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Article

Effect of NH_4^+ exchange on CuY catalyst for oxidative carbonylation of methanol

Yuchun Wang^{a,b}, Huayan Zheng^a, Zhong Li^{a,*}^a Key Laboratory of Coal Science and Technology of Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, Shanxi, China^b Department of Applied Chemistry, Yuncheng University, Yuncheng 044000, Shanxi, China

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ABSTRACT

NaY and ion exchanged NaNH_4Y zeolite with NH_4NO_3 were used as the support to prepare CuY catalysts by a high temperature anhydrous interaction between the support and copper (II) acetylacetonate $\text{Cu}(\text{acac})_2$. The catalysts were used for the oxidative carbonylation of methanol to dimethyl carbonate (DMC) at atmospheric pressure. The textural and acidic properties of NaNH_4Y zeolite and the CuY catalysts were investigated by X-ray diffraction, scanning electron microscopy, N_2 adsorption-desorption, temperature programmed reduction of H_2 , X-ray photoelectron spectroscopy and temperature programmed desorption of NH_3 . With increasing NH_4NO_3 concentration, the NH_4^+ exchange degree increased while the crystallinity of the zeolite remained intact. Crystalline CuO was formed when the NH_4^+ exchange degree of NaNH_4Y was low, and the corresponding CuY catalyst showed low catalytic activity. With increasing of the NH_4^+ exchange degree of NaNH_4Y , the content of surface bound Cu^+ active centers increased and the catalytic activity of the corresponding CuY catalyst also increased. The surface bound Cu^+ content reached its maximum when the NH_4^+ exchange degree of NaNH_4Y reached towards saturation. The CuY exhibited optimal catalytic activity with 267.3 mg/(g·h) space time yield of DMC, 6.9% conversion of methanol, 68.5% selectivity of DMC.

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1. Introduction

Owing to its negligible toxicity, low bioaccumulation and high reactivity, dimethyl carbonate (DMC) has attracted much attention for the so-called ‘sustainable society’ and ‘green chemistry’ chemicals [1–4]. Oxidative carbonylation of methanol is one of the most promising approaches to produce DMC [5,6]. In the process, supported Cu-based catalysts exhibit excellent catalytic activity and has attracted extensive interest. Among these catalysts, copper-exchanged zeolite Y (CuY) is interesting for the oxidative carbonylation of methanol to DMC

[7–9].

It is well known that the surface-bound Cu^+ on the CuY catalyst is the active species for the carbonylation reaction [10–14]. Richter et al. [15] prepared a $\text{CuO}/\text{NH}_4\text{Y}$ zeolite by the deposition-precipitation method. After calcination at 400 °C in static air for 2 h, the zeolite has only marginal activity for the carbonylation reaction. The high activity achieved by the inert activation procedure at 700–750 °C for 15 h is associated with the formation of a favorable active site Cu^+ . Zhang et al. [8] proved that on the CuY catalyst, methanol was absorbed on surface bound Cu^+ to form $\text{Cu}-\text{OCH}_3$ and CO inserted into

^{*} Corresponding author. Tel/Fax: +86-351-6018526; E-mail: lizhong@tyut.edu.cn

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Cu–OCH₃ bonds resulting in the formation of DMC, and insertion of CO is the rate limiting step. However, on Cu-ZSM-5 and Cu-MOR catalysts, because the formation of Cu–OCH₃ on surface bound Cu⁺ was limited due to the strong adsorption of CO, dimethoxy methane (DMM) was the primary product.

The traditional way for the surface bound Cu⁺ active center to be introduced into Y zeolite is that the H⁺ ions (Brönsted acidic sites) of HY are exchanged by Cu⁺ of CuCl during the heating of a physical mixture of CuCl and HY. That is, a solid state ion exchange (SSIE) formed the effective active sites for oxidative carbonylation [16]. The distribution of Brönsted acidic sites in Y zeolite affects the location of the Cu active species, and further affects the catalytic performance of oxidative carbonylation. Huang et al. [17] established a quantitative relationship between the amount of Brönsted acid sites and catalytic activity for oxidative carbonylation over CuY catalysts with different Si/Al ratios. Zhang et al. [18] also investigated the activity of CuY with different Si/Al ratios for the oxidative carbonylation of methanol to DMC systematically by a density functional theory method. They indicated that the CuY zeolite with a Si/Al ratio = 6.5 had the highest catalytic activity.

However, for zeolite Y with different Si/Al ratios, there are differences in not only the Brönsted acid sites, but also other factors in the catalytic activity such as the composition of the framework, bond angle of Si–O–Al and degree of dispersion of the Al ions [19]. Thus, there is a need for a more valid way to evaluate the quantitative relationship between the Brönsted acid sites of the support and catalytic activity of the CuY. Our preliminary investigations [20,21] showed that Cu(acac)₂ adsorbed and highly dispersed in Y zeolite support due to its sublimation. Cu²⁺ of Cu(acac)₂ ion exchanged with NH₄⁺ of NH₄Y at a lower temperature of 174 °C, then during activation, Cu(acac)₂ is easily decomposed and the decomposition products are useful for the Cu⁺ active center, resulting in the formation of more active centers. The unreacted and adsorbed Cu(acac)₂ on Y zeolite decomposed to form CuO species which improved the catalytic activity of the Cu⁺ active center. More importantly, NaY zeolite does not have a solid state ion change with copper (II) acetylacetonate Cu(acac)₂ during the anhydrous heating treatment of the physical mixture. However, an ion exchange reaction between NH₄Y zeolite and Cu(acac)₂ does occur. Compared with SSIE, NH₄⁺ of NaNH₄Y plays the same role as H⁺ of HY, which provides the exchangeable sites for ion exchange of copper ions, and forms surface bound-Cu²⁺ on the CuY. Moreover, the released NH₃ promotes the reduction of surface bound-Cu²⁺ to form the surface bound Cu⁺ active center for oxidation carbonylation of methanol to DMC.

In the present study, we studied the relationship between NH₄⁺ of the NaNH₄Y support and catalytic activity of CuY prepared by high temperature anhydrous interaction (HAI) between Cu(acac)₂ and NaNH₄Y. First, the CuY catalysts from the NaNH₄Y support with different NH₄⁺ ion exchange degrees were prepared by HAI. Then the activities of the CuY catalysts for oxidative carbonylation of methanol were evaluated. Detailed characterization of the CuY catalysts were also performed by X-ray diffraction (XRD), scanning electron microscopy (SEM), N₂ adsorption-desorption, temperature-pro-

grammed reduction of H₂ (H₂-TPR), X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption of NH₃ (NH₃-TPD). The major objectives were to establish the relationship between the catalytic performance and NH₄⁺ exchange degree of NaNH₄Y support.

2. Experimental

2.1. NaNH₄Y preparation

10.003 g commercial NaY zeolite (Si/Al = 2.7) was added to 100.00 mL NH₄NO₃ aqueous solution with the concentration of 0.10, 0.30, 0.50 mol/L, and stirred to ion exchange for 4 h at 30 °C. Then, the suspension was filtered and the resulting cake was washed with deionized water several times and dried at 100 °C for 24 h. The procedure was repeated once and twice in the NH₄NO₃ aqueous solution (0.50 mol/L). The final solid material was designated as NaNH₄Y-X zeolite with the NH₄⁺ exchange degree of X.

2.2. Catalyst preparation

According to the literature [21], the typical preparation of the CuY catalyst included two stages. In the first stage, 5.001 g Y zeolite support and 2.454 g Cu(acac)₂ were mixed and ground well with a mortar and pestle to form an intimate gray-blue mixture. Then the mixture was heated in the muffle furnace from the ambient temperature to 250 °C at 3 °C/min, and then held at 250 °C for 4 h. The mixture turned brown and was named as precursor. In the following activation stage, the precursor material was activated to form the CuY catalyst by heating from the ambient temperature to 650 °C at a heating rate of 3 °C/min and at 650 °C for 4 h. The CuY catalysts were designated as CuY-X. The catalyst support was NaNH₄Y-X zeolite with the NH₄⁺ exchange degree of X. All the prepared catalysts were stored in a desiccator and pressed to 40–60 mesh particles before the catalytic tests.

2.3. Characterization

The sodium content was determined by a VARIAN AA240FS atomic absorption spectroscopy (AAS). The test solution was prepared by the following steps. A mixture of 0.202 g fresh catalyst and 2.012 g KOH was calcined at 500 °C for 6 h. Because the excess base destroyed the crystal structure of Y zeolite, Cu, Si and Al existed in the form of dissolvable compounds in hydrochloric acid. Then the calcined mixture was digested in a hydrochloric acid solution and diluted in a 250.00 mL volumetric flask with deionized water. Then 5.00 mL of this solution was transferred to a 100.00 mL volumetric flask, diluted with deionized water to volume (Cu solution concentration 1–5 mg/L for the AAS experiment). Finally, 50 mL of this solution was used to test the actual Cu content.

XRD patterns were obtained using Cu K_α radiation (λ = 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 65° at a scanning rate of 8°/min.

BET surface areas and pore volume of the CuY catalyst were determined from N₂ physisorption measurements on a Micromeritics ASAP 2010 instrument. The samples were first outgassed under vacuum at 90 °C for 1 h and at 350 °C for 15 h. The total surface area was obtained by the BET equation using the relative pressure range of 0.05–0.16 in the linear part of the nitrogen adsorption isotherm (molecular cross-sectional area for N₂ of 0.162 nm²). The micropore and mesopore volumes were calculated by the *t*-plot and BJH method, respectively.

Morphology analysis was performed by a S-4800 field emission scanning electron microscope (SEM). The powder samples were carefully placed on a double-sided tape with the aluminum stub as the base. The observations were made at different magnifications.

NH₃ temperature programmed decomposition (NH₃-TPDec) of Y zeolite was performed on a Micromeritics Autochem II 2920 chemical adsorption instrument with a thermal conductivity detector (TCD). 0.3003 g sample was loaded in a U-shaped quartz tube and heated from 50 to 600 °C at 10 °C/min in He (30 mL/min). Ammonium gas released from the decomposition was continuously monitored by a TCD. Before detection, the gas flow was conducted through a KOH trap to remove desorbed water.

NH₃-TPD was carried out on a Micromeritics Autochem II 2920 chemical adsorption instrument. 20 mg sample was loaded in a U-shaped quartz tube and first degassed at 300 °C for 0.5 h in He (30 mL/min). After degassing, the temperature was dropped to 50 °C, and then 15 vol% NH₃/He (30 mL/min) was introduced into the sample cell to allow the sample to absorb ammonia. After saturated adsorption, the temperature of the sample was raised from 50 to 600 °C at 10 °C/min. The ammonia gas released by desorption was continuously monitored by a TCD.

H₂-TPR was performed on a Micromeritics Autochem II 2920 chemical adsorption instrument. First, 20 mg sample was loaded in a U-shaped quartz tube and was degassed at 300 °C for 60 min in N₂ (30 mL/min), then cooled to room temperature. The gas was switched to 10 vol% H₂ in argon flow, and the sample was heated to 1000 °C at 10 °C/min. Hydrogen consumption was monitored by a TCD. The effluent gas was passed through a liquid nitrogen cold trap to remove water before detection.

XPS data were collected on an on Scientific ESCALab220i-XL electron spectrometer equipped with a 300 W Al K_α X-ray source with a Thermo-VG. The catalyst holder was placed in a fast entry air load-lock chamber without exposure to air and the pressure was maintained at 3×10⁻⁷ Pa overnight. Then the catalyst holder was transferred to the analysis chamber for XPS study. The binding energy and the Auger kinetic energy scales were referenced to the C1s line at 284.6 eV from adventitious carbon.

2.4. Catalytic tests

Catalytic measurements were performed on a continuous fixed bed microreactor (Φ 8 mm × 500 mm) under atmospheric pressure with an online Agilent 6890 gas chromatograph (GC).

0.6 g (about 1.5 mL) catalyst sample was packed in the tubular reactor and the reactor was positioned in the reactor furnace. 0.05 mL/min methanol was fed into by a constant flow pump (2PB-05) and vaporized in the pre-heater. In the meantime, 55.0 mL/min CO and 5.5 mL/min O₂ were 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 activity test time was 10 h and testing temperature was 140 °C.

The gas products were analyzed by an online GC with three valves and four columns every 12 min. The products flowed through the HP-PLOT/Q capillary column (30 m × 0.53 μm × 40 μm). The organic products were held back. Then the inorganic products flowed through the Poropak-Q packed column: CO₂ first flowed out and entered a TCD and was detected; second, CO and O₂ were separated by the HP-PLOT Molesieve/5A capillary column (30 m × 0.53 μm × 25 μm) and detected by TCD. The products flowed through the HP-INNOWax (30 m × 0.53 μm × 1 μm) capillary column and into a flame ionization detector (FID), thus MeOH, methyl formate (MF), dimethoxymethane (DMM), dimethyl ether (DME) and DMC were detected.

3. Results and discussion

3.1. Characterization

In order to determine the NH₄⁺ exchange degree of NaNH₄Y zeolite, the Na⁺ and NH₄⁺ contents were determined by AAS and NH₃-TPD, respectively. Fig. 1 presents the profiles of NH₃-TPDec from NaNH₄Y with different NH₄⁺ exchange degree (*X*) with temperature rise. There were three peaks over all samples and they were enhanced gradually with the increase of the NH₄⁺ exchange degree. The released NH₃ amount was determined by the peak area. Then combined with the content of the Na⁺ determined by AAS, the NH₄⁺ exchange degree was

Fig. 1. Profiles of NH₃ released from the decomposition of NaNH₄Y with different NH₄⁺ exchange degree during temperature programmed inert heating. Heating rate 10 °C/min, sample weight 0.3 g, He 30 mL/min (1) NaNH₄Y-0; (2) NaNH₄Y-18; (3) NaNH₄Y-46; (4) NaNH₄Y-63; (5) NaNH₄Y-68; (6) NaNH₄Y-69.

Table 1Na⁺ content, NH₄⁺ content and NH₄⁺ exchange degree of NaNH₄Y.

Sample	NH ₄ NO ₃ concentration (mol/L)	Ion exchange times	Na ⁺ content ^a (mmol/g)	NH ₄ ⁺ content ^b (mmol/g)	Exchange degree (%)
NaNH ₄ Y-0	0	1	3.80	0	0
NaNH ₄ Y-18	0.1	1	3.12	0.70	18.3
NaNH ₄ Y-46	0.3	1	2.03	1.76	46.4
NaNH ₄ Y-63	0.5	1	1.41	2.42	63.2
NaNH ₄ Y-68	0.5	2	1.27	2.72	68.1
NaNH ₄ Y-69	0.5	3	1.26	2.77	68.7

^a From AAS; ^b From NH₃-TPDec.

calculated, as listed in Table 1. The initial increase of the NH₄⁺ exchange degree was very obvious. Then the increments were small with further increase of the NH₄NO₃ solution concentration. When the concentration of the NH₄NO₃ solution was 0.5 mol/L and the NaY zeolite ion exchanged twice, the NH₄⁺ exchange degree reached 68.1%, 7.7% higher than that of NaY ion exchanged once. The NH₄⁺ exchange degree of NaY ion exchanged three times only increased 0.9% more. So when NaY zeolite was ion exchanged with 0.5 mol/L NH₄NO₃ solution twice, the NH₄⁺ exchange degree was beginning to stabilize and reached the maximum.

Fig. 2(a) shows the XRD patterns of the NaNH₄Y samples with different NH₄⁺ exchange degrees. Compared with NaNH₄Y-0 zeolite, the diffraction peak intensity of the other NaNH₄Y zeolites decreased slightly. Sato et al. [22] found that ion exchange of NaY with (NH₄)₂SO₄ resulted in structural changes and the relative crystallinity of the NaY decreased by approximately 20% after the first ion exchange. In the second and third ion exchanges, the structural changes depended on the Si/Al ratio of the starting NaY zeolite. Y zeolite with a medium Si/Al ratio of 2.8 retained their high crystallinity. Compared with the results reported by Sato et al. [22], the reduction of the crystallinity of Y zeolite was less in this study. This may be due to the medium Si/Al ratio of 2.7 and the low concentration of the NH₄NO₃ solution. These NaNH₄Y samples with different NH₄⁺ exchange degrees were used as the support to

prepare the CuY catalysts by HAI between NaNH₄Y and Cu(acac)₂. The XRD patterns of the CuY catalysts are presented in Fig. 2 (b). For all the CuY catalysts, the characteristic diffraction peaks of Y zeolite were observed. This indicated that the structure of the Y zeolite remained after the ion exchange of NH₄NO₃ and succeeding heat treatment. It is worth noting that the CuY-68 catalyst exhibited almost no crystalline copper oxide, but other catalysts contain crystalline CuO. CuO (tenorite, synthetic, PDF-Nr. 48-1548) has intense diffraction peaks (relative intensities in parentheses) at $2\theta = 35.418^\circ$ (37), 35.544° (100), 38.709° (99), 38.903° (21) and 48.717° (30). The two most intense diffraction peaks at $2\theta = 35.544^\circ$ and 38.709° can clearly be distinguished. There was no indication for the presence of crystalline Cu₂O or metallic Cu. With the increase of the NH₄⁺ exchange degree, the XRD peak intensities of crystalline CuO decrease gradually. The results may indicate that the content of crystalline CuO decreased or the dispersion of CuO species became better.

The textural properties and porous structure of NaNH₄Y samples with different NH₄⁺ exchange degrees and the CuY catalysts were characterized by N₂ adsorption and the results were shown in Table 2. The specific surface area of the Y zeolite decreased slightly from 797.0 to 775.5 m²/g with increase of the NH₄⁺ exchange degree. This was because the pore structure of the Y zeolite remained intact, which was proved by XRD. After loading of Cu, the surface area of the CuY catalyst was less than that of the support. When the NH₄⁺ exchange degree was zero, the specific surface area of the CuY-0 catalyst dropped to 647.9 from 797.0 m²/g for the support and the pore volume decreased from 0.35 to 0.27 cm³/g. Combined with the H₂-TPR and SEM results, this was because the pores of the Y zeolite have been partly blocked by CuO. With increase of the NH₄⁺ exchange degree, the CuO amount decreased, and there was a reduced specific surface area. That eventually resulted in the increase of the specific surface area of the CuY catalyst with increase of the NH₄⁺ exchange degree.

Fig. 3 shows the SEM images of the CuY catalysts. For all the CuY catalysts, the octahedron morphology with smooth crystal faces and sharp edges was clearly visible, and CuO species were

Fig. 2. XRD patterns of NaNH₄Y with different NH₄⁺ exchange degrees (a) and the prepared CuY catalysts (b).

Table 2

Specific surface area and pore volume of catalysts with different Cu loadings.

Sample	S_{BET}^a (m^2/g)	S_{micro}^b (m^2/g)	S_{meso}^b (m^2/g)	V_{micro}^c (cm^3/g)	V_{meso}^d (cm^3/g)
NH ₄ Y-0	797.0	726.8	70.2	0.35	0.17
NH ₄ Y-18	795.4	737.8	57.5	0.34	0.13
NH ₄ Y-46	785.1	739.2	45.9	0.33	0.10
NH ₄ Y-63	784.2	744.7	39.5	0.33	0.10
NH ₄ Y-68	775.5	732.1	43.4	0.33	0.53
CuY-0	647.9	605.0	42.9	0.27	0.09
CuY-18	653.8	608.3	45.5	0.27	0.10
CuY-46	671.9	629.1	42.8	0.28	0.12
CuY-63	674.6	638.0	36.6	0.30	0.13
CuY-68	720.5	677.4	43.1	0.30	0.32

^a BET surface area calculated using the relative pressure range of 0.05–0.16.

^b The specific surface area of micropore and mesoporous calculated by *t*-plot.

^c The pore of micropore calculated by HK.

^d The pore of mesoporous calculated by BJH.

observed. With increase of the NH₄⁺ exchange degree, the CuO content decreased. This showed that for all the CuY catalysts, the replacement of Na⁺ by NH₄⁺ and the supported copper species did not affect the morphology of the Y zeolite.

In order to investigate the influence of the NH₄⁺ exchanged degree on the distribution of the reducible copper species on the CuY catalysts, H₂-TPR was performed. The results are shown in Fig. 4. The hydrogen consumption peaks from low temperature to high were labeled as peak I, peak II, peak III, and peak IV.

The following facts from the literatures [15,23–25] help to understand the H₂-TPR:

The reduction of ion exchanged Cu²⁺ on zeolite occurs via a two-step mechanism.

Fig. 4. H₂-TPR of CuY catalysts.

The reduction of Cu²⁺ to Cu⁺ is characterized by a H₂-TPR peak below 500 °C. The difficulty of reduction depends on the location of Cu²⁺, in the order of hexagonal prism > sodalite cage > supercage. The second reduction step of Cu⁺ to Cu⁰ occurs above 700 °C.

Reduction of CuO on the CuY catalyst proceeded in one step at 230 °C.

So peak I, peak III, and peak II were ascribed to the reduction of Cu²⁺→Cu⁺ in the supercage and sodalite cage, and CuO→Cu⁰, respectively. Peak IV was assigned to the reduction of Cu⁺→Cu⁰. For the CuY-0 catalyst, there was only peak II of

Fig. 3. SEM images of CuY catalysts. (a) CuY-0; (b) CuY-18; (c) CuY-46; (d) CuY-63; (e) CuY-68.

$\text{CuO} \rightarrow \text{Cu}^0$. This indicated the absence of other reducible copper species besides CuO. With increasing the NH_4^+ exchange degree, peak I, peak III and peak IV increased and peak II decreased gradually. Meanwhile, the reduction temperature of peak IV moved towards low temperature. All these observations suggested that with the increasing NH_4^+ exchange degree, the Cu^{2+} and Cu^+ contents increased and the CuO content decreased, which was in agreement with the XRD results. The Cu^{2+} and Cu^+ contents of CuY-68 catalyst were much higher than these of the CuY-63 catalyst, and the Cu^+ reduction temperature of the CuY-68 catalyst was also lower than other catalysts. Moreover, the catalytic activity of the CuY-68 catalyst was superior to the other catalysts. This indicated that the Cu^+ active center for the oxidative carbonylation of methanol to DMC was formed by HAI between NaNH_4Y and $\text{Cu}(\text{acac})_2$, and the more the NH_4^+ exchange degree, the more Cu^+ active centers were formed and increased the activity of the CuY catalyst.

In order to analyze the copper species distribution on the CuY catalyst surface, XPS was performed. The XPS spectra of Cu 2p and Auger spectra are presented in Fig. 5. Divalent copper can be confirmed by the Cu $2p_{3/2}$ binding energy in 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 [26–29]. Usually, the two peaks from divalent and monovalent copper overlapped. From the different peak shape and relative intensity, the distribution of copper species in the CuY catalysts were different. From the Auger analysis of the Cu species, the kinetic energies for Cu, Cu_2O and CuO are 918.2, 916.0 and 917.6 eV, respectively [30]. In addition, the kinetic energy for Cu^+ in the CuY catalyst was 3 eV below that of Cu_2O , at 913.0 eV [31]. Under the HAI preparation conditions, metallic copper was not possible in the CuY catalyst. Combined with the H_2 -TPR results, the CuY-0 catalyst only contained CuO species, so the two peaks at 912.6 and 916.7 eV in the Auger spectra were assigned to monovalent copper species and divalent copper species, respectively. To determine exactly the content of the copper species on the surface of CuY catalyst, the relative proportion of the peak area of the curve fitting of the Cu $2p_{3/2}$

Table 3

Quantitative analysis of the XPS curve fitting of the CuY catalysts.

Catalyst	Peak area		$\text{Cu}^+/\text{Cu}_{\text{sum}}$ (%)	Cu^+ loading (wt%)
	Cu^+ peak	Cu^{2+} peak		
CuY-0	0	5907.8	0	0
CuY-18	2238.0	3229.2	40.9	4.9
CuY-46	4211.1	5469.5	43.5	5.2
CuY-63	4823.0	5654.4	46.0	5.5
CuY-68	6309.9	3545.3	64.0	7.7

spectra was calculated, i. e., the relative amounts of copper species with different valence states, which are listed in Table 3. With the increasing of the NH_4^+ exchange degree of NaNH_4Y , the monovalent copper content increased and divalent copper content decreased gradually.

To investigate the surface acidity of the CuY catalysts from the NaNH_4Y support with the different NH_4^+ exchange degrees, NH_3 -TPD was performed. The results are presented in Fig. 6. It was only below 250 °C that a NH_3 desorption peak (α) was observed over NaNH_4Y -0, which was attributed to the physically adsorbed and hydrogen-bound NH_3 of Y zeolite [32,33]. There was no desorption of NH_3 at high temperature. The CuY-0 catalyst from the NaNH_4Y -0 support has a similar NH_3 -TPD profile to the NaNH_4Y -0 zeolite. From the H_2 -TPR result (Fig. 4) for the CuY-0 catalyst, there existed only CuO species, and no other copper species. So these provide evidence that CuO species adsorb NH_3 molecule very weakly and the NH_3 adsorption are generally negligible. Besides, for the CuY catalysts from the NaNH_4Y support with different NH_4^+ ion exchange degree, the NH_3 desorption peak below 200 °C was splitted into two overlapped peaks and two NH_3 desorption peaks (β and γ) above 200 °C were observed, which was caused by the introduction of the surface-bound copper ions, as already proposed [25]. That is, the introduction of copper ion into NaY not only creates a more strongly bonded NH_3 adsorption center but also increased the amount of weakly bonded NH_3 centers. In order to quantify the NH_3 desorption capacity of the CuY catalysts, all the NH_3 -TPD curves were processed by

Fig. 5. Cu 2p XPS spectra (a) and Cu Auger spectrum (b) of CuY catalysts.

Fig. 6. NH_3 -TPD profiles of NaNH_4Y -0 and CuY catalysts.

means of a peak-differentiating analysis. The results of the quantitative analysis are listed in Table 4. It can be seen that the NH_3 desorption capacity of the CuY catalyst increased with the increasing of the NH_4^+ exchange degree of NaNH_4Y zeolite. Therefore, there was a positive correlation between the amount of copper ions on the CuY catalyst and the NH_4^+ exchange degree of NaNH_4Y zeolite. Kieger et al. [25] reported that the peak at 327 °C on the NH_3 -TPD is attributed to NH_3 desorbing from Cu^{2+} ions on the Cu^{2+}Y . However, after NH_3 treatment at 500 °C and desorption in He at 500 °C, most of the Cu^{2+} ions on the CuY have been reduced to Cu^+ [34]. A partial reduction of Cu^{2+} to Cu^+ results in the the NH_3 desorption peak above 227 °C shifting toward a low temperature and forming a broad peak from 77 to 327 °C. So the β and γ peak were attributed to surface-bound Cu^+ and Cu^{2+} . It was reported that three NH_3 ligands were bound to Cu^{2+} ions on the CuY catalyst and only two NH_3 ligands were bound to Cu^+ ions on the CuY catalyst [25]. The ion exchange copper ion loading was ob-

Table 4

Quantitative analysis of the NH_3 -TPD profiles of NaNH_4Y -0 and CuY catalysts.

Catalyst	Desorption capacity of NH_3 (mmol/g)				Amount	$\text{Cu}^+ + \text{Cu}^{2+}$ loading (wt%)
	α	β	γ			
NaNH_4Y -0	3.02	0	0		3.02	—
CuY-0	3.12	0	0		3.12	—
CuY-18	1.14	1.45	0.89	0.71	4.19	4.4
CuY-46	0.68	2.56	1.35	1.15	5.74	6.8
CuY-63	0.42	3.45	1.49	1.24	6.60	7.4
CuY-68	0.37	4.29	1.83	1.48	7.97	9.0
CuY-69	0.36	4.31	1.84	1.50	8.01	9.1

α : < 200 °C; β : 200–300 °C; γ : 300–400 °C.

tained and listed in Table 4. For the CuY-0 catalyst, there was no the surface-bound Cu^+ active center instead of CuO. When the NH_4^+ exchange degree was 18.3%, the copper ion loading was 4.4 wt%. With the increasing of the NH_4^+ exchange degree of NaNH_4Y zeolite, the copper ion loading on the CuY catalyst also increased, and reached 9.0 wt%, when the NH_4^+ exchange degree was 68.1%. It was conducive to forming Cu^+ active centers and also will increase the activity of CuY.

3.2. Activity testing

Experiments were undertaken to determine the influence of the NH_4^+ exchange degree on the activity for the oxidative carbonylation of methanol to DMC. The results are showed in Fig. 7. In Fig. 7(a), a plot of the DMC synthesis is given in terms of space time yield (STY_{DMC}) as a function of time on stream. The STY_{DMC} on all the catalysts increased with time on stream, before steadying off within 60 min, then kept constant for 600 min of time on stream. For the CuY-0 catalyst, there existed only CuO species, not the surface-bound Cu^+ active center, so it has no catalytic activity for the oxidative carbonylation of methanol to DMC. Under the same testing reactions, the activities of all the other catalysts from NaNH_4Y support exhibited

Fig. 7. Catalytic activity of CuY catalysts in the vapor phase oxidative carbonylation of methanol to DMC. (a) Time-on-stream performance of CuY catalysts; (b) STY_{DMC} , S_{DMC} and $X_{\text{CH}_3\text{OH}}$. Testing conditions: feed composition 31.8 vol% CH_3OH , 62.5 vol% CO , 5.7 vol% O_2 , GHSV = 3250 h^{-1} , 10 h, 140 °C, atmospheric pressure.

significant increase. The average value of STY_{DMC} , conversion of CH_3OH (X_{CH_3OH}) and selectivity of DMC (S_{DMC}) are presented Fig. 7 (b). It can be seen that with the increase of the NH_4^+ exchange degree, STY_{DMC} and X_{CH_3OH} increased and S_{DMC} decreased slightly. When the NH_4^+ exchange degree was 18.3%, STY_{DMC} , X_{CH_3OH} , and S_{DMC} were 49.1 mg/(g·h), 1.2%, and 73.6%, respectively. When the NH_4^+ exchange degree reached 63.2%, the STY_{DMC} on the CuY-63 catalyst increased to 184.5 mg/(g·h). When the NH_4^+ exchange degree reached 68.1%, it was surprised that the corresponding CuY-68 catalyst has higher activity than the CuY-63 catalyst. Its STY_{DMC} increased about 45% and reached 267.3 mg/(g·h), but S_{DMC} remained unchanged. The catalytic activity of the CuY-69 catalyst from the $NaNH_4Y$ -69 support was a little higher than that of the CuY-68 catalyst. The experimental results can be explained by the following. First, the NH_4^+ exchange degree of 68% has reached the limit. In addition, when the NH_4^+ exchange degree was 63.2%, NH_4^+ was completely ion exchanged by Cu^{2+} of $Cu(acac)_2$, and the ion exchanged copper ions have reached the maximum. When the NH_4^+ exchange degree continued to increase from 63.2% to 68.7%, ion exchange between NH_4^+ and Cu^{2+} does not occur anymore, resulting in the rest of the NH_4^+ remaining on the catalyst precursor. It has been reported that the released NH_3 from NH_4Y decomposition facilitates the reduction of copper species during high temperature treatment [35] and the formation of more Cu^+ active centers [23].

So with the same Cu loading, with the increase of the NH_4^+ exchange degree of $NaNH_4Y$ zeolite, the Cu^+ content increased on the CuY catalyst, which further improved the catalytic activity. This indicated that during the preparation of the CuY catalyst by HAI, the NH_4^+ ion is the exchangeable site of the copper ion, and the Cu^+ active center is related to the distribution of NH_4^+ , which also influenced the reaction performance.

The long term stability and activity of the catalyst are vital for the oxidative carbonylation of methanol to DMC from both the academic and industrial viewpoints. The effects on CuY-18, CuY-63 and CuY-68 catalyst longevity of vapor phase oxidative carbonylation of methanol to DMC were investigated. The results for 60 h are presented in Fig. 8. After an increase of catalytic activity for 1 h, in the next 38 h, the STY_{DMC} values were

Fig. 8. The long-term catalytic performance of CuY catalysts.

maintained constant. Then, the activities of all the CuY catalysts slowly decreased. At the time on stream of 60 h, the deactivation degrees for CuY-18, CuY-63 and CuY-68 catalysts were 19.6%, 32.6%, and 33.3%, respectively.

4. Conclusions

CuY catalysts from a $NaNH_4Y$ support with different NH_4^+ exchange degrees were prepared by high temperature anhydrous interaction and tested for the oxidative carbonylation of methanol. The NH_4^+ of NH_4Y was needed to form the Cu^+ active center and the NH_4^+ exchange degree of $NaNH_4Y$ had a significant influence on the activities of the CuY catalysts. With the increase of the NH_4^+ exchange degree of $NaNH_4Y$, the surface bound- Cu^{2+} and surface bound Cu^+ content of the CuY catalyst increased and the CuO species decreased. The NH_4^+ of $NaNH_4Y$ made copper ion exchange occur more easily and was promoted to form the Cu^+ active centers, which increased the activity of the CuY catalyst for the oxidative carbonylation of methanol to DMC. The surface bound Cu^+ content reached the maximum when the NH_4^+ has almost completely exchanged the Na^+ of NaY zeolite, and this CuY exhibited the optimal catalytic activity.

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Graphical Abstract

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Effect of NH_4^+ exchange on CuY catalyst for oxidative carbonylation of methanol

Yuchun Wang, Huayan Zheng, Zhong Li*

Taiyuan University of Technology; Yuncheng University

A higher NH_4^+ exchange degree in NaNH_4Y zeolite gave a higher amount of the Cu^+ active centers in the CuY catalyst and higher catalytic activity.

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 NH_4^+ 交换度对 CuY 催化剂上甲醇氧化羰基化反应性能的影响王玉春^{a,b}, 郑华艳^a, 李 忠^{a,*}^a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^b运城学院应用化学系, 山西运城 044000

摘要: 碳酸二甲酯 (DMC) 是一种应用极其广泛的绿色化工产品, 其中经济、绿色的甲醇氧化羰基化合成 DMC 工艺极具工业前景, 而 Y 分子筛负载铜 (CuY) 是有效催化剂之一。众所周知, CuY 催化剂上的 Cu^+ 是催化活性中心。 Cu^+ 催化活性中心的引入方式用两种: (1) CuCl 直接与 HY 分子筛固相离子交换; (2) Cu^{2+} 与 NaY 分子筛溶液离子交换, 然后 Cu^{2+} 自还原生成活性中心 Cu^+ 。 在无溶剂条件下制备 CuY 催化剂时, 载体 HY 分子筛中的可交换位 H^+ 量是决定催化剂 CuY 氧化羰基化催化性能的关键因素。 文献通过以不同硅铝比的 HY 分子筛为载体制备的催化剂 CuY, 研究铜离子可交换位 H^+ 量对氧化羰基化的影响, 然而, 硅铝比的不同也直接影响了分子筛骨架的组成、 Si-O-Al 的键角、甚至影响了 Al^{3+} 的分散度, 这些因素都直接影响了 CuY 催化剂活性。 因此, 研究 NaNH_4Y 分子筛载体中的可交换位 (NH_4^+) 的量与 CuY 催化剂活性间的关系具有非常重要的意义。

本文将 NaY 分子筛与不同浓度的 NH_4NO_3 溶液进行离子交换, 制得具有不同 NH_4^+ 交换度的 NaNH_4Y 分子筛, 以其为载体, 以具有易升华、易分解性质的乙酰丙酮铜 $\text{Cu}(\text{acac})_2$ 为铜源, 在无溶剂条件下, 高温热处理二者固相混合物, NaNH_4Y

分子筛中的 NH_4^+ 与 $\text{Cu}(\text{acac})_2$ 中的 Cu^{2+} 发生了离子交换, Cu^{2+} 进一步发生自还原生成活性中心 Cu^+ , 成功地制备了完全无氯的 CuY 催化剂, 应用于催化常压甲醇氧化羰基化合成 DMC 过程, 研究 NaNH_4Y 分子筛中的铜离子可交换位 NH_4^+ 与催化剂 CuY 催化性能间的关系.

通过各种表征及对 CuY 催化剂在甲醇氧化羰基化过程中催化活性分析发现, Y 分子筛经过 NH_4NO_3 溶液离子交换及催化剂的制备过程, 其八面沸石结构和孔道保持良好. 以未经过离子交换的 NaY 负载的 CuY 催化剂上的铜物种完全以 CuO 形式存在, 且没有催化活性. 随着 NH_4^+ 交换度增加, CuY 催化剂表面 CuO 含量逐渐降低, 而活性中心 Cu^+ 含量逐渐增加, 且其催化活性也随之增加. 当 NH_4^+ 交换度趋于极限值时, CuY 催化剂中 Cu^+ 含量达最大, 其催化活性也达最佳, DMC 的时空收率和选择性分别为 267.3 mg/(g·h) 和 68.5%, 甲醇转化率为 6.9%.

因此, 无溶剂条件下, 以 NaNH_4Y 分子筛为载体, $\text{Cu}(\text{acac})_2$ 为铜源, 制备完全无氯 CuY 催化剂时, NH_4^+ 是形成 Cu^+ 活性中心的必须条件, 且 NH_4^+ 交换度直接影响催化剂 CuY 的催化活性.

关键词: 高温无水相互作用; NH_4^+ 交换度; CuY 催化剂; 氧化羰基化; 碳酸二甲酯

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*通讯联系人. 电话/传真: (0351)6018526; 电子信箱: lizhong@tyut.edu.cn

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