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Physico-chemical properties of supported Cu catalysts for production of dimethyl carbonate

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Abstract

The physico-chemical properties of carbon-supported Cu catalysts used for producing dimethyl carbonate were investigated. The specific surface area decreases with increase in the thermal treatment temperature and the Cu content of the catalyst. The molar ratios of OH/Cu also have effect on the specific surface area of the catalysts and their activity. An uniform dispersion of the Cu component and a proper Cu content and molar ratio of OH/Cu are required in order to obtain a high conversion of methanol and high selectivity to DMC.

Keywords: Physico-chemical property; Supported copper catalyst; Dimethyl carbonate

1. Introduction

Dimethyl carbonate (DMC) has been used as a gasoline extender, an octane number improver, an organic solvent, and also has recently been used as a phosgene replacement as a raw material in the process of isocyanates and polycarbonates synthesis. Dimethyl carbonate production by a liquid-phase reaction of methanol with carbon monoxide and oxygen in the presence of a metal halide or a mixed metal halide catalyst were investigated by many researchers [1,2]. However, the process requires the use of elaborate techniques to separate the catalyst and the azeotropic mixtures of dimethyl carbonate formed with water and methanol. Additionally, water accumulates in the solvent and rapidly deactivates the catalyst.

In order to eliminate the above problems, Curnutt [3,4] developed a dimethyl carbonate process by catalytic reaction in the vapor phase. The major work was focused on the catalytic activities of the catalysts, however, little has been reported on the physico-chemical properties of the catalysts. In this work, the physico-chemical properties of carbon-supported Cu catalysts used for producing dimethyl carbonate were investigated in order to gain information about the catalysts.

2. Experimental

2.1. Catalyst preparation

An activated carbon with a particle size between 0.45 and 0.9 mm, and a BET surface area of 1000 m^2/g and a pore volume of 0.87 ml/g

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was used as a carrier. Catalysts with a Cu loading in the range from 3 to 13.5 wt% Cu were prepared by incipient wetness impregnation with an ethanol solution of $CuCl_2$. All impregnated samples were dried under a flow of nitrogen gas at 100°C for 3 h. The dried particles were cooled to room temperature and were further treated by incipient wetness impregnation with an alkali metal- or an alkali earth metal-hydroxide solution. LiOH, NaOH, KOH and $Ba(OH)_2$ were tried as basic components, however, the difference in the alkali and alkali earth metals has no influence on the activity and the physical properties of the catalyst, in consequence all the data in this paper are based on the catalyst doped with NaOH. After impregnation, the sample was subjected to a thermal treatment under a flow of nitrogen gas at 100 to 400°C for 3 h. The molar ratio of OH/Cu is calculated from the moles of impregnated $CuCl_2$ and the moles of OH in the basic solution.

2.2. Catalyst characterization

The activities of catalysts were measured with a micro catalytic reaction system comprising a stainless steel fixed bed reactor of 5 mm inner-diameter, with a molar ratio of carbon monoxide to methanol of 1.3, a molar ratio of oxygen to methanol of 0.3. The reaction temperature was in the range 100 to 150°C and pressure was in the range 0.1 to 1.5 MPa.

The specific surface area measurements of the catalysts were performed by nitrogen at 77 K, using the BET equation on a CHEMBET-3000 instrument. The range of relative pressure of nitrogen was between 0.05 and 0.2. The SEM images of catalysts were produced on a Leica S-360 scanning electron microscope equipped with a Link exl-II EDAX by placing the catalyst particles on the specimen holder and coating with gold. Surface species were checked by means of electron probe. Powder XRD experiments were done using Cu K_α radiation with a D/max diffractometer operated at a working voltage of 40 kV and a working current of 168 mA.

The XPS analysis of the catalysts was carried out on a Perkin-Elmer PHI 1600 ESCA system operated at a pass energy of 23.5 eV with a magnesium X-ray source ($E = 1253.6$ eV). The samples were mounted on the specimen holder by means of double-sided adhesive tape. Spectra were recorded in steps of 0.15 eV. The C1s peak (284.5 eV) was used as the internal standard for binding-energy calibration. The deviation of binding energy was ± 0.15 eV. The pressure during the measurements did not exceed 1.6×10^{-8} Torr and the temperature was approximately 293 K.

3. Results and discussion

Table 1 tabulates the activity and physical properties of the catalysts as well as the thermal

Table 1
The effect of Cu content, OH/Cu ratio and thermal treatment temperature on the surface area and activity [a]

Number of catalyst	Cu content (wt%)	OH/Cu	Thermal treatment temperature (°C)	Specific surface area [b] (m^2/g)		Conversion of methanol (%)	Selectivity to DMC (%)
				B	A		
Z-113	3.0	0.5	300	674.0	539.6	8.3	70.3
Z-121	3.0	1.0	100	633.7	463.8	7.1	78.2
Z-123	3.0	1.0	300	623.8	394.0	9.9	75.3
Z-143	3.0	2.0	300	616.8	335.5	6.2	56.8
Z-323	9.0	1.0	300	459.7	309.9	22.9	78.5
Z-423	13.5	1.0	300	439.6	412.3	14.8	71.4
Z-424	13.5	1.0	400	309.6	224.0	13.0	65.5

[a] Reaction temperature, 130°C; pressure, 0.7 MPa.
[b] B, before reaction; A, after reaction.

treatment temperature. The results showed that the specific surface area decreases with the increase in the thermal treatment temperature at the same Cu content and OH/Cu ratio. The conversion of methanol does not follow the same law, which shows that optimum values of Cu content, OH/Cu and thermal treatment temperature exist. There could be two reasons responsible for the decrease in specific surface area with increase in the thermal treatment temperature, e.g. the sintering of the activated carbon and the plugging effect of the other components. To investigate this, the activated carbon was treated at 300°C for 3 h under a flow of nitrogen, its specific surface area reduced to 776.3 m^2/g. This provided evidence that some

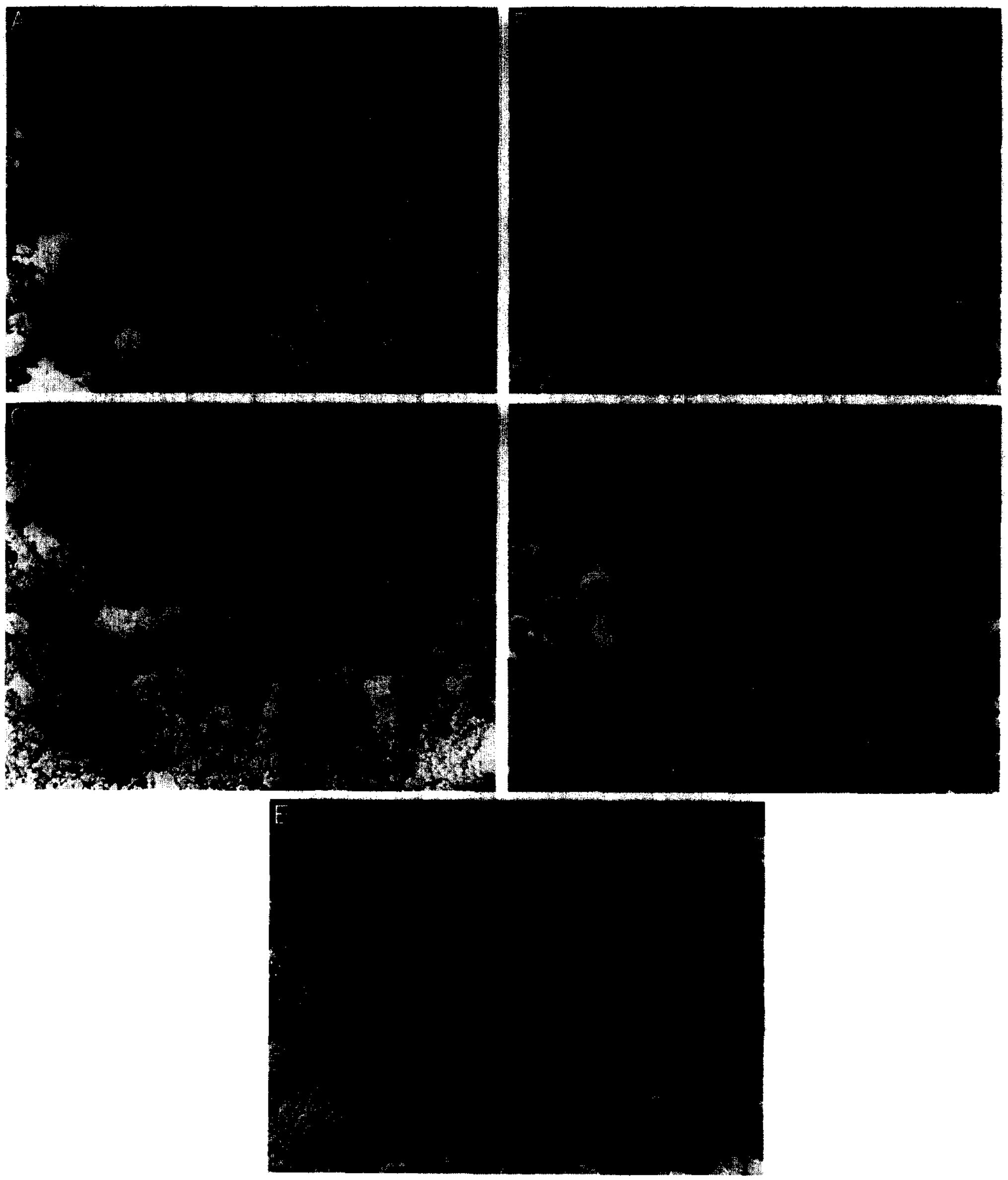

Fig. 1. SEM photographs of the catalysts: A, activated carbon carriers; B, catalyst Z-121 before reaction; C, catalyst Z-121 after reaction; D, catalyst Z-323 before reaction; E, catalyst Z-323 after reaction.

pores of the activated carbon were sintered during the thermal treatment. In the second case, the capillary force in the micropores of the catalyst could cause a build-up of the alkali metal compound because of migration, which causes the pores of the catalyst becoming plugged. It is also demonstrated in Table 1 that the specific surface area decreases with the increase of Cu content in the catalyst. The data of the 3.0 wt% Cu and 300°C treated samples reveal that the specific surface area of the catalyst decreases with the increase of the molar ratio of OH/Cu, however, the catalytic activity increases with the increase of the molar ratio of OH/Cu until the molar ratio of OH/Cu reaches 1.0, beyond which the catalytic activity decreases. It has also been shown that the catalytic activity increases with the increase in Cu content of the catalyst until the Cu content of the catalyst reaches 9.0 wt%, beyond which the catalytic activity decreases. The data in Table 1 shows that all the samples lose quite a lot of specific surface area during the reaction. The results that the specific surface area of the catalysts after reaction is much smaller than that of before reaction may be attributed to further migration of the alkali metal compound during the reaction.

The SEM images of the activated carbon carrier and the supported catalysts before and after reaction are shown in Fig. 1. The activated carbon was very dense and highly microporous with no indication of an open structure as shown in Fig. 1A. The bright particles on the surface could be some impurities coming together with the sample [5]. The SEM photographs of catalyst Z-121 before and after reaction are shown in Fig. 1B and Fig. 1C. The smallest circular particles on the catalyst surface were detected by the electron probe. It proved that they contains a large ratio of Cu and a very small ratio of Na. From comparison of SEM photographs of catalyst Z-121 before and after reaction, the Cu containing particles became smaller and more uniform. The Cu distribution photographs of catalyst Z-121 before (Fig. 2A) and after reaction (Fig. 2B) also indicate that the Cu component distribution became more uniform after reaction than that before reaction. The Cu distribution photographs of other catalysts have also the same results that the Cu component distribution became more uniform after reaction than that of before reaction. This means that there exists redispersion of the Cu component during the reaction because of the chemisorption of reactants and the migration of the sodium salt.

From the analysis of the SEM photographs of catalysts, it was proved that the different alkali metal- or an alkali earth metal-hydroxide has no effect on the dispersion of Cu component on the catalyst surface. It is shown in Fig. 1D, that the Cu containing compound were covered on the carrier surface in the form of a shell over the

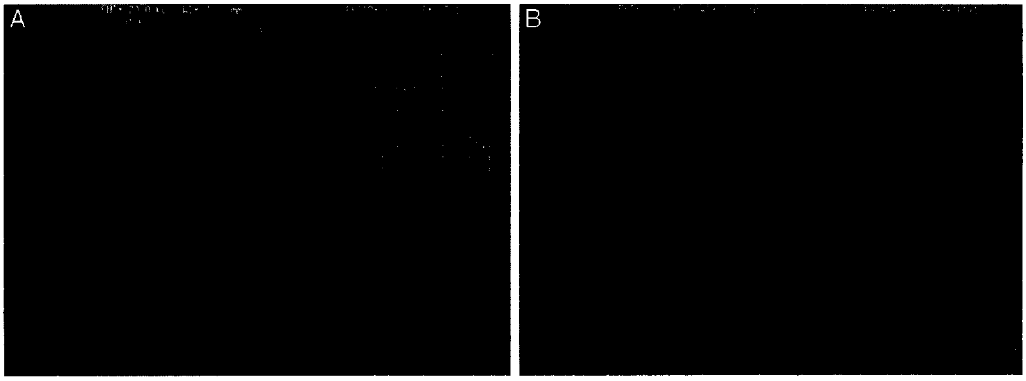

Fig. 2. Cu distribution SEM photographs of the catalysts: A, catalyst Z-121 before reaction; B, catalyst Z-121 after reaction.

carrier before reaction when the Cu content of catalyst reaches 9.0 wt%. After the reaction, the Cu compound was broken into smaller pieces, the sodium compound accumulates in large bodies and rested on the catalyst surface as shown in Fig. 1E. The same experiment shows that when the Cu content of the catalyst reaches 13.5 wt%, after reaction the sodium compound accumulates into larger bodies and almost covered all the surface of catalyst. With the data on methanol conversion and selectivity to DMC, we may conclude that a uniform dispersion of the Cu component and a proper Cu content and molar ratio of OH/Cu are required to obtain a high conversion of methanol and high selectivity to DMC.

The XRD profiles of catalyst Z-323 before and after reaction are illustrated in Fig. 3. It shows that there was NaCl, Cu^0, Cu_2O, $CuCl_2 \cdot 3Cu(OH)_2$ and some CuO in the pattern before reaction, and there was only NaCl, CuO, Cu_2O, $CuCl_2 \cdot 3Cu(OH)_2$ after reaction. It was also observed with other XRD patterns of other samples that the higher the Cu content, the higher the ratio of Cu_2O to Cu^0 was, and when the molar ratio of OH/Cu was 2, the major Cu containing phases observed were $CuCl_2 \cdot 3Cu(OH)_2$ with some Cu_2O, CuO and Cu^0. However, when the molar ratio of OH/Cu is 1, the major Cu containing phases were Cu_2O, CuO and Cu^0. It was also noted that Cu crystals were larger when the thermal treatment temperature was higher.

Typical Cu X-ray photoelectron spectra of the catalyst Z-323 before and after reaction are shown in Fig. 4. The Cu^{2+} is easily identified by the appearance of the shake-up peaks accompanying the peaks with a binding energy of -955.31 ± 0.15 eV ($2p_{1/2}$) and -935.24 ± 0.15 eV ($2p_{3/2}$), respectively. The Cu^0 and Cu^+ were identified by the peaks in their X-ray Auger electron spectroscopy with binding energies of -334.92 ± 0.15 and -337.72 ± 0.15 eV, respectively. After reaction the Cu^0 peak at -334.92 eV in Fig. 4 ZRZ91/Cu2 disappears, which is consistent with the result from XRD

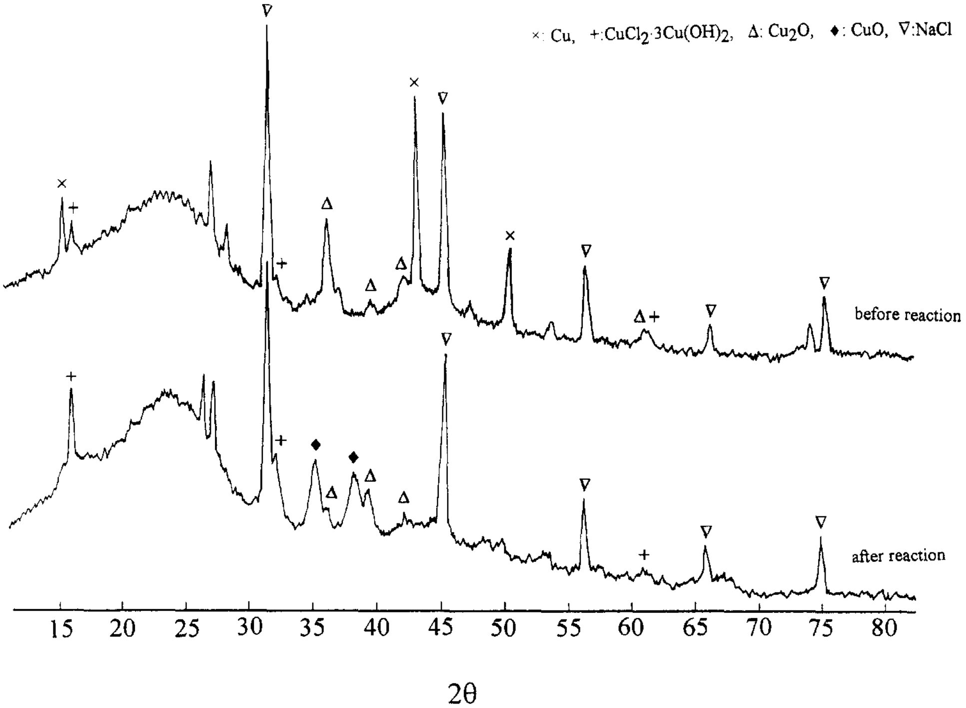

Fig. 3. XRD profiles of catalyst Z-323: ×, Cu; +, $CuCl_2 \cdot 3Cu(OH)_2$; △, Cu_2O; ◆, CuO; ▽, NaCl.

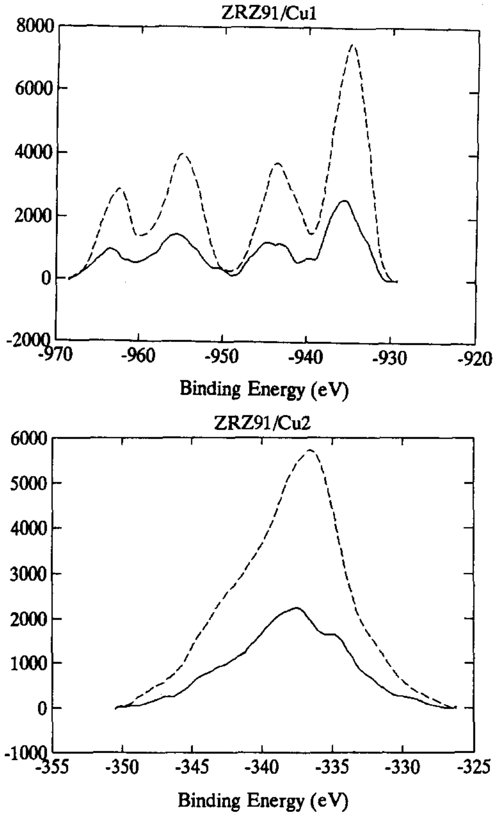

Fig. 4. Cu X-ray photoelectron spectra of the catalyst Z-323: —, before reaction; - - -, after reaction.

that Cu^0 disappears after reaction. The surface composition of the catalysts determined by XPS is given in Table 2. The total amount of Cu increased from 2.83 mol% before reaction to 8.56 mol% after reaction. This result indicates that there is a Cu migration phenomenon during the reaction.

Table 2
The surface composition of catalysts detected by XPS

Catalyst		Surface composition (mol%)				
		C	O	Cu [a]	Na	Cl
Z-323	B [b]	59.49	16.64	2.83	7.20	13.84
	A [b]	44.92	22.89	8.56	5.59	14.03

[a] Total Cu.

[b] B, before reaction; A, after reaction.

4. Conclusions

It has been observed with the activated carbon supported Cu catalyst for the production of dimethyl carbonate that its specific surface area decreases with the increase of the thermal treatment temperature; an optimum thermal treatment temperature exists for catalytic activity, which is 300°C; the specific surface area decreases with the increase in the amount of Cu content of the catalyst. The molar ratio of the OH/Cu has also a strong effect on the specific surface area and their activity, and the best molar ratio of OH/Cu is 1.0. The catalytic activity increases with increase in Cu content of the catalyst until the Cu content of the catalyst reaches 9.0 wt%, beyond which the catalytic activity decreases. A uniform dispersion of the Cu component and a proper Cu content and molar ratio of OH/Cu is required to obtain a high conversion of methanol and high selectivity to DMC.

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