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Effect of Calcination Temperature on Catalytic Activity and Textual Property of Cu/HMOR Catalysts in Dimethyl Ether Carbonylation Reaction

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The effect of calcination temperature on the catalytic activity for the dimethyl ether (DME) carbonylation into methyl acetate (MA) was investigated over mordenite supported copper (Cu/HMOR) prepared by ion-exchange process. The results showed that the catalytic activity was obviously affected by the calcination temperature. The maximal DME conversion of 97.2% and the MA selectivity of 97.9% were obtained over the Cu/HMOR calcined at 430 °C under conditions of 210 °C, 1.5 MPa, and GSHV of 4883 h⁻¹. The obtained Cu/HMOR catalysts were characterized by powder X-ray diffraction, N₂ absorption, NH₃ temperature program desorption, CO temperature program desorption, and Raman techniques. Proper calcination temperature was effective to promote copper ions migration and diffusion, and led the support HMOR to possess more acid activity sites, which exhibited the complete decomposing of copper nitrate, large surface area and optimum micropore structure, more amount of CO adsorption site and proper amount of weak acid centers.

Key words: Dimethyl ether, Methyl acetate, Calcination temperature, Carbonylation, HMOR

I. INTRODUCTION

Due to the environmentally friendly emission, methyl acetate (MA) is becoming widely used as solvent to replace acetone in coatings, inks, resins, adhesives, and so on [1, 2]. While the catalyst applied in the process of typically homogeneous MA synthesis are rare Rh or Ir compounds and corrosive iodide compounds as promoters [3, 4].

Researches on heterogeneous process using solid acid catalysts to reduce pollution and production cost have caused great interest [1, 5–7]. H-mordenite, H-ferrierite, and H-ZSM-5 were tested for iodide-free carbonylation, based on the various acid character zeolites [6, 8]. With the success of dimethyl ether (DME) synthesis from coal, natural gas or biomass-derived syngas, the following catalytic conversion of DME to MA is considered to have economic advantage and has attracted much attention in academia and industry [9–12].

H-mordenite (HMOR) is one of the most promising zeolite catalyst DME carbonylation [10, 13–15]. As reported by Iglesia and co-workers, HMOR shows high activity and selectivity for MA synthesis from DME

carbonylation at low temperature range from 150 °C to 190 °C [10, 14, 15]. According to the mechanism research of carbonylation process, the rate-determining step to form acetyls is the insert of CO (from gas phase or via weakly adsorbed CO species) on the surface methoxy, which is formed by the surface reaction between the hydroxyl groups and DME [16–18]. Thereafter, another DME molecule reacted with the obtained acetyls to produce MA as well as regenerating the surface methoxy [18–20]. Researchers found that the rate-determining step for DME carbonylation occurred more easily inside the 8 member-ring (MR) channel of HMOR due to its specific size and the unusual orientation of methoxy group in the 8MR channels (parallel to the cylinder axis, T3-O33) [12, 21]. The work by Shen *et al.* indicated that pyrimidine pre-adsorbed HMOR could neutralize acid sites and improve the catalytic activity up to 48 h by avoiding heavy hydrocarbon and carbon deposition in 12MR channels of mordenite during DME carbonylation [21]. In order to improve the activity of DME carbonylation, the modification of HMOR was investigated. Cu modified HMOR showed excellent catalytic performance. Nonetheless, the reaction mechanism of Cu/HMOR catalysts is not clear up to now [22–24].

In this work, Cu/HMOR catalysts were prepared by ion-exchange method based on experimental data relevant reported [25]. The effect of calcination tempera-

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ture on its catalytic performance of MA production via DME carbonylation in the fixed-bed reactor was discussed to obtain the proper calcination temperature after the copper ion-exchange step. Particular attention was paid towards its influence on surface area, acidity, CO adsorption properties and carbonylation performance of Cu/HMOR catalysts.

II. EXPERIMENTS

A. Catalyst preparation

Cu-loaded HMOR catalyst was prepared by ion-exchange method. HMOR ($S_{\text{BET}}=574 \text{ cm}^2/\text{g}$, Si:Al=10, Nankai University Catalyst Co. Ltd., China) was mixed with an aqueous solution of copper nitrate, then the mixture was heated at 80 °C for 2 h, followed by washing with distilled water. The ion-exchange process was repeated for three times in order to obtain a desired copper deposition amount on HMOR zeolite. The obtained sample was filtered, washed, dried at 120 °C for 12 h and calcined in batches at 270, 350, 430, 500, and 600 °C for 4 h, followed by granulation into the size of 20–40 mesh. The obtained catalysts were denoted as Cat-270, Cat-350, Cat-430, Cat-500, and Cat-600, respectively.

B. Catalyst characterization

Surface area and textual properties of Cu/HMOR catalysts were measured on a Quantachrome ASIQM002-2 instrument at $-196 \text{ }^\circ\text{C}$ using N_2 as adsorbent. Catalysts were treated at 300 °C for 10 h before N_2 adsorption. Powder X-ray diffraction (XRD) patterns of Cu/HMOR were achieved on a Rigaku D/max- γC using Cu $K\alpha$ radiation ($\lambda=0.154056 \text{ nm}$). The temperature-programmed desorption of ammonia (NH_3 -TPD) was performed at 120–650 °C (0.15 g catalyst, 10 °C/min, 30 mL/min He as carrier flow) on the laboratory-made instrument after being saturated with NH_3 at 120 °C for 20 min. The desorbed- NH_3 was then measured by a thermal conductivity detector (TCD). The process of CO-TPD was conducted similarly to NH_3 -TPD, except that the adsorption temperature and the initial desorption temperature were 80 °C for CO. Laser Raman spectroscopy (LRS) was performed using a laser confocal Raman spectrol system. The excitation source was a 532 nm He-Ar laser beam with a power of 3 mW measured at the analysis spot.

C. Carbonylation reaction

A stainless-steel fixed-bed tubular reactor was adopted to investigate the performance of gas phase carbonylation of DME. In each run, 0.5 g of Cu/HMOR

TABLE I Textural properties of the Cu/HMOR catalysts.

Catalysts	$S_{\text{BET}}^{\text{a}}$	Micropore structure property		
		Area ^b	Volume ^c	Size/nm
Cat-270	495	448	0.175	0.51
Cat-350	507	459	0.179	0.54
Cat-430	521	475	0.184	0.58
Cat-500	511	465	0.182	0.55
Cat-600	503	456	0.185	0.52

^a Surface area (in m^2/g), calculated by BET method.

^b Micropore area (in m^2/g), calculated from desorption branch by t-plot method.

^c Micropore volume (in m^3/g), calculated from desorption branch by t-plot method.

was loaded into the middle of the reactor, then the catalyst was activated *in situ* with 20% H_2 /80% N_2 under conditions of 270 °C, atmosphere and flowing rate of 50 mL/min for 7 h. After activation, the reactor was cooled to 180 °C and purged by syngas with CO/DME ratio of 47% and 4% N_2 as internal standard. The flow rate of reactant gas was adjusted by the Brooks 5850E mass flow controller. The typical operation conditions were $T=210 \text{ }^\circ\text{C}$, $P=1.5 \text{ MPa}$ and $\text{GSHV}=4883 \text{ h}^{-1}$. The tail gas flow rate was regulated by a mass flow meter. Tail gas was heated at 110 °C and analyzed after reaction for 2.4 h by two online gas chromatograph. DME, MA, CH_4 , and MeOH were analyzed by HP-PLOT/Q column with FID detector. CO, N_2 , and CH_4 were analyzed by carbon-sieve column with TCD detector.

III. RESULTS AND DISCUSSION

A. Textural properties of the catalysts

BET surface area and structure properties of Cu/HMOR catalysts calcined at different temperatures from 270 °C to 600 °C are listed in Table I. It is clear that calcination temperature had great effect on the textural properties of the catalysts. The Cat-430 showed the maximum surface area of 521 cm^2/g and micropore area of 475 cm^2/g , while those of the catalysts calcined at lower temperature (270 or 350 °C) and higher temperature (500 or 600 °C) decreased slightly. Moreover, the micropore volume and micropore size of catalysts reached a bigger value at 430 °C, which is similar to the surface area and micropore area, implying that the calcination temperature of 430 °C is not only beneficial to removing impurity in HMOR channel, but also inhibition of pore structures sintering. It is noticeable that the micropore volume of the Cat-600 (0.185 cm^3/g) is a bit bigger than that of Cat-500 (0.182 cm^3/g), which may be due to the removal of decomposition products of copper nitrate or the residues from the inner surface of

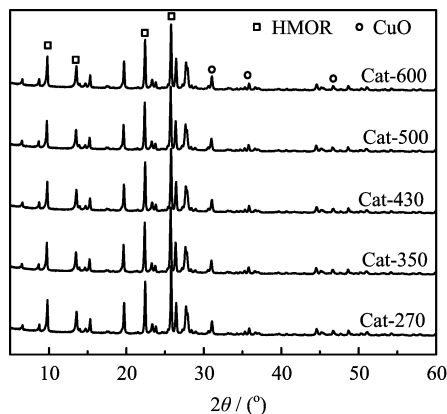


FIG. 1 XRD patterns of the Cu/HMOR catalyst samples before reduction.

the blocked pores. The larger BET, micropore area, micropore volume and micropore size of Cat-430 indicate promoting copper ions migration and diffusion on the surface and in the micropores of HMOR as well as promoting molecular diffusion speed, which may enhance its carbonylation performance mentioned below.

B. Crystalline phase and morphology

Figure 1 illustrates the XRD patterns of catalysts calcined at different temperature without reduction. It exhibited obvious presence of highly crystalline and regular channels of HMOR at $2\theta=9.2^\circ$, 20.5° , and 23.6° for different Cu/HMOR catalysts [14]. The CuO diffraction peaks were detected over Cat-270 as well as these tested at $2\theta=35.5^\circ$, 38.7° , and 48.7° [26] over the other catalysts calcined at higher temperature, showing that copper nitrate was decomposed incompletely to CuO over Cat-270, which agreed with the results of Raman spectra mentioned below.

C. Acid properties

The NH_3 desorption over Cu/HMOR catalysts are shown in Fig.2. Based on these curves, the amount and strength of acidic surface sites were calculated and listed in Table II. Three desorption peaks could be distinguished over Cu/HMOR catalysts calcined at different temperature. The one around 215°C could be attributed to weak desorption of NH_3 on the Bronsted acid site and NH_3 association with Si-OH as reported [27], the desorption peak at about 342°C was ascribed as medium desorption of NH_3 , and the peak around 562°C was assigned to strong desorption of NH_3 adsorbed on the acidic Si-OH-Al groups. The total amount of acid over Cat-270 is 0.64 mmol/g with the three different types of NH_3 adsorption strength of 0.29 , 0.07 and 0.28 mmol/g , respectively. The to-

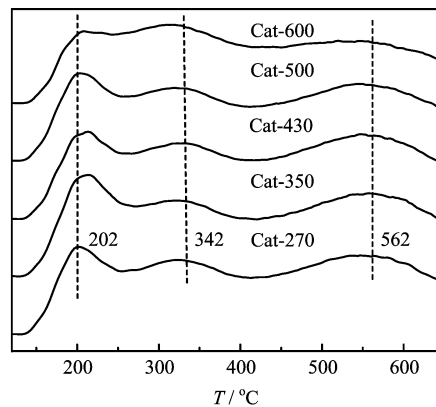


FIG. 2 NH_3 -TPD profiles of the Cu/HMOR catalyst samples.

TABLE II The amount and strength distribution of acidic surface sites and CO adsorption sites over various catalysts.

Sample	Adsorption site ^a /%	Acid amount ^b /(mmol/g)			
		Total	Weak	Medium	Strong
Cat-270	89	0.64	0.29	0.07	0.28
Cat-350	95	0.71	0.34	0.08	0.29
Cat-430	99	0.73	0.35	0.09	0.29
Cat-500	100	0.73	0.34	0.10	0.29
Cat-600	86	0.31	0.10	0.08	0.13

^a CO adsorption of calculated with Gaussian function fit and using Cat-500 as standard.

^b Calculated with Gaussian function fit.

tal amount of acid reached 0.73 mmol/g when the calcined temperature increased from 270°C to 430°C with the amount of weak acid increasing 20.1% (from 0.29 mmol/g to 0.35 mmol/g) and 28.6% for medium acid (from 0.07 mmol/g to 0.09 mmol/g). While, further increase of calcination temperature to 600°C leads to a decrease to 0.31 mmol/g of the total amount of acid over Cu/HMOR, which may be caused by dealumination in the HMOR [28]. Bronsted acid centers and active sites for CO insertion were essential for DME carbonylation catalyst as reported by Volkova and Shen [11, 21]. The large amount of weak acid centers of Cat-430 would be favorable to keep its high catalytic performance.

D. CO adsorption property

The CO-TPD results of different Cu/HMOR catalysts are presented in Fig.3. Based on these curves, the relative amount of CO-adsorbed over the Cu/HMOR catalysts was measured on the basis of the peak area using Cat-500 as standard, as shown in Table II. The CO desorption peak arise at 329°C from all the Cu/HMOR catalysts and the relative amount of CO adsorption was 89% , 95% , 99% , and 86% for Cat-270, Cat-350, Cat-

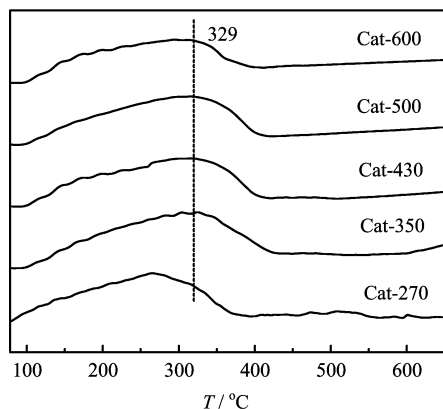


FIG. 3 CO-TPD profiles of the Cu/HMOR catalysts.

430, and Cat-600 respectively. According to the mechanism research reported by Corma and Iglesia [10, 12, 14], surface methoxy groups were easily formed from DME in 8MRs and 12MRs and the attack of CO on the surface methoxy groups is the rate determining step of DME carbonylation to MA. Therefore, more CO adsorption sites prompt the activity and it may lead to the excellent carbonylation performance of Cat-430 and Cat-500 mentioned below.

E. Raman characterization results

This work discussed effect of calcination temperature on the catalytic activity and textual properties of Cu/HMOR catalysts in the carbonylation reaction compared to the work reported by Tsubaki [22–24]. Figure 4 shows Raman spectra of Cu/HMOR catalysts collected at room temperature. Cu/HMOR catalysts exhibit three bands at 405, 470, and 812 cm^{-1} . The band at 405 cm^{-1} is assigned to a five-membered building unit of MOR-structure zeolites, the one at 470 cm^{-1} can be ascribed to four-membered ring and the 812 cm^{-1} band is attributed to the framework symmetric stretching vibration in MOR. Additional distinct band at 1059 cm^{-1} over Cat-270 can be assigned to NO_3^- derived from copper nitrate [29], which disappears for the catalysts calcined at higher temperature. These observations indicate that copper nitrate on HMOR cannot be decomposed completely to CuO at 270 °C. The Cat-600 catalyst shows a weak band at about 343 and 630 cm^{-1} due to the Cu–O stretching mode [30]. However, the 343 cm^{-1} band gets even weaker (for Cat-500) and disappears for catalysts calcined at 430, 350, and 270 °C, which may be due to the smaller CuO particles resulting from lower calcination temperature.

F. Gas-phase carbonylation of DME

Table III shows the comparison of the DME conversion and MA selectivity over Cu/HMOR calcined

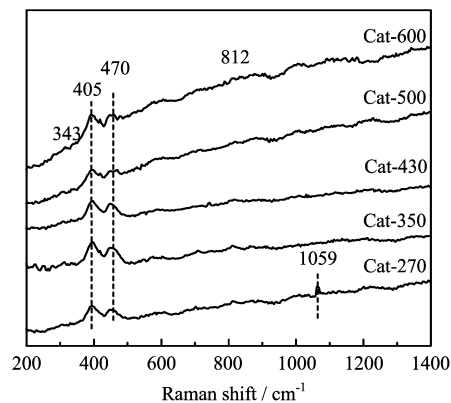


FIG. 4 Raman spectra of various catalysts.

TABLE III DME conversion and selectivity to MA over Cu/HMOR catalyst samples. Reaction condition: $T=483\text{ K}$, $P=1.5\text{ MPa}$, $t=145\text{ min}$.

Sample	DME conversion/%	MA selectivity/%
Cat-270	18.6	75.4
Cat-350	48.0	92.4
Cat-430	97.2	98.8
Cat-500	94.9	97.0
Cat-600	38.8	92.9

at different temperature. A very low DME conversion (18.6%) and MA selectivity (75.4%) was observed over the Cat-270. The residues of undecomposed copper nitrate as detected by the Raman techniques were difficult to be activated by hydrogen at 270 °C. Therefore, the shortage of metal active centers may be the main factor of bad catalytic effect of Cat-270. The activity improved obviously with the catalyst calcinations temperature elevated from 270 °C to 430 °C. DME conversion reached the maximum value of 97.2% and the MA selectivity of 98.8% was obtained over Cat-430. The high activity is deduced from larger surface area, optimum micropore structure, more acid sites and CO adsorption sites over the Cat-430 catalyst [12, 14]. However, further increase of catalyst calcined temperature resulted in a significant drop of activity. As we can see that DME conversion over Cat-600 remained 38.8% and the MA selectivity was 92.9%, which was lower than that of Cat-430 and Cat-500. As the results discussed above, the coupling effect of surface area, CO adsorption, and acid property of the catalysts after about 145 min reaction followed the order: Cat-430 > Cat-500 > Cat-350 > Cat-600 > Cat-270.

IV. CONCLUSION

The Cu/HMOR catalysts calcined at different temperature exhibited distinguishing performances for gas-phase carbonylation of DME to MA. The activity in-

creased with increasing the calcination temperature from 270 °C to 430 °C, and reached the maximal value with 97.2%DME conversion and the 97.9%MA selectivity at calcination temperature of 430 °C. The decrease of activity resulted from further increase of calcination temperature. The surface area and micropore property of the catalyst could be improved at the calcination temperature of 430 °C. The copper nitrate on the surface of the Cat-430 catalyst could be decomposed completely to the corresponding metal oxide, which can be easily activated by H₂ reduction. Cat-430 catalyst possessed large amount of CO adsorption site and acid activity sites. These factors were confirmed to be responsible for the higher catalytic activity of the catalyst calcined at 430 °C in the DME carbonylation reaction.

V. ACKNOWLEDGMENTS

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