Synthesis and characterization of hollow clay microspheres through a resin template approach

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Hollow clay microspheres of high thermal stability were easily fabricated by the adsorption of colloidal clay layers onto the surfaces of a spherical anion exchange resin and calcination of the resulting resin–clay composite.

Hollow spheres of nanometer to micrometer dimensions define an important class of shape-fabricated materials in which the shell of the hollow sphere can be constructed by a variety of materials of high scientific interest and technological importance; magnetic, semiconducting, ceramic, metallic, polymer, composite *etc*.[1–3] Owing to their low density, large specific area, stability and surface permeability, hollow spheres are widely used as controlled release capsules for drugs, dyes, cosmetics and inks, artificial cells, catalysts and fillers. Engineering hollow spheres from porous solids, such as mesoporous silica[4–6] and zeolites,[7] constitutes an important advance in materials, because of the unique properties of these well organized superstructures. Recently, the fabrication of hollow laponite submicrometer spheres (laponite is a synthetic smectite clay) based on the layer-by-layer self-assembly technique, was reported.[8] In this communication we report another approach for easy construction of hollow inorganic spheres, and in particular, describe the synthesis and characterization of thermally stable hollow smectite clay spheres in the micrometer range. In general, the production of clay spheres is expected to be of great value since smectite clays define a known class of layered aluminosilicate minerals that possess unique swelling, intercalative and cation exchange properties.[9] In addition, their thermal stability and chemical inertness make them suitable materials for particle engineering (clay ceramics) and for use as fillers in many industrial applications.[10,11] The method proposed for the morphogenesis of hollow clay microspheres, simply comprises the adsorption of colloidal acid clay layers onto the surfaces of a spherical anion exchange resin (carbonated form), followed by removal of the resin's organic backbone by calcination in air. In principle, our synthetic strategy resembles that of the sacrificial core–shell technique in which hollow spheres are assembled by a controlled adsorption, involving precipitation reactions, sol–gel condensations and layer-by-layer depositions of the desirable material onto the surfaces of an appropriately modified colloidal template (usually a polymer) and subsequent removal of the template by thermal or chemical treatment.[12–15]

In this work, a strongly basic anion exchange resin of a quaternary ammonium chloride type and spherical morphology (Dowex 2, x8 100/200 mesh) was used. The resin was initially treated with 1 M Na_2CO_3 aqueous solutions in order to obtain its carbonated form. Two sources of clay were used. The first, was a naturally occurring montmorillonite from the island of Milos, Greece, denoted Zenith-N. The montmorillonite was fractionated to <2 μm by gravity sedimentation and purified by standard methods to obtain its sodium saturated form with a CEC of 0.8 meq. g^{-1}. The second was a synthetic sodium hectorite (laponite, monovalent cation exchange capacity: CEC = 0.74 meq. g^{-1}) supplied by Laporte Industries Ltd. The resin–clay products were obtained as follows: 1 g of each clay sample was dispersed in 100 ml of deionized water. To each colloidal dispersion, 1–2 drops of concentrated HCl (37%) were added (pH of the mixture *ca*. 3) and the gelatinous mixtures were vigorously stirred for 1 min. After centrifugation of the solids, the supernatant liquids were discarded and the same procedure was repeated twice. Finally, the acid clays were washed once with water, centrifuged and redispersed in 100 ml of deionized water. Each acid clay colloidal dispersion was then slowly added to 4 g of carbonated resin in 20 ml of deionized water and the mixture was heated under vigorous stirring at 80 °C for 30–45 min. During the addition of the acid clay dispersions to the carbonated resin and the thermal treatment, evolution of gas (CO_2) was observed, indicating the binding of the negatively charged clay layers to the positively charged resin surfaces according to eqn. (1) where Resin[+]

$$Resin^+]CO_3^{2-} + 2H^+[^-Clay \rightarrow Resin^+][^-Clay + CO_2 + H_2O \quad (1)$$
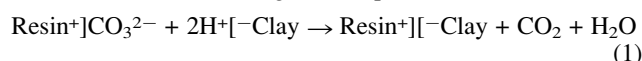
denotes the positively charged surfaces of the resin and [−Clay denotes the negatively charged clay layers. After the thermal treatment, the resin–clay mixtures were centrifuged (4000 rpm, 1 min), washed twice with commercial acetone and dried at 60 °C for 20 min in an oven. Observation of the resin–clay samples under an optical microscope did not reveal the presence of any discrete clay phase but only the presence of transparent resin spheres, suggesting a homogeneous coverage of the resin surfaces by a thin clay coating. The as obtained resin–clay samples were finally calcined in air at 600 °C for 7 h *via* steps of 1 °C min^{-1} to give pure hollow clay microspheres as evidenced by the lack of organic absorptions in IR spectra. The final samples were studied by optical microscopy, SEM and XRD techniques.

Optical microscopy images of the parent anion exchange resin as well as the Zenith-N and laponite clay samples derived after calcination of the corresponding resin–clay composites are shown in Fig. 1. The XRD patterns of the clay samples are also included as inset photos. The parent amorphous resin particles possess a spherical morphology with a non-uniform size distribution of small and large spheres in the range 100–200 μm. On the other hand, both clay samples also consist of spherical particles (Zenith-N spheres: opaque and with rough surfaces, laponite spheres: transparent and with smooth surfaces) with a non-uniform size distribution in the range 20–50 μm. Therefore, the clay samples inherit the shape morphology and size non-uniformity of the parent resin throughout the synthetic process. Accordingly, by controlling the size distribution of the starting resin particles, *e.g.* by sieving the resin, the problem of the size non-uniformity can be eliminated. As far as the observed size shrinkage of the clay samples is concerned, this can be attributed to the removal of the large resin core (at least 100 μm) after calcination of the resin–clay composites. The spheres based on Zenith-N show a weak (001) XRD reflection with a basal spacing (d_{001} = 9.8 Å) characteristic for the collapsed state of the layers in the prime clay particles. In contrast to Zenith-N, the laponite based spheres do not exhibit any (001) reflection that may be attributed to a turbostatic stacking of the
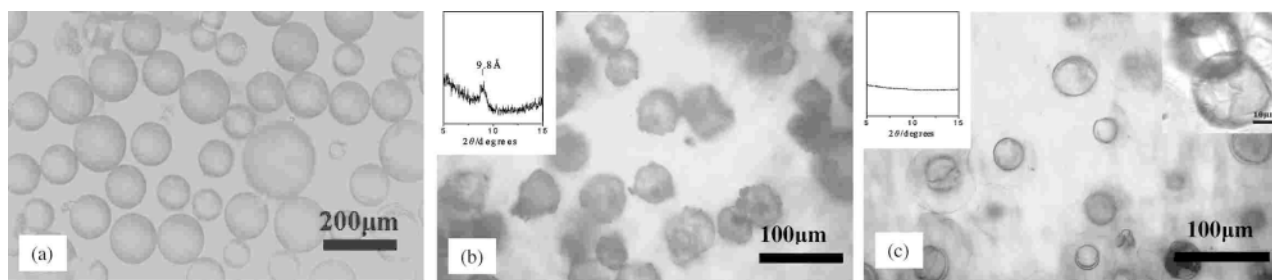
Fig. 1 Optical microscopy pictures of (a) parent resin spheres, (b) Zenith-N clay spheres and (c) laponite clay spheres (the inset photos show XRD patterns of the given clay samples).

layers in the clay particles due to their very small size (*ca.* 0.1 μm *cf. ca.* 1 μm for Zenith-N).

The SEM examination of Zenith-N and laponite samples reveals the presence of compact and intact spheres which are smoother in the latter, Fig. 2. The inset photo, Fig. 2(a), shows a broken sphere that reveals the hollow structure of the spheres. The wall thickness of the spherical cells is rather uniform and varies between 3 and 5 μm for both clay samples. Note that the large majority of the hollow clay spheres are intact at their surfaces. In contrast to this observation, when the clay samples were prepared using the sodium form of Zenith-N and laponite instead of the acid forms, and the chloride form of the resin instead of carbonated form, clay samples consisting primarily of broken specimens with irregular shape and morphology were obtained, features that were more pronounced for the laponite sample. It seems that the resin surfaces are not sufficiently covered by clay layers to form a thick enough coating that remains intact after calcination. This probably arises from the strong electrostatic binding of chloride ions by the positively charged surface of the resin thus making their efficient replacement by the negatively charged clay layers difficult.
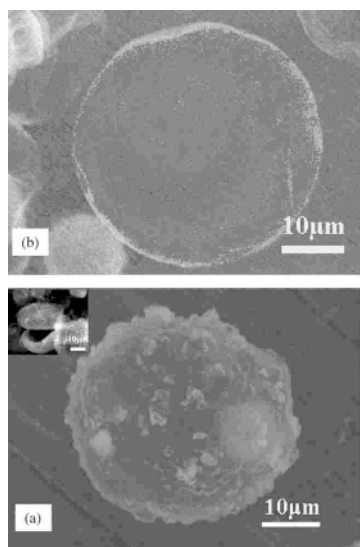

Fig. 2 SEM micrographs of a Zenith-N (a) and laponite (b) hollow clay sphere (the inset photo shows a broken Zenith-N hollow specimen).

Fig. 3 shows XRD patterns of Zenith-N clay spheres before (a) and after (b) treatment with trimethylamine vapor at 80 °C for 3 h. After vapor treatment, the basal spacing of the collapsed clay ($d_{001} = 9.8$ Å) increased to 12.8 Å due to the insertion of trimethylamine molecules into the gallery space of the clay layers *via* interlayer protonation of the base. The results show that the hollow clay spheres can be easily reconstructed to other clay derivatives *via* intercalative patterning of their interlayer space. For laponite, insertion of trimethylamine into the galleries does not alter the amorphous state of the clay shell, even after prolonged exposure. In this case, the lack of layer re-stacking may be attributed to some chemical sintering occurring after calcination, between laponite layers through cross-linking of adjacent broken sites (much greater in number than for
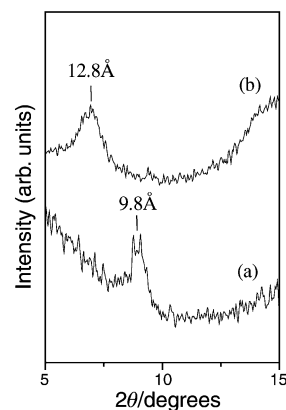

Fig. 3 XRD patterns of Zenith-N hollow spheres (a) before and (b) after trimethylamine vapor treatment.

Zenith-N due to the smaller size of the layers) near their edges.[8] It should be noted that the morphology of the clay samples was preserved after the above mentioned treatments.

In conclusion, thermally stable hollow microspheres (size: 20–50 μm, wall thickness: 3–5 μm) of a naturally occurring and of a synthetic clay were prepared using the sacrificial core–shell technique, in which an anion exchange resin played the role of the core/template and the clay particles the role of the building units of the shell. Intact hollow spheres were obtained only when a carbonated resin and an acid clay were used, as this combination provides an efficient way to sufficiently cover the resin surfaces with the clay layers without screening effects from the counter ions of the resin. The template approach described here can also apply to fabrication of micrometer sized analogues of clay colloidal systems, *e.g.* zeolites and magnetic particles. In a forthcoming publication the ability to synthesize a variety of hollow inorganic microspheres by simply exploiting the exchange properties of the resin will be described.

Notes and references

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