

## Combined Infrared Spectroscopy, Chemical Trapping, and Thermoprogrammed Desorption Studies of Methanol Adsorption and Decomposition on $\text{ZnAl}_2\text{O}_4$ and $\text{Cu/ZnAl}_2\text{O}_4$ Catalysts

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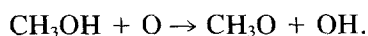
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It is shown that FT-IR spectroscopy permits discrimination to be made between methoxy (methanol) and formate species adsorbed on  $\text{ZnAl}_2\text{O}_4$  and  $\text{Cu-ZnAl}_2\text{O}_4$  catalysts. These species were found to be less stable on copper than on  $\text{ZnAl}_2\text{O}_4$ . The presence of reduced copper promotes methanol transformation into formates and then into  $\text{CO}_2$ : (i) FT-IR results show that copper formate formation from methanol adsorption occurs even at room temperature and that surface oxygen ion participates in its formation; (ii) chemical trapping experiments demonstrate that increasing copper percentage destabilizes formate species, while TPD experiments correlatively indicate an accelerated transformation of formate into  $\text{CO}_2$ . Formyl species are detected by chemical trapping only at the end of the reaction and are therefore assumed not to participate in the decomposition reaction. © 1990 Academic Press, Inc.

### INTRODUCTION

Adsorption and conversion of methanol on  $\text{ZnO}$  (1–5),  $\text{Cu}$  (6–9), and  $\text{Cu/Al}_2\text{O}_3$  (10) have been widely studied. Curiously, these processes on  $\text{Cu/ZnO}$  (11, 12),  $\text{Cu/ZnO/Cr}_2\text{O}_3$  (12), or  $\text{Cu/ZnO/Al}_2\text{O}_3$  (13) have received less attention.

Recently, methanol adsorption on  $\text{ZnO}$  has been found to be localized on  $\text{Zn-O}$  pairs as methoxy species (14). Bowker and Madix (15) have observed that methanol is adsorbed dissociatively on the clean  $\text{Cu}(110)$  surface at 270 K with formation of a methoxy species. Wachs and Madix (16) observed that when the surface was pre-dosed with oxygen atoms, the hydroxyl proton of  $\text{CH}_3\text{OH}$  was removed by the oxygen and water desorbed from the surface at low temperature, thus leaving on the surface a species of stoichiometry  $\text{CH}_3\text{O}$ :



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The decomposition of this entity was observed to take place at 370 K, yielding formaldehyde, hydrogen, and some methanol.

Formate species located on copper desorb as  $\text{CO}_2$  and  $\text{H}_2$  at 440 K. Wachs and Madix (8) interpreted the low formaldehyde production on the clean  $\text{Cu}(110)$  surface as due to the nondissociation of methanol in that case, this dissociation being induced by preadsorbed oxygen. This work shows that oxygen acts as a “sink” for protons on the surface, leaving only methoxy species present above 270 K.

On  $\text{Cu}(100)$ , Sexton (17) has shown by electron energy loss spectroscopy (EELS) experiments that methoxy species are chemisorbed through their oxygen end; Ryberg (18) concluded that these species are tilted and Outka and Madix (19) have calculated the angles to have a value equal to  $32 \pm 10^\circ$  with respect to the normal surface. Moreover, methoxy transformation into formate has been cited in the literature on  $\text{ZnO}$  (2,

5), Cu (7, 20), Cu/Al<sub>2</sub>O<sub>3</sub> (10), Cu/ZnO (12), and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> (13). The reaction mechanism generally accepted for this transformation involves formaldehyde followed by dioxymethylene species as intermediates (4, 21). The latter has been recently characterized on ZnAl<sub>2</sub>O<sub>4</sub> and Cu/ZnAl<sub>2</sub>O<sub>4</sub> (22).

The aim of this work is to study the adsorption and conversion of methanol of  $x\%$  Cu/ZnAl<sub>2</sub>O<sub>4</sub> ( $x = 0, 15, \text{ and } 30 \text{ wt}\%$ ), by FT-IR spectroscopy, chemical trapping, and thermoprogrammed desorption. The characterization of surface species after methanol adsorption and decomposition and the study of their chemical changes can be helpful in understanding methanol synthesis mechanism(s) on Cu/Zn/Al catalysts.

## EXPERIMENTAL

### A. Catalyst Preparation

Samples (zinc aluminate, 15% Cu/zinc aluminate, and 30% Cu/zinc aluminate) were prepared by the coprecipitation technique already published (23–25). Precipitation of the metal nitrates (copper, aluminum, zinc) by sodium carbonate in 0.5–1.5 M aqueous solutions was carried out under controlled and constant pH conditions between 333 and 363 K. The precipitate was subsequently washed, dried, and air-calcined. All samples were heated under a hydrogen flow (2 liters h<sup>-1</sup> g cat<sup>-1</sup>, 1 K min<sup>-1</sup>) up to 523 K, and kept at this temperature for 12 h before cooling to room temperature.

The catalysts were characterized by both XRD and STEM of thin foils of the solids as already detailed (24), since it has been clearly shown that XRD characterization on its own would have led to incomplete or erroneous conclusions about the sample composition (24). This allowed us to check for the presence of only the ZnAl<sub>2</sub>O<sub>4</sub> spinel phase in the support with a platelet morphology. This spinel mixed oxide phase is produced from a pure hydrotalcite-like

phase having the same morphology and Zn/Al ratio, as already published (23, 24).

### B. Fourier Transform Infrared Spectroscopy

Samples for IR analysis (30 mg) were pressed into 16-mm-diameter disks under a pressure of  $2 \times 10^8$  Pa. The activation was performed in an IR cell in the following manner. While maintaining a vacuum of  $1.3 \times 10^{-3}$  Pa, the samples were heated from ambient temperature to 523 K over a 2-h period. The temperature was kept at 523 K for an additional 2 h, then cooled to room temperature over a period of approximately  $\frac{1}{2}$  h.

For reduced samples, reduction was effected by heating the samples to 523 K over a 5-h period under a flow of hydrogen (40 cm<sup>3</sup> min<sup>-1</sup>). The samples were allowed to rest at this temperature for an additional 10 h, then degassed at  $1.3 \times 10^{-3}$  Pa before cooling to room temperature.

Before introduction to the cell in the vapor phase, methanol and formic acid were trapped at the temperature of liquid nitrogen, degassed, and then heated to room temperature.

CH<sub>3</sub><sup>18</sup>OH was prepared by hydrolysis at 378 K of trimethyl phosphate by H<sub>2</sub><sup>18</sup>O, obtained from the Commissariat à l'Energie Atomique (26). The isotopic purity was about 92%.

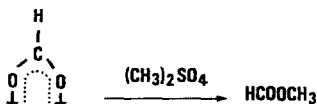
The spectra reported in the figures are those obtained after subtraction of the background.

### C. Chemical Trapping

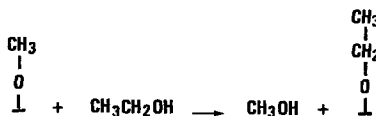
A surface intermediate adsorbed on the surface of the catalyst is brought into contact with an appropriate agent, giving rise to a compound which can be detected by gas chromatography of high sensitivity.

Knowledge of the compounds formed yields information on the adsorbed species, as indicated:

1. Methyl formate formation by reaction with dimethylsulfate indicates the presence of adsorbed formate species:



2. Methanol formation in the presence of ethanol is due to the reaction with adsorbed methoxy species:



*Procedure.* The catalysts were heated under a hydrogen flow (2 liters  $\text{h}^{-1}$   $\text{g cat}^{-1}$ ) up to 523 K (1 K  $\text{min}^{-1}$ ) and kept at this temperature for 12 h before cooling to room temperature. The catalysts were then evacuated to  $10^{-1}$  Pa, the background gas being hydrogen.

*Formation of methoxy, formate, and acetate species from methanol or ethanol.* Methanol or ethanol (25  $\mu\text{mol}$ ) was introduced into a bulb containing the catalyst (100 mg) at a background pressure of  $10^{-1}$  Pa. The pressure was restored to atmospheric pressure with argon gas at room temperature. The samples were then heated to the desired temperature (given in the captions to the Figures).

*Formation of methoxy, formate, and acetate species, from  $\text{CO} + \text{H}_2$  or  $\text{CO}_2 + \text{H}_2$ .* At a background pressure of  $10^{-1}$  Pa, a 1:2  $\text{CO}:\text{H}_2$  or  $\text{CO}_2:\text{H}_2$  gas mixture was introduced into a bulb containing 100 mg of catalyst until atmospheric pressure was reached. The sample was then heated to the experimental temperatures (see captions to the Figures).

*Formate, acetate, and methoxy trapping conditions.* An excess of dimethyl sulfate (1 ml) was introduced at room temperature into the first bulb to reveal formates and acetates. The bulb was kept at 383 K for 1 h.

An excess of ethanol (1 ml) was injected into the second bulb to reveal methoxy species. Protonation of the methoxy groups was immediate at room temperature.

Methyl formate or acetate and methanol

(products formed after chemical trapping of formate or acetate and methoxy species, respectively) are identified by gas chromatography. In the pretreatment with  $\text{CO}_2 + \text{H}_2$  at 403 K, only formates are formed and no methoxy species are observed. In the methanol adsorption experiments, the appearance of formates and the disappearance of methoxy species are followed, as given later in Figs. 9 and 12. Surface species, under these conditions, reacted totally with trapping agent(s) and the reaction yields were quantitative [within experimental error ( $\sim 10\%$ )] (27).

#### D. Thermoprogrammed Desorption

Catalyst samples (500 mg) were charged into a tubular quartz reactor, and reduced as described above (Section A). After being cooled to 313–318 K, the samples were exposed to a partial pressure of methanol ( $1.3 \times 10^3$  Pa) in a He flux (2 liters  $\text{h}^{-1}$   $\text{g cat}^{-1}$ ) for 15 min. The system was degassed under a flow of helium at the same temperature for 4–5 h (until neither methanol nor  $\text{CO}_2$  or CO was detected by gas chromatography). The temperature was then increased to 773 K (6 K  $\text{min}^{-1}$ ) under the carrier gas (helium) (4 liters  $\text{h}^{-1}$   $\text{g cat}^{-1}$ ). A Gow-Mac cells system allowed the detection of desorbed molecules from the catalytic surface. Desorption products were detected by two on-line gas chromatographs equipped with heated multiposition sampling valves, one for methanol (FID, Chromosorb 102) and the other for CO and  $\text{CO}_2$  (katharometer, Chromosorb 102);  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , and HCHO were not analyzed. The gases were carefully dried on silica gel and molecular sieve and traces of oxygen were eliminated by the deoxo device.

## RESULTS

Before undertaking methanol adsorption and decomposition we characterized the infrared spectra of formate species and studied the changes induced by heating ("thermal evolution").

TABLE 1

Wavenumbers (cm<sup>-1</sup>) of Formate Species Formed from HCOOH Adsorption on ZnO, Al<sub>2</sub>O<sub>3</sub>, ZnAl<sub>2</sub>O<sub>4</sub>, and Reduced Copper

ZnO	Al <sub>2</sub> O <sub>3</sub>	ZnAl <sub>2</sub> O <sub>4</sub>	Reduced Cu	Assignment
2960	2970	2970	<sup>a</sup>	$\nu_3(\text{COO}^-) + \delta(\text{CH})$
2882	2905	2900	<sup>b</sup> $\left\{ \begin{array}{l} 2850 \\ 2930 \end{array} \right.$	$\nu(\text{CH})$
2740	2750	2770	<sup>a</sup>	$\nu_2(\text{COO}^-) + \delta(\text{CH})$
1580	1595	1590	<sup>a</sup>	$\nu_2(\text{COO}^-)$
1382	1395	1395	<sup>a</sup>	$\delta(\text{CH})$
1365	1380	1375	1352	$\nu_3(\text{COO}^-)$

<sup>a</sup> The "surface dipole selection rule" explains the inactivity of these vibrational modes (40).

<sup>b</sup> The  $\nu(\text{CH})$  vibration is in Fermi resonance interaction (see text).

## A. CHARACTERIZATION AND THERMAL EVOLUTION OF FORMATE SPECIES

### 1. ZnAl<sub>2</sub>O<sub>4</sub>

Irreversible adsorbed surface species resulting from formic acid adsorption at room temperature are characterized (Fig. 1) by bands at (i) 1590 cm<sup>-1</sup> (with a weak shoulder at 1620 cm<sup>-1</sup>); (ii) 1372 and 1378 cm<sup>-1</sup> (with a weak shoulder at 1395 cm<sup>-1</sup> and a broad one at 1330 cm<sup>-1</sup>); and (iii)  $\nu(\text{CH})$  at 2900 cm<sup>-1</sup> accompanied by two broad bands at 2770 and 2970 cm<sup>-1</sup>.

The frequencies of the bands are compared (Table 1) with those we obtained from HCOOH adsorption on ZnO and Al<sub>2</sub>O<sub>3</sub>. The small shifts observed on Al<sub>2</sub>O<sub>3</sub>, ZnO, and ZnAl<sub>2</sub>O<sub>4</sub> are significant enough to conclude that species formed on ZnAl<sub>2</sub>O<sub>4</sub> are indeed characteristic of a mixed phase and not due to the adsorption on one component, alumina or zinc oxide. Salomatin *et al.* (28) reported the appearance of bands at 1600, 1395, and 1380 cm<sup>-1</sup> from HCOOH adsorption on alumina. They are very close to those we observe on the same oxide (Table 1) and were assigned to formate species (28). Salomatin *et al.* also noted two other bands at 1630 and 1320 cm<sup>-1</sup>, assigned to a chemisorbed formic acid-type

species. The band we observe at 1620 cm<sup>-1</sup> on ZnAl<sub>2</sub>O<sub>4</sub> (Fig. 1) appears as a broad shoulder after evacuation at 323 K. It therefore corresponds to species resistant to heating at 403 K. We assign it to another type of formate species, probably bidentate or bridged formates, as suggested by their thermal stability (29).

The evolution of formates formed from CO<sub>2</sub>-2H<sub>2</sub> at 403 K was followed as a function of time by chemical trapping. As shown in Fig. 2a, formation of formates reached a maximum value ( $\approx 10^{-4}$  mol g<sup>-1</sup>) after about 7 h. A stationary state is observed with further contact.

### 2. 15% Cu/ZnAl<sub>2</sub>O<sub>4</sub>

Adsorption of formic acid at room temperature on reduced 15% Cu/ZnAl<sub>2</sub>O<sub>4</sub> previously evacuated at 523 K (Fig. 3) led to a strong band at 1595 cm<sup>-1</sup>, with a shoulder at 1620 cm<sup>-1</sup>, and to a complex absorption in the 1350 cm<sup>-1</sup> range characterized by at least three bands: 1390 (shoulder), 1370, and 1352 (very sharp) cm<sup>-1</sup>. We also note the presence of a broad band at 1330 cm<sup>-1</sup>. In the  $\nu(\text{CH})$  range, the band at 2890 cm<sup>-1</sup> is accompanied by two sharp and relatively strong bands at 2850 and 2930 cm<sup>-1</sup>. The three sharp bands at 1352, 2850, and 2930

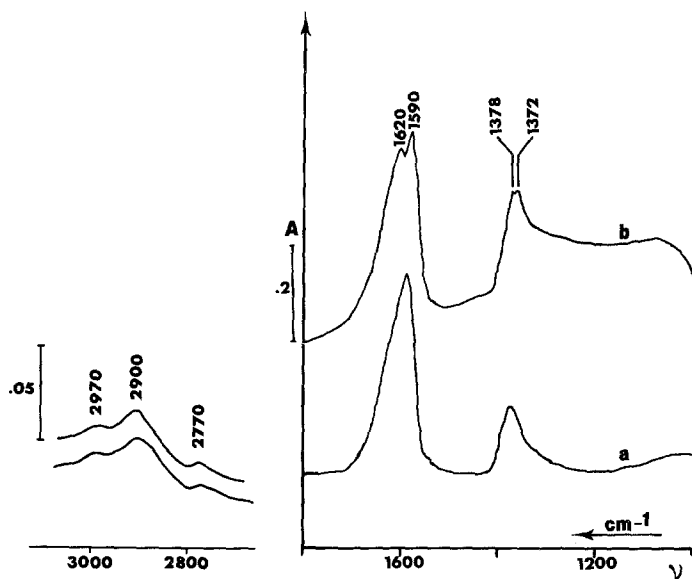


FIG. 1. Species formed after adsorption of  $30 \mu\text{mol g}^{-1}$  formic acid on  $\text{ZnAl}_2\text{O}_4$  (a) at room temperature and (b) after heating for 1 h at 323 K, followed by evacuation at 323 K.

$\text{cm}^{-1}$  decreased in intensity after heating at 323 K and disappeared completely at 403 K. At 403 K, strong bands at 1230, 1430, and  $1650 \text{ cm}^{-1}$  (hydrogen carbonates),  $1530 \text{ cm}^{-1}$  (carbonates), 1375, 1395, and  $2900 \text{ cm}^{-1}$  (similar to formates on  $\text{ZnAl}_2\text{O}_4$ ), and  $2095 \text{ cm}^{-1}$  (CO) became apparent.

We consider the sharp bands at 1352, 2850, and  $2930 \text{ cm}^{-1}$  to be characteristic of formate species on the copper surface, in

agreement with the literature (17, 30, 31). Such species were not thermally very stable and transform into  $\text{CO}_2$  and CO, which could explain the formation of other formate species close to those observed on  $\text{ZnAl}_2\text{O}_4$  (Table 1). The presence of CO could be explained by the further reaction of  $\text{CO}_2$  with hydrogen.

Formate production, from  $\text{CO}_2 + 2\text{H}_2$  at 403 K (chemical trapping), is shown in Fig. 2b. Formate concentration in this case is 20 times higher than that on  $\text{ZnAl}_2\text{O}_4$ , indicating that the presence of copper has a promoting role in their formation. The chemical trapping was made directly on the samples which were kept under a  $\text{CO}_2 + \text{H}_2$  atmosphere until just before the trapping experiments. The amount of formates trapped is constant and corresponds to the amount of formates at equilibrium. When a catalyst containing more copper is used [ $\sim 50\%$  Cu (32)] a maximum is observed in the first minutes of contact at 403 K. Afterward, only the equilibrium state is reached, thus showing that on these catalysts, formates on copper are formed and rapidly decomposed. This was not observed on the

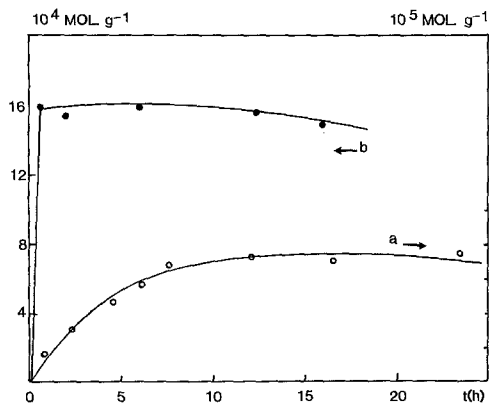


FIG. 2. Formation of formates from  $\text{CO}_2\text{-H}_2$  versus time ( $t$ ) (temperature = 403 K) on (a)  $\text{ZnAl}_2\text{O}_4$  and (b) 15% Cu/ $\text{ZnAl}_2\text{O}_4$ .

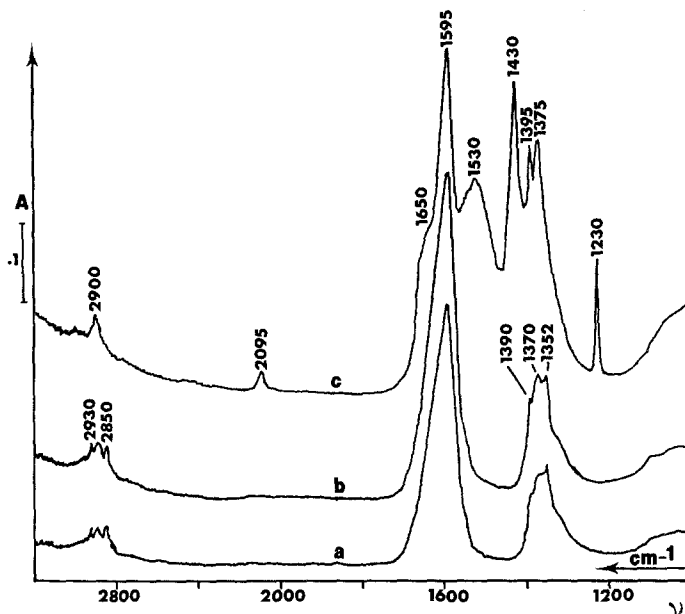


FIG. 3. Species resulting from the adsorption of  $30 \mu\text{mol g}^{-1}$  formic acid on reduced 15% Cu/ZnAl<sub>2</sub>O<sub>4</sub> (a) at room temperature, (b) after 1 h at 323 K, and (c) after 1 h at 403 K.

15 wt% Cu/ZnAl<sub>2</sub>O<sub>4</sub> catalyst. However, the influence of copper on the amount of formate formed is clearly seen in Fig. 2.

## B. CHARACTERIZATION AND THERMAL CHANGES INDUCED IN METHOXY SPECIES

### 1. ZnAl<sub>2</sub>O<sub>4</sub>

Methanol adsorption on Al<sub>2</sub>O<sub>3</sub> has already been studied (33). In the  $\nu(\text{CH})$  range, essentially two bands at 2944 and 2825 cm<sup>-1</sup> have been observed, and in the  $\nu(\text{CO})$  range (below 1200 cm<sup>-1</sup>), bands at 1190 (weak) and 1095 (strong) cm<sup>-1</sup> have been observed (Fig. 4b).

On ZnO calcined at 723 K and reduced under H<sub>2</sub> at 523 K for one night, irreversible adsorption of CH<sub>3</sub>OH at room temperature led to two sharp bands at 2932 and 2818 cm<sup>-1</sup>, accompanied by shoulders at 2910, 2895, and 2790 cm<sup>-1</sup> (Fig. 4a). In the region below 1200 cm<sup>-1</sup>, a broad band at 1076 cm<sup>-1</sup> with shoulders at 1058 and 1040 cm<sup>-1</sup> was observed. They are due to the  $\nu(\text{CO})$  band of methoxy species since adsorption of CH<sub>3</sub><sup>18</sup>OH leads to corresponding bands

at 1050, 1028, and 1014 cm<sup>-1</sup>. We therefore conclude that three types of methoxy species are formed. With the activation procedure used, no formate species appears at room temperature. The band near 1600 cm<sup>-1</sup> (Fig. 4a) is due to the formation of a small amount of water, and disappears by heating at 403 K, while formate species (band at 1580 cm<sup>-1</sup>) are then detected.

In the case of ZnAl<sub>2</sub>O<sub>4</sub>, the irreversibly adsorbed methanol species are characterized by bands at 2940 and 2820 cm<sup>-1</sup> with shoulders at 2915 and 2895 cm<sup>-1</sup> [ $\nu(\text{CH})$  bands] and at 1185 (weak) and 1095 cm<sup>-1</sup> with a shoulder at 1040 cm<sup>-1</sup> (Fig. 4c).

The 1185 and 1095 cm<sup>-1</sup> absorption bands are very close to those observed in the case of Al<sub>2</sub>O<sub>3</sub>. A broad and very weak band between 1500 and 1400 cm<sup>-1</sup> [ $\delta(\text{OH})$ ] indicates that one part of the species is not dissociated at room temperature (Fig. 4c). Upon the addition of methanol, the intensity of this band increased together with that of the 1040 cm<sup>-1</sup> band, indicating the formation of undissociated reversible species. Two types are possible, either hydro-

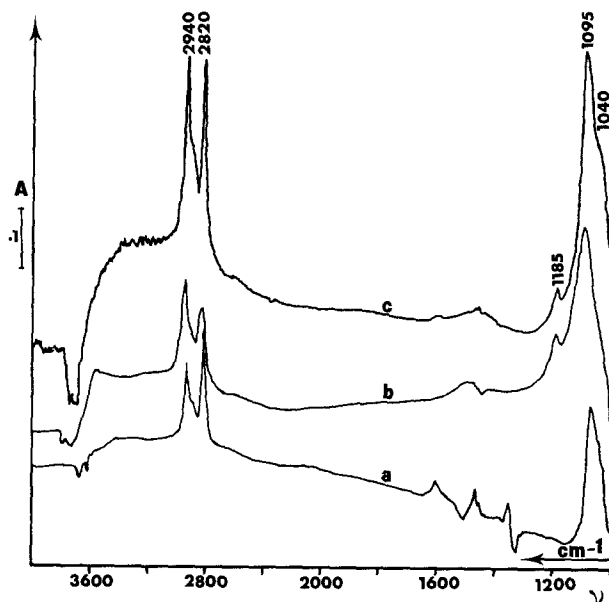


FIG. 4. Species resulting from the irreversible adsorption of methanol at room temperature on (a) 100 mg ZnO, (b) 100 mg  $\text{Al}_2\text{O}_3$ , and (c) 30 mg  $\text{ZnAl}_2\text{O}_4$ .

gen-bonded to basic sites (A species) or coordinatively bonded to Lewis acid sites (B species). In such a case the wavenumber of the broad OH deformation vibration would be in favor of a supplementary interaction between the hydroxyl group and a Lewis basic site (B species), as already proposed on  $\text{Al}_2\text{O}_3$  (33):



Methoxy species were not affected by heating at 403 K (Fig. 5, Ia); this has been confirmed by chemical trapping results showing that formate species are not formed under these conditions. After 1 h heating at 523 K, methoxy bands notably decreased in intensity, and formate (1621, 1592, 1392, and 1375  $\text{cm}^{-1}$ ), carbonate (broad band at 1530  $\text{cm}^{-1}$ ), and hydrogen carbonate bands (1230  $\text{cm}^{-1}$ ) appeared (Fig. 5, Ib).

Under an argon atmosphere, the evolution of the number of methoxy species, followed by chemical trapping at 483 K, shows that about 50% of methoxy species disappeared after 3 h, whereas about 10% of formates formed (Fig. 6a). CO and  $\text{CO}_2$  were detected in the gas phase but their amount was not quantitatively measured, due to possible readsorption on the surface. Similar results were observed under a hydrogen atmosphere.

Thermoprogrammed desorption of products resulting from adsorption of methanol on  $\text{ZnAl}_2\text{O}_4$  is shown in Fig. 7. At temperatures lower than 400 K, methanol (d) and  $\text{CO}_2$  (b) desorbed, whereas at higher temperatures,  $\text{CO}_2$  (b), CO (c), and traces of methanol desorbed (600–620 K). CO and  $\text{CO}_2$  result from the decomposition of formate species formed from methoxy species on the surface of  $\text{ZnAl}_2\text{O}_4$ . These results confirm the presence of reversibly and irreversibly adsorbed methanol on the surface.

## 2. Copper-Based Catalysts

### a. Unreduced 15% Cu/ $\text{ZnAl}_2\text{O}_4$ . Metha-

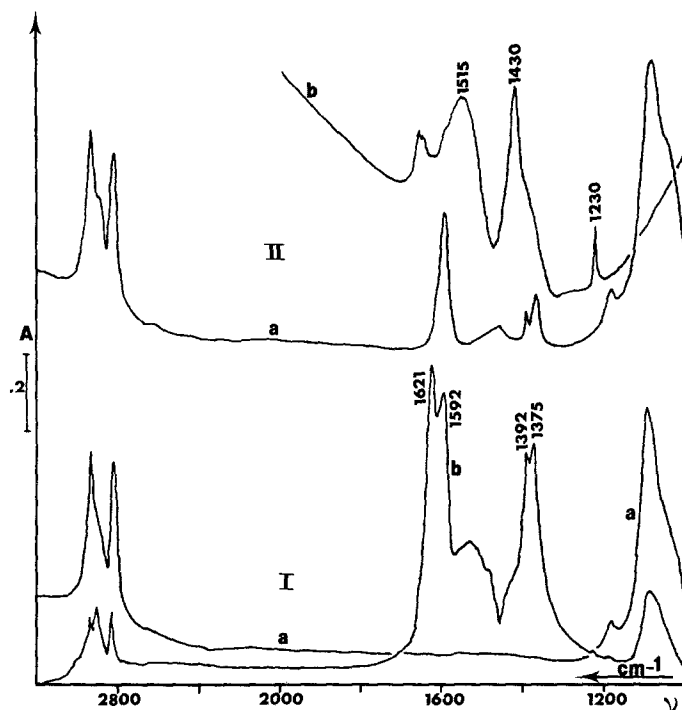


FIG. 5. Changes induced on heating species resulting from the irreversible adsorption of methanol on (I) ZnAl<sub>2</sub>O<sub>4</sub> (a) after 1 h at 403 K and (b) after 1 h at 523 K; and (II) unreduced 15% Cu/ZnAl<sub>2</sub>O<sub>4</sub> (a) after 1 h at 403 K and (b) after 1 h at 523 K.

nol adsorption at room temperature led to results similar to those observed on ZnAl<sub>2</sub>O<sub>4</sub>. However, after 1 h heating at 403 K, formate species were observed (1595, 1395, and 1372 cm<sup>-1</sup>) (Fig. 5, IIa).

After heating at 523 K, methoxy species completely disappeared and CO<sub>2</sub> formation as carbonates (1515 cm<sup>-1</sup>) or hydrogen carbonates (1230 cm<sup>-1</sup>) was observed (Fig. 5, IIb). It is therefore impossible to detect

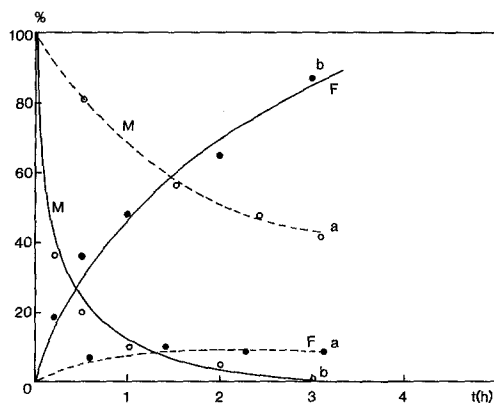


FIG. 6. Methanol decomposition versus time in the presence of argon at 483 K on (a) ZnAl<sub>2</sub>O<sub>4</sub> and (b) 15% Cu/ZnAl<sub>2</sub>O<sub>4</sub>. F, formate; M, methoxy.

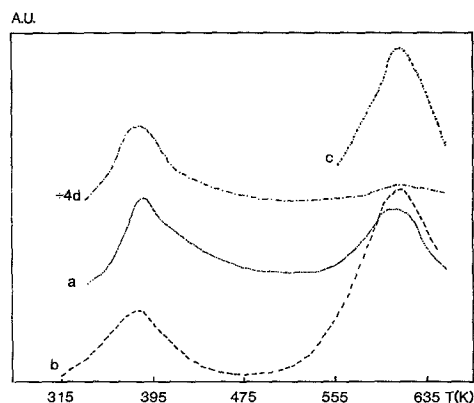


FIG. 7. TPD of products resulting from methanol adsorption on ZnAl<sub>2</sub>O<sub>4</sub> at room temperature. (a) Katharometer signal, (b) CO<sub>2</sub>, (c) CO, (d) methanol.



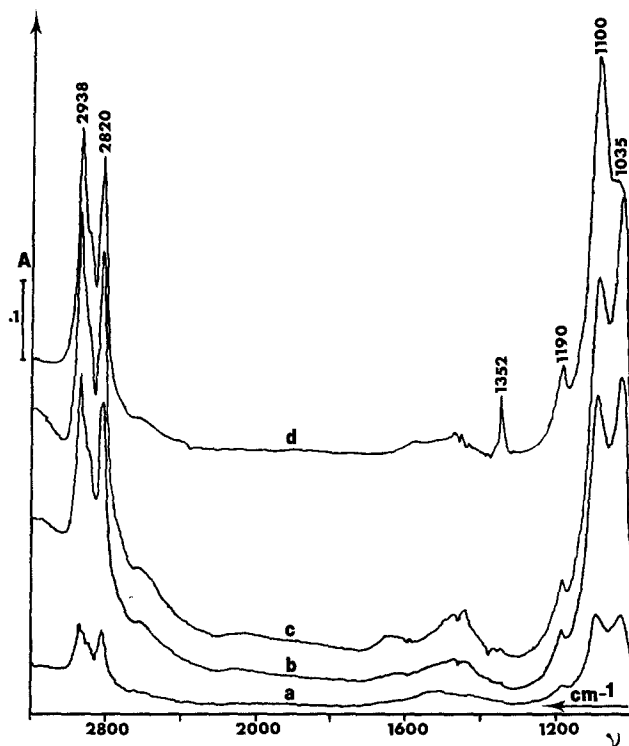


FIG. 8. Species resulting from the introduction of methanol on nonreduced 15% Cu/ZnAl<sub>2</sub>O<sub>4</sub>. (a) 90  $\mu\text{mol g}^{-1}$ , (b) 300  $\mu\text{mol g}^{-1}$ , (c) 400  $\mu\text{mol g}^{-1}$ , (d) after evacuation at room temperature.

bands due to methanol adsorption on copper ions of the oxidized catalyst. The only conclusion that can be drawn is a decrease in the thermal stability of methoxy species adsorbed on ZnAl<sub>2</sub>O<sub>4</sub> due to the presence of copper oxide.

*b. Reduced 15% Cu/ZnAl<sub>2</sub>O<sub>4</sub>. FT-IR results.* Methanol addition led to the appearance of three IR bands below 1200  $\text{cm}^{-1}$ , at 1190 (very weak), 1100, and 1035  $\text{cm}^{-1}$  (Fig. 8). The intensity of the latter two was almost equal until about 300  $\mu\text{mol g}^{-1}$  methanol was introduced. Supplementary addition of methanol preferentially increased the 1035  $\text{cm}^{-1}$  band intensity which significantly diminished upon evacuation at room temperature (Fig. 8). In the  $\nu(\text{CH})$  range, mainly two strong bands at 2938 and 2820  $\text{cm}^{-1}$  appeared with, at low coverage, three shoulders at 2920, 2890, and 2840  $\text{cm}^{-1}$ . It is clear that the catalyst reduction increases the intensity of the reversible band at 1035

$\text{cm}^{-1}$ , which therefore corresponds, at least partly, to methanol adsorption on copper.

We also noted the appearance of a weak band at 1352  $\text{cm}^{-1}$ . This band was even detected at room temperature and appeared more clearly after evacuation; it was generally accompanied by a shoulder at 1340  $\text{cm}^{-1}$  which disappeared after evacuation. Heating for 1 h at 323 K increased the intensity of the 1352  $\text{cm}^{-1}$  band (Fig. 9). After heating for 1 h at 403 K, bands associated with formate species of ZnAl<sub>2</sub>O<sub>4</sub> type [2900, 1620 (sharp), 1590, 1392 (sharp) and 1370  $\text{cm}^{-1}$ ] were found. Such species essentially resulted from methanol entities characterized by the 1035  $\text{cm}^{-1}$  band, involving methanol adsorption on copper sites. On the other hand, the intensity of the 1095  $\text{cm}^{-1}$  band due to methoxy species on the support has not been affected. After heating for 1 h at 523 K, methanol species as well as species characterized by the 1352

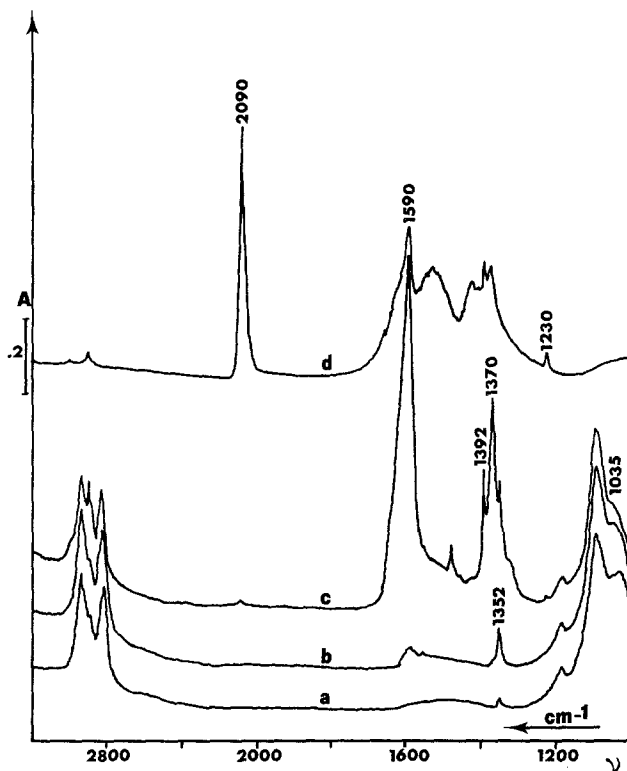


FIG. 9. Changes induced on heating species resulting from the irreversible adsorption of methanol on reduced 15% Cu/ZnAl<sub>2</sub>O<sub>4</sub> (a) at room temperature, (b) after 1 h at 323 K, (c) after 1 h at 403 K, and (d) after 1 h at 523 K.

cm<sup>-1</sup> band had completely disappeared, while ZnAl<sub>2</sub>O<sub>4</sub>-type formate species had decreased; on the other hand, the presence of CO<sub>2</sub> (carbonates and hydrogen carbonates) and CO (very intense band at 2090 cm<sup>-1</sup>, Fig. 9d) was noted.

When CH<sub>3</sub><sup>18</sup>OH is used instead of CH<sub>3</sub><sup>16</sup>OH, the low-energy absorptions (below 1200 cm<sup>-1</sup>) are shifted from 1190, 1100, and 1035 cm<sup>-1</sup> to 1190, 1070, and 1010 cm<sup>-1</sup>, indicating that the absorption at 1190 cm<sup>-1</sup> is insensitive to the isotopic substitution. This vibration does not involve a C–O mode but is due to a  $r/(CH_3)$  mode, as already suggested, while the other two correspond to the  $\nu(CO)$  vibration of two different methanol species.

After treatment with CH<sub>3</sub><sup>18</sup>OH, the 1352 cm<sup>-1</sup> band, assigned to a formate adsorbed on the copper surface, is accompanied by

two bands, one at 1330 cm<sup>-1</sup> (similar intensity) and another one, very weak, at 1315 cm<sup>-1</sup> (Fig. 10). They could be assigned to HC<sup>16</sup>O<sup>18</sup>O and HC<sup>18</sup>O<sup>18</sup>O species, respectively. The very weak intensity of the latter shows that formate oxygens do not come from methanol only, but that surface oxygens participate in formate formation.

*Chemical trapping and TPD results.* Chemical trapping experiments (Fig. 6b), on this catalyst, showed a quick decrease in the number of methoxy species with time and a concomitant formation of formate species; after 3 h the amount of formate species formed represents  $\approx 85\%$  of the initial amount of methoxy species. CO and CO<sub>2</sub> were detected in the gas phase ( $\approx 7\%$ ) and traces of formyl were also observed but only after at least 2 h of trapping (after CO formation).

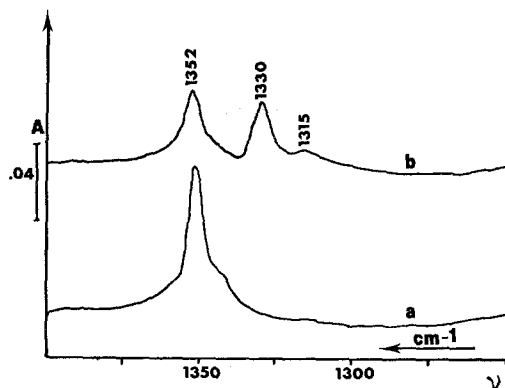


FIG. 10. Spectra of formate species formed on reduced 15% Cu/ZnAl<sub>2</sub>O<sub>4</sub> after addition of CH<sub>3</sub><sup>16</sup>OH (a) or CH<sub>3</sub><sup>18</sup>OH (b) at room temperature.

Thermoprogrammed desorption of products resulting from methanol adsorption is shown in Fig. 11. Methanol desorption mainly occurred at two different temperatures, 395 and 475 K, with traces of desorption at 515–530 K. The desorption at 395 K probably corresponds to nondissociatively adsorbed methanol on the surface; meanwhile, a possible hydrogenation of methoxy species on copper (8) or on ZnO (2, 6) can exist. The desorption at 475 K can probably be assigned to hydrogenation of formates on copper surfaces.

CO<sub>2</sub> desorption occurred at three temper-

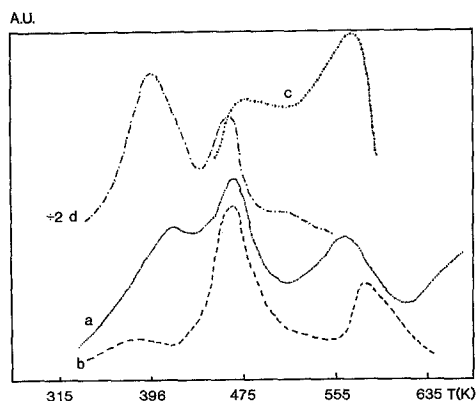


FIG. 11. TPD products resulting from methanol adsorption on 15% CuZnAl<sub>2</sub>O<sub>4</sub> at room temperature. (a) Katharometer signal, (b) CO<sub>2</sub>, (c) CO, (d) methanol.

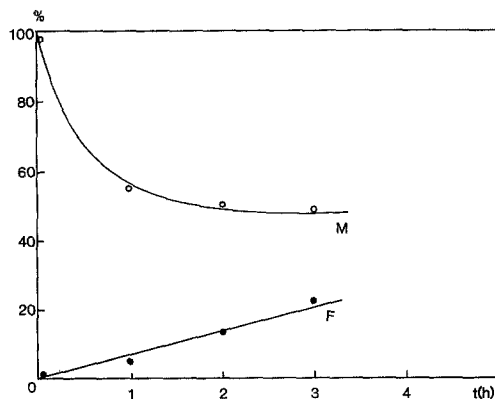


FIG. 12. Methanol decomposition versus time in the presence of argon on 30% Cu/ZnAl<sub>2</sub>O<sub>4</sub> at 403 K. F, formate; M, methoxy.

atures; the first desorption is below 410 K, the second at 475 K is characteristic of formate decomposition on copper (7, 34), and the third at 570–590 K is probably due to the decomposition of formates on the ZnAl<sub>2</sub>O<sub>4</sub> surface. Similar results have recently been reported by Bowker *et al.* (35). Furthermore we detected two peaks of CO desorption. The first at 480 K is similar to that observed by Chan and Griffin (11) on Cu/ZnO(0001); the second one, at 565–575 K, comes from ZnAl<sub>2</sub>O<sub>4</sub> formate decomposition.

*c. Reduced 30% Cu/ZnAl<sub>2</sub>O<sub>4</sub>.* As this catalyst did not have sufficient transparency for IR analysis, it was used only for chemical trapping and TPD experiments.

At 483 K, all methoxy and formate species were completely decomposed into CO and CO<sub>2</sub> ( $t \leq 15$  min). At 403 K (Fig. 12), the number of methoxy species decreased to about 50%, while the number of formate species increased to 25% of initial methoxy species after 3 h of reaction. CO and CO<sub>2</sub> were also detected in the gas phase and traces of formyl species were observed after 2 h.

Thermoprogrammed desorption of products resulting from methanol adsorption (Fig. 13) is similar to that obtained on 15% Cu/ZnAl<sub>2</sub>O<sub>4</sub>. Three different and important

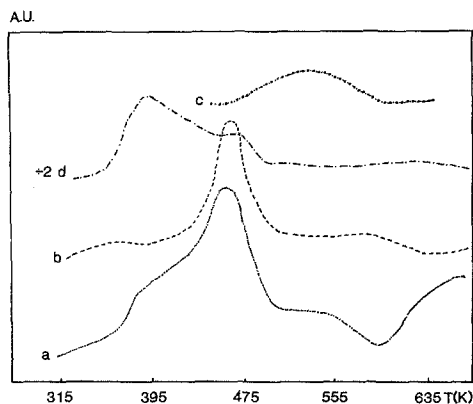


FIG. 13. TPD of products resulting from methanol adsorption on 30% Cu/ZnAl<sub>2</sub>O<sub>4</sub> at room temperature. (a) Katharometer signal, (b) CO<sub>2</sub>, (c) CO, (d) methanol.

points may, however, be noted: (i) methanol desorption at 475 K is less important than that on 15% Cu/ZnAl<sub>2</sub>O<sub>4</sub> (compared to CO<sub>2</sub> desorption at the same temperature); (ii) CO desorption is not so well defined; and (iii) CO<sub>2</sub> desorption (at 560–600 K) is much less important.

#### DISCUSSION

Formic acid adsorption enables the differentiation of formate species formed on ZnAl<sub>2</sub>O<sub>4</sub> and on the copper surface. The latter is well characterized by the  $\nu(\text{CH})$  band at 2850 and 2930 cm<sup>-1</sup> and by a sharp band at 1352 cm<sup>-1</sup>. The 1352 cm<sup>-1</sup> band is very close to that reported by Salomatin *et al.* (28), while formate bands formed from CO<sub>2</sub>+H<sub>2</sub> on copper catalysts seem quite different: 2950, 1657, and 1318 cm<sup>-1</sup> (36). The latter wavenumber values are close to those reported on Cu(100), while ours are comparable to those presented by copper formate salts (29). It is important to note that the  $\nu_a(\text{COO}^-)$  mode expected to be situated in the frequency range between 1600 and 1550 cm<sup>-1</sup> is not well apparent. This result agrees with a very recent one from Ghiotti *et al.* (30) who invoke the "metal surface selection rule" to explain the inactivity of such a mode. The two CH bands observed at 2930 and 2850 cm<sup>-1</sup> are

assigned to a Fermi resonance between the  $\nu(\text{CH})$  fundamental and a combination band of the same symmetry. Assuming a C<sub>2v</sub> or C<sub>s</sub> symmetry, the latter would correspond to  $\nu_a(\text{COO}^-) + \delta(\text{CH})$ .

Edwards and Schrader (12) did not report the formation of copper formate species by adsorption of formic acid or formaldehyde on CuO/ZnO and Cu/ZnO/Cr<sub>2</sub>O<sub>3</sub> catalysts. This could be due to the following reasons: (i) the copper content of catalysts used was low (less than 10%), and (ii) adsorptions were carried out at relatively high temperatures ( $T > 348$  K). The present results indicate that this temperature is sufficiently high to initiate the transformation of copper formate species into formate on the support, CO<sub>2</sub> and CO.

FT-IR spectroscopic analysis indicates a specific adsorption of methanol on reduced copper, characterized by a band at 1035 cm<sup>-1</sup>. The corresponding species is weakly adsorbed and does not resist evacuation at 323 K.

Methanol decomposition led to formate species (under inert gas or under hydrogen) as indicated in the literature (1–3, 10, 12). This process is more pronounced on reduced catalysts since it occurred even at room temperature (IR results). As shown from Fig. 10, at least one part of the formate species on copper was formed by the participation of surface oxygen. This implies that the reduction treatment used is not sufficient enough to completely reduce copper. Such a result is in agreement with Bowker *et al.* (35) who, using copper samples reduced by H<sub>2</sub> at 520 K, also found residual copper oxide responsible for formaldehyde transformation into formate species. We therefore propose the following mechanism, in agreement with a previous paper (22): (a) methanol adsorption on metallic copper sites; (b) dehydrogenation into formaldehyde on metallic copper, this step not being possible on a completely oxidized sample, since formaldehyde formation would be inhibited; (c) adsorption of formaldehyde on a residual oxygen site of the copper surface.

Chemical trapping experiments confirm that methanol decomposition is greatly enhanced by increasing the copper loading. Methoxy species were totally decomposed after 15 min at 483 K on 30% Cu/ZnAl<sub>2</sub>O<sub>4</sub>, whereas total methoxy decomposition needs 3 h, within experimental error, to be complete on 15% Cu/Al<sub>2</sub>O<sub>3</sub> and reaches 55% only after the same duration on ZnAl<sub>2</sub>O<sub>4</sub> (Fig. 11).

Our results are in agreement with those of Frohlich *et al.* (37) who showed that maximum methoxy decomposition on Cu/ZnO catalysts occurred for the following composition: 30% Cu–70% ZnO. TPD experiments show partial CO<sub>2</sub> desorption below 400 K, as already found by Chan and Griffin (11). As expected, the quantity of CO<sub>2</sub> arising from ZnAl<sub>2</sub>O<sub>4</sub> formate decomposition (570–590 K) was less important in the case of the higher copper loading due to the important copper coverage. Similar results have already been observed on Cu/ZnO(0001) film (11).

We also note, on both Cu catalysts, that CO desorption in the ZnAl<sub>2</sub>O<sub>4</sub> formate region occurred at lower temperature than CO<sub>2</sub> desorption. This result suggests that two different formate species may exist on the surface, in agreement with the IR results (presence of a shoulder at 1620 cm<sup>-1</sup> and a band at 1590 cm<sup>-1</sup>, Fig. 9).

Formate formation, which has been well characterized by the three techniques used in the present study, can occur either from direct oxidation of methoxy species on the surface or from recombination of CO, CO<sub>2</sub>, and H<sub>2</sub> formed from methanol decomposition (via a formyl route, for instance).

It is difficult to determine which path is followed on ZnAl<sub>2</sub>O<sub>4</sub>, since formate formation occurs at a relatively high temperature and because, under such conditions, CO and CO<sub>2</sub> are also detected. On copper catalysts, direct oxidation occurs because of the following:

i. Ethanol decomposition on 15% Cu/ZnAl<sub>2</sub>O<sub>4</sub> gives only acetate species after 15 min of reaction at 483 K (38), while in the case of decomposition into CO + H<sub>2</sub>, for-

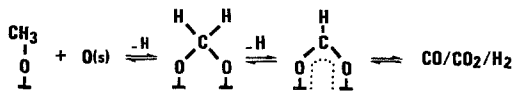
mate species should also be formed. This has not been found under our experimental conditions.

ii. The IR study shows that copper formate is formed from methanol adsorption even at room temperature while under such conditions CO + H<sub>2</sub> coadsorption does not lead to copper formate (39).

iii. In a previous study (22), we characterized dioxymethylene species on the same catalysts from either methanol or formic acid adsorption. Therefore, such species could be intermediates between methoxy and formate species.

iv. As formyl species have been detected only at the end of the reaction, after CO and CO<sub>2</sub> formation, they can be precluded as intermediate species in the methanol decomposition mechanism.

We therefore propose a scheme for methanol decomposition on reduced supported copper catalysts:



#### ACKNOWLEDGMENTS

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