Functionalized nanohybrid materials obtained from the interlayer grafting of aminoalcohols on kaolinite†

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New robust functionalized nanohybrid materials were prepared by the interlayer covalent attachment of aminoalcohols to the octahedral sheets of kaolinite.

The intimate mixing at the molecular level of organic and inorganic units can result in functional nanohybrid materials designed for specific purposes, with control of their physical and chemical properties.[1] Clay minerals, particularly the smectite group, are attractive as inorganic units since they are widely available, show intercalation and swelling properties, and can be delaminated to produce nanocomposite materials.[2] The covalent grafting of organic units on an inorganic surface leads to materials combining functionalities and specific properties of the support.[3] These functionalized inorganic solids have a potential as "intelligent" materials.[3]

Kaolinite, $Al_2Si_2O_5(OH)_4$, a widely available mineral, is a dioctahedral 1 : 1 layered aluminosilicate made up of two types of interlayer surfaces, consisting, on one side, of $(SiO)_6$ macrorings and, on the other side, of aluminol groups.[4] This asymmetry provides kaolinite with a large cohesive energy, making intercalation of guest molecules more challenging than in the case of the smectites. However, once access to the interlayer spaces is provided to the reagent, the aluminol layer is a good candidate for grafting organic moieties, creating consequently a functionalized, non-centrosymmetric, two-dimensional supramolecular organizing medium. A few reports have appeared in the last decade describing the synthesis and the characterization of kaolinite modified by the grafting of organic units on the aluminol interlayer surfaces.[5] In all the cases reported so far, the grafted organic units were alcohols, polyols or ether–alcohols. It is highly desirable to extend the range of functionalities, such as with pendant amine groups, in order to attach in further steps larger molecules to the interlayer surfaces of kaolinite. The grafting of a series of aminoalcohols to the aluminol surface of boehmite was reported previously[6] and an attempt was made at grafting ethanolamine to the internal aluminol surfaces of kaolinite.[7]

In this work, the synthesis and the characterization of nanohybrid materials resulting from the grafting of aminoalcohols on the interlayer surfaces of kaolinite are reported, providing, for the first time, a grafted, amino-functionalized kaolinite derivative. It is shown that, under the reported experimental conditions, diethanolamine (DEOA) and triethanolamine (TEOA) are covalently grafted, while ethanolamine (EOA) is intercalated, but not grafted on the surface. The organo-kaolinite derivatives are robust nanohybrid materials, decomposing at temperatures above 300 °C and resisting hydrolysis.

The intercalate of dimethyl sulfoxide (DMSO) in kaolinite (DMSO-K) was used as starting material.[8] The reactions of EOA, DEOA and TEOA† with DMSO-K were performed at 170 °C in the case of EOA and at 180 °C for DEOA and TEOA during 2 h under nitrogen. In a typical set of experiments, 1 g of DMSO-K was dispersed in 6 g of the aminoalcohol. The temperature of the mixture was then increased slowly from room temperature to 170 or 180 °C and maintained stable during 2 h. The resulting nanohybrids were recuperated after three series of centrifugation following washing with isopropanol (3 × 50 ml). They were dried at 60 °C overnight.

Fig. 1 shows the oriented XRD patterns of the materials recovered after the centrifugation, washing and drying process.

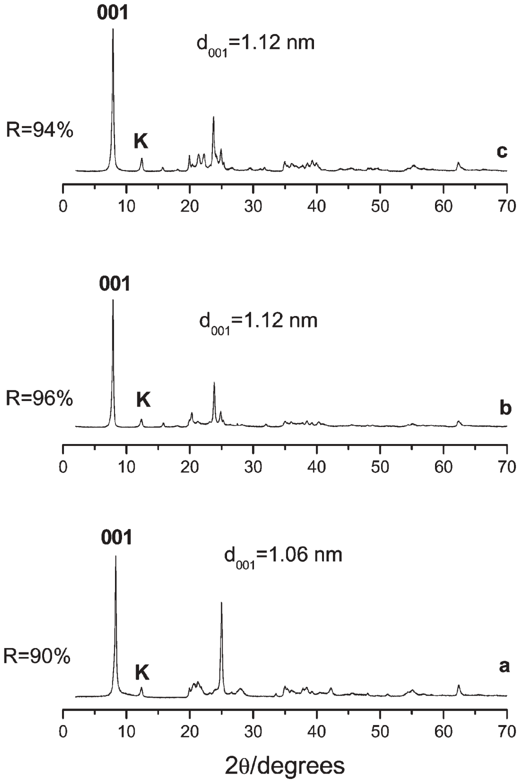

Fig. 1 Oriented XRD patterns (2–70° 2*θ*) of kaolinite intercalated and reacted with (a) EOA, (b) DEOA, (c) TEOA. (kaolinite and DMSO-K patterns are shown on Fig. S1(a)–(e), as ESI†).

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They are characterized by an intense 001 reflection at 1.06 nm (EOA) and at 1.12 nm (DEOA and TEOA). In all the cases, the d_{060} reflection of kaolinite remains at 1.49 Å, characteristic of a dioctahedral clay mineral, showing that the structure of the layers of kaolinite is largely unaffected by the intercalation and reaction process. Since the d_{001} of DMSO-K is 1.10 nm, very close to the observed d_{001} of the products, the XRD patterns can not give direct indications on the replacement of DMSO by the ethanolamines. This is however demonstrated by the ^{13}C MAS NMR spectra (see Fig. 4 below), since the DMSO signal has completely or largely disappeared in the three cases. The intercalation ratios (obtained as an approximation, from the relative intensities of the d_{001} peaks of the intercalate and of the non-intercalated kaolinite) are at least 90%. In all three cases, an intercalation has taken place since the interlayer distance is in the order of 4 Å, corresponding to a monolayer of the alcoholamines. Is the intercalated organic compound grafted or not on the aluminol surface?

Intercalates of kaolinite can usually be displaced by washing with water to recover the original kaolinite or to form a kaolinite hydrate.[9] However, in strong contrast, the grafted derivatives of kaolinite, resulting from esterification of the aluminol surfaces, are stable towards extensive washing.[5b,h] This property was used to test the formation of grafted species. Fig. 2 shows the oriented XRD patterns for EOA-K, DEOA-K and TEOA-K as obtained after drying (see above). The three samples were then dispersed and stirred in water at room temperature.

After 1 h already in the case of EOA-K, the d_{001} peak of EOA-K had disappeared, being replaced by the characteristic d_{001} peak of kaolinite. EOA-K is not resistant to hydrolysis. In the experimental conditions of the reaction between kaolinite and EOA, an intercalate is formed, but the reaction does not proceed further to the grafting on the aluminol surface. In strong contrast, when DEOA-K and TEOA-K were dispersed and stirred in water at room temperature for 48 h, there were only minor changes on the XRD pattern. The d_{001} peaks were slightly shifted to lower values, to 1.07 and 1.08 nm respectively, from their original values at 1.12 nm. The two samples were then refluxed under water for 16 h, still with no major changes noticed on the XRD pattern. A small increase of the original d_{001} peak of kaolinite can be seen in the case of DEOA-K, suggesting a minor hydrolysis reaction followed by deintercalation of DEOA. This experiment gives strong indications that the two organic compounds with higher local hydroxyl group concentrations have reacted with the internal aluminol surfaces. Further evidence can be obtained from the TGA/DTG traces.

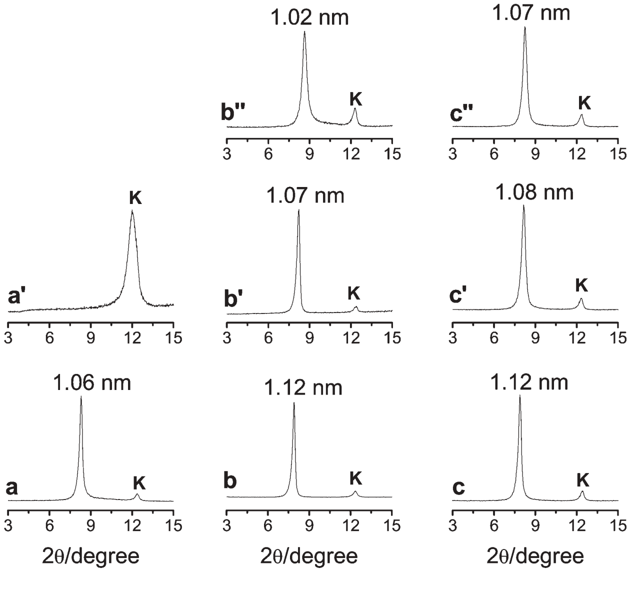

Fig. 2 Oriented XRD patterns (2–15° 2θ) of (a) EOA-K, (b) DEOA-K, (c) TEOA-K. The three samples were treated with water at RT for (a′) 1 hr (b′, c′) 48 h. (b″, c″) The samples were then refluxed under water for 16 h.

Fig. 3 shows the DTG traces of the three materials obtained under N_2 flow. In all three cases, the dehydroxylation of kaolinite is observed at a temperature slightly below that characteristic of pure kaolinite, 497, 502 and 509 °C respectively, to be compared with typically 515 °C for kaolinite. This is a well-known observation, attributed to the lower crystallinity of the grafted materials.[5h] In addition to dehydroxylation, a major weight loss is observed at 198 °C in the case of EOA-K, attributed to the removal of the intercalated EOA. For comparison, the deintercalation of DMSO from the DMSO-K preintercalate occurs at 180 °C.[8b] In contrast, the removal of TEOA appears at higher temperatures, in three steps, at 308, 356 and 426 °C, which are attributed to the decomposition of TEOA. The case of DEOA is intermediate, with a weight observed at 222 °C, followed with the same pattern as for TEOA, with three peaks in the temperature range 300 to 450 °C. The DTA shows corresponding endothermic peaks for the thermolysis of the organic groups under nitrogen as well as the exothermic transition metakaolinite–mullite which can be observed near 1000 °C in all cases.[10] On the basis of the percentage of weight loss of water and organics to form metakaolinite $Al_2O_3{\cdot}2SiO_2$, the TGA data allow the calculation of the formula unit of EOA-K as $Al_2Si_2O_5(OH)_4(EOA)_{0.90}$. This stoichiometry is in good agreement with data reported for similar intercalates.[5,8] In the cases of DEOA and TEOA, one can observe on the DTG a qualitative decrease of the intensity of the dehydroxylation peak, in agreement with the grafting process. The following idealized formula can also be calculated for TEOA-K: $Al_2Si_2O_5(OH)_3[H{-}(OCH_2CH_2)_3N]_{0.51}$. TEOA is grafted to one aluminol group of each unit structure, consequently bridging two adjacent unit structures. Plausibly, the third hydroxyl group,

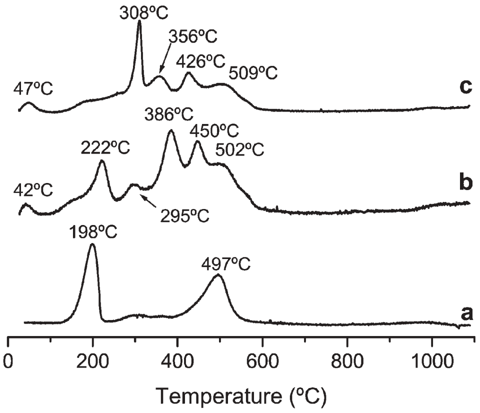

Fig. 3 DTG traces (RT–1100 °C) of (a) EOA-K, (b) DEOA-K, (c) TEOA-K. The maxima are indicated. (kaolinite and DMSO-K traces are shown on Fig. S3(a)–(e), as ESI†).

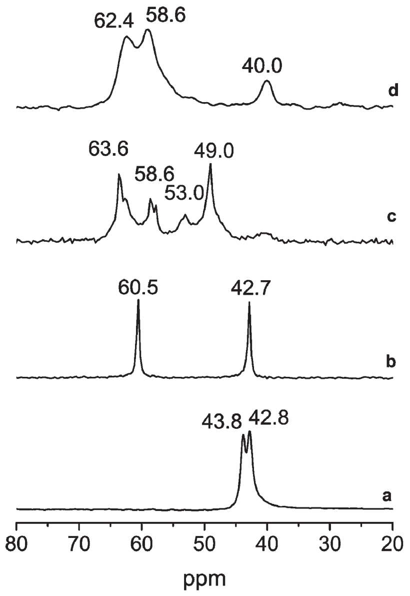

Fig. 4 Solid-state ^{13}C CP/MAS NMR spectra for (a) the starting material (DMSO-K), (b) EOA-K, (c) DEOA-K, (d) TEOA-K.

non-grafted, interacts with the siloxane macroring of the opposing layer. These stoichiometries are in fair agreement with the results of the elemental analysis (see experimental part in ESI†).

The ^{13}C CP/MAS NMR spectra are given on Fig. 4. The two signals characteristic of DMSO-K are replaced by the two signals of EOA-K, with chemical shift values close to the solution spectrum of EOA. In the case of TEOA-K, the two ^{13}C signals are broadened. The signal at 58.6 ppm is in the expected chemical shift range for a tertiary amine. Some residual DMSO can be observed at 40.0 ppm. In the case of DEOA, one can observe the superposition of at least two different species that are attributed to DEOA intercalated and grafted through one or two hydroxyl groups. The signals at 49 and 53 ppm are in the range expected for a secondary amine. The NMR data are in agreement with the TGA data, showing a mixture of intercalated and grafted DEOA. The ^{27}Al MAS NMR spectra at 11.7 T are given as ESI† (Fig. S5). They show in all three cases a disymmetric signal in the chemical shift range of octahedral aluminum. The IR spectra are given as ESI† (Fig. S6). They show in all cases the presence of the band at 3621 cm^{-1} for the kaolinite interlayer hydroxyls, and of the band at 3695 cm^{-1} for the hydroxyl groups not parallel to the *c*-direction, and consequently not expected to be involved in the grafting process, while the two AlOH groups oriented parallel to the *c*-direction are involved in the grafting process. The modifications of the 2800–4000 cm^{-1} region is in agreement with previously reported spectra for intercalated and grafted species.[5]

In conclusion, new robust functionalized nanohybrid materials were prepared by the interlayer covalent attachment of aminoalcohols to the octahedral sheet of kaolinite. The case of triethanolamine is particularly interesting since it consists in a well structured material with two organic arms covalently bridging two vicinal structure units of the mineral, leaving the third arm and the amino group available for further modifications.

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Notes and references

1 *Functional Hybrid Materials*, ed. P. Gómez-Romero and C. Sanchez, Wiley-VCH, Weinheim, 2004.

2 (*a*) E. Ruiz-Hitzky and A. Van Meerbeek, Clay Mineral- and Organoclay-polymer Nanocomposite, in *Developments in Clay Science, 1, Handbook of Clay Science*, ed. F. Bergaya, B. K. G. Theng and G. Lagaly, Elsevier, Amsterdam, 2006, ch. 10.3, pp. 583–621; (*b*) K. A. Carrado, Polymer–Clay Nanocomposites, in *Advanced Polymeric Materials: Structure–Property Relationships*, ed. G. Shonaike and S. Advani, CRC Press, Boca Raton, FL, 2003; (*c*) *Polymer–Clay nanocomposites*, ed. T. J. Pinnavaia and G. Beall, Wiley Series in Polymer Science, Wiley, New York, 2000; (*d*) M. Alexandre and P. Dubois, *Mater. Sci. Eng., R*, 2000, **28**, 1–63.

3 (*a*) E. Ruiz-Hitzky, *Chem. Rec.*, 2003, **3**, 88–100; (*b*) A. Stein, B. J. Melde and R. C. Schroden, *Adv. Mater.*, 2000, **12**, 1403–1419.

4 (*a*) R. F. Giese, Jr., in *Hydrous Phyllosilicates*, ed. S. W. Bailey, Mineralogical Society of America, Washington, DC, 1988, pp. 28–66; (*b*) M. F. Brigatti, E. Galan and B. K. G. Theng, Structures and Mineralogy of Clay Minerals, in *Developments in Clay Science, 1, Handbook of Clay Science*, ed. F. Bergaya, B. K. G. Theng and G. Lagaly, Elsevier, Amsterdam, 2006, ch. 2, pp. 19–86.

5 (*a*) J. J. Tunney and C. Detellier, *Chem. Mater.*, 1993, **5**, 747–748; (*b*) J. J. Tunney and C. Detellier, *Clays Clay Miner.*, 1994, **42**, 552–560; (*c*) J. J. Tunney and C. Detellier, *J. Mater. Chem.*, 1996, **10**, 1679–1685; (*d*) Y. Komori, H. Enoto, R. J. Takenawa, S. Hayashi, Y. S. Sugahara and K. Kuroda, *Langmuir*, 2000, **16**, 5506–5508; (*e*) T. Itagaki and K. Kuroda, *J. Mater. Chem.*, 2003, **13**, 1064–1068; (*f*) K. B. Brandt, T. A. Elbokl and C. Detellier, *J. Mater. Chem.*, 2003, **13**, 2566–2572; (*g*) J. Murakami, T. Itagaki and K. Kuroda, *Solid State Ionics*, 2004, **172**, 279–282; (*h*) J. E. F. C. Gardolinski and G. Lagaly, *Clay Miner.*, 2005, **40**, 537–546; (*i*) J. E. F. C. Gardolinski and G. Lagaly, *Clay Miner.*, 2005, **40**, 547–556; (*j*) T. A. Elbokl and C. Detellier, *Clay Sci., Suppl. 1*, 2005, **12**, 38–46; (*k*) M. Janek, K. Emmerich, S. Heissler and R. Nüesch, *Chem. Mater.*, 2007, **19**, 684–693.

6 (*a*) M. Inoue, H. Tanino and K. Kondo, *Clays Clay Miner.*, 1991, **39**, 151–157; (*b*) M. Inoue, M. Kimura and T. Inui, *Chem. Mater.*, 2000, **12**, 55–61.

7 J. J. Tunney and C. Detellier, *Can. J. Chem.*, 1997, **75**, 1766–1772.

8 (*a*) S. Letaief and C. Detellier, *J. Mater. Chem.*, 2005, **15**, 4734–4740; (*b*) S. Letaief and C. Detellier, *J. Mater. Chem.*, 2007, **17**, 1476–1484.

9 J. J. Tunney and C. Detellier, *Clays Clay Miner.*, 1994, **42**, 473–476.

10 L. A. Pérez-Maqueda, J. L. Pérez-Rodriguez, G. W. Scheiffele, A. Justo and P. J. Sánchez-Soto, *J. Therm. Anal.*, 1993, **39**, 1055–1067.