

FORMATION OF 0.84 NM HYDRATED KAOLINITE AS AN ENVIRONMENTALLY FRIENDLY PRECURSOR OF A KAOLINITE INTERCALATION COMPOUND

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Abstract—Creating an environmentally friendly precursor to form a kaolinite intercalation compound is important for promoting the applications of nanohybrid kaolinite in electrochemical sensors, low- or zero-toxicity drug carriers, and clay-polymer nanocompounds. In the present study, a stable hydrated kaolinite pre-cursor with $d_{001} = 0.84$ nm was prepared successfully by heating the transition phase, the as-prepared kaolinite-hydrazine intercalate, at temperatures between 40 and 70°C. The structure of the hydrated kaolinite was characterized by X-ray diffraction and infrared spectroscopy. The morphology was examined using scanning electron microscopy. The results showed that the hydrated hydrazine of the transition phase was easy to decompose to hydrazines and water molecules in the interlayer at 40–70°C. Hydrazine molecules de-intercalated gradually, and water molecules remained in the ditrigonal holes of the silicate layer with sufficient stability, finally forming the stable 0.84 nm hydrated kaolinite in the system with a success rate of 80–90%. The 0.84 nm hydrated kaolinite may become an excellent precursor for the preparation of other kaolinite intercalates. A degree of intercalation of ~100% was obtained for the kaolinite-ethylene glycol intercalate, and a degree of intercalation of ~80% was obtained for the kaolinite-glycine intercalate from the 0.84 nm hydrated kaolinite precursor.

Key Words—Environment-friendly Precursor, Hydrated Kaolinite, Hydrazine, Intercalation.

INTRODUCTION

The individual layers in kaolinite are linked together through hydrogen bonds between the aluminol groups of the octahedral sheet on one side and the siloxane macro-ring sheets on the other. Kaolinite has a much greater density of hydroxyl groups than other clay minerals, which causes strong interactions with organic molecules. In recent years, nanohybrid materials, in which functional molecules (which can be used for specific purposes, *e.g.* in medicines, adsorbents, cosmetics, anti-microbial agents, *etc.*) are intercalated into the kaolinite interlayers, have attracted considerable attention, *e.g.* in electrochemistry (Tonle *et al.*, 2007, 2009) as electrochemical sensors for the detection of toxic species (in environmental protection); in low- or zero-toxicity drug carriers for controlling drug delivery (Chakraborti *et al.*, 2011; Vaiana *et al.*, 2011); in clay-polymer nanocompounds consisting of inorganic nanolayers of clay and organic polymer (Li *et al.*, 2008) to improve tensile and gas-barrier properties, thermostability, flame retardance, and anti UV-degradation of the composites (Cabeda *et al.*, 2004); and in the field of catalysis (Bizaia *et al.*, 2009) in which the nanohybrid is used as an oxidation catalyst for the epoxidation of

cyclooctene. The nanohybrid is relatively inexpensive, selective, and reusable, unlike catalysts that do not interact with kaolinite.

These types of nanohybrids also have the advantage of combining both the structural properties of the clay mineral and the chemical properties of the functional molecule as the intercalated species. The most important aspect is that, as a host structure for the intercalated molecules, the clay mineral has properties, such as chemical and thermal stability, ion-exchange ability, and interlayer hydroxyl groups as active sites, which can strongly interact with many functional molecules that are stabilized in the interlayer. To obtain such functional nanohybrids, precursors are generally necessary, and these are prepared initially via intercalation of a polar molecule (Deng *et al.*, 2003; Li *et al.*, 2009), such as potassium acetate, hydrazine hydrate, formamide, dimethylsulfoxide, and urea, into the interlayer of the kaolinite to overcome the strong binding force between the interlayers which prevents the insertion of some of the desired functional molecule, in which the stronger polarization of the polar molecule promotes the binding of the molecule with ions existing in the interlayer rather than binding of existing ions in the layers. The polar molecules in the interlayer can be replaced by the desired functional molecules to form the intercalation compounds. Therefore, the polar molecule-intercalated kaolinite appears to be a suitable precursor in the preparation of the desired intercalation compound.

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However, most of the polar molecules, such as hydrazine hydrate, are not environmentally safe. In recent years, a new type of intercalate referred to as ‘hydrated kaolinite’ has been reported; this type of intercalate is artificial and formed from kaolinite by the insertion of water into the interlayer (Tunney and Detellier, 1994; Frost *et al.*, 1999; Komori *et al.*, 1999; Naamen *et al.*, 2003; Xu *et al.*, 2011). Hydrated kaolinite can be used as a precursor for further intercalation (Costanzo and Giese, 1990; Sato, 1999), and it is stable in air and environmentally safe. Furthermore, water can offer more hydroxyls in the interlayer as reactive sites to react with the functional molecules to form a highly effective intercalate. However, the efficiency of the intercalation of the water and the length of time taken to form the hydrated kaolinite are still not satisfactory for use as a precursor for kaolinite intercalation compounds.

Hydrazine hydrate can be intercalated into kaolinite (Johnston and Stone, 1990; Frost *et al.*, 1998, 2002). If the hydrazines can be removed from the interlayer space and the water left there, hydrated kaolinite would thus be obtained. In the present study, hydrazine hydrate is proposed as an intermediate in the formation of hydrated kaolinite, with a short reaction duration. Stable hydrated kaolinite with $d_{001} = 0.84$ nm was synthesized successfully and effectively with a short reaction time. The degree of intercalation of the water reached 80–90%. Guest molecules then replaced the water to form the desired kaolinite intercalation compounds, *e.g.* kaolinite-ethylene glycol, which had a degree of intercalation of ~100%, and kaolinite-glycine, which had a degree of intercalation of 80%.

EXPERIMENTAL

The raw material used was kaolinite mined from the Yangshan mining district of Suzhou, China, by China Kaolin Company, with the trade name ‘Water-Washed Kaolin Clay, T5-1.’ The particle-size distribution was 1–2 μm and the chemical composition (%) was SiO_2 46.29, Al_2O_3 38.79, Fe_2O_3 0.27, SO_3 0.75, K_2O 0.20, Na_2O 0.04, and H_2O 1.07. The hydrazine hydrate A (85% weight ratio), ethanol, and glycine were obtained as analytically pure chemicals from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). About 3 g of the kaolinite-hydrazine intercalate was synthesized initially by mixing 3 g of the oven-dried raw kaolinite powders with 60 mL of hydrazine hydrate solution (85% in concentration) (mass:volume ratio = 1:20) in an ampoule for 24 h reaction at room temperature during which a magnetic stirring bar was used in the ampoule for continuous stirring. The kaolinite-hydrazine intercalate was then separated from the liquid by centrifugation at a speed of $2220 \times \text{g}$ and washed twice with ethanol and separated using centrifugation several more times leaving just the intercalate without hydrazine on its surface. Finally, the hydrated

kaolinite was obtained after the wet kaolinite-hydrazine intercalate was heated in the atmosphere at a temperature between ambient and 150°C for different time periods.

The microstructure of the raw kaolinite was characterized by X-ray powder diffraction (XRD) using an X’Pert PRO X-ray diffractometer (Almelo, The Netherlands) ($\text{CuK}\alpha$ radiation = 1.5418 \AA operating at 40 kV and 40 mA) and by Fourier-transform infrared (FTIR) spectroscopy (Nexus 670, Boston, USA) using the KBr pellet method. The raw kaolinite was a dried powder, and the kaolinite-hydrazine intercalate and the hydrated kaolinite powders were from T5-1 and from moist, as-synthesized powder, respectively. The samples were placed on glass substrates for XRD analysis. The morphology of the kaolinite particles was observed using a field emission scanning electron microscope (FEI, FESEM, S-4800, Hillsboro, USA) with a magnification of $30,000 \times$ and a working distance of $7900 \mu\text{m}$.

RESULTS AND DISCUSSION

The XRD pattern of the raw kaolinite showed the typical d_{001} peak of 0.72 nm (Figure 1a). For kaolinite mixed with hydrazine hydrate for 24 h at room temperature (Figure 1b), a new peak at $d_{001} = 1.04$ nm was observed, while the peak at $d_{001} = 0.72$ nm decreased in intensity. The FTIR spectra revealed the distinctive bands of the raw kaolinite and the kaolinite mixed with hydrazine hydrate (Figure 2). The bands at 3695 , 3668 , and 3652 cm^{-1} were all stretching vibrations of hydroxyls in the inner-surface of the kaolinite, which were easy to exchange with the interlayer environment because of the direct exposure of the hydroxyls to other ions in the interlayer. Compared with those of the raw kaolinite (Figure 2a), the hydroxyl stretching bands in the hydrazine-kaolinite did not shift,

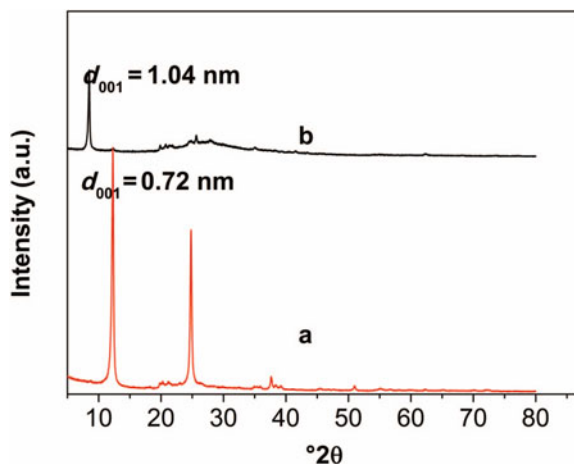


Figure 1. XRD patterns of (a) kaolinite and (b) kaolinite-hydrazine intercalate.

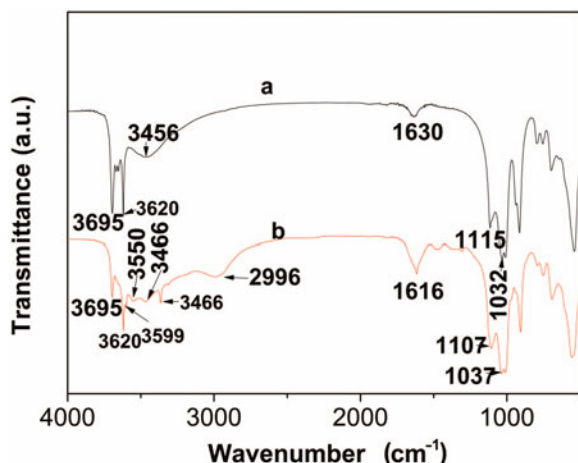


Figure 2. FTIR spectra of (a) kaolinite and (b) kaolinite-hydrazine intercalate.

although they decreased significantly in intensity (Figure 2b). The band at 3620 cm^{-1} is attributed to the stretching vibrations of the inner hydroxyls of the kaolinite and this band did not change significantly with changes in the interlayer. The Si–O stretching band shifted from 1115 cm^{-1} for raw kaolinite to 1107 cm^{-1} for the kaolinite reacted with hydrazine hydrate. The broad band at 3456 cm^{-1} and the sharp one at 1630 cm^{-1} are due to adsorbed H_2O . Bands at 3466 cm^{-1} and 3363 cm^{-1} in the hydrazine-kaolinite belong to the stretching and anti-stretching vibrations, respectively, of the NH_2 in hydrazine; the band at 1616 cm^{-1} was attributed to shearing vibrations of NH_2 . Furthermore, the bands at 3599 cm^{-1} and 3550 cm^{-1} indicated the presence of water in the interlayer (Komori *et al.*, 1999).

Scanning electron microscopy (SEM) images, as expected, revealed lamellar and tubular particles in the original kaolinite (Figure 4a). The size of the kaolinite particles, which were distributed homogeneously, was $\sim 1\text{--}2\text{ }\mu\text{m}$. Some nanosheets and small tube-like kaolinite agglomerates could be seen in the kaolinite-hydrazine intercalate (Figure 4b). The morphologies of the samples heat-treated in the atmosphere over a temperature range of ambient to 120°C (Figure 4c–e) showed that the particle size of the intercalated and heat-treated kaolinite was insignificantly smaller than that of raw kaolinite.

As has been shown previously (Deng *et al.*, 2003; Frost *et al.*, 2002), the increase in the d spacing of the kaolinite indicates the probable intercalation of hydrated hydrazine into the interlayer. The NH_2 -related bands at 3466 cm^{-1} and 3363 cm^{-1} and the interlayer water-correlated bands at 3599 cm^{-1} and 3550 cm^{-1} appearing in the kaolinite that reacted with hydrazine hydrate (Figure 2b) indicated that water molecules existed in the interlayer of the kaolinite. Furthermore, the Si–O band at 1115 cm^{-1} , which shifted to 1107 cm^{-1} , revealed a decrease in the bonding force of Si–O; this perturbation could have been due to interaction or even hydrogen

bonding of the hydrated hydrazine with the basal surface oxygens (Figure 2). These results are consistent with previous studies that showed intercalation of hydrated hydrazine into kaolinite (Frost *et al.*, 1998, 1999, 2002).

Heating the kaolinite-hydrazine intercalation compounds in the atmosphere between room temperature and 150°C caused changes in the XRD patterns (Figure 3). At room temperature (Figure 3b), the 1.04 nm diffraction peak of the kaolinite-hydrazine intercalation compound disappeared, while the intensity of the $d_{001} = 0.72\text{ nm}$ peak from the raw kaolinite increased significantly. After heat treatment at 30°C (Figure 3c), a new weak peak at 0.84 nm appeared in addition to the main peak at 0.72 nm . As the treatment temperature increased from 40 to 70°C , the peak at 0.84 nm increased in intensity while the main peak at 0.72 nm remained almost the same except for a loss of intensity between 30 and 40°C (Figure 3c,d,e,g). When the heating temperature increased to 90 and 120°C , however, the intensity of the 0.72 nm peak was enhanced significantly, while new peaks at 0.77 nm and 0.75 nm appeared (Figure 3h,i). Finally, when the temperature increased to 150°C , only the peak with 0.72 nm was present (Figure 3j).

The hydrazine hydrate intercalated in the kaolinite disappeared almost completely from the interlayer space of the kaolinite-hydrazine intercalation compound heated in atmospheric conditions at a temperature between ambient and 30°C or at 150°C (Figure 3b,c,j). When the heat treatment temperature was between 40 and 70°C , however, the XRD pattern indicated a new phase with $d_{001} = 0.84\text{ nm}$, while the phase with $d_{001} = 1.04\text{ nm}$ disappeared. This new phase was actually the molecular water which existed in the interlayer space of kaolinite and formed a hydrated kaolinite with $d_{001} = 0.84\text{ nm}$, which was also found in previous studies (*e.g.*

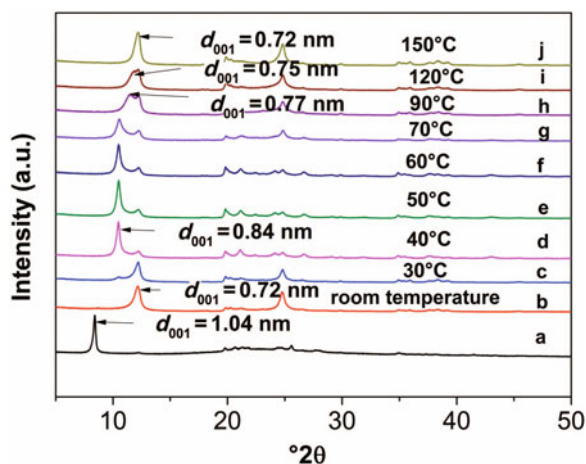


Figure 3. XRD patterns of kaolinite-hydrazine intercalate heated in atmospheric conditions at (a) room temperature for 0 h, (b) room temperature for 7 days, (c) 30°C for 7 days, (d) 40°C for 24 h, (e) 50°C for 24 h, (f) 60°C for 24 h, (g) 70°C for 24 h, (h) 90°C for 24 h, (i) 120°C for 6 h, and (j) 150°C for 6 h.

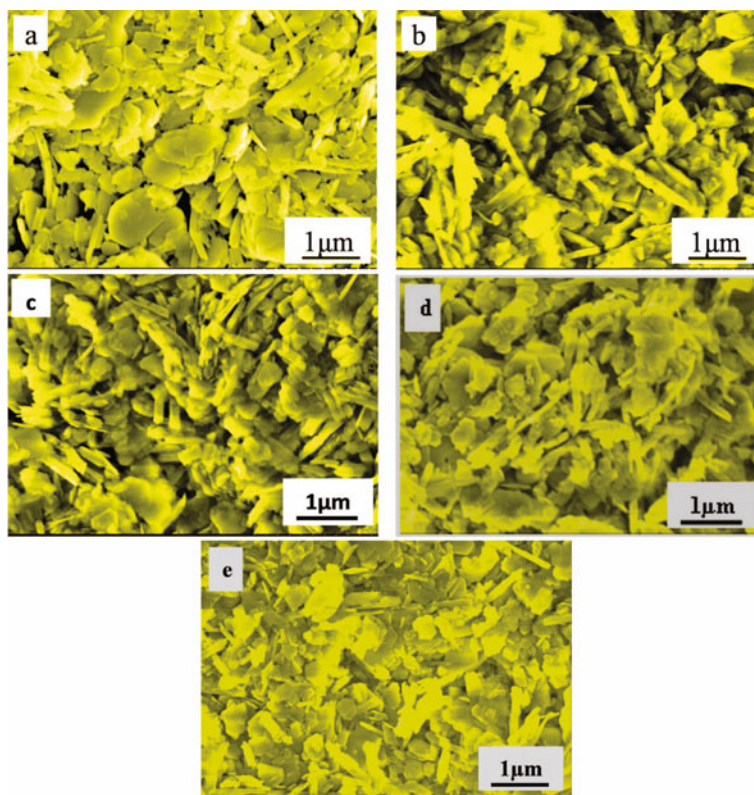


Figure 4. SEM images of (a) kaolinite and (b) kaolinite-hydrazine as-synthesized intercalate and of kaolinite-hydrazine intercalate heated in atmosphere at (c) room temperature for 7 days, (d) 60°C for 24 h, and (e) 120°C for 6 h.

Costanzo and Giese, 1990; Komori *et al.*, 1999; Naamen *et al.*, 2003; Xu *et al.*, 2011). In fact, in the present study, the molecular water was believed to be inserted into the ditrigonal holes of the silicate layer, and the distance of 0.12 nm between the layers was, thus, less than the size of molecular water, ~ 0.264 nm. From the Fourier-transform IR (FTIR) patterns (Figure 5a), the appearance of absorption bands of 3545 cm^{-1} and 1653 cm^{-1} , which corresponded to the hydroxyl stretching and bending vibrations, respectively, of interlayer water, verified the existence of the new phase of hydrated kaolinite, which was also obtained using methanol-kaolinite intercalation (Komori *et al.*, 1999) and using glycol-kaolinite intercalation (Tunney and Detellier, 1994). Apparently, the hydrated kaolinite with $d_{001} = 0.84$ nm was formed by heating the kaolinite-hydrazine intercalate at a temperature between 40°C and 70°C. Furthermore, after heating at 90 and 120°C, new phases with d_{001} spacings of 0.77 nm and 0.75 nm appeared. According to Costanzo and Giese (1985), the phase with a crystal lattice from 0.72 nm to 0.79 nm is a kind of hydrated kaolinite containing only a small amount of molecular water distributed randomly between the layers. The statistical layer distance detected was, thus, much smaller than that in the structure with $d_{001} = 0.84$ nm. The IR spectra of the

two new phases ($d_{001} = 0.77$ nm and 0.75 nm) of kaolinite (Figure 5b,c) showed no typical new absorption peaks related to the molecular water compared with that of the hydrated kaolinite (Figure 5a). The new phases might still be the same as those obtained by Costanzo. The absorption peaks of 3545 cm^{-1} associated with

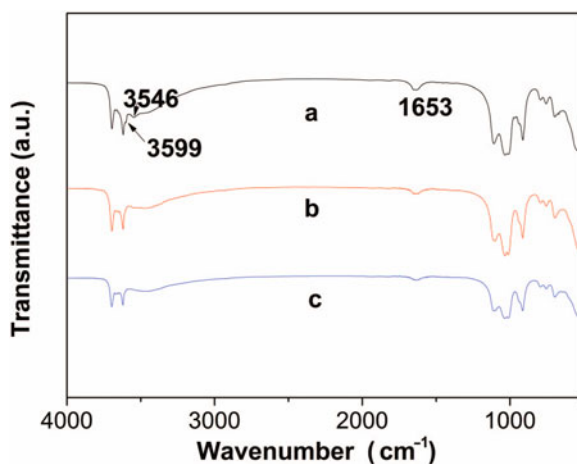


Figure 5. FTIR spectra of hydrated kaolinite with an interlayer distance, d_{001} , of (a) 0.84 nm, (b) 0.77 nm, and (c) 0.75 nm.

molecular water seemed to disappear in the two new phases because the amount of interlayer water molecules was below detection limits. In the case of the high treatment temperature between 90 and 120°C, therefore, only a small amount of water molecules was likely to be embedded in the ditrigonal holes of the tetrahedral sheet. The $d_{001} = 0.72\text{--}0.79$ nm hydrated kaolinite formed as a consequence.

The formation of hydrated kaolinite from the kaolinite-hydrazine intermediate was analyzed based on the XRD patterns. The XRD patterns of the kaolinite-hydrazine intercalation compound treated at 60°C for different amounts of time (Figure 6) illustrated the process of transformation from the intermediate to hydrated kaolinite. The 0.72 nm peak began to form after 10 min of heat treatment under atmospheric conditions, while the typical peak of $d_{001} = 1.04$ nm of the kaolinite-hydrazine intercalation compound decreased slightly (Figure 6b). The typical 1.04 nm peak disappeared until the treatment time of 20 min (Figure 6c), while a broad peak of 0.96 nm appeared and the 0.72 nm peak increased slightly. Then, when increasing the treatment time to 40 min, the 0.96 nm peak became broader. Meanwhile, it shifted to a larger 2θ value (Figure 6d). When the treatment time was further increased to 1 h, the new 0.84 nm peak formed steadily, with the complete disappearance of the 0.96 nm peak (Figure 6d). After that, the 0.84 nm peak increased significantly when the heating time was between 1 and 2 h and remained almost unchanged above 2 h. For all of the samples heat treated from 20 min to 24 h the intensity of the 0.72 nm peak was almost perfectly stable.

For the kaolinite-hydrazine intercalation compound heated at 60°C, molecular hydrazine hydrate de-intercalated from the interlayer during heat treatment, but most of the molecules probably remained in the interlayer, especially in the large particles, if the

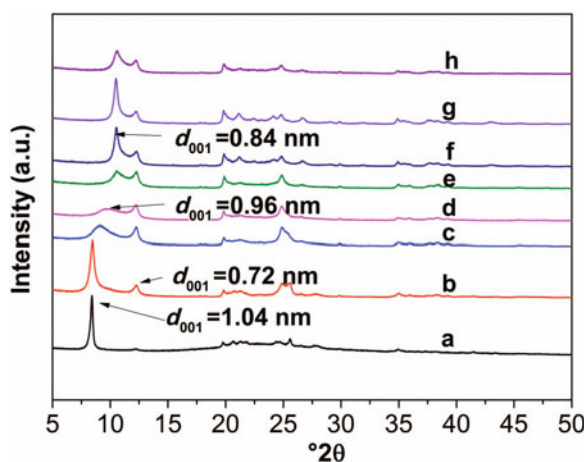


Figure 6. XRD patterns of (a) kaolinite-hydrazine intercalate heated at 60°C for (b) 10 min, (c) 20 min, (d) 40 min, (e) 1 h, (f) 1.5 h, (g) 2 h, and (h) 24 h.

duration of the heat treatment was short enough. Therefore, most of the kaolinite-hydrazine intercalation compound remained stable in the case of $d_{001} = 1.04$ nm and only a small amount was restored to the raw kaolinite when heating for only 10 min (Figure 6b). After 20 min of heat treatment, however, the hydrazine hydrate in the interlayer seemed to decompose. A new phase with the interlayer distance of $d_{001} = 0.96$ nm began to form; some of the hydrazine-kaolinite intercalate was transferred to raw kaolinite (Figure 6c). In the present study, the new phase was due to the decomposition of hydrazine hydrate in the interlayers. The decomposition caused the layers of kaolinite to collapse, forcing the -NH_2 group of hydrazine into the ditrigonal hole and probably generating molecular water in the interlayers (Johnston and Stone, 1990). In the present case, the hydrazine molecules without OH groups would diffuse from the interlayers, but molecular water would be relatively stable in the ditrigonal holes with increasing processing time. By de-intercalating the hydrazine molecules continually, the 0.96 nm peak, thus, became broader and shifted gradually to a larger 2θ value to form a new phase with $d_{001} = 0.84$ nm (Figure 6c,e). The new phase was seen clearly in samples heat treated beyond 1 h, in which only molecular water was inside the interlayer. Thus, a hydrated kaolinite with $d_{001} = 0.84$ nm formed perfectly and more completely with a heating time of between 1 and 2 h (Figure 6e,f,g). Beyond 2 h, the transformation from $d_{001} = 0.96$ nm into $d_{001} = 0.84$ nm was completed. The hydrated kaolinite content no longer increased with heating time in the system. Obviously, 2 h of heat treatment was sufficient to form the stable hydrated kaolinite with a yield rate of 80–90%. The schematic drawing of the formation of hydrated kaolinite is shown in a ball-and-stick model (Figure 7). Three days or more were often needed to complete the hydration process in previous studies (Tunney and Detellier, 1994; Komori *et al.*, 1999; Naamen *et al.*, 2003), but only ~2 h were needed here to form the hydrated kaolinite.

The kaolinite-hydrazine intercalate was heated at room temperature and at 120°C for different periods of time (Figures 8, 9). For the kaolinite-hydrazine intercalate, the intensity of the 0.72 nm peak increased with increasing heating time up to 7 days in air at room temperature (Figure 8). Meanwhile, the intensity of the 1.04 nm peak decreased with time and disappeared completely after 7 days of heat treatment. In addition, the 1.04 nm peak of the kaolinite-hydrazine intercalate disappeared completely when heated at 120°C for 5 min (Figure 9b), while the 0.72 nm peak increased significantly and a new 0.77 nm peak appeared. The 0.77 nm peak then shifted to 0.75 nm with heating time from 5 min to 2 h, and the relative intensity of the 0.75 nm peak remained unchanged beyond a heating time of 2 h (Figure 9c,d).

The hydrazine hydrate molecules appeared to de-intercalate directly from the interlayer space of the

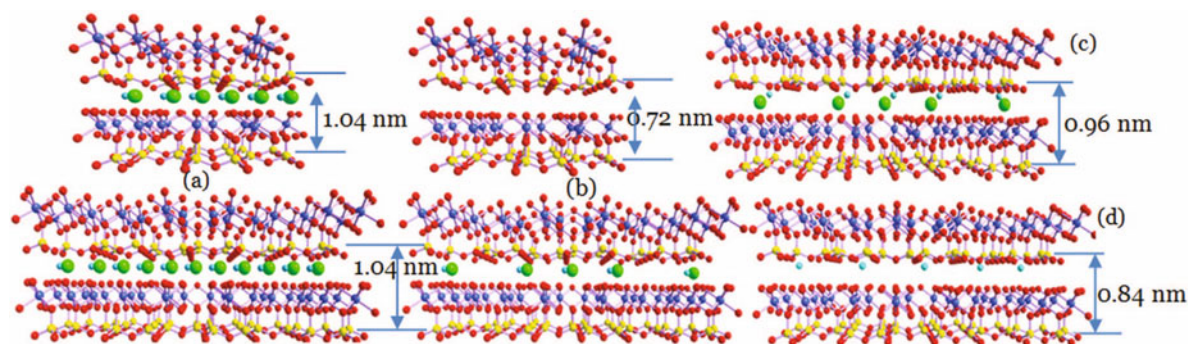


Figure 7. Schematic drawing of the formation of hydrated kaolinite at 60°C for (a) <math><10\text{ min}</math>, (b) $>10\text{ min}$: partial de-intercalation of hydrazine hydrates, (c) $>20\text{ min}$: decomposition of hydrazine hydrates, (d) $>1\text{ h}$: de-intercalation of hydrazine molecules and remaining water inside.

kaolinite-hydrazine intercalate with increase in processing time (Figure 8) at room temperature, in contrast to the compound treated at 60°C (Figure 6). The hydrazine hydrate molecules intercalated in the kaolinite did not appear to decompose to form the hydrated kaolinite at a temperature of 28°C in this case. In fact, room temperature was too low to decompose the hydrazine hydrate molecules intercalated in the kaolinite. The hydrazine hydrate was, thus, moved directly out of the interlayer with a long period of diffusion. After 7 days, all of the intercalated kaolinite with $d_{001} = 1.04\text{ nm}$ was transformed to raw kaolinite with $d_{001} = 0.72\text{ nm}$.

Furthermore, the de-intercalating rate of the hydrazine hydrate molecules from the kaolinite increased as the temperature increased to 120°C (Figure 9). In addition, the hydrazine hydrates had sufficient driving force to be decomposed at high temperatures before moving out of the interlayer of the kaolinite. However, the as-decomposed molecules, including hydrazine and water, diffused quickly and left the interlayer of the

kaolinite easily. The 1.04 nm diffraction peak, thus, disappeared after only 5 min of heating with only a small amount of the water molecules decomposed from hydrazine hydrate remaining in the interlayer. As only a small amount of water was left inside in the interlayer, the layer distance could not be supported at the conventional value, as in the phase with $d_{001} = 0.84\text{ nm}$. Thus, a layer space showing the phase with $d_{001} = 0.77\text{ nm}$ appeared after 5 min of heating and then transformed into 0.75 nm with a further decrease in the amount of water molecules after 2 h of heating (Figure 9b,c). The phase was maintained at $d_{001} = 0.75\text{ nm}$, showing the same result as that in a previous study (Costanzo and Giese, 1985). The intensity of the 0.75 nm peak remained stable after 2 h in the case of heating at 120°C (Figure 9d).

As a result, the hydrated hydrazine in the interlayer of kaolinite was volatile at 20–30°C and tended to evaporate and de-intercalate while exposed to air. The hydrated hydrazine decomposed to molecules of hydrazine and water in the interlayer, however, in which the

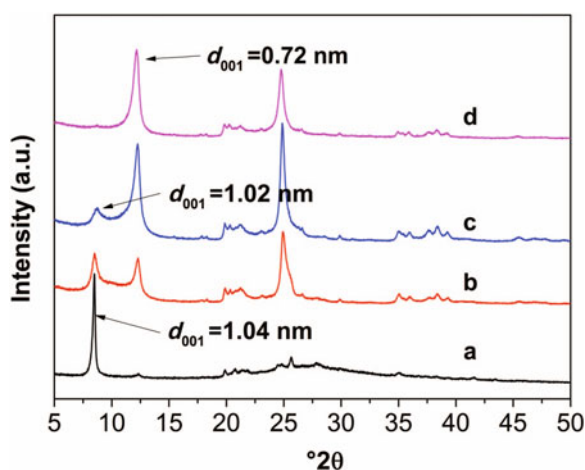


Figure 8. XRD patterns of kaolinite-hydrazine intercalate treated at room temperature for: (a) 0 h, (b) 12 h, (c) 3 days, and (d) 7 days.

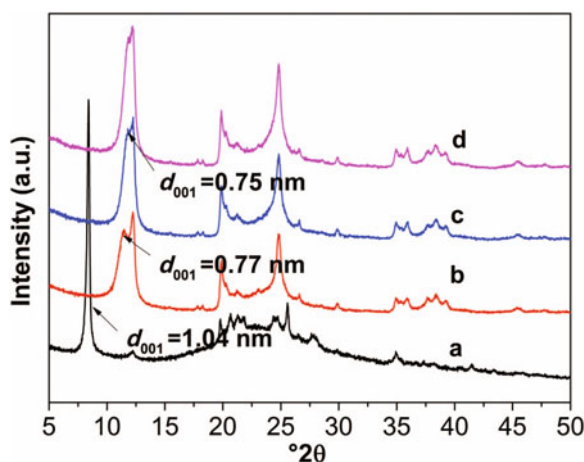


Figure 9. XRD patterns of: (a) kaolinite-hydrazine intercalate without heating and at 120°C for (b) 5 min, (c) 2 h, and (d) 6 h.

hydrazine molecules might have de-intercalated gradually, and the water remained stable in the ditrigonal holes of the silicate layer at 40–70°C, forming stable $d_{001} = 0.84$ nm hydrated kaolinite. Of course the interlayer hydration of the kaolinite will decrease a little with increasing temperature from 40 to 70°C as shown in Figure 3 due to the gradual increase in de-intercalating water molecules. At high temperatures of 90–120°C, however, the hydrated hydrazine decomposed sharply, and both molecules de-intercalated quickly from the interlayer except for a small number of water molecules remaining in the ditrigonal holes of the silicate layer randomly and, thus, forming a stable hydrated kaolinite with a lattice distance of $d_{001} = 0.77$ – 0.75 nm. Beyond 150°C, hydrazine hydrate was decomposed significantly and de-intercalated completely to form kaolinite without intercalation due to the intense evaporation of hydrazine and water molecules. In this case, the kaolinite particles after intercalation were slightly smaller in size compared with the raw kaolinite (Figure 4).

The glycol-kaolinite and the glycine-kaolinite intercalation were prepared by reacting hydrated kaolinite with ethylene glycol and glycine, respectively (Figure 10). As shown, the 0.84 nm diffraction peaks of hydrated kaolinite disappeared completely and a new 1.09 nm diffraction peak appeared (Figure 10a), which is consistent with the literature (Janek *et al.*, 2007). The ethylene glycol-kaolinite intercalate was, thus, proven to form in this case. A strong 1.03 nm diffraction peak appeared after the hydrated kaolinite reacted with glycine (Figure 10b), which indicated that glycine was successfully intercalated into kaolinite (Sato, 1999). This result demonstrated that the hydrated kaolinite with $d_{001} = 0.84$ nm prepared by the heat treatment of kaolinite-hydrazine intercalate in air at 60°C was acceptable and appropriate for further intercalation with other molecules.

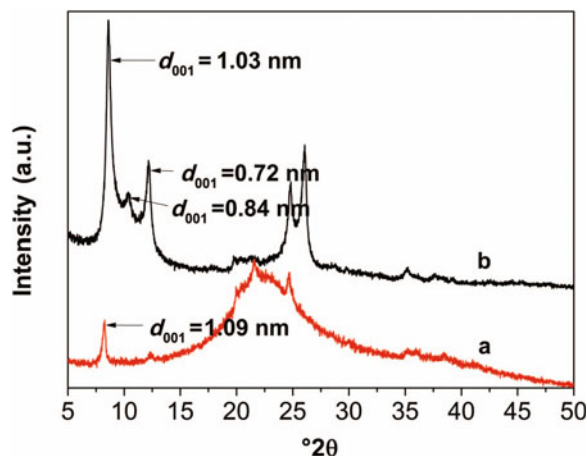


Figure 10. XRD patterns of: (a) ethylene glycol-kaolinite intercalate; and (b) glycine-kaolinite.

CONCLUSIONS

Hydrazine hydrate was intercalated into the interlayers of kaolinite and formed a kaolinite-hydrazine hydrate intercalation via new hydrogen bonds with O in SiO_4 sheets, resulting in expansion of the interlayer distance of the raw kaolinite from $d_{001} = 0.72$ nm to $d_{001} = 1.04$ nm. The hydrated hydrazine hydrate in the interlayer of kaolinite was volatile at 20–30°C and tended to de-intercalate while exposed. The hydrazine hydrate decomposed to molecules of hydrazine and water, in which the hydrazine molecules de-intercalated gradually, and water remained stable in the ditrigonal holes of the silicate layer at 40–70°C, forming stable $d_{001} = 0.84$ nm hydrated kaolinite. At high temperatures, between 90 and 120°C, the hydrazine hydrate decomposed rapidly, and both molecules de-intercalated quickly from the interlayer except for a small number of water molecules remaining randomly in the ditrigonal holes of the silicate layer and, thus, forming a stable hydrated kaolinite with a lattice constant of $d_{001} = 0.77$ – 0.75 nm. Beyond 150°C, hydrazine hydrate decomposed significantly and de-intercalated completely to form kaolinite without intercalation due to the evaporation of hydrazine and water molecules. The 0.84 nm hydrated kaolinite was suitable for use as a precursor for the preparation of new kaolinite intercalation compounds without using other polluting organic molecules, indicating that the hydrated kaolinite is an environmentally friendly precursor suitable for further intercalation.

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