

The mechanism of dimethyl carbonate synthesis on Cu-exchanged zeolite Y

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Abstract

The mechanism of dimethyl carbonate (DMC) synthesis from oxidative carbonylation of methanol over Cu-exchanged Y zeolite has been investigated using *in situ* infrared spectroscopy and mass spectrometry under transient-response conditions. The formation of DMC is initiated by reaction of molecularly adsorbed methanol with oxygen to form either mono- or di-methoxide species bound to Cu^+ cations. Reaction of the mono-methoxide species with CO produces monomethyl carbonate (MMC) species. DMC is formed via two distinct reaction pathways—CO addition to di-methoxide species or by reaction of methanol with MMC. The rate-limiting step in DMC synthesis is found to be the reaction of CO with mono-methoxide or di-methoxide species. The first of these reactions produces MMC, which then reacts rapidly with methanol to produce DMC, whereas the second of these reactions produces DMC directly. Formaldehyde was identified as an intermediate in the formation of dimethoxy methane (DMM) and methyl formate (MF). Both byproducts are thought to form via a hemiacetal intermediate produced by the reaction of methanol with adsorbed formaldehyde at a Cu^+ site.

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1. Introduction

Dimethyl carbonate (DMC) has many potential applications. It can serve as an oxygen-containing fuel additive, a precursor for synthesis of carbonic acid derivatives, a methylating agent, and as an intermediate in the synthesis of polycarbonates and isocyanates [1–3]. Cu-exchanged zeolites are particularly attractive catalysts for the synthesis of DMC, because they promote the oxidative carbonylation of methanol to DMC in the gas phase [4–9]. Previous investigations have shown that Cu-X and Cu-Y are the most active catalysts for producing DMC, whereas Cu-ZMS-5 and Cu-MORD are less active and exhibit a high selectivity to producing dimethoxy methane (DMM).

Several studies of the mechanism and kinetics of DMC synthesis over Cu-exchanged zeolites have been reported. Based on evidence from *in situ* IR spectroscopy, King [4,5] has proposed that methanol adsorbs on extra-framework Cu cations in Cu-Y and reacts with oxygen to form methoxide groups.

When CO is present in the gas phase, new bands appeared which were attributed to carbomethoxide species ($\text{CH}_3\text{OCO}-$); however, a definitive assignment of these features could not be made. DMC was envisioned to form upon reaction of methanol with the carbomethoxide species. The rate-limiting step was proposed to be CO addition to adsorbed methoxide species to form carbomethoxide species. These findings are supported by the studies of Anderson and Root [6,7], which show that the rate of DMC over Cu-X is first order in CO partial pressure and nearly zero order in both methanol and oxygen partial pressures. More recently, we have carried out studies of the kinetics of DMC synthesis on a fully characterized sample of Cu-Y prepared by dry exchange of H-Y with CuCl [8–10]. Analysis of the catalyst after preparation showed that all of the protons in H-Y had been exchanged one-for-one by Cu, and XANES data confirmed that all of the exchanged Cu was present as Cu^+ . In agreement with the work, of Anderson and Root, it was also shown that the kinetics of DMC formation are nearly first order in CO partial pressure, whereas the dependencies on methanol and oxygen partial pressures are nearly zero order. *In situ* infrared spectra revealed that while CO is strongly adsorbed by extra-framework Cu^+ cations, this adsorbate is almost com-

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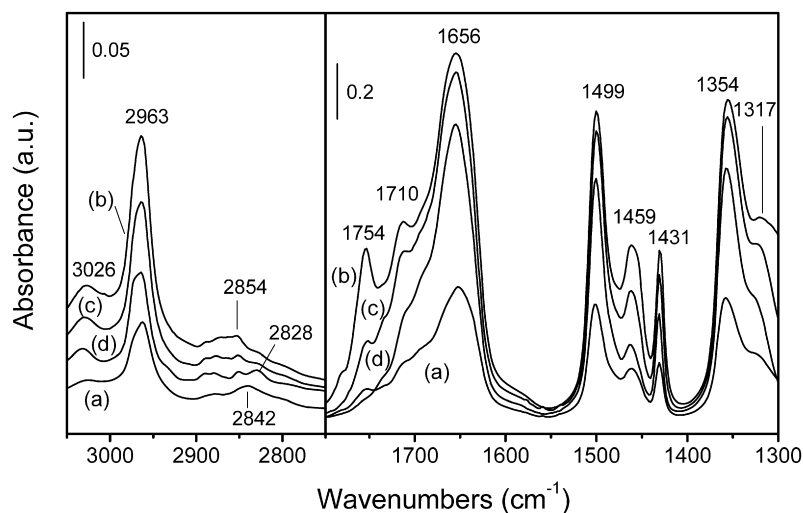


Fig. 1. IR spectra of Cu-Y exposed to DMC (5.57 kPa): (a) 12 s and (b) 20 min; and flushing with He: (c) 1.7 min and (d) 20 min.

pletely displaced by methoxide groups when methanol and oxygen are present together with CO.

The present study was undertaken to elucidate the mechanism for DMC formation on Cu-Y. The same catalyst sample was used as in our previous work [8,10]. Transient-response IR spectroscopy was used in combination with measurements of the temporal evolution of products in the gas phase, to identify the sequence of elementary steps involved in the formation of DMC. Additional transient-response experiments were conducted to gain information on the pathways for forming DMM and methyl formate (MF), the byproducts of DMC synthesis.

2. Experimental

2.1. Catalyst preparation

Cu-Y zeolite was prepared by solid-state ion exchange of H-Y zeolite (Si/Al = 2.5) with CuCl at 923 K [8]. A detailed discussion of the extent of cation exchange and the oxidation state of Cu in the sample of Cu-Y used for the present study has been presented previously [8,10]. This work demonstrated that all of the Brønsted acid protons are replaced quantitatively by Cu⁺ cations during solid-state exchange of H-Y by CuCl. The presence of Cu⁺ cations as the exclusive form of Cu was confirmed by the observation of a well-defined, Cu K-pre-edge peak at 8983.8 eV by XANES. Analysis of EXAFS data demonstrated that the Cu⁺ cations are coordinated to framework oxygens with a coordination number of ~2.1 at a distance of 1.99 ± 0.02 Å.

2.2. Transient-response IR and mass spectrometry experiments

Transient-response IR experiments were carried out using 15 mg of catalyst pressed into a 20 mm-diameter pellet. The pellet was placed into an *in situ* IR cell, and spectra were recorded using a Thermo-Nicolet NEXUS 670 FTIR spectrometer. Eight scans were averaged using a resolution of 4 cm^{-1} . Prior to adsorbate exposure, the catalyst was heated in He at

673 K. The products formed during transient-response experiments were monitored by mass spectrometry (MKS Mini-Lab quadrupole). In a typical experiment, the temperature was reduced to 403 K prior to the introduction of CH₃OH (12.12 kPa). All flow rates were approximately $40 \text{ cm}^3 \text{ min}^{-1}$. After 30 min of exposure to CH₃OH, 2.02 kPa O₂ was added into the stream. Once steady-state was reached, the stream was switched to He in order to remove gas-phase CH₃OH and O₂ from the atmosphere, as well as any weakly adsorbed species. A flow of CO (20.2 kPa, balance He) was then introduced for a fixed period of time after which the cell was again flushed with He. Next, a flow of CH₃OH/O₂ (12.12 kPa CH₃OH, 2.02 kPa O₂) was reintroduced into the cell. Finally, a flow of CH₃OH/O₂/CO/He (4.0/1.0/9.0/19.3) was passed through the cell at the rate of $40 \text{ cm}^3 \text{ min}^{-1}$. Since the concentration of reaction products leaving the infrared cell was too small to measure accurately, a parallel experiment was carried out using a larger amount of catalyst (150 mg) [9]. The same protocol used for the transient-response IR experiments was used for the observation of products formed during the transient-response reaction experiments. Separate experiments were carried out to identify the formation for DMM/MF. In this case, a He stream containing formaldehyde was introduced into the system, after which was switched to one containing methanol and formaldehyde. The flow of formaldehyde was turned off and turned on again to identify the role of formaldehyde in the formation for DMM and MF.

3. Results

3.1. Infrared spectra of adsorbed DMC and DMM

Infrared spectra of DMC and DMM adsorbed on Cu-Y were recorded to aid the interpretation of the spectra observed under transient-response conditions. Spectra of DMC adsorbed on Cu-Y at 403 K are shown in Fig. 1. After a contact time of 12 s, bands appear at 3026 and 2963 cm^{-1} , due to the anti-symmetric and symmetric C–H stretching vibrations of the CH₃

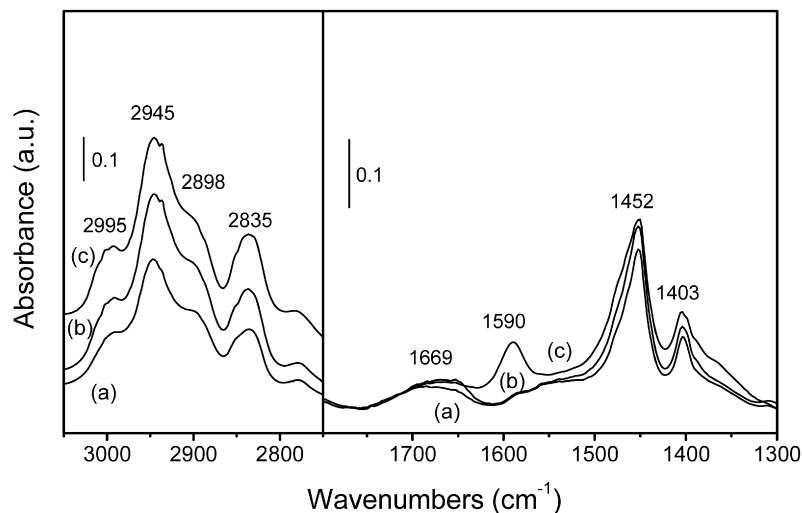


Fig. 2. IR spectra of Cu-Y exposed to DMM (43.4 kPa): (a) 0.8, (b) 1.1, and (c) 20 min.

in DMC, respectively [11,12]. A weak band is also seen at 2842 cm^{-1} , which is likely due to adsorbed methanol formed via the decomposition of DMC on Cu-Y. The bands at 1656 , 1499 , and 1354 cm^{-1} are attributable to C=O stretching, C-H bending, and O-C-O stretching modes of monomethyl carbonate (MMC) species associated with the Cu^+ cations in Cu-Y. This assignment is supported by the work of Beutel [12], who investigated the adsorption of DMC on Na-Y. Since the C-H stretching vibrations for DMC are totally coincident with those of MMC, it is impossible to identify the presence of DMC by inspection of the C-H stretching portion of the spectrum. Evidence for adsorbed DMC is given by the bands observed at 1459 and 1431 cm^{-1} , which can be assigned to asymmetric and symmetric bending vibrations of CH_3 groups in adsorbed DMC [11,13]. The C=O and O-C-O signals for this species exist as shoulders located on the high- and low-frequency sides of the bands for MMC, respectively. It is noted, though, that the band at 1431 cm^{-1} could also be due to CH_3 deformation vibrations of MMC.

After 20 min of exposure to DMC, the intensity of the C-H stretching bands at 3026 and 2963 cm^{-1} increased, together with the intensities of the C=O and C-O stretching features, indicating a higher occupancy of Cu^+ cations by adsorbed DMC and MMC. At the same time, a set of weak bands appeared above 2854 cm^{-1} , which are tentatively assigned to a combination of symmetric CH_3 stretching bands for gaseous DMC. The band at 1710 cm^{-1} due to C=O vibration of DMC adsorbed on Cu^+ became well resolved as well as the band at 1317 cm^{-1} for asymmetric O-C-O vibrations. Physically adsorbed DMC exhibits a C=O band at 1754 cm^{-1} . After 20 min of flushing in He, physisorbed DMC was removed, as was confirmed by the disappearance of the band at 1754 cm^{-1} . The bands at 1710 and 1317 cm^{-1} diminished upon He flushing, and concurrently, a band appeared at 2828 cm^{-1} due to C-H stretching vibrations of methoxide species [12].

Fig. 2 displays the spectra observed during exposure of Cu-Y to DMM at 403 K . Bands are seen at 2995 , 2945 , 2898 and 2835 cm^{-1} . The band at 2995 cm^{-1} is due to anti-symmetric

C-H vibrations of CH_3 groups, and the doublet at 2945 is due to a mixture of anti-symmetric C-H vibrations of CH_2 groups and a combination of the fundamental for the symmetric C-H vibrations of CH_3 groups and the overtone of methyl deformation of methoxide groups. The band at 2898 cm^{-1} is assigned to symmetric C-H vibrations of CH_2 groups [14]. The band at 2835 cm^{-1} cannot be assigned unambiguously, but may be due possibly to an overtone of deformation vibrations. In the C-H deformation region, features at 1452 and 1403 cm^{-1} are attributable to anti-symmetric vibrations of CH_3 and CH_2 groups, respectively. A new band appeared at 1590 cm^{-1} after 20 min of exposure to DMM, which can be assigned to formate species [15].

3.2. Transient-response studies of DMC, DMM, and MF formation

The infrared spectrum of Cu-Y exposed to methanol (12.12 kPa) in He at 403 K is shown by the circled points in Fig. 3a. Bands are seen at 2952 and 2844 cm^{-1} due to the anti-symmetric and symmetric C-H stretching vibrations of molecularly adsorbed methanol, at 1458 cm^{-1} for the deformation of methyl groups, and at 1366 cm^{-1} for the deformation of OH groups [16]. Upon addition to the flow of methanol, O_2 reacts rapidly with the adsorbed methanol to form methoxide species, which exhibit asymmetric and symmetric CH_3 stretching vibrations at 2925 and 2824 cm^{-1} , respectively. The band at 1458 cm^{-1} , attributed to methyl deformation, increases in intensity and is accompanied by a decrease in intensity of the OH deformation band for molecular methanol at 1366 cm^{-1} .

The products observed during the course of an analogous experiment carried out with a larger amount of catalyst are shown in Fig. 5. DMM is the principal product formed, together with smaller amounts of MF and CO_2 . The turnover frequency (TOF) for DMM formation is $7.3 \times 10^{-6}\text{ s}^{-1}$, that for MF is $1.9 \times 10^{-6}\text{ s}^{-1}$, and that for CO_2 is $1.0 \times 10^{-6}\text{ s}^{-1}$. The rate of DMC formation is nearly two orders of magnitude lower than that of DMM formation ($1.1 \times 10^{-7}\text{ s}^{-1}$). Fig. 4a displays the

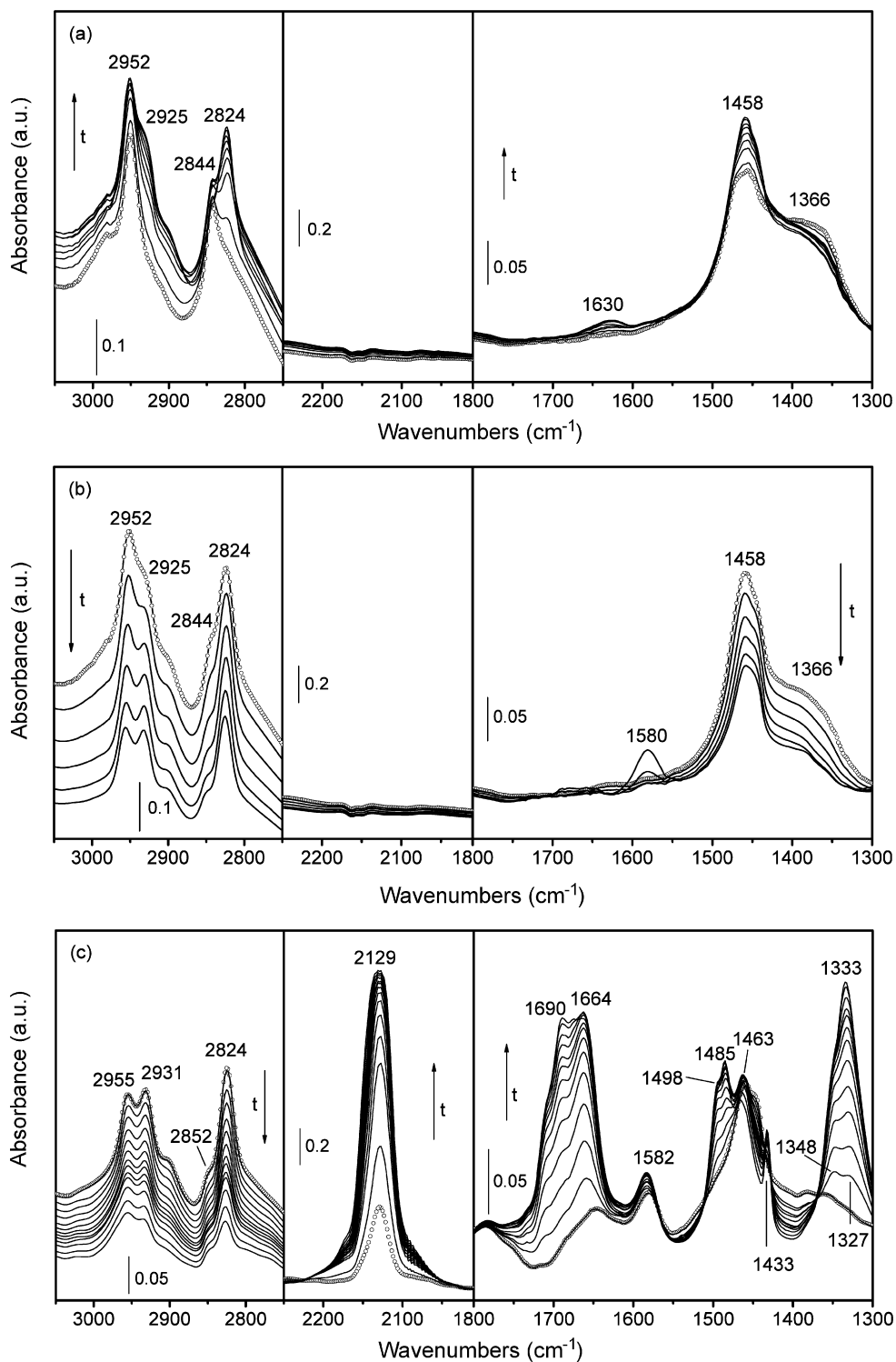


Fig. 3. IR spectra recorded during transient-response experiments: (a) exposure to CH_3OH (12.12 kPa) and O_2 (2.02 kPa) for 1.68 ks; (b) He flushing for 1.8 ks; (c) exposure to CO (20.2 kPa) for 1.72 ks; (d) He flushing for 1.8 ks; (e) exposure to CH_3OH (12.12 kPa) and O_2 (2.02 kPa) for 1.7 ks; (f) exposure to CH_3OH (12.12 kPa), CO (20.2 kPa), and O_2 (2.02 kPa) for 1.8 ks.

rate of methoxide species formation rate as a function of time (after the addition of O_2 to the flow of methanol) based on the growth in the intensity of the band at 2824 cm^{-1} associated with C–H symmetric stretching vibration of $\text{Cu-CH}_3\text{O}$. The formation of methoxide species on Cu-Y in the presence of O_2 occurs with an apparent first-order rate coefficient of $1.7 \times 10^{-2}\text{ s}^{-1}$.

Flushing the infrared cell with He at 403 K removes CH_3OH and O_2 from the gas phase as well as weakly adsorbed CH_3OH . The disappearance of the molecularly adsorbed methanol is evidenced by the progressive decrease in the intensities of the bands at 2952, 2844, 1458, and 1366 cm^{-1} , as seen in Fig. 3b. By contrast, the bands at 2925 and 2824 cm^{-1} as-

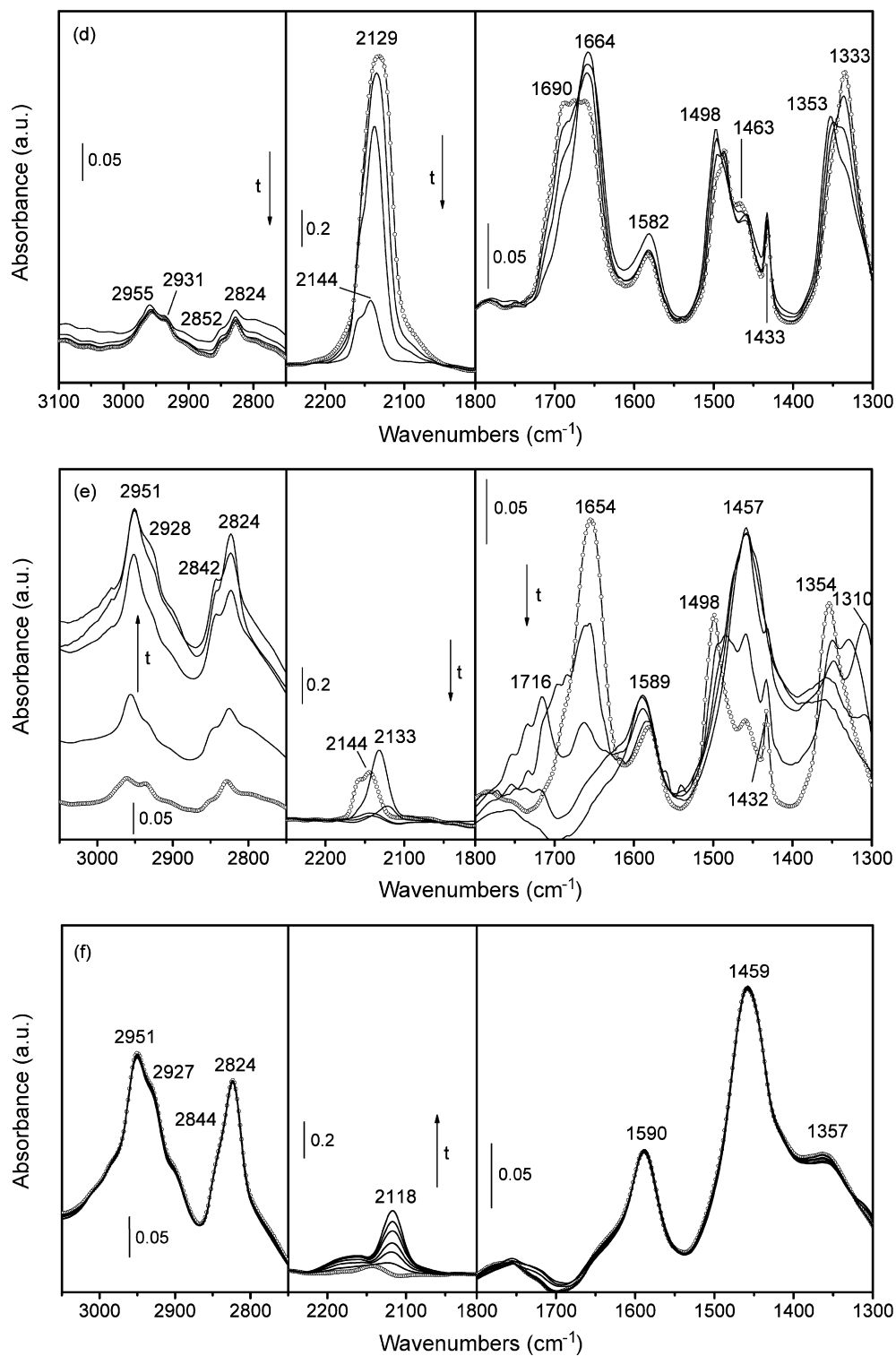


Fig. 3. (continued)

sociated with adsorbed methoxide species remain essentially constant in intensity. A new band appears at 1580 cm^{-1} , attributable to the formation of small amount of formate species [15]. Fig. 5 shows that during He flushing of the larger charge of catalyst, the rates of DMM and MF formation rapidly decline, as do the rates of DMC and CO_2 formation.

Passage of CO (20.2 kPa) over the catalyst previously exposed to CH_3OH and O_2 and then flushed with He produces significant changes in the infrared spectrum, as seen in Fig. 3c. The bands for methoxide species (2931 and 2824 cm^{-1}) decrease in intensity and new features appear at 1690 , 1664 , 1498 , 1485 , 1463 , 1433 , 1348 , and 1327 cm^{-1} , as well as a shoulder at 1354 cm^{-1} . The bands at 1690 , 1463 , and 1327 cm^{-1} can be

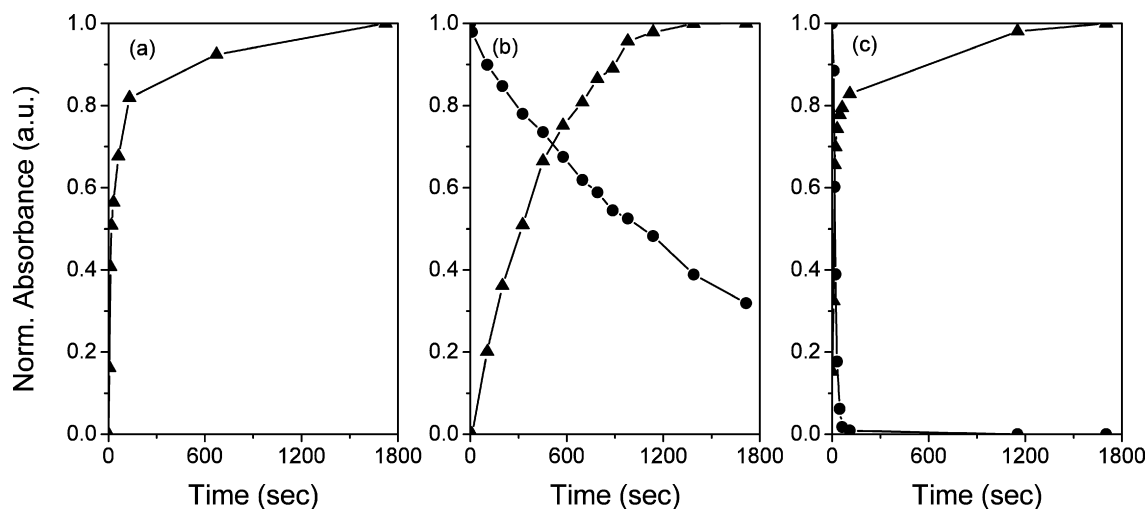


Fig. 4. Dynamics of band appearance or disappearance during transient-response experiments. Reaction conditions are those given in the caption for Fig. 3: (a) the formation rate of Cu methoxide species (▲); (b) the disappearance of methoxide species (●) and the formation of MMC (▲); (c) the formation rate of methoxide species (▲) and the disappearance of MMC (●).

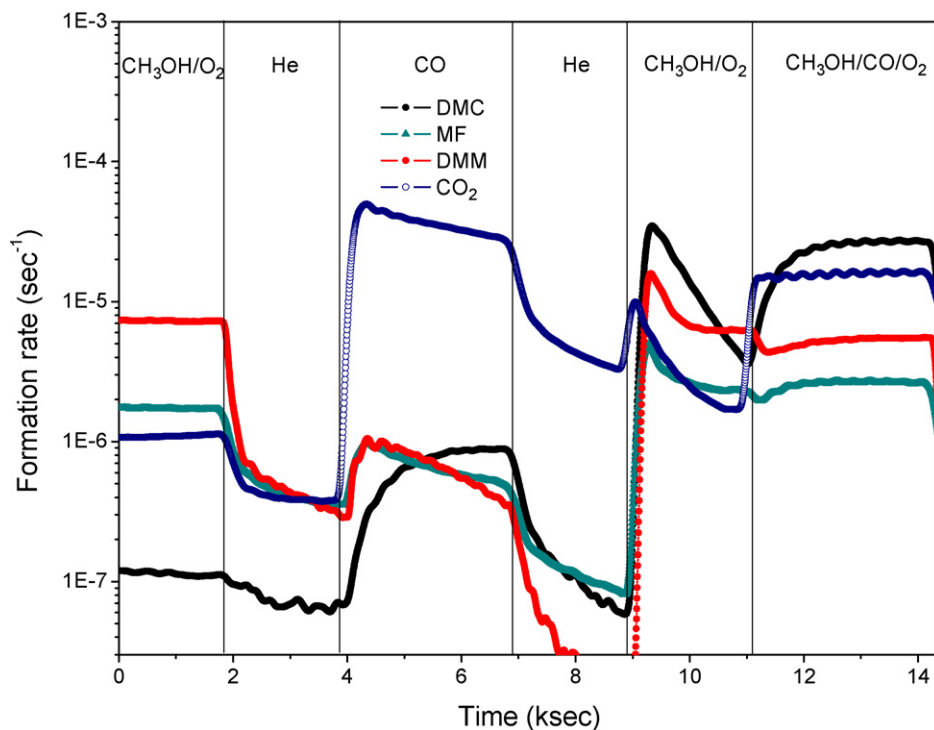


Fig. 5. Rates of product formation during transient-response studies aimed at understanding the mechanism of DMC formation. The reaction conditions used for each panel are identical to those used for the experiments shown in Figs. 3a–3f.

assigned to adsorbed DMC, whereas the bands at 1664, 1485, and 1348 cm^{-1} can be assigned to MMC. It is also noted that a carbonyl band (Cu^+-CO) appears at 2129 cm^{-1} . With increasing exposure of the sample to CO, the bands for adsorbed DMC, MMC and CO increase in intensity. The band at 1348 cm^{-1} slowly evolves into a shoulder on the high frequency side of the band of 1333 cm^{-1} . The bands at 1664 and 1348 cm^{-1} do not show any changes in intensity during the last several scans, suggesting that the formation of MMC has reached a maximum. However, slow increases in the intensity of the C=O and O–C–O stretching vibrations for DMC are still detectable.

The frequency of the C–O stretching band for adsorbed CO is red shifted by 9 cm^{-1} relative to that observed when CO is adsorbed on Cu–Y in the absence of other species. As discussed earlier [10], the red shift in the position of the CO band is due to the coadsorption of methanol or methoxide species. The band of constant intensity appearing at 1582 cm^{-1} during carbon monoxide exposure is assigned to asymmetric vibrations of O–C–O in formate ions [15] formed during He flushing. Fig. 4b shows the dynamics of methoxide consumption and MMC formation. The rates of methoxide species consumption and MMC formation are comparable and both are significantly lower than

the rate of methoxide group formation. The apparent first-order rate coefficient for the MMC formation is $2.5 \times 10^{-3} \text{ s}^{-1}$. As seen in Fig. 5, the introduction of CO causes a small increase in the rates of DMM and MF formation, which then slowly decline, whereas the rate of DMC formation increases steadily with time. Over the same interval of time, the rate of CO_2 formation increases to $6.0 \times 10^{-5} \text{ s}^{-1}$ and then steadily declines.

After the passage of CO over the catalyst, it was again flushed with He. The infrared spectrum taken at the onset of He flushing is illustrated by circled points in Fig. 3d. A number of changes in the spectrum are observed: (1) the position of the CO band shifts to 2144 cm^{-1} caused by the desorption and/or consumption of methanol/methoxide species; (2) the bands at 1690, 1463, and 1333 cm^{-1} , attributable to adsorbed DMC, decrease in intensity; and (3) the bands at 1664, 1498, and 1433 cm^{-1} , due to adsorbed MMC, retain their intensity. The removal of CO from the gas phase causes an immediate decrease in the production of DMC, DMM, MF, and CO_2 , as seen in Fig. 5.

Fig. 3e shows that when the sample is exposed to a stream containing CH_3OH and O_2 , a number of changes occur in the infrared spectrum. The bands for molecularly adsorbed methanol ($2951, 2842, 1457 \text{ cm}^{-1}$) grow in intensity, whereas the band for adsorbed CO first shifts to 2133 cm^{-1} and then rapidly disappears. These changes are accompanied by a loss in the intensity of the bands for MMC ($1654, 1498, 1354 \text{ cm}^{-1}$) and the concurrent increase and then decrease in the intensity of the bands due to adsorbed DMC ($1690, 1463, \text{ and } 1333 \text{ cm}^{-1}$), as well as the loss in intensity of the bands for gas-phase DMC ($1716 \text{ and } 1310 \text{ cm}^{-1}$). The latter pattern suggests that DMC is formed via the consumption of adsorbed MMC with methanol. With increasing time, the bands for adsorbed DMC diminish completely and the surface becomes dominated by the features of molecularly adsorbed methanol and methoxide species. Fig. 4c shows that the rates for the disappearance of adsorbed MMC and the formation of methoxide groups are rapid and essential equivalent. The disappearance of the adsorbed MMC has an apparent first-order rate coefficient of $6.3 \times 10^{-2} \text{ s}^{-1}$.

Fig. 5 demonstrates that when the sample is exposed to a mixture of CH_3OH and O_2 , after previously being exposed separately to mixture of CH_3OH and O_2 and then to CO, a burst of DMC, DMM and MF formation occurs, after which the rate of formation of all three products declines monotonically, with that of DMC occurring most rapidly. The rate for DMC formation quickly reaches a maximum of $3.8 \times 10^{-5} \text{ s}^{-1}$ and then decreases to $3.1 \times 10^{-6} \text{ s}^{-1}$. Maxima of $1.6 \times 10^{-5} \text{ s}^{-1}$ and $6.1 \times 10^{-6} \text{ s}^{-1}$ are detected in the rates of DMM and MF formation, respectively. After ~ 10 min, the formation rates approached a constant value of $6.4 \times 10^{-6} \text{ s}^{-1}$ and $2.5 \times 10^{-6} \text{ s}^{-1}$ for DMM and MF, respectively. Over the same period the rate for CO_2 formation rises rapidly to $1.0 \times 10^{-5} \text{ s}^{-1}$ and then rapidly decreases at a rate paralleling the decrease in the DMC formation.

In the last segment of the transient-response experiment, all of the reactants required for DMC synthesis are introduced into the reactor simultaneously. Fig. 3 shows that in this case the only bands observed are those for molecularly adsorbed methanol ($2951, 2844, 1459, \text{ and } 1357 \text{ cm}^{-1}$), methoxide

species ($2927 \text{ and } 2824 \text{ cm}^{-1}$), and adsorbed CO (2118 cm^{-1}). No features for MMC or DMC are observed under steady-state reaction conditions in agreement with our previous report [8,10]. The observation of only a small, red-shifted band for adsorbed CO at 2118 cm^{-1} indicates that the formation of methoxide groups inhibits the adsorption of CO. Fig. 5 shows that upon introduction of the $\text{CH}_3\text{OH}/\text{CO}/\text{O}_2$ mixture, the rate of DMC formation rises rapidly to $2.7 \times 10^{-5} \text{ s}^{-1}$, whereas the rates of DMM and MF formation rate rise to $5.5 \times 10^{-6} \text{ s}^{-1}$ and $2.8 \times 10^{-6} \text{ s}^{-1}$, respectively. CO_2 is formed at a rate only slightly lower than that for the formation of DMC ($1.8 \times 10^{-5} \text{ s}^{-1}$).

Fig. 6 shows the products formed during transient-response experiments aimed at elucidating the pathways leading to DMM and MF. DMM and MF are detected when formaldehyde alone is passed over the catalyst. The rate of DMM formation reaches a maximum of $8.7 \times 10^{-6} \text{ s}^{-1}$ and then decreases monotonically with further reaction time. The highest rate of MF formation is $1.3 \times 10^{-6} \text{ s}^{-1}$. After reaching a maximum, the rate decreases to $4.8 \times 10^{-6} \text{ s}^{-1}$ and then increases slowly again. When methanol is added in the feed stream together with formaldehyde, the rates of DMM and MF formation increases rapidly to $2.1 \times 10^{-4} \text{ s}^{-1}$ and $2.3 \times 10^{-5} \text{ s}^{-1}$, respectively. Without the presence of formaldehyde, the rates of DMM and MF formation decrease. The rates of formation of DMM and MF recover when formaldehyde is re-introduced in the system together with methanol. The data shown in Fig. 6 demonstrate that DMM and MF are formed at significant rates only when methanol and formaldehyde are present together.

4. Discussion

The results presented in Figs. 3–5 suggest that the mechanism of DMC formation proceeds via the steps shown in Fig. 7. Methanol first adsorbs molecularly on extra-framework Cu^+ cations, species **1**, to form species **2**. When oxygen and methanol are present in the gas phase, molecularly adsorbed CH_3OH reacts to form methoxide species, as evidenced by the appearance of bands for these species in the infrared spectra shown in Fig. 3a. The elementary processes by which methoxide groups are formed cannot be identified from the results of the present study. However, it is reasonable to suppose that upon reaction with O_2 , adsorbed methanol forms species **3**, in which a methoxide and a hydroxide group are both attached to a single Cu cation. The reaction of **3** with a second molecule of CH_3OH results in the release of water and the formation of species **5**, which contains two methoxide groups. As shown in Fig. 5, the formation of methoxide groups is relatively rapid and occurs with a time constant of $1.7 \times 10^{-2} \text{ s}$.

Passage of CO over Cu-Y previously exposed to CH_3OH and O_2 results in the slow consumption of methoxide species and the concurrent formation of MMC (see Fig. 3c). DMC also appears in the gas phase at about the same rate as that for the formation of adsorbed MMC (see Figs. 4b and 5). Fig. 7 illustrates how adsorbed MMC (species **4**) could form by the reaction of CO with **3**, and how DMC could form by reaction of CO with **5** to form species **6**, adsorbed DMC. Desorption of

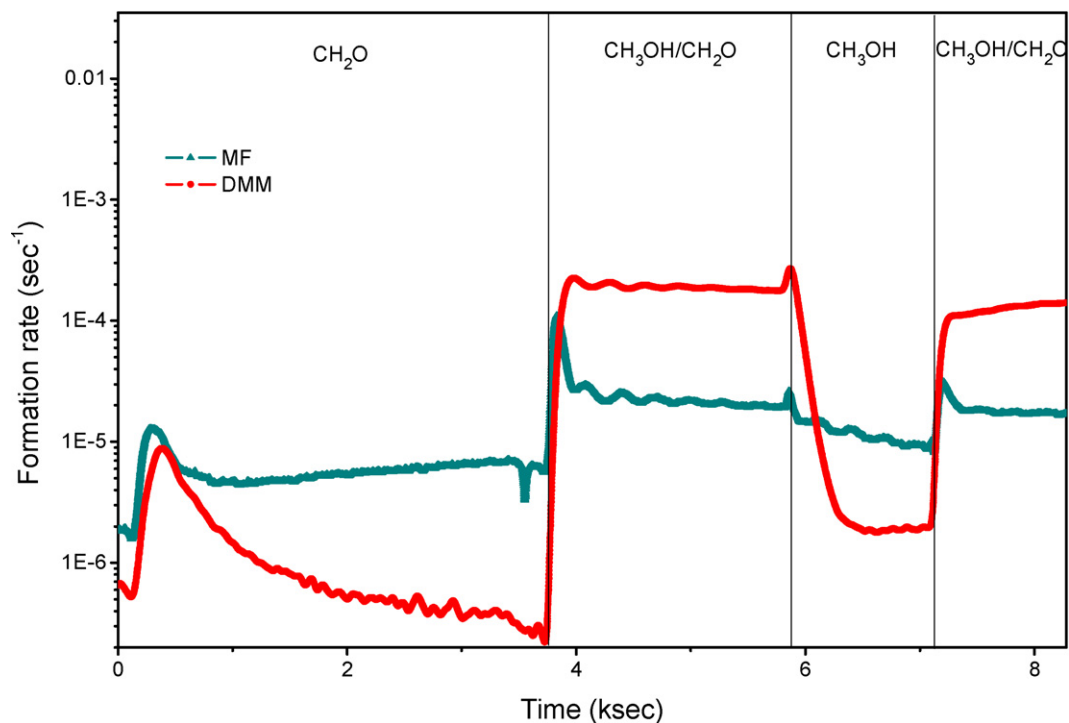


Fig. 6. Rates of product formation during transient-response experiments aimed at understanding the mechanism of DMM and MF formation. The partial pressures of CH_2O and CH_3OH are 6.06 and 0.96 kPa, respectively.

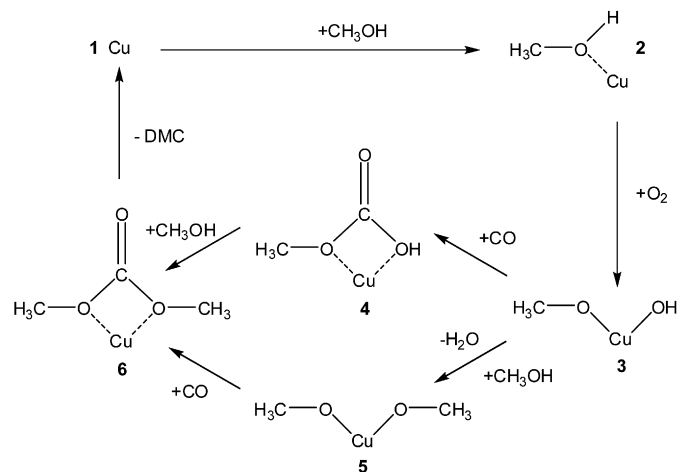


Fig. 7. Mechanism for the formation DMC.

DMC from **6** results in the restoration of **1**. The reaction of **3** to form **4** is viewed as the source of adsorbed MMC seen by IR (see Figs. 3c, 3d, and 4b), whereas the reaction of **5** to form **6** is viewed as the source of gas-phase DMC. The similarity in the rates of forming adsorbed MMC and gas-phase DMC suggests that the dynamics of the elementary processes involved in these two products are comparable. The large amount of CO_2 observed during this phase of the transient response sequence (see Fig. 5) is likely due to the reaction of CO with adsorbed atoms of O. Fig. 5 shows that the formation of DMC ceases as soon as gas-phase CO is flushed from the reactor by He. However, when the catalyst is next exposed to a mixture of CH_3OH and O_2 , the formation of DMC begins almost immediately, passes

through a maximum, and then decreases slowly. Fig. 3e suggests that the formation of DMC occurs as a consequence of the reaction of adsorbed MMC reacting with CH_3OH , i.e., the reaction of **4** to **6** shown in Fig. 7.

The proposed reaction mechanism for the oxidative carbonylation of methanol to DMC is similar to that proposed by King [4,5] but differs in two respects. The first and most important is the identity of the intermediate formed upon the interaction of CO with methoxide groups. In contrast with the interpretation proposed by King, we propose that the intermediate is MMC (see Fig. 7), rather than a carbomethoxy species. The formation of MMC is proposed on the basis of the close similarity in the bands observed when CO is added to methoxide species bonded to Cu^+ cations (see Fig. 3c) to those observed upon adsorption of DMC at reaction temperature (see Fig. 1). The scheme proposed in Fig. 7 then naturally allows for an explanation of both DMC synthesis and its decomposition upon adsorption. Another difference between the mechanism shown here and that proposed by King is the hypothesis that DMC may also form by CO addition to dimethoxy species. The inclusion of this step is supported by the observation of DMC formation upon passage of CO over Cu-Y previously exposed to methanol and oxygen (see Figs. 3c and 4b). The pathway via MMC cannot explain this observation, since reaction of MMC with gas-phase methanol is required to form DMC from MMC.

The data presented in Fig. 6 strongly suggest that the formation of DMM and MF involves the reaction of CH_3OH with CH_2O . While CH_2O was not observed as a product during the reaction of CH_3OH with O_2 , it is an expected intermediate in the oxidation of methanol to CO_2 . A possible mechanism for the formation of DMM and MF is shown in Fig. 8. The coad-

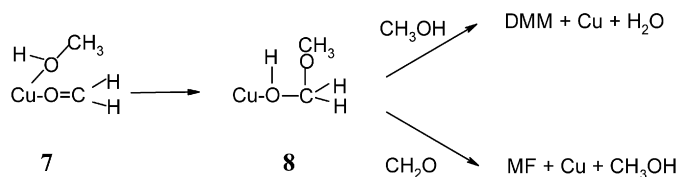


Fig. 8. Mechanism for the formation of DMM and MF.

sorption of CH_2O and CH_3OH produces species **7**, which can react to form a hemiacetal, species **8**. The reaction of **8** with CH_3OH would produce DMM and H_2O , whereas the reaction of **8** with CH_2O would produce MF and CH_3OH . MF could also be produced by the Tishchenko reaction of two molecules of CH_2O , but the data shown in Fig. 6 suggest that this process is much less effective than the reaction of CH_2O with CH_3OH , since the rate of MF formation from CH_2O alone is much lower than that when CH_2O and CH_3OH are both present in the gas phase. This conclusion is further supported by the data in Fig. 5, which show that when CH_3OH and O_2 are passed over the catalyst the rate of DMM formation is significantly higher than the rate of MF formation. This is also true when CO is present in the feed gas.

It is interesting to observe that while CO readily adsorbs on Cu^+ cations in Cu-Y, the concentration of adsorbed CO decreases significantly when CH_3OH and O_2 are present in the gas phase together with CO (see Fig. 3). This observation is a direct consequence of the effect of methoxide groups on the adsorption of CO. As noted in our earlier work [10], the adsorption energy for CO is decreased significantly by the presence of methoxide species bound to Cu^+ cations in Cu-Y. The red shift in the frequency of CO coadsorbed in the presence of CH_3OH and O_2 is another indicator that CO adsorbs on Cu^+ sites containing either methoxide species or molecularly adsorbed CH_3OH , both of which serve as electron donors to Cu^+ . The increased charge density on Cu^+ results in greater back donation of charge to the π^* antibonding orbitals of CO, which, in turn, causes the red shift in the C–O stretching frequency.

The infrared spectra presented in Fig. 3f show that under steady-state conditions of DMC synthesis, the dominant species associated with Cu^+ cations are methoxide species. However, it is not possible to determine whether these species are in the form of species **3** (mono-methoxide) or **4** (di-methoxide). As reported previously [10], the kinetics of DMC formation are nearly first order in CO partial pressure and are nearly zero-order in the partial pressures of CH_3OH and CO. Taken together, these observations strongly suggest that the rate of DMC formation is limited by the reaction of species **3** to **4** or **5** to **6**. The reaction of species **3** with CO to form species **4** results in the formation of MMC as an intermediate, and, as discussed above, the reaction of **4** (adsorbed MMC) with gas-phase methanol is very rapid relative to the rate at which DMC is formed.

Under conditions of very low methanol conversion (<1%), the rate of DMC formation is an order of magnitude faster than the rate of DMM or MF formation (see Fig. 5). This means that the processes leading to DMM and MF are much slower than

those leading to DMC. The results of Fig. 6 show that in the absence of CO and O_2 , and with methanol and formaldehyde partial pressures of 6.06 and 0.96 kPa, respectively, the rate of DMM is more than an order of magnitude higher than during DMC synthesis. This suggests that in the later case, the concentration of formaldehyde produced by the partial oxidation of methanol may be only 0.1 kPa.

5. Conclusions

The elementary steps involved in the oxidative carbonylation of methanol to form DMC on Cu-Y were investigated by combining information obtained from infrared spectroscopy and mass spectrometry under transient-response conditions. Characterization of Cu-Y indicates that the Cu/Al ratio is unity and that all of the Cu is present as Cu^+ cations. Transient-response IR experiments show that methanol adsorbs molecularly and then reacts with O_2 to form methoxide species. While CO adsorbs on Cu^+ more strongly than methanol, the formation of methoxide groups inhibits the adsorption of CO significantly. With CO present in the gas phase, the methoxide species react slowly to form monomethyl carbonate species. The latter species react rapidly with methanol to form DMC. The overall mechanism of DMC formation is summarized in Fig. 7. DMM and MF are the principal byproducts of DMC synthesis. The formation of both byproducts is hypothesized to proceed via a hemiacetal intermediate formed by the reaction of formaldehyde, produced by the partial oxidation of methanol. As shown in Fig. 8, reaction of the hemiacetal with methanol leads to DMM, whereas reaction of this intermediate with additional formaldehyde produces MF. These pathways are supported by transient-response experiments involving the reaction of formaldehyde with methanol.

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