The high dispersion of $CuCl_2$ in NaZSM-5 by using microwave technique

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By using microwave technique, the high dispersion of $CuCl_2$ in NaZSM-5 zeolite ($CuCl_2 \cdot 2H_2O$/NaZSM-5 ratio of 0–0.50 g/g) has been prepared. The mechanical mixture of $CuCl_2 \cdot 2H_2O$ and NaZSM-5 ($CuCl_2 \cdot 2H_2O$/NaZSM-5 ratio of 0–0.50 g/g) shows characteristic XRD peaks of both NaZSM-5 and crystalline $CuCl_2 \cdot 2H_2O$. Notably, after reaction of the above samples in a microwave oven for 10 min, the sample XRD patterns only exhibit the peaks assigned to NaZSM-5, while the peaks assigned to crystalline $CuCl_2 \cdot 2H_2O$ disappear completely, indicating that $CuCl_2 \cdot 2H_2O$ no longer exists in the crystalline state in the $CuCl_2 \cdot 2H_2O$/NaZSM-5 samples. Additionally, in DTA curves, we cannot observe the melting point of $CuCl_2$ in a $CuCl_2 \cdot 2H_2O$/NaZSM-5 sample ($CuCl_2 \cdot 2H_2O$/NaZSM-5 ratio of 0–0.5 g/g) treated in a microwave oven, indicating that there is no $CuCl_2$ crystalline phase in the $CuCl_2 \cdot 2H_2O$/NaZSM-5 samples ($CuCl_2 \cdot 2H_2O$/NaZSM-5 ratio of 0–0.50 g/g).

Keywords: dispersion; $CuCl_2$; ZSM-5; zeolite; microwave

1. Introduction

The copper ion-exchanged ZSM-5 zeolite is a very effective catalyst for the selective reduction of nitrogen monoxide (NO) by hydrocarbons [1–6]. The activity and selectivity are strongly influenced by the copper loading in the zeolites. Notably, CuZSM-5 is usually prepared by using the ion-exchange or "excessive ion-exchange" method [2,5,6], with Cu/Al ratio from 0 to near 1.0 (the exchange level is taken as 100% when Cu/Al = 1.0, i.e. one copper ion has replaced on sodium ions).

On the other hand, in this decade, commercially available microwave ovens have been used in many laboratory procedures [7], including organic synthesis [8], the reaction of solids in synthesis of inorganic compounds [9], and the crystallization of zeolites [10], etc. Recently, we have successfully synthesized several types of molecular sieves [11] at ambient temperature with short reaction time (5–30 min) by using the microwave technique.

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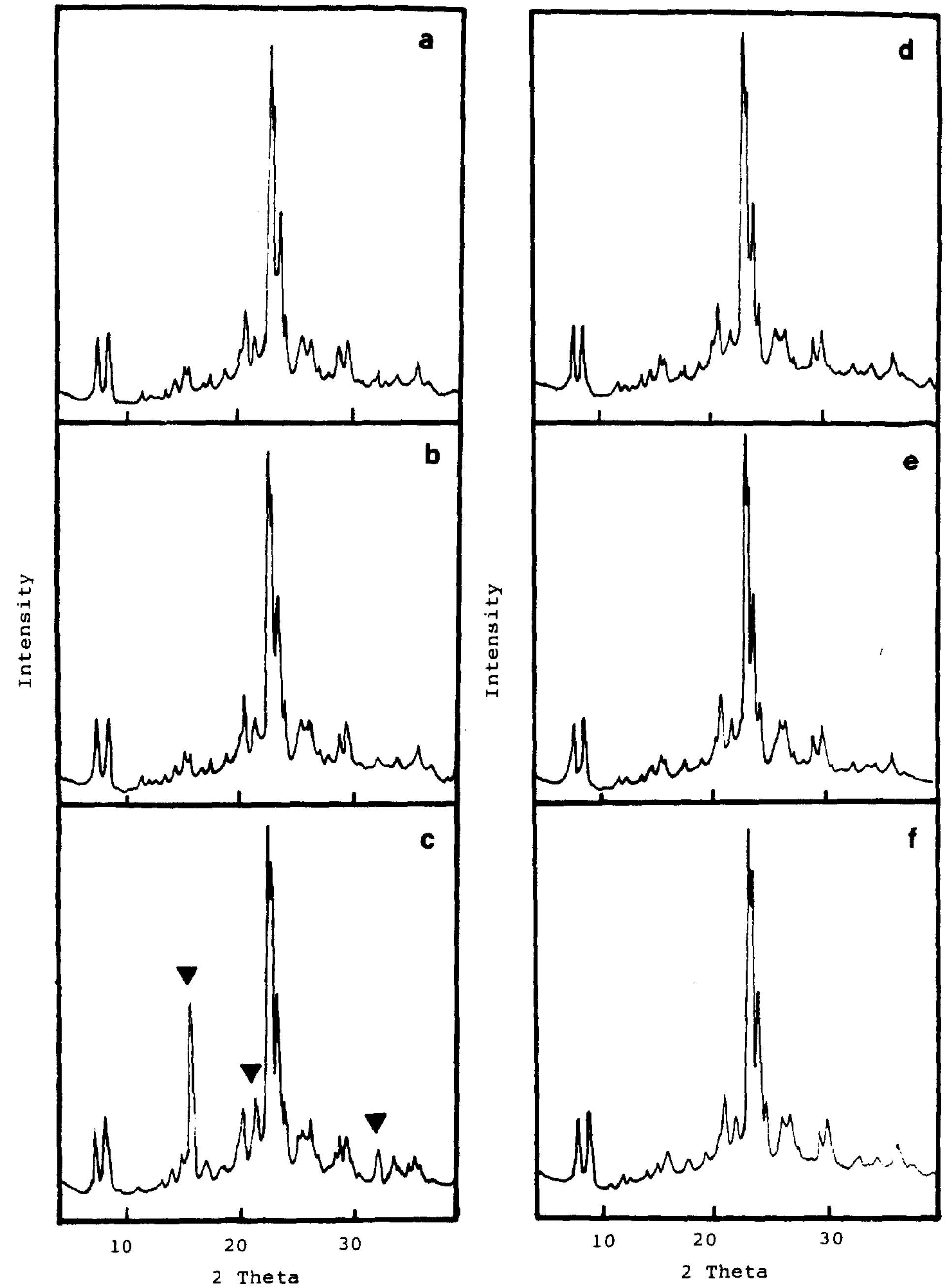

Fig. 1. XRD patterns of NaZSM-5 and $CuCl_2 \cdot 2H_2O$ at various conditions: (a) NaZSM-5; (b) NaZSM-5 treated in microwave oven for 60 min; (c) mechanical mixture of $CuCl_2 \cdot 2H_2O$ and NaZSM-5 with $CuCl_2 \cdot 2H_2O$ loading of 0.10 g/g (Cu/Al = 1.5); (d) after (c), the sample was treated in microwave oven for 10 min; (e) mechanical mixture of $CuCl_2 \cdot 2H_2O$ and NaZSM-5 with $CuCl_2 \cdot 2H_2O$ loading of 0.20 g/g (Cu/Al = 3.0) treated in microwave oven for 10 min; (f) mechanical mixture of $CuCl_2 \cdot 2H_2O$ and NaZSM-5 with $CuCl_2 \cdot 2H_2O$ loading of 0.30 g/g (Cu/Al = 4.5) treated in microwave oven for 10 min;

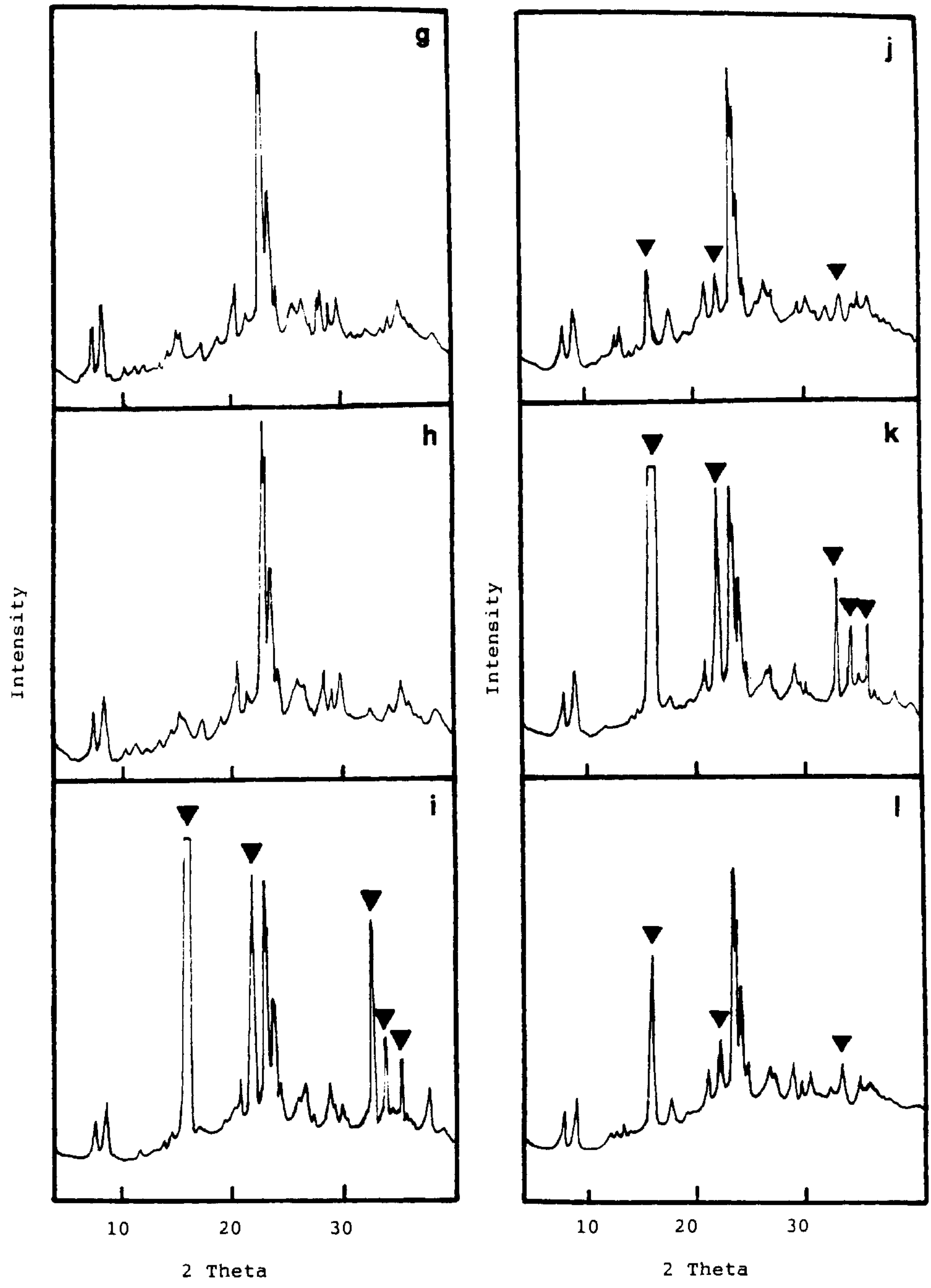

Fig. 1. (g) mechanical mixture of $CuCl_2{\cdot}2H_2O$ and NaZSM-5 with $CuCl_2{\cdot}2H_2O$ loading of 0.40 g/g (Cu/Al = 6.0) treated in microwave oven for 10 min; (h) mechanical mixture of $CuCl_2{\cdot}2H_2O$ and NaZSM-5 with $CuCl_2{\cdot}2H_2O$ loading of 0.50 g/g (Cu/Al = 7.5) treated in microwave oven for 10 min; (i) mechanical mixture of $CuCl_2{\cdot}2H_2O$ and NaZSM-5 with $CuCl_2{\cdot}2H_2O$ loading of 0.60 g/g (Cu/Al = 9.0); (j) after (i), the sample was treated in microwave oven for 20 min; (k) mechanical mixture of $CuCl_2{\cdot}2H_2O$ and NaZSM-5 with $CuCl_2{\cdot}2H_2O$ loading of 0.70 g/g (Cu/Al = 10.5); (l) after (k), the sample was heated in microwave oven for 20 min (▼, characteristic peaks of $CuCl_2{\cdot}2H_2O$).

In the present study, we try to develop a new route for the dispersion of $CuCl_2$ in ZSM-5 zeolite by using the microwave technique, and it was found that the $CuCl_2$ highly disperses in the channel of NaZSM-5 with Cu/Al of 0–7.5.

2. Experimental

The NaZSM-5 zeolite was synthesized by reacting an aluminosilicate gel containing Na and tetrapropylammonium (TPA) cations. The procedure is described in detail elsewhere [12]. After calcination for removing organic template (TPA) and ion-exchange in NaCl solution, the NaZSM-5 zeolite was further characterized by X-ray diffraction, adsorption of probing molecules, and chemical analysis. The parameters were as follows: Si/Al = 40; surface area 500 m^2/g; crystallinity over 95%; and $H^+/Na^+ < 0.03$.

$CuCl_2$/NaZSM-5 was prepared from $CuCl_2 \cdot 2H_2O$ (purity >99.99%) with NaZSM-5. At first, the NaZSM-5 ($H^+/Na^+ < 0.01$) powder (2.0 g) was mixed mechanically with crystalline $CuCl_2 \cdot 2H_2O$ (0–1.6 g), and the mixed sample was ground for 10 min at 298 K. Then, the sample was placed into the microwave oven (Microwave Products Co., Shunde, China; model E-100Ea; frequency 2450 MHz; power 800 W). After reaction for 10–60 min in a microwave oven, the sample was characterized by X-ray diffraction (D/max-IIIA, Rigaku Co.) and differential thermal analysis (DTA) (PE-1700, programmed heating rate of 10 K/min).

The *n*-hexane isotherms on various samples were carried out by using a Cahn-2000 electron recording balance. At first, 0.20 g of the sample was placed into the sample cell, and evacuated at 473 K for 3 h. After the sample cooled down to 298 K, *n*-hexane was exposed to the sample and the weight change of the sample was recorded.

3. Results and discussion

Fig. 1 shows the XRD patterns of NaZSM-5 zeolite with $CuCl_2 \cdot 2H_2O$ under microwave condition. As observed in figs. 1a and 1b, the two XRD patterns give the same peaks at 7.9, 8.9 and 23.1, being characteristic of NaZSM-5, which indicates that the framework structure of NaZSM-5 is stable under microwave condition. The mechanical mixture of $CuCl_2 \cdot 2H_2O$ and NaZSM-5 ($CuCl_2 \cdot 2H_2O$/NaZSM-5 = 1.0, Cu/Al = 1.5) shows the peaks at 16.3, 21.9 and 34.0, assigned to $CuCl_2 \cdot 2H_2O$ crystal, in addition to those of NaZSM-5, as shown in fig. 1c. It is of interest to note that the characteristic peaks assigned to $CuCl_2 \cdot 2H_2O$ crystal disappear completely when the sample is treated in microwave oven for 10 min, as given in fig. 1d. The disappearance of the XRD peaks of $CuCl_2 \cdot 2H_2O$ crystal in $CuCl_2 \cdot 2H_2O$/NaZSM-5 might be explained by the high dispersion of $CuCl_2 \cdot 2H_2O$ in the channel of NaZSM-5 zeolite, where the $CuCl_2 \cdot 2H_2O$ no longer exists in the crystalline state [13,14]. Increasing the $CuCl_2{\cdot}2H_2O$ loading in NaZSM-5 to 0.5 g/g (Cu/Al = 7.5), we observed that the XRD peaks of NaZSM-5 still keep their positions, but we could not observe the XRD peaks of crystalline $CuCl_2{\cdot}2H_2O$, as shown in figs. 1e–1h. Upon further increase of $CuCl_2{\cdot}2H_2O$ loading in NaZSM-5 up to 0.60–0.70 g/g (Cu/Al = 9.0–10.5), the characteristic peaks assigned to $CuCl_2{\cdot}2H_2O$ appear, indicating the presence of $CuCl_2{\cdot}2H_2O$ crystalline in the $CuCl_2{\cdot}2H_2O$/NaZSM-5, as given in figs. 1i–1l.

Fig. 2 shows the curves of DTA for various samples. The sample of NaZSM-5 shows one peak at 361 K, which is assigned to the desorption of water adsorbed on NaZSM-5. The DTA curve of $CuCl_2{\cdot}2H_2O$ shows two peaks at 400 and 773 K, which are attributed to dehydration of $CuCl_2{\cdot}2H_2O$ and the melting point of $CuCl_2$, respectively. The mechanical mixture of $CuCl_2{\cdot}2H_2O$ with NaZSM-5 (Cu/Al = 1.5) gives two strong peaks at 390 and 603 K, as shown in fig. 2c. The peak at 390 K is very similar to the peak at 400 K in fig. 2b, and thus we assigned it to the dehydration of the sample. The peak at 603 K may be explained by "monolayer dispersion" of $CuCl_2$ in the NaZSM-5 by heating from 573 to 723 K. Similar phenomena have been extensively studied by Xie et al. [13]. It is very interesting that after the reaction of the $CuCl_2{\cdot}2H_2O$/NaZSM-5 sample in the microwave oven for 10 min, the sample profile only exhibits the peaks at 380 K, and the peaks at 603 K in fig. 2c and 773 K in fig. 2b completely disappeared. These results may be interpreted as that the $CuCl_2$ highly disperses in the channel of NaZSM-5 zeolite under microwave condition [13]. Upon a further increase of $CuCl_2{\cdot}2H_2O$ loading in NaZSM-5 up to 0.60 g/g (Cu/Al), followed by treatment in the microwave oven for 20 min, the sample profile gives the peaks at 400 and 770 K. The peak at 400 K is assigned to dehydration of the sample, and the peak at 770 K is assigned to the melting point of $CuCl_2$ because of the residual crystalline $CuCl_2$ on the sample. The above phenomena are similar to those of $CuCl_2$/zeolites prepared with the "monolayer dispersion" method [13], which have demonstrated that the $CuCl_2$ highly disperses in the channel of NaZSM-5, and the saturated amount for $CuCl_2{\cdot}2H_2O$ dispersion in NaZSM-5 is about the weight ratio of $CuCl_2{\cdot}2H_2O$/NaZSM-5 of 0.50 g/g (Cu/Al = 7.5).

Furthermore, we recorded the *n*-hexane isotherms on various samples in an attempt to understand the change in zeolite channels. Basically, all samples exhibit Langmuir-type isotherms [15], but there are some obvious features. For the mechanical mixtures of $CuCl_2{\cdot}2H_2O$ with NaZSM-5 powder (weight ratio of $CuCl_2{\cdot}2H_2O$/NaZSM-5 of 0–0.50), the shape of the *n*-hexane isotherms is the same as that of NaZSM-5, but the adsorption amount for *n*-hexane reduced obviously because $CuCl_2{\cdot}2H_2O$ does not adsorb *n*-hexane. Notably, when the above samples were treated in a microwave oven for 10 min, the hexane adsorption requires higher *n*-hexane pressure to reach the saturated adsorption. This phenomenon may be interpreted as that the copper salt enters the zeolite channels, resulting in the change in channel circumstance.

The IR spectra of CO adsorbed on $CuCl_2{\cdot}2H_2O$/NaZSM-5 have been

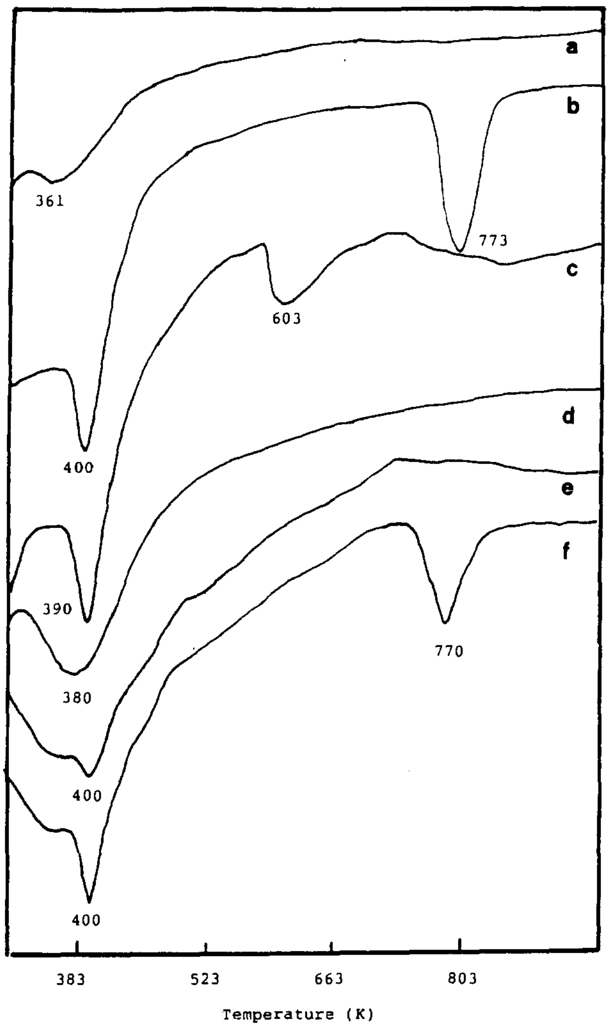

Fig. 2. DTA curves of (a) NaZSM-5 after treatment in microwave oven for 10 min; (b) $CuCl_2 \cdot 2H_2O$; (c) mechanical mixture of $CuCl_2 \cdot 2H_2O$ and NaZSM-5 with $CuCl_2 \cdot 2H_2O$ loading of 0.10 g/g (Cu/Al = 1.5); (d) mechanical mixture of $CuCl_2 \cdot 2H_2O$ and NaZSM-5 with $CuCl_2 \cdot 2H_2O$ loading of 0.10 g/g (Cu/Al = 1.5), followed by treatment in microwave oven for 10 min; (e) mechanical mixture of $CuCl_2 \cdot 2H_2O$ and NaZSM-5 with $CuCl_2 \cdot 2H_2O$ loading of 0.30 g/g (Cu/Al = 4.5), followed by treatment in microwave oven for 10 min; (f) mechanical mixture of $CuCl_2 \cdot 2H_2O$ and NaZSM-5 with $CuCl_2 \cdot 2H_2O$ loading of 0.60 g/g (Cu/Al = 9.0), followed by treatment in microwave oven for 20 min.

recorded, and it was found that the adsorbility for CO increases remarkably, as compared with that of CuZSM-5 prepared with ion-exchange method. The study on IR characterization and catalysis will be reported in the future.

In contrast to those prepared by using the copper ion-exchange method, the Cu/NaZSM-5 prepared by using the microwave technique exhibits the following obvious features: (i) The dispersion loading of $CuCl_2$ in NaZSM-5 is very large. By using ion-exchange or "excessive ion-exchange" Cu/NaZSM-5 method, it has been reported that the maximum for Cu/Al in CuZSM-5 zeolite is at near 1.0. But, by using microwave technique, we can prepare the $CuCl_2{\cdot}2H_2O$/NaZSM-5 with $CuCl_2{\cdot}2H_2O$ loading up to 0.50 g/g (Cu/Al = 7.5). (ii) Reaction time is very short. Generally, the dispersion of $CuCl_2{\cdot}2H_2O$ in NaZSM-5 under microwave condition takes only 10 min. (iii) The preparation of samples is very simple without stirring in solution, dryness and calcination. (iv) By using the microwave technique, $CuCl_2{\cdot}2H_2O$ can easily disperse in silicalite-I zeolite which has no ion-exchange capability. In contrast, we cannot prepare the Cu/silicate-I sample via the ion-exchange method.

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