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Investigation of the interaction between Cu(acac)₂ and NH₄Y 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) acetylacetonate Cu(acac)₂ and NH₄Y 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 NH₄Y is heated from ambient temperature to 230 °C, Cu(acac)₂ firstly sublimates and then is adsorbed immediately on the surface of the Y zeolite. Simultaneously the ion exchange between Cu(acac)₂ and NH₄Y occurs at about 174 °C. During the activation process from 230 to 500 °C, the exchanged Cu²⁺ is reduced to the Cu⁺ active center, and the adsorbed and unreacted Cu(acac)₂ on the NH₄Y 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/NH₄Y catalyst. It is strongly proved that during heat treatment, the solid state ion-exchange between Cu(acac)₂ and NH₄Y 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 being 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.¹⁻⁴ DMC is also more valuable as a green organic intermediate to substitute the toxic phosgene dimethyl sulfate.^{5,6} Of course, many innovation strategies to synthesize DMC have being developed.^{7,8} Among them, the oxidative carbonylation of methanol was considered as an environmentally friendly synthesis of DMC and has been widely investigated.^{8,9} As early as 1980s, the Enichem Company (Italy) had demonstrated the oxidative carbonylation of methanol to DMC by cuprous chloride CuCl catalyst.⁷ 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.¹⁰

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 Cu⁺Y 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}, H β zeolite¹⁵, HZSM-5 zeolite¹⁶, SiO₂-Al₂O₃¹⁷, SiO₂-ZrO₂¹⁸, and SiO₂-TiO₂¹⁹, 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.²⁰⁻²⁵ 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 Cu₂O¹², Cu(NO₃)₂²⁶⁻³¹ and Cu(CH₃COO)₂³². The CuY catalyst prepared by heating the powder mixture of Cu₂O and HY zeolites at 650°C for 70 h with helium purge was active to produce DMC, but its activity was very low and quickly decreased.¹² In our previous work²⁸⁻³⁰, it was showed that when the Cu²⁺Y zeolite material prepared by liquid solution ion exchange (LSIE) of NaY zeolite with Cu(NO₃)₂ cuprammonia was heated at high temperature, Cu²⁺ in the supercages was auto-reduced to active Cu⁺ and the activated materials showed superior activity. Furthermore, during high temperature activation of the Cu(NO₃)₂/Y zeolite prepared by incipient wetness impregnation (IWIM), HY is easier to ion-exchange with Cu²⁺ 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

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deposition-precipitation (DP) of $\text{Cu}(\text{CH}_3\text{COO})_2$ on NH_4Y zeolite in aqueous solution, the ion exchange does occur to form Cu^{2+} on the surface of Y zeolite and the released NH_3 is favor to reduce Cu^{2+} to Cu^+ .

Recently, an organometallic compound $\text{Cu}(\text{acac})_2$ has been demonstrated the unique charm in the field of copper material preparation due to its properties of sublimation and decomposition at low temperature.³³⁻³⁶ Goel et al.³³ reported that, by chemical vapor deposition of $\text{Cu}(\text{acac})_2$ precursor, Cu_2O and CuO generated at the temperature of 195 °C to 430 °C respectively, but at 285 °C, both Cu_2O and CuO did coexist. Nasibulin et al.³⁵ found when the oxygen concentration of the oxygen/nitrogen carrier gas was 0.5%, by $\text{Cu}(\text{acac})_2$ vapor decomposition, nanoparticles Cu_2O and CuO was 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 0.0003%, 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 NH_4Y zeolite, it is also expected that when a physical mixture of NH_4Y zeolite and $\text{Cu}(\text{acac})_2$ is heated in a muffle furnace, $\text{Cu}(\text{acac})_2$ would sublimate and be adsorbed on the NH_4Y surface several times to be dispersed uniformly, then NH_4Y zeolite decompose to HY zeolite and $\text{Cu}(\text{acac})_2$ decompose to Cu_2O , and simultaneously SSIE between HY zeolite and Cu_2O was happened to form the Cu^+Y catalyst. The decomposed gases such as CO , NH_3 , N_2 , CO_2 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 work³⁷, the chlorine-free CuY catalysts were successfully prepared by high temperature anhydrous interaction (HAI) between $\text{Cu}(\text{acac})_2$ and NH_4Y 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 $\text{Cu}(\text{acac})_2$ and NH_4Y under anhydrous condition and the formation of Cu catalytic active centres was investigated in more detail by TG/DSC, XRD, H_2 -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 NH_4NO_3 (AR, Tianjin Chemical Reagent NO. 3 Factory), $\text{Cu}(\text{acac})_2$ (AR, Sinopharm Chemical Reagent Co. Ltd), CH_3OH (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 NH_4NO_3 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 NH_4Y zeolite.

Then, part of the prepared NH_4Y zeolite was packed in a crucible and then put into a muffle furnace in order to calcinate NH_4Y 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 $\text{Cu}/\text{NH}_4\text{Y}$ catalyst was prepared by heating treatment of a mixture of $\text{Cu}(\text{acac})_2$ and NH_4Y according to following two stages. In the first stage, 2.045 g $\text{Cu}(\text{acac})_2$ and 5.000 g NH_4Y 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 $\text{Cu}(\text{acac})_2$ dispersed very well on the surface of NH_4Y zeolite to form the precursor. In the second stage, the precursor material was activated to form $\text{Cu}/\text{NH}_4\text{Y}$ 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 $\text{Cu}/\text{NH}_4\text{Y}$ catalysts were denoted as $\text{Cu}/\text{NH}_4\text{Y}$ -300, $\text{Cu}/\text{NH}_4\text{Y}$ -400 and $\text{Cu}/\text{NH}_4\text{Y}$ -500 respectively.

According to the above procedure, NaY and HY were also used to substitute of NH_4Y 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 omnistar 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 (H_2 -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. % H_2 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 $\text{CuK}\alpha$ radiation ($\lambda=0.154056$ nm) on a Rigaku D/max 2500 diffractometer at 40 kV target voltage and 100 mA tube current in the 2θ 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 grinded 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 K α 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 2.0g 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 ($\Phi 6 \text{ mm} \times 450 \text{ mm}$) under atmospheric pressure with on-line Agilent 6890 gas chromatograph (GC). 0.45 g catalyst (about 1.0 mL) was packed in the tubule reactor and the reactor was positioned in the furnace. $0.02 \text{ mL}\cdot\text{min}^{-1}$ methanol was introduced by a constant-flux pump (2PB-05) and vaporized in the pre-heater. In the meantime, $28.0 \text{ mL}\cdot\text{min}^{-1}$ carbon monoxide and $2.8 \text{ mL}\cdot\text{min}^{-1}$ 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

($30\text{m}\times 0.53\mu\text{m}\times 40\mu\text{m}$), the organic products were hold back. And then the excurrent inorganic products flowed through the Propack-Q packed column: CO_2 firstly flowed out and entered into a thermal conductivity detector (TCD) and was detected; secondly, CO and O_2 were separated by the HP-PLOT Molesieve/5A capillary column ($30\text{m}\times 0.53\mu\text{m}\times 25\mu\text{m}$) and detected by TCD. The products flowed through the HP-INNOWax ($30\text{m}\times 0.53\mu\text{m}\times 1\mu\text{m}$) 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 NH_4Y zeolite is heated at 400 °C, NH_3 is dissociated, and NH_4Y zeolite converts to HY zeolite³⁸.

Then the dehydroxylation of silicol on the surface of the HY zeolite takes place at the heating temperature above 450 °C.^{38,39} The TG/DTG-DSC curves of the as-prepared NH_4Y 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 phenomenon⁴⁰; between 200-440 °C, the dissociation of NH_3 from NH_4Y 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.

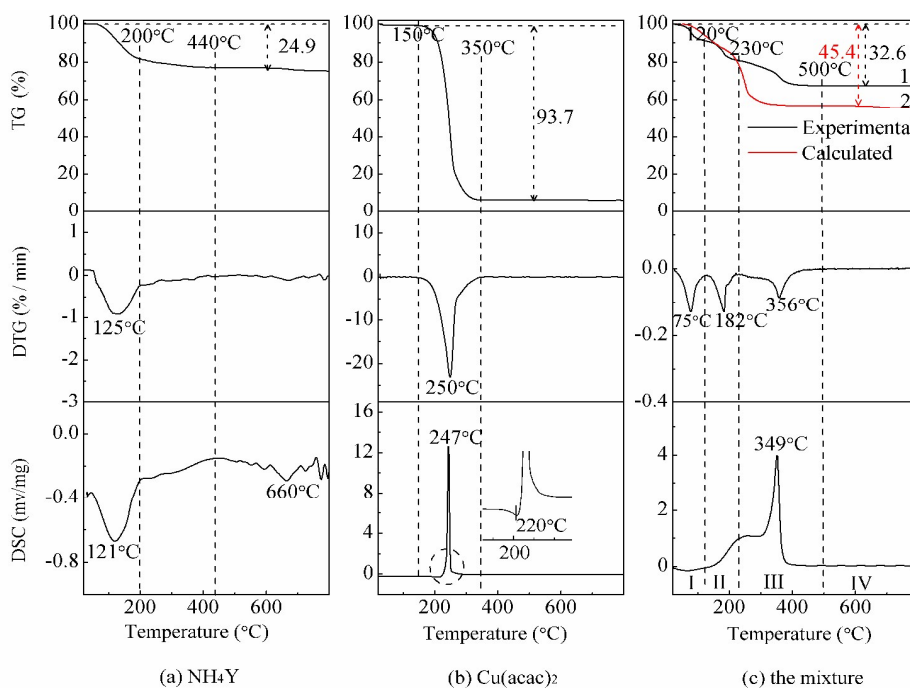


Fig. 1 TG/DTG-DSC curves of samples

* The curve 2 is the TG of an addition of the TG of $\text{Cu}(\text{acac})_2$ and NH_4Y

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For $\text{Cu}(\text{acac})_2$ 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 $\text{Cu}(\text{acac})_2$ decomposed at 150–350 °C, because there is no further weight loss and no heat changes above 350 °C. The final material of $\text{Cu}(\text{acac})_2$ decomposition should be CuO , and the theoretical weight loss is 69.4%. But the actual weight loss of TG in Fig. 1(b) is as high as 93.7%. If the DSC curve is enlarged as showed in Fig 1(b), a weak endothermic peak at 220 °C is clearly observed before the strong exothermic peak at 247 °C. It must be caused by the sublimation of $\text{Cu}(\text{acac})_2$. Therefore, it is concluded that $\text{Cu}(\text{acac})_2$ firstly sublimates and then decomposes to CuO at the temperature from 150 °C to 350 °C.

But for a well physical mixture of NH_4Y with 28.6 wt.% $\text{Cu}(\text{acac})_2$, 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_4Y zeolite. This water desorption peak temperature on the curve 1 is obviously lower than that of pure NH_4Y and on the curve 2. It is indicated that some of $\text{Cu}(\text{acac})_2$ 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 $\text{Cu}(\text{acac})_2$ begins to sublimated and was partly absorbed on NH_4Y . 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 $\text{Cu}(\text{acac})_2$. 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 $\text{Cu}(\text{acac})_2$ and NH_4Y during heat treatment.

To obtain more detail information during heat treatment of the mixture of $\text{Cu}(\text{acac})_2$ and NH_4Y , 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_2O 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.⁴¹ During heat treatment of the mixture, water is released at 76 °C below the water desorption peak temperature (121 °C) of pure NH_4Y , 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_4Y zeolite decomposes and releases NH_3 . So it was proved that the ion exchange between Cu^{2+} of $\text{Cu}(\text{acac})_2$ and NH_4^+ of NH_4Y 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_4Y 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_2O .

According to the above analysis, during heat treatment of the mixture, (a) in the temperature zone I, the zeolite-adsorbed water of NH_4Y is released; (b) in the temperature zone II, $\text{Cu}(\text{acac})_2$ sublimates and $\text{Cu}(\text{acac})_2$ vapor is mostly adsorbed on Y zeolite, in the meantime, ion exchange between $\text{Cu}(\text{acac})_2$ and NH_4Y occurs; (c) in the temperature zone III, the

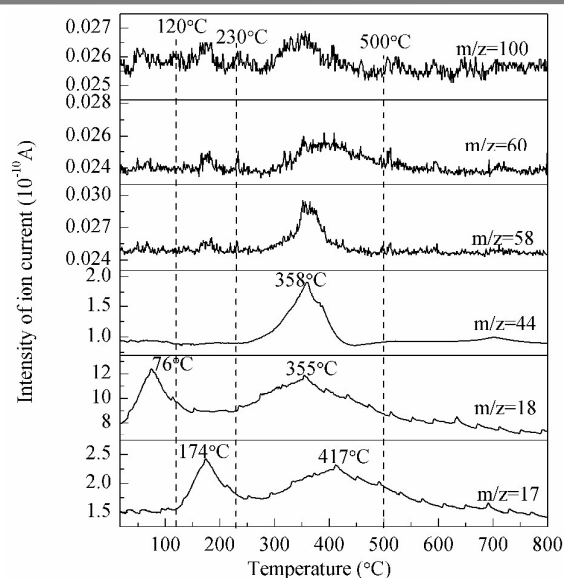


Fig. 2 MS spectra of gaseous products of the physical mixture of NH_4Y and $\text{Cu}(\text{acac})_2$

decomposition of adsorbed $\text{Cu}(\text{acac})_2$, residual NH_4^+ decomposition of NH_4Y .

Structural properties of CuY catalysts

The XRD patterns of samples are compared in Fig. 3. For the mixture, diffraction peaks of $\text{Cu}(\text{acac})_2$ and NH_4Y are simultaneously observed. However, the diffraction peaks of the precursor and the $\text{Cu}/\text{NH}_4\text{Y}$ 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 zeolite⁴². As can be seen in Fig. 3, compared with NH_4Y , 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_4Y zeolite by the ion exchange between Cu^{2+} of $\text{Cu}(\text{acac})_2$ and NH_4^+ of NH_4Y . I_{111} , I_{220} and I_{311} also decrease for $\text{Cu}/\text{NH}_4\text{Y}$ catalysts, yet compared with the precursor, I_{111} and I_{220} increase more slightly. The difference indicates that, adsorbed $\text{Cu}(\text{acac})_2$ decomposes to copper oxide and copper ions migrate from supercages to small cages during activation, so the particles of copper species in $\text{Cu}/\text{NH}_4\text{Y}$ catalysts become more smaller and uniformly, resulting in less

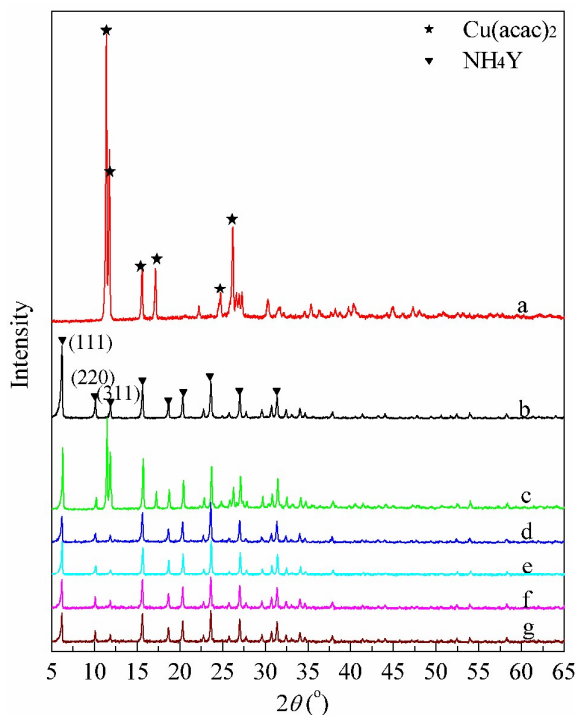


Fig. 3 XRD patterns of $\text{Cu}(\text{acac})_2$ (a), NH_4Y (b), mixture (c), the precursor (d), $\text{Cu}/\text{NH}_4\text{Y}$ -300 (e), $\text{Cu}/\text{NH}_4\text{Y}$ -400 (f) and $\text{Cu}/\text{NH}_4\text{Y}$ -500 (g).

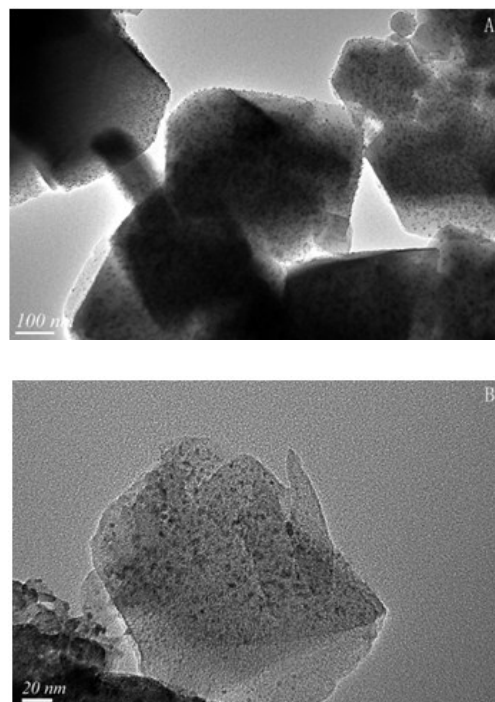


Fig. 4 TEM images of the $\text{Cu}/\text{NH}_4\text{Y}$ -400 catalyst

impact on the zeolite structures.

Fig. 4 presents the TEM images of the $\text{Cu}/\text{NH}_4\text{Y}$ -400 catalyst. Richter et al.²⁶ 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 $\text{Cu}/\text{NH}_4\text{Y}$ 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-differencing 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^{26,28-30,43-45} 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)

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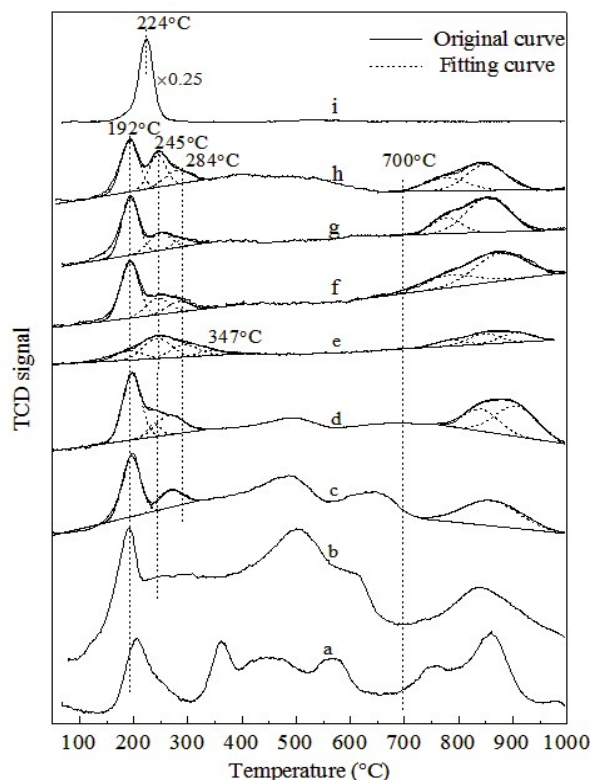


Fig. 5 H₂-TPR profiles: Cu/NH₄Y-200 (a), Cu/NH₄Y-220 (b), Cu/NH₄Y-250 (c), Cu/NH₄Y-280 (d), Cu/HY-400 (e), Cu/NH₄Y-300 (f), Cu/NH₄Y-400 (g), Cu/NH₄Y-500 (h), Cu/NaY-400 (i)

The reduction of dispersed CuO to Cu⁰ occurs around 250 °C. (iii) The exchanged Cu⁺ is reduced at distinctly higher temperature. So for H₂-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 Cu²⁺ 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/NH₄Y and Cu/HY-400 catalysts belong to the reduction of CuO to Cu⁰ in one step. The reduction peaks above 700 °C are attributed to the reduction of Cu⁺ to Cu⁰. Thus it can be seen that there exist only CuO on the Cu/NaY-400, ion-exchanged Cu²⁺, Cu⁺ besides CuO on the Cu/NH₄Y 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/NH₄Y catalysts, until the activation temperature reaches to 280 °C, the hydrogen consumption peaks of CuO and Cu⁺ species appear on the H₂-TPR profile of Cu/NH₄Y-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 H₂-TPR profile of Cu/NH₄Y, and there are some undetermined hydrogen consumption peaks from 300 °C to 700 °C. This suggests that the initial temperature of exchanged Cu²⁺ 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/NH₄Y-400 with Cu/HY-400, it is found that the content of CuO and Cu²⁺ of Cu/NH₄Y-400 is lower than that of Cu/HY-400, but the content of Cu⁺ in the supercages of Cu/NH₄Y-400 is more than doubled that of Cu/HY-400.

Table 1 Quantitative analysis of the H₂-TPR profiles of the catalysts

Catalyst	H ₂ consumption /cm ³ ·g ⁻¹								Cu mass /%			Cu ⁺ / Cu _{sum} %
	H _{2sum}	Cu ²⁺ →Cu ⁺			CuO→Cu ⁰	Cu ⁺ →Cu ⁰			Cu ²⁺	Cu ⁺	CuO	
		Sup.	Sod.	Hex.		Sup.	Sod.	Hex.				
Cu/NaY-400	28.4	0	0	0	28.4	0	0	0	---	---	8.1	0
Cu/NH ₄ Y-250	19.8	8.9	1.1	0	0	9.8	0	0	---	---	0	0
Cu/NH ₄ Y-280	25.8	9.1	1.3	0	0.7	5.7	9.0	0	5.9	2.5	0.2	32.9
Cu/NH ₄ Y-300	26.3	8.7	0.6	0	1.4	3.3	12.3	0	5.3	3.6	0.4	38.7
Cu/NH ₄ Y-400	25.5	7.4	0.4	0	2.4	5.2	10.1	0	4.5	4.3	0.7	45.3
Cu/NH ₄ Y-500	27.3	6.3	0.7	0	7.4	2.5	10.4	0	4.0	3.4	2.1	35.8
Cu/HY-400	26.7	3.2	3.1	2.1	7.0	2.5	4.6	4.2	4.8	1.7	2.0	20.0

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% Cu²⁺ ions on the Cu/NH₄Y-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.⁴⁸ Fig. 6 presents Cu 2p_{3/2} XPS spectra and the Cu LMM Auger spectra of Cu/NH₄Y. It was reported that the kinetic energy of the Cu LMM Auger electrons at 913.7eV and 916.6eV is ascribed to Cu⁺ and Cu²⁺,³² and the kinetic energy of Cu0 is at the range from 918 to 920 eV.²⁹ 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 Cu²⁺ with a kinetic energy of 915.9 eV, and there is no peak of Cu0 in the range from 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} The XPS spectra of Cu 2p (Fig. 6) shows an overlapping Cu 2p_{3/2} signal, by the curve-fitting of the Cu 2p_{3/2} spectra, it can be fitted into two peaks at 933.4 eV attributed to Cu⁺ and 935.7 eV attributed to Cu²⁺ respectively. By the proportion of area percentage, the calculated Cu⁺ percent content of catalysts is 46.9%, 52.5%, and 39.1% respectively when the activation temperature is 300 °C, 400 °C and 500 °C. The change trend coincides with that of the Cu⁺ percent content which is discussed in H₂-TPR (Table 1).

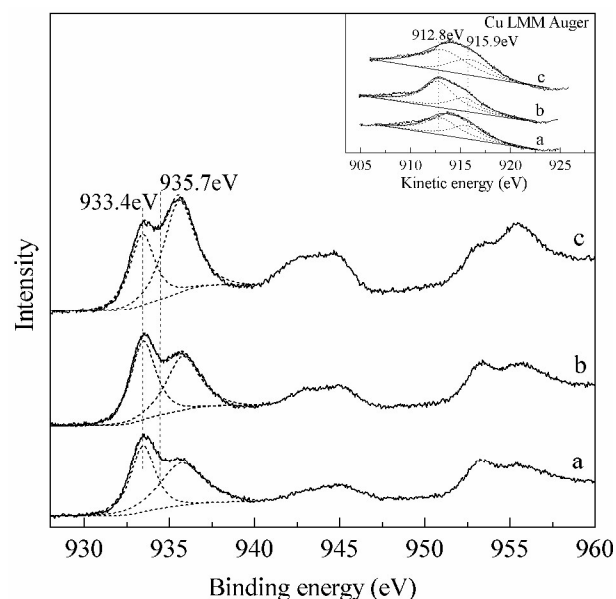
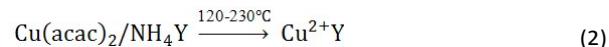
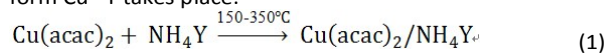
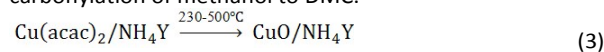


Fig. 6 Cu2p XPS and Cu LMM Auger spectra of Cu/NH₄Y-300 (a), Cu/NH₄Y-400 (b), Cu/NH₄Y-500 (c).

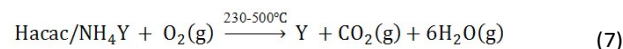
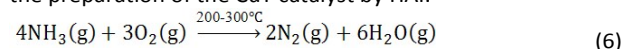
As indicated above, it is deduced that the main reactions are as follows: During heat treatment, Cu(acac)₂ sublimates and is adsorbed on the NH₄Y surface firstly, and in the meantime the ion exchange between Cu²⁺ of Cu(acac)₂ and NH₄⁺ of NH₄Y to form Cu²⁺Y takes place.



At the stage of activation, the adsorbed unreacted Cu(acac)₂ starts to decompose, at the same time, NH₄Y decomposes to form HY and releases NH₃. Meanwhile ion exchanged Cu²⁺ is auto-reduced to form the active centre Cu⁺ for oxidative carbonylation of methanol to DMC.



In addition, Lu et al.⁵¹ reported CuY is the most active catalyst for NH₃ oxidation from 200 °C to 300 °C. And organic ligands and their products react with oxygen in the air and generate CO₂ and H₂O. So the following reactions are possible during the preparation of the CuY catalyst by HAI.



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^{24,28,32} 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/NH₄Y-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 NH₄⁺ of NH₄Y can introduce Cu²⁺ into extraframework cation location of zeolite Y by ion exchange between Cu²⁺ of Cu(acac)₂ and NH₄⁺ of NH₄Y, and the decomposed NH₃ from NH₄Y facilitates the reduction of Cu²⁺ to Cu⁺ to form more active centres. Compared with the Cu/HY catalyst, more copper ions on the Cu/NH₄Y catalyst locate in the supercages accessible to reactants. However, Na⁺ of NaY can't exchange with Cu²⁺ 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/NH₄Y catalysts with different activation temperature (300 °C, 400 °C, 500 °C), when the activation temperature is 300 °C, the conversion of methanol (X_{CH₃OH}) and the space-time yield of DMC (STY_{DMC}) is 7.5% and 137.2 mg·g⁻¹·h⁻¹ for Cu/NH₄Y-300 respectively. However, the Cu/NH₄Y-400 catalyst activated at 400 °C exhibits an excellent catalytic activity with 8.2% X_{CH₃OH} and 153.0 mg·g⁻¹·h⁻¹ STY_{DMC}. When the activation temperature is 500 °C, X_{CH₃OH} and STY_{DMC} have decreased to

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Table 2 Catalytic activity of the catalysts in oxidative carbonylation of methanol^a

Catalysts	Preparation	Support/Activation temperature (°C)	Cu (wt.%)	STY _{DMC} (mg·g ⁻¹ ·h ⁻¹)	X _{CH₃OH} (%)	S _{DMC} (%)	Ref.
Cu/NaY-400	HAI	NaY/400	8.2 ^c	0	0	0	
Cu/NH ₄ Y-300	HAI	NH ₄ Y/300	9.5 ^c	137.2	7.5	61.2	
Cu/NH ₄ Y-400	HAI	NH ₄ Y/400	9.5 ^c	153.0	8.2	61.9	
Cu/NH ₄ Y-500	HAI	NH ₄ Y/500	9.5 ^c	113.3	6.2	60.9	
Cu/HY-400	HAI	HY/400	8.5 ^c	65.4	3.5	60.7	
Cu/NaY(L)-600	LSIE	NaY/600	6.3 ^c	131.4	6.5	68.5	28
Cu/HY(I)-600	IWIM	HY/600	10.0 ^d	95.6	5.1	62.0	28
Cu/NaY(I)-600	IWIM	NaY/600	10.0 ^d	16.3	1.1	50.7	28
Cu/HY(S)-650	SSIE	HY/650	12.2 ^c	97.3	4.4	74.6	24
Cu/NH ₄ Y(D)-400 ^b	DP	NH ₄ Y/400	10.0 ^d	0	0	0	32
Cu/NH ₄ Y(D)-750 ^b	DP	NH ₄ Y/750	10.0 ^d	84.4	8.1	53.5	32

^a Reaction conditions: V_{CH₃OH}:V_{CO}:V_{O₂} = 4:10:1, GHSV = 2520 h⁻¹, T = 140 °C, P = 0.1MPa.

^b Reaction conditions: V_{CH₃OH}:V_{CO}:V_{O₂} = 6:8:1, 1% Ar (He balance), GHSV = 3000 h⁻¹, T = 140 °C, P = 0.1MPa. The Cu/NH₄Y(D)-400 catalyst prepared by DP has a NH₄Y 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/NH₄Y-500 respectively. The H₂-TPR and XPS characteriation have shown that the Cu/NH₄Y-400 catalyst has the highest content of Cu⁺ active center.

In addition, it also is found that the catalytic activity of the Cu/NH₄Y-400 catalyst is better than those of the chloride-free CuY catalysts prepared by LSIE²⁸, IWIM²⁸ or DP³² and the Cu/HY(S)-650 catalyst prepared by SSIE²⁴. For example, the STY_{DMC} of the Cu/NH₄Y-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 IWIM²⁸, including the Cu/HY(I)-600 catalyst with 95.6 mg·g⁻¹·h⁻¹ STY_{DMC} and the Cu/NaY(I)-600 catalyst with 16.3 mg·g⁻¹·h⁻¹ STY_{DMC}. And even the STY_{DMC} of the Cu/NH₄Y-400 catalyst is higher 57.2% than that of the Cu/HY(S)-650 catalyst with 12.2 wt.% Cu loading prepared by SSIE²⁴. The Cu/NH₄Y(D)-400 catalyst has no catalytic activity, and the Cu/NH₄Y(D)-750 catalyst has 84.4 mg·g⁻¹·h⁻¹ STY_{DMC} that it is also lower 44.8% than that of the Cu/NH₄Y-400 catalyst. For the Cu/NaY(L)-600 catalyst with 131.4 mg·g⁻¹·h⁻¹ STY_{DMC} prepared by LSIE²⁸, the 6.3 wt.% Cu loading is the maximum permissible loading for LSIE once, and

the STY_{DMC} is lower 14.4% than that of the Cu/NH₄Y-400 catalyst.

According to the previous studies²³, the proposed mechanism for the oxidative carbonylation of methanol to dimethyl carbonate can be concluded as follows. Firstly, CH₃OH 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 monomethyl carbonate species (MMC) as intermediate. Last, the MMC species react with methanol to form DMC. The reaction of carbon monoxide into the methoxide is the rate-limiting step. And, Cu⁺ of CuY has been demonstrated to improve the adsorption energy of co-adsorbed CO in co-adsorbed CO/CH₃O system, stabilizes the transition state for the reaction of CO insertion to produces monomethyl carbonate (MMC) species.⁵²⁻⁵⁴ In our experiment, the content of Cu⁺ has attained the highest for the Cu/NH₄Y-400 catalyst, which exhibits the best catalytic performance. 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.³⁷ 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 $\text{Cu}(\text{acac})_2$ and NH_4Y , from 120 °C to 230 °C, $\text{Cu}(\text{acac})_2$ sublimates and $\text{Cu}(\text{acac})_2$ vapor is mostly adsorbed and well dispersed on the surface of Y zeolite. In the meantime, ion exchange between $\text{Cu}(\text{acac})_2$ and NH_4Y occurs in the supercages. Above 230 °C, the unreacted $\text{Cu}(\text{acac})_2$ decomposes to form copper oxides, simultaneously NH_4Y decomposes and releases NH_3 , which facilitates the reduction of Cu^{2+} to Cu^+ . Above 500 °C, no physical or chemical processes occur.

For NaY zeolite, no solid state ion-exchange occurs between $\text{Cu}(\text{acac})_2$ 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 $\text{Cu/NH}_4\text{Y}$ catalyst. The distribution of Cu^{2+} , Cu^+ and CuO on the $\text{Cu/NH}_4\text{Y}$ catalyst highly depends on the activation temperature. When the activation temperature is 400 °C, the content of Cu^+ has attained the highest, the corresponding $\text{Cu/NH}_4\text{Y-400}$ 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 $\text{mg}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ respectively.

Acknowledgements

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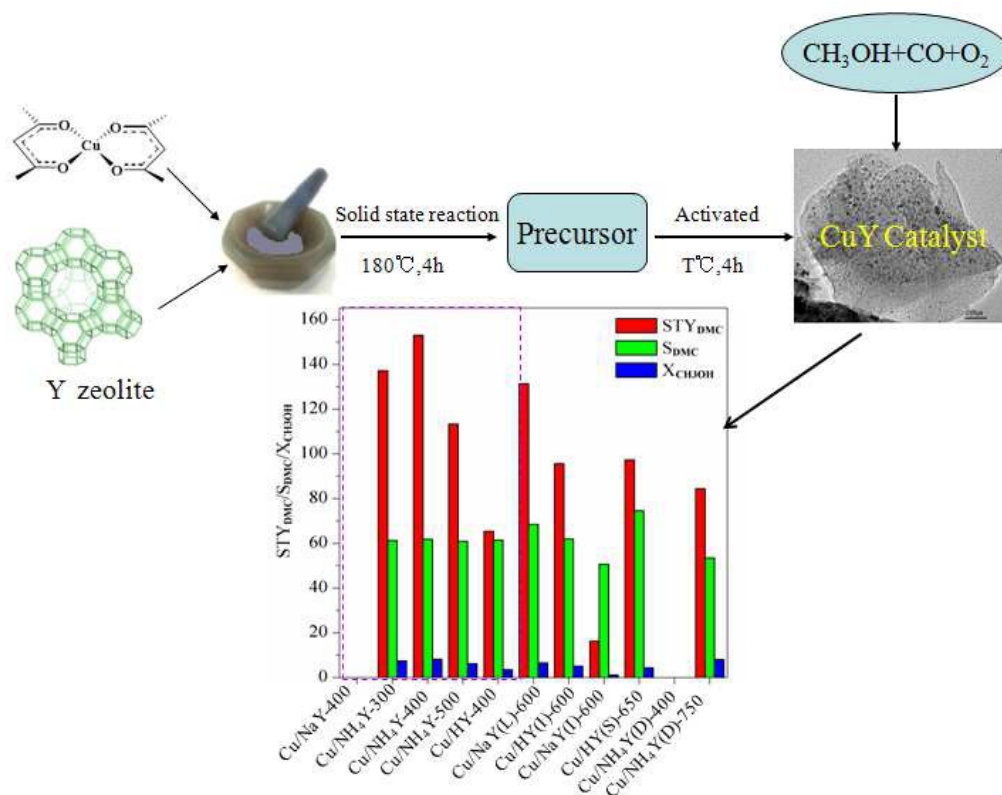
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The high temperature anhydrous interaction between copper (II) acetylacetonate $\text{Cu}(\text{acac})_2$ and NH_4Y was investigated to prepare a chlorine-free CuY catalyst for the oxidative carbonylation of methanol to dimethyl carbonate. The Cu/NH₄Y-400 catalyst shows superior catalytic activity.