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Oxidative carbonylation of methanol to dimethyl carbonate by solid-state ion-exchanged CuY catalysts

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Abstract

The chloride free ion-exchanged Cu(II)Y is inactive for oxidative carbonylation of methanol to dimethyl carbonate. However, the Cu(I)Y as prepared from a solid-state ion-exchange method is very active. Ammonia can facilitate the copper migration into zeolite cages at low temperature (150°C). The reaction mechanism was studied by in-situ FTIR. The formation of copper methoxide in the zeolite cages during the oxidation of methanol is the first step. The insertion of carbon monoxide into copper methoxide is the rate-limiting step. Methanol is required for the desorption of dimethyl carbonate (DMC) in zeolite cages.

Keywords: Dimethyl carbonate; DMC; Carbonylation; Zeolites; Copper; Catalysis; FTIR; Infrared spectroscopy

1. Introduction

Dimethyl carbonate (DMC) has a high oxygen content and can be used as an oxygenate in gasoline. It can also be used as an intermediate to substitute phosgene and dimethyl sulfate in many industrial processes [1]. Romano et al. [1] developed a two-step slurry process to make DMC from the oxidative carbonylation of methanol. The first oxidation step is the formation of cupric methoxychloride:

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

The isolated cupric methoxychloride is reacted with carbon monoxide in the second reduction step to form DMC:

$$2(CH_3O\text{-}Cu)^+Cl^- + CO \rightarrow (CH_3O)_2CO + 2CuCl \quad (2)$$

Cuprous chloride is the catalyst in the reactions above. A gas-phase one-step process is more desirable because it is more economical than the liquid phase batch operation. Curnutt [2] developed a gas-phase one-step continuous flow process using a carbon-supported cupric chloride catalyst. However, such $CuCl_2$/carbon catalyst suffers deactivation due to the loss of chloride [2]. Lee and Park [3] reported a slurry one-step batch process using the ion-exchanged Cu(II)/zeolites X and Y as catalysts. The exchanges were conducted in the aqueous $CuCl_2$ and $Cu(NO_3)_2$ solutions. The faujasite structure of the zeolite X was destroyed after the catalyst preparation, their Cu/zeolite X catalysts were actually the copper chloride on amorphous silica-alumina support. All their catalysts as prepared from copper chloride solution showed activity. But the catalysts as prepared from the $Cu(NO_3)_2$ solution were not active. We have

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also verified in this work that the ion-exchanged Cu(II)Y catalyst, as prepared from the aqueous solution of $Cu(NO_3)_2$, showed almost no activity. Although these results seem to indicate that the chloride is a necessary component in oxidative carbonylation of methanol to DMC, in this work it has been found that the chloride is not required in zeolite catalyst for such reactions if the catalyst is prepared properly. This finding is important for the development of a commercial gas-phase process because the zeolite-anchored copper can be very stable and also avoids the problem of chloride loss as indicated in Curnett's work [2].

The work by Romano et al. [1] clearly showed that cupric methoxychloride is the intermediate which is formed from the oxidation of cuprous chloride [Eq. (1)]. However, cupric chloride is also active in the one-step process [2,3]. This implies that the oxidation and the reduction were combined in the one-step process and the starting Cu(II) chloride can be reduced to Cu(I) during the reaction and participates in the Cu(I)/Cu(II) redox cycle locally on the surface of the catalyst. The reason that the Cu(II)Y catalyst, as prepared from the Cu^{2+} exchange in $Cu(NO_3)_2$ aqueous solution, have no activity may be attributed to the high stability of Cu^{2+} which resists the reduction at 130°C and cannot form copper methoxide intermediate. This work is to show that the Cu(I)/zeolites have very good activities for oxidative carbonylation of methanol. The Cu(I)/zeolite can not be prepared from aqueous solution because the cuprous salts have very low solubility in water. Maxwell et al. [4] exchanged Cu(I) in ammonia solution of cuprous iodide. The amount of Cu exchanged into zeolite Y in CuI/ammonia solution was only 28% of the theoretical capacity. Such low exchanged Cu(I)Y was not stable during oxidation [4]. In this work, the Cu(I)/zeolite catalysts were prepared by heating the solid mixture of cuprous chloride or oxide with zeolites to achieve the so-called high temperature solid-state ion-exchange which was first observed by Rabo et al. [5] and Clearfield et al. [6]. Xie and et al. [7] applied the high temperature solid-state ion-exchange method to prepare Cu(I)/zeolites as adsorbents for carbon monoxide and unsaturated hydrocarbons. Others have also used this high temperature solid-state ion-exchange method to prepare catalysts for studying different aspects of catalysis [8,9]. For the convenience of the discussion below, the high temperature solid-state ion-exchange or high temperature anhydrous reaction is abbreviated as HAR.

2. Experimental

The Y zeolites, Y52, LZ-20M and LZ-Y85 were obtained from UOP. The Y zeolite HSZ-330 was obtained from TOSOH. Zeolite Y52 is a NaY ($SiO_2/Al_2O_3 = 5$). Zeolite LZ-20M is an acidic Y ($SiO_2/Al_2O_3 = 22$). The catalysts ExY52 and ExLZ-20M were prepared by ion-exchange of zeolite Y in an aqueous solution of $Cu(NO_3)_2$ repeatedly at room temperature to achieve the maximum exchange. The Cu contents in ExY52 and ExLZ-20M were 7.7 and 2.3 wt% respectively. The HAR catalysts were prepared by heating the powder mixture of copper chloride or oxides and acidic zeolites in a quartz tube at 650°C for 70 h with helium purge. For copper chloride mixture, such prolonged heating can remove the excess copper chloride. The excess copper chloride from the mixture sublimed and condensed at the exit of the quartz tube. Hydrogen chloride in the exist gas was also detected by IR method. The IR bands of the OH groups in the region 3800–3200 cm^{-1} disappeared after the HAR treatment. The copper loss decreases asymptotically with time during the high temperature heating until a stable copper content in the zeolite was reached. This stable copper content is very close to the theoretical value of the maximum Cu(I) exchange capacity of the correspondent zeolite. The HAR-CuCl/LZ-20M catalyst was prepared from the mixture of 24 wt% CuCl with LZ-20M. The neutron activation analysis showed that the HAR-CuCl/LZ-20M catalyst contained 7.3 wt%

Cu and 1.1 wt% Cl. The X-ray analysis indicated no destruction of the crystal structure of the zeolite after the HAR treatment. The final catalyst showed white color in the absence of moisture. This indicated that the copper in zeolite was not in metallic form. The HAR-Cu_2O/LZ-20M catalyst was prepared from the mixture of 21 wt% Cu_2O with LZ-20M. Copper oxides are not volatile at 650°C, the excess copper oxide was left on the catalyst after the HAR treatment. The final HAR-Cu_2O/LZ-20M catalyst contained 18 wt% Cu. HAR-CuCl/LZ-Y85 ($SiO_2/Al_2O_3 = 11$) catalyst was prepared similarly to that of HAR-CuCl/LZ-20M. The $CuCl_2$/carbon catalyst was prepared by the procedures as given in [2] and contained 4.5 wt% Cu.

The activities of the catalysts for gas-phase oxidative carbonylation of methanol to DMC were tested in a heated quartz tube (3.5 mm i.d.) at 130°C. The catalyst powder was packed in the tube to occupy 0.63 cc of volume. The feed was a gaseous mixture of methanol/CO/air with a mole ratio of 0.9/1.6/1. The total gas flow rate was 8.7 cc/min. The products and the unreacted reactants were analyzed by a on-line GC.

The surface species on the catalyst were studied by an in-situ FTIR technique which has been described elsewhere [10]. The catalyst wafer was heated in the in-situ IR cell and the spectrum of the catalyst was recorded as the background. After the reactant was introduced and the spectrum was recorded, a subtraction operation was performed by the computer to cancel the spectrum due to the catalyst background. All the IR spectra in this paper show only the net spectral change on the surface of the catalyst.

3. Results and discussion

Fig. 1 is a comparison of the gas-phase oxidative carbonylation activities among the three catalyst samples. Copper oxides by themselves have no activity. Fig. 1(a) shows that the HAR-Cu_2O/LZ-20M is very active to produce DMC. This result indicates that the dispersed copper is responsible for such an activity. Since HAR-Cu_2O/LZ-20M catalyst contained no chloride, it proved that the chloride was not required.

Copper chlorides have much lower melting points than copper oxides and can achieve more complete exchange than oxides under the same HAR treatment [7]. For example, the maximum amount of Cu(II) which was exchanged into LZ-20M by aqueous method in this study, was

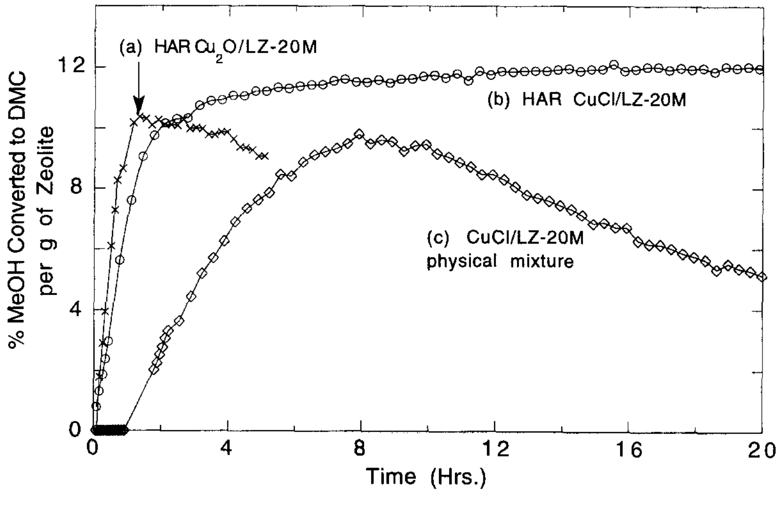

Fig. 1. Comparison of the activities between catalysts at 130°C. Feed composition: methanol/CO/air (0.9/1.6/1 mole ratio).

2.3 wt%. The HAR-CuCl/LZ-20M catalyst contained 7.3 wt% Cu, which is about 100% of the theoretical exchange capacity for Cu(I) in LZ-20M. The loss of the OH IR bands and the release of HCl during HAR treatment indicates the following reaction between CuCl and H^+ on the zeolite frame work (Ze^-):

$$CuCl + Ze^-H^+ \rightarrow Ze^-Cu^+ + HCl \qquad (3)$$

One may argue that the observed activity for HAR-CuCl/LZ-20M was due to copper chloride since 1.1 wt% Cl was detected. Even if this residual Cl were in the form of copper chloride, the level would be too low to account for the observed high activity (see later discussion). If the observed 1.1 wt% Cl were copper chloride, the amount of anchored Cu in zeolite would still be 5–6 wt%. Such level of copper ions in HAR-CuCl/LZ-20M zeolite is much higher than the maximum Cu(II) exchange capacity and they must be in Cu(I) state. Fig. 1(b) shows that HAR-CuCl/LZ-20M is a better catalyst than HAR-Cu_2O/LZ-20M because HAR-CuCl/LZ-20M shows no deactivation. The deactivation of HAR-Cu_2O/LZ-20M catalyst [Fig. 1(a)] may be attributed to the incomplete exchange sites which can cause coke formation.

The activity of $CuCl_2$/carbon catalyst is proportion to the copper content if the loading is below 5% [2]. This implies that all the monolayer dispersed copper on carbon are active. If the reaction rates of the copper ion site on carbon and in zeolite are similar, the high activities for HAR zeolite catalysts indicate that most of the copper ions present in zeolite, which is Cu(I), must be active.

As mentioned above, a large portion of inert copper oxide was left in the catalyst HAR-Cu_2O/LZ-20M. (Similarly, the physical mixture of CuCl/LZ-20M [Fig. 1(c)] contained a large quantity of the excess crystalline CuCl.) It will be misleading to compare the true site activities among catalysts if the activities were normalized to either total copper weight or total catalyst weight. Therefore, the activity in Fig. 1 is expressed as the percent methanol conversion to DMC per gram of net zeolite since the copper ions in zeolite are responsible for the observed activities.

It is interesting to see that the physical mixture of CuCl/LZ-20M [Fig. 1(c)] also shows a good activity after a long induction period. Cuprous chloride solid salt has a very low surface area and has very low activity by itself at

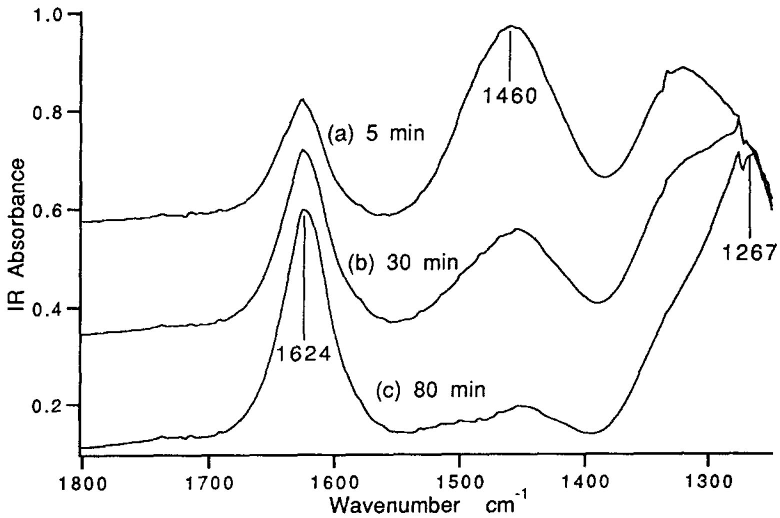

Fig. 2. IR spectra of NH_4^+ and the Cu/NH_3 complex during the heating of a physical mixture of CuO (15 wt%) and acidic HSZ-330 zeolite at 150°C in NH_3.

130°C. The long induction period may be attributed to either the ion exchange in zeolite cages or the dispersion of copper chloride over the zeolite surface. Usually, the temperature of HAR treatment was in the range of 400–700°C. The copper migration as shown in Fig. 1(c) at low temperature must be assisted by the reactants and/or products of the reaction system. It was found in this work that NH_3 can also assist the migration of copper into the zeolite cages very efficiently. This was observed by in-situ FTIR experiment. The wafer of a physical mixture of CuO and acidic Y (HSZ-330) was heated in the IR cell to 150°C. When NH_3 was first introduced into the IR cell, the neutralization of the acidic sites in zeolite by NH_3 was observed as indicated by the instantaneous formation of the NH_4^+ band at 1460 cm^{-1} [Fig. 2(a)]. However, the intensity of this NH_4^+ band decreased with time at 150°C as indicated by the spectral change from (a) to (c) in Fig. 2. The IR bands at 1624 and 1267 cm^{-1}, caused by the formation of Cu/NH_3 complex in zeolite cages, increased with time. The intensity decrease of the 1460 cm^{-1} band correlated very well with the increase of the 1267 cm^{-1} band intensity (Fig. 3). This low temperature treated catalyst also showed good activity for oxidative carbonylation of methanol after the adsorbed NH_3 was removed by the helium purge at a higher temperature. Presumably, the Cu(II) in CuO was reduced to Cu(I) by NH_3 and the Cu/NH_3 complex facilitated the migration of copper into the zeolite cages.

The positive charges of Cu^{2+} ion in Cu(II)/zeolite are balanced by two negative charges on zeolite frame work (Ze^-). The reduction of Cu^{2+} with a hydrogen source generates a pair of Cu^+ and acidic site (H^+Ze^-):

$$Cu^{2+}(2Ze^-) + \tfrac{1}{2}H_2 \rightarrow Cu^+Ze^- + H^+Ze^- \quad (4)$$

This reaction can be easily monitored by in-situ IR when NH_3 is used as the reducing agent. A wafer of ExY52 was heated in the IR cell to 120°C. Fig. 4(a) shows the IR spectrum after NH_3 was introduced. Almost no NH_4^+ band was observed since Cu(II)Y had very little acidic site. The wafer was then heated in NH_3 at 413°C for 30 minutes to reduce Cu(II) into Cu(I). After the temperature was reduced to 120°C with NH_3 in cell, spectrum showed the formation of NH_4^+ band at 1450 cm^{-1} [Fig. 4(b)]. This indicates the formation of the Cu^+Ze^- and H^+Ze^- pair. The $Cu^{2+}(2Ze^-)$ site in Cu(II)Y may be very stable and resist the reduction under the oxidative carbonylation conditions at 130°C. This may explain that the exchanged Cu(II)Y (without chloride) is inac-

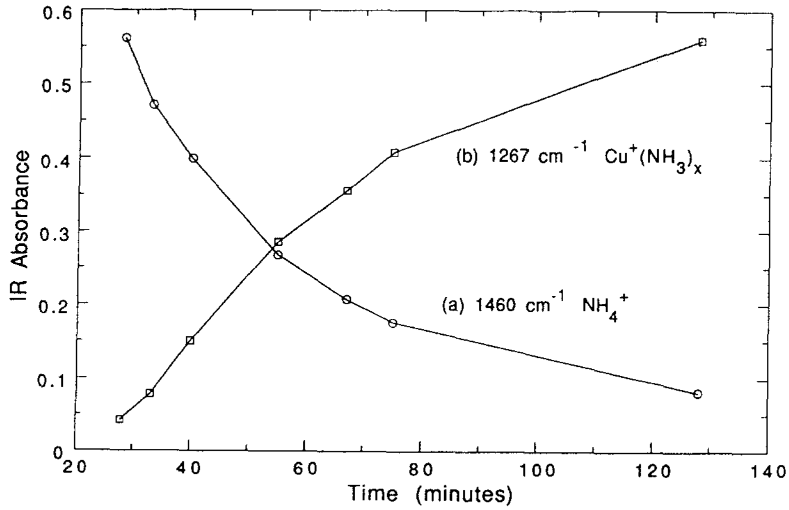

Fig. 3. The changes of the IR intensities of the NH_4^+ and the Cu/NH_3 complex bands as shown in Fig. 2.

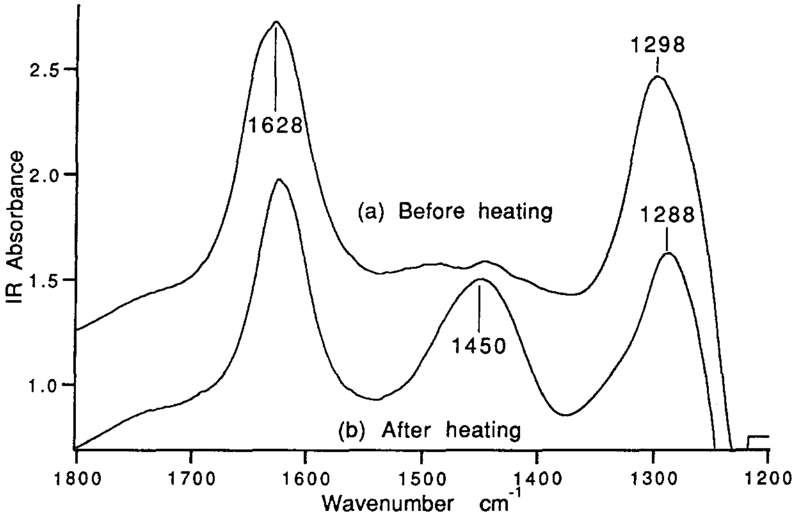

Fig. 4. IR spectra recorded at 120°C in the presence of NH_3 (a) before and (b) after NH_3 reduction of the ExY52 catalyst at 413°C.

tive for oxidative carbonylation of methanol. On the other hand, the oxidation of the fully exchanged HAR Cu(I)Y catalyst by methanol/CO/air feed does not form $Cu^{2+}(2Ze^-)$ since every Ze^- site is already occupied by one copper. The formation of the active copper methoxide intermediate, $(CH_3O\text{-}Cu)^+Ze^-$, becomes more favorable.

The organic species on catalyst surface during the reaction were also studied by in-situ FTIR. The catalyst wafer of HAR-CuCl/LZ-20M was heated in the IR reactor to 130°C with the helium purge. Then the helium was switched to methanol/air feed and the formation and the change surface species were monitored by IR as shown in Fig. 5. The IR bands at 2955 and 2847 cm^{-1} are due to the physically adsorbed methanol. The IR bands at 2932 and 2826 cm^{-1} are due to the surface methoxide. The stronger symmetric $-CH_3$ stretching band at 2826 cm^{-1} than the asymmetric $-CH_3$ stretching band at 2932 cm^{-1} is a good evidence for the surface

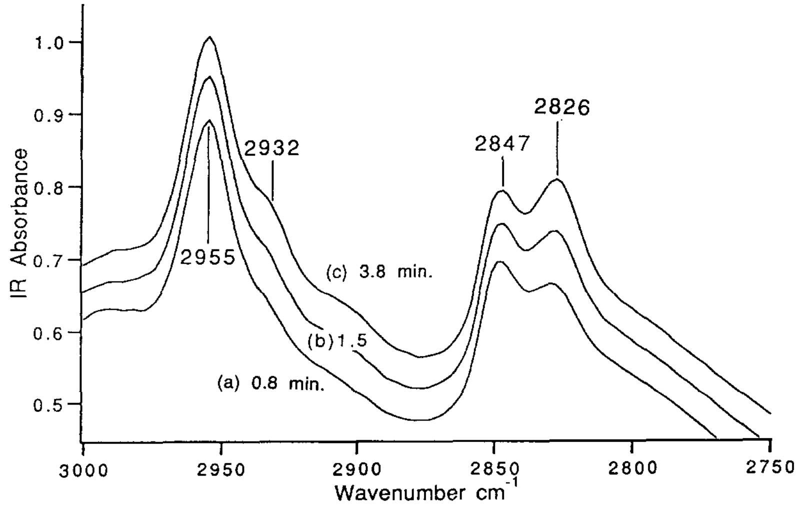

Fig. 5. IR spectra during the methanol reaction in the channels of HAR-CuCl/LZ-20M catalyst at 130°C.

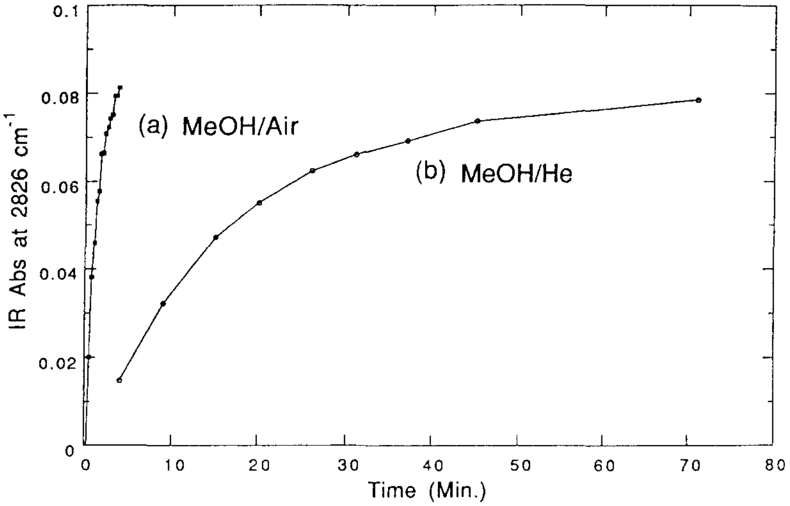

Fig. 6. The rates of $(CH_3O\text{-}Cu)^+Ze^-$ formation at 130°C, (a) in the presence of air, (b) in the absence of air.

methoxide structure [11]. The intensity change with time was plotted in Fig. 6(a). The same reaction was repeated with only methanol without air, similar IR spectra were observed except that the increase of the surface methoxy band was at a very slow rate [Fig. 6(b)]. Clearly, the following reaction was taking place:

$$2CH_3OH + \tfrac{1}{2}O_2 + 2Cu^+Ze^- \rightarrow 2(CH_3O\text{-}Cu)^+Ze^- + H_2O \quad (5)$$

The reason that the formation of copper methoxide was also observed in the absence of gaseous oxygen may attribute to the residual oxygen which was trapped in the zeolite.

After the formation of $(CH_3O\text{-}Cu)^+Ze^-$ reached the maximum as shown in Fig. 6, the methanol/air feed was purged out by helium and the CO was introduced. The surface species with IR bands at 1665,1495, 1433 and 1348 cm^{-1} [Fig. 7(a)] was formed first. Then the species with IR bands at 1694, 1487, 1433 and 1333 cm^{-1} grew with time to reach the maxi-

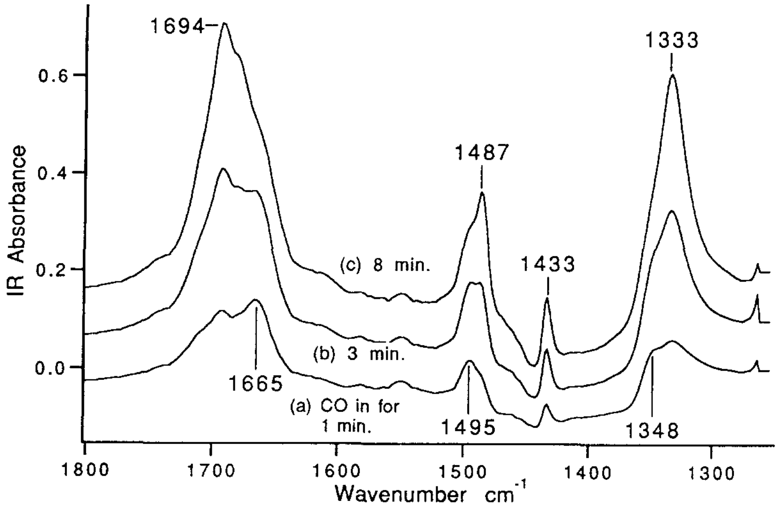

Fig. 7. IR spectra of the surface species during the CO insertion into $(CH_3O\text{-}Cu)^+Ze^-$ at 130°C, (a) 1 min, (2) 3 min and (c) 8 min.

mum intensity in about 10 min [Fig. 8(b) and Fig. 7(c)]. Very little DMC was detected in the gas phase during this time. In a separate experiment, a pulse of DMC vapor was introduced to the same catalyst at 130°C. After the physically adsorbed DMC was purged out, the more stable species left in the cages of zeolite had similar IR spectra as shown in Fig. 7. The IR spectra as shown in Fig. 7 may be assigned to either the strongly bonded DMC in zeolite cages or to the formation of carbomethoxide, $(CH_3O\text{-}CO\text{-}Cu)^+Ze^-$, which was proposed by Romano et al. [1]:

$$(CH_3O\text{-}Cu)^+Ze^- + CO \rightarrow (CH_3O\text{-}CO\text{-}Cu)^+Ze^- \tag{6}$$

The spectrum in Fig. 7(a) is also consistent with the structure of monomethyl carbonate, which can be formed from the decomposition of DMC if there are some Cu(II) ions present:

$$(CH_3O)_2CO + Cu^{2+}(2Z^-) + H_2O \leftrightarrow (CH_3O\text{-}COO)\text{-}Cu^{2+}Ze^- + H^+Ze^- + CH_3OH \tag{7}$$

Further studies are necessary to identify these surface species more positively. Those species as shown in Fig. 7(c) were stable in CO at 130°C. After CO was purged out by helium and methanol/air feed was switched in, all the IR bands as shown in Fig. 7(c) disappeared instantaneously and a large pulse of DMC was observed in the exited gas by a second IR spectrometer. If those species were strongly bonded DMC in the channels, methanol would be needed to desorb them. If those species were carbomethoxide, the following reaction might take place to produce DMC:

$$2(CH_3O\text{-}CO\text{-}Cu)^+Ze^- + 2CH_3OH + \tfrac{1}{2}O_2 \rightarrow 2(CH_3O)_2CO + H_2O + 2Cu^+Ze^- \tag{8}$$

If the formed species were monomethyl carbonate, then the reverse reaction of Eq. (7) might take place to produce DMC. However, the reversed reaction of Eq. (7) could not be the major pathway because the formation of Cu(II) at this step might interrupt the redox cycle.

After the desorption of DMC, further reaction with methanol and air showed the formation of copper methoxide again as indicated in Fig. 5.

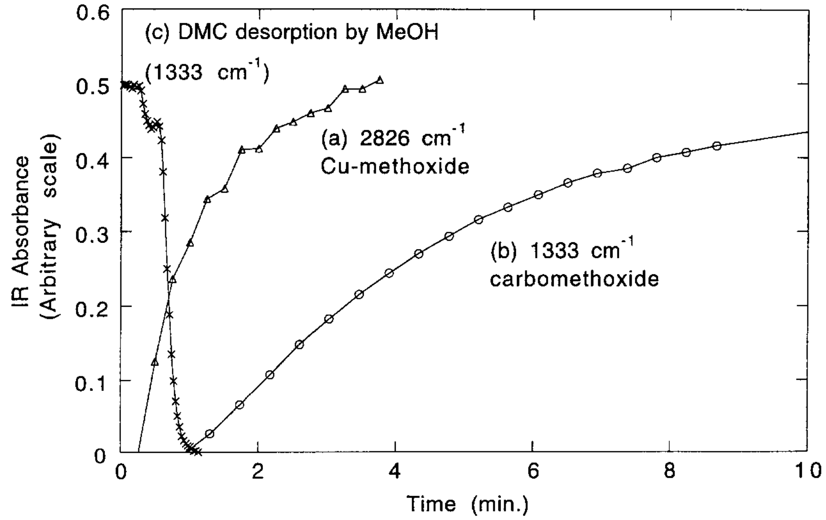

Fig. 8. The comparison of the IR band intensity changes which correspond to the rates of (a) copper methoxide formation (2826 cm^{-1} band in Fig. 5), (b) CO insertion to form carbomethoxide (1333 cm^{-1} band in Fig. 7), and (c) formation and desorption of DMC by methanol (1333 cm^{-1} band in Fig. 7) at 130°C. The absorbances were normalized to an arbitrary scale so that all curves can be plotted with comparable intensities.

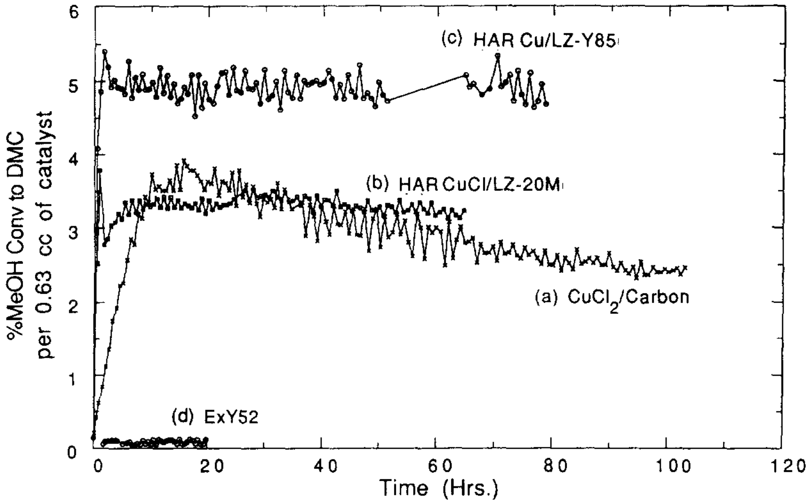

Fig. 9. The comparison of the DMC activity between (a) $CuCl_2$/carbon, (b) HAR-CuCl/LZ-20M, (c) HAR-CuCl/LZ-Y85, and (d) ExY52.

This redox cycle was repeated many times without any sign of deactivation.

Fig. 8 compares the rates of copper methoxide formation (a), the CO insertion to form carbomethoxide (b), and the desorption of carbomethoxide into DMC by methanol (c). The results indicate that the CO insertion is the slowest step.

Fig. 9 compares the activities between $CuCl_2$/carbon and the zeolite catalysts. The $CuCl_2$/carbon [Fig. 9(a)] showed a long induction period and deactivation after the maximum activity was reached. The long induction period might attribute to the spread of copper chloride crystals on carbon to a monolayer dispersion. The deactivation was attributed to the loss of chloride [2]. The HAR catalysts [Fig. 9(b) and Fig. 9(c)] show very short induction period and no deactivation. Apparently the HAR treatment of the CuCl/Y zeolite catalyst provides the maximum Cu(I) loading in zeolite so that the catalysts show maximum activities at the very beginning of the reaction. The copper is well-anchored in the zeolite and shows no deactivation. The zeolite LZ-Y85 had a higher exchange capacity than LZ-20M and a higher activity was observed [Fig. 9(c)]. Fig. 9(d) shows the inactive ExY52 for comparison.

Besides DMC and water, other by-products were methylal, methyl formate and carbon dioxide. Most of the carbon dioxide was from the oxidation of CO. For HAR zeolite Y catalysts, the selectivities of the organic products were 80 wt% DMC, 20 wt% methylal and a trace of methyl formate. For $CuCl_2$/carbon catalyst, the selectivities of the organic products were 55 wt% of DMC, 40% methyl formate and 5 wt% methylal after 40 h on stream.

Due to the short duration of this research project, the in-situ FTIR work on the methanol/air reactions in the cages of the ExY52 or ExLZ-20M catalysts was not done. The proposed mechanism discussed above predicts that the copper methoxide can not be formed in those catalysts at 130°C. Further work should be done to verify such predictions.

4. Conclusions

For the oxidative carbonylation of methanol to DMC by Cu/zeolite catalysts, the presence of chloride is not required. However, the zeolite has to be exchanged with maximum amount of Cu(I) which can participate in the redox cycle by forming the active copper methoxide intermediate, $(CH_3O\text{-}Cu)^+Ze^-$. If the starting catalyst is the exchanged Cu(II)/zeolite, the stable $Cu^{2+}(2Ze^-)$ may resist reduction and may not form the proper intermediate. The best way to prepare the Cu(I)/zeolite catalyst is to apply the HAR treatment to the mixture of cuprous chloride or oxide with zeolite. The organic and inorganic ligands, such as NH_3, can facilitate the copper migration into zeolite channels at low temperature. The insertion of CO into copper methoxide is the rate limiting step. Methanol is required for the desorption of DMC in zeolite channels.

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