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Reaction Mechanism of Oxidative Carbonylation of Methanol to Dimethyl Carbonate in Cu–Y Zeolite

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The Cu(I)Y catalyst, as prepared by solid-state ion exchange at 650°C, shows higher productivity and less deactivation than the known carbon-supported $CuCl_2$ catalyst for gas-phase oxidative carbonylation of methanol to make dimethyl carbonate. The ion-exchanged Cu(II)Y showed very little activity for the same reaction. An *in situ* FTIR technique was applied to elucidate the reaction mechanism. The first step is the oxidation of methanol and Cu(I) to from Cu(II)–methoxide. The insertion of CO to Cu(II)–methoxide, forming probably a carbomethoxide, is the rate-limiting step. Finally, methanol and oxygen react with carbomethoxide to from dimethyl carbonate.

I. INTRODUCTION

Dimethyl carbonate (DMC) has a high oxygen content and has potential for use as an oxygenate in gasoline. It can also be used as an intermediate to substitute phosgene and dimethyl sulfate in many applications. The best way to produce DMC is by oxidative carbonylation of methanol. A liquid-phase slurry process employing a copper chloride catalyst has been practiced commercially (1). However, a gas-phase process is more desirable because the copper chloride is corrosive in the liquid phase. A gas-phase process was first developed by Curnutt using a copper chloride catalyst on a carbon support (2). However, the $CuCl_2$/carbon catalyst suffers deactivation due to loss of chloride. In this work, it has been found that the chloride is not necessary for copper to catalyze the oxidative carbonylation of methanol. Therefore, a better solid catalyst can be prepared by replacing chloride with zeolite. The copper/zeolite catalysts, which were prepared by heating a mixture of copper chlorides or oxides with Y zeolites at 650°C (high-temperature anhydrous reaction, or HAR, in this paper), were found to be excellent catalysts for gas-phase DMC synthesis. The HAR type of Cu/zeolite catalysts is not only more productive and selective than the $CuCl_2$/carbon catalyst, but also shows very little deactivation. The HAR treatment to achieve the solid-state ion exchange was first observed by Rabo *et al.* (3) and Clearfield *et al.* (4). Xie *et al.* (5) applied this technique to prepare Cu(I)/zeolites as adsorbents for carbon monoxide and unsaturated hydrocarbons. Others have also used the same method to prepare catalysts for studying different aspects of catalysis (6–10). The HAR type of Cu/zeolite catalysts is also unique for the oxidative carbonylation of methanol because the conventional ion-exchanged Cu(II)/zeolite does not catalyze the same reaction. An *in situ* FTIR technique has been applied to elucidate the reaction mechanism. This paper summarizes the results.

II. EXPERIMENTAL

The zeolites Y52, LZ-Y85, and LZ-20M were obtained from UOP. Y52 was a NaY zeolite with a Si/Al_2 ratio of 5. The catalyst ExY52 was prepared by exchanging Cu(II) into the Y52 zeolite using an aqueous solution (0.25 *M*) of $Cu(NO_3)_2$ at 25°C. The catalyst was dried under vacuum at 120°C. The final amount of Cu in ExY52 was 7.7 wt%.

The LZ-Y85 and LZ-20M were both Y zeolites in the acidic form with Si/Al_2 ratios of 12 and 22, respectively. The catalyst CuCl/LZ-20M was a mechanical mixture of 24% CuCl with the LZ-20M powder. The catalyst CuCl/LZ-20M(HAR) was made by heating CuCl/LZ-20M in a helium stream at 650°C for 70 h. About 5 g of the mixed powder was packed in a quartz tube with 1 in. i.d. for such HAR treatment. The excess copper chloride was observed to condense at the exit of the quartz tube. Hydrogen chloride in the exist gas was also detected by IR method. The OH groups on zeolite disappeared after the HAR treatment as indicated by the loss of the IR bands in the region 3800–3200 cm^{-1}. The copper content in the zeolite reached a stable constant amount after the prolonged heating. The final CuCl/LZ-20M(HAR) catalyst contained 7.3 wt% Cu and 1.1 wt% Cl. No change of the crystalline structure before and after the HAR treatment was detected by X-ray analysis. The catalyst CuCl/LZ-Y85(HAR) was prepared by HAR treatment of a CuCl/LZ-Y85 mixture. The catalyst Cu_2O/LZ-20M(HAR) was also prepared by HAR treatment of a mixture of 21% Cu_2O with LZ-20M zeolite. The final Cu content in Cu_2O/LZ-20M(HAR) was 18%. Since the Cu_2O is not volatile, most of the copper in catalyst Cu_2O/LZ-20M(HAR) should still be in the copper oxide form. The catalyst $CuCl_2$/carbon was prepared by standard impregnation techniques as given in reference (2). A commercial

0021-9517/96 $18.00

TABLE 1

List of Catalysts Catalyst

Catalyst	Preparation method	Cu wt%
ExY52	Ion exchange using $Cu(NO_3)_2$	7.7
CuCl/LZ-20M	Physical mixture with 24% CuCl	
CuCl/LZ-20M(HAR)	HAR treatment of Cu/LZ-20M	7.3
CuCl/LZ-Y85(HAR)	HAR treatment of CuCl(24%)/LZ-Y85	
Cu_2O/LZ-20M(HAR)	HAR treatment of Cu_2O(21%)/LZ-20M	18.0
$CuCl_2$/carbon	Ref. (2)	4.5

activited carbon (DARCO) was impregnated with $CuCl_2$ from an ethanol solution. The copper content in $CuCl_2$/-carbon catalyst was 4.5 wt%. Table 1 shows a list of the catalysts studied in this work.

The catalysts were pressed into 1-cm-diameter wafers for IR studies. The IR cell used in this work is described elsewhere (11). The conversion and selectivity of the catalysts were determined in a quartz tube reactor (4 mm i.d.) at 130°C. The catalyst powder was packed in the tube to occupy 0.63 cc volume. The feed composition was methanol/CO/air with a ratio of 0.9/1.6/1. The total gas glow was 8.7 cc/min. An on-line GC was used to analyze the effluent from the reactor.

III. RESULTS AND DISCUSSION

In the slurry reaction system with the copper chloride catalyst, Romano *et al.* (1) have shown that the oxidative carbonylation of methanol to form DMC can be separated in two separate steps. The first step is the oxidation to form cupric methoxychloride:

$$2CH_3OH + \tfrac{1}{2}O_2 + 2Cu^+Cl^- \rightarrow 2(CH_3O\text{–}Cu)^+Cl^- + H_2O. \quad [1]$$

The second step is to reduce the cupric methoxychloride with carbon monoxide to form DMC:

$$2(CH_3O\text{–}Cu)^+Cl^- + CO \rightarrow (CH_3O)_2CO + 2Cu^+Cl^-. \quad [2]$$

If the chloride ions in the above reactions do not participate in the redox cycle of copper, the same redox cycle can be carried out inside the channels of Cu/zeolite (Ze^-) as shown below

$$2CH_3OH + \tfrac{1}{2}O_2 + 2Cu^+Ze^- \rightarrow 2(CH_3O\text{–}Cu)^+Ze^- + H_2O. \quad [3]$$

$$2(CH_3O\text{–}Cu)^+Ze^- + CO \rightarrow (CH_3O)_2CO + 2Cu^+Ze^-. \quad [4]$$

(A) Formation of Methoxide

After the wafer of catalyst CuCl/LZ-20M(HAR) was dried with a helium purge at 130°C, methanol vapor was introduced into the helium stream. Figure 1 shows the IR spectra of the physically adsorbed methanol (2955 and 2847 cm^{-1}) and the formation of methoxide (2932 and 2826 cm^{-1}). The symmetric C–H stretching band (s-ν_{CH_3}) of physically adsorbed methanol (2847 cm^{-1}) has a lower

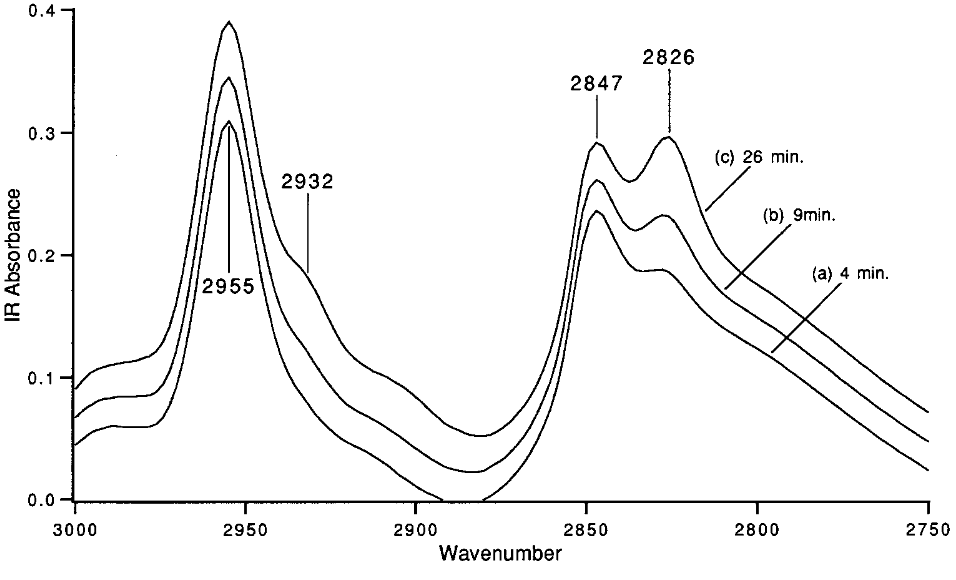

FIG. 1. Methanol reactions in the channels of CuCl/LZ-20M(HAR) catalyst without air at 130°C.

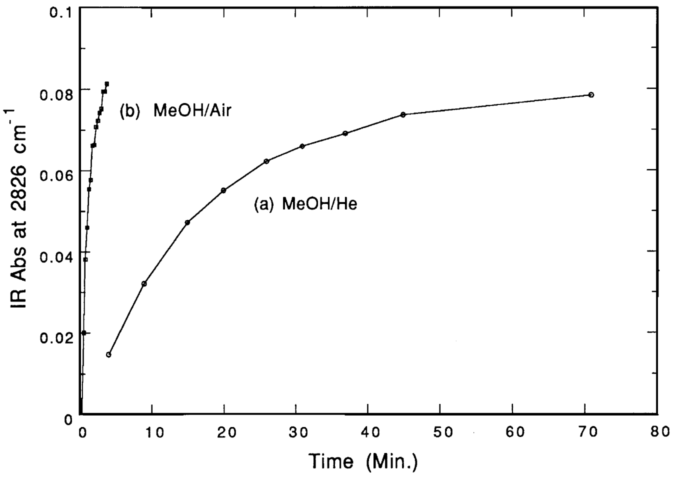

FIG. 2. The rates of Cu–methoxide formation from methanol reaction at 130°C: (a) without air; and (b) with air.

intensity than the antisymmetric band (a-ν_{CH_3}, 2955 cm^{-1}). However, the surface methoxide should have a strong s-ν_{CH_3} band than the a-ν_{CH_3} band (12). The 2826 cm^{-1} band in Fig. 1 is more intense than the 2932 cm^{-1} band, indicating the formation of a surface methoxide. The methoxide was formed on the copper sites because the zeolite without copper did not form such methoxide under the same reaction conditions. The physically adsorbed methanol saturated the zeolite instantaneously as indicated by the constant intensities of the 2955 and 2847 cm^{-1} bands. On the other hand, the formation of copper methoxide is a slower process and the intensity of 2826 cm^{-1} band increased with time as shown in Figs. 1 from a to c. This change is also plotted in Fig. 2a.

In a separate experiment using the same catalyst, the methanol vapor was carried into the cell by air instead of helium. Similar IR spectra as shown in Fig. 1 were observed. However, the rate of intensity increase of the 2826 cm^{-1} band is much faster in the presence of air (Fig. 2b) than in the helium (Fig. 2a). This indicates that the oxygen is needed for the formation of copper methoxide as shown by Eq. [3]. The reason that the formation of copper methoxide was also observed in the absence of gaseous oxygen (Fig. 2a) may be attributed to the residual oxygen which was trapped in the zeolite.

(B) DMC Reaction in Zeolite

The insertion of CO to copper methoxide is the second step to form DMC. Before the discussion of such an insertion reaction, the IR spectra to DMC in the Cu–Y zeolite channels are examined first to help the interpretation of the IR spectra as shown in later sections. Figure 3 shows the IR spectra of DMC in the channels of a CuCl/LZ-20M(HAR) catalyst at 130°C. The DMC vapor was carried into the cell by a helium stream. Figure 3a is the IR spectrum which was recorded with the DMC/He feed in the IR cell. The IR bands at 1761, 1454, and 1290 cm^{-1} are due to be physically adsorbed DMC in the zeolite channels. The 1761 and 1290 cm^{-1} bands are due to the C=O and C–O stretching modes ($\nu_{C=O}$, $\nu_{C\text{-}O}$) of DMC respectively. The 1454 cm^{-1} band is the antisymmetric CH$_3$ deformation (a-δ_{CH_3}) mode. After the physically adsorbed DMC was purged out by helium, the species left in the zeolite channels shows a different spectrum (Figs. 3b and 3c). The $\nu_{C=O}$, $\nu_{C\text{-}O}$, and a-δ_{CH_3} bands shifted to 1653, 1352, and 1500 cm^{-1}, respectively. The down shift of the $\nu_{C=O}$ mode and the up shift of the

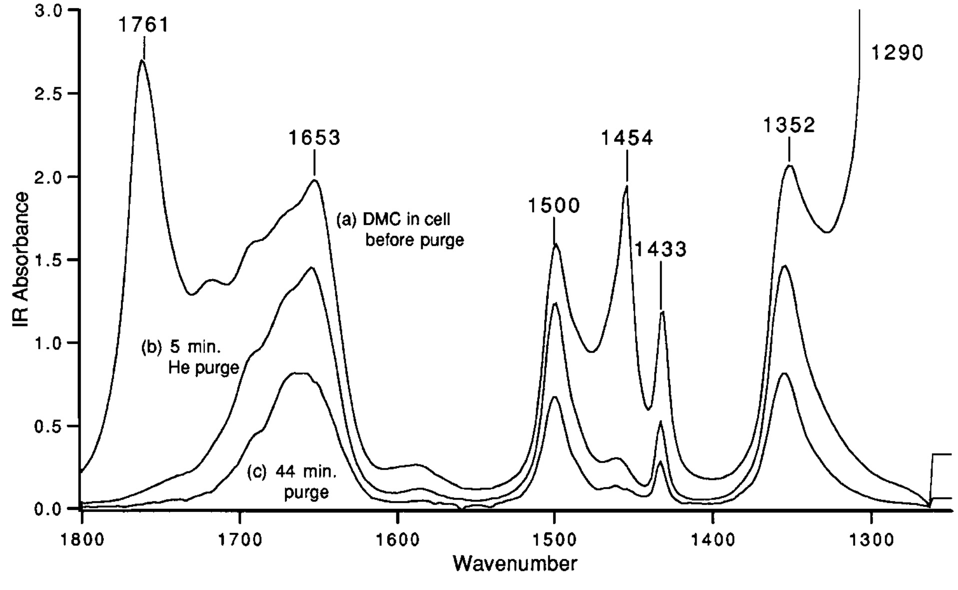

FIG. 3. DMC adsorption and reaction in the channels of CuCl/LZ-20M(HAR) catalyst at 130°C: (a) before helium purge; (b) after 5 min; and (c) 44 min of helium purge.

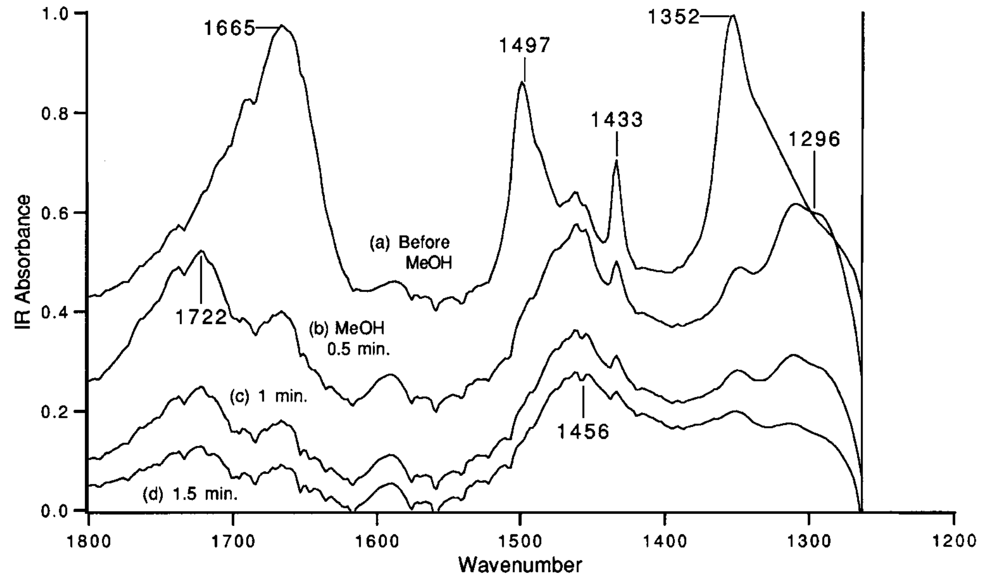

FIG. 4. DMM reaction with methanol at 130°C: (a) DMM before the introduction of methanol; (b) after 0.5 min; (c) 1 min; and (d) 1.5 min of methanol reaction.

$\nu_{\mathrm{C–O}}$ mode indicate the move of electrons from the C=O bond to C–O bond. This implies the change from the carbonyl to a carboxylate structure, such as monomethyl carbonate (MMC). For example, $(CH_3O\text{–}COO)^-NA^+$ has the $\nu_{\mathrm{C=O}}$ and $\nu_{\mathrm{C–O}}$ modes at 1630 and 1372 and $\delta_{\mathrm{CH_3}}$ mode at 1470 cm^{-1}, respectively. One possible explanation is that the DMC decomposes into methanol and MMC due to the presence of residual water in the zeolite.

$$(CH_3O)_2CO + Cu^+Ze^- + H_2O \longleftrightarrow (CH_3O\text{–}COO)^-Cu^+ + H^+Ze^- + CH_3OH \quad [5]$$

or

$$(CH_3O)_2CO + Cu^{++}(Ze^-)_2 + H_2O \longleftrightarrow (CH_3O\text{–}COO)^-Cu^{++}Ze^- + H^+Ze^- + CH_3OH. \quad [6]$$

To prove that Eqs. [5] or [6] are reversible, methanol vapor was passed through the cell to react with the species as shown in Fig. 3c. Figure 4a shows the MMC spectrum before the methanol vapor reached the IR cell. The MMC changed to DMC instantaneously when methanol reached the catalyst as indicated by the change from Figs. 4a to 4b. The IR spectra from b to d in Fig. 4 (also in Fig. 5) show the desorption of DMC. DMC desorbs easily at 130°C in contrast to DMM (Fig. 3(b, c)). The band at 1433 cm^{-1} in Figs. 3 and 4 can be assigned to the s-$\delta_{\mathrm{CH_3}}$ mode which shows the same frequency for both DMC and MMC.

The formation of H^+Ze^- (or OH groups), as indicated by Eqs. [5] or [6], implies the appearance of IR bands in the 3800–3200 cm^{-1} region. However, the recorded IR spectrum did not provide a definitive answer because only a broad band was observed in the region 3600–3300 cm^{-1}.

(C) Insertion of CO to Methoxide

The insertion of CO to the cupric methoxide chloride $((CH_3O\text{–}Cu)^+Cl^-)$ to form a carbomethoxide intermediate, $(CH_3O\text{–}CO\text{–}Cu)^+Cl^-$, has been postulated by Romano *et al.* (1) in their slurry CuCl system. They did not identify this carbomethoxide intermediate. If this is a true mechanism and the carbomethoxide is stable, the insertion of CO to $(CH_3O\text{–}Cu)^+Ze^-$ should show the formation of $(CH_3O\text{–}CO\text{–}Cu)^+Ze^-$. After the maximum copper methoxide was formed by methanol/air reaction as indicated by Fig. 2b, methanol/air was purged out and CO

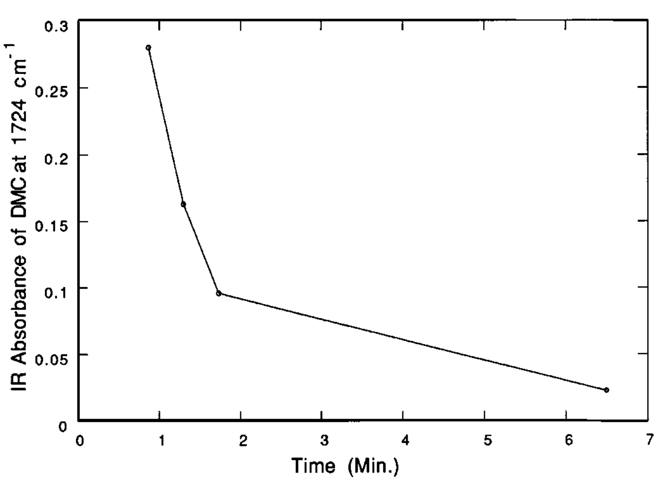

FIG. 5. Rate of DMC desorption from CuCl/LZ-20M(HAR) catalyst at 130°C in the presence of methanol.

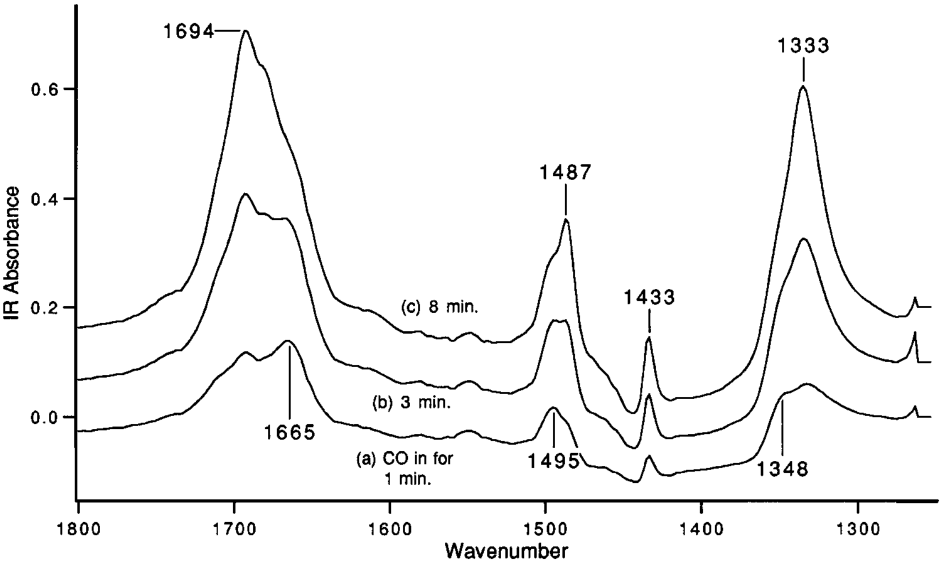

FIG. 6. Reactions of CO with the Cu–methoxide in CuCl/LZ-20M(HAR) catalyst at 130°C: (a) CO in for 1 min; (b) 3 min; and (c) 8 min.

was switched on. Figure 6a shows the first IR spectrum after CO reached the catalyst. The bands at 1665, 1495, 1433, and 1348 cm^{-1} are similar to the spectrum of MMC (Fig. 3c). This implies that the initial insertion of CO forms DMC which decomposes into MMC instantaneously. After the first contact of CO, Figs. 6b and 6c show that a new species grew with time as indicated by the bands at 1694, 1487, 1433, and 1333 cm^{-1}. The change from 1665 to 1694 cm^{-1} indicates the increase of the π character of the C=O double bond. This new species can be interpreted as DMC in the narrow channels where the C=O bond of DMC is strongly perturbed by the copper or zeolite. The difficulty of this interpretation is that this species did not desorb at 130°C. The DMC should desorb fairly easily at this temperatures as indicated by Fig. 5. In addition, the perturbation of the C=O bond of DMC alone should not cause the large shift of the a-δ_{CH_3} band from 1454 cm^{-1} (Fig. 3a) to 1487 cm^{-1} (Fig. 6c). Another possible interpretation of the observed results is the formation of carbomethoxide, $(\text{CH}_3\text{O–CO–Cu})^+\text{Ze}^-$ as suggested by Romano *et al.* (1).

$$(\text{CH}_3\text{O–Cu})^+\text{Ze}^- + \text{CO} \rightarrow (\text{CH}_3\text{O–CO–Cu})^+\text{Ze}^-. \quad [7]$$

Although no IR reference of carbomethoxide can be found in the literature, the spectrum in Fig. 6c is consistent with such structure. The formation of carbomethoxide (increase of 1333 cm^{-1} band intensity) correlates well with the loss of copper methoxide (decrease of the 2826 cm^{-1} band) during the CO insertion as shown in Fig. 7.

(D) Methanol Reaction with Carbomethoxide

After the maximum IR intensity of the 1333 cm^{-1} band was reached as shown in Fig. 7b, the CO was replaced by methanol/air again. Carbomethoxide reacts very rapidly with methanol/air to form DMC as indicated by the fast decrease of the 1333 cm^{-1} band (Fig. 6c) and fast formation of the IR bands similar to the spectrum in Fig. 4b. The fast change from carbomethoxide to DMC is shown in Fig. 8a. This fast reaction may be expressed as

$$2(\text{CH}_3\text{O–CO–Cu}^+\text{Ze}^- + 2\text{CH}_3\text{OH} + \tfrac{1}{2}\text{O}_2$$
$$\rightarrow 2(\text{CH}_3\text{O})_2\text{CO} + \text{H}_2\text{O} + 2\text{Cu}^+\text{Ze}^-. \quad [8]$$

The desorption of DMC into the gas phase (Fig. 9a) was monitored by another FTIR spectrometer. Equation [8] implies that the oxygen is necessary for methanol to react with carbomethoxide. When the methanol/He was used instead

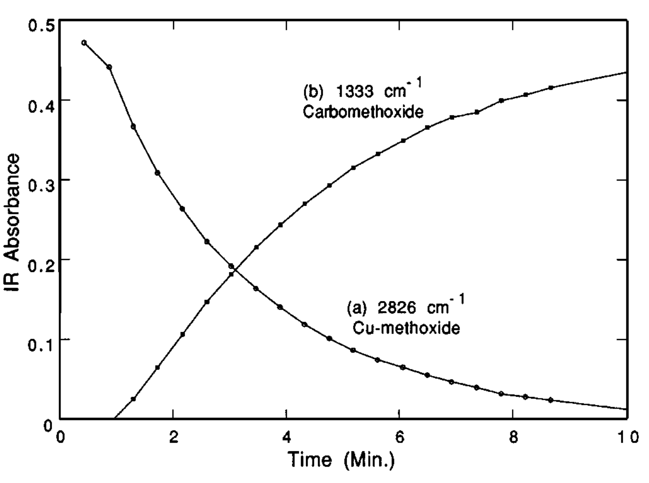

FIG. 7. The plot of IR intensity changes of carbomethoxide band at 1333 cm^{-1} (with a 4 × expansion) (a) and Cu–methoxide band at 2826 cm^{-1} (b) from Fig. 6.

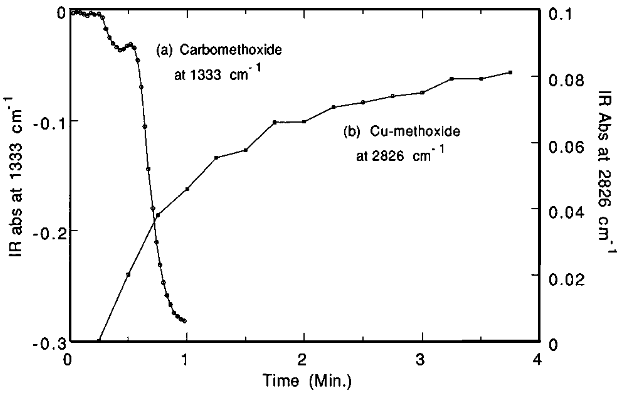

FIG. 8. (a) The disappearing rate of carbomethoxide and (b) the formation rate of Cu–methoxide during the reaction with methanol at 130°C.

of methanol/air in the above experiment, only about one–third as much DMC was produced as shown in Fig. 9b. The reason that DMC was made without oxygen in the feed may be attributed to the residual oxygen in the system. The IR cell may not be sealed completely during the experiment.

The rate of the copper methoxide formation during the above experiment was also monitored as shown in Fig. 8b, which is similar to Fig. 2b. The formation of copper methoxide (Fig. 8b) is slower than the methanol/air reaction with carbomethoxide (Fig. 8a) indicating that the methoxide formation is a separate step from DMC formation as shown by Eq. [3]. After the copper methoxide was formed, the CO was inserted again the repeat the redox cycle. This redox cycle was repeated many times and no deactivation was detected.

The CO insertion is the slowest step in this oxidative carbonylation of methanol to DMC process as indicated by the slower change of the slope of the curves in Fig. 7 than in Fig. 8.

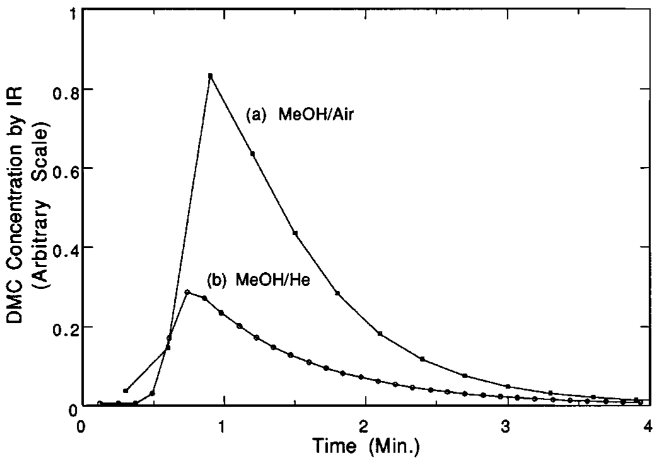

FIG. 9. The DMC productions from the methanol reaction with carbomethoxide at 130°C: (a) with air; and (b) without air.

(E) Carbon Monoxide Interaction with Copper

Carbon monoxide forms a complex with Cu(I) but not with Cu(II)(13). Romano suggested that CO forms a monocarbonyl complex with cuprous chloride. COCuCl, which interacts with copper methoxide to form carbomethoxide. The carbomethoxide further reacts with another copper methoxide to form DMC. During the CO insertion into copper methoxide as shown in Fig. 6, the IR spectra of the Cu(I)CO complex was also monitored as shown in Fig. 10. The band at 2136 cm^{-1} indicates the formation of Cu(I)CO complex in the zeolite supercage (14). However, the intensity of this band increase with time (Figs. 10a–10c). Figure 11 shows the plot of intensity changes of the 1333 cm^{-1} band (the formation of carbomethoxide) against the change of the 2136 cm^{-1} band (the formation of Cu(I)CO complex). Although the increase of intensities correlates linearly between these two bands, the line does not pass through the origin. It is not clear that the observed Cu(I)CO complex is responsible for the CO insertion into carbomethoxide. In the presence of methanol, the IR band of the Cu(I)CO complex shifted from 2136 to 2126 cm^{-1} as indicated by Fig. 10d. This shows that both methanol and CO interact with the same copper site. However, the exact mechanism of CO transfer from gas phase to the carbomethoxide is not clear.

(F) Comparison of the Activities between Different Catalysts

The catalyst CuCl/LZ-20M(HAR) contained 1.1% chloride. The above results based on catalyst CuCl/LZ-20M(HAR) cannot preclude that the chloride plays an active role in this catalytic process. However, the catalyst Cu_2O/LZ-20M(HAR) did not contain chloride. Figure 12 compares the methanol conversion to DMC at 130°C between Cu_2O/LZ-20M(HAR) (Fig. 12a) and CuCl/LZ-20M(HAR) (Fig. 12b) catalysts. Since the catalyst Cu_2O/LZ-20M(HAR) had a high level of copper oxide, a fair comparison of activities is to normalize the conversion with the same amount of zeolite used. Figure 12 shows that both Cu_2O/LZ-20M(HAR) and CuCl/LZ-20M(HAR) catalysts have similar initial activities. Clearly, the chloride itself is not participating in this copper-catalyzed DMC synthesis. The catalyst Cu_2O/LZ-20M(HAR) started to deactivate after 1.5 h on stream due to either the formation of a copper phase which consumed oxygen to oxidize CO into CO_2, or the coking. The well-dispersed copper inside the zeolite by HAR treatment shows good activity without deactivation (Fig. 12b). Without HAR treatment, such as the catalyst CuCl/LZ-20M, deactivation was observed (Fig. 12c).

The Y zeolite LZ-Y85 had a higher aluminum content than LZ-20M. Figure 13 shows that the catalyst CuCl/LZ-Y85(HAR) had a higher activity than CuCl/LZ-

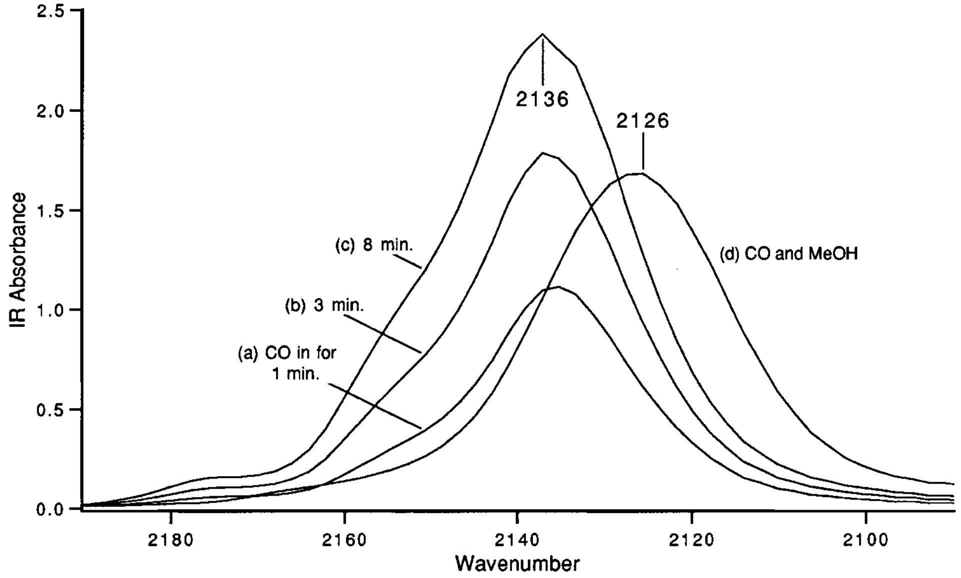

FIG. 10. CO interaction with Cu(I) in zeolite at 130°C: (a), (b), and (c) without methanol; and (d) with methanol.

20M(HAR). This should be attributed to the higher capacity of LZ-Y85 to accommodate copper. The Cu(II)-exchanged Y52, even with 7.7% Cu, shows very little activity to produce DMC (Fig. 13c). This may be attributed to the relatively high stability of $Cu^{2+}(Ze^-)$ in zeolite which resists the reduction at 130°C. On the other hand, the Cu–Y catalysts, as prepared by HAR treatment, contain the maximum amount of Cu(I) which occupy all of the Ze^- sites. Thus the oxidization of such Cu(I)Y at 130°C does not form $Cu^{2+}(2Ze^-)$ but $(CH_3O{-}Cu)^+Ze^-$ as shown in Eq. [3]. Although the oxidation state of Cu in the HAR catalyst was not directly determined in this work, the observation as given in the Experimental section indicate the formation of Cu(I)Y. The stable final Cu content after the HAR treatment is consistent with the theoretical maximum Cu(I) exchange capacity. The loss IR bands of the OH groups and the production of HCl also point to the reaction between CuCl and H^+Ze^-. (An attempt to make Cu(II)Y without Cu(I) by HAR treatment of $CuCl_2$/zeolite Y mixture for comparison was unsuccessful due to the “auto reduction” of Cu(II) to Cu(I) during heating (15)).

The catalyst $CuCl_2$/carbon as prepared by the method given in Ref. (2) shows not only a lower activity than CuCl/LZ-Y85(HAR) but also deactivation. The deactivation of $CuCl_2$/carbon catalyst can be attributed to the loss of chloride due to the formation of either volatile chlorine compounds or a different chlorine bond to the support. Reference (2) indicated that the $CuCl_2$/carbon catalyst has to

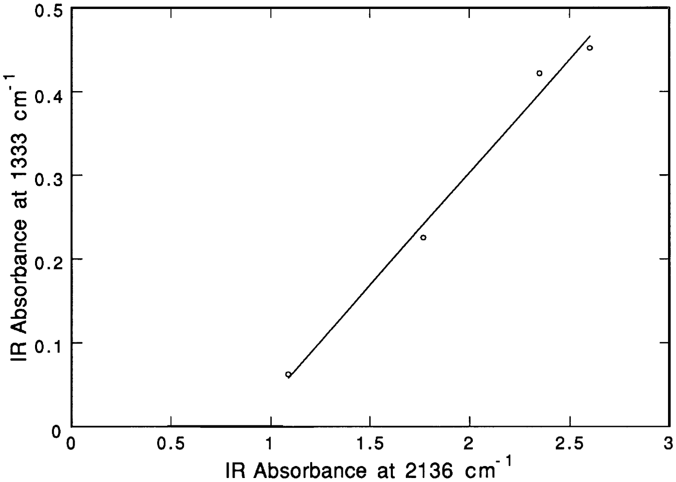

FIG. 11. Correlation between 2136 (from Fig. 10) and 1333 (from Fig. 6) cm^{-1} bands.

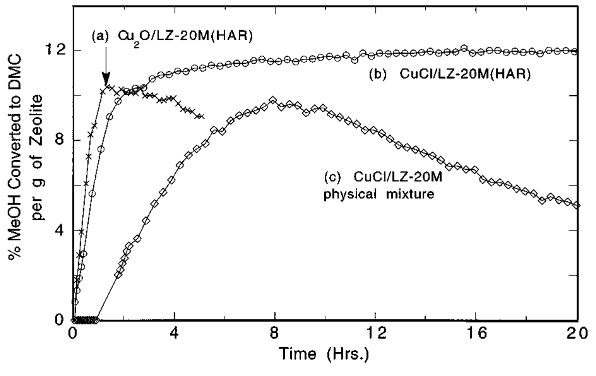

FIG. 12. The comparison of the DMC activities between (a) Cu_2O/LZ-20M(HAR); (b) CuCl/LZ-20M(HAR); and (c) CuCl/LZ-20M catalysts at 130°C with a MeOH/CO/air (0.9/1.6/1) feed of 8.7 cc/min total gas flow rate.

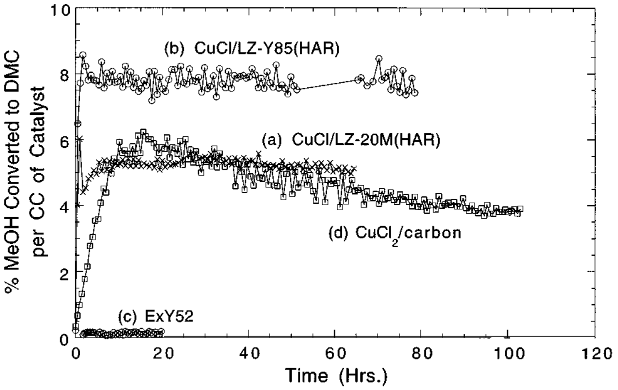

FIG. 13. The comparison of the DMC activities between (a) CuCl/LZ-20M; (b) Cu/LZ-Y85; (c) ExY52; and (d) $CuCl_2$/carbon catalysts at 130°C with a MeOH/CO/air (0.9/1.6/1) feed of 8.7 cc/min total gas flow rate.

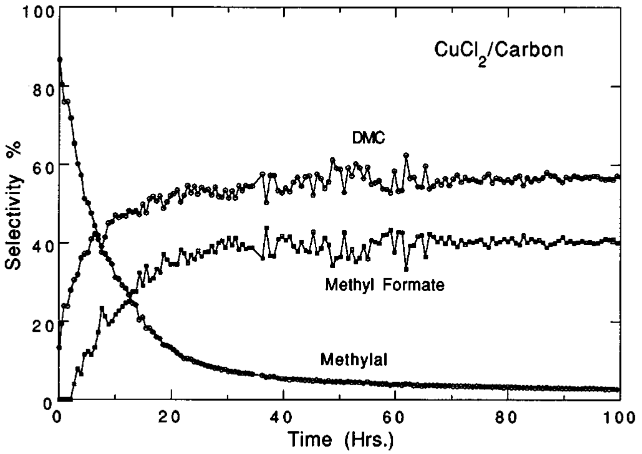

FIG. 15. Selectivities for $CuCl_2$/carbon catalyst.

be regenerated frequently by HCl. The activities in Fig. 13 are normalized to the same bulk volume of catalyst used.

(G) Other Side Reactions

Besides the DMC, methylal and methyl formate are two major by-products from the oxidative carbonylation of methanol. The CO_2 is mostly due to the oxidation of CO. Figures 14 and 15 show the selectivities of the organic components from catalysts CuCl/LZ-Y85(HAR) and $CuCl_2$/carbon, respectively. The CuCl/LZ-Y85(HAR) system produced about 20% methylal and a trace quantity of methyl formate. On the other hand, the $CuCl_2$/carbon system produced about 40% methyl formate and 5% methylal after 100 h on stream.

The induction period in the first 15 h for $CuCl_2$/carbon system (Fig. 15) may be attributed to the change from a milder oxidation site to a stronger oxidation side. The milder oxidation site may come from the isolated Cu on the highly dispersed surface. Presumably, the amount of oxygen on such copper sites is only enough to oxidize methanol to formaldehyde, which couples methanol to methylal:

$$CH_3OH + \tfrac{1}{2}O_2 \rightarrow CH_2O + H_2O. \qquad [9]$$

$$2CH_3OH + CH_2O \rightarrow (CH_3O)_2CH_2 + H_2O. \qquad [10]$$

After the copper forms bigger aggregates, more oxygen congregates on copper to oxidize methanol further into formic acid, which is the precursor for methyl formate:

$$CH_2O + \tfrac{1}{2}O_2 \rightarrow CHOOH \qquad [11]$$

$$CHOOH + CH_3OH \rightarrow CHOOCH_3 + H_2O. \qquad [12]$$

When only methanol was passed over a fresh $CuCl_2$/carbon catalyst, the methylal was observed as shown in the first part of Fig. 16. Apparently, there was enough residual oxygen

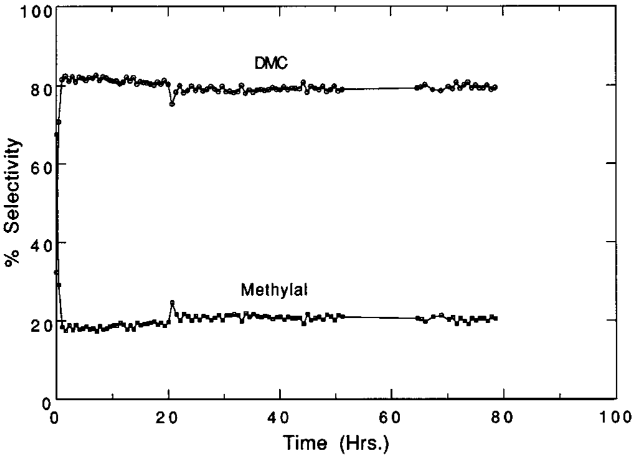

FIG. 14. Selectivities for CuCl/LZ-Y85(HAR) catalyst.

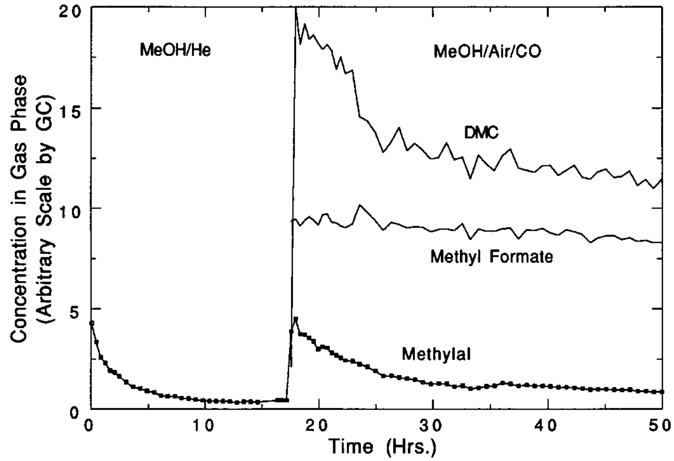

FIG. 16. Reactions of methanol and methanol/air/CO feed over the $CuCl_2$/carbon catalyst at 130°C.

on the catalyst to oxidize methanol (Eqs. [9] and [10]). The methanol pretreatment also created the sites for DMC and methyl formate so that when the methanol/air/CO feed was switched on, all sites became active at the start (Fig. 16).

IV. CONCLUSIONS

1. In the catalytic process of oxidative carbonylation of methanol to form DMC by $CuCl_2$, the chloride does not participate in the catalytic cycle of copper and can be replaced by zeolites. The deactivation of the carbon-supported $CuCl_2$ catalyst, which is due to the loss of chloride, can be avoided in the copper/zeolite catalysts.

2. Only the Cu/zeolite catalysts as prepared by the high-temperature anhydrous reaction (or solid-state ion exchange) of copper chlorides or oxides with zeolites show excellent activities to produce DMC without deactivation. This may be attributed to the formation of Cu(I)/zeolite. The ion-exchanged Cu(II)Y is almost inactive, which may be attributed to the high stability of Cu^{2+} in Cu(II)Y at 130°C and cannot be reduced under the reaction conditions.

3. The first step of the reaction is to form cupric methoxide from the oxidation of methanol on a copper site. The insertion of CO to cupric methoxide forms probably a carbomethoxide. This CO insertion is the rate limiting step. Methanol and oxygen react with carbomethoxide to form DMC.

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