
Goethite and kaolinite are ubiquitous in natural environments. In soils they are often cemented together as a binary association, which has a significant influence on the structure and properties of soils. In this study, the mineralogy (using X-ray diffraction [XRD], thermal analyses, and infrared analysis), interactions, and stability of a goethite–kaolinite association (GKA) and a goethite–kaolinite mixture (GKM) were investigated. In GKA, goethite almost completely coated the surface of kaolinite, whereas for GKM the coating was partial. Infrared (IR) spectra showed that the vibrational frequencies of ≡Fe–OH in GKM and GKA shifted to higher wave numbers and those of ≡Al–OH, O–Al–O, Al–O–Si, and Fe–O shifted to lower wave numbers. Magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy demonstrated that interactions between goethite and kaolinite increased the chemical shifts of $^{29}$Si and $^{27}$Al. The shifts of both the IR and the MAS NMR parameters were larger for GKA than for GKM. In addition, the IR bands of ≡Al–OH and the XRD peaks of goethite were weaker with GKA than with GKM. As expected, particle size distributions showed that GKA had a higher mechanical stability than GKM. The thermal stability of the kaolinite in GKA was higher than that of GKM, but that of goethite in GKA was lower than that in GKM. These results imply that: (i) kaolinite and goethite interact by electrostatic attraction, anion ligand exchange, surface coordination, and hydrogen bonds; (ii) the interaction strength was much stronger for GKA than for GKM; (iii) a cation exchange reaction and isomorphous substitution of Fe by Al for goethite occurred in GKA.

Abbreviations: DTG, differential thermogravimetry; EDS, energy dispersive X-ray spectrometry; FTIR, Fourier transform infrared; GKA, goethite-kaolinite association; GKM, goethite-kaolinite mixture; MAS NMR, magic angle spinning nuclear magnetic resonance; SEM, scanning electron microscopy; TEM, transmission electron microscopy; TG, thermogravimetry; XRD, X-ray diffraction.

Iron oxides and kaolinite are often simultaneously present in soils, where they tend to form associations that are cemented together by various interactions (e.g., Bigham et al., 2002; Davey et al., 1975; Qafoku et al., 2000). These associations are important constituents of tropical and subtropical soils and they contribute to the structure and properties of aggregates in soils and sediments (Bronick and Lal, 2005; Duiker et al., 2003; Fitzpatrick, 1988; Rhoton et al., 1998; Teixeira and Misra, 1997). Knowledge of the formation mechanisms and microstructures of iron oxide–kaolinite associations is of significance for soil and water conservation, fertility cultivation, and environmental restoration of tropical and subtropical zones.

Iron oxides exist in a variety of structures, polymorphs, and hydration states, but the basic structural unit for all iron oxides is an octahedron, in which each Fe atom is surrounded either by six oxygens (Navrotsky et al., 2008; Schwertmann and Cornell, 2000). Iron oxides possess a high reactivity due to the large amount of active surface sites, such as iron hydroxyls (≡Fe–OH) and Fe atoms (Herbert,
Kaolinite is a well-defined 1:1-type phyllosilicate with the chemical composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. One layer of kaolinite consists of a silica/oxygen tetrahedral sheet and an alumina/oxygen dioctahedral sheet that share a common plane of oxygen atoms. The surface sites of kaolinite are mainly silanol ($\equiv\text{Si}–\text{OH}$) and aluminol ($\equiv\text{Al}–\text{OH}$) groups situated at the edges and at the hydroxyl-terminated planes of the clay lamellae (Ioannou and Dimirkou, 1997; Landry et al., 2009). In addition, permanently charged sites ($\equiv\text{X}^–$) on basal surfaces of kaolinite arise from isomorphic substitution of the Si and Al ions in the crystal structure for lower valence cations, but the number of these sites is generally much fewer than that of edge sites (e.g., Landry et al., 2009; Tombácz et al., 2004).

When kaolinite and iron oxides are simultaneously present in a suspension they interact. In the pH range 4 to 7, iron oxides have a positive surface charge and kaolinite has a negative surface charge; therefore, electrostatic attraction occurs and this may lead to heterocoagulation and formation of iron oxide–kaolinite aggregates (e.g., Hou et al., 2007; Osei and Singh, 1999; Tombácz et al., 2004). In time, iron oxide–kaolinite aggregates become cemented together by various surface reactions (Golden and Dixon, 1985; Goldberg and Glaubig, 1987; Nachtegaal and Sparks, 2004). The IR and MAS NMR spectra have shown that the interactions between the aggregates hydrogen bonds might occur between the $\equiv\text{Fe}–\text{OH}$ on the iron oxide surface and the $\equiv\text{Si}–\text{OH}$ or $\equiv\text{Al}–\text{OH}$ on the kaolinite surface (Cheng et al., 1995, 1996; Ioannou and Dimirkou, 1997). Mössbauer and X-ray photoelectron spectroscopy (XPS) have revealed that interactions between iron oxides and kaolinite may increase the magnetic hyperfine field of Fe atoms and decrease the binding energy of Si2p and Al2p electrons (Bigham et al., 1978; Eusterhues et al., 2008; Goldberg and Glaubig, 1987). These results confirm that the chemical environment of some Fe, Si, and Al elements in the minerals can be changed by reactions between the surface groups. In the binary system of iron oxides and kaolinite, iron oxides can coat the kaolinite surface and also intercalate into the interlayer spaces of kaolinite. Iron ions present in solutions can even cause a small amount of Fe ion incorporation into the crystal structure via the isomorphic substitution of the structural Si and Al ions (Bentabol et al., 2009; Ma and Pierre, 1998; Saleh and Jones, 1984). Once iron oxide particles are cemented to kaolinite particles, aggregates appear that have a relatively high stability (Bronick and Lal, 2005; Duiker et al., 2003). Soil structure consists of an aggregate formed by the arrangement of soil particles, and depends on the interactions between primary particles to form stable aggregates (Bronick and Lal, 2005; Igwe et al., 1999). Thus, the recognition of the interactions, size distribution, and stability of soil aggregates is important to properly interpret soil structure.

Goethite ($\alpha$-FeOOH) is one of the most common iron oxides in soils and the isomorphic substitution of Fe by Al is very common (Bigham et al., 1978, 2002; Fitzpatrick and Schwertmann, 1982; Schwertmann and Cornell, 2000). Although Al is 17% smaller than Fe, up to one-third of the Fe can be replaced by Al in natural goethite. Generally, the mole ratio of the substitution increases with soil development. The substitution of Fe by Al typically has a marked effect on the properties of goethite: crystallinity, thermal stability, unit cell volume, particle size, specific surface area, surface hydroxyls, morphology, solubility and spectral and magnetic characteristics (e.g., Bigham et al., 2002; Fitzpatrick, 1988; Fitzpatrick and Schwertmann, 1982).

In the literatures, most attention has been paid to the association of goethite and kaolinite. To investigate the structures and properties of these associations the binary systems of goethite and kaolinite have been prepared in the laboratory by: (i) mechanically mixing crystallographically pure goethite in a suspension with kaolinite (Hou et al., 2007; Ioannou and Dimirkou, 1997) and (ii) synthesizing goethite in a suspension in which kaolinite is present (Saleh and Jones, 1984; Schwertmann, 1988; Violante et al., 1998). The interactions of the systems obtained by the first method are very weak and differ considerably from those of natural goethite–kaolinite associations. The samples prepared by the second method were closer to the natural associations found in soils. However, it was difficult to prepare goethite–kaolinite associations of a sufficiently high purity and quantity because in the presence of kaolinite the formation of goethite is inhibited (e.g., Bigham et al., 2002; Cornell and Schwertmann 2003; Schwertmann, 1988).

Recently, Wei et al. (2011) have found that Fe(II) can accelerate the synthesis of goethite in the presence of kaolinite at weakly acidic pH and temperatures of 50 to 60°C. Therefore, in the present study Wei et al.’s procedure will be used to prepare a GKA. The properties of GKA will be compared with those of pure goethite and kaolinite and with that of a GKM. The methods of analysis included X-ray diffraction (XRD), scanning electron microscope/energy dispersive X-ray spectrometry (SEM/EDS), transmission electron microscopy (TEM), Fourier transform infrared (FTIR), MAS NMR, particle size analysis, and thermogravimetry/differential thermogravimetry (TG/DTG) to obtain information on the structure, the interactions, and the stability of GKA and GKM. With this information a better understanding of the formation and structure of natural goethite–kaolinite associations is obtained and such understanding is important in the fields of agriculture, geochemistry, and environmental chemistry.

**MATERIALS AND METHODS**

**Materials**

Analytical grade reagents and distilled water were used in all experiments. The polyethylene flasks, syringes, and distilled water needed for the preparation of goethite and the goethite–kaolinite association were all flushed with pure N$_2$ to remove the dissolved oxygen and to avoid Fe(II) oxidation. The FeCl$_2$ solution was filtered through a 0.22-µm membrane filter in a cabinet flushed with N$_2$ to remove particulate contaminants.

Raw kaolinite was purchased from the Maoming Kaolin Clay Company (Guangdong Province, China) and pretreated.
product was centrifuged, washed, dried, ground, and stored in 5 d, followed by a rest period of 30 d at room temperature. The sealed and the suspension was aged in a glycerin bath of 55°C for 5 d. The polyethylene flask was sealed, stirred with a magnetic stirrer for 2 d, and then the total volume was adjusted to 1 L with distilled water. The polyethylene flask, magnetic stirring for 5 min and ultrasonic dispersion for 30 min. The pH of the suspension was adjusted back to 6 with a dilute NaOH solution, and then the total volume was adjusted to 1 L with oxygen-free distilled water. After another 30 min, both the stirring and N2 supply were stopped. The polyethylene flask was tightly sealed and the suspension was aged in a glycercin bath of 55°C for 5 d. The final product was centrifuged and washed with oxygen-free distilled water until the conductivity of the supernatant was <6 μS/cm. The precipitated goethite was dried at 40°C, ground to pass a 100-mesh sieve, and stored in a desiccator.

Pure goethite was prepared according to the procedure described by Schwertmann and Cornell (2000) and Wei et al. (2011). A solution of 6 mol/L NaOH was added drop by drop to 100 mL of 1 mol/L FeCl3 solution in a 1 L polyethylene flask under vigorous magnetic stirring until pH 6 was reached. Subsequently pure N2 was flowed through the suspension at a rate of 100 mL/min. After 30 min, 2 mL of 1 mol/L FeCl3 solution was injected into the suspension with a syringe. The pH of the suspension was adjusted back to 6 with a dilute NaOH solution, and then the total volume was adjusted to 1 L with oxygen-free distilled water. After another 30 min, both the stirring and N2 supply were stopped. The polyethylene flask was tightly sealed and the suspension was aged in a glycercin bath of 55°C for 5 d. The final product was centrifuged and washed with oxygen-free distilled water until the conductivity of the supernatant was <6 μS/cm. The precipitated goethite was dried at 40°C, ground to pass a 100-mesh sieve, and stored in a desiccator.

For the preparation of the GKA, 100 mL oxygen-free distilled water was added to 7.985 g kaolinite in a 1 L polyethylene flask, followed by vigorous stirring for 5 min and ultrasonic dispersion for 30 min. Then 100 mL of 1 mol/L FeCl3 solution was poured into the kaolinite suspension under vigorous magnetic stirring. These amounts of kaolinite and FeCl3 were selected to reach a theoretical mass ratio (1:1) of goethite to kaolinite. The pH of the suspension was adjusted to 6 with a 6 mol/L NaOH solution; thereafter pure N2 was flowed through the suspension at a rate of 100 mL/min. After 30 min, 6 mL of 1 mol/L FeCl3 solution was injected into the suspension with a syringe. The pH of the suspension was adjusted back to 6 with a dilute NaOH solution, and then the total volume was adjusted to 1 L with oxygen-free distilled water. After a reaction time of 30 min both the stirring and N2 supply were stopped. The polyethylene flask was tightly sealed and the suspension was aged in a glycercin bath of 55°C for 5 d, followed by a rest period of 30 d at room temperature. The product was centrifuged, washed, dried, ground, and stored in the same way as the goethite.

For the preparation of the GKM, 50 mL distilled water was added to 0.5 g goethite mixed with 0.5 g kaolinite in a 1 L polyethylene flask, magnetic stirring for 5 min and ultrasonic dispersion for 30 min. The pH of the suspension was adjusted to 6 with a dilute NaOH solution, and then the total volume was adjusted to 100 mL with distilled water. The polyethylene flask was sealed, stirred with a magnetic stirrer for 2 d, and then aged at rest for 30 d at room temperature. The mixture was centrifuged, washed, dried, ground, and stored in the same way as the goethite.

**Sample Analysis and Identification**

X-ray diffraction patterns were obtained with a German Bruker D8 ADVANCE X-ray diffractometer. Random powder samples were taken into the notch of a plastic board and lightly pressed against a filter paper. The diffractometer was operated at 40 kV tube voltage and 40 mA tube current with a graphite monochromator using CuKα radiation (λ = 0.15406 nm), a diffracting rate of 2°/min, and step intervals of 0.02°.

Morphology and main elements of the samples were characterized using a field emission scanning electron microscope (FE-SEM; JEOL JSM-6700F) integrated with an energy dispersive X-ray spectrometer (Bruker QUANTAX). The surface of the samples was coated with C before analysis. The EDX analysis of samples was performed at selected micro-areas of the SEM images.

Transmission electron microscopy analysis was performed with a Philips-CM12 TEM operated at an accelerating voltage of 100 kV. The samples were gently crushed to powder, and then dispersed in absolute alcohol and sonicated before deposition on a holey copper film and dried in air.

Fourier transform infrared spectra were recorded on a Bruker Equinox 55 spectrophotometer. The samples were mixed very gently with KBr (0.5% sample weight) in an agate mortar and pelletized. Each sample was determined in the spectral range 4000 to 380 cm⁻¹ with a transmittance mode, a resolution of 4 cm⁻¹ and 64 scans. The data were analyzed using the OPUS software.

The 29Si and 27Al MAS NMR spectra were obtained at 11.7 T using a Varian INOVA 600 spectrometer and Doty probe. The Al spectra were measured using a 4 mm rotor spinning at 9 kHz, operated at a frequency of 156.28 MHz. A 1 s recycle delay and a 1.2 μs pulse were employed. For each spectrum 500 scans at the same conditions were collected. The final 27Al spectra were referenced against the spectrum of Al(H2O)6 3+ in a 1 mol/L Al(NO3)3 solution. The 29Si MAS NMR spectra were obtained with a 6 mm rotor at a spinning rate of 7.0 kHz and operated at a frequency of 119.15 MHz. A 5 s recycle delay and a 2 μs pulse were employed. For each spectrum 1000 scans at the same conditions were collected. The final 29Si spectra were referenced against the spectrum of tetrathemethylsilane (TMS).

**Mechanical and Chemical Stability of the Samples**

The mechanical stability of the samples was analyzed by subjecting their suspensions to ultrasonic dispersion. About a 1-g sample in a flask was moistened by slowly adding 10 mL distilled water along the inner wall of the flask and then kept at rest for 10 min; thereafter another 10 mL distilled water was added. The suspension was dispersed using an ultrasonic generator with a frequency of 22 ± 1 kHz and power of 750 W at 25°C for 30 and 120 min. After the treatment, the particle size distribution of the dispersed sample was measured within a total range of...
diameters between 0.01 and 100 μm using a laser particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd., Malvern, Worcestershire, UK). The analyzer quantitatively measures the mean diameter and the corresponding volume content of each particle fraction of the sample using the common mode based on the assumption that the particles are spherical.

The thermal stability of the samples was measured by TG analysis using a NETZSCH TG 209 instrument. About 10-mg sample was subjected to an argon stream with a flow-rate of 20 mL/min; the heating rate was 10°C/min. The TG curves were recorded from 40 to 800°C and the DTG curves are the derivatives of the TG data. Alumina was used as the reference standard.

RESULTS

X-Ray Diffraction Analysis

The XRD patterns of the samples are shown in Fig. 1. The peaks of the kaolinite and goethite matched well with the file cards of kaolinite (JCPDS-89–6538) and of goethite (JCPDS-81–0464) respectively, indicating that both pure samples are of a good crystallinity and high purity. The background intensities of all samples were close to each other, but the peak intensities of kaolinite and goethite in the binary systems (GKM and GKA) were much lower than those of the kaolinite and goethite. This can be attributed to the fact that in kaolinite–goethite systems the two minerals partially masked the mineral surfaces and also affected the preferred orientation of each other (Dimirkou et al., 2002; Schwertmann and Cornell, 2000; Violante and Huang, 1994). Compared to GKM, GKA showed weaker peaks for kaolinite and lower and broader peaks for goethite. This illustrates that: (i) in GKA the coating of the kaolinite surface with goethite particles is larger than in GKM (Dimirkou et al., 2002; Violante and Huang, 1994) and (ii) goethite in GKA possesses a relatively poor crystallinity (Bigham et al., 2002; Schwertmann, 1988; Wei et al., 2011).

Scanning Electron Microscopy, Transmission Electron Microscopy, and Energy Dispersive X-ray Spectrometry Analysis

In the SEM image of GKM (Fig. 2a), the nanorod-like goethite particles were mostly located in the gaps between the adjacent flake-like kaolinite particles but rarely on the kaolinite surface. For GKA (Fig. 2b), the kaolinite particles were mostly coated by goethite particles or by small goethite aggregates. In the TEM image of GKM (Fig. 2c), only a small amount of star- or rod-like goethite nanoparticles were located on the kaolinite surface, while in that of the GKA (Fig. 2d), nearly all goethite particles were attached to the kaolinite surface and only a few free goethite particles were observed.

The SEM–EDS data of the selected micro-areas are listed in Table 1. In GKM, the bare kaolinite surface (Panel 1 in Fig. 2a) contained traces of Fe and a rich amount of Si, Al, and O. The elements found in the gaps between the kaolinite particles (Panel 2 in Fig. 2a) were mainly Fe and O, with a Fe/O atom ratio of 1:2.17, which is close to the Fe/O atom ratio (1:2) of α-FeOOH. In GKA, the area of kaolinite coated with only a few goethite particles (Panel 3 in Fig. 2b) contained 11.42% Fe and that of kaolinite with many goethite particles (Panel 4 in Fig. 2b) 40.49% Fe.

Fourier Transform Infrared Spectrophotometry

The FTIR spectra of the samples are depicted in Fig. 3. According to the literatures (Beauvais and Bertaux, 2002; Cornell and Schwertmann, 2003; Qtaitat and Al-Trawneh, 2005; Weckler and Lutz, 1998), the vibrational assignments are listed in Table 2. The IR spectra of the binary systems were different from those of the kaolinite and goethite for the following bands:

1. In the IR spectrum of the kaolinite, a set of bands appeared at around 3695, 3660, 3626, 1110, 1037, 938, 912, 797, 755, 542, and 469 cm⁻¹. In the binary systems these bands shifted to lower wave numbers. The bands around 1015, 698, and 425 cm⁻¹ for the kaolinite shifted to lower wave numbers for GKA but they remained unchanged for GKM.

2. The vibrational bands that appeared at around 3130, 892, and 790 cm⁻¹ in the IR spectrum of the goethite showed an upward tendency in the spectra of GKA and GKM. The band at 641 cm⁻¹ for the goethite shifted to lower wave numbers for GKA but they remained unchanged for GKM.

Magic Angle Spinning Nuclear Magnetic Resonance Spectra of the Samples

The ²⁹Si and ²⁷Al MAS NMR spectra of the kaolinite, GKM and GKA are depicted in Fig. 4. The peaks of ²⁹Si appeared in the range from −90 to −92 ppm.
and those of $^{27}$Al in the range of 3 to 6 ppm. The peak positions of $^{29}$Si and $^{27}$Al indicated that the three samples possessed a tetrahedral coordinated Si and an octahedral coordinated Al (He et al., 2004; Xu and Van Deventer, 2002). The chemical shifts of both $^{29}$Si and $^{27}$Al for the kaolinite, GKM and GKA were close to each other, meaning that interactions between goethite and kaolinite changed little the basic structure of kaolinite. Compared to the kaolinite sample, the peaks of $^{29}$Si and $^{27}$Al shifted to the positive side in the binary systems, for GKM by 0.40 and 0.82 ppm, respectively and for GKA by 1.14 and 2.74 ppm, respectively. Clearly, interactions between goethite and kaolinite increased the chemical shifts of $^{29}$Si and $^{27}$Al.

Table 1. Scanning electron microscopy energy dispersive X-ray spectrometry (SEM-EDS) analysis of goethite–kaolinite mixture (GKM) and goethite–kaolinite association (GKA).

<table>
<thead>
<tr>
<th>Elements</th>
<th>GKM</th>
<th>Elemental content, %</th>
<th>GKA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Panel 1 in Fig. 2a</td>
<td>Panel 2 in Fig. 2a</td>
<td>Panel 3 in Fig. 2b</td>
</tr>
<tr>
<td>O</td>
<td>66.74</td>
<td>38.75</td>
<td>61.56</td>
</tr>
<tr>
<td>Si</td>
<td>16.02</td>
<td>2.06</td>
<td>13.75</td>
</tr>
<tr>
<td>Al</td>
<td>15.37</td>
<td>1.93</td>
<td>13.27</td>
</tr>
<tr>
<td>Fe</td>
<td>1.87</td>
<td>57.26</td>
<td>11.42</td>
</tr>
</tbody>
</table>
Stability of the Samples

Particle Size Distributions and Mechanical Stability

The particle size distributions of the dispersed samples after ultrasonic dispersion for 30 min are presented in Fig. 5a and Table 3. All the distributions were about bimodal with the first distribution presenting the “single” particles and the second the aggregates. The single particle population might also include some small particles clusters. For the goethite the single particle peak position is at 0.13 µm, and the weaker peak of the aggregates is at 1.45 µm. With the kaolinite the peak position of the single particles is at 0.19 µm, the similar peak at 4.37 µm is due to the aggregates of kaolinite.

With GKM, the large first part of the distribution (0.05–0.83 µm) covered both the single goethite and kaolinite particles and accounted for a volume content of 80.24%; the peak position (0.13 µm) is very close to that of the goethite particles. The second part of the distribution (1.00–27.54 µm; aggregates) with a peak at 4.37 µm accounted for a volume content of 19.52%. The diameter at the peak of the aggregates is similar to that of the pure kaolinite aggregates. With GKA, the first part of the distribution (0.05–1.20 µm) with a peak position at 0.23 µm accounted for a volume content of 66.56%. The diameter at the peak position is somewhat larger than that of kaolinite. This indicates that next to single goethite and kaolinite particles also single kaolinite particles that are partly covered with goethite are present. The part of the distribution that covers the aggregates (1.45–47.86 µm; peak at 5.25 mm) accounted for a volume content of 32.53%.

Some information on the mechanical stability of the aggregates can be obtained by comparing the above results with those after an ultrasonic treatment of 120 min duration. With the goethite only one prominent peak was present at 0.13 µm for single particles. All goethite particles were well dispersed. With the kaolinite, the particle size range 0.04 to 1.00 µm (single particles) with a peak at 0.19 µm corresponded to a volume content of 69.39% and the aggregated particles (1.20–22.91 µm) with a peak at 3.63 µm to 28.53%. Although the degree of dispersion was improved, 120 min was still insufficient to fully disperse the kaolinite.

With GKM, the single particles (0.05–1.00 µm) with a peak at 0.16 µm accounted for the dominant content of 90.04%. The volume content of the aggregates (1.20–10.97 µm) with a peak at 3.63 µm was 9.96%. Evidently, about 50% of the aggregates that existed after 30 min sonication could be dispersed by 120 min sonication. Moreover, the shift of the peak position of the single particles toward lower particle sizes indicates that small particle clusters were also affected. In GKA, the single particles (0.05–1.20 µm) accounted for 74.15% of the volume content; with a peak at 0.23 µm. The volume content of the aggregates (1.45–57.54 µm) with a peak at 4.37 µm was 25.63%. The long sonication shifted the distributions in favor of the single particles by about 8%.

Thermal Stability

The TG and DTG curves of the kaolinite are depicted in Fig. 6a. The physically adsorbed water was released below 120°C. Dehydroxylation occurred from 120 to 650°C, with a peak at 501°C and a mass loss of 13.92%. With further increasing temperature, the total mass loss was up to 15.13% at 800°C. For the goethite (Fig. 6b)
the mass loss of 1.62% below 130°C can be attributed to dehydration. Dehydroxylation occurred in the range of 130 to 350°C with a peak at 256°C and a mass loss of 13.68%. The total mass loss was 17.94% at 800°C. These features of mass loss for the kaolinite and goethite are consistent with the literatures (Plante et al., 2009; Subbanna et al., 2003; Vágvolgyi et al., 2008).

For GKM (Fig. 6c), the physically adsorbed water was driven off below 140°C, corresponding to a mass loss of 0.78%. With increasing temperature from 140 to 380°C, a mass loss of

Table 3. Parameters of particle size distributions of kaolinite, goethite, goethite–kaolinite mixture (GKM) and goethite–kaolinite association (GKA) after ultrasonic dispersion for 30 and 120 min.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Particle size</th>
<th>Dispersion for 30 min</th>
<th>Dispersion for 120 min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Particle size</td>
<td>Particle content</td>
<td>Peak position</td>
</tr>
<tr>
<td></td>
<td>µm</td>
<td>%</td>
<td>µm</td>
</tr>
<tr>
<td>Goethite</td>
<td>0.06–0.40</td>
<td>84.90</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>0.48–19.06</td>
<td>15.01</td>
<td>1.45</td>
</tr>
<tr>
<td></td>
<td>0.05–0.83</td>
<td>52.38</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>1.20–27.54</td>
<td>47.32</td>
<td>4.37</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>0.05–0.83</td>
<td>80.24</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>1.00–27.54</td>
<td>19.52</td>
<td>4.37</td>
</tr>
<tr>
<td>GKM</td>
<td>0.05–1.20</td>
<td>66.56</td>
<td>0.23</td>
</tr>
<tr>
<td>GKA</td>
<td>1.45–47.86</td>
<td>32.53</td>
<td>5.25</td>
</tr>
</tbody>
</table>
4.43% occurred with a peak at 271°C due to the dehydroxylation of goethite. The structural hydroxyls of kaolinite were lost over the temperature range from 380 to 640°C, with a prominent peak at 504°C and a mass loss of 9.47%. With further increasing temperature, the total mass loss increased gradually to 14.76% at 800°C. For GKA (Fig. 6d), physically adsorbed water was released below 140°C, with a mass loss of 0.63%. The dehydroxylation of goethite in the range of 140 to 390°C resulted in a mass loss of 5.48% and a peak at 265°C. The structural hydroxyls of kaolinite were removed between 390 and 640°C, with a mass loss of 9.61% and a peak at 508°C. The mass loss of GKA was 16.37% at 800°C.

**DISCUSSION**

**Interactions between Goethite and Kaolinite**

Interaction mechanisms between goethite and kaolinite are revealed by the IR and MAS NMR spectra of the samples. The lower IR vibrational wave numbers of $\equiv$Al–OH in the binary systems, compared to the kaolinite, indicate that interactions between goethite and kaolinite decreased the polarity of $\equiv$Al–OH (Ioannou and Dimirkou, 1997; Pokrovski et al., 2003). Because the surfaces of goethite and kaolinite have an amount of $\equiv$Fe–OH and $\equiv$Al–OH, respectively, hydrogen bond formation ($\equiv$Al–O(H)...H–O–Fe, $\equiv$R–O–H...H–O–Fe) is possible in the binary systems. Moreover, the points of zero charge (PZC), determined by potentiometric titration in the present study, of the kaolinite and goethite were 4.0 and 8.2, respectively. Therefore, in a suspension of pH 6, positive charge occur on the goethite surface and negative charges on the kaolinite surface, resulting in electrostatic attraction between the two types of surfaces. Both hydrogen bond formation and electrostatic attraction likely weakened the polarity of O–H in $\equiv$Al–OH and eventually decreased the IR vibrational frequency of $\equiv$Al–OH. The shifts of the IR vibrational bands of O–Al–O, Al–O–Si, Fe–O, and $\equiv$Fe–OH in the binary systems may be due to the coordination between the O atoms of the kaolinite surface and the Fe atoms of the goethite surface. According to the literatures (Bentabol et al., 2009; Dimirkou et al., 2002; Petit and Decarreau, 1990), this coordination directly weakens the polarity of O–Al–O, Al–O–Si, and Fe–O, and thus decreases the vibrational frequencies; at the same time the polarity of O–H in $\equiv$Fe–OH is strengthened, resulting in a higher frequency.

The increase of the chemical shifts of $^{29}$Si and $^{27}$Al in the binary systems implies that interactions between goethite and kaolinite decreased the extranuclear electron density of Si and Al atoms. The surface interactions between goethite and kaolinite include hydrogen bonds, electrostatic attraction, and anion ligand exchange (Cheng et al., 1995, 1996; Dimirkou et al., 2002, Ioannou and Dimirkou, 1997). The first two were already suggested above. The anion ligand exchange means that the functional groups with a negative charge ($\equiv$R–O$^-$, R stands for Si or Al) on the kaolinite surface have replaced the bound hydroxyl ions on the goethite surface ($\equiv$R–O$^-$ + HO–Fe$^+$ $\rightarrow$ $\equiv$R–O–Fe$^+$ + OH$^-$). These interactions decrease the extranuclear electron density of the O and R atoms in the $\equiv$R–O groups, and resulted
in an increase of the chemical shifts of $^{29}\text{Si}$ and $^{27}\text{Al}$ (Cheng et al., 1995, 1996; Dimirkou et al., 2002).

**Microstructure of Goethite–Kaolinite Mixture and Goethite–Kaolinite Association**

Our XRD, SEM/EDS, and TEM results indicated that with GKA the kaolinite surface is strongly coated by goethite and with GKM this coating is poor. Both the IR vibrational bands of $=\text{Al}–\text{OH}$, $=\text{Fe}–\text{OH}$, $\text{O}–\text{Al}–\text{O}$, $\text{Al}–\text{O}–\text{Si}$, and $\text{Fe}–\text{O}$ groups and the MAS NMR peaks for $^{29}\text{Si}$ and $^{27}\text{Al}$ had similar shifts in GKM and GKA. However, the peak shifts in GKA were more than those in GKM. This indicates that, although similar interactions occurred in both samples, in GKA the strength of interactions between kaolinite and goethite was much greater.

The IR transition intensity of $=\text{Al}–\text{OH}$ in GKA was considerably weaker than that in GKM (Fig. 3). This can best be explained by a cation exchange reaction (Dimirkou et al., 2002; Petit and Decarreau, 1990). In the formation process of GKA, some $\text{H}^+$ ions in the $=\text{Al}–\text{OH}_2^{0.5+}$ on the kaolinite surface were likely replaced by other cations, such as $\text{Fe}^{x+}(\text{OH})_y(3x–y)$ and $=\text{Fe}_2\text{OH}_4^{2+}$ $(n=1, 2, 3)$ on the goethite surface, which decreased the amount of $=\text{Al}–\text{OH}_2^{0.5+}$, resulting in a relatively weak vibrational band. Furthermore, a large amount of goethite particles covered the surface of kaolinite in GKA, which also decreased the IR transition intensity of $=\text{Al}–\text{OH}$. On the contrary, the transition intensity of $=\text{Fe}–\text{OH}$ in GKA was slightly greater than that in GKM. This can be attributed to the fact that the poorly crystalline goethite in GKA contained many structural hydroxyls (Bigham et al., 1978, 2002; Cornell and Schwertmann, 2003; Fitzpatrick and Schwertmann, 1982). The poorly crystalline goethite in GKA is likely due to: (i) the isomorphous substitution of Al (originated from kaolinite) for Fe in the goethite structure (Bigham et al., 1978, 2002; Fitzpatrick, 1988; Fitzpatrick and Schwertmann, 1982) and (ii) inhibition of the formation of goethite due to the presence of kaolinite (Cornell and Schwertmann, 2003; Schwertmann, 1988; Wei et al., 2011).

**Mechanical and Chemical Stability of the Samples**

After ultrasonic dispersion, the particle size of the binary systems was greater than the average value of the kaolinite and goethite (Table 3). This illustrates that aggregation of kaolinite and goethite had occurred in the binary systems, which improved the stability against ultrasonic dispersion. The peaks of mass loss for dehydroxylation of kaolinite and goethite in the binary systems were higher than those of the kaolinite and goethite alone (Fig. 6), which indicated that the binary systems exhibited a higher stability against thermal treatment. These results are consistent with the literatures (Duiker et al., 2003; Teixeira and Misra, 1997; Wilson et al., 2006).

After ultrasonic dispersion for 30 min, the volume content of aggregates and the peak positions of the particle size distributions of GKA were all slightly greater than those of GKM. With prolonged ultrasonic dispersion, significant changes in the particle size distributions were observed for GKM and only small changes for GKA (Fig. 5 and Table 3). This reveals that a more significant breakdown of aggregates occurred in GKM compared to GKA. The peak temperature for dehydroxylation of kaolinite in GKA was higher than those in GKM (Fig. 6), which indicated that the kaolinite in GKA exhibited a higher thermal stability. In general, the stability of these binary systems is positively correlated with the strength of interactions between goethite and kaolinite (Bronick and Lal, 2005; Duiker et al., 2003). Therefore, the stability results confirm that stronger interactions occurred in GKA than in GKM.

In the binary systems, the peak temperature for dehydroxylation of goethite in the GKA sample was lower than that in GKM and the corresponding mass loss was GKA > GKM. This indicates that the goethite in GKA possessed a lower stability and more structural hydroxyls. According to the literatures (e.g., Bigham et al., 2002; Cornell and Schwertmann 2003; Fitzpatrick and Schwertmann, 1982), this can be ascribed to the fact that the goethite in GKA was an Al-substituted poorly crystalline product.

**CONCLUSIONS**

With GKA, goethite was mainly present as a protective coating on the kaolinite surface, and with GKM, goethite and kaolinite existed mainly separately. The IR and MAS NMR spectra of the systems containing goethite and kaolinite showed that electrostatic attraction, surface coordination, hydrogen bonding, and anion ligand exchange caused the relatively strong interactions between goethite and kaolinite in GKA, whereas with GKM these interactions played only a small role. In addition, a cation exchange reaction and the isomorphous substitution of Al for Fe in the goethite structure occurred in GKA. Interactions between goethite and kaolinite increased the mechanical and chemical stability of the binary systems. Compared with GKM, in GKA the stability of kaolinite was higher but that of goethite was lower.

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