



Covalent porous materials from hybrid silica particles



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ABSTRACT

Three-dimensional porous materials are routinely prepared from molecular precursors. We describe here a study of a much less explored route, namely of using of sub-micron particles as building blocks which are reacted with each other to form covalent porous materials. The motivation for such an approach is the expectation that shifting from molecules to particles is a potential source of new type of 3D-covalent porosity. This was indeed proven by employing two covalent linking reactions: Radical-initiated cross-linking of hybrid particles of polyethylene@silica (PE@silica), and the bridging of PE@aminosilica particles with the bi-functional suberoyl dichloride in a condensation–aggregation reaction. These resulted in the mesoporous materials (XPE@SiO₂)_n and (PE@amidosilica)_n, respectively. The resulting mesoporous materials were investigated in detail, and the kinetics of their formation was followed by various methodologies. SEM shows that the geometry of the covalently aggregated particles is different from simple physical aggregation, and these stable structures could be achieved only through the strong covalent bonds. Real-time movies monitoring (links are provided) allowed the direct follow-up of the radical processes and condensation–polymerizations and identify their different routes. Applications in the fields of separation, supports for catalysis, and matrices for release, are envisaged.

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1. Introduction

Covalent porous materials are commonly prepared from molecular precursors – MOFs, sol–gel materials, porous polymers are some high well known examples. Much less explored is the route which uses sub-micron particles as precursors which are covalently linked to each other to form a 3D porous network. Directed aggregation has been used especially in the design 2D of photonic crystals [1,2], but the common focus has been on various physical interactions [3–11], not on covalent-bonds which form a macroscopically covalent material. We show here that intentional covalent aggregation reactions of particles – namely, the 3D connection of particles by covalent bonds – is a generic approach for the preparation of new porous materials. Interestingly, while the term “covalent aggregation” is well known in biochemistry and refers there to proteins binding [12], to the best of our knowledge, the term has not been yet adopted in the field of chemistry of materials. We describe two general synthetic routes for the fabrication of covalent aggregates: The first route uses a cross-linking reaction between the particles, and the second links them covalently with a bridging linker molecule. The resulting materials are with porous architectures that cannot be obtained by regular

simple physical aggregation. Detailed characterization of the resulting materials is accompanied by following the individual particles and their dynamics of binding to each other, including real-time follow-up of the reaction in movies which are part of this report.

The sub-micrometer hybrid building-block particles we use in this study are of two types: polyethylene PE@silica hybrids [13–15]; and (the previously unreported) PE@aminosilica particles. We briefly recall that PE@silica is an interesting hybrid material which represents the hybridization of extremes: It intimately combines one of the most hydrophobic organic polymers – PE – with one of the most hydrophilic polymeric oxides – silica.

2. Experimental details

2.1. Materials

Tetraethyl orthosilicate (TEOS) 98%, linear low-density polyethylene (PE, density 0.932 g/mL, melt index 55 g/min) and polyethylene-block-poly(ethylene glycol) (PE-b-PEG, Mw 1400, 50% (w/w) PEG) were purchased from Sigma–Aldrich. 3-Aminopropyltriethoxysilane (APTES) 99%, suberoyl chloride 97% and dodecane mixture of isomers were purchased from Acros Organics. The cross-linker bis(3,5,5-trimethylhexanoyl)peroxide (THP, dissolved

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in isododecane, 75% by weight) was kindly donated by M. Shuster, Carmel Olefins Ltd., Haifa.

2.2. Synthesis of the hybrid particles

PE@aminosilica particles were prepared by an emulsion polymerization as follows: The hydrophobic phase consisted of 0.2 g PE and 0.2 g PE-b-PEG dissolved in a boiling mixture of 4.0 mL xylenes, 2.6 mL TEOS and 1.4 mL APTES (mol ratio TEOS:APTES 1:2). After dissolution, the solution was rapidly poured into the hydrophilic dispersing phase consisting of 100 mL ethanol and 60 mL ammonium hydroxide (25% w/w) warmed to 78 °C, under vigorous magnetic stirring. A white emulsion formed immediately which was then stirred under heat for about 30 min. Then the heating was turned off and the emulsion gradually cooled down to room temperature and was kept stirred for 24 h. The formed particles were collected after centrifugation of the dispersion at 6000 rpm for 20 min. The precipitate was air-dried for 24 h.

The building block PE@silica particles were synthesized according to the procedure of Ref. [13], using emulsion polymerization of TEOS.

2.3. Inter-particles reactions

The covalent cross-linking of PE@silica particles: 0.072 g of PE@silica particles powder was initially heated in order to expel some PE chains onto the particles surface [14,15]. Heating was carried out by placing the particles powder in a round bottom flask which was immersed in an oil-bath and fitted with an argon line. The powder was heated for 30 min at 130 °C. Next, the bath temperature was cooled to 120 °C and 2.0 mL of the cross-linking agent, THP 75% in *i*-dodecane, was transferred into the reaction flask. Heating was removed after 20 min and the suspension gradually reached room temperature. The cross-linked particles powder was separated from the solvent. A reference sample was prepared by replacing the cross-linking agent, THP in *i*-dodecane, with neat *i*-dodecane containing no THP.

Covalent aggregation of PE@aminosilica particles: 0.25 g of PE@aminosilica particles powder was placed in a vial into which a solution of 0.2 mL suberoyl chloride in 2.0 mL THF was added. 24 h later, the suspension was filtered through a Büchner filter and the powder was thoroughly washed with ethanol and air-dried.

2.4. Real-time follow-up of the covalent-aggregate formation

The reaction of PE@silica particles: For the follow up of the inter-particle reaction, NanoSight LM12 by nano-particles image analysis system was used. A 1.25×10^{-4} g/mL particle suspension in ethanol was injected into the measurement cell and the initial particle size was recorded. Then, the suspension was drained out of the measurement cell into a vial, into which 0.2 mL of the cross-linking agent was introduced. The vial was placed on a hot plate for a few minutes to affect the cleavage of the THP into radicals and then was re-injected into the measurement cell. Real-time inter-particle reaction was recorded at timed intervals. The aggregate size evaluation is based on the Stokes–Einstein equation. The aggregate-size measurement was conducted for 20 min, beyond which the particles are too large for detection by this method.

The reaction of PE@aminosilica particles: This was followed up by two methods: In the first method the on-line nano-tracking analysis mentioned above was used by injecting a diluted ethanol particle suspension (2×10^{-4} g/mL) into the measurement cell. The initial particle size was determined and then to that suspension either 40 μ L or 80 μ L of the linker molecule, suberoyl-chloride was added. Real-time inter-particle reaction and particle-size evolution were followed for 20 and 5 min respectively (the size at

20 min reaches the limits of reliable readings). The second method applied an analytical centrifuge (LumiFuge 114, separation analyzer by L.U.M. GmbH) as follows: 0.5 mL of PE@aminosilica particles suspension in ethanol (1×10^{-3} g/mL) was transferred into the centrifuge tube. Then, 0.1 mL of linker molecule solution in THF was added. The reaction was performed at four volume fractions of linker molecule in THF: 0.1 mL of THF and no suberoyl chloride; 0.05 mL of THF and 0.05 mL of suberoyl chloride; 0.02 mL of THF and 0.08 mL of suberoyl chloride; and 0.1 mL containing only suberoyl chloride. The measurement was performed at 300 rpm for 2 h.

2.5. Instrumentation

High-resolution scanning electron microscopy (HR-SEM) observations were performed with a Sirion (FEI) microscope, operating at 5 and 10 kV. Samples were prepared by placing the centrifuged, air-dried powder on an aluminum stub for SEM using a double sided carbon tape. Scanning-transmission electron microscopy (STEM) observations were performed on a MagellanTM XHR SEM microscope operating at 2 and 5 kV. Samples for STEM observation were prepared by re-dispersing the resultant powder in ethanol by ultra-sonication for 24 h and placing a drop of that dispersion on Formvar/carbon 300 mesh copper grid. The dispersion was air dried for 1 min and the excess solution was wiped off. Atomic force microscopy (AFM) measurements were conducted with Nanoscope Dimension 3100 with the Nanoscope V controller (Veeco company) the measurements used the Nanomanipulation mode in order to move the probe along the surface. Sample suspension was placed on a mica surface. The probe used was RTSP type with spring constant of 20 Nt/m. Specific surface area and the nominal BJH pore diameters were calculated (multiple point calculation) from nitrogen adsorption/desorption isotherms determined at 77 K using Micromeritics ASAP 2020 surface analyzer. Outgassing for these measurements was carried out for 24 h at 100 °C. IR measurements were carried out using a Bruker Tensor 27 spectrometer. The samples were tested in a disk form obtained by grinding the powder with KBr and pressing under 10 atm.

3. Results and discussion

3.1. Covalent aggregation-reaction of PE@silica particles leading to $(XPE@SiO_2)_n$ material

3.1.1. The radical cross-linking polymerization reaction of the particles building blocks

The elevated temperature at which the cross-linking agent, THP, is added to the particles dispersion results in three events (Scheme 1): the cleavage of THP molecules into two radicals; hydrogen radical abstraction from the PE chain; inter-particle C–C bond formation, similar to the solution PE cross-linking reaction. Unlike solution, however, this reaction continues all around each particle, resulting in a covalently bound 3D structure. The maximal number of nearest neighbor particles to each particle is that of a hexagonal packing, that is 12 other particles. However, such close packing requires that the process be reversible, which it is not. Therefore, the first particles bind covalently at random, and the later particles must fit in large enough vacancies on the surface. As a result one may expect a covalent packing which is less than the maximal, which is indeed the case (next).

3.1.2. Microscopy evidence for the covalent aggregation and formation of $(XPE@SiO_2)_n$

The resulting material of the multiple inter-particle reactions is presented in Fig. 1. Fig. 1a shows, for comparison, the starting

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