

LOCATION AND MIGRATION OF CATIONS IN Cu^{2+} -ADSORBED MONTMORILLONITE

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Abstract — Location of Cu^{2+} ion in Cu^{2+} -adsorbed montmorillonite have been studied by electron paramagnetic resonance (EPR), supplemented by X-ray diffraction (XRD) and differential thermal analysis (DTA). In the EPR spectra of Cu^{2+} -adsorbed montmorillonite, three signals, corresponding to Cu^{2+} ion, have been simultaneously recorded. Some Cu^{2+} ion seemed to replace the original interlayer metal cations and some entered into the hexagonal cavities. A small fraction of Cu^{2+} ion penetrated into the octahedral vacancies. There were two ways for the adsorption of Cu^{2+} ion by montmorillonite — exchangeable and specific. On heating, the hydrated Cu^{2+} ion in the interlayer loses the coordinating water and then enters into the hexagonal cavities. When the heating temperature further increased, dehydroxylation occurs, which facilitates Cu^{2+} ion in the hexagonal cavities to penetrate into the octahedral vacancies.

Key words —Cu ion, DTA, EPR, Montmorillonite, XRD,

1. Introduction

The contamination of soil and aquatic bodies by industrial effluents rich in heavy metals has received much attention in recent years. While some of the heavy metals are essential for metabolic activity of cells at certain levels, they exert toxic effects at concentrations encountered in polluted environments. Adsorption of heavy metals is one of the major processes governing the fate of trace metals in soils and other environmental systems. Adsorption occurs via selective and non-selective processes. Selective sorption is also termed as specific or non-exchangeable sorption while non-selective sorption as exchangeable sorption (Schindler and Stumm, 1987). Although clay minerals adsorbing metals has been widely studied, there are many debates on the adsorption mechanism, especially on the precise location of metal ions (Stadler and Schindler, 1993; Srasra et al., 1994; Heller-Kallai et al., 1995; Madejova et al., 1996; Bahranowski et al., 1996; Mosser et al., 1997; Theng et al., 1997). Recently, studies on Cu-montmorillonite, Li-montmorillonite and their heating products (Srasra et al., 1994; Heller-Kallai et al., 1995; Mosser et al., 1997) have shown

that small monovalent and divalent compensating ions in montmorillonite may behave differently on heating. The monovalent Li ions may penetrate into the octahedral vacancies before dehydroxylation (Srasra et al., 1994), whereas the divalent Cu^{2+} ion, with a similar ionic radius to Li, do not (Heller-Kallai et al., 1995). Heller-Kallai et al. (1995) proposed that a minor fraction of Cu^{2+} ion could penetrate into octahedral vacancies on heating based on the infrared spectra, however, they could not distinguish the Cu^{2+} ion in the hexagonal cavities and octahedral vacancies in their EPR spectra.

We prepared the samples of montmorillonite that adsorbed Cu^{2+} ion in an aqueous solution with very low Cu^{2+} concentration that is similar to those in some environmental systems and different from those used in the previous studies. Cu^{2+} ion is chosen based on the following reasons: 1) The effect of copper on microorganisms and other aquatic fauna is ecologically very significant. 2) The speciations of copper have significant effects on its bioavailability. 3) Cu^{2+} ion is an excellent probe and its local environment can be monitored accurately by EPR spectroscopy. In this paper, a group of hyperfine structure lines corresponding to the Cu^{2+} ion is reported for the first time in the non-pillared Cu-montmorillonite. This research is of paramount importance for understanding the precise location of Cu^{2+} ion in Cu^{2+} -adsorbed montmorillonite and migration on heating.

2. Materials and Methods

The montmorillonite sample used in this study was from Guangdong, China, and is referred to as "FM0". Its structural formula determined from chemical analysis is $[\text{Na}_{0.106}\text{K}_{0.089}\text{Ca}_{0.457}\text{Mg}_{0.067}][\text{Fe}^{2+}_{0.002}\text{Fe}^{3+}_{0.037}\text{Mg}_{0.347}\text{Al}_{1.656}][\text{Si}_{3.794}\text{Al}_{0.206}]\text{O}_{10}(\text{OH})_2\text{nH}_2\text{O}$. The cation exchange capacity (CEC) of the clay was 84.4 mmol per 100g, determined by leaching with 1M ammonium acetate at pH 7, washing with 90% ethanol, displacing the NH_4^+ with 1M NaCl and measuring the amount displaced with an autoanalyzer (Theng et al., 1997). The surface area was $56.37\text{m}^2/\text{g}$, measured on NOVA Ver. 3.70n by N_2 adsorption at 77K and application of BET equation (Stadler and Schindler, 1993).

Cu^{2+} -adsorbed montmorillonite was prepared using the following method: 2g of clay were dispersed in 1L of 4×10^{-6} copper sulfate. The pH of the solutions was adjusted to 3.0, 4.5 and 6.0, respectively. The adsorption time was 6h. Then the clays were separated by centrifugation and dried in an oven at 80°C . These Cu^{2+} -adsorbed montmorillonite samples are referred to as "FM0-Cu-3.0", "FM0-Cu-4.5" and "FM0-Cu-6.0", respectively.

Thermal analysis was conducted on ICT differential thermal balance. 200mg sample was heated in a Pt crucible from room temperature to desired temperature at a heating rate of $20^\circ\text{C}/\text{min}$ and was maintained at the desired temperatures for 1h (Mosser et al., 1997). Sample "FM0-Cu-6.0-300" represents FM0-Cu-6.0 that was heated to 300°C . The other samples were referred to in the same way.

Sample FM0-Cu-4.5-400(W) and FM0-Cu-6.0-400(W) were prepared following EPR measurement by adding demineralized water into samples FM0-Cu-4.5-400 and FM0-Cu-6.0-400, respectively, in the quartz tubes. The samples were soaked for 4d, then dried in an oven at 80°C.

X-ray diffraction patterns were obtained on randomly oriented powder specimens using a D/MAX-1200 diffractometer with Cu K α radiation.

The EPR spectra were obtained at room temperature with an X-Band Brüker ECS106 spectrometer on randomly oriented powders. The spectrometer settings were 9.76GHz frequency and 3mW microwave power. Spectra were recorded in the magnetic field range of 0.025–0.575T with central field of 0.3T. Equal sample masses were packed in quartz tubes and these tubes were placed in the same position in the microwave cavity (Mosser et al., 1997).

3. Results

3.1 X-ray diffraction

The XRD patterns of FM0 and FM0-Cu-6.0 are shown in Figure 1. The d(001) value of FM0-Cu-6.0 is 1.523nm, which is obviously different from that of FM0 (d(001)=1.479nm), but similar to that of Cu-montmorillonite obtained from Ca-montmorillonite by ion exchange in 0.5M copper sulfate (Yang et al. 1994; He, 1999), indicating the presence of fully hydrated hexaaqua-copper ion in the interlayer of montmorillonite.

Figure 1. XRD patterns of FM0 and FM0-Cu-6.0.

3.2 DTA

The DTA and TG curves of the four samples are shown in Figure 2. The curve corresponding to FM0 exhibits a first endothermic peak centered at 153°C (between 67°C and 209°C), corresponding to the loss of physisorbed water and the water molecules bound to the interlayer cations. The second endothermic peak centered at 517°C (between 461°C and 561°C) and the third endothermic peak centered at 630°C (between 562°C and 662°C) correspond to the dehydroxylation of the layer silicate minerals. The sharp exothermic peak around 921°C may correspond to the phase change of montmorillonite. The dehydroxylation of FM0-Cu-3.0, FM0-Cu-4.5 and FM0-Cu-6.0 occurs at higher temperature as compared to sample FM0, revealing the stronger interaction between OH and the metal ions of the octahedral sheet in Cu²⁺-adsorbed montmorillonite. This change indicates a different composition of the octahedral sheet after Cu²⁺ exchange.

Figure 2. DTA and TG curves of FM0, FM0-Cu-3.0, FM0-Cu-4.5 and FM0-Cu-6.0.

3.3 EPR

Figure 3 shows the EPR spectra of FM0 and Cu²⁺-adsorbed montmorillonite. In the EPR spectrum of FM0, the signal around g=4.14 corresponds to the octahedral Fe(III) ion, and the signal with g=2.0009 to the hydrated Fe(III) ion in the interlayer of montmorillonite (Goodman et al., 1994). Compared with the EPR spectrum of FM0, three new signals were simultaneously recorded on the spectra of Cu²⁺-adsorbed montmorillonite. These signals include two fine structure lines around g=2.07 and g=2.14, respectively, and a group of weak hyperfine structure lines with g=2.20-2.65. As the three new signals only occur in the spectrum of Cu²⁺-adsorbed montmorillonite, we suggest that they correspond to Cu²⁺ ions.

Figure 3. EPR spectra of FM0, FM0-Cu-3.0, FM0-Cu-4.5 and FM0-Cu-6.0.

Figures 4 and 5 are the EPR spectra of FM0-Cu-6.0 that was heated to different temperatures. A signal around g=2.07 occurs in the EPR spectra of the samples treated at different temperatures, revealing that Cu²⁺ ion is in a restricted environment (Heller-Kallai et al. 1995; Mosser et al. 1997). At room temperature, there is a signal with g=2.14 which is associated with hydrated Cu²⁺ ion in the interlayer (Heller-Kallai et al. 1995). When the temperature increases to 300°C, the signal of g=2.14 disappears, which is similar to the results reported by Heller-Kallai et al. (1995) and Mosser et al. (1997).

Figure 4. EPR spectra of FM0-Cu-6.0 and its thermal products.

Figure 5. Enlarged EPR spectra of FM0-Cu-6.0 and its thermal products.

In the EPR spectra of the samples after calcination, the hyperfine structure lines become clearer. A group of relatively stronger signals with g values of 2.20, 2.33, 2.47 and 2.65, respectively, were recorded for the samples treated at 600°C, which suggests that dehydroxylation would facilitate the migration of Cu²⁺ ion, and some Cu²⁺ ion may have entered into the octahedral sheet. However, when the treating temperature further increases, the signals became less clear.

Figure 6 is the EPR spectra of FM0-Cu-4.5-400(W) and FM0-Cu-6.0-400(W). As compared with the EPR spectra of FM0-Cu-4.5-400 and FM0-Cu-6.0, a weak signal with g=2.14 was regained, which reflects that this signal corresponds to the rehydration of Cu²⁺ ion.

Figure 6. EPR spectra of FM0-Cu-4.5-400(W) (A) and FM0-Cu-6.0-400(W)(B).

4. Discussion

Three different signals corresponding to three types of Cu^{2+} ion located in different structural environment is evident from the EPR spectra of FM0-Cu-3.0, FM0-Cu-4.5 and FM0-Cu-6.0. XRD result of FM0-Cu-6.0 shows that its $d(001)$ value is 1.523nm that is different from that of FM0, indicating the presence of free, fully hydrated hexaaqua-copper ions in the interlayer of montmorillonite. On heating to 300°C, the signal with $g=2.14$ disappears and the intensity of the signal with $g=2.07$ is greatly increased, revealing a change of environment of Cu ions. As DTA results show that the physisorbed water and the water molecules bounded to the interlayer cations are eliminated below 300°C, we suggest that the signal with $g=2.14$ may correspond to the hydrated Cu^{2+} ion in the interlayer, which is confirmed by the studies on the rehydrated samples. In the EPR spectra of FM0-Cu-4.5-400(W) and FM0-Cu-6.0-400(W), a weak signal with $g=2.14$ is regained, which demonstrates that the signal with $g=2.14$ corresponds to the hydrated Cu^{2+} ion in the interlayer.

Previous studies (Heller-Kallai et al., 1995; Madejova et al., 1996; Mosser et al., 1997) concluded that metal ions might migrate into hexagonal cavities, and some of these ions might penetrate into octahedral vacancies. Heller-Kallai et al. (1995) and Mosser et al. (1997) supposed that, on heating, some Cu^{2+} ion that initially entered into the hexagonal cavities eventually penetrated into the octahedral vacancies corresponding to the signal with $g=2.07$. In the EPR spectra of the three Cu^{2+} -adsorbed samples, there is a strong signal with $g=2.07$, which indicates that some of the Cu^{2+} ion have migrated into the hexagonal cavities before heating. With the disappearance of the signal with $g=2.14$ after heating, the intensity of the signal with $g=2.07$ is obviously increased, indicating that Cu^{2+} ion migrated into the hexagonal cavities from the interlayer when losing the coordinating water on heating. This result is in agreement with that reported by Heller-Kallai et al. (1995).

In the EPR spectra of FM0-Cu-3.0, FM0-Cu-4.5 and FM0-Cu-6.0, a group of four weak hyperfine structure lines with $g=2.20-2.65$ was recorded. These lines have never been reported in the previously published papers on Cu-montmorillonites. In the EPR study of Al-, Ti- and Zr-pillared Cu^{2+} -adsorbed montmorillonite and their thermal products, Bahranowski et al. (1996) recorded a group of hyperfine structure lines similar to those recorded in this study. They proposed that the hyperfine structure lines corresponded to square planar tetraaqua-complexes $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ in the interlayer before dehydroxylation and to the copper ions linking with the pillars after dehydroxylation. However, in this study, montmorillonite has not been pillared. Thus, it is impossible that this signal correspond to copper ions linking with pillars after dehydroxylation. Also, as discussed above, the copper species present in montmorillonite are hexaaqua-complexes $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, not square planar tetraaqua-complexes $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$. Bahranowski et al. (1996) proposed that hexaaqua-complexes $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ could give isotropic resonance around $g=2.17$, which is in agreement with our results.

The study by Srasra et al. (1994) demonstrated that Li entered octahedral vacancies before dehydroxylation. Although the radius of Cu^{2+} ion is similar to that of Li ion, Heller-Kallai et al.

(1995) suggested that the two ions behaved differently, i.e., Cu^{2+} ion did not penetrate into the octahedral vacancies before dehydroxylation as Li did. Through the IR study, Heller-Kallai et al. (1995) and Mosser et al. (1997) proposed that Cu^{2+} ion might penetrate into octahedral vacancies after dehydroxylation, but they only recorded the signal around $g=2.07$. After losing coordinating water, copper ion may be located at the following sites: (1) entering into the hexagonal cavities in the Si-O sheet; (2) penetrating into the octahedral vacancies. As discussed above, possibility (1) has been demonstrated. If the situation (2) occurs, more and more Cu^{2+} ion will penetrate into octahedral vacancies and the hyperfine structure lines will become stronger as dehydroxylation proceeds. From room temperature to 400°C , the intensity of this group signal did not change obviously, but the intensity of the signal with $g=2.07$ was greatly increased. DTA results showed that the dehydroxylation of montmorillonite occurred above 461°C , indicating that most of the Cu^{2+} ion may enter into the hexagonal cavities during losing coordinating water. When heating to higher temperatures, a change in environment of the Cu^{2+} ion occurred, which was evidenced by the intensity increase of the signal of the hyperfine structure lines as expected. When sufficient energy was provided, dehydroxylation removed the obstacle to the penetration of the Cu^{2+} ion into octahedral sheets (Heller-Kallai et al., 1995; Mosser et al., 1997). At 600°C , the hyperfine structure lines are very clear. MAS NMR study of montmorillonite and its thermal products indicated that around 700°C a vigorous microstructural change of Al and Si atoms in montmorillonite might occur (Wu, 1998). Below 700°C , dehydroxylation plays an important role in effecting the structural change of montmorillonite, and 4-, 6-fold Al occur in the octahedral sheets, and a segregation of Al_2O_3 and SiO_2 occurs above 700°C (Wu, 1998), indicating that montmorillonite began to transfer to other phases at about 700°C . Therefore, when the heating temperatures further increased, the signals of superfine structure lines with $g=2.20-2.65$ become vague.

Integration of the results suggests that the Cu^{2+} ion may be at the following sites: most of the Cu^{2+} ion have replaced the original interlayer cations or migrated into hexagonal cavities, some Cu^{2+} ion have penetrated into octahedral vacancies.

5. Conclusion

In Cu-montmorillonite, most of the Cu^{2+} ion replace the original metal ions in the interlayer or move into hexagonal cavities of Si-O sheet. A small fraction penetrate into the octahedral vacancies. This result indicates that there are three different occurrences of Cu^{2+} ion in montmorillonite: (1) entering into the interlayer; (2) adsorbed in the hexagonal cavities; (3) penetrating into the octahedral vacancies. The first is attributed to the exchangeable adsorption,

the second and the third to the specific adsorption.

The hydrated Cu^{2+} ion will lose the coordinating water and migrate into the hexagonal sites when heating the Cu^{2+} -adsorbed montmorillonite. Further heating will result in dehydroxylation, and some Cu^{2+} ion will penetrate into the octahedral vacancies from the hexagonal cavities. Dehydroxylation facilitates the Cu^{2+} ion to migrate into the octahedral vacancies.

Owing mostly to the similarity of their ionic radii, Li and Cu in montmorillonite behave similarly. This conclusion is different from that of the published studies (Heller-Kallai et al., 1995; Mosser et al., 1997).

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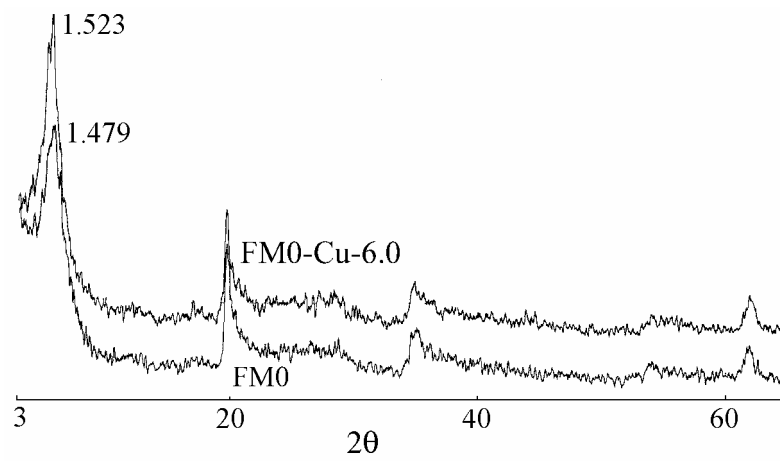


Fig.1

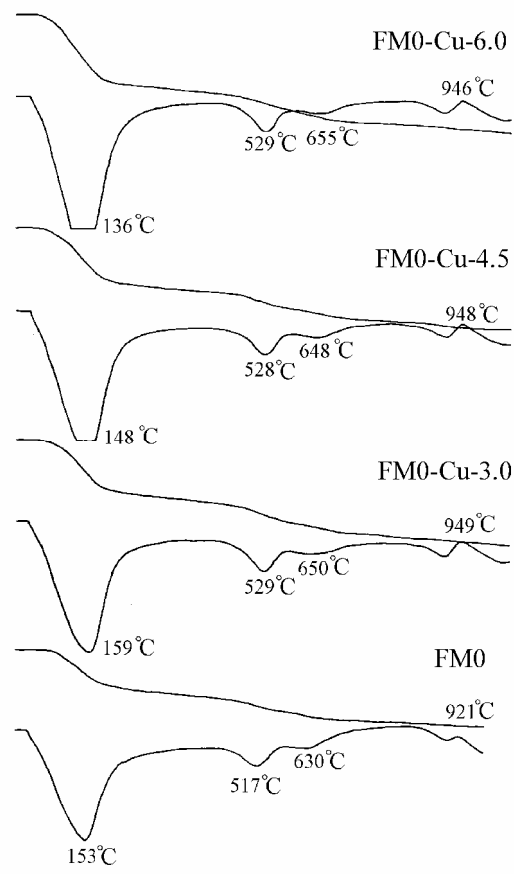


Fig.2

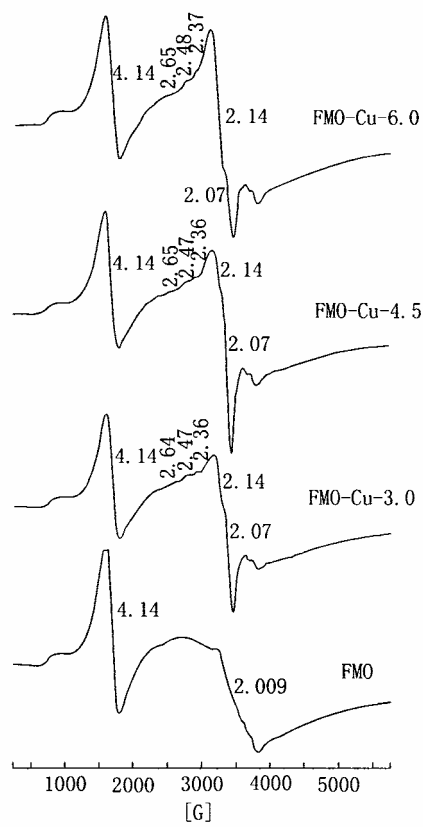


Fig.3

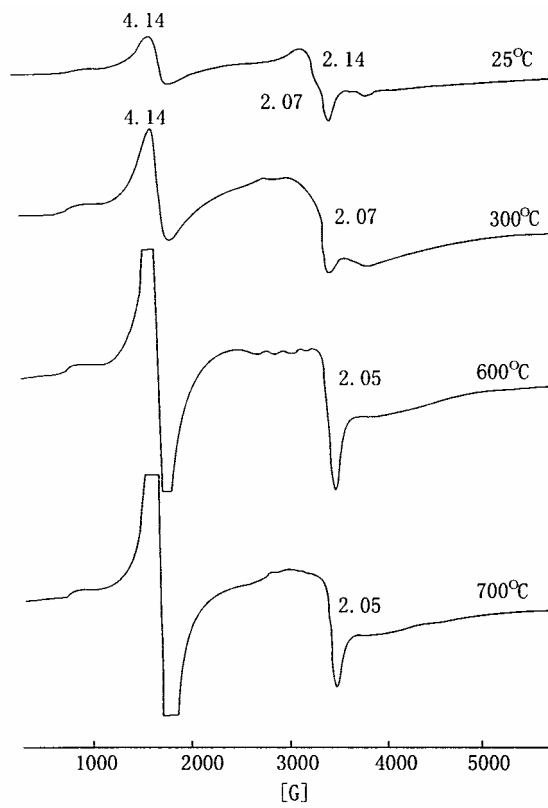


Fig.4

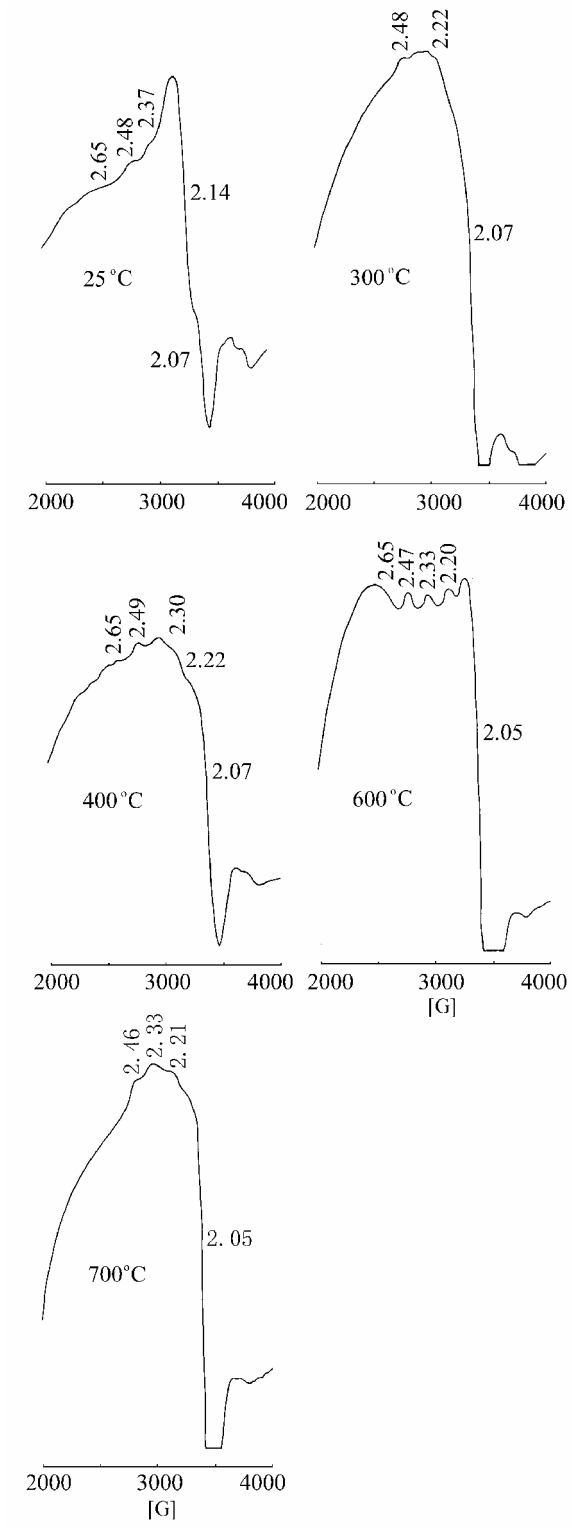


Fig.5

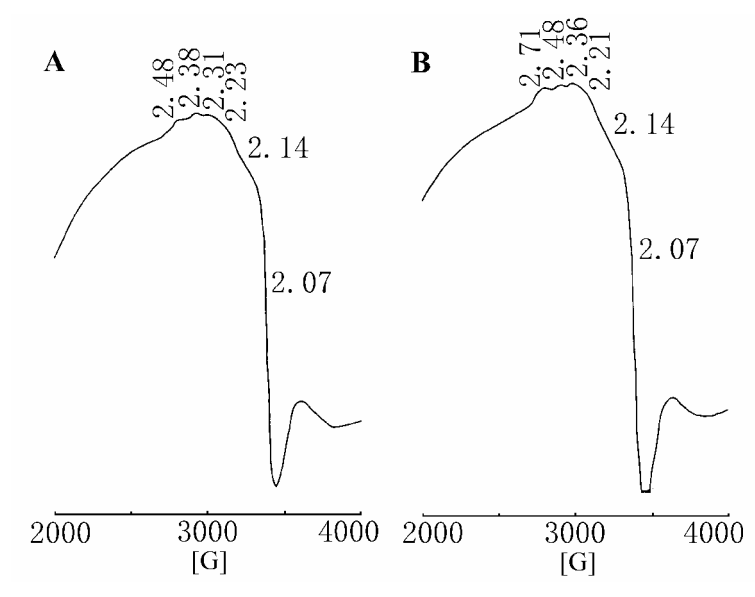


Fig.6