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Adsorption Behavior for CO on Modified MCM-41 with Zn and CuCl

Nong Yue HE[1,2]*, Qi Hong SHI[3], Fei GAO[3], Yi Bing SONG[3], Yang YU[3], Hui Lin WAN[4]

[1]Key Lab of New Materials and Technology of China National Packaging Corporation,
Zhuzhou Engineering College, Zhuzhou 412008
[2]Key Laboratory for Molecular and Biomolecular Electronics of Ministry of Education,
Southeast University, Nanjing 210096
[3]Department of Chemistry , Shantou University , Shantou 515063
[4]The State key Laboratory for Physical Chemistry of Solid Surfaces, Xiamen University,
Xiamen 361005

Abstract: The Zn-Cu(I)/HMCM-41 catalysts were successfully prepared in laboratory scale by solid-state ion exchange with CuCl salt, together with introduction of Zn to improve the dispersion degree of the active component Cu(I) on the surface. With increase of the amounts of Zn and CuCl from 0% to 9.0% and 25.0% respectively, CO adsorption the amounts of increased from 10.6 μmol/g to 183.0 μmol/g correspondingly. The *in situ* FT-IR spectra for CO adsorption demonstrated that there existed two dynamic equilibriums between surface carbonyl complexes: $Cu(CO)_3^+ \Leftrightarrow Cu(CO)_2^+ + CO$ and $Cu(CO)_2^+ \Leftrightarrow Cu(CO)^+ + CO$. The equilibriums can be shifted reversibly by changing the temperature and pressure. Due to the modified MCM-41 mesoporous materials possess both of the acidic and metallic carbonyl centers, this kind of material can be developed into mesoporous bifunctional catalysts for carbonylation reactions, in which larger molecules are involved.

Keywords: MCM-41, carbon monoxide, adsorption, carbonylation, cuprous.

The synthetic method of tertiary monocarboxylic acids has following deficients: the difficult separation and the use of strong acid necessity of waste treatment. It is necessary to develop heterogeneous catalysts[1]. We have successfully synthesized the C_5 carboxylic acid using butanol and carbon monoxide as starting materials, metal-containing and enzyme–like zeolites as catalysts under mild conditions (~523 K, atmospheric pressure)[2-4]. However, the and HZSM-5 parent zeolites with small pore size (<1.0 nm) is limited to use in the synthesis of tertiary monocarboxylic acid with a longer carbon chain, for example, C_9 carboxylic acid, which is a wonderful paint for car. Based on our previous studies on mesoporous materials[5-10], here we report the preparation of Zn-Cu(I)/HMCM-41 bifunctional catalysts with large enough pore admitting the reversible adsorption of carbon monoxide molecules. This kind of material can be developed to the catalyst which can be used in the reaction of carbon monoxide and bulky organic molecules.

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*E-mail: nyhe@seu.edu.cn

The HMCM-41 sample with a SiO_2/Al_2O_3 ratio of 32 was prepared as described previously[6]. The Zn-Cu(I)/HMCM-41 sample was prepared as below: Given amount of HMCM-41 sample was added into given amount of absolute alcohol containing given amount of $ZnCl_2$ under stirring until the alcohol was completely vaporized at ambient temperature, followed by drying at 393 K in an oven for 6 h. Then the sample was transferred into a muffle oven and was calcined at 843 K for 4.5 h to obtain the Zn/HMCM-41 sample. Given amount of Zn/HMCM-41 was mixed with given amount of CuCl in a mortar with pestle, then calcined in a quartz tube in a nitrogen flow at 623 K for 4 h to get the Zn-Cu(I)/HMCM-41 samples. The CO-TPD-MS investigation was conducted on a temperature programmed desorption instrument adapted from the Blazers GSD 3000 02 mass spectrometer (MS). The *in situ* FT-IR spectra were acquired on a PE-Spectrum 2000 *in situ* FT-IR spectrometer with a resolution of 2 cm^{-1}.

The loading amounts of Zn and CuCl and CO adsorption capacity on a series of samples are listed in **Table 1**. It was found that after loading CuCl or Zn, the CO adsorption amount was significantly increased in comparison with the parent HMCM-41 sample 12, and the CO adsorption capacity on CuCl-loaded sample 11 was much greater than that on Zn-loaded sample 10. On the other hand, comparing the data for sample 2, 5, 8 and 11 possessing the same amount of CuCl, we can find that after loading Zn the CO adsorption capacity increased more than the sample 11 which was only loaded CuCl. From the data we also found that the positive influence of Zn on the CO adsorption capacity increased from 3.0% to 9.0% of the loading amount of Zn and decreased from 9.0% to 12.0%, *i.e.*, the most optimized loading amount of Zn is 9.0. It seemed that the loaded Zn occupied part of adsorption sites of CuCl and, therefore, the CO adsorption capacity decreased when the loading amount of Zn increased from 9.0% to 12.0%.

For the samples with the same Zn loading amount and varying loading amount of CuCl (20.0%, 25.0% and 30.0%), the CO adsorption capacity behaviors are different from each other. When the loading amount of Zn is ≤9.0%, the CO adsorption capacities on samples with a CuCl loading amount of 25.0% are the greatest. Whereas, due to that a fraction of adsorption sites were occupied by Zn species, the CO adsorption capacity decreased with the increase in the loading amount of CuCl for those samples with 12.0% of Zn (see sample 7-9).

Table 1 The influence of the loading amounts of Zn and CuCl on CO adsorption capacity of the Zn-Cu(I)/HMCM-41

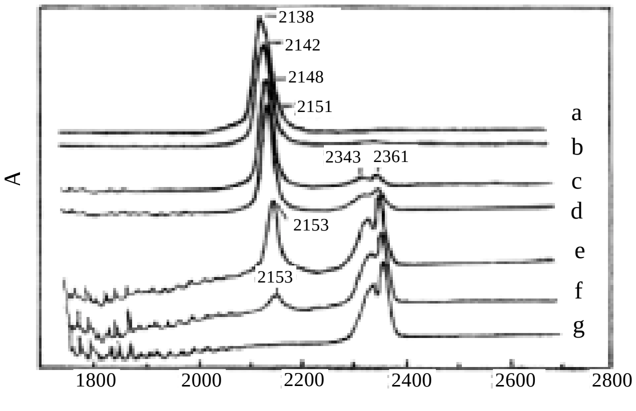
Samples	Zn loading content (wt%)	CuCl loading content (wt%)	CO adsorption capacity (μmol/g)
1	3.0	20.0	68.84
2	3.0	25.0	80.77
3	3.0	30.0	71.05
4	9.0	20.0	139.71
5	9.0	25.0	182.99
6	9.0	30.0	142.54
7	12.0	20.0	107.91
8	12.0	25.0	87.52
9	12.0	30.0	83.34
10	6.0	0.0	26.05

11	0.0	25.0	59.57
12	0.0	0.0	10.61

The influence of Zn species on the CO adsorption capacity of CuCl-loaded samples is worthy of some discussion. It is well known that under the same composition conditions, the population of reactive sites and, therefore, the activity, increases with the decrease in the size of particles and the increase in surface area of particles. Because there is a strong interaction between the Zn species and CuCl species on Zn-Cu(I)/HMCM-41 samples prepared by solid-state ion exchange[11], the sintering and agglomeration of Cu species can be prevented and Cu(I) species highly dispersed on the surface of channel wall of HMCM-41. This leads us to the conclusion that adding Zn species can increase the dispersion degree and, therefore, increase the population of reactive sites resulting from Cu(I) species. Thus the CO adsorption capacity increased for those samples loaded with both Zn and CuCl species.

The *In situ* FT-IR spectra of CO sample 8 are shown in **Figure 1** before and after evacuation at different temperature. Five bands were detected at 2138, 2142, 2148, 2152 and 2153 cm^{-1}, respectively. They were assigned to $Cu(CO)^+$ (2135 cm^{-1}), $Cu(CO)_2^+$ (2148 and 2151 cm^{-1}) and $Cu(CO)_3^+$ (2138 and 2140 cm^{-1}), respectively[12]. It was shown that the sample prepared by solid-state ion exchange approach, $Cu(CO)_3^+$ was formed at low temperature (323 K). When the temperature was increased or the CO partial pressure was decreased, all the bands shifted towards high wavenumber direction, $Cu(CO)_3^+$ was destabilized and its special band gradually vanished. If the temperature was increased to 573 K, all the bands owing to the CO adsorption completely disappeared (spectrum g in **Figure 1**), meaning CO can not be adsorbed at such a high temperature. When the temperature was increased to 373 and 473 K respectively, correspondingly $Cu(CO)_2^+$ and $Cu(CO)_3^+$ were formed respectively. Upon decrease of temperature from 473 K to 373 and 323 K, the spectra were recovered to the same as that obtained before increasing the temperature. It seemed that some reversible and dynamic equilibriums existed among $Cu(CO)_3^+$, $Cu(CO)_2^+$ and $Cu(CO)_1^+$ upon the changes in temperature and pressure. It is believed that a carbonylation reaction takes place

Figure 1 IR spectra of CO absorbed on Zn-Cu(I)/HMCM-41



(a) and (b): Before and after evacuation at 323 K; (c) and (d): Before and after evacuation at 373 K; (e) and (f): Before and after evacuation at 473 K; (g): Before evacuation at 573 K.

Wavenumber (cm^{-1})

accompanying the adsorption and release of CO as follows:

$$Cu(CO)_3^+ \Leftrightarrow Cu(CO)_2^+ + CO \qquad (I)$$
$$Cu(CO)_2^+ \Leftrightarrow Cu(CO)_1^+ + CO \qquad (II)$$

Recently we observed that the solid-state acid centers in bifunctional Cu(I)/HY, Cu(I)/Hβ or Cu(I)/HZSM-5 can work in cooperation with the above metal carbonyl centers under mild conditions (523 K and atmospheric pressure) to convert the alcohol into tertiary monocarboxylic acid ($\leq C_5$) by carbonylation reaction. Because the modified MCM-41 samples not only have pore size of 1.6-3.2 nm but also possess both solid-state acid sites and metal carbonyl active centers, it is promising to develop these materials into carbonylation catalysts for bulk molecules.

From **Figure 1** we can also observe that after evacuation at 323 K, two bands at 2361 and 2343 cm^{-1} assigned to CO_2 appeared and the intensities of them increased with the increase in temperature and decrease in partial pressure of CO. It was the result of the reduction of Cu(I) on Zn-Cu(I)/MCM-41 to release CO_2:

$$Cu^+ + CO \rightarrow Cu^0 + CO_2$$

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