



Kaolin intercalated by urea. Ceramic applications



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HIGHLIGHTS

- The intercalation degree of kaolinite by urea is 69% when aqueous mixing is used.
- Bonds are formed between inner-surface hydroxyls of kaolinite and NH groups of urea.
- Intercalation increases the densification rate and reduces the sintering temperature.
- Intercalated kaolinite behaves similarly to intensively grounded kaolinite.
- A high intercalation degree of kaolin can be attained in industrial processes.

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ABSTRACT

Kaolinite–urea complexes were prepared with kaolinite from KGa-1 kaolin by two techniques, mixing and ball-milling at room temperature in water. The intercalation degree was found to be 72% and 69% respectively. Urea-intercalated kaolinite has potential applications in industry, since it change most of the chemical and thermal behaviors. Particularly, ion intercalation into kaolinite structure changes the amount of reactive acidic and basic sites on the internal and external surfaces. In this study XRD patterns and infrared spectroscopy of kaolinite–urea complexes confirm the intercalation of urea into kaolinite by the expansion of the basal spacing of kaolinite from 0.715 nm to 1.069 nm. The expansion of kaolinite is due to entering urea into interlayers that confirms the occurrence of hydrogen bonding between urea and kaolinite. Thermal analyses (TG, DSC and thermogravimetry) evidence changes in transformation temperatures of intercalated kaolinite. The sintering densification is shifted to lower temperature and kaolinite–urea complexes can be used in new ceramics for building with lower CO₂ specific emission.

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1. Introduction

Industries are major users of clays since it use about 70 wt% of commercial clays. Clay properties of interest in the silicate ceramics industry are plasticity, molding ability, detailed chemical and mineralogical compositions, refractoriness, surface interaction with liquids, thermal and sintering behaviors, and color. They have several applications in construction and in manufacturing, and are also used in the calcined form as fillers (chamotte). As clays are fundamental raw materials for all ceramic compositions, many studies were devoted to improving the role of clays in thermal transformations leading to silicate ceramics having better properties but at a lower cost.

In all countries, considerable amounts of silicate ceramics containing clays are sintered between 900 °C and 1400 °C, in large scale industrial processes. It requires significant amounts of energy and causes significant CO₂ emissions of about 0.25 kg of CO₂ per kg of final product. In particular, the total annual emission of the French bricks and tiles industry is about 1.2 million tons of CO₂ [1,2]. One way to limit emissions is to lower the sintering temperatures, which can be obtained by modifying the behavior with temperature of clays used in compositions, including kaolinite.

In kaolinite mineral, layers are bounded by reactive hydrogen bonds [3–6] and are not easily delaminated [7]. Kaolinite properties can be improved by mechanochemical activation and by intercalation, since they change the surface area, ion-exchange capacity, crystal structure, crystallinity degree and rate of solubility [8,9]. Kaolinite intercalation is due to surfaces interaction with organic molecules and is known for decades [10,11]. Actual researches

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are mostly in polymers nano-composites and in inorganic materials. The thermal behavior is also studied since a heating treatment of intercalated kaolinite is necessary for ceramic applications [12]. Different intercalated systems have been reported by many authors but one of the most studied systems is the intercalation of a synthetic polymer, such as kaolinite–potassium acetate [13], kaolinite–formamide [14,15], or kaolinite–urea [9]. In general, methods for the preparation of kaolinite–organic complexes include pressurization, pyrogenation, or mixing of a liquid media [16]. However in industrial processes it is critical to use a low cost and simple method [17], and it has been demonstrated that the mixing of an aqueous suspension is very convenient [18].

In this study, the proposed method is the intercalation of kaolinite by urea, since it is abundantly available at low cost, while having a low environmental impact during its production. With urea, kaolinite can attain a high degree of intercalation with a significantly increased interlayer space. With increasing temperature, the kaolinite–urea complex undergoes very specific structural transformations, which differ from those of a non-intercalated kaolinite. In particular, it leads to a process of dehydroxylation at lower temperature (down to ~ 350 °C instead of ~ 550 °C). After dehydroxylation, intercalated kaolinite becomes a more reactive component, with lower temperatures of structural and microstructural transformations inherent in the formation of silicate ceramics. However, the exact role of urea in these changes is not yet established.

In this work, we demonstrate that simple intercalation method can be used with a representative kaolinite, which is the most frequent material in silicate ceramic industries. We study in details the role of the intercalation process on the thermal and structural transformations, and on the sintering behavior up to 1300 °C. We also study how intercalation of kaolinite is able to reduce the firing temperature of a kaolinite containing composition used in industrial silicate ceramics.

2. Materials and methods

The reference Kga-1b kaolin is supplied by the Mineralogical Society. Chemical and mineralogical compositions are reported in Table 1 [19]. The Kga-1b kaolin contains 95 wt% of kaolinite, associated with minor phases such as quartz, hematite and gibbsite. Kga-1b kaolin was used as received and sieved at 63 μm .

Urea used for this experiment is from VWR. Urea formula is $\text{CO}(\text{NH}_2)_2$ with a Molar Mass of 60.06 (g/mol). Solubility of urea in water is high, about 105 g/100 mL at 20 °C.

For sample preparation, two intercalation methods were carried out with kaolinite. Firstly we added 3 g of kaolinite into 7 mol/L urea aqueous solution at 20 °C by stirring during 48 h. To separate the excess solution, solid was removed by centrifugation and dried at 75 °C for 24 h. A second method is mechanochemical intercalation by mixing 5 g of kaolinite with the same aqueous urea solution, but grounded by ball milling during 1 h (porcelain jar and balls). The mixture is subsequently centrifuged and dried at 75 °C for 24 h.

Thermal transformation and sintering up to 1300 °C were studied with the initial Kga-1b kaolin and with the intercalated Kga-1b kaolin. Additional experiments were performed with a ceramic composition containing mostly the Kga-1b kaolin. The composition is a representative triaxial mixture containing Kga-1b kaolin (50 wt%), fine quartz (25 wt%) and alkaline feldspar (25 wt%). Whereas the considerable spread of compositions for silicate ceramics, this simple mixture is representative of industrial ceramics for floor tiles, sanitary and building materials [20]. Samples were prepared by wet ball milling during 2 h, drying the mixture at 80 °C, granulating at 500 μm through a sieve and pressing in a metallic mold to form small barrels for sintering experiments. The objective is to validate the ceramic application of intercalated kaolinite, using similar processes than that of industries.

Characterizations of all samples by X-ray diffraction (XRD) were carried out with a Philips X'Pert type diffractometer equipped with a $r = 240$ mm goniometer. We used Cu K α radiation ($K\alpha = 1.541874$ Å) operating at 40 kV and 40 mA. Scanning rate was 2°/min in the 2 θ range of 2–65° for powders and 2–35° for oriented preparations.

Thermal analyses were carried out with a thermo balance TG–DSC SETARAM (SetSys evolution) under air atmosphere at 10 °C/min heating rate and 20 °C/min cooling rate. Alumina as reference material and platinum crucibles were used for the experiments.

FTIR analyses were with a Spectrometer Nicolet 760 Magna IR, with the Nicolet's OMNIC software. We used this spectrometer in the mid-IR range of 400–4000 cm^{-1} .

Dilatometry analyses were carrying out with a horizontal dilatometer 402PC NETZSCH. This technique is for the measurement of expansion or shrinkage during a controlled temperature/time program. We used alumina sample holder and push-rod, and air atmosphere in the kiln. Sample of powder compacts were preliminary pressed into cylinder of 3 mm diameter and controlled length. Temperature range was 25–1200 °C with 5 °C/min for heating and cooling rates.

3. Results

The XRD patterns for samples are given in Fig. 1 (a–c), for kaolinite (Kga-1) and for kaolinite–urea. Fig. 1a displays the common basal [001] distance of kaolinite of 7.2 Å, and in Fig. 1b and c for intercalation complexes, a new peak appears with a d value of 10.7 Å. It demonstrates that inter-layers contain some guest molecules leading to the expansion of the basal spacing of kaolinite by intercalation. The relative intensity of the 7.2 Å peak indicates that intercalation is not fully completed. To compare the two processing methods, the intercalation ratios were obtained from peak heights [6]. They attain 69% from mixing and 75% from ball-milling techniques. The FWHM value of the 10.7 Å peak is broader for the mechanochemical intercalation (Fig. 1b) than for intercalation by the aqueous suspension [9]. It is related to the increase of the structural disorder and the reduction of crystallite size during the intense mechanochemical grinding.

The reduction of intensity of non-basal peaks is also due to urea intercalation causing disorder in kaolinite stacking [21]. XRD of Fig. 1b and c also show that the second basal reflection of kaolinite is superposed with the third basal reflection of the urea–intercalated complex.

The significant expansion of basal distance of kaolinite is accompanied by a significant change in kaolinite surface properties. Intercalation process is firstly explained by a diffusion process within layers. Then existing hydrogen bonds between kaolinite outer hydroxyl groups and O of the adjacent silica layer are broken, and new hydrogen bonds through their respective H and O atoms with the O atom of tetrahedral sheets and H atom of octahedral sheets [22].

Infrared studies were performed with the urea–kaolinite complex to observe any changes at kaolinite interlayers. Experiment of pure kaolinite in Fig. 2a and b shows IR absorption bands commonly observed with well-ordered kaolinite. In the high wavenumber region, OH stretching bands are observed at 3695, 3670, 3652 and 3620 cm^{-1} [23]. They correspond to the inner OH stretching (3620 cm^{-1}), to the anti-phase stretching of inner-surface OH groups (3670, 3652 cm^{-1}) and to in-phase stretching of the three inner-surface OH groups (3695 cm^{-1}) [24].

In the lower wavenumber region, bands at 1032 and 1009 cm^{-1} are anti-symmetric stretching Si–O–Si vibrations. Beside, bands at 1114 and 1102 cm^{-1} are from symmetric stretching of outer Si–O

Table 1
Chemical composition of Kga-1b kaolin (wt%) [19].

SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	FeO	MnO	MgO	Na ₂ O	K ₂ O	F	P ₂ O ₅
44.2	39.7	1.39	0.13	0.08	0.002	0.002	0.013	0.05	0.013	0.034

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