An investigation of carbon-supported CuCl\(_2\)/PdCl\(_2\) catalysts for diethyl carbonate synthesis

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**ABSTRACT**

The synthesis of diethyl carbonate (DEC) by the oxidative carbonylation of ethanol was investigated using catalysts prepared by the dispersion of CuCl\(_2\) and PdCl\(_2\) on amorphous carbon promoted with KCl and NaOH. Catalysts were characterized extensively by XRD, XAFS, SEM and TEM with the aim of establishing their composition and structure after preparation, pretreatment, and use. It was observed that after preparation and pretreatment in He at 423 K copper is present almost exclusively as Cu(I), most likely in the form of [CuCl\(_2\)]\(^-\) anions, whereas palladium is present as large PdCl\(_2\) particles. Catalysts prepared exclusively with copper or palladium chloride are inactive for DEC synthesis, indicating that both components must be present together. Evidence from XANES and EXAFS suggests that the DEC synthesis may occur on [PdCl\(_2\)_x][CuCl\(_2\)]\(_y\) species deposited on the surface of the PdCl\(_2\) particles. As-prepared catalysts exhibit an increase in DEC synthesis activity and selectivity with time on stream, but then reach a maximum activity and selectivity, followed by a slow decrease in DEC activity. The loss of DEC activity is accompanied by a loss in Cl from the catalyst and the appearance of paratacamite.

**1. Introduction**

Diethyl carbonate (DEC) is a potential fuel oxygenate additive with characteristics that are superior to alternatives, such as dimethyl carbonate (DMC) or ethanol (see Table 1) [1]. Compared with characteristics that are superior to alternatives, such as DMC, DEC has higher energy content, lower vapor pressure, better distribution into gasoline versus water, and safer hydrolysis products. DEC is also useful for carbonylation and ethylation, or as an intermediate for the synthesis of diphenyl carbonate (used for the production of polycarbonate plastic). Conventional synthesis of dialkyl carbonates can be carried out by reaction of alcohols with phosgene. The use of phosgene can be avoided by oxidative carbonylation of alcohols in a slurry containing copper chloride salts [2]. However, this approach involves corrosive materials and difficulties in product separation. Thus, it would be desirable to develop a gas-phase process for producing DEC.

Various catalysts have been investigated for promoting the synthesis of DEC via the oxidative carbonylation of ethanol, Eq. (1) [3–10].

\[
2\text{CH}_3\text{CH}_2\text{OH} + \text{CO} + \frac{1}{2}\text{O}_2 \rightarrow (\text{CH}_3\text{CH}_2\text{O})_2\text{CO} + \text{H}_2\text{O} \quad (1)
\]

Virtually all of these materials are prepared by dispersing CuCl\(_2\) or CuCl\(_2\) and PdCl\(_2\) onto a support. Early studies showed that activated carbon (AC) was a particularly good catalyst support [5,11]. A comparison of CuCl\(_2\)/PdCl\(_2\) supported on silica, alumina, and AC revealed that a 10-fold higher activity to DEC could be achieved using AC rather than silica or alumina as the support [4]. The type of AC has been shown to have a significant impact on catalytic activity in DMC synthesis [3], as well as pretreatment of the AC support with HNO\(_3\), KOH, H\(_2\)O, air or H\(_2\) before adding the catalytically active components [12].

Various promoters, such as alkali chlorides, hydroxides, and acetates, have been found to improve catalyst activity and stability [4,8,10–15]. Alkali chlorides are thought to reduce the loss of Cl from the catalysts, one of the mechanisms by which DEC activity is lost (vide infra), whereas alkali hydroxides are thought to reduce support acidity, which can contribute to the decomposition of DEC. Alkali hydroxides have also been hypothesized to promote the formation of copper hydroxychlorides, such as paratacamite, Cu\(_2\)Cl(OH)\(_3\). The roles of these species are discussed below.

A number of investigators have noted that AC-based catalysts deactivate with time. Explanations of the cause of deactivation have focused on the loss of chlorine as a primary culprit [8,10,11,16]. Catalyst activity can be regenerated by offline treatment with a chlorine-containing gas, such as HCl [11] or methyl chloroacetate [8]. It is also interesting to note that chlorine loss also occurs during catalyst activation when a freshly prepared
catalyst is first exposed to reactants, suggesting that an optimal Cl/Cu ratio may exist [6]. Three other deactivation modes have been proposed. These include sintering of CuCl and reduction of PdCl₂ for a CuCl-PdCl₂/AC catalyst [17] and a transformation from one copper hydroxochloride phase to another [16].

The composition and structure of the active species for DEC synthesis and their relationship to the composition of the precursors used for catalyst preparation are not well understood. Several studies of CPAC catalysts have concluded that copper hydroxochlorides are formed during preparation and that these Cu species promote the synthesis of DEC or promote the reoxidation of Pd⁰ [4,8,10,13,15,16,18,19]. Structural characterization of CPAC-type catalysts [6,8,10–13,15,16,19] has shown that CuCl₂ and PdCl₂ are well dispersed on the catalyst surface. After pretreatment or reaction, the Cl/Cu has been observed to decline relative to that in the as-prepared catalyst and the formation of copper hydroxochlorides has been reported in some cases. While significant progress has been made towards identifying an active catalyst for the gas-phase synthesis of DEC, reports of high DEC yields on activated carbon-based catalysts are tempered by the observation that activity declines with time on stream. In addition, there is a lack of consensus regarding the identity and structure of active species in these catalysts. The aim of the present investigation was to carry out a detailed study of the factors affecting catalyst activity, selectivity, and stability for DEC. Measurements of catalyst activity and selectivity were combined with structural characterization using XRD, TEM, SEM-EDS, XANES, and EXAFS. Our results provide new evidence regarding the nature of Cu and Pd species in CPAC catalysts, as well as the role of KCl and NaOH additives.

2. Experimental

2.1. Catalyst preparation

Activated carbon (Darco, 12–20 mesh) was purchased from Aldrich and hand-ground for 3–4 min to produce a fine powder. CuCl₂ (anhydrous, Acros), PdCl₂ (Aldrich), and KCl (Fisher) were also hand ground and mixed with the activated carbon. The powder was transferred to 100 mL of refluxing methanol. The solution was stirred vigorously for 4 h, and then the methanol was removed by evaporation. NaOH (Merck) was then added by physical mixing and subsequent stirring in refluxing methanol for 4 h. After evaporating the methanol for the second time, the catalyst was dried in ambient air at 383 K for 10 h. Catalysts made by this technique are listed in Table 2. An abbreviated name and the loadings of each component are also listed.

2.2. Catalytic activity and selectivity

Catalyst performance was evaluated in a flow reaction system comprising a 1/4 in. stainless steel tubular reactor connected to a flow manifold. A back pressure regulator (Go, BP-8 model) was used to maintain the reaction pressure at 3.1 bar. Because the catalyst activity and selectivity changed significantly during the course of the reaction, a new sample of catalyst was used for each experiment. A run was initiated by loading 150 mg of catalyst into the reactor and then heating it to 423 K in 60 cm³/min of He. For experiments with no additional pretreatment, the flow of reactants was started immediately upon reaching 423 K. This reaction temperature was chosen after preliminary studies to optimize DEC activity. Samples pretreated at elevated temperatures in He were cooled to 423 K before starting reaction gases. The reactant feed composition was chosen to favor activity towards DEC. High CO pressure and low O₂ pressure helped suppress undesired oxidation reactions (see Eqs. (2), (4), and (5) below). Except where noted, the reactant gases CO (61%), O₂ (5%) and He (24%) were passed over the catalyst at 69 cm³/min (STP). Ethanol was supplied to the gas stream from a bubbler maintained at 329 K. After reaction, catalysts were cooled in He and then stored at ambient conditions. All catalysts were tested for 9 h.

The reaction products were identified and quantified by gas chromatography (Agilent 6890GC) at 19-min intervals for at least 8 h after the reaction gases were introduced to the catalyst. The gas chromatograph (GC) was equipped with two columns: a packed column (Alltech, Haysep DB packing) connected to a TCD detector for measuring CO, O₂, and CO₂; and a capillary column (Alltech, AT Aquawax; polyethylene glycol stationary phase) connected to an FID detector for measuring ethanol, DEC, and other organic byproducts. GC peak areas were converted to product concentrations by direct calibration for CO, O₂, CO₂, and ethanol. Concentrations of DEC, acetaldehyde, and 1,1-diethoxyethylene (acetal) were calculated using relative response factors and the ethanol calibration. Because the identity of the active species in these catalysts was unclear, activities were normalized to the weight of catalyst used, reported in units of (mmol product/gm catalyst/h). Only a portion of the Cu may be active in catalyzing the synthesis of DEC and acetaldehyde, or CO₂. Some catalysts may also take place on Pd species.

CO₂, acetaldehyde and 1,1-diethoxyethane (acetal) were the only significant byproducts detected. While water was observed in the reaction products, its concentration was not measured. For selectivity calculations, CO₂ was considered to be derived from the combustion of CO (Eq. (1); or via Eqs. (2) and (3) combined), whereas acetaldehyde and acetal were considered byproducts derived from ethanol (Eqs. (4) and (5), respectively). Eq. (6) was used to calculate selectivities from ethanol or CO. In this equation, α is the net moles of ethanol or CO required to make the ith product; ri is the rate of formation of the ith product; and the

Table 1

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>DMC</th>
<th>DEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower heating value</td>
<td>MBtu/gal</td>
<td>55.6</td>
<td>74.3</td>
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<tr>
<td>Density</td>
<td>gm/cm</td>
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<tr>
<td>Melting point</td>
<td>°C</td>
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</tr>
<tr>
<td>Boiling point</td>
<td>°C</td>
<td>90</td>
<td>126</td>
</tr>
<tr>
<td>Vapor pressure @ 37.8°C</td>
<td>mmHg</td>
<td>81</td>
<td>–0</td>
</tr>
<tr>
<td>Blending octane (R + M)/2</td>
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<td>103–116</td>
<td>104–106</td>
</tr>
<tr>
<td>Gasoline/water</td>
<td></td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>Distribution coefficient</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Hydrolysis products</td>
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<td>Ethanol, CO₂</td>
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</table>

Table 2

<table>
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<tr>
<th>Abbreviation</th>
<th>CuCl₂</th>
<th>PdCl₂</th>
<th>KCl</th>
<th>NaOH</th>
<th>BET</th>
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<tr>
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<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>545</td>
</tr>
<tr>
<td>KNCPC-3</td>
<td>2.3</td>
<td>0.22</td>
<td>1.3</td>
<td>0.52</td>
<td>412</td>
</tr>
<tr>
<td>KNCPC-HP</td>
<td>3.2</td>
<td>0.83</td>
<td>1.0</td>
<td>1.04</td>
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<tr>
<td>KNCPC-LP</td>
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<td>0.11</td>
<td>1.0</td>
<td>1.01</td>
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<tr>
<td>KNCAC</td>
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<td>–</td>
<td>0.9</td>
<td>1.01</td>
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</tr>
<tr>
<td>KNCPC-HC</td>
<td>6.5</td>
<td>0.26</td>
<td>1.0</td>
<td>0.96</td>
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<tr>
<td>KNCPC-LC</td>
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<td>0.25</td>
<td>1.2</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>PCAP</td>
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<td>0.23</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KCPAC</td>
<td>2.3</td>
<td>0.24</td>
<td>1.3</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>KPAC</td>
<td>–</td>
<td>0.25</td>
<td>1.0</td>
<td>–</td>
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</tr>
</tbody>
</table>

* On a wt % metal basis.  
* Molar ratio of promoter/Cu.  
* Nominal values (elemental analysis not measured).
sumption is over all products.

\[
\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2
\]

2.3. X-ray absorption fine structure (XAFS)

2.3.1. Cu K edge experiments

X-ray absorption spectroscopy was carried out using beamline 2-3 at the Stanford Synchrotron Radiation Laboratory (SSRL). Catalyst powder was pressed into a rectangular pellet (4.3 mm × 1.86 mm) and mounted in a stainless steel cell designed for measuring x-ray absorption spectra in transmission mode under gas and temperature treatments [20]. Eq. (7) was used to calculate the sample weight \( w \). In this equation \( A_{\text{ps}} \) is the pellet cross sectional area and \( \text{PCS} \) is the photoabsorption cross section (tabulated for each element at www-cxro.lbl.gov). The sample absorbance, \( A_n \), is the desired absorbance at 50 eV past the absorption edge, and was set at 2.5 to optimize the signal to noise ratio in the XAFS data.

\[
w = \frac{A_n}{\frac{\text{PCS}}{A_0}}
\]

The x-ray energy was selected using a double crystal Si(111) monochromator. The monochromator was detuned by 30% at 500 eV above the Cu K-edge to eliminate harmonic x-ray energies. Slits were situated before the first detector to constrain the beam size to a 10 mm rectangle. Three ionization chambers filled with N\(_2\) were used to measure the x-ray intensity (i) incident to the sample; (ii) after passing through the sample and before passing through a Cu foil standard; (iii) after passing through the Cu foil standard. The Cu foil was used as a reference to align experimental data spectra.

Because of constraints associated with the EXAFS experimental setup, the reaction conditions were modified from those used in the lab. CO (66%), O\(_2\) (3%), EtOH (5%), and He (balance) were flowed at 67 cm\(^3\)/min and a total pressure of 1 bar. The temperature was maintained at 423 K. Further details of the x-ray absorption experiment have been reported earlier [21].

To assess the effect of the high-energy x-ray beam on the catalyst, we took several EXAFS scans of the as-prepared catalyst over a period of hours before applying any gas or temperature treatments. There were no changes in the x-ray absorption spectrum of the catalyst during this period, confirming that significant changes in the catalyst did not occur due to interactions with the x-ray beam.

2.3.2. Pd K edge experiments

The experimental setup for Pd K edge experiments was identical to those for the Cu K edge, except that the post-edge absorbance \( A_n \) could not be constrained to 2.5 in the catalyst samples, due to low Pd loading. For these samples, the post-edge absorbance was set at 0.3. While this value is far outside the optimal range (2.5–4), useful EXAFS data could still be collected and analyzed.

2.3.3. Cl K edge experiments

Cl XANES were measured in fluorescence mode on beamline 9.3.1 at the Advanced Light Source, located at the Lawrence Berkeley National Laboratory. Powder samples were pressed onto carbon tape and mounted in a vacuum chamber (1 × 10\(^{-8}\) Torr). The XANES signal was extracted by taking the ratio of fluorescent photons to incident photons, as in Eq. (8).

\[
A = \frac{I}{I_0}
\]

2.3.4. XAFS data analysis

XANES and EXAFS data were analyzed using the Athena and Artemis applications in the IFEFFIT software package [22], as described previously [23].

2.4. X-ray diffraction

Identification of crystalline species in the catalyst was accomplished by x-ray diffraction, using a Siemens D5000 diffractometer, which is equipped with a Cu Kα \((\lambda = 1.54718 \text{ Å})\) radiation source and a graphite monochromator. Samples were mounted on a low-background holder with Vaseline as a binding agent. The x-ray angle was stepped in 0.05° increments from 2θ = 10°–70° with a count time of 6 s. Line broadening analysis was carried out using the Scherrer equation (9), where \( \lambda \) is the wavelength of the x-ray radiation, \( B \) is the full 2θ width at half maximum (in radians), and \( \theta \) is the peak position.

\[
t = \frac{0.9\lambda}{B\cos(\theta)}
\]

2.5. Scanning electron microscopy (SEM)

The catalyst surface composition and structure was examined by scanning electron microscopy using a S-4300SE/N (Hitachi, USA) scanning electron microscope equipped with energy dispersive spectroscopy (EDS). Noran System Six software was used to calculate elemental concentrations from x-ray emission profiles. Catalyst samples were mounted on carbon tape and measurements were taken at \( \sim 10^{-4} \) Pa. The absence of surface charging established that the activated carbon was sufficiently conductive without further modification.

2.6. Transmission electron microscopy

Transmission electron microscopy of two catalyst samples – as-prepared KNCPAC catalyst and KNCPAC after about 9 h of reaction – was obtained using the TECNAI TEM at the National Center for Electron Microscopy (NCEM). Both samples were prepared by diluting about 1 mg catalyst in about 10 mL ethanol, and then applying a small drop of the ethanol solution onto holey carbon-coated copper grids (SPI Supplies).

3. Results

3.1. Catalytic activity and selectivity

The catalytic activity of KCl-NaOH-CuCl\(_2\)-PdCl\(_2\)/activated carbon (KNCPAC) is illustrated in Fig. 1. The activity of this catalyst increases to a maximum of 4.8 mmol DEC/gm catalyst/h at 2 h of time on stream and then slowly loses activity thereafter. Acetaldehyde is produced at a stable rate, indicating that the active site for oxidative carbylation of ethanol differs from the site for acetaldehyde synthesis. In fact, activated carbon itself
CO₂/gm catalyst/h. By contrast, when ethanol is added to the feed, provide additional support for this hypothesis. Without ethanol
Removing PdCl₂ altogether resulted in a loss of more than 80% of changes in Pd loading (with Cu held at 3.0 wt%) are shown in Fig. 2. 3.1.1. Variation of Pd and Cu loadings
the combustion of CO to CO₂. DEC formation, leading to the conclusion that ethanol suppresses formation, suggesting that the processes for DEC and CO₂ synthesis (because of acidic and basic functional groups present on its surface) has been identified as a catalyst for conversion of ethanol to acetaldehyde and acetal. In a study of ethanol reactivity over carbon surfaces, acetal was observed only when acid sites were present on the carbon surface [24]. Therefore, the formation of some acetal suggests the presence of acid sites on the catalysts investigated.
There is a strong correlation between the rates of CO₂ and DEC formation, suggesting that the processes for DEC and CO₂ synthesis may share a common active site. The results of CO oxidation in the absence of ethanol (CO 70%, O₂ 6%, 60 cm³/min, 423 K, 3.1 bar) provide additional support for this hypothesis. Without ethanol present, CO oxidation achieves a steady rate of about 2.6 mmol CO₂/gm catalyst/h. By contrast, when ethanol is added to the feed, CO₂ formation declines with time in a manner similar to that for DEC formation, leading to the conclusion that ethanol suppresses the combustion of CO to CO₂.

3.1.1. Variation of Pd and Cu loadings
The variations of activity and selectivity towards DEC with changes in Pd loading (with Cu held at 3.0 wt%) are shown in Fig. 2. Removing PdCl₂ altogether resulted in a loss of more than 80% of the DEC activity relative to the sample loaded with 0.22 wt% Pd. CO₂ activity also declined, while acetaldehyde activity increased. Adding more Pd (0.83 wt%) increased the rates of all products, but the selectivities to DEC from ethanol and CO were highest for a Pd loading of 0.22 wt%.

3.2. X-ray diffraction
The XRD data for KNCPAC are summarized in Fig. 6. The as-prepared sample exhibits features for activated carbon (very broad background peaks at 23° and 43°), KCl, and NaCl, as well as silica...
impurities in the activated carbon support. The absence of any features for Cu reflects the high dispersion of this component, whereas the absence of features for Pd may be due to the low loading of this element. It is evident that some of the NaOH from the preparation is converted to NaCl, possibly via Eq. (10) or (11).

\[
\text{NaOH} + 2\text{CuCl}_2 \rightarrow 3\text{NaCl} + \text{Cu}_2\text{Cl}_3 \quad \Delta H^\circ = -291 \text{ kJ/mol (10)}
\]

\[
2\text{NaOH} + \text{CuCl}_2 \rightarrow 2\text{NaCl} + \text{Cu(OH)}_2 \quad \Delta H^\circ = -164.5 \text{ kJ/mol (11)}
\]

Three changes occur after the catalyst has been exposed to reaction conditions: (i) after 2 h, the NaCl peak height increases considerably, and then decreases after 10 h; (ii) some reduction in the KCl peak height takes place; (iii) a peak at \(2\theta = 16.3^\circ\) (probably paratacamite; vide infra) appears after 2 h and grows significantly after 10 h. The slight increase in NaCl is likely due to reaction of the remaining NaOH in the sample with CuCl\(_x\) species via Eq. (10), which could also account for growth of the peak at 16.3°. The loss of intensity for the KCl peak may be due to increased dispersion on the support or to the interaction of KCl with CuCl to form a molten salt mixture \(T_m = 423 \text{ K}\). Eq. (12) describes one of the reactions purported to take place in KCl-CuCl systems [27]. (As discussed below, CuCl\(_2\) is converted to a Cu(I) chloride species under reaction conditions.)

\[
2\text{KCl} + \text{CuCl} \rightarrow \text{K}_{2}\text{CuCl}_3 \quad (12)
\]

Paratacamite or related copper compounds may be responsible for the peak at 16.3°. In KNCAP samples with a Cu loading of 6.0 wt% (data not shown), the appearance of a second peak at 32.4° helps to identify this species as paratacamite \((\text{Cu}_2\text{Cl(OH)}_3)\). Other authors have identified \(\text{Cu}_2\text{Cl(OH)}_3\) as the active species in CuCl\(_2/\)
PdCl$_2$ catalyst systems (vide supra, Introduction). The data in Fig. 6 indicate that paratacamite begins to form XRD-visible crystals at the time that the catalyst reaches its peak activity for DEC formation. And as the DEC activity declines, paratacamite-like species increase in concentration. This observation suggests that paratacamite may not be the active species for DEC formation, but an inactive phase formed during deactivation of the catalyst. On the other hand, if paratacamite is, indeed, the active Cu phase, the increase in paratacamite peak intensity during deactivation could also be attributed to sintering of paratacamite particles and a resulting loss in surface area for reaction.

Line broadening analysis was carried out for KCl and NaCl. For the as-prepared catalyst, average particle sizes of 56 and 37 nm were calculated for KCl and NaCl, respectively. After He pretreatment, the average size of KCl and NaCl particles decreased by about 25%; no further decrease in particle size was observed after reaction.

3.3. TEM and SEM-EDS

Fig. 7 shows a TEM image of the as-prepared catalyst. Some stacking of carbon layers is evident from the TEM image. The inset of Fig. 7 shows the fast Fourier transform (FFT) of the TEM image, revealing faint diffraction bands probably associated with weakly graphitic features of the activated carbon [28]. No evidence for crystalline copper species was observed, providing further evidence for the very high dispersion of copper on the support. The catalyst was also examined by TEM after reaction (not shown). The same features were observed as those seen for the as-prepared catalyst.

In addition to graphitic features, large (~20–50 nm) crystalline particles of PdCl$_2$ were seen dispersed throughout the catalyst (Fig. 8). The particles were identified by comparison of FFT patterns with the reciprocal lattice of PdCl$_2$ and other possible compounds. This suggests that most of the PdCl$_2$ introduced during catalyst
preparation forms large crystals. Additional evidence supporting this conclusion is presented below.

The SEM images of KNCPAC taken before and after reaction are shown in Figs. 9 and 10. The attached tables list the elemental analyses for Cu, Na, K, Cl at the specified areas on each sample. The as-prepared catalyst (Fig. 9a) consists of carbonaceous particles with rather inhomogeneous surface characteristics. Some regions of the catalyst particles look relatively smooth, while others (not shown here) are decorated by large crystallites, principally KCl and NaCl. The size of the KCl and NaCl crystals observed by SEM were generally in the range from 25 to 100 nm, in agreement with the sizes determined from XRD. The KCl and NaCl regions are distinct and segregated from one another in many cases, indicating incomplete dispersion. However, some sodium and potassium is detected in regions where there are no large crystals, suggesting that these elements are dispersed throughout the catalyst.

Because elemental analysis in SEM relies on x-ray emission from a finite region of the catalyst, rigorous interpretation of the concentrations tabulated in Figs. 9 and 10 is unwarranted; however, the changes from point to point, and at different conditions are relevant. Various levels of Al, Si and S (from the activated carbon support) were encountered throughout the catalyst. However, Pd was not detected. While Cu was found throughout the entire surface of the catalyst, no Cu-containing particles could be identified. The surface of the as-prepared catalyst has a remarkably uniform distribution of these four species, with elements present in the order Cl > Cu > K > Na.

Fig. 10 shows SEM images taken after exposure of the catalyst to reaction conditions. The catalyst surface after reaction was smoother, and exhibited fewer patches of inorganic material. Elemental analysis showed a change in the distribution of the catalyst components, with Cu > Cl > K > Na. For the sampling of points in Figs. 9 and 10, the surface concentration of Cl decreased by at least 50% after the reaction relative to what was seen for the as-prepared catalyst.
3.4. XAFS

3.4.1. Cu XAFS

Cu XANES and EXAFS were collected in situ during He pretreatment and DEC synthesis. As the catalyst was heated in He from the as-prepared state, the XANES and EXAFS spectra changed continuously towards a stable spectrum that was reached after about 2 h. When reaction gases were subsequently introduced to the catalyst, the XANES and EXAFS spectra changed continuously, and a stable spectrum was obtained only after about 4–5 h reaction. The data shown here were acquired after the XAFS spectra stopped changing under the following conditions: (1) as-prepared, (2) after He pretreatment at 423 K, (3) after subsequent treatment under modified (see Section 2) reaction conditions.

Fig. 11 shows Cu XANES of as-prepared KNCPAC and after He pretreatment and exposure to reaction conditions at 423 K. XANES spectra of CuCl, Cu₂O, and CuCl₂ standards are also shown for comparison. The spectrum of the as-prepared catalyst has a distinct peak at 8983 eV characteristic Cu(I) species [29]. Previous studies have reported that Cu(I) species have a sharp absorption edge around 8983 eV, whereas the absorption edge for Cu(II) species occurs at >8985 eV. This distinction is well illustrated by the three copper standards shown in Fig. 11. Because the spectrum of the as-prepared catalyst has a distinct peak in the Cu(I) absorption edge region, it is clear that significant reduction from Cu(II) to Cu(I) species occurred during catalyst preparation. After treatment in He or exposure to reaction conditions, the feature for Cu(I) increased in intensity, indicating an increase in Cu(I) character, as well as a decrease in Cu coordination. The absorption at 8983 eV corresponds to the 1s → 4p transition [29]. The normalized absorption intensity of this peak can be correlated roughly with the Cu coordination number, with 2-coordinate Cu having an intensity of about 1.0 and 3-coordinate Cu having an intensity of about 0.7. Therefore, Cu in KNCPAC, under He flow or...
reaction conditions, has an estimated average coordination number of a little less than 3. The only evidence for Cu(II) is a weak feature around 8978 eV observed in the derivative spectrum shown in the inset of Fig. 12. This feature is attributable to the $1s \rightarrow 3d$ electronic transition that is partially allowed for d$^9$ Cu(II) compounds with broken symmetry. The data indicate, therefore, that while copper is introduced to the catalyst as CuCl$_2$, most of the Cu(II) is reduced to Cu(I) during catalyst preparation. It is noted further that the initial leading edge of the Cu XANES spectra for He-pretreated KNCPAC and for KNCPAC after reaction closely resembles that for CuCl. The absence of x-ray diffraction peaks for CuCl suggests that upon the reduction of CuCl$_2$ highly dispersed CuCl species are formed on the catalyst surface. The structure of these species is discussed below.

The Fourier-transformed, non-phase corrected, $k^3$-weighted Cu EXAFS data for KNCPAC are shown in Fig. 12. Fits to these data are shown in Fig. 13 and the fitting parameters are listed in Table 3. Each EXAFS spectrum is characterized by a single scattering contribution at about $R = 1.7 \text{ Å}$. The average Cu–Cl bond length increased from 2.08 Å in the as-prepared sample to 2.12 Å upon heating in He or exposure to reaction conditions at 423 K. Concurrent with the slight increase in bond length, the average Cu–Cl coordination number decreased from 2.7 in the as-prepared sample to 1.8 after heat treatment in He, and to 1.7 after exposure to reaction conditions. This decrease in coordination is qualitatively consistent with the observed increase in the intensity of the $1s \rightarrow 4p$ peak seen in the XANES data (Fig. 11).

It is worth noting that the quality of the fit, as indicated by the R-factor, improved after the catalyst was treated in He and then in the reaction mixture. This indicates that the coordination environment of Cu in the fresh catalyst is less homogeneous than that in the catalyst pretreated in He or exposed to reactants. In none of the EXAFS data is there any evidence for a separate Cu–O coordination shell, as there would be if a large portion of the Cu were present as Cu$_2$Cl(OH)$_3$. However, it is not possible to confirm or reject the existence of a (small) Cu–O contribution overlapping the Cu–Cl shell.

As noted above, Cu XANES showed that the Cu species in KNCPAC catalysts are almost exclusively Cu(I). These Cu(I) species are highly dispersed as suggested by the XRD and SEM-EDS data. While the nature of the Cu(I) species cannot be identified definitively, we propose that all or part of the species are chlorocuprate anions, such as [CuCl$_2$]$^-$, [CuCl$_3$]$^{2-}$, and [Cu$_2$Cl$_3$]$^{2-}$. Such anions have been observed in aqueous and organic solutions [30], and can be crystallized together with moderately large cations, for example tetraalkylammonium cations in these studies [31,32]. Chlorocuprate anions are readily distinguished by their Cu–Cl bond lengths, as indicated in Table 5 [30]. Clearly, [CuCl$_2$]$^-$ is the only chlorocuprate anion that matches the Cu EXAFS data taken after catalyst pretreatment in He or exposure to reaction conditions (Table 3). We suggest, therefore, that [CuCl$_2$]$^-$ anions could be the dominant Cu species present in the sample after He pretreatment and after reaction.

The Cu species in the as-prepared sample is probably a mixture of mostly [CuCl$_3$]$^-$ anions, together with some unreduced CuCl$_2$. Quantum chemical calculations of the geometry of CuCl$_2$ and [CuCl$_2$]$^-$ predict that the Cu–Cl bond length for linear CuCl$_2$ monomers is 0.06–0.08 Å less than that for [CuCl$_2$]$^-$ [33]. Consistent with this, it is observed that the as-prepared sample KNCPAC had a lower average Cu–Cl bond length than the catalyst characterized after exposure to reaction conditions.
3.4.2. Pd EXAFS

The Fourier-transformed, non-phase corrected, $k^2$-weighted Pd EXAFS data for KNCPAC are shown in Fig. 14 for as-prepared KNCPAC and after subsequent pretreatment of this material in He or exposure to reaction gases. The spectra for PdCl$_2$ and Pd are also shown for comparison. Fits to the EXAFS spectra are shown in Fig. 15, and the corresponding EXAFS fitting parameters are given in Table 4. The as-prepared catalyst strongly resembles crystalline PdCl$_2$. Upon He pretreatment or exposure to reaction gases at 423 K, the Pd–Cl coordination number decreased from 3.7 to 3.0 (compared to 4.0 for PdCl$_2$) and the disorder parameter, $\Delta \sigma^2$, increased, indicating an increase in the disorder of the Pd–Cl coordination shell. However, this change is not accompanied by an increase in Pd–Pd coordination (a scattering contribution would be expected at $\sim$2.5 Å) that would signal the reduction of Pd(II) to Pd(0).

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**Fig. 9.** SEM images of the as-prepared KNCPAC catalyst at a magnification of (a) 400×, (b) 4000×. Numbers indicate points where elemental analysis was measured. Values in the tables are concentrations in mol%.

**Fig. 10.** SEM images of the KNCPAC catalyst after reaction conditions at a magnification of (a) 400×, (b) 4000×. Numbers indicate points where elemental analysis was measured. Values in the tables are concentrations in mol%.

**Fig. 11.** Cu XANES for KNCPAC and three Cu standards. The inset shows the derivative spectrum for the XANES in the region where the 1s → 3d transition occurs for Cu(II) compounds.

**Fig. 12.** Non-phase corrected, $k^2$-weighted $\chi(k)$ spectra of the Cu EXAFS for KNCPAC. Spectra are shown before reaction and during in situ treatment with He or reaction gases. Each of the spectra is characterized by a single scattering shell at $\sim$1.7 Å.
3.4.3. Cl XAFS

The Cl K XANES for KNCPAC, CuCl and CuCl₂ are shown in Fig. 16. CuCl₂ is distinguished by the sharp peak at 2821 eV. The peak at 2821 eV in the as-prepared catalyst was very small and even smaller after exposure to reaction conditions. This observation provides further evidence that Cu(I) is the dominant copper species in the catalyst. It is noted, though, that while the Cl XANES edge energies for as-prepared KNCPAC and KNCPAC observed after reaction were very similar, they differ from that of CuCl. Therefore, as discussed above, we suggest that Cu(I) species are present primarily as [CuCl₂]⁻ anions.

Normalized XANES spectra are characterized by an “edge step,” calculated from the absolute difference in the mass absorption coefficient before and after the absorption occurring at an x-ray absorption edge. For x-ray fluorescence experiments with thin samples and low absorber concentrations, the magnitude of the edge step is proportional to the concentration of the absorbing element in a sample, and can therefore be used to determine changes in the concentration of the absorbing element [34]. The magnitude of the edge step in the Cl XANES spectrum was used as a qualitative measure of the Cl content before and after reaction. Before reaction, the edge step was 0.27 and after reaction, the edge step decreased to 0.12, confirming that a loss of Cl from the catalyst had occurred during reaction. The decrease of 56% agrees well with the loss of Cl observed by SEM-EDS (vide supra).

4. Discussion

The results presented in this study clearly demonstrate that as-prepared catalysts exhibit little activity initially for the formation of DEC, but slowly activate over several hours under reaction conditions, reach a maximum activity, and then lose activity. The major organic byproduct of DEC is acetaldehyde, and the rate of formation of this product rises slowly with time on stream but does not reach a maximum during 10 h of reaction. While KNCPAC shows a modest activity for DEC synthesis, the rate of DEC synthesis and the selectivity to DEC based on ethanol are significantly enhanced by the inclusion of PdCl₂ in the catalyst formulation. PdCl₂ supported on activated carbon shows no activity for DEC synthesis, but only a low activity for acetaldehyde synthesis. Increasing the ratio of CuCl₂ to PdCl₂ in the catalyst formulation increases the rate of DEC formation, but also the rate of acetaldehyde formation. As a consequence, the selectivity to DEC from ethanol passes through a maximum at a CuCl₂/PdCl₂ ratio of about 10/1. The addition of KCl to the catalyst formulation enhances somewhat the maximum rate of DEC formation, without affecting the rate of acetaldehyde formation, contributing to an increase in the maximum selectivity to DEC from ethanol. Pretreatment of fresh KNCPAC in He at 573 K for 1 h enhances the maximum rate of DEC formation and to an even greater degree, the rate of acetaldehyde formation, leading to a decrease in the maximum DEC selectivity from ethanol. He pretreatment also accelerates the rate of activity loss after the maximum in the rate of DEC formation is attained.

The observed changes in DEC activity with time on stream suggest that changes occur in the catalyst composition and structure with increasing exposure of the catalyst to reaction conditions. This view is supported by the observed changes in the physical characteristics of the catalyst. XANES and EXAFS clearly show that while copper is introduced as CuCl₂, the Cu(I) cations are reduced to Cu(I) cations during catalyst preparation. This change is accompanied by a decrease in the Cu–Cl coordination bonds.

| Table 3 | Summary of Cu EXAFS fitting parameters for KNCPAC. The Cu–Cl bond distances for CuCl and CuCl₂ are shown for comparison. |
| Scatterer | N | R (Å) | Δx² | ΔE₀ | R-factor |
| As prepared | Cl | 2.7 | 2.08 | 0.0074 | -8.9 | 0.008 |
| 423 K in He | Cl | 1.8 | 2.12 | 0.0066 | -1.6 | 0.006 |
| 423 K in EtOH/O₂/CO | Cl | 1.7 | 2.12 | 0.0073 | -1.8 | 0.002 |
| CuCl | Cl | 4 | 2.34 |
| CuCl₂ | Cl | 4 | 2.26 |

| Table 4 | Pd EXAFS fitting parameters. |
| Scatterer | N | R (Å) | Δx² | ΔE₀ | R-factor |
| As prepared | Cl | 3.7 | 2.29 | 0.0036 | 2.9 | 0.018 |
| 423 K in He | Cl | 3.2 | 2.29 | 0.0056 | 1.9 | 0.046 |
| 423 K in EtOH/O₂/CO | Cl | 3.0 | 2.29 | 0.0108 | 1.6 | 0.071 |
| PdCl₂ | Cl | 4 | 2.31 |
| Pd | Pd | 12 | 2.74 |

| Table 5 | Cu–Cl bond lengths for various chlorocuprate anions in the literature [30]. |
| Anion | Approximate bonding arrangement | Cu–Cl (Å) |
| CuCl₂⁻ | Linear | 2.07–2.12 |
| CuCl₃⁻ | Trigonal | 2.20–2.27 |
| Cu₂Cl₄⁻ | Trigonal | 2.24 |
| Cu₂Cl₃⁻ | Tetrahedral | 2.36–2.42 |

Fig. 13. Fits to Cu EXAFS data for KNCPAC (a) as prepared, (b) under reaction conditions. Experimental data (symbols) are shown with the corresponding fits (lines).
number and reduction in the intensity of the Cl XANES signal. After exposure to DEC synthesis conditions, the Cu–Cl coordination number decreases further and the Cu(I) pre-edge feature in the XANES spectrum increases in intensity. TEM and SEM micrographs, as well as XRD data, show no evidence for crystalline CuCl, either in the freshly prepared catalyst or after exposure of the catalyst to reaction conditions, leading to the conclusion that CuCl species are very highly dispersed. While these species could not be imaged, the Cu–Cl bond distance determined by analysis of Cu K-edge EXAFS data acquired after catalyst use suggest that Cu is present in the form of [CuCl₂]⁻ anions. By contrast, TEM shows that Pd is present in the form of 30 nm crystallites of PdCl₂, a conclusion that is also supported by analysis of Pd K-edge EXAFS data. These data also show a small decrease in the Pd-Cl coordination number upon exposure of the catalyst to reaction conditions. Combining the data obtained on the structure and form of the dispersed CuCl and PdCl₂ species together with the observation that the presence of Pd strongly enhances the formation of DEC, we hypothesize that the active centers for DEC synthesis may be species of the form [PdCl₂/C₄H₆O₃][CuCl₂]ₐ formed on the surface of PdCl₂ crystallites.

The pattern of catalyst activation up to a maximum DEC activity followed by a loss in activity has been reported previously [11,12], but the causes for this evolution in catalyst activity are poorly understood. We propose that activation involves the further dispersion of CuCl species on the surface of activated carbon, which may in part be facilitated by the reaction of CuCl with KCl to form K₂CuCl₃, a compound that has a melting point of 423 K, the temperature at which DEC synthesis is carried out. It is noted, though, that no direct evidence for K₂CuCl₃ was observed. The formation of [PdCl₂/C₄H₆O₃][CuCl₂]ₐ is also likely to occur, or be enhanced during exposure of the catalyst to reaction conditions. The loss in catalyst activity is accompanied by a decrease in the Cl content of the catalyst, observed by SEM, Cl-XANES, and the presence of C₂H₅Cl in the reaction products. Similar attributions of activity loss have been reported in the literature [11], and it has been noted that catalyst activity can be restored by treatment of the catalyst with a Cl-containing compound, such as HCl. Another loss mechanism that has been proposed is the conversion of CuCl to paratacamite, Cu₂Cl(OH)₃. Evidence for the formation of paratacamite was observed in the XRD patterns of spent catalyst, and it can be hypothesized that this compound is formed by the reaction 2CuCl + 0.5O₂ + H₂O + C₂H₅OH → Cu₂Cl(OH)₃ + C₂H₅Cl, where CuCl may be formed by abstraction of chlorine from [CuCl₂]⁻ by a cationic species such as H⁺.

5. Conclusion

The present investigation has shown that carbon-supported catalysts prepared from CuCl₂ and PdCl₂ are active for the synthesis of DEC by oxidative carbonylation, but undergo
significant changes in both activity and selectivity with time. The DEC activity and selectivity of a freshly prepared catalyst at first increase with time, then reach a maximum, and finally steadily decrease. The structure of the catalyst is complex and changes with pretreatment and exposure to reaction conditions. While copper is introduced as Cu(II) in the form of CuCl₂, it is almost completely reduced to Cu(I) in the form of highly dispersed Cu₂Cl(OH)₃. Deactivation is also accompanied by the appearance of paratacamite that is believed to form via the overall reaction 2 CuCl + 0.5 O₂ + H₂O → Cu₂Cl(OH)₃ + C₂H₅Cl. The addition of NaOH to the catalyst enhances its DEC activity.

The addition of KCl to the catalyst involves the formation of [PdCl₂]⁻ anions, during catalyst preparation. Palladium, on the other hand, which is introduced as PdCl₂, retains its oxidation state and is present in the form of large PdCl₂ particles. It is further observed that, alone, neither PdCl₂ nor [CuCl₂]⁻ species are active for DEC synthesis and that DEC synthesis activity is observed only when both species are present together. It is hypothesized that the active form of the catalyst involves the formation of [PdCl₂₋ₓ][CuCl₂ₓ] species on the surface of the PdCl₂ particles. The loss of DEC activity is accompanied by a loss in Cl content of the catalyst and the appearance of small amounts of C₂H₅Cl. Deactivation is also accompanied by the appearance of paratacamite that is believed to form via the overall reaction 2 CuCl + 0.5 O₂ + H₂O → Cu₂Cl(OH)₃ + C₂H₅Cl. The addition of KCl to the catalyst enhances its DEC activity slightly, but NaOH addition has little effect on the DEC activity.

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