Modification of kaolinite structure through intercalation

PhD THESIS

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Introduction and Aim of Research

Nowadays, the modification of kaolinite structure through intercalation is an important research field, where, among others, kaolinite plates can be converted into nanotubes, which can be applied in advanced nanocomposite and nanohybrid materials. These nanotubes are produced by multi-step intercalation, where first, a suitable guest molecule (e.g. dimethyl sulfoxide, urea, potassium or ammonium acetate) is inserted into the interlayer space of kaolinite, and subsequently it is displaced by other compounds. Using intercalation and deintercalation steps, kaolinite layers can be exfoliated, i.e. they can be separated into individual double layers. To compensate stresses due to misfit of tetrahedral and octahedral sheets, the exfoliated kaolinite layers curl and then frequently roll to form nanotubes.

The main purpose of this work was to improve the existing multi-step intercalation procedures of kaolinite in such a way that kaolinite nanotubes can be produced in shorter time, by using fewer intercalation steps and less reagent volume. First, the direct intercalation procedure of kaolinite and potassium acetate (KAc), ammonium acetate (AAc), urea and dimethyl sulfoxide (DMSO) was further developed and refined. Here, the homogenization method worked out for the KAc was applied in the case of other intercalating reagents. Next, the methanol intercalation procedure of the synthesized precursors was improved for the frequently applied solution/stirring method and the rarely applied solvothermal one. Finally, the stirring and solvothermal intercalation methods with cetyltrimethylammonium chloride (CTAC) were further developed towards a more efficient production of kaolinite-CTAC complexes and kaolinite nanotubes. The formed complexes, as well as the effects of treatment parameters and combination of the intercalation steps on the intercalation were investigated using modern material analyzing and testing methods such as X-ray powder diffraction, thermogravimetry, Fourier transform infrared spectroscopy, transmission electron microscopy, and scanning electron microscopy.
Thesis points

1. A simple and cost-efficient homogenization method was developed for the direct intercalation of ammonium acetate (AAc), dimethyl sulfoxide (DMSO) as well as urea into kaolinite. This method improves the shortcomings of the conventional solution and mechanochemical methods. (Related publications: [1, 2, 3, 5].)

   a) I revealed that the homogenization procedure (by simple wetting the clays with mixture of intercalation reagent and distilled water) requires an order of magnitude lower amount of reagents to prepare complexes, which have identical structure to those obtained by the solution method and have a high degree of intercalation.

   b) I established that the so far less investigated stable 1.7-nm kaolinite-AAc complex has higher water content than the 1.4-nm one. I verified that the 1.7-nm complex can easily transform to the 1.4-nm complex, when removing extra water molecules from the interlayer space. At room temperature, the degree of intercalation of both complexes generally increases with aging time, but the 1.4-nm complex is present in the samples only up to 6 weeks, while the 1.7-nm complex appears only after 4 weeks.

   c) For the kaolinite-AAc complexes, it was concluded that cooling below 0°C helps to meaningfully accelerate the intercalation and significantly increase the degree of intercalation. Furthermore, the cooling reduces the influence of kaolinite crystallinity and halloysite content on the intercalation.

   d) Comparing the studied intercalation parameters of precursors, I proved that the aging temperature and the use of closed or open sample holder can increase the intercalation rate and the degree of intercalation. These parameters strongly correlate to the stability of the intercalating reagent and the role of water molecules during the intercalation. I established and explained that, while the highest degree of intercalation of AAc was obtained by cooling (at -24°C), that of DMSO and urea was obtained by heating (at 60°C and 90°C, respectively). I also demonstrated that, due to the lower stability of AAc, the use of closed sample holder results in the highest degree of intercalation with this reagent. On the contrary, the highest degree of intercalation of urea and DMSO was achieved by ageing in an open sample holder. The intercalating reagent to water mass ratio, as well as the
kaolinite content (where the intercalating reagent content is higher than the theoretical content reported in the literature) have weaker influence on the intercalation reaction than the type of sample holder.

2. **Solution/stirring and solvothermal methods were developed to prepare the technologically favorable kaolinite-methanol complex from the kaolinite-urea precursor.** (Related publications: [2, 4, 5].)

   a) I proved that the solvothermal treatment is much more efficient than the weeks-long conventional solution/stirring treatment to form the kaolinite-methanol complex. Also, the original solvothermal methodology developed for the kaolinite-DMSO precursors can be simplified and shortened in the case of the kaolinite-urea precursor, because methanol can easier displace urea than DMSO at 100°C.

   b) The basal spacing of the kaolinite-methanol complex was established as 1.12 nm in methanol-wet state, which decreased to 0.83-0.84 nm after drying at 150°C, showing no dependence on the type of precursor. It was confirmed that rewetting of the dried kaolinite-methanol complex with fresh methanol can recover the 1.12-nm complex.

   c) The chemical formula of the kaolinite-methanol complex dried at 150°C was described as Al$_2$Si$_2$O$_5$(OH)$_{3.7}$(OCH$_3$)$_{0.3}$.

3. **Simple and effective two-step and three-step (solution/stirring and solvothermal) methods were developed to produce the kaolinite-cetyltrimethylammonium chloride (kaolinite-CTAC) complex and kaolinite nanoscrolls from the kaolinite-urea precursor.** (Related publications: [4, 5].)

   a) I presented that the CTAC molecules enter into the interlayer spaces without causing loss of periodicity in the stacking of kaolinite layers, and expand the basal spacing to 3.82 nm. My estimation for the formula of the kaolinite-CTAC complex was Al$_2$Si$_2$O$_5$(OH)$_{3.7}$(OCH$_3$)$_{0.3}$(CTAC)$_{1.6}$(Me)$_{1.6}$, which means that the interlayer molecular ratio of methanol (Me) to CTAC is 1:1. It was confirmed that the degree of intercalation of the precursor (e.g. urea) can determine the degree of intercalation of the kaolinite-methanol and kaolinite-CTAC complexes in the case of the two-step and three-step methods.
b) It was demonstrated that the short-term three-step solvothermal synthesis (without refreshing the methanol) at 100°C required an order of magnitude less time and reagent volume than the commonly applied solution/stirring method.

c) I verified that the formation of the kaolinite-CTAC complex from the kaolinite-urea precursor can proceed directly without preliminary methanol treatment using our own two-step solvothermal method at 100°C. This conceptually new method, utilizing supposed cointercalation of methanol and CTAC, is suitable for a cost-efficient production of kaolinite nanoscrolls through the exfoliation of kaolinite. I also demonstrated that the two-step solvothermal method cannot be applied in the case of the kaolinite-DMSO precursor, because the interaction of DMSO with the kaolinite layers remains prohibitively strong at 100°C.

d) For the two-step solvothermal method, it was shown that the formation of the kaolinite-CTAC complex, besides the type of precursor, also strongly depends on the reaction time and temperature. The 16-h solvothermal treatment of kaolinite-urea precursor at 100°C was found to be the most favorable one to synthesize the kaolinite-CTAC complex (and to produce kaolinite nanoscrolls), since there is no additional increase in degree of intercalation with increasing reaction time and temperature.
International publications related to the thesis


Cumulated impact factors of publications: ≈ 14.4

Conference proceedings, posters, and oral presentations


Other publication related to the thesis


Publication not related to the thesis