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Investigation of the interaction between Cu(acac)$_2$ and NH$_4$Y in the preparation of chlorine-free CuY catalysts for oxidative carbonylation of methanol to a fuel additive

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The high temperature anhydrous interaction between copper (II) acetylacetone Cu(acac)$_2$, and NH$_4$Y was investigated to prepare a chlorine-free CuY catalyst for the oxidative carbonylation of methanol to dimethyl carbonate. When a physical mixture of Cu(acac)$_2$, and NH$_4$Y is heated from ambient temperature to 230 °C, Cu(acac)$_2$ firstly sublimes and then is adsorbed immediately on the surface of the Y zeolite. Simultaneously the ion exchange between Cu(acac)$_2$, and NH$_4$Y occurs at about 174 °C. During the activation process from 230 to 500 °C, the exchanged Cu$^{+2}$ is reduced to the Cu$^+$ active center, and the adsorbed and unreacted Cu(acac)$_2$, on the NH$_4$Y surface decomposes to nano CuO. For NaY zeolite, no solid state ion-exchange occurs between Cu(acac)$_2$, and NaY during the heat treatment and only CuO exists on the Cu/NaY catalyst surface. While for HY zeolite, the ion-exchanged Cu$^+$ is less in the supercages. The Cu/NaY catalyst has no catalytic activity and the Cu/HY catalyst exhibits lower activity than the Cu/NH$_4$Y catalyst. It is strongly proved that during heat treatment, the solid state ion-exchanged between Cu(acac)$_2$, and NH$_4$Y occurs and makes more Cu$^+$ locate in the supercages accessible to reactants.

Introduction

In the last decades, a nontoxic and easily biodegraded dimethyl carbonate (DMC), has been found huge potential applications. Compared with the conventional octane enhancing additive of methyl tert-butyl ether (MTBE), DMC is more suitable component of reformulated fuels owing to its good blending properties, high oxygen content and significant pollutants reduction in the exhaust gas. DMC is also more valuable as a green organic intermediate to substitute the toxic phosgene dimethyl sulfate. Of course, many innovation strategies to synthesize DMC have been developed. Among them, the oxidative carbonylation of methanol was considered as an environmentally friendly synthesis of DMC and has been widely investigated. As early as 1980s, the Enichem Company (Italy) had demonstrated the oxidative carbonylation of methanol to DMC by cuprous chloride CuCl$_2$ catalyst. But during the catalytic process, the catalyst suffers from losing of chlorine to form HCl, which results in the catalytic deactivation and the equipment corrosion seriously. Then, the supported Cu-based catalysts were considered to reduce the influence of chlorine and have been explored widely.

King$^{11,12}$ reported that when heating a physical mixture of CuCl and HY zeolite at high temperature, the solid state ion exchange (SSIE) of Cu$^+$ of CuCl with H$^+$ of HY was happened, and the formed CuY catalyst catalyzed the oxidative carbonylation of methanol to DMC with more than 5% conversion of methanol and 80% DMC selectivity. It means that without chlorine, Cu$^+$ also has the catalytic activity. After that, many solid acids, such as MCM-41$^{13,14}$, Hβ zeolite$^{15}$, HZSM-5 zeolite$^{16}$, SiO$_2$-Al$_2$O$_3$$^{17}$, SiO$_2$-ZrO$_2$$^{18}$, and SiO$_2$-TiO$_2$$^{19}$ were employed to prepare Cu$^+$ supported catalysts by SSIE. Among them, HY is of great interest to many researchers due to the special supercages microstructure and large surface area. However, a little of chlorine is remained inevitably and then forms HCl to corrode the equipment.

To avoid the negative effects of chlorine, intensive efforts have been made to prepare a chlorine-free CuY catalyst by non-chloric copper salts, such as Cu$_2$O$^{12}$, Cu(NO$_3$)$_2$$^{26-31}$ and Cu(CH$_3$COO)$_2$.$^{32}$ The CuY catalyst prepared by heating the powder mixture of Cu$_2$O and HY zeolites at 650°C for 7 h with helium purge was active to produce DMC, but its activity was very low and quickly decreased. In our previous work$^{28-30}$, it was showed that when the Cu$^{+2}$Y zeolite material prepared by liquid solution ion exchange (LSIE) of NaY zeolite with Cu(NO$_3$)$_2$ cuprammonia was heated at high temperature, Cu$^{+2}$ in the supercages was auto-reduced to active Cu$^+$ and the activated materials showed superior activity. Furthermore, during high temperature activation of the Cu(NO$_3$)$_2$-Y zeolite prepared by incipient wetness impregnation (IWIM), HY is easier to ion-exchange with Cu$^{+2}$ than NaY and the former exhibited a better catalytic activity. Richter et al.$^{32}$ also found that in the heat treatment above 700 °C of the CuY zeolite prepared by...
In this study, the interaction process of heating the mixture of catalytic activities highly depend on the heating temperature. Recently, an organometallic compound Cu(acac)₂ has been demonstrated the unique charm in the field of copper material preparation due to its properties of sublimation and demonstrated the unique charm in the field of copper material preparation. It is reported that, by chemical vapor deposition of Cu(acac)₂ precursor, Cu₂O and CuO generated at the temperature of 195 °C to 430 °C respectively, but at 285 °C, both Cu₂O and CuO did coexist. Nasibulin et al. found when the oxygen concentration of the oxygen/nitrogen carrier gas was 0.5%, by Cu(acac)₂ vapor decomposition, nanoparticles Cu₂O and CuO were prepared at 432 °C and 705 °C respectively; when the oxygen concentration is above 10.0%, above 596 °C only CuO nanoparticles generated; When the oxygen concentration is below 0.003%, only Cu nanoparticles generated. What’s more, oxygen plays very important role in removing impurities. Therefore, similarly to the process of SSIE between CuCl and NH₄Y zeolite, it is also expected that when a physical mixture of NH₄Y zeolite and Cu(acac)₂ is heated in a muffle furnace, Cu(acac)₂ would sublimate and be adsorbed on the NH₄Y surface several times to be dispersed uniformly, then NH₄Y zeolite decompose to HY zeolite and Cu(acac)₂ decompose to Cu₂O, and simultaneously SSIE between HY zeolite and CuO was happened to form the CuY catalyst. The decomposed gases such as CO, NH₃, N₂, CO₂ form the reduce atmosphere in the heating process, which is favorable to Cu⁺ keeping. To the best of our knowledge, this novel process to prepare a chlorine-free Cu⁺ catalyst has not been reported previously. In our recent work, the chlorine-free CuY catalysts were successfully prepared by high temperature anhydrous interaction (HAI) between Cu(acac)₂ and NH₄Y and used in the oxidation carbonylation of methanol. It was found that the catalytic activities highly depend on the heating temperature. In this study, the interaction process of heating the mixture of Cu(acac)₂ and NH₄Y under anhydrous condition and the formation of Cu catalytic active centres were investigated in more detail by TG/DSC, XRD, H₂-TPR, XPS, TEM and etc.

Experimental Section

Materials

NaY zeolite with a Si/Al molar ratio of 2.7 was purchased from Nankai Catalyst Factory. Reagents like NH₄NO₃ (AR, Tianjin Chemical Reagent NO. 3 Factory), Cu(acac)₂ (AR, Sinopharm Chemical Reagent Co. Ltd), CH₃OH (AR, Tianjin Kemiou Chemical Reagent Company) as well as carbon monoxide (99.99%, Beijing Haipu Beifen Gas Industry Co., LTD), oxygen, nitrogen and hydrogen (99.99%, TISCO) were used.

Catalyst preparation

Firstly, 30.0 g NaY zeolite was added to 300 mL 0.5 mol·L⁻¹ NH₄NO₃ aqueous solution and stirred to ion exchange for 4 h at 30 °C, and dried at 100 °C. Then the procedures were repeated once and the final solid material was NH₄Y zeolite. Then, part of the prepared NH₄Y zeolite was packed in a crucible and then put into a muffle furnace in order to calcinate NH₄Y zeolite to HY zeolite. The furnace temperature was firstly raised from the ambient temperature to 200 °C at 3 °C min⁻¹, then raised from 200 °C to 500 °C at 1 °C min⁻¹ and held constantly at 500 °C for 6 h. Finally, the cooled solid material was HY zeolite.

The Cu/NHY catalyst was prepared by heating treatment of a mixture of Cu(acac)₂ and NH₄Y according to following two stages. In the first stage, 2.045 g Cu(acac)₂ and 5.000 g NH₄Y was mixed and ground well with a mortar and pestle to form an intimate gray-blue mixture. Then the mixture was heated in a muffle furnace from the ambient temperature to 180 °C at 3 °C min⁻¹, and then held at 180 °C for 4 h to make Cu(acac)₂ dispersed very well on the surface of NH₄Y zeolite to form the precursor. In the second stage, the precursor material was activated to form Cu/NHY catalyst by heating at the temperature of 300, 400, or 500 °C for 4 h from the ambient temperature at heating rate of 3 °C min⁻¹. The activated Cu/NHY catalysts were denoted as Cu/NHY-300, Cu/NHY-400 and Cu/NHY-500 respectively.

According to the above procedure, NaY and HY were also used to substitute of NH₄Y to prepare Cu/NaY-400 and Cu/HY-400 catalysts respectively. The activation temperature was 400 °C. All catalysts were stored in a dryer, and pressed to 40-60 mesh particles before catalytic tests.

Characterization techniques

Thermogravimetric analysis (TG/DSC) were performed on a SETSYS Evo 16/18 thermogravimetric analyzer (Setaram) under an air flow rate of 100 ml min⁻¹, employing a heating rate of 10 °C min⁻¹ up to a final temperature of 800 °C. The evolved gas analysis of the decomposition reaction was monitored with an omnispec quadrupole Pierre mass spectrometer (MS) linked to the thermobalance. The MS operated on 40 eV of ionization energy, using a Channeltron detector (1000 V). Temperature-programmed reduction (H₂-TPR) was performed on a Micromeritics Autochem II 2920 chemical adsorption instrument. 20 mg sample was loaded in a U-shaped quartz tube, and then heated at 10 °C min⁻¹ to 300 °C with 30 ml min⁻¹ argon for 30 min to remove adsorbed moisture. After cooling to room temperature, the gas was switched to 10 vol. % H₂ in argon flow, and the sample was heated to 1000 °C. The hydrogen consumption was monitored by a thermal conductivity.

X-ray diffraction (XRD) data were collected by using CuKa radiation (λ=0.154056 nm) on a Rigaku D/max 2500 diffractometer at 40 kV target voltage and 100 mA tube current in the 20 range from 5 ° to 80 ° at a scanning rate of 8°/min.

Transmission electron microscope (TEM) photographs were carried out using a JEOL JEM-2100F electron microscope operating at 200 kV. Exposition times were confined to about 2 s due to the beam sensitivity of the samples. Sample preparation was carried out by dispersing 5 mg grounded powder in 5 mL ethanol by ultrasonic, and then followed by dropping the suspension on a rounded carbon-coated Cu-Grid mesh and drying at room temperature.

X-ray photoelectron spectroscopy (XPS) data were collected on an AXIS ULTRA DLD electron spectrometer by using a 150 W monochromatic Al Kα radiation source operating at 1486.6 eV.
The binding energy and the Auger kinetic energy scales were referenced to the C1s line at 284.8 eV from adventitious carbon.

Atomic absorption spectroscopy (AAS) was used to determine the Cu loading of the prepared catalyst by using a VARIAN AA240FS equipment. The testing solution was prepared by following steps: 0.2 g fresh catalyst was calcined with 2.0 g potassium hydroxide at 500 °C for 6 h, and digested in a hydrochloric acid solution, and diluting to a 250 mL volumetric flask with deionized water. Then transfer 5.0 mL of this solution to a 100 mL volumetric flask, dilute with deionized water to volume, and mix.

**Catalytic tests**

Catalytic measurements were performed in a continuous fixed bed micro reactor (Φ6 mm × 450 mm) under atmospheric pressure with on-line Agilent 6890 gas chromatograph (GC). 0.45 g catalyst (about 1.0 mL) was packed in the tube reactor and the reactor was positioned in the furnace. 0.02 mL·min⁻¹ methanol was introduced by a constant-flux pump (2PB-05) and vaporized in the pre-heater. In the meantime, 28.0 mL·min⁻¹ carbon monoxide and 2.8 mL·min⁻¹ oxygen was introduced into the pre-heater and mixed well with vaporized methanol, and then the mixed reactants were fed into the catalyst bed to catalyze oxidative carbonylation of methanol. The temperature and time of the catalytic reaction was 140 °C and 10 h respectively.

The thermal gas products were analyzed by an on-line GC with three valves and four columns every 20 minutes. The products flowed through the HP-PLOT/Q capillary column (30m×0.53μm×40μm), the organic products were hold back. And then the excurrent inorganic products flowed through the Propack-Q packed column: CO₂ firstly flowed out and entered into a thermal conductivity detector (TCD) and was detected; secondly, CO and O₂ were separated by the HP-PLOT Molesieve/5A capillary column (30m×0.53μm×25μm) and detected by TCD. The products flowed through the HP-INNOWax (30m×0.53μm×1μm) capillary column and entered into a flame ionization detector (FID), thus MeOH, methyl formate (MF), dimethoxymethane (DMM), dimethyl ether (DME) and DMC were detected.

**Results and discussion**

**Thermal Analysis**

It is well known that when NH₄Y zeolite is heated at 400 °C, NH₃ is dissociated, and NH₄Y zeolite converts to HY zeolite. Then the dehydroxylation of silicol on the surface of the HY zeolite takes place at the heating temperature above 450 °C. The TG/DTG-DSC curves of the as-prepared NH₄Y zeolite are illustrated in Fig. 1(a). It is clearly showed that when the temperature is below 200 °C, the desorption of zeolite-adsorbed water causes an obvious weight loss and endothermic phenomenon; between 200-440 °C, the dissociation of NH₃ from NH₄Y zeolite causes a slight weight loss with endothermic phenomenon; above 440 °C the dehydroxylation of silicol on the surface of the HY zeolite causes another slight weight loss with endothermic phenomenon.

![Fig. 1 TG/DTG-DSC curves of samples](image_url)

*The curve 2 is the TG of an addition of the TG of Cu(acac)₂ and NH₄Y*
For Cu(acac)$_2$ sample, only one obvious weight loss peak on the DTG at around 250 °C and only one strong exothermic peak on the DSC at 247 °C is observed in Fig. 1(b). It is strongly indicated that Cu(acac)$_2$ decomposed at 150-350 °C, because there is no further weight loss and no heat changes above 350 °C. The final material of Cu(acac)$_2$ decomposition should be CuO, and the theoretical weight loss is 69.4%. But the actual sublimation of Cu(acac)$_2$ exothermic peak at 247 °C. It must be caused by the complicated interaction between Cu(acac)$_2$ and the mixture of Cu(acac)$_2$ and NH$_4$Y. Therefore, it is concluded that Cu(acac)$_2$ firstly sublimes and then decomposes to CuO at the temperature from 150 °C to 350 °C.

But for a well physical mixture of NH$_4$Y with 28.6 wt.% Cu(acac)$_2$, the thermal behavior is so complicated that it is not the simple addition of two raw materials, and TG of the mixture and the simple addition is labeled as curve 1 and curve 2 respectively, as showed Fig. 1(c). It is clear that the weight loss undergoes four steps according to the TG/DTG curves of the mixture. In the first step, the temperature is below 120 °C as zone I, the weight loss of 8.8% with the peak at 75 °C must be contributed to loss of the adsorbed water in the NH$_4$Y zeolite. This water desorption peak temperature on the curve 1 is obviously lower than that of pure NH$_4$Y and on the curve 2. It is indicated that some of Cu(acac)$_2$ would have adsorbed on the surface of zeolite and facilitate the release of zeolite-adsorbed water. In the second step, the temperature is between 120 °C and 230 °C as zone II, the weight loss of 10.1% with the peak at 182 °C on the curve 1 is lower than 13.1% on the curve 2, it is perhaps because Cu(acac)$_2$ begins to sublimated and was partly absorbed on NH$_4$Y. In the third step, the temperature is between 230 °C and 500 °C as zone III, the rate of weight loss on the curve 1 is slower and lower than that on the curve 2, so the weight loss of 13.7% with a broad peak at 356 °C is assigned to the mild decomposition of Cu(acac)$_2$. In the fourth step, the temperature is above 500 °C as zone IV, nearly no weight loss is observed. In the total range of temperature, the actual weight loss is 32.6% on the curve 1 and much less than 45.4% on the curve 2. Moreover, endothermic and exothermic peaks on the DSC curve of the mixture are overlapping and the largest exothermic peak also shifts from 247 °C to 349 °C. It is showed that there exists a complicated interaction between Cu(acac)$_2$ and NH$_4$Y during heat treatment.

To obtain more detail information during heat treatment of the mixture of Cu(acac)$_2$ and NH$_4$Y, TG-MS measurement was performed and the results are shown in Fig. 2. The signals at m/z = 17, 18 and 44 are assigned to the main volatile products of NH$_3$, H$_2$O and CO$_2$ respectively, and the signals at m/z = 58, 60 and 100 are ascribed to the trace organic products of acetone, propyl alcohol and acetylacetone respectively. During heat treatment of the mixture, water is released at 76 °C below the water desorption peak temperature (121 °C) of pure NH$_4$Y, which has been demonstrated from TG/DTG. With the increase of heat treatment temperature, the release of NH$_3$ proceeds in two steps from the curve of m/z = 17. In the first step, NH$_3$ is released at 174 °C, simultaneously, a trace amount of organic products are also observed. Additionally, only above 200 °C, NH$_4$Y zeolite decomposes and releases NH$_3$. So it was proved that the ion exchange between Cu$^{2+}$ of Cu(acac)$_2$ and NH$_4$+ of NH$_4$Y does occur at 174 °C. In the second step, at the temperature of 417 °C, the release of NH$_3$ comes from the residual NH$_4$+ decomposition of NH$_4$Y or desorption of adsorbed NH$_3$ from ion exchange. When the heat treatment temperature reaches about 360 °C, the organic products of acetone, propyl alcohol and acetylacetone were observed in addition to CO$_2$ and H$_2$O.

According to the above analysis, during heat treatment of the mixture, (a) in the temperature zone I, the zeolite-adsorbed water of NH$_4$Y is released; (b) in the temperature zone II, Cu(acac)$_2$ sublimates and Cu(acac)$_2$ vapor is mostly adsorbed on Y zeolite, in the meantime, ion exchange between Cu(acac)$_2$ and NH$_4$Y occurs; (c) in the temperature zone III, the

![Fig. 2 MS spectra of gaseous products of the physical mixture of NH$_4$Y and Cu(acac)$_2$](Image)
decomposition of adsorbed Cu(acac)$_2$, residual NH$_4^+$ decomposition of NH$_4$Y.

**Structural properties of CuY catalysts**
The XRD patterns of samples are compared in Fig. 3. For the mixture, diffraction peaks of Cu(acac)$_2$ and NH$_4$Y are simultaneously observed. However, the diffraction peaks of the precursor and the Cu/NH$_4$Y catalysts are similar to those of Y zeolite and no diffraction peaks of the corresponding Cu species are observed. It proves Cu species are well dispersed on the surface of Y zeolite during the preparation of the CuY catalyst. In addition, these results also indicate that the preparation of the CuY catalyst does not have significant effects on the framework structure of zeolite, only the diffraction peak intensity is slightly weakened.

Owing to the ion-exchanged ions substituting Na$^+$ of NaY and undergoing rearrangement, the alteration of the relative intensities of (220) and (311) crystal planes of Y zeolite is observed. As can be seen in Fig. 3, compared with NH$_4$Y, I$_{111}$ of the precursor decreases obviously, I$_{220}$ and I$_{311}$ also decrease slightly, but I$_{220}$ decreases more greatly than I$_{311}$. It illustrates that Cu$^{2+}$ substitutes NH$_4^+$ of NH$_4$Y zeolite by the ion exchange between Cu$^{2+}$ of Cu(acac)$_2$ and NH$_4^+$ of NH$_4$Y. I$_{111}$, I$_{220}$ and I$_{311}$ also decrease for Cu/NH$_4$Y catalysts, yet compared with the precursor, I$_{111}$ and I$_{220}$ increase more slightly. The difference indicates that, adsorbed Cu(acac)$_2$ decomposes to copper oxide and copper ions migrate from supercages to small cages during activation, so the particles of copper species in Cu/NH$_4$Y catalysts become more smaller and uniformly, resulting in less

**Fig. 3** XRD patterns of Cu(acac)$_2$ (a), NH$_4$Y (b), mixture (c), the precursor (d), Cu/NH$_4$Y-300 (e), Cu/NH$_4$Y-400 (f) and Cu/NH$_4$Y-500 (g).

Impact on the zeolite structures.

Fig. 4 presents the TEM images of the Cu/NH$_4$Y-400 catalyst. Richter et al. reported the CuY samples suffered major modifications during imaging of TEM. In order to suppress the influence of the electron beam, it imaged immediately after the beam was focused. From Fig. 4A, the faujasite structure of zeolite Y is unbroken, and nanosized copper particles disperse well on the surface of zeolite Y, the particle sizes are in a range of 2-6 nm. From Fig. 4B, light grey Cu species with 1-2 nm are observed in the channel of zeolite Y. In the meantime, there also exists some larger black Cu species caused by incident electron beam.

**Analysis of copper valence and state**
To determine the distribution of the reducible copper species on CuY catalyst, the H$_2$-TPR was carried out and the profiles are showed in Fig. 5. The H$_2$-TPR profile of Cu/NaY-400 catalyst only appears a sharp reduction peak at around 224 °C. However, the profiles of Cu/NH$_4$Y and Cu/HY-400 catalysts exhibit more than one reduction peaks from ambient temperature to 1000 °C. In order to investigate the content and location of the reducible copper species, the H$_2$-TPR profiles are studied by means of peak-differenating analysis (dotted line in Fig. 5).

As for the reduction of the reducible copper species on the CuY, many researchers have discussed and the following conclusions are accepted: (i) The reduction of exchanged Cu$^{2+}$ to Cu$^+$ occurs from 200 °C to 300 °C, and the reduction temperature depends highly on the location and in the order: supercages < sodalite cage < hexagonal prism. (ii)
The reduction of dispersed CuO to Cu\(^0\) occurs around 250 °C.

(iii) The exchanged Cu\(^+\) is reduced at distinctly higher temperature. So for H\(_2\)-TPR of the as-prepared CuY catalyst in Fig.5, the peaks at 192 °C, 284 °C and 347 °C are attributed to reduction of Cu\(^{2+}\) to Cu\(^+\) located in supercages, sodalite cage and hexagonal prism of Y zeolite, respectively. The peaks at 224 °C of the Cu/NaY-400 catalyst and at 245 °C of Cu/NH\(_4\)Y and Cu/HY-400 catalysts belong to the reduction of CuO to Cu\(^0\) in one step. The reduction peaks above 700 °C are attributed to the reduction of Cu\(^+\) to Cu\(^0\). Thus it can be seen that there exist only CuO on the Cu/NaY-400, ion-exchanged Cu\(^{2+}\), Cu\(^+\) besides CuO on the Cu/NH\(_4\)Y and Cu/HY-400. The hydrogen consumption and the relative contents of reducible Cu species are calculated by the area of hydrogen consumption peak and listed in Table 1.

From Fig.5, for the Cu/NH\(_4\)Y catalysts, until the activation temperature reaches to 280 °C, the hydrogen consumption peaks of CuO and Cu\(^+\) species appear on the H\(_2\)-TPR profile of Cu/NH\(_4\)Y-280. When the activation temperature is lower than 280 °C, the hydrogen consumption peaks of CuO and Cu\(^+\) species are not observed on the corresponding H\(_2\)-TPR profile of Cu/NH\(_4\)Y, and there are some undetermined hydrogen consumption peaks from 300 °C to 700 °C. This suggests that the initial temperature of exchanged Cu\(^{2+}\) reduced to the Cu\(^+\) active center is 280 °C. When activation temperature is 400 °C, the CuY catalyst has the highest Cu\(^+\) content of 4.3 wt.% (Table 1). Compare Cu/NH\(_4\)Y-400 with Cu/HY-400, it is found that the content of CuO and Cu\(^{2+}\) of Cu/NH\(_4\)Y-400 is lower than that of Cu/HY-400, but the content of Cu\(^+\) in the supercages of Cu/NH\(_4\)Y-400 is more than doubled that of Cu/HY-400.

**Table 1** Quantitative analysis of the H\(_2\)-TPR profiles of the catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(H_2) consumption /cm(^3) g(^{-1})</th>
<th>(Cu^{2+}\rightarrow Cu^+)</th>
<th>(Cu^O\rightarrow Cu^0)</th>
<th>Cu mass %</th>
<th>(Cu^+)/(Cu^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/NaY-400</td>
<td>28.4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>8.1</td>
</tr>
<tr>
<td>Cu/NH(_4)Y-250</td>
<td>19.8</td>
<td>8.9</td>
<td>1.1</td>
<td>0</td>
<td>3.2</td>
</tr>
<tr>
<td>Cu/NH(_4)Y-280</td>
<td>25.8</td>
<td>9.1</td>
<td>1.3</td>
<td>0</td>
<td>5.9</td>
</tr>
<tr>
<td>Cu/NH(_4)Y-300</td>
<td>26.3</td>
<td>8.7</td>
<td>0.6</td>
<td>0</td>
<td>5.3</td>
</tr>
<tr>
<td>Cu/NH(_4)Y-400</td>
<td>25.5</td>
<td>7.4</td>
<td>0.4</td>
<td>0</td>
<td>5.2</td>
</tr>
<tr>
<td>Cu/NH(_4)Y-500</td>
<td>27.3</td>
<td>6.3</td>
<td>0.7</td>
<td>0</td>
<td>4.0</td>
</tr>
<tr>
<td>Cu/HY-400</td>
<td>26.7</td>
<td>3.2</td>
<td>3.1</td>
<td>2.1</td>
<td>4.8</td>
</tr>
</tbody>
</table>
It’s worth mentioning that many works have shown the exchanged copper ions on the CuY were populated preferentially in small cages.46,47 However, Cu(acac)$_2$ cannot enter into small cages because of the steric hindrance, so up to 95% Cu$^{2+}$ ions on the Cu/NH$_4$Y-400 catalyst locate in the supercage accessible to reactants. This is an advantage of preparing the CuY catalyst with high catalytic activity for oxidation carbonylation of methanol to DMC.

XPS as a surface analysis technique, however, due to the large voids of zeolite Y, the sampling depth is higher in zeolite and the effective depth is about 5-10 unit cells of zeolite below the surface.46 As seen in Fig.6, The Cu LMM Auger spectra strongly supports the presence of Cu$^+$ with a kinetic energy of 912.8 eV and Cu$^{2+}$ with a kinetic energy of 915.9 eV, and there is no peak of Cu0 in the range of 918 to 920 eV. The characteristics of divalent copper can be further confirmed by the Cu 2p$_{3/2}$ binding energy within the range of 933.0 – 936.0 eV and the shake-up satellite peak. Monovalent copper can be assigned to the binding energy of the XPS peaks ranging from 932.0 to 933.0 eV without any shake-up satellite peaks.49,50

As indicated above, it is deduced that the main reactions are as follows: During heat treatment, Cu(acac)$_2$ sublimates and is adsorbed on the NH$_4$Y surface firstly, and in the meantime the ion exchange between Cu$^{2+}$ of Cu(acac)$_2$ and NH$_4^+$ of NH$_4$Y to form Cu$^{2+}$Y takes place.

\[
\text{Cu(acac)}_2 + \text{NH}_4\text{Y} \xrightarrow{156-350^\circ C} \text{Cu(acac)}_2/\text{NH}_4\text{Y}. \tag{1}
\]

\[
\text{Cu(acac)}_2/\text{NH}_4\text{Y} \xrightarrow{120-230^\circ C} \text{Cu}^{2+}Y \tag{2}
\]

At the stage of activation, the adsorbed unreacted Cu(acac)$_2$ starts to decompose, at the same time, NH$_4$Y decomposes to form HY and releases NH$_3$. Meanwhile ion exchanged Cu$^{2+}$ is auto-reduced to form the active centre Cu$^+$ for oxidative carbonylation of methanol to DMC.

\[
\text{Cu(acac)}_2/\text{NH}_4\text{Y} \xrightarrow{236-500^\circ C} \text{Cu}^0/\text{NH}_4\text{Y} \tag{3}
\]

\[
\text{NH}_4\text{Y} \xrightarrow{200-400^\circ C} \text{HY} + \text{NH}_3 \tag{4}
\]

\[
\text{Cu}^2+\text{Y} \xrightarrow{300-500^\circ C} \text{Cu}^+\text{Y} \tag{5}
\]

In addition, Lu et al.51 reported CuY is the most active catalyst for NH$_3$ oxidation from 200 °C to 300 °C. And organic ligands and their products react with oxygen in the air and generate CO$_2$ and H$_2$O. So the following reactions are possible during the preparation of the CuY catalyst by HAI.

\[
4\text{NH}_3(g) + 30_2(g) \xrightarrow{200-300^\circ C} 2\text{N}_2(g) + 6\text{H}_2\text{O}(g) \tag{6}
\]

\[
\text{Hacac}/\text{NH}_4\text{Y} + 0_2(g) \xrightarrow{236-300^\circ C} \text{Y} + \text{CO}_2(g) + 6\text{H}_2\text{O}(g) \tag{7}
\]

**Catalytic properties of CuY catalysts**

Catalytic properties of the as-prepared CuY catalysts in the direct gas phase oxidative carbonylation of methanol to DMC are listed in Table 2. For comparison, some CuY catalysts in the literatures are also listed in Table 2 as reference. The as-prepared Cu/NaY-400 catalyst has no catalytic activity, and the catalytic activity of the Cu/NH$_4$Y-400 catalyst with 153.0 mg·g$^{-1}$·h$^{-1}$ STY$_{DMC}$ is better than that of the Cu/HY-400 catalyst with 65.4 mg·g$^{-1}$·h$^{-1}$ STY$_{DMC}$. The above analytic results have shown that NH$_4^+$ of NH$_4$Y can introduce Cu$^{2+}$ into extraframework cation location of zeolite Y by ion exchange between Cu$^{2+}$ of Cu(acac)$_2$ and NH$_4^+$ of NH$_4$Y, and the decomposed NH$_3$ from NH$_4$Y facilitates the reduction of Cu$^{2+}$ to Cu$^+$ to form more active centres. Compared with the Cu/HY catalyst, more copper ions on the Cu/NH$_4$Y catalyst locate in the supercages accessible to reactants. However, Na$^+$ of NaY can’t exchange with Cu$^{2+}$ of Cu(acac)$_2$ under the same experimental condition, and there is no Cu$^+$ active center on the Cu/NaY-400 catalyst, only CuO species.

As for Cu/NH$_4$Y catalysts with different activation temperature (300 °C, 400 °C, 500 °C), when the activation temperature is 300 °C, the conversion of methanol ($X_{CH_3OH}$) and the space-time yield of DMC (STY$_{DMC}$) is 7.5% and 137.2 mg·g$^{-1}$·h$^{-1}$ for Cu/NH$_4$Y-300 respectively. However, the Cu/NH$_4$Y-400 catalyst activated at 400 °C exhibits an excellent catalytic activity with 8.2% $X_{CH_3OH}$ and 153.0 mg·g$^{-1}$·h$^{-1}$ STY$_{DMC}$. When the activation temperature is 500 °C, $X_{CH_3OH}$ and STY$_{DMC}$ have decreased to...
Table 2 Catalytic activity of the catalysts in oxidative carbonylation of methanol\(^a\)

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Preparation</th>
<th>Support/Activation temperature (°C)</th>
<th>Cu (wt.%)</th>
<th>STY(_{\text{DMC}}) (mg·g(^{-1})·h(^{-1}))</th>
<th>(X_{\text{CH}_3\text{OH}}) (%)</th>
<th>STY(_{\text{DMC}}) (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/NaY-400</td>
<td>HAI</td>
<td>NaY/400</td>
<td>8.2(^d)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Cu/NH(_4)Y-300</td>
<td>HAI</td>
<td>NH(_4)Y/300</td>
<td>9.5(^d)</td>
<td>137.2</td>
<td>7.5</td>
<td>61.2</td>
<td></td>
</tr>
<tr>
<td>Cu/NH(_4)Y-400</td>
<td>HAI</td>
<td>NH(_4)Y/400</td>
<td>9.5(^d)</td>
<td>153.0</td>
<td>8.2</td>
<td>61.9</td>
<td></td>
</tr>
<tr>
<td>Cu/NH(_4)Y-500</td>
<td>HAI</td>
<td>NH(_4)Y/500</td>
<td>9.5(^d)</td>
<td>113.3</td>
<td>6.2</td>
<td>60.9</td>
<td></td>
</tr>
<tr>
<td>Cu/HY-400</td>
<td>HAI</td>
<td>HY/400</td>
<td>8.5(^d)</td>
<td>65.4</td>
<td>3.5</td>
<td>60.7</td>
<td></td>
</tr>
<tr>
<td>Cu/NaY(L)-600</td>
<td>LSIE</td>
<td>NaY/600</td>
<td>6.3(^d)</td>
<td>131.4</td>
<td>6.5</td>
<td>68.5</td>
<td>28</td>
</tr>
<tr>
<td>Cu/HY(I)-600</td>
<td>IWIM</td>
<td>HY/600</td>
<td>10.0(^d)</td>
<td>95.6</td>
<td>5.1</td>
<td>62.0</td>
<td>28</td>
</tr>
<tr>
<td>Cu/NaY(L)-600</td>
<td>IWIM</td>
<td>NaY/600</td>
<td>10.0(^d)</td>
<td>16.3</td>
<td>1.1</td>
<td>50.7</td>
<td>28</td>
</tr>
<tr>
<td>Cu/HY(S)-650</td>
<td>SSIE</td>
<td>HY/650</td>
<td>12.2(^d)</td>
<td>97.3</td>
<td>4.4</td>
<td>74.6</td>
<td>24</td>
</tr>
<tr>
<td>Cu/NH(_4)Y(D)-400(^d)</td>
<td>DP</td>
<td>NH(_4)Y/400</td>
<td>10.0(^d)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>32</td>
</tr>
<tr>
<td>Cu/NH(_4)Y(D)-750(^d)</td>
<td>DP</td>
<td>NH(_4)Y/750</td>
<td>10.0(^d)</td>
<td>84.4</td>
<td>8.1</td>
<td>53.5</td>
<td>32</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: \(V_{\text{CH}_3\text{OH}}:V_{\text{CO}:V_{\text{O}_2}} = 4:10:1\), GHSV = 2520 h\(^{-1}\), \(T = 140\) °C, \(P = 0.1\) MPa.

\(^b\) Reaction conditions: \(V_{\text{CH}_3\text{OH}}:V_{\text{CO}:V_{\text{O}_2}} = 6:8:1\), 1% Ar (He balance), GHSV = 3000 h\(^{-1}\), \(T = 140\) °C, \(P = 0.1\) MPa. The Cu/NH\(_4\)Y(D)-400 catalyst prepared by DP has a NH\(_4\)Y support and is activated at 400 °C, the naming rules are used to name other catalyst from literature.

\(^c\) The actual Cu loading is determined by atomic absorption spectrometry.

\(^d\) The theoretical Cu loading is calculated by copper addition.

6.2% and 113.3 mg·g\(^{-1}\)·h\(^{-1}\) for Cu/NH\(_4\)Y-500 respectively. The H\(_2\)-TPR and XPS characterization have shown that the Cu/NH\(_4\)Y-400 catalyst has the highest content of Cu\(^+\) active center. In addition, it also is found that the catalytic activity of the Cu/NH\(_4\)Y-400 catalyst is better than those of the chloride-free CuY catalysts prepared by LSIE\(^{28}\), IWIM\(^{28}\) or DP\(^{27}\) and the Cu/HY(S)-650 catalyst prepared by SSIE\(^{24}\). For example, the STY\(_{\text{DMC}}\) of the Cu/NH\(_4\)Y-400 catalyst with 9.5 wt.% Cu loading reaches to 153.0 mg·g\(^{-1}\)·h\(^{-1}\), which is higher than those of the CuY catalysts with 10.0 wt.% Cu loading prepared by IWIM\(^{28}\), including the Cu/HY(I)-600 catalyst with 95.6 mg·g\(^{-1}\)·h\(^{-1}\) STY\(_{\text{DMC}}\) and the Cu/NaY(L)-600 catalyst with 16.3 mg·g\(^{-1}\)·h\(^{-1}\) STY\(_{\text{DMC}}\). And even the STY\(_{\text{DMC}}\) of the Cu/NH\(_4\)Y-400 catalyst is higher 57.2% than that of the Cu/HY(S)-650 catalyst with 12.2 wt.% Cu loading prepared by SSIE\(^{24}\). The Cu/NH\(_4\)Y(D)-400 catalyst has no catalytic activity, and the Cu/NH\(_4\)Y(D)-750 catalyst has 84.4 mg·g\(^{-1}\)·h\(^{-1}\) STY\(_{\text{DMC}}\) that is also lower 44.8% than that of the Cu/NH\(_4\)Y-400 catalyst. For the Cu/NaY(L)-600 catalyst with 131.4 mg·g\(^{-1}\)·h\(^{-1}\) STY\(_{\text{DMC}}\) prepared by LSIE\(^{28}\), the 6.3 wt.% Cu loading is the maximum permissible loading for LSIE once, and the STY\(_{\text{DMC}}\) is lower 14.4% than that of the Cu/NH\(_4\)Y-400 catalyst.

According to the previous studies\(^{23}\), the proposed mechanism for the oxidative carbonylation of methanol to dimethyl carbonate can be concluded as follows. Firstly, CH\(_2\)OH with oxygen adsorbs on Cu\(^+\) Lewis sites by formation of either mono- or di-methoxide species bound to Cu\(^+\) cations. Then, adsorption and insertion of carbon monoxide into the methoxide species leads to the formation of DMC directly or through the reaction of CO insertion to produce monomethyl carbonate (MMC) species.\(^{52-54}\) In our experiment, the content of Cu\(^+\) has attained the highest for the Cu/NH\(_4\)Y-400 catalyst. Besides, Engeldinger et al.\(^{27,31}\) also approve that the formation of DMC...
is initiated by reaction of molecularly adsorbed methanol on Cu⁺ cations. More significantly, they found that CuOx agglomerates in the supercages favors oxidation and oxocarbonylation reactions of methanol and enhances the formation of DMC. According to our studies, the Cu/NaY catalyst, only containing CuO species, has no catalytic activity. And when Cu loading is too high, excessive amounts of CuOx agglomerates cover the Cu⁺ active centers, resulting in decrease in catalytic activity of the CuY catalyst. Therefore, we suggest that the Cu⁺ ions on the CuY catalyst are the active centers for oxidation carbonylation of methanol to DMC and a modest amount of CuOx agglomerates contribute lattice oxygen to the formation of DMC to improve of catalytic performance.

Conclusions
During heat treatment of the physical mixture of Cu(acac)₂ and NH₄Y, from 120 °C to 230 °C, Cu(acac)₂ sublimes and Cu(acac)₃ vapor is mostly adsorbed and well dispersed on the surface of Y zeolite. In the meantime, ion exchange between Cu(acac)₃ and NH₄Y occurs in the supercages. Above 230 °C, the unreacted Cu(acac)₂ decomposes to form copper oxides, simultaneously NH₄Y decomposes and releases NH₃, which facilitates the reduction of Cu²⁺ to Cu⁺. Above 500 °C, no physical or chemical processes occur. For NaY zeolite, no solid state ion-exchange occurs between Cu(acac)₃ and NaY during heat treatment, and the as-prepared Cu/NaY catalyst has no catalytic activity. For HY zeolite, the ion-exchanged Cu⁺ is less in the supercages and the as-prepared Cu/HY catalyst exhibits lower activity than the Cu/NH₄Y catalyst. The distribution of Cu²⁺, Cu⁺ and CuO on the Cu/NH₄Y catalyst highly depends on the activation temperature. When the activation temperature is 400 °C, the content of Cu⁺ has attained the highest, the corresponding Cu/NH₄Y-400 catalyst also shows the best catalytic activity, and the conversion methanol, selectivity of DMC and the DMC space-time yields is 8.2%, 61.9% and 153.0 mg·g⁻¹·h⁻¹ respectively.

Acknowledgements
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References
The high temperature anhydrous interaction between copper (II) acetylacetonate Cu(acac)$_2$ and NH$_4$Y was investigated to prepare a chlorine-free CuY catalyst for the oxidative carbonylation of methanol to dimethyl carbonate. The Cu/NH$_4$Y-400 catalyst shows superior catalytic activity.