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Article

Synthesis of dimethyl carbonate over starch-based carbon-supported Cu nanoparticles catalysts

Jun Ren*, Changjiang Guo, Leilei Yang, Zhong Li

Key Laboratory of Coal Science and Technology of Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, Shanxi, China

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ABSTRACT

Carbon-supported Cu (Cu/C) catalyst was prepared from $\text{Cu}(\text{NO}_3)_2$ and starch, by the sol-gel method, subsequent high temperature carbonization and KOH activation. Catalyst samples were characterized by scanning and transmission electron microscopies, X-ray diffraction, thermogravimetric analysis, N_2 adsorption-desorption and CO temperature-programmed desorption. Their catalytic performance in the oxidative carbonylation of methanol to dimethyl carbonate (DMC) in a fixed-bed reactor was investigated. The activation temperature and KOH content greatly influenced the catalyst microstructure and catalytic performance. The Cu/C catalyst prepared at activation temperature of 850 °C and KOH/C mass ratio of 1 exhibited the best catalytic activity. Its specific surface area and mean Cu particle size were 1690 m^2/g and 30.4 nm, respectively. The space time yield was 235.7 $\text{mg}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, and the methanol conversion and selectivity for DMC were 1.6% and 76.5%, respectively.

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1. Introduction

Methanol is a heavy chemical made from coal or natural gas, and developing the deep processing of methanol is a focus of many countries. Dimethyl carbonate (DMC) is a downstream product of methanol and has received much recent attention. DMC can be used as a substitute for toxic or carcinogenic chemicals such as phosgene, dimethyl sulfate and chloroformate in many organic syntheses. DMC also has potential as a chemical intermediate and fuel additive [1]. Ever-increasing vehicle emission standards hint at good commercial prospects for DMC as a fuel additive.

The oxidative carbonylation of methanol utilizes methanol, CO and O_2 to produce DMC. This green process contrasts to typical national alternatives where coal is used as the energy

source. The process has low production costs and high product selectivity [2]. The DOW Chemical Co., USA, first employed $\text{CuCl}_2\text{-KCl/AC}$ (where AC denotes activated carbon) as an industrial scale catalyst to prepare DMC from methanol and CO. A drawback was the loss of Cl⁻, causing corrosion and decreased activity [3]. The activity of $\text{PbCl}_2\text{-CuCl}_2/\text{AC}$ was reported to be higher than that of CuCl_2/AC . Adding CH_3COOK resulted in its interaction with PdCl_2 or CuCl_2 to form KCl, which limited the loss of chlorine [4]. Higher reaction rates and better catalytic stability have been obtained for CuCl_2 on amino-functionalized in comparison with CuCl_2 on non-functionalized supports under identical conditions. This was attributed to accelerated redox processes of $\text{Cu}^{2+}/\text{Cu}^+$ to complex species in the presence of amino groups [5]. The $\text{Cu}_2(\text{OH})_3\text{Cl/AC}$ catalyst gradually converted to CuO and CuCl_2 , thus decreasing activity [6].

*Corresponding author. Tel/Fax: +86-351-6018598; E-mail: renjun@tyut.edu.cn

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King [7] reported that Cu(I)Y catalysts made by a solid-state ion-exchange method exhibited higher initial productivity. The deactivation rate was significantly reduced compared with CuCl_2/AC , indicating that Cl^- was not essential for the reaction. Li et al. [8] synthesized $\text{CuCl}/\text{MCM-41}$, and this catalyst exhibited 100% selectivity for DMC in the conversion of methanol. Anderson et al. [9] reported that Cu(I)X exhibited higher activity and selectivity for DMC than Cu(I)ZSM-5, which was attributed to the formation of more active sites Cu(I). Zhang et al. [10] reported that the superior activity and selectivity of Cu-Y for DMC were associated with its weaker adsorption of CO. Under identical conditions, Cu(I)Y exhibited higher selectivity for DMC than Cu(I)ZSM-5 or Cu(I)MOR. However, the operating conditions necessary for solid-state ion-exchange were extremely harsh, requiring temperatures $> 550^\circ\text{C}$ and calcination for > 15 h in an inert atmosphere to achieve satisfactory results [7–10]. Zhang et al. [11] reported that ~ 10 wt% of the copper zeolite was occluded as CuCl clusters within channels and intersections; this fraction being incapable of ion-exchange. This confirmed that the presence of residual chlorine was inevitable. High temperature treatments have also resulted in the loss of Al from zeolite frameworks [8]. Such drawbacks limit the use of Cu(I)Y catalysts on the industrial scale.

Chlorine-free catalysts have been investigated as a means of avoiding catalyst inactivation by Cl^- loss. $\text{Cu}_2\text{O}/\text{Y}$ catalyst prepared by King [7] exhibited high initial activity but deactivated rapidly 1.5 h later. Richter et al. [12] prepared chloride-free Cu/zeolite Y catalysts with Cu loading by precipitation from aqueous $\text{Cu}(\text{CH}_3\text{CO}_2)_2$. The catalyst exhibited considerable activity in oxidative carbonylation. Li et al. [13–15] prepared highly active $\text{Cu}_2\text{O}/\text{AC}$ catalysts by heat treatment of $\text{Cu}_2(\text{NO}_3)(\text{OH})_3/\text{AC}$ in an inert atmosphere. Catalyst activity was promoted by modifying the AC with HNO_3 or NH_3 [16,17]. The coadsorption of CO and CH_3O on the $\text{Cu}_2\text{O}(111)$ surface has been investigated with density functional theory and periodic models. The mode of action between CO and CH_3O on the catalyst surface and the interaction of the adsorbed molecules were determined.

The sol-gel method can quantitatively introduce trace elements into catalysts and achieve uniform doping [18]. Starch has been widely used to prepare carbon source and gel materials [19,20]. Herein, a starch-based carbon-supported Cu (Cu/C) catalyst was prepared from starch and KOH activation [21–24]. The oxidative carbonylation of methanol to DMC was investigated. The effect of temperature and KOH dosage on pore structure, crystal structure and catalytic performance were investigated.

2. Experimental

2.1. Catalyst preparation

In a typical procedure, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Tianjin Guangfu Technology Development Co. Ltd., 2.00 g) was dissolved in 50 mL of deionized water. The solution was stirred at $60\text{--}80^\circ\text{C}$, soluble starch (Tianjin BASF Chemical Co., Ltd., 10.65 g) was added, and the mixture continued to stir until a stable colloid

formed. The obtained wet-gel was aged for 10 d at 25°C , transferred to a vacuum oven and dried under vacuum at 80°C for 12 h. The product was calcined at 500°C and held there for 2 h under a $30\text{--}40$ mL/min flow of N_2 . The carbonized product was ball-milled, and the powder passed through a 100 mesh sieve. This raw material was mixed with KOH in varying mass ratios to yield Cu-KOH/C. Cu-KOH/C was activated in a $30\text{--}40$ mL/min H_2 flow at $650\text{--}900^\circ\text{C}$ for 2 h. After cooling, washing and drying, the Cu/C catalyst was obtained. Samples are denoted as Cu/C- t , where t is activation temperature ($500, 650, 750, 850$ and 900°C), and $t = 500^\circ\text{C}$ indicates the catalyst precursor.

2.2. Catalyst characterization

Differential thermogravimetric analysis (TG-DTG) was conducted on a thermogravimetric analyzer, STA-409C (NETZSCH), at a heating rate of $10^\circ\text{C}/\text{min}$ and N_2 flow rate of 50 mL/min. X-Ray diffraction (XRD) patterns were recorded on a Rigaku D-Max 2500 diffractometer, using Cu K_α radiation ($\lambda = 0.154$ nm) at 40 kV and 100 mA, with a scanning rate of $8^\circ/\text{min}$ at 2θ of $5^\circ\text{--}80^\circ$. Scanning electron microscopy (SEM) was carried out using a JEOL JSM-6701F instrument. Transmission electron microscopy (TEM) was carried out using a Tecnai G2F20 S-Twin microscope operating at 200 keV. TEM samples were prepared by immersing C-coated Cu grids in ethanol solutions of samples, and drying at room temperature.

N_2 adsorption-desorption isotherms were measured with a JW-BK122W adsorption analyzer at -196°C . Specific surface area (A_{BET}), micropore specific surface area (V_{micr}), mesopore size distribution (D_{BJH}) and micropore size distribution (D_{HK}) values were calculated from isotherms using the BET, t -plot, BJH, and HK methods, respectively.

X-ray photoelectron spectroscopy (XPS) was carried out using an ESCALab220i-XL (Thermo-VG Scientific) spectrometer equipped with a monochromatised Al K_α (1486.6 eV, 300 W) source. The C $1s$ line (284.6 eV) was taken as a reference to correct for electrostatic charging.

Cu contents were determined by elemental analyses using iodometry, in which samples were dissolved in $\text{HCl}/\text{H}_2\text{O}_2$. The solution was boiled to remove H_2O_2 , and ammonia was promptly added once the solution had precipitated. HAc , NH_4HF and KI were added in turn, and the resulting solution was titrated against a standard $\text{Na}_2\text{S}_2\text{O}_3$ solution until it appeared faint yellow. Starch indicator and NH_4SCN solution were added, and the resulting solution was titrated against standard $\text{Na}_2\text{S}_2\text{O}_3$ solution until the blue color had disappeared.

CO temperature-programmed desorption (CO-TPD) measurements were performed in a U-shaped Pyrex tube furnace, using a FINESORB-3010 apparatus. Samples were degassed at 200°C for 0.5 h under a 50 mL/min He flow, to remove water and physisorbed organic species. The temperature was lowered to 35°C , and a 50 mL/min flow of 10% CO- 90% He was introduced to allow CO adsorption. The temperature was increased from 50 to 600°C at a rate of $10^\circ\text{C}/\text{min}$ under a 50 mL/min flow of He. CO was released as was continuously monitored by TCD.

2.3. Catalyst activity evaluation

DMC synthesis was carried out in a fixed-bed reactor. A stainless steel tube reactor of inner diameter of 5 mm was used. The catalyst loading was 0.2 g. Methanol was introduced by a micro-pump and then heated sufficiently to vaporize. CO and O₂ were mixed, preheated and then regulated by a mass-flow controller. Liquid products were analyzed by flame ionization detector (FID) gas chromatography (GC-950, Shanghai Haixin, China) using a HP-INNO-WAX (30 m × 530 μm × 1 μm) column (able to analyze methanol, DMC, methyl formate and dimethoxymethane). Conditions in the fixed-bed reactor were 140 °C and 0.5 MPa over a duration of 10 h. Reactant flow rates were CH₃OH = 0.056, CO = 55 and O₂ = 5 mL/min.

3. Results and discussion

3.1. TG/DTA and TG/DTG analysis

Carbonization is the pyrolysis of organic and inorganic species in raw materials under an inert atmosphere and high temperature, and involves thermal decomposition and polycondensation [25]. The purpose is usually to increase the porosity and mechanical strength of materials. A lower heating rate favors the formation of initial pores, and sufficient duration at constant temperature ensures that raw materials completely carbonize, forming an ideal surface structure.

DTG and differential thermogravimetric analysis (DTA) curves of the Cu(NO₃)₂/starch composite colloid under a N₂ flow are shown in Fig. 1. There were three obvious weight losses in the DTG curve. The first occurred from ambient temperature to 138 °C and was a 1.6% weight loss of residual water, corresponding to an endothermic peak. At 138–184 °C, Cu(NO₃)₂ was pyrolyzed to CuO, NO₂ and O₂. Pyrolysis proceeded violently at 160 °C, as formed NO₂ and O₂ immediately combusted. The release of NO₂ and O₂ resulted in a weight loss of 11.9%, indicated by the peak at ca. 160 °C in the DTG curve. Weight loss at 240–290 °C was due to the pyrolysis of starch, releasing H₂O and CO₂ [26–28]. A faster pyrolysis of starch occurs at 300–440 °C. This was similar to the reported pyrolysis of polysaccharides, which produce CO, CO₂, H₂O, CH₄, C₂H₄ and

Fig. 1. TG/DTA (a) and TG/DTG (b) curves of Cu(NO₃)₂/starch co-gel.

formaldehyde [28,29]. The release of these gaseous products resulted in an 83.2% weight loss. The sample mass remained nearly constant at > 500 °C, indicating incomplete pyrolysis. However, the DTA curve suggested weakly endothermic behavior during this stage, attributed to the gradual transformation of amorphous to graphitic carbon, resulting in a well-ordered carbon structure [30].

3.2. Porosity

N₂ adsorption-desorption isotherms of Cu/C catalysts prepared at different activation temperatures are shown in Fig. 2(a). The isotherm morphology of Cu/C-500 and Cu/C-650 remained nearly constant, suggesting no pore structure within these catalysts. Those of Cu/C-750, Cu/C-850 and Cu/C-900 exhibited a mixture of type I and type IV isotherms, with a wid-

Fig. 2. N₂ adsorption-desorption isotherms (a), mesopore size distribution (b) and micropore size distribution (c) of Cu/C catalysts with different activation temperatures.

Table 1

Specific surface area and pore volume of Cu/C catalysts with different activation temperatures.

$t/^{\circ}\text{C}$	A_{BET} (m^2/g)	V_{tot} (cm^3/g)	V_{micr} (cm^3/g)	D_{BJH} (nm)	D_{HK} (nm)
500	4	0.01	0	7.68	1.10
650	8	0.01	0	4.22	1.12
750	734	0.44	0.35	2.41	0.55
850	1690	0.88	0.64	2.09	1.05
900	1217	0.61	0.54	1.99	1.04

er knee exhibited at relative pressure (p/p_0) < 0.1. This indicated wider micropores [31]. An obvious capillary condensation step (hysteresis loop) at $p/p_0 > 0.4$ indicated that a considerable amount of mesoporous was also present. Mesopore and micropore size distributions calculated by the BJH and HK methods, respectively, are shown in Fig. 2(b) and (c), respectively. Specific surface areas and pore structure parameters of the Cu/C catalysts are summarized in Table 1. From the pore size distributions it can be seen that Cu/C catalysts exhibited a high percentage of micropores, and the pore size distribution was predominantly 0.5–1.2 nm. A certain amount of mesopores were also formed during activation. Figure 2(c) shows that surface areas first increased and then decreased with increasing activation temperature, but pore size was nearly constant with a maximum at 850 °C. Table 1 shows that the Cu/C catalysts were typical microporous materials. A small amount of micropores could accelerate reactant sorption in the catalyst channels and potentially improve efficiency.

Concerning catalyst textures, A_{BET} , V_{micr} and V_{tot} initially increased and then decreased with increasing activation temperature. Catalysts had a largely constant average pore diameter (D). The TGA results suggest that colloid depolymerization and pyrolysis occurred at 240 °C, and a cross-linked aromatic ring system subsequently formed at higher temperature through a series condensation and cyclization reactions.

When activation temperature increased, activated C atoms of the carbonized material were more reactive towards KOH. This meant that more pores were created by corrosion of KOH, resulting in an increased pore volume. As activation temperature reached 850 °C, the surface area, total pore volume and microporosity obtained their highest values of 1690 m^2/g , 0.88 cm^3/g and 72.4%, respectively. When activation temperature was increased further, over-reaction between KOH and activated C atoms collapsed the pore structure, and the pore volume decreased.

N_2 adsorption-desorption isotherms of Cu/C catalysts activated at 850 °C with different KOH/C mass ratios are shown in Fig. 3, and textural parameters are summarized in Table 2. A_{BET} , V_{micr} and V_{tot} initially increased and then decreased as the KOH/C ratio increased from 0.5 to 3. D_{BJH} remained nearly constant, and D_{HK} fluctuated around 1 nm. When the KOH/C ratio was 0.5, A_{BET} was only 535 m^2/g . Increasing the ratio from 0.5 to 1.0 caused the surface area, total pore volume and microporosity to obtain their highest values. During activation, KOH is thought to have reacted with the carbonized material via chemical etching. This created new pores and widened existing ones, favoring the pyrolysis of carbon material to some

Fig. 3. N_2 adsorption-desorption isotherms of the Cu/C-850 catalyst with different KOH/C mass ratios.

degree [32]. Further increasing the ratio led to a decrease in A_{BET} and V_{tot} . Over-activation of KOH covered the carbonized material surface and inhibited its pyrolysis. A_{BET} and V_{tot} subsequently decreased, and there was a balance between chemical etching and pyrolysis of the carbonized material during activation. At KOH:C = 3, A_{BET} and V_{tot} decrease to 579 m^2/g and 0.34 cm^3/g , respectively.

3.3. XRD results

XRD patterns of the precursor and Cu/C catalysts after activation in H_2 at various temperatures are shown in Fig. 4. The precursor consisted of crystallized Cu with weak diffraction peaks at 2θ of 43.11°, 50.45° and 73.92°. This was presumably

Table 2

Textural parameters of the Cu/C-850 catalyst with different KOH/C mass ratios.

KOH:C mass ratio	A_{BET} (m^2/g)	V_{tot} (cm^3/g)	V_{micr} (cm^3/g)	D_{BJH} (nm)	D_{HK} (nm)
0.5	535	0.28	0.26	2.06	0.64
1	1690	0.88	0.64	2.09	1.05
2	1149	0.57	0.54	2.00	0.62
3	579	0.34	0.28	2.33	0.72

Fig. 4. XRD patterns of Cu/C catalysts with different activation temperatures.

because of the partial reduction of CuO and Cu₂O, the decomposition products of Cu(NO₃)₂, by support surface carbon at 500 °C [16]. All catalysts treated in H₂ at > 650 °C exhibited patterns with predominant diffraction peaks, confirming the presence of Cu⁰. The intensity of Cu⁰ diffraction peaks increased with increasing temperature, indicating that Cu⁰ particle size also increased. The particle size estimated from the Scherrer equation increased with increasing activation temperature. It was found to be 28.3, 30.4 and 34.4 nm for catalysts activated at 650, 850 and 900 °C, respectively. Cu⁰ particles sintered into larger clusters at higher activation temperatures.

3.4. SEM and TEM results

Figure 5(a) and (b) shows typical SEM and TEM images of the Cu/C catalyst prepared at 850 °C. Figure 5(a) shows that an abundant pore structure formed throughout the entire sample. During oxidative carbonylation of methanol to DMC, macropores and mesopores favor the fast diffusion of reactants inside the catalyst. A quantity of micropores accelerates reactant sorption in the catalyst channels and improves efficiency. Cu particles were evenly distributed over the activated carbon surface and generally exhibited a spherical shape. Their diameter distribution was 11–26 nm, and their average size was 17 nm, as calculated by Nano Measurer Software from TEM image analysis. This differed slightly from those estimated from the XRD results.

3.5. XPS and elemental analysis

XPS and elemental analyses of the Cu/C catalysts prepared at different activation temperatures are shown in Table 3. Table 3 shows that the Cu 2p_{3/2} binding energies of the catalysts were centered at 933 eV, and corresponded to Cu⁰ and Cu⁺. The binding energies of Cu⁰ and Cu⁺ are similar, so distinguishing

Table 3

XPS and elemental analysis results of Cu/C catalysts with different activation temperatures.

<i>t</i> /°C	Cu 2p _{3/2} (eV)	CuLMM (eV)	α' (eV)	Cu concentration (wt%)
500	932.6	918.1	1850.7	12.56
650	933.1	917.0	1850.1	12.35
750	932.9	917.1	1851.0	13.52
850	933.2	914.3	1847.5	14.13
900	932.6	916.1	1848.7	20.03

them from the Cu 2p_{3/2} binding energy is difficult. α' values calculated from the sum of the kinetic and binding energies were instead used. α' of Cu⁰ and Cu⁺ are 1847 and 1851 eV, respectively [33]. A 2–3 eV shift toward lower binding energy occurred when Cu⁰ was highly dispersed and strongly interacted with the support. α' for catalysts activated at 500, 650 and 700 °C were 1850.7, 1850.1 and 1851.0 eV, respectively, and were attributed to Cu⁰.

α' exhibited significant decreases to 1847.5 or 1848.7 eV when activation temperature was increased to 850 or 900 °C, respectively. This was attributed to a stable graphitic layer dispersion and was caused by the polycondensation of carbon material surface functional groups at high temperature, resulting in a high degree of graphitization.

Element analyses in Table 3 show that Cu content changed little, as activation temperature increased from 650 to 850 °C. Cu content increased by ca. 7% for Cu/C-900 because collapse of the carbon structure brought about C–C bond cleavage. Negatively charged carbon atoms reacted with H₂ and resulting in an 'apparent' increased Cu content.

3.6. CO-TPD

Figure 6 shows CO-TPD profiles of Cu/C catalysts activated at different temperatures. Two major desorption features were exhibited by all catalysts. Catalysts activated at 750 and 850 °C exhibited desorption peaks at ca. 80–200 and 350–500 °C, respectively, with maxima of 122 and 402, and 107 and 417 °C, respectively. Peak maxima shifted to slightly higher temperatures for the catalyst activated at 900 °C. The lower temperature desorption peak was attributed to CO desorption from Cu⁰

Fig. 5. SEM (a) and TEM (b) images of the Cu/C-850 catalyst.

Fig. 6. CO-TPD profiles of Cu/C catalysts with different activation temperatures.

sites that were highly dispersed on the support surface [6,34–36]. The higher temperature desorption peak corresponded to the high temperature peak in the earlier TGA curve. It was attributed to CO desorption from alternative Cu^0 sites, which strongly interacted with the support. This indicated an enhanced adsorption ability of CO. The second desorption area of the Cu/C-850 was larger than that for any other temperature. This suggested that Cu^0 bonding with the support has occurred. The surface structure of the carbon support began to convert to graphitic carbon at higher temperature, which inhibited the rapid desorption of CO.

3.7. Catalytic activity

The effect of activation temperature on catalytic activity is shown in Fig. 7. Figure 7(a) and (b) shows that catalysts activated at $> 850^\circ\text{C}$ exhibited the highest activity and selectivity. Catalytic activity, as judged from STY_{DMC} and S_{DMC} , increased dramatically with increasing activation temperature. S_{DMC} and STY_{DMC} exhibited maximum values of 76.5% and 235.7 $\text{mg}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, respectively, at 850°C . Cu/C-900 exhibited a slight decrease in activity compared to Cu/C-850, presumably because of the formation of larger Cu^0 particles at higher temperature. The effect of activation temperature on activity was attributed to the surface area and total pore volume of the support. These two parameters of activated carbon greatly affect the STY and selectivity for DMC. They first increased and then decreased with increasing temperature and exhibited maximum values at 850°C . Activity was largely in accordance with the N_2 sorption results in Table 1. Further analysis showed that

gaseous K would diffuse into the carbon layer to form a new pore structure with activation temperature $> 760^\circ\text{C}$ (the boiling point of K). This was predominantly attributed to the intercalating and etching of KOH [37]. Part of the micropore structure expanded, resulting in a slight increase in micropore and mesopore volume. A higher temperature would destroy the pore structure, decreasing the surface area and total pore volume.

Micropores are important in the vapor phase oxidative carbonylation of methanol to DMC. Micropores accelerate the sorption of CH_3OH , CO and O_2 , and improve efficiency. Mesopores favor the fast diffusion of reactants inside the catalyst. The combination effect of these two factors results in the maximum catalytic activity of the Cu/C-850 sample in the synthesis of DMC, which is consistent with results of Li et al. [17]. They reported an AC support higher with specific surface area benefited the formation of active centers by the dispersion of copper salts.

Catalysis of the oxidative carbonylation of methanol to DMC by Cu/C catalysts activated at 850°C with different KOH/C mass ratios is shown in Fig. 8. S_{DMC} and STY_{DMC} first increased and then decreased as the KOH/C ratio changed from 0.5:1 to 3:1. When the ratio was 1:1, S_{DMC} and STY_{DMC} obtained their highest values of 76.4% and 233.8 $\text{mg}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, respectively. This is consistent with the results in Fig. 7, indicating that this method has good repeatability.

4. Conclusions

A $\text{Cu}(\text{NO}_3)_2/\text{starch}$ composite colloid was obtained using the

Fig. 7. The catalytic activities of Cu/C catalysts with different activation temperatures in the oxidative carbonylation of methanol. (a) STY of DMC; (b) DMC selectivity.

Fig. 8. The catalytic activities of Cu/C catalysts with different KOH/C mass ratios in the oxidative carbonylation of methanol. (a) STY of DMC; (b) DMC selectivity.

sol-gel method. After aging, drying, carbonization and KOH activation, a series of Cu/C catalysts were prepared, in which the Cu particle size was 10–30 nm. Activation temperature was important in forming the Cu/C catalyst pore structure. Surface area, micropore volume and total pore volume first increased and then decreased with increasing activation temperature. Micropore size remained largely constant. The optimized preparation conditions were a carbonization temperature of 500 °C, KOH/C mass ratio of 1:1 and activation temperature of 850 °C. A resulting surface area of 1690 m²/g and microporosity of 72.4% were achieved, from which the catalyst exhibited the highest activity. The Cu particle size and catalyst surface structure can be controlled using this method, and it has potential for wider use in catalysis.

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Graphical Abstract

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Synthesis of dimethyl carbonate over starch-based carbon-supported Cu nanoparticles catalysts

Jun Ren*, Changjiang Guo, Leilei Yang, Zhong Li
Taiyuan University of Technology

Carbon-supported copper nanocatalysts (Cu/C) were prepared from Cu(NO₃)₂ and starch by the sol-gel method, followed by high temperature carbonization and KOH activation.

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淀粉基炭负载纳米铜催化合成碳酸二甲酯

任 军*, 郭长江, 杨雷雷, 李 忠

太原理工大学煤科学与技术教育部和山西省重点实验室, 山西太原030024

摘要: 以硝酸铜和可溶性淀粉为原料, 经过溶胶-凝胶化过程、高温炭化和KOH活化得到炭负载铜催化剂(Cu/C), 采用扫描电镜、透射电镜、X射线衍射、热重-差热分析仪、 N_2 吸附和CO程序升温脱附对催化剂结构进行了表征, 并考察了它在甲醇氧化羰基化合成碳酸二甲酯(DMC)反应中的催化活性. 结果表明, 活化温度和KOH用量对催化剂的表面结构及金属铜粒子尺寸影响显著, 当活化温度为850 °C, KOH:C = 1 (质量比)时, Cu/C催化剂的比表面积达到1690 m^2/g , 铜纳米粒子平均晶粒尺寸为30.4 nm, 催化活性最高, DMC时空收率达到235.7 $mg \cdot g^{-1} \cdot h^{-1}$, 甲醇转化率和DMC选择性分别为1.6%和76.5%.

关键词: 淀粉; 溶胶凝胶法; 炭载体; 氢氧化钾活化; 碳酸二甲酯

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*通讯联系人. 电话/传真: (0351)6018598; 电子信箱: renjun@tyut.edu.cn

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1. 前言

甲醇是一种以煤或天然气为原料生产的大宗化学品, 其深度加工是许多国家竞相开发的重要研究领域. 在众多甲醇下游产品中, 绿色化学品碳酸二甲酯(DMC)近年来受到了极大的关注. DMC用途极为广阔, 可以取代光气、硫酸二甲酯、氯甲酸甲酯等剧毒或致癌化学品进行有机合成, 也可以作为高品质溶媒或燃油添加剂^[1]. 随着我国对机动车排放标准的进一步升级, DMC用于燃油添加剂的市场发展空间十分巨大.

在众多DMC合成工艺中, 甲醇气相氧化羰基化法以甲醇、CO和O₂为原料, 生产成本低, 产物选择性高, 是一条符合我国以煤为主要能源的重要绿色化工路线^[2]. 美国DOW化学公司最早使用CuCl₂-KCl/AC作为工业催化剂来生产DMC, 但是反应过程中Cl⁻容易发生流失, 导致设备腐蚀和活性逐渐下降^[3]. 双组分催化剂PbCl₂-CuCl₂/AC的活性高于CuCl₂/AC, 添加CH₃COOK会与PdCl₂或CuCl₂发生作用形成KCl, 可以抑制Cl⁻流失^[4]; 引入氨基^[5]有利于促进Cu²⁺/Cu⁺之间的氧化还原循环, 从而改善催化剂活性和稳定性. Cu₂(OH)₃Cl/AC催化剂在反应过程中Cu₂(OH)₃Cl逐渐转变为CuO和CuCl₂, 从而导致活性逐渐下降^[6].

King^[7]采用固态离子交换法制备的Cu(I)Y型分子筛在反应中初始活性高, 失活速度比CuCl₂/AC显著降低,

说明Cl⁻并非反应所必需. Li等^[8]制备的CuCl/MCM-41分子筛上DMC的选择性接近100%. Anderson等^[9]指出, Cu(I)X比Cu(I)ZSM-5催化活性高的原因在于形成了更多的Cu(I)活性位. Zhang等^[10]认为, Y型分子筛独特的结构使得CO容易与甲氧基结合离开催化剂表面, 因此Cu(I)Y比Cu(I)ZSM-5或Cu(I)MOR具有更高的DMC选择性. 采用固态离子交换法制备Cu(I)分子筛操作条件极为苛刻, 通常需要在高温(>550 °C)和惰性气体保护条件下进行长时间(>15 h)焙烧才能达到比较理想的效果^[7-10]. 然而, Zhang等^[11]研究发现, 仍然有~10 wt%的CuCl堵塞在分子筛孔道内, 不能发生离子交换作用, 证明Cl⁻的残留是不可避免的, 而处理温度过高则会导致分子筛骨架脱铝^[8], 成为Cu(I)分子筛应用难以逾越的瓶颈.

完全无氯的铜基催化剂可以从根本上克服Cl⁻流失导致的失活问题. King^[7]制备的Cu₂O/Y催化剂具有较高的初始活性, 但反应1.5 h后催化剂活性迅速下降. Richter等^[12]将Cu(NO₃)₂或Cu(OH)₂浸渍在Y型分子筛上得到无氯的Cu/Y分子筛催化剂, 在甲醇氧化羰基化反应中表现出高活性. 李忠等^[13-15]研究发现, 采用高温热分解醋酸铜、硝酸铜可以制备出高活性的Cu₂O/AC催化剂, 通过硝酸或氨水对活性炭载体进行改性可进一步提高催化活性^[16,17]. 此外, 基于密度泛函理论, 采用广义梯度近似方法结合周期平板模型, 对Cu₂O(111)非极性表面上CO和CH₃O的吸附和共吸附进行了系统的研究, 为甲醇

氧化碳基化反应中CO和CH₃O与催化剂表面作用方式以及表面吸附分子间的相互作用提供了重要的信息。

溶胶-凝胶法容易在催化剂中均匀定量地掺入一些微量元素,实现分子水平上的均匀掺杂^[18]。以淀粉为碳源和凝胶材料被广泛应用于新型炭材料的制备^[19,20]。本文以淀粉为原料,采用KOH活化法^[21–24]制备了淀粉基炭载铜催化剂,用于甲醇气相氧化碳基化合成DMC反应中,考察了活化温度及KOH用量对催化剂孔隙结构、晶体结构及催化性能的影响。

2. 实验部分

2.1. 催化剂制备

将2.00 g Cu(NO₃)₂·3H₂O (AR, 天津市光复科技发展有限公司)溶于50 mL蒸馏水中,然后加入10.65 g可溶性淀粉(AR, 天津市巴斯夫化工有限公司),在搅拌条件下升温到60–80 °C,直至形成稳定的胶体;湿凝胶在25 °C老化10 d,置于真空烘箱中在80 °C干燥12 h,然后放入管式炉内在N₂气流(30–40 mL/min),于500 °C炭化处理2 h;样品冷却后在球磨机中进行研磨,取100目筛以下物作为原料,将KOH (AR, 天津市风船化学试剂科技有限公司)与原料按照不同的质量比进行混合,放入管式炉内在H₂气流(30–40 mL/min)中加热至不同温度(650, 750, 850和900 °C),恒温活化处理2 h,自然冷却至室温后取出,用去离子水洗涤至中性,烘干后得到Cu/C催化剂。样品记为Cu/C-*t*, *t*为活化温度(500, 650, 750, 850和900 °C)。 *t* = 500 °C的样品为催化剂前驱体。

2.2. 催化剂表征

采用德国NETZSCH公司的STA-409C型热分析仪进行热重(TG-DTG)分析, N₂流量50 mL/min, 升温速率10 °C/min。

采用日本理学D/max 2500型粉末X射线衍射(XRD)仪进行晶体观察。 Cu K_α 射线($\lambda = 0.154$ nm), 石墨单色器, 管电压40 kV, 管电流100 mA, 扫描速率8°/min, 扫描范围 $2\theta = 5^\circ - 80^\circ$ 。

采用日本JEOL JSM-6701F型扫描电子显微镜进行表面形貌观察。

样品颗粒经研磨后悬浮在乙醇溶液中, 并经超声波震荡分散在铜网上, 采用荷兰Tecnai G2 F20型场发射透射电子显微镜(HR-TEM)观察表面形貌和粒度大小。

采用北京精微高博科学技术有限公司的JW-BK122W型吸附仪, 以N₂为吸附质, 在-196 °C下测定试样的吸附等温线, 采用BET法计算样品的总比表面积,

t-plot法计算微孔的比表面积, BJH法求得试样的中孔孔径分布, 微孔孔径分布通过HK法计算。

样品用VG Scientific ESCALab220i-XL型光电子能谱(XPS)仪分析, 激发源为Al K_α X射线, 功率约300 W。电子结合能用污染碳的C 1s峰(284.6 eV)校正。

Cu 含量元素分析采用碘量法检测, 样品用HCl+H₂O₂溶解, 加热煮沸除去H₂O₂, 加氨水调节pH至刚刚有沉淀生成; 依次加入HAc, NH₄HF和KI后用Na₂S₂O₃溶液滴定至淡黄色, 加入淀粉指示剂和NH₄SCN溶液, 继续以Na₂S₂O₃溶液滴定, 终点为蓝色消失。

采用FINESORB-3010型全自动吸附仪(浙江泛泰仪器有限公司)进行CO程序升温脱附(CO-TPD)实验, He气流速50 mL/min, 以5 °C/min的速率升温至200 °C, 恒温吹扫30 min, 降温至35 °C, 再切换成10% CO-90% He混合气(流速50 mL/min), 系统稳定后, 以10 °C/min的速率升温至600 °C, 用TCD检测CO脱附信号。

2.3. 催化剂的评价

催化剂活性评价在固定床反应器中进行, 称取0.20 g催化剂装入内径5 mm, 管长500 mm的反应管内, 甲醇由微量进样泵引入, 随着CO和O₂两路气体混合进入汽化室, 汽化混合后进入反应器, 流过催化剂床层, 反应后的混合物经气液分离器分离, 液相混合物用GC-950型气相色谱仪分析。在标准状态下, 原料气CO和O₂流量分别为55和5 mL/min, 甲醇进料流量0.056 mL/min, 于140 °C 0.5 MPa条件下, 反应10 h。液相混合物中的甲醇、DMC、甲酸甲酯、二甲氧基甲烷用毛细管柱HP-INNO-WAX柱(30 m × 530 μm × 1 μm)分离, FID检测器检测。

3. 结果与讨论

3.1. TG/DTA和TG/DTG分析

炭化的实质是材料中的有机物和无机物在惰性气氛下发生高温热裂解的物理化学过程, 包括热分解反应和缩聚反应^[25], 以增加材料的孔隙率和机械强度。在炭化过程中, 较慢的升温速率有利于初始孔隙的形成, 使样品中的挥发组分和分解产物相继逸出, 保持足够的恒温时间, 可以确保原材料发生完全炭化, 形成理想的表面结构。

图1为Cu(NO₃)₂/淀粉复合胶体的TG/DTA和TG/DTG曲线。可以看出, 复合胶体的热失重过程主要分为三个阶段: (1)室温–138 °C范围内, 归结为胶体内在水分的挥发所致, 在DTA曲线上有一个明显的吸热峰, 失重率为1.6%; (2) 138–184 °C, 是由于Cu(NO₃)₂剧烈分

解引起的, 其中160 °C时热解反应最剧烈, 在此期间样品逐渐分解为CuO, NO₂和O₂, 生成的气体产物不断逸出, 热失重为11.9%; (3) 240–290 °C, 对应于淀粉发生热裂解释放出气体产物为H₂O和CO₂^[26–28]. 淀粉在300–440 °C时热解速率较高, 反应过程与多糖热解类似, 释放出的气体产物主要是CO, CO₂, H₂O, CH₄, C₂H₄和甲醛^[28,29], 样品在该温度段的失重率达到83.2%; 此外, 500 °C以上样品质量几乎没有发生变化, 说明热解过程已经结束, 但DTA曲线显示此过程仍有较弱的吸热行为, 这是因为高温下炭的结构逐渐向石墨化方向转变, 形成非常有序的碳结构^[30].

3.2. N₂吸附分析

图2(a)为不同活化温度下制备的Cu/C催化剂样品的N₂吸附-脱附等温曲线. 可以看出, 经过500和650 °C活化的样品没有形成明显的孔结构, 在750 °C以上活化的样品的吸-脱附等温线表现为I型和IV型的混合类型, 在 $p/p_0 < 0.1$ 的范围内吸附量急剧增加, 说明存在大量的微孔^[31]; 在 $p/p_0 > 0.4$ 的区域内吸附量逐渐增加, 并出现明显的脱附滞后回环, 说明样品中形成了部分介孔. 图2(b)和(c)是分别采用BJH法和HK法计算的催化剂样品的介孔和微孔孔径分布曲线, 表1为各催化剂样品的结构参数. 可以看出, Cu/C催化剂的孔道以微孔为主, 其尺寸主要分布在0.5–1.2 nm, 同时存在一定量的介孔结构. 表1结果表明, 所有催化剂样品属于典型的微孔材料, 其微孔比表面积都很大, 而大量的微孔结构可以使反应物分子快速地在通道里吸脱附从而提高反应效率. 由图2(c)可知, 随着活化温度的升高, 催化剂的微孔孔径变化不大, 微孔的比表面积先增加后减小, 于活化温度为850 °C时达到最大值. 从表1可以看出, 随着活化温度的升高, 催化剂的比表面积、微孔孔容和总孔容先增大后减小, 但平均孔径几乎不变. 由TG/DTA结果可知, 复合胶体在240 °C开始发生解聚和热解反应, 并在较高温时发生分子的缩聚、环化等一系列反应, 形成交联的芳香环体系. 活化温度升高, 淀粉基炭材料中活性碳原子数较多, 与KOH反应活性增强, 因此孔容不断增加. 当活化温度达到850 °C时, 催化剂的比表面积达到最大值, 为1690 m²/g, 总孔容达到0.88 cm³/g, 此时微孔率达到72.4%. 然而, 当活化温度过高时, 由于炭材料中大量的活性碳原子与KOH过度反应, 形成的孔隙孔径过多, 从而引起结构的部分坍塌, 孔容降低.

在850 °C活化制备的不同KOH/C质量比的催化剂样品的N₂吸附-脱附等温曲线见图3, 样品的结构参数见

表2. 由表2可知, 随着KOH/C质量比的提高, 样品的 A_{BET} , V_{micr} 和 V_{tot} 先增大后减小, 但 D_{BJH} 几乎不变, D_{HK} 为1 nm左右. 当KOH:C = 0.5时, A_{BET} 仅为534 m²/g; 当KOH/C从0.5升到1时, 样品的比表面积迅速增加, 达到1690 m²/g, 总孔容达到0.88 cm³/g, 同时微孔率达到72.4%, 这是炭材料的高温热解过程和足量KOH化学蚀刻共同作用的结果^[32]. 随着KOH含量的进一步提高, 过多的KOH就会覆盖原本比表面积(4 m²/g)很小的炭表面, 抑制炭材料的热解, 尽管过量的KOH会促进化学蚀刻, 但总体上仍使比表面积和总孔体积降低, 当KOH:C = 3时, A_{BET} 和 V_{tot} 分别降为579 m²/g和0.34 cm³/g.

3.3. XRD结果

图4为不同活化温度下制备的Cu/C催化剂及其前驱体的XRD谱. 可以看出, 前驱体存在较弱的单质铜晶相衍射峰(43.11°, 50.45°和73.92°), 这是由于炭化温度达到500 °C时, 载体表面上的一部分炭将Cu(NO₃)₂的分解产物CuO或Cu₂O还原所致^[16]. 随着活化温度的升高, 样品中单质铜的衍射峰逐渐增强, 表明Cu⁰晶粒逐渐长大. 根据Scherrer公式计算可知, 在650, 850和900 °C活化的催化剂上Cu⁰晶粒大小分别为28.3, 30.4和34.4 nm. 可见, 升高活化温度导致催化剂表面的Cu⁰晶粒聚集长大.

3.4. SEM和TEM结果

图5(a)和(b)分别为850 °C活化条件下制备的Cu/C催化剂的SEM和TEM照片, 由图可观察到样品表面形成丰富的孔洞结构. 在甲醇氧化羰基化合成DMC反应中, 大孔和中孔可以使反应物分子快速的传输, 而大量的微孔结构能使反应物分子快速地在通道里吸脱附从而提高反应效率.

由图5(b)可见, 该样品Cu呈准球形, 均匀分散在炭材料表面. 用Nano Measurer软件统计出来的晶粒尺寸为11–26 nm, 平均尺寸为17 nm, 这与XRD的分析结果略有差别.

3.5. XPS和元素分析

不同活化温度Cu/C催化剂的Cu 2p_{3/2}和Cu LMM峰值见表3. 由于Cu⁺和Cu⁰的结合能非常接近, 由Cu 2p_{3/2}峰难以区分, 因此我们依据Cu LMM俄歇谱线的动力学能与Cu 2p_{3/2}峰的结合能之和, 即 α' 值来鉴别样品中的Cu⁺和Cu⁰化学态. 一般情况下, Cu⁺和Cu⁰的 α' 值分别为1847和1851 eV, 当Cu⁰以高度分散态存在并且与载体产生极强的相互作用时, α' 值会降低2–3 eV^[37]. 由表3可见, 在500, 650和700 °C活化制得的催化剂样品的 α' 值分别为1850.7, 1850.1和1851.0 eV, 显然属于Cu⁰. 当活化温

度升到850和900 °C时, α' 值依次降低为1847.5和1848.7 eV. 分析认为, 随着活化温度升高, 炭材料表面官能团在高温下进一步发生缩聚反应, 石墨化程度逐渐增高, C–C键之间的作用力增强, 芳香环越来越稳定, 在这种情况下 Cu^0 趋向于石墨层水平方向上的稳定分散, 因此导致 α' 值显著下降.

还可以看出, 650–800 °C活化温度下制得的Cu/C催化剂中Cu含量变化不大, 但900 °C时的增加了7%左右. 这是因为高温下炭结构的坍塌促使了C–C键之间的断裂, 带负电的碳原子与 H_2 反应使Cu元素的相对含量提高.

3.6. CO-TPD分析

图6为不同活化温度下制备的Cu/C催化剂的CO-TPD谱. 由图可见, 所有催化剂都出现两个CO脱附峰, 750和800 °C活化的催化剂样品的脱附峰出现在80–200和350–500 °C的两个温度区间, 最高值分别为122和402 °C及107和417 °C, 而900 °C活化的催化剂的两个脱附峰温明显升高. 分析认为, 低温脱附峰归属于吸附在炭表面的高分散单质Cu上CO的脱附^[6,33–35]. 此外, 各Cu/C催化剂在400 °C处还出现一个明显的脱附峰, 与TG曲线中高温失重峰相对应, 归属于吸附在与载体发生强相互作用的Cu上CO的脱附, 说明形成强相互作用的Cu吸附CO的能力有所增强. 而850 °C活化制得催化剂中形成强相互作用的Cu明显最多. 当活化温度达到900 °C, 炭材料表面上的结构在高温下趋向于石墨化, 从而不利于CO的快速脱附.

3.7. 催化活性

图7为不同活化温度下制备的Cu/C催化剂上甲醇氧化羰基化反应结果. 可以看出, 未经活化的催化剂无活性; 在 H_2 气氛中, 当催化剂于650 °C活化后, DMC的选择性和STY也没有明显的变化, 催化剂也没有活性. 当活化温度大于750 °C时, 甲醇的转化率和DMC的时空收率迅速增加, 分别为65.2%和156.7 $\text{mg} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$. 当热处理温度升至850 °C时, 相应催化剂活性进一步提高, DMC选择性和时空收率分别达到76.5%和235.7 $\text{mg} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$. 当活化温度为900 °C时, 催化剂活性有所降低, 这是由于较高温度制备的催化剂中 Cu^0 的晶粒较大所致. 由前文

可知, 随着活化温度的升高, 活性炭的比表面积和总孔体积均是先增大后减小, 于850 °C时达到最大, 因此活性与表1中 N_2 吸附的测试结果是一致的. 由此可见, 当活化温度较低时, 载体的比表面积和孔容都较小, 而催化剂的活性和选择性与载体的这两个参数密切相关. 当活化温度超过金属钾沸点760 °C时, 钾蒸气会扩散入碳层内部形成新的孔结构, 同时部分微孔被扩大, 因此微孔和中孔体积均有所增加. 然而, 当温度过高时, 导致孔结构遭破坏, 孔体积和比表面积又大幅下降.

对于甲醇氧化羰基化合成DMC反应, 微孔起着最为重要的作用, 大量的微孔结构能使反应物小分子(CH_3OH , CO 和 O_2)在通道中快速吸脱附, 从而提高反应速率; 一定量的介孔结构有利于反应物分子快速传输, 但太多又不利于反应物分子有效的接触, 二者共同作用使得Cu/C-850样品的催化活性达到最高, 与李忠等^[17]的活性炭载体较高的比表面积有利于铜盐的分散而形成更多的活性中心的研究结果相吻合.

图8为不同KOH与炭的质量比于850 °C热处理制备的Cu/C催化剂上甲醇氧化羰基化反应10 h内DMC时空收率和选择性. 可以看出, 随着KOH与炭质量比的升高, DMC的选择性和时空收率均先增加后降低至1时达最大, 分别为76.4%和233.8 $\text{mg} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, 与上文结果一致(76.5%和235.7 $\text{mg} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$), 说明用该法制备Cu/C催化剂重复性很好.

4. 结论

采用溶胶-凝胶法制备出 $\text{Cu}(\text{NO}_3)_2$ /淀粉复合胶体, 经过老化、干燥、高温炭化和KOH活化得到炭负载纳米铜催化剂(Cu/C), 铜纳米粒子尺寸为10–30 nm. 活化温度对催化剂孔隙结构的形成起着关键作用, 随着活化温度从500升至900 °C, 比表面积、微孔孔容和总孔容先增大后减小, 而微孔的孔径变化不大. 在炭化温度为500 °C、 $\text{KOH}:\text{C} = 1$ 、活化温度为850 °C条件下制备的Cu/C催化剂的比表面积高达1690 m^2/g , 微孔孔容率为72.4%, 该催化剂在甲醇氧化羰基化反应中的催化活性最高. 此法可以方便调控Cu/C催化剂的表面结构和金属Cu粒子的尺寸, 有望广泛应用于催化领域.