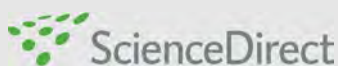


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Article

Surface reactions of CuCl₂ and HY zeolite during the preparation of Cu^I catalyst for the oxidative carbonylation of methanol

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ABSTRACT

A Cu^I/Y catalyst was prepared for the vapor phase oxidative carbonylation of methanol to dimethyl carbonate (DMC). The surface solid-state interactions of CuCl₂ with HY zeolite were studied using thermogravimetry. The surface properties and morphologies of catalyst samples were analyzed by thermogravimetry, X-ray photoelectron spectroscopy, and elemental analysis, and their catalytic performance was assessed in a fixed-bed reactor. Both CuCl and CuCl₂ were found to co-exist on the external surface of the catalyst, while ion-exchanged Cu^I along with small amounts of adsorbed CuCl were contained in the internal Y zeolite cage structures. Both the CuCl and CuCl₂ were active species during the DMC synthesis. Compared with a conventional Cu^I/Y catalyst prepared by heating a mixture of CuCl and HY zeolite, the Cu^I/Y catalyst prepared by heating a mixture of CuCl₂ and HY zeolite showed increased catalytic activity for the oxidative carbonylation of methanol, even though it had lower Cu and Cl contents.

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1. Introduction

The solid-state ion exchange (SSIE) of CuCl with solid acid supports to produce Cu^I supported catalysts is an important reaction. CuCl has a low melting point and is easily dispersed over the support surface when heated, with the spontaneous formation of either a mono or multilayer [1–5]. He et al. [2] modified mesoporous silica (SBA-15) by incorporating alumina and found that the resulting material could be used to support CuCl. The same study determined that isolated cuprous species generated by SSIE between CuCl and Brønsted acid sites formed on the silica host were effective at promoting the dispersion of CuCl. The ion exchange of the Cu^I in solid CuCl with

the H⁺ in HY zeolite has been shown to occur at temperatures in excess of 300 °C, with the maximum ion exchange rate achieved at 340 °C. During this process, HCl gas is produced and any excess CuCl sublimates from the solid catalyst surface [6,7].

King [8,9] reported that a Cu^I/Y catalyst prepared by the SSIE of CuCl and HY zeolite was more active and more stable than catalysts prepared by the solution ion exchange of Cu(NO₃)₂ with HY zeolite during the oxidative carbonylation of methanol to dimethyl carbonate (DMC). Anderson et al. [10,11] prepared Cu^I/X and Cu^I/ZSM-5 catalysts by the SSIE of CuCl and HX or HZSM-5 zeolites and found that the reduced adsorption of CO on Cu^I/X as compared with Cu^I/ZSM-5 favored the synthesis of DMC. The Cu-O species formed on these materials

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were proposed as the active species during the catalytic reaction [12–14]. DMC was the primary product over Cu^I/Y, whereas dimethoxy methane (DMM) was the majority product generated over Cu^I/ZSM-5 and Cu^I/MOR. The higher activity and selectivity of the Cu^I/Y catalyst were attributed to the weaker adsorption of CO onto the Cu^I cations in this material. Huang et al. [15] prepared a series of Cu^I/FAU catalysts with varying SiO₂/Al₂O₃ molar ratios and found that the locations of the Cu active sites were related to the distribution of Brønsted acid sites, which also influenced the performance of the catalyst during oxidative carbonylation. In addition to the H-type zeolite, other Brønsted acids have also been used to prepare heterogeneous Cu^I catalysts by SSIE with CuCl; studies have investigated the use of SiO₂-Al₂O₃, SiO₂-TiO₂, SO₄²⁻/ZnO, and S₂O₈²⁻/ZnO solid acids to prepare Cu^I/SiO₂-Al₂O₃ [16], Cu^I/SiO₂-TiO₂ [17,18], Cu^I/SO₄²⁻/ZnO, and Cu^I/S₂O₈²⁻/ZnO [19] catalysts, respectively. The obtained catalysts exhibited excellent catalytic activity during the oxidative carbonylation of methanol to DMC.

Notwithstanding the substantial utility of CuCl, it is well known that this material readily oxidizes in air to form Cu(II), and thus it is difficult to be produced commercially. CuCl₂, however, is more stable in air and thus easier to obtain and less expensive than CuCl. In addition, CuCl₂ quickly decomposes to CuCl and Cl₂ gas when heated to high temperatures. We have therefore previously attempted to prepare a Cu^I catalyst by the SSIE method using CuCl₂ as the Cu source instead of CuCl [20]. In this prior work, the catalyst formation process as well as the microstructure and active site locations of the catalyst were not completely elucidated, and consequently a series of systematic experiments were performed in the present study to obtain further information with regard to these aspects of the catalyst.

2. Experimental

2.1. Solid materials made by heating a mixture of CuCl₂ and HY

NaY zeolite (Si/Al = 8.1, Qilu Branch Research Institute, Sinopec, China) was twice subjected to ion exchange with a NH₄NO₃ solution (0.5 mol/L) for a 4 h time span and then calcined at 500 °C in air to produce the HY zeolite. CuCl₂·2H₂O was subsequently thoroughly mixed with either the HY or NaY zeolite (at a 1:1 mass ratio), and the mixture was heated in a tube furnace (Φ 60 mm × 1000 mm) at a rate of 5 °C/min to 650 °C and held at that temperature for 4 h under N₂. After cooling to ambient temperature, the solid materials, designated as either the Cu^I/Y or Cu^I/NaY catalyst, were obtained. The same procedure was also applied to mixtures of CuCl₂·2H₂O or CuCl with HY zeolite (again at a 1:1 mass ratio), which were heated at various temperatures under N₂ to obtain either Cu^I/Y(CuCl₂) or Cu^I/Y(CuCl) catalyst.

2.2. Solid material characterization

Thermogravimetric (TG/DTG) analysis was carried out using a Netzsch STA409C instrument (Selb, Germany), applying a heating rate of 10 °C/min under N₂ (50 mL/min). X-ray photo-

electron spectroscopy (XPS) was performed with an ESCALAB-250 spectrometer at a chamber pressure of 7.0 × 10⁻⁸ Torr with an X-ray beam generated by bombarding an Al target with electrons at 1486.6 eV. Samples were fixed onto double-sided adhesive tape and then placed into a specimen holder. A C 1s binding energy of 284.6 eV was adopted as the internal reference. Elemental analysis (EA) of Cu in the solid materials was carried out by the iodometric method using an SP-723P spectrophotometer while the mercury thiocyanate spectrophotometric method provided in the DZG-93-01 standard was applied for analysis of the Cl content of the catalysts.

2.3. Vapor phase oxidative carbonylation of methanol

The synthesis of DMC via the vapor phase oxidative carbonylation of methanol was investigated at atmospheric pressure in a fixed-bed reactor (Φ 6 mm × 450 mm). In a typical process, 0.45 g catalyst sample (approximately 1.0 mL) was packed into the reactor tube and placed in the center of the reactor furnace. A thermocouple was inserted into the middle of the furnace to ensure accurate control of the reaction temperature. The reactor was heated from room temperature to 140 °C over 40 min and then held at that temperature for the reaction. The furnace temperature was controlled with a precision of ± 0.5 °C by a time programmed temperature controller (SK-II, Shanxi Institute of Coal Chemistry, Chinese Academy of Sciences). Liquid methanol was pumped at a rate of 0.02 mL/min using a constant flux micro-pump (2PBOOC, Beijing Weixing Co., China) and vaporized in a pre-heater at 130 °C. The resulting constant flux of methanol vapor was thoroughly mixed with CO (28 mL/min) and O₂ (2.8 mL/min, standard atmosphere), each of which was controlled individually by mass gas flow controllers (MFC, Seven Star Huachuang Co., China). The hot gas mixture subsequently flowed into the catalyst bed where the catalytic oxidative carbonylation of methanol to DMC took place. The effluent gas was routed to an Agilent 6890 gas chromatograph (GC) for online analysis of the products. The GC was equipped with an HP-INNOWAX capillary column connected to a flame ionization detector (FID) as well as a series consisting of a PORAPAK-Q packed column and HP-PLOT/Q carbon sieve and HP-PLOT Molesieve/5A capillary columns connected to a thermal conductivity detector (TCD). Methanol, DMC, methylformate (MF), DMM, and traces of dimethyl ether (DME) in the products were detected by the FID, whereas CO, O₂, and CO₂ were detected by TCD. The gaseous products were sampled and analyzed automatically every 20 min throughout the reaction. The catalytic activity was reported as methanol conversion as well as the space-time yield (STY) of DMC, while product selectivity (*S*) was measured as the sum of the quantities of DMC, DMM, and MF produced.

3. Results and discussion

3.1. Interaction between CuCl₂ and the HY zeolite

The TG/DTG plots obtained for the mixtures of HY or NaY zeolite with CuCl₂·2H₂O under N₂ are shown in Fig. 1. To avoid

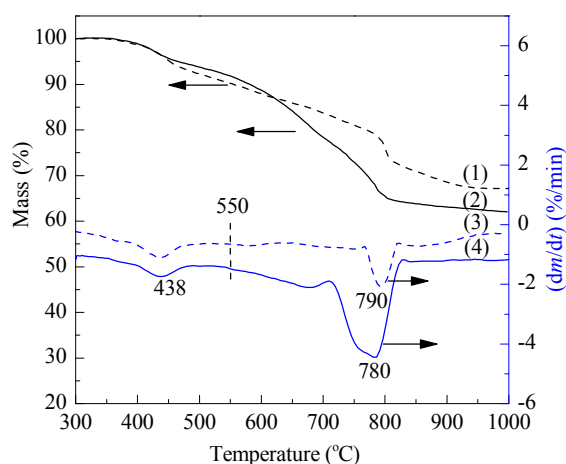


Fig. 1. TG/DTG plots of 50 wt% mixtures of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with HY (1, 3) or NaY (2, 4).

the effects of moisture contained in the zeolites, samples were dehydrated by heating at 300 °C for 1 h prior to analysis. The anhydrous samples were then heated from 300 to 1000 °C at a rate of 1 °C/min. In the case of both materials, there are two obvious mass loss peaks in the DTG profile, occurring at approximately 438 and 780 °C. With regard to the NaY mixture, the first peak can be attributed to the release of Cl_2 during the decomposition of CuCl_2 to CuCl , while the second peak results from the sublimation of CuCl . In contrast, the HY mixture exhibits a more pronounced mass loss between 300 and 550 °C and a lower mass loss between 550 and 1000 °C. This is due to the SSIE reaction of CuCl formed from the decomposition reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with the HY zeolite [14]. The release of HCl results in the additional mass loss between 300 to 550 °C while the lower mass loss is caused by the subsequent sublimation of CuCl . Calculations based on these plots indicate that the extent of ion exchange that CuCl underwent with HY and the amount of Cu^I loaded on the Y zeolite during the heating process were 53.3% and 6.3 g/g, respectively.

The catalytic performance of the Cu^I/Y and Cu^I/NaY catalysts during the gas phase oxidative carbonylation of methanol to DMC were evaluated in the fixed-bed reactor, and the resulting STY and S_{DMC} values are shown in Fig. 2. Both STY and S_{DMC} increased in the initial reaction stages and reached equilibrium levels after approximately 3 h. The Cu^I/Y catalyst exhibited higher catalytic activity than the Cu^I/NaY catalyst; STY and S_{DMC} were 100 mg/(g·h) and 72.56% over Cu^I/Y and 70 mg/(g·h) and 67.71% over Cu^I/NaY . In addition to the highly dispersed CuCl present in the Y zeolite structure, the Cu^I/Y catalyst had also been loaded with ion-exchanged Cu^I . It therefore appears that both the CuCl and the ion-exchanged Cu^I are active during DMC formation and that the ion-exchanged Cu^I improves the catalytic activity.

3.2. Effect of Cu precursor on the catalytic performance of Cu^I/Y catalysts

The catalytic activities of the Cu^I/Y materials prepared from different Cu salts are compared in Fig. 3, which summarizes the

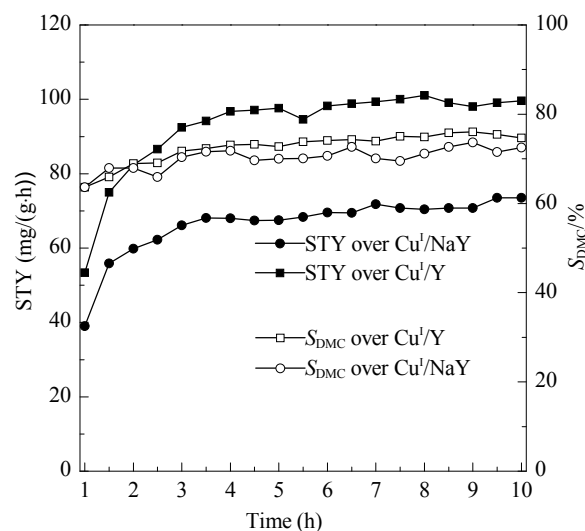


Fig. 2. Variations in STY and S_{DMC} with on-stream reaction time over Cu^I/Y and Cu^I/NaY catalysts.

STY and S_{DMC} values obtained from catalysts prepared at different temperatures. These data suggest that the activities of the two Cu^I/Y catalysts increased with increasing processing temperatures. At a processing temperature of 250 °C, the $\text{Cu}^I/\text{Y}(\text{CuCl}_2)$ catalyst shows lower activity than $\text{Cu}^I/\text{Y}(\text{CuCl})$ although the former has a faster rate of increase of both STY and S_{DMC} . At 450 °C, $\text{Cu}^I/\text{Y}(\text{CuCl}_2)$ exhibits better catalytic activity than $\text{Cu}^I/\text{Y}(\text{CuCl})$. The STY and S_{DMC} of the $\text{Cu}^I/\text{Y}(\text{CuCl}_2)$ catalyst were 38.16 mg/(g·h) and 60.27%, respectively, both of which are higher than those of $\text{Cu}^I/\text{Y}(\text{CuCl})$. With further increases in processing temperature, $\text{Cu}^I/\text{Y}(\text{CuCl}_2)$ exhibits an improved STY and similar S_{DMC} compared with the $\text{Cu}^I/\text{Y}(\text{CuCl})$ catalyst. Analysis of X-ray diffraction of the catalysts (not shown) indicated that higher processing temperatures resulted in improved dispersion of CuCl_2 or CuCl on the catalyst surfaces. The specific surface areas of the prepared catalyst also increased, leading to the observed improvements in the catalytic activity of the Cu^I/Y materials.

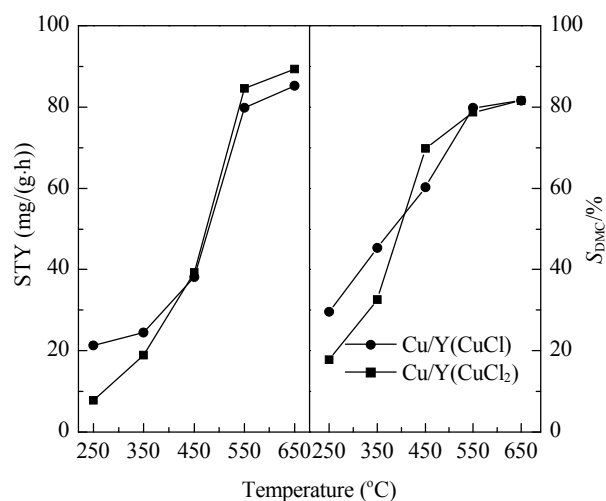


Fig. 3. Effects of preparation temperature on the activities of Cu^I/Y catalysts.

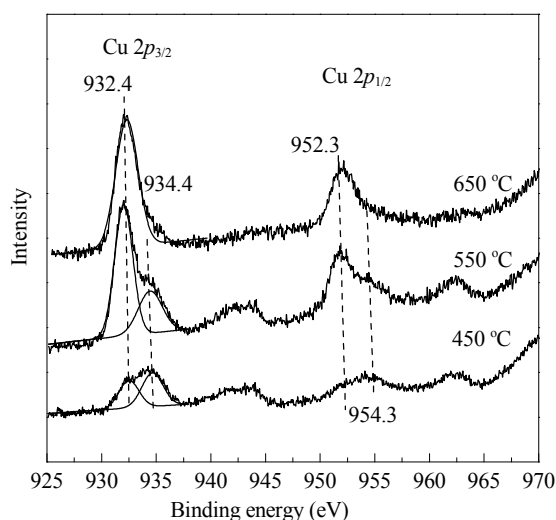


Fig. 4. Cu 2p XPS spectra of Cu/Y(CuCl₂) catalyst prepared at different temperatures.

Figure 4 presents the Cu 2p XPS spectra of the Cu/Y(CuCl₂) catalyst prepared at various temperatures. These results demonstrate that the Cu 2p_{3/2} and Cu 2p_{1/2} binding energies for these catalyst samples were within the ranges of 930–938 and 950–957 eV, while the divalent Cu satellite peak was at 940–945 eV. Through curve-fitting of the Cu 2p_{3/2} spectra, two peaks attributed to Cu^I (932.4 eV) and Cu^{II} (at 934.4 eV) were identified, and the results are shown in Table 1. It indicates that with increasing processing temperatures the Cu^I content on the catalyst surfaces increased while the Cu^{II} decreased. As an example, the atom percentages of Cu^{II} on the surfaces of the catalysts prepared at 450 and 550 °C were 56.75% and 29.90%, respectively. Thus Cu^I rather than Cu^{II} is the dominant species on the catalyst prepared at 650 °C. The Cl content is also seen to decrease while the molar ratio of Cu to Cl increased with rising processing temperatures. The apparent presence of Cu^{II} on the surfaces of catalysts prepared at 450 and 550 °C could be due to incomplete decomposition of CuCl₂ because these materials exhibit surface Cu/Cl atomic ratios below 1. On the surface of the Cu/Y(CuCl₂) catalyst prepared at 650 °C, only Cu^I was present and the Cu/Cl atomic ratio was 1.08, indicating that the Cu on the surface of this catalyst is primarily in the form of CuCl.

The Cu/Y samples prepared from different Cu salts were analyzed by elemental analysis, with the results shown in Table 2. The Cu content in Cu/Y(CuCl) catalyst is higher than that of Cu/Y(CuCl₂). However, both have Cu/Cl atom ratios above 1, and this ratio increases further with higher heating tempera-

Table 1
Surface elemental analysis results for Cu/Y catalysts based on XPS data.

Preparation temperature (°C)	Atomic percentage Cu 2p _{3/2} (%)		Atomic percentage (%)		Cu/Cl atomic ratio
	Cu ^I	Cu ^{II}	Cu	Cl	
450	43.25	56.75	1.62	3.47	0.47
550	70.10	29.90	1.46	1.56	0.93
650	100	0	1.85	1.71	1.08

Table 2
Elemental analysis data for the Cu/Y catalysts.

Catalyst	Preparation temperature (°C)	Mass content (%)		Mole content (mol/g)		Cu/Cl atomic ratio
		Cu	Cl	Cu	Cl	
Cu/Y(CuCl)	550	19.70	7.69	0.31	0.22	1.4
	650	19.50	6.33	0.34	0.18	1.89
Cu/Y(CuCl ₂)	550	10.86	3.88	0.17	0.11	1.54
	650	11.84	3.22	0.19	0.09	2.11

tures. Comparison of the Cu/Cl atom ratios indicates that the ratio calculated on the basis of the XPS surface elemental analysis is less than 1, while the ratio in the bulk phase of the catalyst is much higher. The dominant compounds on the catalyst surface are therefore CuCl and CuCl₂, while the ion-exchanged Cu^I is in the internal cage structure of the zeolite. Thus Cu exists in the form of both CuCl and CuCl₂ on the external surface of the Y zeolite, while the ion-exchanged Cu^I and small amounts of adsorbed CuCl are in the Y zeolite cage structures [21]. The catalyst prepared at 650 °C has only Cu^I derived from the small amount of adsorbed CuCl (0.09 mol/g) and ion-exchanged Cu^I (0.1 mol/g).

3.3. Stability of the Cu/Y(CuCl₂) catalyst

Figure 5 shows the dependence of the steady-state catalytic activity on the Cu loading of the Cu/Y(CuCl₂) catalysts. With increases in the CuCl₂·2H₂O content, the STY and selectivity for DMC increased, although this effect decreased at CuCl₂·2H₂O contents above 30 wt%. Both STY and S_{DMC} eventually plateaued and did not increase any further with higher CuCl₂·2H₂O content, likely owing to the saturation of Brönsted acid sites with Cu⁺ from dispersed CuCl in the zeolite.

Figure 6 depicts the dependence of the catalytic performance on reaction time over Cu/Y(CuCl₂) catalyst. It shows that the formation rate of DMC increases with the on-stream time, reaching an equilibrium value after 3 h. After 200 h of reaction time, the STY and selectivity for DMC were approximately 85 mg/(g·h) and 80%, respectively. About 3 h was required for the

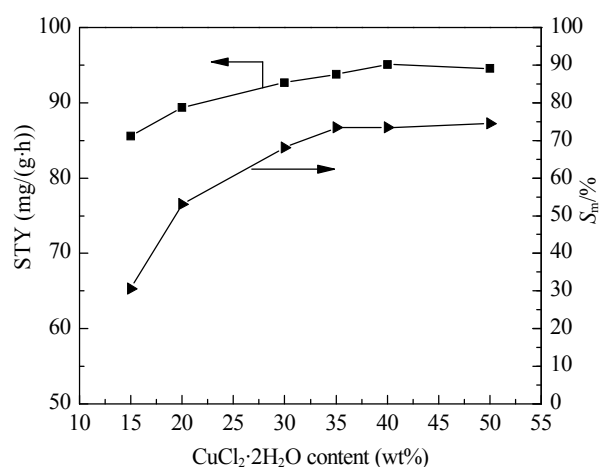


Fig. 5. Variation in steady-state activity during DMC synthesis using Cu/Y(CuCl₂) catalysts as a function of CuCl₂·2H₂O content.

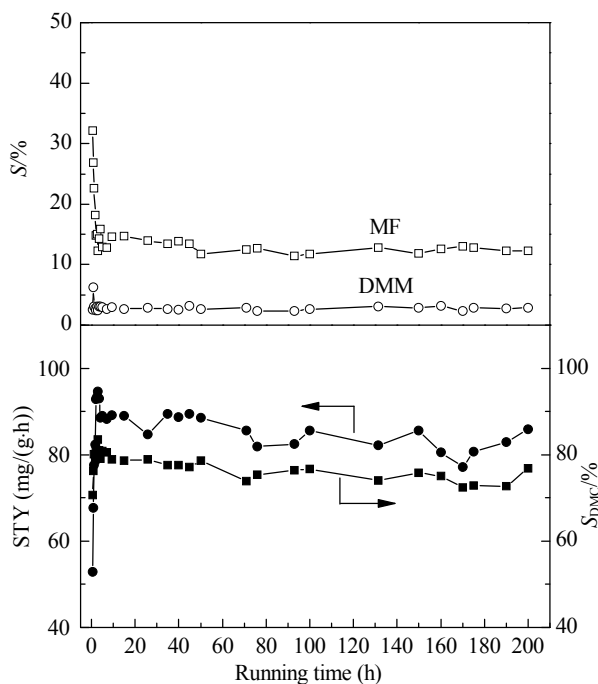


Fig. 6. Variation in catalytic performance with on-stream reaction time over Cu/Y(CuCl₂) catalysts.

MF and DMM formation rates to plateau, at which point their selectivities were 15% and 2%, respectively.

4. Conclusions

A Cu/Y catalyst was prepared by the SSIE method using a combination of CuCl₂ and HY zeolite. The highly dispersed CuCl and ion-exchanged Cu⁺ in the zeolite were both active in DMC synthesis from methanol. CuCl and CuCl₂ were found to co-exist on the external surface of the catalyst, while ion-exchanged Cu⁺ or small amounts of adsorbed CuCl were contained in the internal cage structure of the Y zeolite. Compared with the Cu⁺/Y

catalyst prepared by heating a mixture of CuCl and HY, the Cu/Y catalyst synthesized by heating a mixture of CuCl₂ and HY showed higher catalytic activity during the oxidative carbonylation of methanol, even though the latter material had lower Cu and Cl contents.

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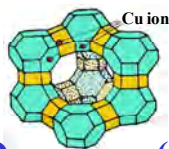
Graphical Abstract

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Surface reaction of CuCl₂ and HY zeolite during the preparation of CuY catalyst for the oxidative carbonylation of methanol

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China University of Mining and Technology; Taiyuan University of Technology



A Cu/Y(CuCl₂) catalyst was prepared by heating a combination of CuCl₂ and HY zeolite, and exhibited higher catalytic activity for the oxidative carbonylation of methanol compared with a conventional Cu/Y catalyst generated by heating a mixture of CuCl and HY zeolite, even though it had lower Cu and Cl contents. In this catalyst, both CuCl and CuCl₂ were present on the surface and ion-exchanged Cu⁺ and low levels of adsorbed CuCl were in the internal Y zeolite cage structure.

CuCl₂和HY分子筛的表面反应及Cu/Y分子筛的制备及其催化甲醇氧化羰基化

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摘要: 以CuCl₂为前驱物与HY分子筛进行固相离子交换制备了Cu/Y催化剂, 采用热重方法研究了CuCl₂与HY分子筛的表面固相离子交换反应, 结合活性测试表明催化剂中高度分散的CuCl和离子交换形式的Cu⁺物种是甲醇氧化羰基化合成碳酸二甲酯的催化活性中心. X射线光电子能谱表征和元素分析结果表明, 活性金属Cu主要以CuCl形式存在于分子筛外表面, 而在分子筛笼内则以交换的Cu⁺和少量吸附的CuCl形式存在. 与以CuCl为交换铜源所制催化剂相比, 以CuCl₂为铜源制备的催化剂Cu含量低, 催化活性更高.

关键词: 氯化铜; 固相离子交换; 催化剂; 氧化羰基化; 甲醇; 碳酸二甲酯

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