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高岭石插层效率评价

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摘要:用基于 X 射线衍射分析(XRD)的插层率、基于热重分析(TGA)的热失重率和基于红外光谱分析(FTIR)的 3 600 cm^{-1} 谱带与 3 700 cm^{-1} 谱带强度比值对高岭石/二甲基亚砜(DMSO)插层复合物和高岭石/*N*-甲基甲酰胺(NMF)插层复合物的插层效率进行了综合评价。结果表明,当插层反应进行到 1、6 和 25 d,高岭石/DMSO 的插层率分别为 5%、52%和 89%;而高岭石/NMF 的插层率则分别为 93%、94%和 95%。与此同时,高岭石/DMSO 的热失重率分别为 1.06%、8.06%和 17.46%;而高岭石/NMF 的失重率分别为 6%、6.5%和 14.2%。在红外光谱图中,高岭石/DMSO 复合物的 3 600 与 3 700 cm^{-1} 带强度比分别为 1.03,1.141 和 1.628,而高岭石/NMF 复合物分别为 1.403,1.433 和 1.612。3 种评价方法显示很好的一致性,相对而言,在插层作用的初期,XRD 方法比较灵敏,而在插层作用的后期,TGA 和 FTIR 方法则显得更为灵敏和有效。

关键词:高岭石;插层效率;综合评价
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Evaluation of Kaolinite Intercalation Efficiency

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Abstract: The intercalation efficiency of kaolinite/dimethyl sulfoxide(DMSO) and kaolinite/*N*-methyl formamide (NMF) was evaluated by intercalation ratio from XRD, weight loss from TGA and intensity ratio of 3 600 to 3 700 cm^{-1} from FTIR. The results show that, for the 1, 6 and 25 d intercalation compounds, the intercalation ratio of kaolinite/DMSO is 5%, 52% and 89%, respectively, and 93%, 94% and 95%, respectively, for kaolinite/NMF intercalation, the weight loss of kaolinite/DMSO is 1.06%, 8.06% and 17.46%, while that of kaolinite/NMF intercalation is 6%, 6.5% and 14.2%, respectively, the intensity ratio of 3 600 to 3 700 cm^{-1} for kaolinite/DMSO is 1.03, 1.141 and 1.628, reapectively, and 1.403, 1.433 and 1.612 for kaolinite/NMF intercalation. The results from three different evaluation methods are agreed well. The XRD method is more sensitive than TGA and FTIR at low intercalation stage, however, when the intercalation increases, TGA and FTIR methods become more sensitive than XRD method.

Key words: kaolinite; intercalation efficiency; comprehensive evaluation

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0 Introduction

Intercalation reaction, occurring by the topotactic insertion of mobile guest species into the accessible crystallographically defined vacant sites located between the layers in the layered host structure, has been well known as a method for forming inorganic - organic nanocomposites under mild conditions with layered minerals as starting materials. In such intercalation compounds, strong covalent bonds occur in the layers and weak interactions between host lattice and guest species or co-intercalated solvents[1].

Montmorillonite, layered double hydroxide and kaolinite are typical layered clay materials. Montmorillonite and layered double hydroxide were known as cationic and anionic clay minerals, respectively, because their interlayer compensation ions are cation and anion. They are easier to be expanded by organic and inorganic ions. kaolinite is a non swellable 1∶1 phyllosilicate containing a gibbsite octahedral layer and a silicon oxide tetrahedral sheet with two distinct interlayer surface, has strong hydrogen bonds between the aluminol and Si-O groups, holding adjacent lamella to each other, and consequently makes the intercalation process inside the basal space difficult, in particular, because of the absence of any exchangeable cations inside the basal space[2]. Only a limited number of polar guest species such as dimethyl sulfoxide(DMSO), formamide(FA), N-methyl formamide (NMF), dimethylfomamide(DMF), K-acetate, hydrazine-hydrate can directly be intercalated [3-6]. Some large organic molecules were intercalated by using a small molecule intercalation compounds as the intermediate[7-8].

The key for intercalation in kaolinite is a right selection of a suitable guest precursor (intermediate) and a solvent. Thus, any matching in the guest intermediate and the solvent will result in abortive intercalation or even deintercalation of the guest species. Some works reported the method to delaminate kaolinite in the solution of formamide[9], but exfoliation and delamination of kaolinite is relatively difficulty and with low productivity comparing to montmorillonite and layered double hydroxide.

It is very important to evaluate the intercalation efficiency for kaolinite intercalation because of the difficulty in intercalation. The intercalation ratio based on XRD is a common method to evaluate the intercalation efficiency of kaolinite. The first order diffraction from XRD of kaolinite usually has a corresponding $d_{(001)}$ spacing of 0.717 nm, and will shift to a larger $d_{(001)}$ value after intercalation. The intercalation degree can be estimated from the ratio of $I_I/(I_I+I_K)$, where the I_I represents the $d_{(001)}$ spacing peak intensity of the intercalation compound and the I_K represents that of unintercalation kaolinite in the compound[10]. Actually, after the interlayer of a kaolinite was expanded, the organic molecules can continue intercalating it. Although the amounts of interlayer organic molecule keep on increase but intercalate ratio increase a little. So the intercalate ratio can not be used to characterize the amounts of organic molecules introduced into interlayer of kaolinite especially during the later intercalation stage. We report here the evaluation of intercalation efficiency of kaolinite/DMSO and kaolinite/NMF intercalation compounds by XRD, TGA and FTIR.

1 Experimental

1.1 Materials

N-methyl formamide(reagent grade), was purchased from the Sigma-Aldrich Chemical Company Ltd. Kaolinite and dimethyl sulfoxide (reagent grade) were obtained from Fluka, Purum. All of the materials were used as received without further purification.

1.2 Preparation

A kaolinite/NMF and kaolinite/DMSO intercalation compounds were prepared following, with minor modification, the method of Komori et al [8]. Firstly, in a 200 mL flask equipped with a stirrer and heater, 20 g kaolinite was dispersed in 100 mL NMF or DMSO solution containing 10% wt water with vigorous stirring at room temperature for 25 d. At a given interval, about 10 mL sample was pumped from the solution and centrifuged and dried at 50 ℃ in a vacuum oven for 24 h, the dried sample was used for characterization with XRD, TGA and FTIR.

1.3 Characterization

XRD patterns were recorded on a Rigaku Miniflex II desktop X-ray powder diffractometer with Cu $K\alpha$ radiation (λ=0.154 18 nm), accelerating voltage was 50 kV at a current of 20 mA. Scans were taken at 2θ=2°~70° at 0.1° step size. FTIR spectroscopic analyses were carried out on a Nicolet 560 Fourier transform infrared spectrometer using the KBr method. Spectra were recorded between 400 and 4 000 cm^{-1} at a resolution of 4 cm^{-1}. Thermogravimetric analysis (TGA) was performed on an SDT 2960 machine at 12~14 mg scale under a flowing nitrogen atmosphere at a ramp rate of 20 ℃·min^{-1}.

2 Results and discussion

2.1 XRD

The XRD patterns of kaolinite/DMSO and kaolinite/NMF intercalation compounds are shown in Fig.1 and 3. The intercalation ratios, calculated according to the equation of IR=$I_i/(I_i+I_k)$, as a function of intercalation time are shown in Fig.2 and 4, respectively. The pristine kaolinite has the first order reflection (with a d_{001} value of 0.707 nm), second order reflection (with a d_{002} value of 0.355 nm) and third order reflection (with a d_{003} value of 0.178 nm). The DMSO intercalation expands the basal spaceing of the first order reflection from 0.707 nm to 1.08 nm. With the progress of intercalation, the intensity of the first order reflection (1.08 nm) increases, and those of the second and third reflections decrease and then disappear. A new peak with a d-value of 0.386 nm appears in the intercalation compounds, which suggests that there may be more than one type of molecular arrangements in the interlayer. The increment of the kaolinite basal spacing is 0.31 nm which is less than the van der Waals diameter (0.35 nm) of CH_3 group in DMSO molecule. This evidence supports the assumption that parts of the DMSO molecule key into the kaolinite ditrigonal hole, which is similar to the kaolinite/formamide intercalation [3]. The intercalation efficiency increases with the time (Fig.3). There is almost no intercalation within one day, the intercalation ratio is 52%, 81%, 89% and 91% at 6,10, 20 and 25 d, respectively. After 25 d, there is no more enhancement in the intercalation efficiency. Kaolinite/NMF intercalation compound has a much higher intercalation rate than that of kaolinite/DMSO. The intercalation ratio of kaolinite/NMF at 2 h and 10 h is 7% and 69%, respectively. The intercalation after 24 h reaches a relatively saturation state, the intercalation ratio at 1 d, 6 days and 25 d is 93%, 94% and 95% (Fig.3 and 4). It is interesting to note that the XRD pattern is different at 2θ about 24 between kaolinite/DMSO and kaolinite/NMF. DMSO intercalattion kaolinite brings a small peak with basal spacing of 0.368 nm and the intensity of the peak increases with intercalation process. But this peak does not emerge in kaolinite/NMF compounds. This

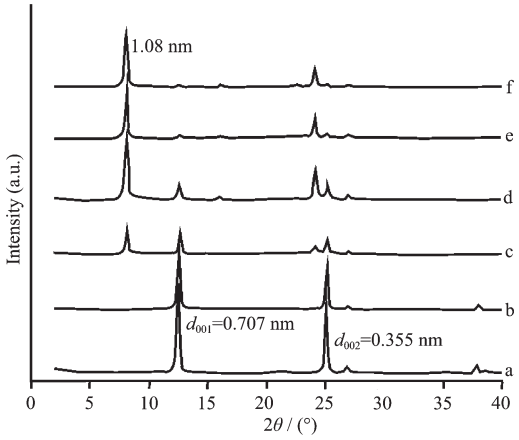

Fig.1 XRD patterns of (a) kaolinite; (b) kaolinite/DMSO intercalation for 1 d;(c) kaolinite/DMSO intercalation for 6 d;(d) kaolinite/DMSO intercalation for 10 d; (e) kaolinite/DMSO intercalation for 20 d; (f) kaolinite/DMSO intercalation for 25 d

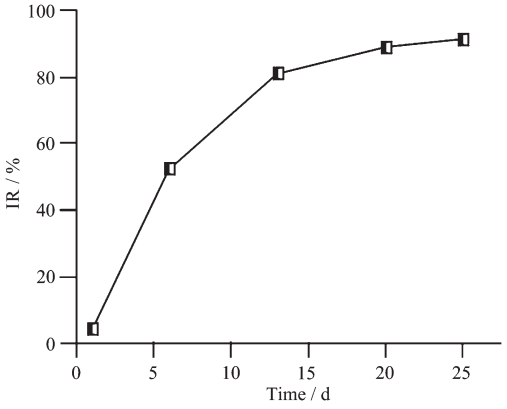

Fig.2 kaolinite/DMSO intercalation ratio(IR) as a function of intercalation time

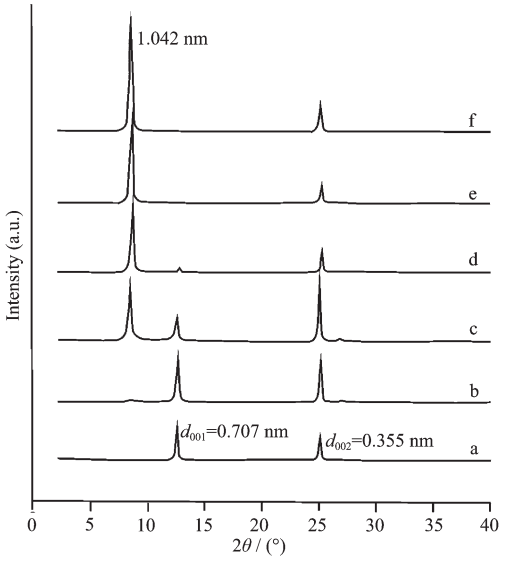

Fig.3 XRD patterns of (a) kaolinite, (b) kaolinite/NMF intercalation for 2 h, (c) kaolinite/NMF intercalation for 10 h, (d) kaolinite/NMF intercalation for 1 d, (e) kaolinite/NMF intercalation for 6 d, (f) kaolinite/NMF intercalation for 25 d

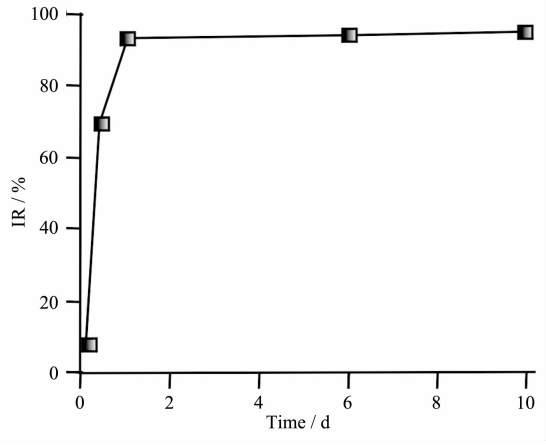

Fig.4 kaolinite/NMF intercalation ratio as a function of intercalation time

difference may imply the different direction and arrangement characteristics of DMSO and NMF in the interlayer of kaolinite. For the structure of kaolinite, the two sides of interlayer consist of hydroxyl groups (aluminol) and oxygen atoms (siloxane surface), respectively. The aluminol side can donor proton to form a hydrogen bond and the siloxane side can accept proton to form hydrogen bond during intercalation. For the structure of NMF, the oxygen atoms can accept the proton from aluminol site and NH group can donor proton to siloxane of kaolinite. So NMF molecule can get a high order direction and with only one kind arrangement in the interlayer of kaolinite due to the formation of hydrogen bonds with the two sites of kaolinite interlayer. On the other hand, although the oxygen atom of DMSO can form hydrogen bonds with aluminol of kaolinite, the other side of DMSO molecule consists of two CH_3 groups which can penetrate into the kaolinite ditrigonal hole but can not form hydrogen bond and the two CH_3 groups have some changes when penetrate in ditrigonal hole. So kaolinite/DMSO intercalation compounds have lower order direction and more than one kind arrangement in the interlayer of kaolinite.

2.2 TGA

Fig.5 and 6 show the thermal stability of kaolinite and its intercalates with DMSO and NMF. One of the main features of pristine kaolinite is the major endotherm near 550 ℃ that is attributed to the loss of water due to the dehydroxylation, i.e. formation of meta-kaolinite. This endotherm roughly corresponds to 10.5% mass loss in TG, which is also related to a maxium in the DTG. There are almost no changes of the TG and DTG curves in the range of 450~650 ℃ after DMSO and NMF intercalation comparing to pristine kaolinite. The losses in the range of 130~200 ℃ are typical of the kaolinite intercalates of DMSO and NMF. The intercalation for kaolinite/DMSO is very slow in the first two days. The weight loss of 1 d, 6 d and 25 d

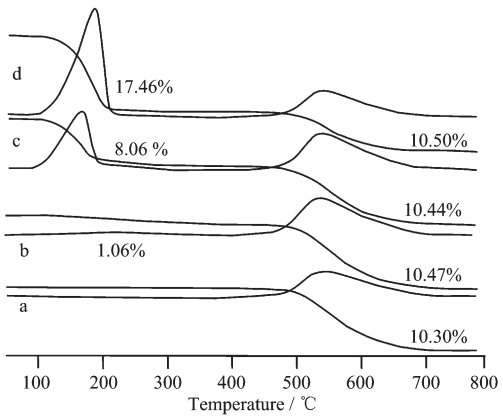

Fig.5 TG and DTG curves of (a) kaolinite, (b) kaolinite/DMSO intercalation for 1 d, (c) kaolinite/DMSO intercalation for 6 d and (d) kaolinite/DMSO intercalation for 25 d

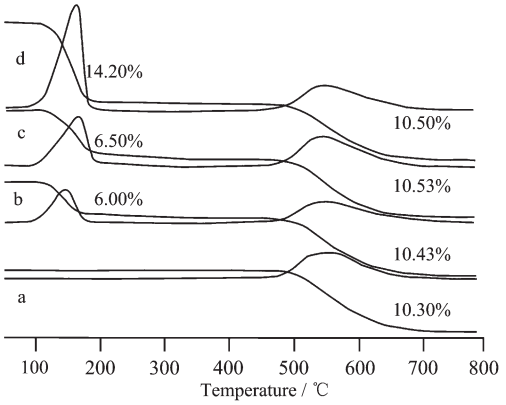

Fig.6　TG and DTG curves of (a) kaolinite, (b) kaolinite/ NMF intercalation for 1d, (c) kaolinite/ NMF intercalation for 6 d and (d) kaolinite/ NMF intercalation for 25 d

intercalates is 1.06%, 8.06% and 17.46%, respectively. In contrast, the intercalation for kaolinite/NMF is much faster during the first two days. The weight loss of 1 d, 6 d and 25 d intercalates is 6%, 6.5% and 14.2%, respectively. The weight loss of 25 d NMF intercalate is lower than that of DMSO, although the 25 d intercalation ratio from XRD of kaolinite/NMF is slightly higher than that of the kaolinite/DMSO intercalate. This may imply that the kaolinite/NMF intercalate has more ordered structure than that of the kaolinite/DMSO intercalate, because the structure of NMF makes it easy to orientate in the interlayer of kaolinite and get a higher intercalation ratio from XRD patterns than DMSO, but the amount of NMF molecules in the interlayer of kaolinite is less than that of DMSO.

2.3　FTIR

Figs.7 and 8 show the FTIR specta of kaolinite and its intercalates. Kaolinite shows four OH-stretching bands at 3 700, 3 670, 3 650 and 3 620 cm^{-1}. The bands 3 700 and 3 650 cm^{-1} hydroxyls, the inner-surface(outer) hydroxyls, are regarded as forming the interlayer hydrogen-bonds that bind the lamellae together in the crystals, whereas the 3 670 cm^{-1} hydroxyl, also outer hydroxyl, is relatively "free". The outer hydroxyl groups are situated on the surface of the lamellae, which are accessible for hydrogen bonding with the appropriate intercalated molecules. Therefore, the outer hydroxyl stretching bands are influenced by interlayer modification. The band at 3 620 cm^{-1} is attributed to the stretching frequency of the internal (inner) hydroxyl groups of kaolinite, which lie within the lamellae in the plane common to both the tetrahedral and octahedral sheets. Being within the layers, the inner hydroxyl cannot participate in hydrogen-bonding to intercalated molecules. So, the inner hydroxyl stretching band is not usually influenced by the interlayer modification of kaolinite[11-13].

FTIR spectra show that the intensity of the 3 700, 3 670, and 3 650 cm^{-1} bands decrease upon the intercalation of DMSO and NMF. New and weaker bands appear at lower frequencies. These are assigned to perturbed kaolinite hydroxyls and thus organic compounds in kaolinite hydrogen-bond to 3 700, 3 670, and 3 650 cm^{-1} hydroxyls. If the intensity of the inner

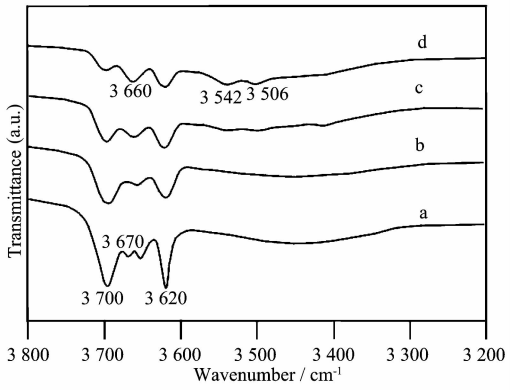

Fig.7　FTIR spectra of (a) kaolinite, (b) kaolinite/DMSO intercalation for 1 d, (c) kaolinite/DMSO intercalation for 6 d and (d) kaolinite/DMSO intercalation for 25 d

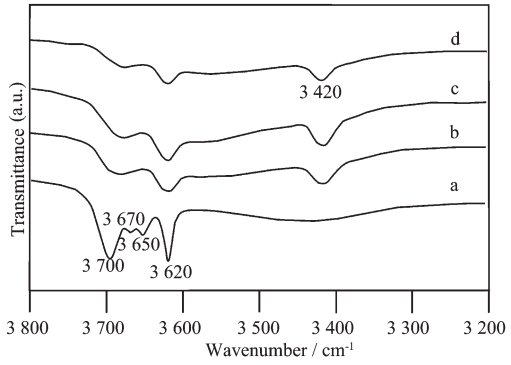

Fig.8　FTIR spectra of (a) kaolinite, (b) kaolinite/NMF intercalation for 1 d, (c) kaolinite/ NMF intercalation for 6 d and (d) kaolinite/ NMF intercalation for 25 d

Table 1 Summary of intercalation efficiency

Samples		Intercalation efficiency		
		Intercalation ratio(%) from XRD	Weight loss at the range of 130~200 ℃(%) from TGA	Intensity ratio of 3 620/ 3 700 cm^{-1} from FTIR
Kaolinite		0	0	1.035
DMSO	1 d	5	1.06	1.030
Intercalation	6 d	52	8.07	1.141
Complex	25 d	89	17.46	1.628
NMF	1 d	93	6.00	1.403
Intercalation	6 d	94	6.50	1.433
Complex		25 d	95	14.20

hydroxyl stretching band, 3 620 cm^{-1}, can be assumed to be unaffected on complex formation, the ratio of intensities of other bands to the 3 620 cm^{-1} band in the complex, compared to that in pristine kaolinite, could give an indication of changes in band intensities occurring on intercalation into kaolinite. These changes could give useful information of intercalation efficiency on kaolinite. The results show that for pristine kaolinite, the ratio of 3 620 cm^{-1} to 3 700, 3 670, and 3 650 cm^{-1} is 1.035, 1.547 and 1.491, respectively. For the one day DMSO intercalation complex, the ratio of the intensities of 3 620 cm^{-1} band to that of 3 700 cm^{-1} is 1.030, the 3 670 and 3 650 cm^{-1} bands incorporated to 3 660 cm^{-1}. For 6 d intercalation complex, the ratios of 3 620 to 3 670 and 3 660 cm^{-1} are 1.414 and 1.267, and for 25 d intercalation complex, they are 1.628 and 1.139. These data show that the ratio of 3 620 to 3 700 cm^{-1} increases with the progress of intercalation. The incorporation of 3 670 and 3 650 cm^{-1} bands results in the increase of ratio of 3 620 to 3 660 cm^{-1}.Whereas for kaolinite/NMF intercalation, the bands of 3 650 and 3 670 cm^{-1} totally disappear. The ratio of 3 620 to 3 700 cm^{-1} increases gradually from 1.035 of pristine kaolinite to 1.403, 1.433 and 1.612 of 1 d, 6 d and 25 d intercalation complexes, respectively.

3 Conclusions

The method of k aolinite intercalation efficiency evaluation based on XRD is more intuitionic than those based on TGA and FTIR. The XRD method is preferred in evaluating the ratio of intercalated particles to unintercalated particles. After most of the particles are intercalated, the intercalation ratio increases very slowly. But the intercalation efficiency based on TGA and FTIR show that the mass loss and intensity ratio of 3 620 to 3 700 cm^{-1} still increase. This implies that the organic molecules continue to intercalate into the interlayer after the layer is expanded. The XRD method can be affected by the crystallinity of kaolinite and the order degree of intercalation in the interlayer of kaolinite. The TGA method may be influenced by molecules adsorbed on the surface and side face of kaolinite. The method based on XRD, TGA and FTIR can evaluate the expanded degree of kaolinite, the order degree of intercalation complex, the molecular adsorbtion and arrangement of molecules in the interlayer of kaolinite.

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