

A Practical Approach Toward Processing of Mesoporous Organosilica Powder as Composites for Industrial Applications

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Abstract: Despite the extent of research on preparation of mesoporous silica and their functional derivatives, the powder nature of the material as obtained from sol-gel synthesis have remained an issue for commercial usability. In addition to technological issues, restrictions in both handling and material recycling for further treatment or reuse also arise. Toward this end, amine-functionalized mesoporous silica powders (of MSU family) were coated on or melt blended with a polystyrene support matrix. Both surface coating and melt blends of the silica powder with polymer were successful in preparing composites with adsorption properties comparable to those of the native powder-form adsorbents, as determined from gold adsorption tests from simulated hydrometallurgical solutions.

Key words: *Mesoporous silica, organosilica, sol-gel synthesis, silica-polymer composite, adsorption*

INTRODUCTION

Since the mid-1990's, functionalized mesoporous silicas prepared by surfactant assembly (designated MCM-41, HMS, SBA and MSU) have attracted significant attention for the development of highly effective adsorbents because of their high specific surface area ($\sim 1000 \text{ m}^2\text{g}^{-1}$), open framework nm-scale pore structure, and ease of synthesis and functionalization.[1] In spite of their promise for a wide range of environmental and industrial application, the fine powder morphology of these materials often limits their practical use in industry-scale processes.

Controlling the morphology of mesoporous silica has proven to be a challenge for materials chemists.[2] Various synthesis strategies yielding micrometer to millimeter-sized spherical geometries obtained through microemulsion sol-gel synthesis have been reported[3-7], while larger spheres, films and coatings[8-11] and monolithic morphologies [12-18] have been demonstrated by careful control of synthesis conditions. In fabrication of monolithic mesostructures through direct templating to obtain cast monoliths or membranes, inadequate diffusion of the inorganic moieties within the preformed lyotropic phase as well as uncontrolled phase separation have caused certain heterogeneities during synthesis that adversely affected the structural characteristics of the material.[2] Moreover, the necessity of compatibility and proper interaction among added co-solvents, oils and other

emulsifying agents with the main structure-directing agent and synthesis conditions adds to the complication of controlling the construction of highly ordered structures in syntheses based on phase separation. For example it has been found that alkanes with different chain lengths interact with co-polymer surfactant among which only those of suitable chain length (ranging from hexane to decane) are good matches with the co-polymer.[19,20]

A simpler and more generalized approach to achieve size control is to blend the powdered adsorbents in a suitable polymer, in which the mesoporous silica are combined within polymer matrices as functional nano-fillers.[21,22] In this research, the polymer was regarded only as either a substrate (for coating the silica powder) or as the blend matrix in a physical composite. The idea of using polymer beads as substrates for coating of the micron-sized powder material originated from the use of ion-exchange resins in commercial applications such as hydrometallurgical pre-concentration of metal ions. In this work, the preparation of amino-functionalized mesoporous silica/polystyrene composites, both as blends and coated particles, is investigated and tested for the uptake of gold thiosulfate from simulated hydrometallurgical leachate solutions.

MATERIALS AND METHODS

Chemicals

Igepal® CO-720 was used as surfactant (structure directing agent), while TMB (mesitylene or 1,3,5 trimethyl benzene) was used as swelling agent, both provided by Sigma-Aldrich® (St. Louis, MO, U.S.A.). TEOS (tetraethoxysilane) as the silica precursor was from Gelest Inc. (Morrisville, PA, U.S.A.). Functional silane 3-aminopropyl-triethoxysilane (APTES) > 98% was purchased from Sigma-Aldrich® (St. Louis, MO, U.S.A.). Sodium fluoride (reagent A.C.S.) was provided by Matheson Coleman & Bell manufacturing chemists (East Rutherford, NJ, U.S.A.). All other chemicals including acid (HCl) and solvents (ethanol, 1-butanol and toluene) were of reagent grade. Polystyrene beads were graciously provided by Prof. Eduard Guerra from the Bharti School of Engineering, Laurentian University.

Synthesis of mesoporous silica powder and related hybrids

MSU-2 mesoporous silica prepared through previously described two-step (separate hydrolysis and condensation) synthesis procedure.[23] Typically, a 0.02 M surfactant solution was prepared in the desired volume of DI water which was acidified with appropriate amounts of dilute HCl to pH \approx 2-2.5. Swelling agent (TMB/surfactant molar ratio=1) was also added at this stage. After the solution became homogenous by magnetic stirring at ambient temperatures, TEOS (Si/surfactant molar ratio= 8) was added as silica precursor. After an hour of hydrolysis, sodium fluoride (molar NaF/Si =0.04) was introduced to the solutions to catalyze the condensation of silica at elevated temperature (55 °C) in a thermostated water bath overnight without any disturbance of the solution. After filtration and air oven drying, the template was removed by solvent extraction using hot ethanol in a Soxhlet apparatus (for 48 h). Post-synthesis amine grafting was performed by adding the as-obtained mesoporous material together with 3-aminopropyl-triethoxysilane (equal masses of each) into dry toluene and refluxing for 16 hours. After drying in air, the functionalized material was ready for coating/blending with the polymer beads.

Hybrid mesoporous silica blending with polymer

Different approaches were considered in making the mesoporous silica-polymer physical composites. The first method consisted of lidded zirconium metal pots in which polystyrene beads (diameter: 3-4 mm) were embedded in layers of amine-functionalized MSU-2 mesoporous silica and let to stay in an oven in air for

certain periods of time at temperatures reaching as high as 180 °C (3-4 hours).

The second composite preparation methods consisted of a *dynamic* coating process in which an appropriate amount of beads (weight polymer/mesoporous silica = 20) was heated in aluminum pans using a gun heater, while the pan was simultaneously kept in an orbital rotating motion (@ 200 rpm) to ensure homogenous coating of the surface of the beads. Experiments lasted 15-30 minutes and temperature varied 135-175 °C. The mechanical impact was expected to provide the necessary pressure for the penetration of hybrid powder into the partially melted (softened) surfaces of the polymer bead. After coating, the beads were rinsed with DI water several times to remove any loosely attached particles. The schematic setup of the experiment is shown in Figure 1.

Additional experiments were performed in which the amino-functionalized MSU-2 silica was melt blended with softened polymer into different morphologies such as pressed pads (plates), threads/tapes and complete mixtures of random shapes. The blends were mixed and shaped mainly by hand and common laboratory utensils (e.g. spatulas). Thread/tape morphologies were prepared by extrusion of the mixture using an LME laboratory mixing extruder (Dynisco).

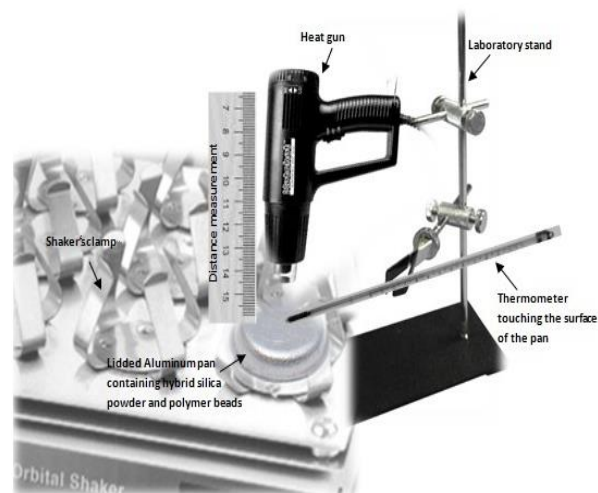


Figure 1: Schematics of the experimental set-up in the polymer bead dynamic coating experiments.

Materials Characterization

N₂ adsorption isotherms were measured for MSU-2 silica at 77 K using Micromeritics® ASAP 2010 apparatus in order to determine the successful preparation of the mesoporous substrate. Specific surface areas for MSU-2 were measured as 1119 m²g⁻¹ using the BET method. The mean pore size of the

material was determined to be 4.4 nm, as determined using the integrated DFT Plus[®] software in which the Broekhoff de Boer model for cylindrical pores was employed for pore size distribution analysis and pore volume calculation. These values confirm the successful preparation of a mesoporous silica with uniform nanoscale porosity.[23]

Gold adsorption by composites.

Simulated gold thiosulfate solutions (10 mg/L Au) were stirred by orbital shaking (150 rpm) with composite beads prepared by method 2 (dynamic coating method) for 24 hours. The treated solutions were analyzed for Au by flame AAS (Laurentian University Central Analytical Facility) in order to quantify the amount of gold adsorbed by the composites.

RESULTS AND DISCUSSION

Because of the attractiveness of adsorbent beads with spherical morphology for industrial applications such as adsorption and catalysis, the manufacture of composites by adsorbent coating on polystyrene bead surfaces was of particular interest for this study. The free (unblended) contact of the hybrid powder with polystyrene polymer beads, though resulting in a high degree of bead coverage with the adsorbent, resulted in yellowish color change. Such color change was attributed to possible degradation of the amine functions when exposed to prolonged heating in the air atmosphere of oven which recurred even in the absence of polymer beads. Further, as shown in Figure 2, the top portion of the beads was not coated despite it was fully covered with the powder during heat treatment. The latter was considered to be due to lack of dynamics (enough pressure) between the powder and softened (partially molten) top “hydrophobic” surface of the polymer bead. In contrast, the dynamic coating process (method 2) afforded materials with much better control of composition and surface morphology, as shown in Table 1

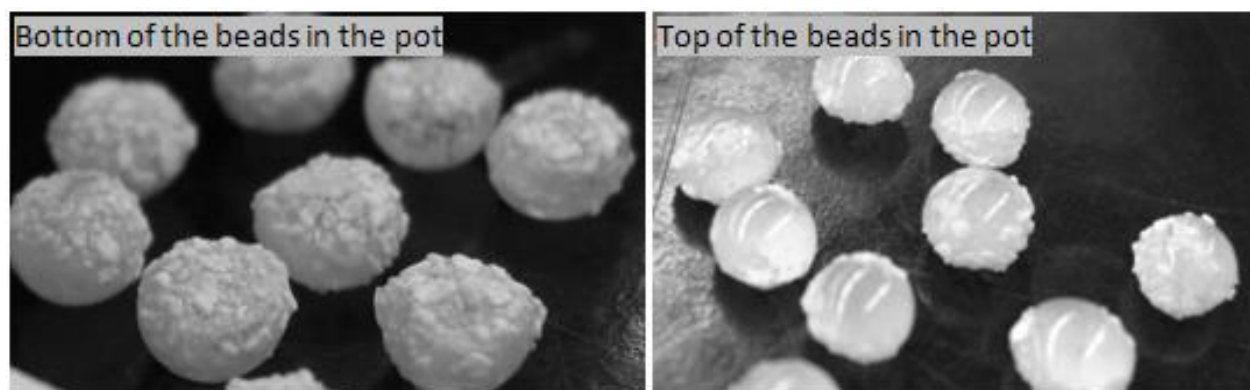


Figure 2: Coating of polystyrene beads with amino-functionalized MSU-2 mesoporous silica powder aggregates after static heating in air atmosphere oven and being rinsed with DI water

Table 1: Weight gain of on the polymer bead after being coated in different conditions of dynamic coating tests

Test	Distance of the gun tip to the surface of the pan (cm)	Temperature at the surface of the pan (°C)	Duration of experiment (min)	Weight gain of the beads (%)
C1	15	135	15	0.035
C2	15	135	30	0.115
C3	15	135	50	0.160
C4	10	155	10	0.210
C5	10	155	20	0.220
C6	5.5	175	15	0.285
C7	5.5	175	30	0.525

The temperature measured at the surface of aluminum pan containers, was a direct function of the distance of

the gun tip to the pan surface as observed in Table 1. It was also evidenced that the loading of the beads with

the mesoporous silica increased as a function of applying higher temperatures and/or longer duration of experiment. None of the coated beads in these tests had experienced color changes due to degradation of the material composition. Although the translucency of the beads was lost after being coated with the hybrid material, not much difference was observable to the naked eye among the coated polymer beads with different loadings of hybrid mesoporous silica (Figure 3).



Figure 3: The polystyrene beads before and after being coated with hybrid mesoporous silica powder in the dynamic coating experiments

The performances of coated beads in gold adsorption tests were essentially proportional to the loading of hybrid silica on the beads. Gold recoveries from simulated thiosulfate leach solutions ranged from 44-63% for C1-C7, compared to 70% for the native amino-functionalized MSU-2 powder (Figure 4). The more highly coated composites were therefore shown to exhibit adsorption properties only slightly reduced compared to the native adsorbent. The amount of MSU silica loss due to detachments from the bead surfaces under the agitation conditions used (24 h, 150 rpm) was also determined by weighing the dried samples after stirring in deionized water. The lowest loss of powder was recorded for C1 (< 2 mg/24 h) and for C6 it was near 4.5 mg/24 h in the adsorption experiments. In both cases, the loss of adsorbent from the composites was relatively minor, and exhibited little effect on the adsorption performance of the overall composite.

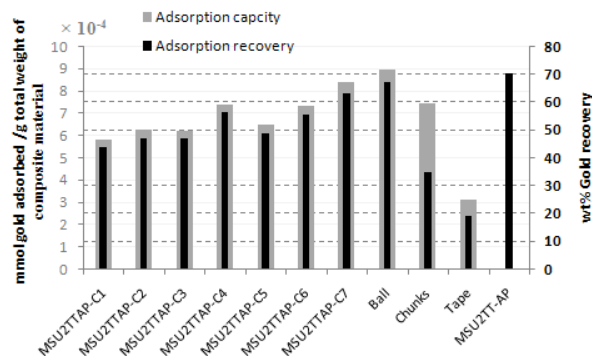


Figure 4: Gold adsorption capacities and recoveries by different mesoporous silica composites (Method 1: C1-C7, method 2: ball, chunks, tape) compared with those obtained

for pristine aminopropyl-functionalized MSU-2 powder (MSU2TT-AP).

Figure 5 shows other melt-blended composite materials that were processed in different shapes and morphologies. In all samples, amine-functionalized silica powder was added to the polymer which was only heated toward softening temperature while being shaped by hand into the desired morphology. There was no apparent sign of functional degradation of the mesoporous silica from the applied heat during melt mixing in any of the created morphologies. Although precise quantification of the amount of silica relative to polymer in the composites were not measured, their performance were evaluated by the gold adsorption tests. Based on metal recovery values per weight of the composite material (Figure 4), fully mixed composite samples (with either balled or chunk geometry) showed the adsorption capacities comparable to those of the coated composites, although gold recovery (expressed as % weight) were markedly lower for the chunk morphologies. The tape/thread extruded composites fare worse than the other sample studied, with only 24% gold recovery, and less than half of the adsorption capacity of the other samples. The blended samples, on the other hand, were advantageous from the point of view of structural integrity, exhibiting lowered attrition of MSU powder in stirring tests (about 1 mg/24 h) compared to that of the coated beads.

The poor performance of some of the composite blends can be attributed to the better dispersion of the adsorbent powder into the softened polystyrene matrix when fully blended, occluding access of some of the adsorbent particles to the contact solution. The hydrodynamics during an agitated adsorption system might also be improved in some of the full blends owing to defects in “random” 3-dimensional morphologies such as balls and chunks, providing more surface exposure to functional material in all directions when contacted with target specie(s) in solution. The tape (or thread) morphology gave better results when prepared by hand mixing and shaping rather than by extrusion, but overall it was the least performing composite among those studied, both in terms of metal recovery from solution and loss/detachment of powder from stirring.

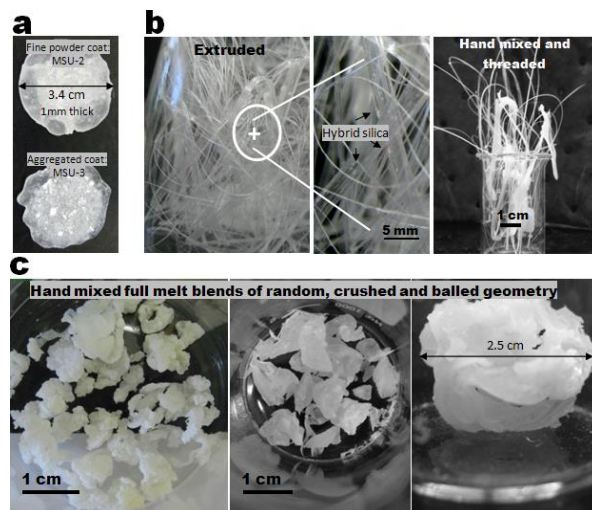


Figure 5: Different morphologies of mesoporous silica-polystyrene composites prepared by partial or complete melt blending; a) pressed as balls/pads, b) threaded/taped and c) fully blended into random shapes (chunks).

CONCLUSION

Surface coating of polymer beads with hybrid silica powder was very effective in obtaining a smooth homogeneous coating on the polymer surface while preserving its spherical geometry. The laboratory set-up in these experiments could possibly be replaced by tumble dryer or similar equipment in a real process so that the amount of heat and rotational impact are controlled more precisely. Complete melt-blends of hybrid mesoporous silica with an inert polymer (e.g. polystyrene) proved to be an efficient way to prepare composite adsorbents that expose significant amount of functional material for an application such as adsorption of metals.

It was shown that during the coating/blending process of amine-functionalized mesoporous silica and polymer, short exposures of the mixture to air and temperatures reaching up to 180 °C would not cause noticeable material degradation or loss of adsorption capacity. As the melt blending in this research was performed mostly by hand, the efficiency of an industrial substitute for such process must be accurately evaluated. For example, the use of extrusion (as applied in some of these tests) might not be feasible due to high viscosity of the paste resulting from high powder/polymer loading ratios.

As demonstrated by the gold adsorption studies, the processing of mesoporous silica-based adsorbent materials into polymer matrices, either by coating or by melt blending, results in morphologically-controlled composites with properties comparable to (although somewhat reduced in some cases) to the native powdered materials. This is useful when

considering the application of these materials in real-life industrial situations.

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