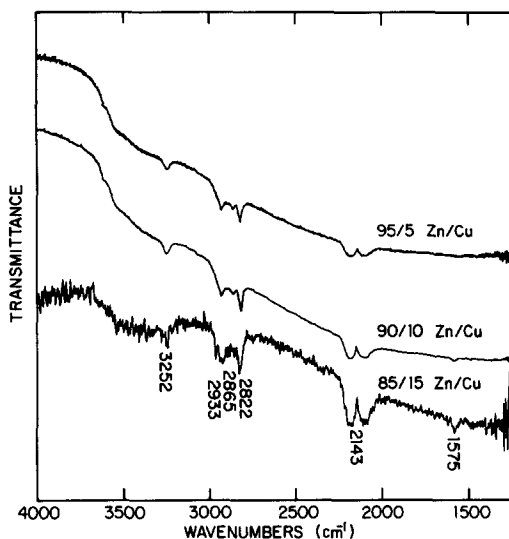


FIG. 5. Adsorption of CO-H<sub>2</sub> mixtures on binary oxides at 50 atm and 200°C.

95/5 Zn/Cu catalyst at 200°C and 50 atm for various feed compositions that were previously established from reactor studies to be satisfactory for methanol synthesis. A feed mixture of 66/27/7 H<sub>2</sub>/CO/CO<sub>2</sub> produced surface species that were identical with those using only H<sub>2</sub> and CO in the feed. The additional band at 2350 cm<sup>-1</sup> was absorption by gaseous carbon dioxide. A feed mixture of 50/50 H<sub>2</sub>/N<sub>2</sub> containing some formic acid solution (73% HCOOH, 27% H<sub>2</sub>O) also produced formate (band at 2870 cm<sup>-1</sup>) and methoxy groups (bands at 2935 and 2820 cm<sup>-1</sup>). Because the feed had some water and a low formic acid concentration, the isolated hydroxyls (bands at 3660 and 3620 cm<sup>-1</sup>) were not completely displaced by methoxy groups.

#### Infrared Spectra of Ternary Catalysts

The ternary Zn-Cu-Cr oxide catalysts, which were also restricted to low copper contents, were superior to the binary catalysts in high-pressure infrared experiments because the transmittance remained high throughout the mid-infrared range. Better surface detail provided more information

for identifying adsorbed species during methanol synthesis conditions.

The reaction of carbon monoxide and hydrogen on a 90/5/5 Zn/Cu/Cr catalyst at 200°C and 50 atm is shown in Fig. 7. The initial surface species on the reduced catalyst (pretreatment 1) after exposure to a 2/1 H<sub>2</sub>/CO mixture (Fig. 7a) were formate groups (bands at 2963, 2872, 1582, 1381, and 1360 cm<sup>-1</sup>), adsorbed formaldehyde species (bands at 2934 and 2843 cm<sup>-1</sup>), and methoxy groups (bands at 2934 and 2824 cm<sup>-1</sup>). The adsorbed formaldehyde species disappeared and the amount of methoxy groups reached a maximum in an hour (Fig. 7b), followed by a gradual decrease in methoxy groups (Fig. 7c). A pressure drop to 1 atm (Fig. 7d) revealed an adsorbed carbonyl species at 2010 cm<sup>-1</sup>.

The reaction of carbon monoxide and hydrogen (H<sub>2</sub>/CO = 2/1) on a 80/10/10 Zn/Cu/Cr catalyst (pretreatment 1) at 200°C and 50 atm is shown in Fig. 8. The initial spectrum (Fig. 8a) showed formate groups (bands at 2870, 1576, 1381, and 1360 cm<sup>-1</sup>), methoxy groups (bands at 2932 and 2822 cm<sup>-1</sup>), and a carbonyl species at 2089 cm<sup>-1</sup>. The methoxy groups reached a steady-state

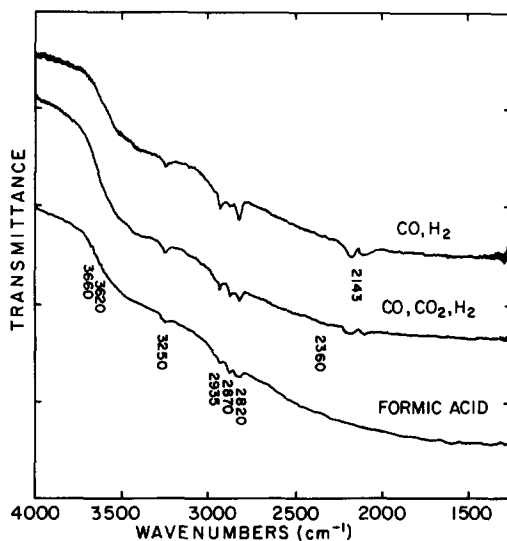


FIG. 6. Adsorption of various feed mixtures on 95/5 Zn/Cu oxide at 50 atm.

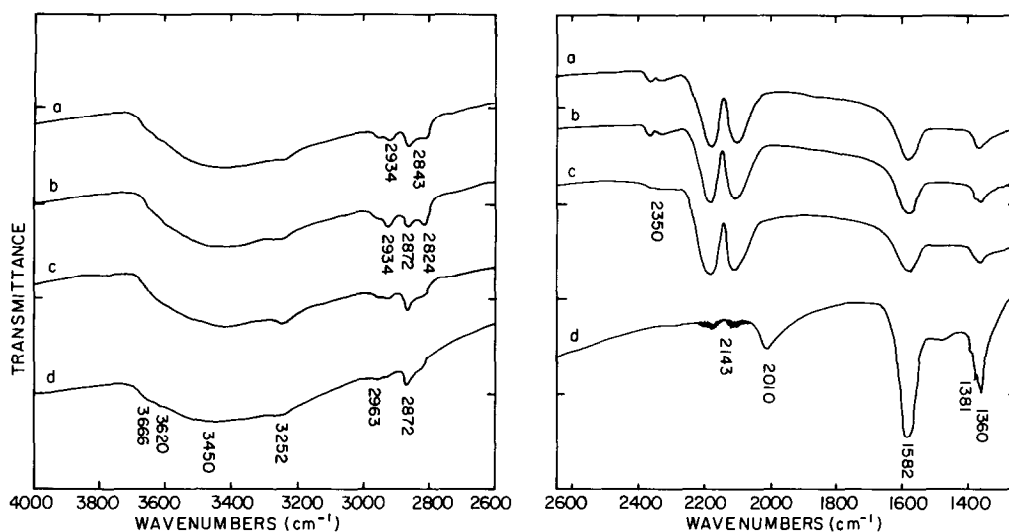


FIG. 7. Adsorption of CO-H<sub>2</sub> mixture on 90/5/5 Zn/Cu/Cr oxide at 50 atm and 200°C. (a) Exposure for 15 min, (b) exposure for 30 min, (c) exposure for 8 h, and (d) after pressure drop.

condition within an hour (Fig. 8b). The carbonyl species shifted from 2089 to 2021 cm<sup>-1</sup> (Fig. 8c). A pressure drop to 1 atm (Fig. 8d) revealed in sharper detail a carbonyl species at 2010 cm<sup>-1</sup>.

The reactor tests established that although a binary catalyst was active for formic acid hydrogenation to methanol, the 80/

10/10 Zn/Cu/Cr catalyst was inactive for this reaction during the same operating conditions. The adsorption of formic acid solution (73% HCOOH, 27% H<sub>2</sub>O) in a carrier gas of 50/50 H<sub>2</sub>/N<sub>2</sub> on a 80/10/10 Zn/Cu/Cr catalyst (pretreatment 1) at 200°C and 50 atm is shown in Fig. 9. A carbonyl species (band at 1983 cm<sup>-1</sup>) and minor amounts

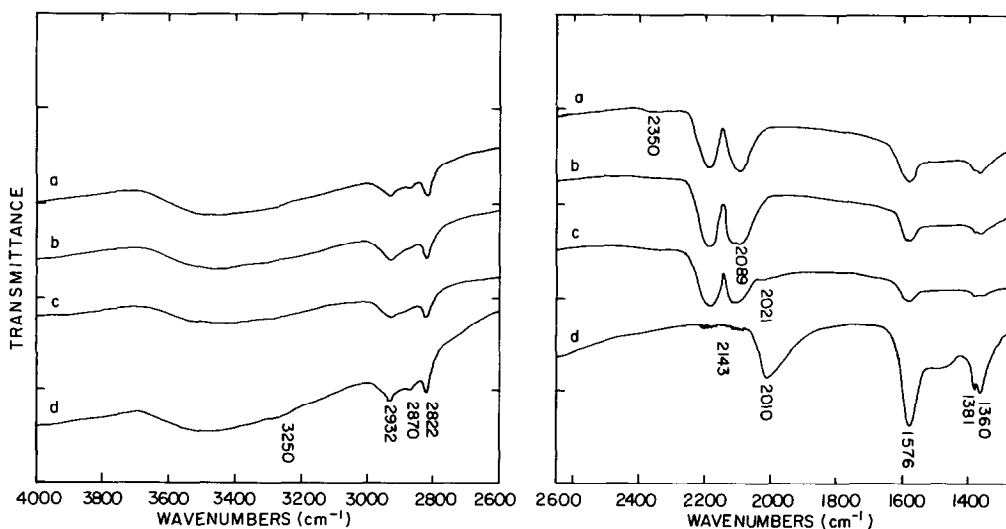


FIG. 8. Adsorption of CO-H<sub>2</sub> mixture on 80/10/10 Zn/Cu/Cr oxide at 50 atm and 200°C. (a) Exposure for 15 min, (b) exposure for 1 h, (c) exposure for 4 h, and (d) after pressure drop.



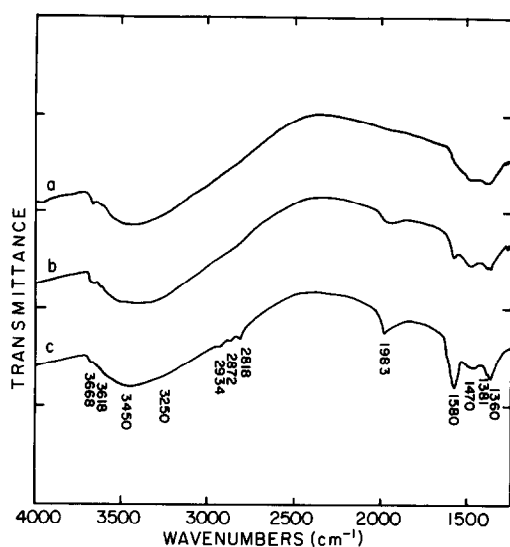


Fig. 9. Adsorption of formic acid on 80/10/10 Zn/Cu/Cr oxide at 50 atm and 200°C. (a) Reduced surface, (b) exposure for 1 h, and (c) exposure for 3 h.

of formate groups (bands at 2872, 1580, 1381, and 1360  $\text{cm}^{-1}$ ) were the only adsorbed species formed within the first hour of exposure (Fig. 9b). Some methoxy groups (bands at 2934 and 2818  $\text{cm}^{-1}$ ) were produced after prolonged exposure (Fig. 9c), but the concentration was low since the isolated hydroxyls (bands at 3668 and 3618  $\text{cm}^{-1}$ ) were not completely displaced. Thus the poor methanol synthesis activity of Zn-Cu-Cr catalysts when using formic acid in the feed mixture was due to the difficulty of formic acid decomposition into formate groups and adsorbed hydrogen at high pressures.

## DISCUSSION

### Band Assignments

The identification of adsorbed species on methanol synthesis catalysts by the analysis of infrared bands has been presented previously (15). Infrared bands at 3665, 3620, 3550, and 3450  $\text{cm}^{-1}$  were assigned to residual hydroxyls on different crystal planes of zinc oxide. The band at 3520  $\text{cm}^{-1}$ , observed during carbon monoxide adsorption (Fig. 3), was assigned to a Type

I zinc hydroxyl species (16). The corresponding Type I zinc hydride was observed at 1660  $\text{cm}^{-1}$ . The band at 3252  $\text{cm}^{-1}$  was assigned to a bulk hydroxyl species associated with a reduced state of copper.

Surface carbonate groups had infrared bands at 1515, 1470, 1376, and 1323  $\text{cm}^{-1}$ . Based on the general assignments for unidentate and bidentate carbonate complexes given by Nakamoto (17), the bands at 1470 and 1376  $\text{cm}^{-1}$  were assigned to the asymmetric and symmetric OCO stretching frequencies of a unidentate carbonate species, while the bands at 1515 and 1323  $\text{cm}^{-1}$  were assigned, respectively, to the asymmetric and symmetric OCO stretching frequencies of a bidentate carbonate species.

The infrared bands at 2875, 1381, 1575, and 1360  $\text{cm}^{-1}$  were assigned to the fundamental CH stretching, CH bending, asymmetric OCO stretching, and symmetric OCO stretching frequencies, respectively, of a bidentate formate species. Additional bands at 2969 and 2731  $\text{cm}^{-1}$  (Fig. 3) were assigned to combinations of fundamental frequencies: the former band was a combination of the CH bending and asymmetric OCO stretching frequencies, while the latter band was a combination of the CH bending and symmetric OCO stretching frequencies. Infrared bands at 2935, 2840, and 2731  $\text{cm}^{-1}$  were assigned to the  $\text{CH}_2$  scissoring overtone, asymmetric  $\text{CH}_2$  stretching, and symmetric  $\text{CH}_2$  stretching frequencies, respectively, of an adsorbed formaldehyde species. The concentration of adsorbed formaldehyde in these experiments was too low to observe the CO stretching frequency. The infrared bands at 2935 and 2820  $\text{cm}^{-1}$  were assigned to the asymmetric and symmetric  $\text{CH}_3$  stretching frequencies, respectively, of a methoxy species.

The band near 2090  $\text{cm}^{-1}$  (Fig. 8) that shifted to 2010  $\text{cm}^{-1}$  at high pressures was assigned to the stretching frequency of a carbonyl species adsorbed on a reduced copper site whose oxidation state may be either +1 or 0. Prolonged exposure to carbon monoxide at high pressure (Fig. 3) or

formic acid decomposition (Fig. 9) can produce a carbonyl species whose band has shifted as low as  $1975\text{ cm}^{-1}$ .

### *Methanol Synthesis*

The reactor experiments established that these coprecipitated binary and ternary catalysts were active and highly selective for methanol synthesis at 50 atm and 200–250°C, even though the copper contents were much lower than those used in industrial catalysts. The methanol synthesis reaction was far from equilibrium in these experiments. The small addition of some water into a CO–H<sub>2</sub> feed stream produced an effluent with carbon dioxide rather than water, indicating that the water-gas shift reaction was near equilibrium. The addition of some carbon dioxide to the CO–H<sub>2</sub> feed stream generally decreased the methanol yield at 200°C. The initial low value for the CO<sub>2</sub> concentration in the reactor effluent and the release of relatively large amounts of CO<sub>2</sub> when the pressure was reduced suggested that carbon dioxide was adsorbed by the catalyst. Relatively high concentrations of CO<sub>2</sub> in the catalyst pores apparently inhibited the rate of methanol synthesis. At 250°C the addition of carbon dioxide to the CO–H<sub>2</sub> feed stream increased the reaction rate. The increased temperature improved the methanol yields in all tests conducted; a strong promotional effect was observed when an oxidant was added to the CO–H<sub>2</sub> feed stream.

Infrared spectra taken at 50 atm in CO/H<sub>2</sub> mixtures had much less transmission than previous spectra taken at atmospheric pressure (15). However, despite some lack of detail in the high-pressure spectra, it was apparent that the types of surface species were essentially the same at both pressures. Thus band assignments that were given to adsorbed species on these metal oxides at atmospheric pressure could be applied to surface species at 50 atm. The primary effect of elevated pressure on adsorbed species was to stabilize the surface hydroxyl at  $3520\text{ cm}^{-1}$  and to weaken the

carbon–oxygen bond of the surface carbonyl (band shift to lower frequency).

Information about the sequence of reaction steps and adsorption sites was obtained from transient experiments. Despite the low activity of these catalysts at 200°C, the infrared spectra showed that steady-state surface conditions were quickly reached when a 2/1 H<sub>2</sub>/CO feed mixture was used. The surface reactions could be slowed by decreasing the amount of hydrogen in the feed mixture. Even in the extreme case of having only carbon monoxide in the gas phase, gradual hydrogenation of surface species occurred because the residual hydroxyls were a source of hydrogen. This demonstrated that hydrogen (possibly as protons) was mobile on the surface at 200°C. Formate groups were clearly formed before formaldehyde and methoxy groups. The order of formaldehyde and methoxy formation at high pressure was difficult to establish because the intensity of the formaldehyde bands was low, but results from the atmospheric studies (15) suggested that the formaldehyde species was the precursor of the methoxy species.

The spectra of Zn/Cu/Cr ternary catalysts during methanol synthesis conditions provided the most detailed information on surface species. At steady state the 80/10/10 Zn/Cu/Cr catalyst had mainly methoxy groups, some formate groups, and no observable formaldehyde groups on the surface (Fig. 8). The adsorbed carbonyl had shifted from  $2089$  to  $2021\text{ cm}^{-1}$ , indicating a weakening of the carbon–oxygen bond without changing the nature of the carbonyl (linear bonded). Unfortunately, the hydroxyl region was too indistinct to detect any band at  $3520\text{ cm}^{-1}$ .

The steady-state spectrum of surface species on a binary catalyst during methanol synthesis using a feed with formic acid was very similar to the spectra for feed mixtures of CO/H<sub>2</sub> or CO/CO<sub>2</sub>/H<sub>2</sub> (Fig. 6). Because the spectrum from the formic acid experiment showed no carbonyl species or gaseous carbon monoxide, the evidence for

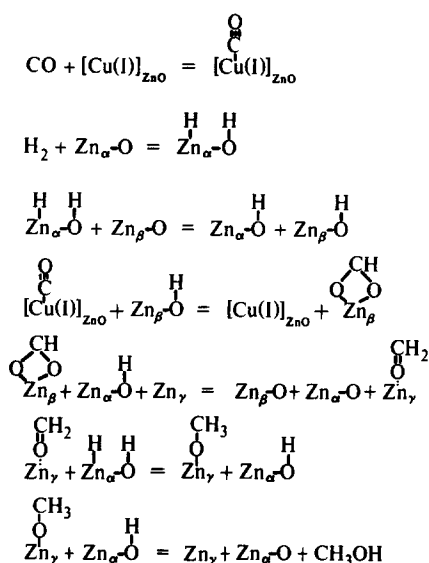


FIG. 10. Methanol synthesis mechanism.

a reaction sequence involving formate and methoxy intermediates was strengthened. A reaction pathway involving carbon-bonded intermediates is unlikely since the lack of formate decomposition provides no carbon monoxide for this synthesis route. Alternatively, a ternary catalyst was unsatisfactory for methanol synthesis using a feed with formic acid. The infrared spectra showed very little formate and methoxy groups on this catalyst, apparently because formic acid decomposition was difficult at these conditions.

A proposed mechanism for methanol synthesis based on the results from this study and atmospheric experiments (15, 18) is shown in Fig. 10. Carbon monoxide is adsorbed on Cu(I) sites in the zinc oxide lattice to form a linear carbonyl species (band at 2020  $\text{cm}^{-1}$ ). Hydrogen is adsorbed dissociatively on adjacent zinc-oxygen sites to form a hydroxyl and hydride species (Type I adsorption). During methanol synthesis conditions the hydroxyl (band at 3520  $\text{cm}^{-1}$ ) and hydride (band at 1660  $\text{cm}^{-1}$ ) were difficult to detect, suggesting that these species were not very stable. Hydrogen could migrate to other sites to form

other types of hydroxyl species (bands at 3550 and 3450  $\text{cm}^{-1}$ ) which were more stable at these conditions. The surface carbonyl can insert into a hydroxyl group to form a bidentate formate species (bands at 2875, 1575, 1381, and 1365  $\text{cm}^{-1}$ ). Hydrogenation of the formate species produces an adsorbed formaldehyde species (bands at 2935, 2840, 2740, and 1610  $\text{cm}^{-1}$ ) which is on a different surface site than the formate species. The formaldehyde species is quickly hydrogenated to form a methoxy species (bands at 2935 and 2820  $\text{cm}^{-1}$ ). The rate-determining step is the hydrogenation of the methoxy species to methanol.

The various zinc sites proposed to be involved in this mechanism can be associated with specific crystal planes of zinc oxide (18). The isolated hydroxyls (bands at 3665 and 3620  $\text{cm}^{-1}$ ) are on the same sites as formaldehyde and methoxy species. These isolated hydroxyl sites ( $\text{Zn}_\gamma$ ) have been associated with polar ZnO surfaces (19). The formate groups occupy a portion of the hydrogen-bonded hydroxyl sites ( $\text{Zn}_\beta$ ) which have been associated with nonpolar ZnO surfaces. The hydrogen-bonded hydroxyls have bands at 3550 and 3450  $\text{cm}^{-1}$ . The site of hydrogen adsorption ( $\text{Zn}_\alpha$ ), which produces a hydroxyl band at 3520  $\text{cm}^{-1}$ , is proposed to be a stepped surface between polar and nonpolar planes of zinc oxide.

#### ACKNOWLEDGMENTS

This work was conducted through the Ames Laboratory which is operated for the U.S. Department of Energy by Iowa State University under Contract W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Chemical Sciences Division.

#### REFERENCES

1. Herman, R. G., Klier, K., Simmons, G. W., Finn, B. P., Bulko, J. B., and Kobylinski, T. P., *J. Catal.* **56**, 407 (1979).
2. Mehta, S., Simmons, G. W., Klier, K., and Herman, R. G., *J. Catal.* **57**, 339 (1979).
3. Bulko, J. B., Herman, R. G., Klier, K., and Simmons, G. W., *J. Phys. Chem.* **83**, 3118 (1979).
4. Herman, R. G., Simmons, G. W., and Klier, K., in "Proceedings, 7th International Congress on

- Catalysis" (T. Seiyama and K. Tanabe, Eds.), p. 475. Elsevier, New York, 1981.
5. Okamoto, Y., Fukino, K., Imanaka, T., and Teranishi, S., *J. Phys. Chem.* **87**, 3740 (1983).
  6. Okamoto, Y., Fukino, K., Imanaka, T., and Teranishi, S., *J. Phys. Chem.* **87**, 3747 (1983).
  7. Deluzarche, A., Kieffer, R., and Muth, A., *Tetrahedron Lett.* **38**, 3357 (1977).
  8. Vedage, G. A., Pitchai, R., Herman, R. G., and Klier, K., "Proceedings, 8th International Congress on Catalysis." Vol. II, p. 47. DEHEMA, Frankfurt am Main, 1984.
  9. Henrici-Olive, G., and Olive, S., *J. Mol. Catal.* **17**, 89 (1982).
  10. Kung, H. H., *Catal. Rev.-Sci. Eng.* **22**, 235 (1980).
  11. Cheng, W. H., and Kung, H. H., *Surf. Sci.* **122**, 21 (1982).
  12. Cheng, W. H., Akhter, S., and Kung, H. H., *J. Catal.* **82**, 341 (1983).
  13. Edwards, J. F., and Schrader, G. L., *Appl. Spectrosc.* **35**, 559 (1981).
  14. Stiles, A. B., U.S. Patent 4,111,847 (Sept. 5, 1978); assigned to E. I. du Pont de Nemours and Co.
  15. Edwards, J. F., and Schrader, G. L., *J. Phys. Chem.* **88**, 5620 (1984).
  16. Dent, A. L., and Kokes, R. J., *J. Phys. Chem.* **73**, 3772 (1969).
  17. Nakamoto, K., "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3rd ed. Wiley, New York, 1978.
  18. Edwards, J. F., and Schrader, G. L., *J. Phys. Chem.* **89**, 782 (1985).
  19. Atherton, K., Newbold, G., Hockey, J. A., *Discuss. Faraday Soc.* **52**, 33 (1971).