Functionalized Emulsion and Suspension Polymer Particles: Nanoreactors for the Synthesis of Inorganic Materials

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Cross-linked acrylic emulsion polymers are prepared from ethyl acrylate, methacrylic acid, and allyl methacrylate in aqueous media. The carboxylate groups on these polymers readily form ionic complexes with cation species. These cation-loaded polymers can be burned in air to yield pure oxides at temperatures as low as 150 °C. In an analogous fashion, commercially available suspension particles composed of styrene and divinylbenzene can be functionalized by reacting with sulfuric acid. The resultant sulfonic groups have a different selectivity for cation species. This novel synthetic technique may be used with most metallic elements, and it is demonstrated here for the formation of ZrO_2, CeO_2, $LiMn_2O_4$, and $Ba_2YCu_3O_7$, as well as catalysts in the Au/Pt and Pt/CeO_2 systems. The rapid, intimate mixing of metal ions results in low formation temperatures of nanosized materials, and the myriad of potential processing techniques enables isolation of inorganic oxide powders, precipitation of isolated inorganic clusters within a polymer matrix, and the coating of substrates with nanoparticulate inorganic materials.

Introduction

As chemists studied increasingly larger metal clusters and diminishingly smaller particles, it became inevitable that nanotechnology should emerge. The terminology is hackneyed, but the chemistry has afforded a stunning variety of materials with physical properties reminiscent of both the atom and the conventional bulk solid but quite distinct from each. The impressive mechanical strength, strong magnetic response, dramatically reduced sintering temperatures, increased catalytic activity, and enhanced optical properties of nanometer-sized particles are all motivations for their study.[1]

There are quite a number of techniques available for the isolation of nanometer-sized materials. Physical methods include gas condensation,[2] molecular beam epitaxy,[3] high-energy ball milling,[4] chemical vapor deposition,[5] mechanical alloying,[6] and simple coprecipitation.[7] Chemical methods include spray pyrolysis,[8] flame and plasma synthesis,[9] sol−gel techniques,[10] Pechini's method,[11] hydrothermal precipitation,[12] use of inverse microemulsions,[13−16] and even protein[17] or liquid crystal[18] templating. Some of these processes yield broad particle size distributions or intermediate products which require further calcination to obtain the desired product.

The interaction of polymers with inorganics has been intensely studied, particularly for use in ion-exchange processes for purification.[19] Block copolymers have been used to form inorganic materials,[20−23] and there are studies employing the combustion of emulsions to isolate inorganic materials.[24,25] We extend these studies[26] considerably to include functionalized, cross-linked acrylic emulsion polymers which afford excellent control

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over the stoichiometry, size, shape, and structure of inorganic materials. The general strategy is depicted in Figure 1.

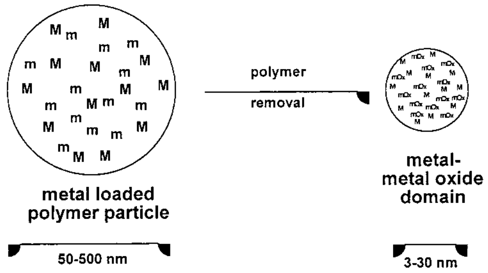

Figure 1. Schematic of nanoscale reactors and the production of inorganic materials using them. The letters M and m represent various metallic species which can bind to polymer particles.

Experimental Section

Particle size measurements were carried out on a Matec Applied Sciences CHDF-1100, which separates particles of different size on the basis of the hydrodynamic effects of particles undergoing Poiseulle flow within a capillary tube. Chemical composition was measured using inductively coupled plasma (ICP) spectroscopy on a Bausch and Lomb 3510. Thermogravimetric analysis (TGA) was performed on a DuPont 2200 analyzer. Surface area measurements were carried out on a Micromeritics ASAP2400 analyzer using the BET method. X-ray diffraction (XRD) data were collected on a Philips APD3720 diffractometer using a copper target. Transmission electron microscopy (TEM) was carried out on a JEOL JEM 1200EX. Residual carbon content was measured on a Leico IR-412 unit.

Polymer Synthesis. Standard emulsion polymerization techniques were used.[27,28] A typical monomer emulsion was formed by combining 200 g of water, 7 g of Rhodapon L-22, 90 g of ethyl acrylate, 90 g of glacial methacrylic acid, and 7.5 g of allyl methacrylate. The mixture was shaken vigorously to form a monomer emulsion. A 2 L round-bottom flask was charged with 250 g of water and heated to 80 °C under flowing nitrogen. The solution was agitated throughout the reaction by a Teflon paddle which developed a 1 in. vortex in the liquid. Ammonium persulfate (0.06 g) and 34 g of the monomer emulsion were added to the reaction flask, and the mixture was allowed to react for about 10 min. As this initial dose of monomer emulsion polymerized, the solution turned from opalescent to nearly translucent. The remaining 360 g of monomer emulsion and 32.2 g of ammonium persulfate solution (as a 0.027 M aqueous solution) were added to the flask at rates of 4 and 0.35 g/min, respectively. After the feeds were completed, the vessel was maintained at 80 °C for 20 min and cooled to 60 °C, and tert-butyl hydroperoxide (0.1 g) and sodium formaldehyde sulfoxylate (0.06 g) were added to reduce the amount of unconverted monomers. A typical particle size measurement is shown in Figure 2. Three batches produced with this procedure yielded particles of average size 117−121 nm with peak width at half-height of 82−107 nm. The size and distribution of the latex particles is influenced by the amount of surfactant, speed of agitation, amount of initial monomer emulsion charge, and amount of persulfate used. This cross-linked polymer has a theoretical loading capacity of 5.6 mequiv of carboxylic acid groups per dry gram and was the polymer used throughout this study, except as noted.

The synthesis of a quaternary-amine-functionalized emulsion polymer, here called polymer B, was described previously.[29] To summarize, a methacrylic acid (60%), styrene (35%), and divinylbenzene (5%) emulsion polymer was formed in a manner analogous to that given above and was dried. In an *extremely hazardous reaction*, the polymer was functionalized by reaction with chloromethyl methyl ether and propylene dichloride and then with dimethylethylamine.

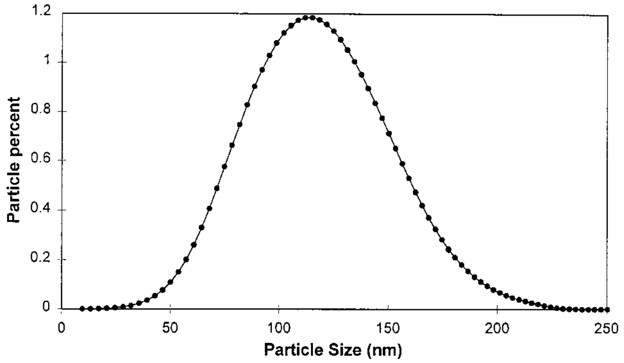

Figure 2. Polymer particle size distribution measured on a Matec CHDF-1100. The weight distribution indicates an average particle size of 120 nm and a peak width at half-height of 82 nm.

Synthesis of ZrO_2. A 31 g portion of a 16 wt % emulsion (26.3 mequiv) was combined with 13.6 mL of 0.9 M NH_4OH (12 mequiv) to adjust the pH to 8.2. Aqueous zirconium nitrate (0.42 g, 5 mequiv) was slowly added to the emulsion, while the pH was maintained near 8.2. The product was spray dried, and the polymer portion was removed using a thermal treatment of 600 °C for 2 h in air.

In an alternate synthesis, 34 g of a 29 wt % styrene (65%)/divinylbenzene (35%) emulsion polymer, Biocryl BPA-2100, of average size 210 nm (50 mequiv) and 20 g of water were charged to a glass jar. To the stirred mixture was added 11.3 mL of a 2.2 M solution of zirconyl chloride (25 mequiv). The mixture was stirred for 46 h and rinsed with water until the pH was neutral. A small portion of the beads was removed and pyrolyzed at 650 °C to yield a white solid in 22% yield. To the remaining resin were added 10 g of 19 N NaOH and 20 g of water. The stirred mixture was heated at 80 °C for 2 h, cooled to room temperature, rinsed with water until the pH was neutral, and charged with an additional 10 mL of zirconyl chloride solution. After reaction, the beads were rinsed to neutrality and a small portion was removed and pyrolyzed to yield white particles in 31% yield. This procedure was repeated four additional times with 41%, 42%, 46%, and 49% yield, respectively.

To prepare yttria-stabilized zirconia, 500 g of an 11.2 wt % emulsion, Biocryl BPA-2100, with a mean particle size of 230 nm, was stirred. A 500 mL portion of a 0.19 M zirconium oxynitrate and 0.007 M yttrium nitrate aqueous solution was added dropwise over 2 h. The pH of the reaction mixture was maintained at 3.4 with the addition of 150 mL of 1 M NH_4OH solution. An aliquot was ultracentrifuged, and the supernatant was found to contain 0.26% (0.24 mg) of the Zr in solution. Yttrium was not detected. The metal-loaded polymer was isolated by adding 250 mL of deionized water and then adding dropwise 65 mL of an aqueous solution of acrylic strong base polymer particle emulsion, Biocryl BPA-1000, with a mean particle size of 150 nm and a solids content of 9.46%. The flocculated mass was collected by filtration and dried at 110 °C overnight. The material was heated at 250 °C for 1 h, at 350 °C for 1 h, and then at 500−1000 °C for 4 h.

Synthesis of CeO_2. A 31 g sample of a 16 wt % emulsion (26.3 mequiv) was combined with 13.6 mL of 0.9 M NH_4OH (12 mequiv) to adjust the pH to 8.2. Aqueous cerium acetate (0.53 g, 5 mequiv) was slowly added to the emulsion, while the pH was maintained near 8.2. An aliquot was ultracentrifuged, and the supernate was found to contain 0.11 ppm cerium ion. Nanocrystalline CeO_2 was isolated by dewatering

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the emulsion (e.g., by spray drying) and heating the resultant powder to 150 °C for 6 h in air. To deagglomerate the material, 20 g of CeO_2 and 80 mL of water were rolled at 20 rpm for 24 h in a 500 mL ceramic jar, half-filled with 0.5 mm zirconia beads.

In an alternate synthesis, 37.0 g of a 27 wt % emulsion (50 mequiv) was combined with 3.7 g of cerium(III) carbonate hydrate (14.4 mequiv) and 53.0 g of water in a round-bottom flask containing a magnetic stir bar and fitted with a gas outlet tube. The gas outlet was directed to a water-filled, graduated cylinder inverted in a container of water. The reaction was monitored by evolution of carbon dioxide. After stirring the quiescent mixture overnight at room temperature, it was heated at 65 °C until the vigorous gas evoloution subsided. The reaction was heated at 85 °C for 2 h and cooled to room temperature. No residue was observed in the reaction flask, and ICP analysis showed only 34 ppm cerium (<1%) remained in solution. The material was spray dried, and an 8.7 g sample of the dried material was pyrolyzed at 650 °C for 4 h to yield 1.5 g of pale yellow CeO_2.

An intriguing alternative to pyrolysis is the in situ formation of CeO_2. As before, 31 g of a 16 wt % emulsion (26.3 mequiv) was loaded with 5 mequiv of Ce^{3+} as an acetate solution. Excess H_2O_2 was added to the loaded emulsion at 80 °C. The reaction mixture changed color during the reaction from a milky white to a creamy tan, indicative of the formation of CeO_2.

Synthesis of CdS. A 37.55 g sample of a 26.6 wt % emulsion (56 mequiv) was neutralized by adding 48.5 mL of 1 M NH_4OH to adjust the pH to 8.2. The mixture was stirred for 10 min and then 56.79 mL of a 0.2 M $CdCl_2$ solution (23.8 mequiv) was added dropwise with continuous stirring of the mixture. The mixture was stirred for an additional 10 min, the pH was measured at 6.0, and then 2 aliquots were removed. These aliquots were ultracentrifuged, and the clear supernatant was analyzed by ICP and found to contain 1065 ppm of Cd. Since 0.186 mg of Cd or 8.5% of the total cadmium remained in solution, the mixture was dialyzed using an Amicon TCF-10 ultrafiltration unit to remove the unloaded cadmium. Ultrafiltration of the solution resulted in the removal of some of the metal from the polymer as well, since an equilibrium is set up between the polymer and the aqueous phase. A 46 mg portion of cadmium was collected in 560 mL of deionized water.

To the stirred mixture was added 2.0 mL of a 20% ammonium sulfide solution. The mixture was stirred for an additional 30 min and allowed to settle. A darker yellow orange layer formed on the bottom of the flask. The canary yellow polymer emulsion was decanted from the precipitate.

Synthesis of $LiMn_2O_4$. A 147 g portion of a 27.2 wt % emulsion (194 mequiv) was diluted to 5 wt % solids. Aqueous 1.75 M LiOH solution (110.4 mL, 193 mequiv) was slowly added to the emulsion. Some of the lithium ions were displaced from the resin by the dropwise addition of 0.8 M $Mn(NO_3)_2$ solution (98.6 mL, 158 mequiv). The solids were collected by centrifugation for 90 min at 15 000 rpm on a Sorvall Automatic Superspeed centrifuge and dried overnight at 100 °C. Pure, crystalline $LiMn_2O_4$ was isolated by heating the resultant powder to 400 °C for 2 h in air.

Synthesis of $Ba_2YCu_3O_7$. A wet macroreticular styrene-divinylbenzene suspension polymer (250 g, Rohm & Haas IRC-718) was placed in a 2 L, polyurethane-lined steel jar along with 500 cm^3 of $^3/_8$ in. alumina balls and 500 mL of deionized water. The can was sealed and shaken on a Sweco Vibro-energy wet grinding mill (model M18−5) for 20 h. The material was reduced to a particle size of less than 500 nm. To 24.98 g of this iminodiacetic acid-containing polymer were added 337.02 g of deionized water and 9.15 g of $Cu(NO_3)_2 \cdot 2.5H_2O$. The suspension was stirred for 2 h at room temperature. The pH of the solution was buffered to 4.5 by the addition of ammonium acetate.

A sulfonated styrene/divinylbenze emulsion polymer, Biocryl BPA-2100, was used which had an average particle size of 230 nm. To 500 g of a 10.8 wt % emulsion was added an aqueous solution containing 6.85 g of barium nitrate and 5.02 g of yttrium nitrate. The pH of the emulsion was controlled between 5 and 6 with the addition of ammonium hydroxide. The emulsion was stirred an additional 2 h.

Table 1. Strong Metal Support Interactions Prepared Using Nanoscale Reactors

metal	support	temp (°C) at 50% conversion	reaction catalyzed
Au	MnO_2	RT	$CO + O_2 \rightarrow CO_2$
Pd	BaO_x	250	$NO_x + CO \rightarrow N_2 + CO_2$
Rh	ZrO_2/CeO_2	250	$NO_x + CO \rightarrow N_2 + CO_2$
Pt	CeO_2	180	$CO + HC + O_2 \rightarrow CO_2 + H_2O$
Pt	ZrO_2/CeO_2	250	$CO + O_2 \rightarrow CO_2$

The metal-loaded polymer suspension and the metal-loaded emulsion polymer were mixed together. To the mixture was added 15 mL of a 9.57 wt % aqueous emulsion of the quaternary amine-functionalized emulsion polymer B containing dimethylaminoethyl methacrylate (60%), styrene (35%), and divinylbenzene (5%). The polymers flocculated to form a blue mass which was collected by filtration and dried under vacuum at 40 °C overnight. ICP analysis of the filtrate indicated that the flocculated mass contained a molar ratio of Ba:Y:Cu of 1.99:1.0:3.0. Black powdered $Ba_2YCu_3O_{7-x}$ was formed by heating the dried polymer mixture to 350 °C for 1 h, 500 ° for 2 h, and 750 °C for 1 h. The sample contained <0.1% carbon.

Synthesis of Supported Catalysts. A typical synthesis was to form Pt supported on CeO_2. To a flask containing 0.50 g of platinum as aqueous hexachloroplatinic acid was added 261.23 g of a 9.57 wt % aqueous emulsion polymer B. To a second flask was added 303.83 g of the standard 16.45 wt % aqueous emulsion. The polymer was neutralized by the addition of 150 mL of 1.0 M NH_4OH, and 5.0 g of cerium as aqueous cerium nitrate solution was added.

A beaker was charged with 122.11 g of the cerium-loaded polymer, and 30 g of the Pt-loaded emulsion was added dropwise. Water was added to avoid excess thickening of the mixture, and the pH was maintained at 8.0 by the addition of NH_4OH. A flocculated mass formed which was collected by filtration and dried overnight at 110 °C. ICP analysis indicated that the metal ions remained with the polymer mass (1.47 ppm Pt and 0.05 ppm Ce found in 800 mL of filtrate). The dried powder was heated in air to 250 °C for 1h, 350 °C for 1 h, and 500 °C for 4 h.

Similar supported materials can be formed by loading Pt, Pd, Rh, or Au onto the quaternary amine-functionalized emulsion and Mn, Ba, Zr, or Ce onto the standard acrylic-based emulsion. These materials can be used in other strong metal support interactions (SMSI) applications. A representative sampling of the materials formed via this approach are given in Table 1.

Results

ZrO_2. X-ray diffraction patterns collected from several materials indicate that either tetragonal or cubic zirconia is formed when the Zr-loaded emulsion polymer is burned at 600 °C, remarkably in the absence of stabilizers such as yttrium (see Figure 3). The XRD peaks are broad, so the tetragonal and cubic forms cannot be distinguished. Use of the Scherrer equation on these data, however, suggests a crystallite size of 4 nm, while TEM shows a slightly larger primary particle of 5−7 nm. The surface area of zirconia powder prepared at 500 °C via this technique can be as high as 77 m^2/g (see Table 2). Helium pycnometry indicates that the domains have little or no microporosity. Nevertheless, heat treatment of the zirconia at 1000 °C results in the transformation to the thermodynamically favored monoclinic phase. As expected, the addition of

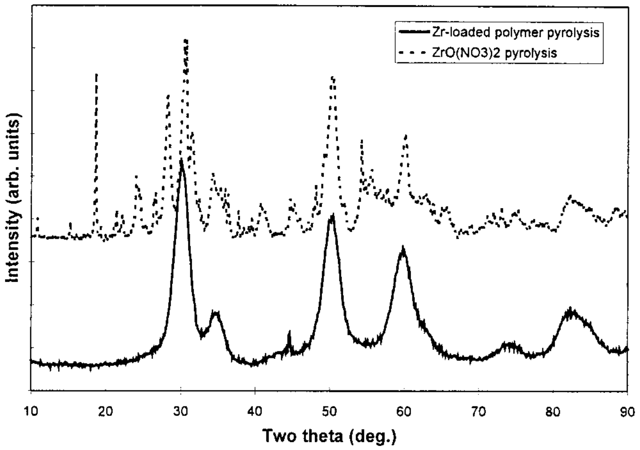

Figure 3. X-ray diffraction patterns for polymer-derived ZrO_2 (solid) and for ZrO_2 derived from the pyrolysis of $ZrO(NO_3)_2$ (dashed). The peak at 44° is an artifact of the sample holder.

Table 2. Surface Area of Polymer-Derived Zirconia after 4 h Heat Treatments

ZrO_2		$Y_{0.03}Zr_{0.97}O_2$	
temp (°C)	surface area (m^2/g)	temp (°C)	surface area (m^2/g)
500	77.2	500	43.8
800	47.7	800	14.2
1000	14.7	1000	0.90

3% yttrium to zirconium results directly in a cubic material.

Treatment of the zirconium-loaded suspension polymer with aqueous sodium hydroxide causes the precipitation of an insoluble zirconium species within the polymer matrix. This procedure serves to free the binding sites of the polymer, so that they can be reloaded with zirconium ion. The regenerative cycle of loading, precipitation, and reloading can be done repeatedly with no apparent damage to the polymer matrix. This procedure enables the yield of inorganic nanocrystals harvested from the polymer matrix to be more than doubled!

CeO_2. TGA experiments were conducted in flowing air. The halcyon removal of the polymer was accomplished even during an isothermal hold at 250 °C (see Figure 4). This proves to be too low a removal temperature for most other systems, indicating a certain catalytic effect of some metallic species on the decomposition of the polymeric material. X-ray diffraction patterns collected from these materials indicate the formation of pure CeO_2.

TEM indicates a uniform particle size of about 7 nm with a dispersion of only a few nanometers. About 80 particles are formed from each 100 nm diameter nanoreactor, and these tend to form as 1–2 micron, raspberry-like agglomerates during the polymer removal process. However, the agglomerates are friable and can be shattered readily with soft media to a primary crystallite size of 7 nm. Uniformly sized CeO_2 is especially useful in polishing applications.[30]

The formation of CeO_2 nanoparticles from insoluble, basic cerium carbonate is an attractive synthetic route. The strong affinity of the emulsion for cerium rapidly destroys the cerium carbonate and causes the release of carbon dioxide during reaction at 65 °C. This route to CeO_2 eliminates the need to neutralize the emulsion, uses a solid salt in place of an acidic cerium solution, simplifies the synthetic process, and precludes the formation of ammonium nitrate as a byproduct.

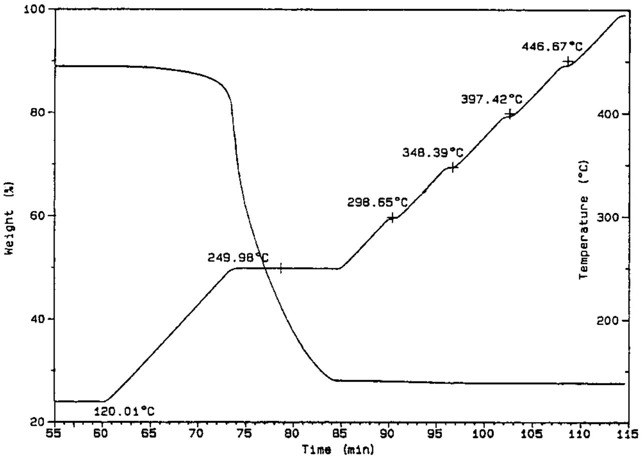

Figure 4. Thermogravimetric analysis of Ce-loaded nanoreactors. The polymer portion is removed smoothly during an isothermal hold at 250 °C in 15 min.

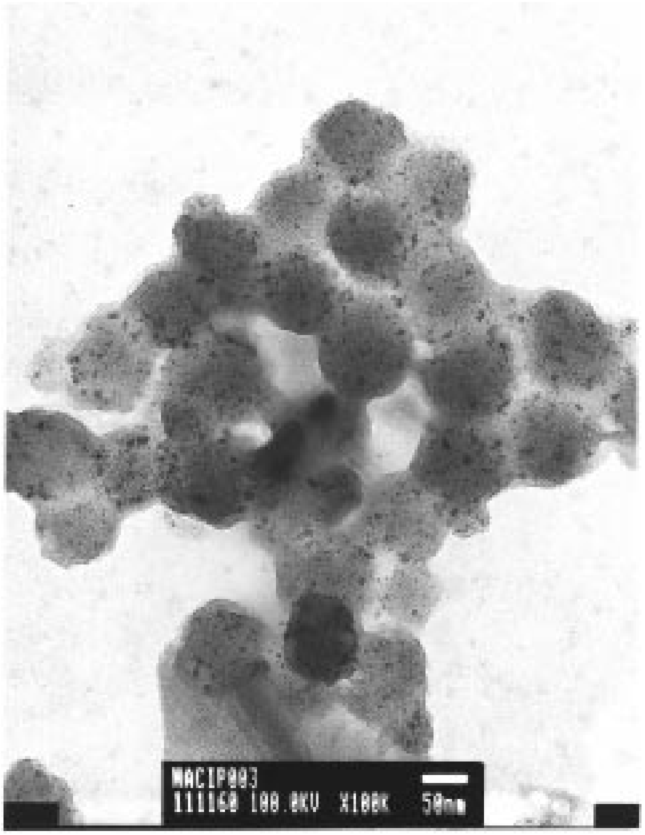

Figure 5. TEM image of CeO_2 formed within a polymer matrix by the addition of peroxide. The binding sites of this polymer can be repeatedly loaded and regenerated in this fashion.

The formation of CeO_2 nanoparticles by the addition of H_2O_2 to metal-loaded emulsion polymer particles is shown in Figure 5. This emulsion does not withstand exposure to strong base, but peroxide treatment serves the same function as the base treatment of zirconium-loaded suspension polymers. Removal of the metal ions

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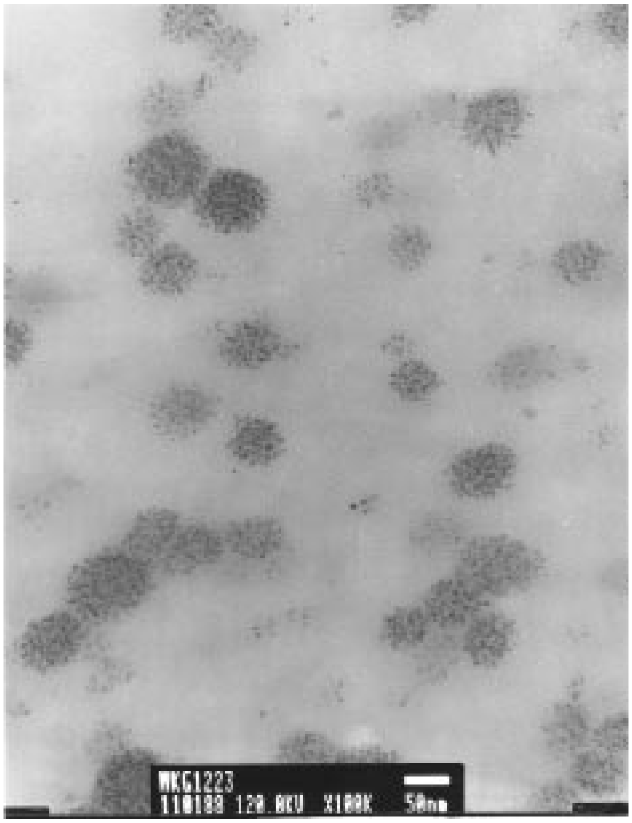

Figure 6. TEM image of CdS particles dispersed within an emulsion polymer particle.

from the binding sites of the nanoreactors should regenerate those sites.

CdS. Transmission electron microscopy shows that a large number of roughly 5 nm diameter CdS particles are produced during the reaction with $(NH_4)_2S$, and the particles are uniformly distributed throughout the polymer matrix (see Figure 6). The aqueous emulsion polymer particle solution develops an intense canary yellow color (absorption $\lambda_{max} = 462$ nm) upon addition of the ammonium sulfide, which corresponds to an average spherical particle size of 5 nm.[31,32] As expected, lowering the cadmium concentration in the nanoreactors results in the formation of smaller crystallites of CdS with a corresponding shift in the absorption spectrum to higher energy.[33] We have observed that ZnS and its solid solutions (i.e., $Zn_xCd_{1-x}S$) can be formed in a similar fashion.

$LiMn_2O_4$. A typical X-ray diffraction pattern is given in Figure 7. Surface area is affected by heat treatment and can be adjusted from 2 to 24 m²/g (see Table 3).

Electrodes for electrochemical testing were fabricated by mixing 80 parts $LiMn_2O_4$, 13 parts Essegri Super S carbon, and 7 parts Atochem KynarFlex 2801-00 poly(vinylidene difluoride) binder prepared as a 10 to 12% solution in 1-methyl-2-pyrrolidinone (NMP). The paste was cast onto 18 μm thick aluminum foil using a doctor blade with a 250 μm gap. The film was dried in a forced-air oven at 80 °C for 1 h and pressed between two polished steel plates at 1.4 MPa for 2 min. Electrode disks, 1.2 cm in diameter, were punched from the film and kept under vacuum at 140 °C for 16 h. Electrochemical testing was carried out in a Swagelock T-fitting constructed of Teflon. The cell was assembled in an argon-filled drybox by placing lithium foil on one stainless steel rod, the $LiMn_2O_4$ electrode on another, and inserting at least one Hoechst Celguard polypropylene separator between the two. A few drops a standard 1 M $LiBF_4$ solution in ethylene carbonate/diethyl carbonate was added, and the electrodes were squeezed together. Additional solvent was added, and the cell was sealed.

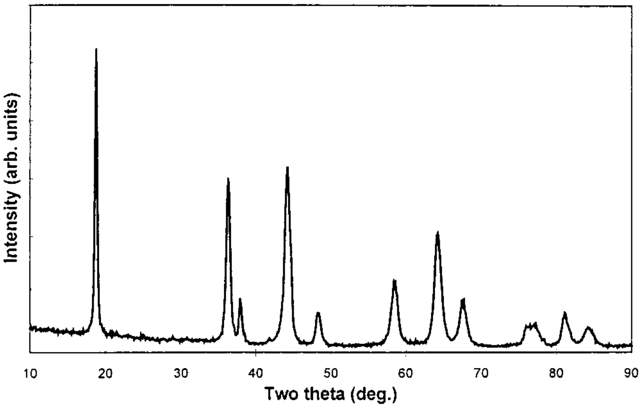

Figure 7. X-ray diffraction pattern for polymer-derived $LiMn_2O_4$.

Table 3. Surface Area of Polymer-Derived $LiMn_2O_4$

temp (°C)	time (h)	surface area (m²/g)	temp (°C)	time (h)	surface area (m²/g)
850	18	2.0	600	18	11.1
800	2	5.3	500	18	12.3
750	2	8.0	375	2	23.5

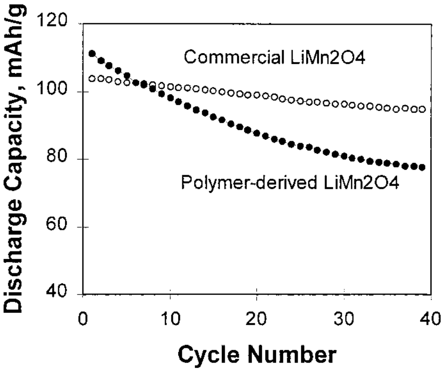

Figure 8. Discharge capacity for polymer-derived $LiMn_2O_4$ (solid circles) and commercially available material (open circles). Cycling was carried out from 3 to 4.5 V at 50 °C with a 5 h charge/discharge rate.

Electrochemical testing was conducted on a battery tester manufactured by Arbin Instruments. Testing was done in a constant current mode from 3 to 4.3 V at 50 °C with a 5 h charge/discharge rate. The polymer-derived cathode materials have electrochemical capacities of 110−120 mAh/g, which compare favorably to the capacity of 100−130 mAh/g of some commercially available materials (see Figure 8).

$Ba_2YCu_3O_{7-x}$. X-ray diffraction showed the material to be quite similar to a commercial sample (see Figure 9). Crystallite size is affected by calcination time and

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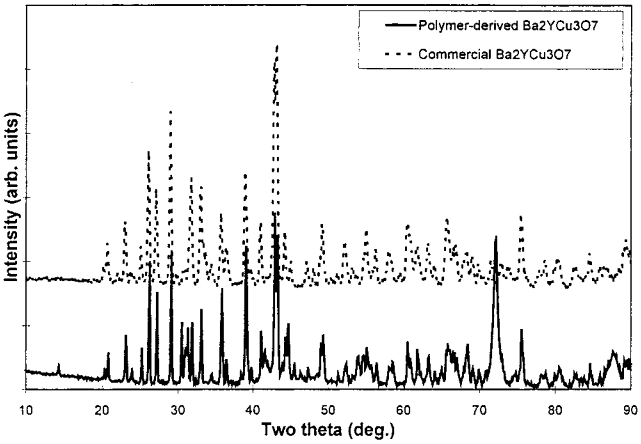

Figure 9. X-ray diffraction patterns for polymer-derived $Ba_2YCu_3O_{7-x}$ (solid) and commercially available material (dashed).

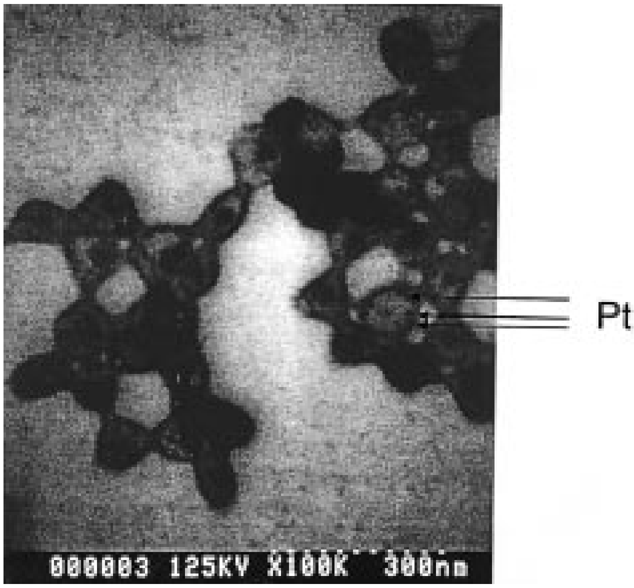

Figure 10. TEM image of Pt supported on CeO_2 domains. Polymer was removed by heating at 350 °C in air for 10 min. Arrows denote some of the Pt particles.

temperature. The powder was pressed into a 0.5 in. diameter pellet and heated in oxygen at 750 °C for 1 h followed by heating at 910 °C for 1 h. The pellet was cooled in air to room temperature, and copper electrodes were connected with indium. The resistivity was measured using a four-point method and found to disappear by 77 K.

Metals Supported on Metal Oxides: Pt/CeO_2. TEM images of Pt supported on CeO_2 are given in Figure 10. Each cluster of domains results from a single nanoreactor, thus the domains shown in the micrograph are the result of two emulsion polymer particles.

Except for the Au/MnO_{2-x} system, all the samples were all evaluated at elevated temperatures using a model reactor to simulate the processing of automotive exhaust gas (see Table 1). The importance of SMSI is clearly demonstrated by the ability of these materials to lower the lightoff temperature for a given reaction or to allow a change in reactant stoichiometry. For example, in CO oxidation, a standard platinum supported on alumina catalyst has a lightoff temperature of 250 °C, while the same amount of platinum supported on ceria prepared using this technology has a much lower lightoff temperature of 180 °C. Similarly, supporting palladium on barium oxide enables this catalyst to reduce nitric oxides at higher oxygen concentrations than is possible when palladium is supported on alumina. This is in agreement with work conducted by Toyota.[34]

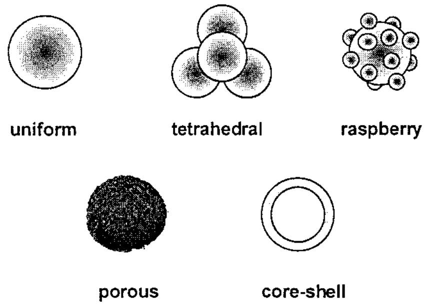

Figure 11. Some potential shapes and structures of emulsion polymers.

We have been able to coat nonconventional catalyst supports, such as metal foils, metal gauzes and metal oxide powders. Owing to the high charge density on the surface of these particles, even perfluorinated polymers can be coated with a monolayer of emulsion polymer particles!

Discussion

The ability to tailor the characteristics and structures of emulsion and suspension polymer particles is a direct result of the extensive research effort that has been carried out over the past 75 years.[35] Numerous techniques have been developed during this time to modify and to control the particle size, degree and type of chemical functionality, and the shape and internal structure of emulsion polymer particles (see Figure 11).[36,37] These modifications were partially motivated by the utility of concentrating metallic species, notably in waste treatment and purification processes. The present work leverages that robust technology but uses it for a completely different purpose. We concentrate metallic species, most notably as stoichiometric mixtures, to promote the formation of valuable inorganic materials. The polymers have become “nanoreactors” to bind metallic species.

The generality of the process makes it quite powerful. Most elements in the periodic table can be loaded into a nanoscale reactor, although we illustrated the technique with a limited number of examples. Our proletarian, cross-linked polymer has weak acid (carboxylic) functionality, and its selectivity generally tracks with the known hydrolysis constants[38,39] of the ionic species in water. The carboxylic groups bind most strongly to

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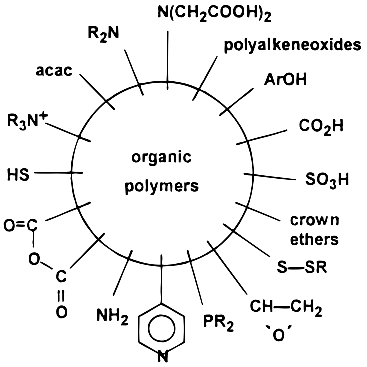

Figure 12. Functional group possibilities for emulsion polymers.

hard Lewis acids, those cations with a high charge-to-size ratio.[40] For example, some Cd^{2+} ($pK_a = 10.1$) migrated off a metal-loaded polymer particle during ultrafiltration, while Y^{3+} ($pK_a = 7.7$) is largely retained.

Functionalization of the particles after polymerization can enhance the selectivity for certain metal species. Readily available alternative functionalities include sulfonic acid and quaternary amine groups, which bind soft acids more effectively. To form $Ba_2YCu_3O_7$, for example, the sulfonic acid containing resin, BPA-2100, is much more effective at binding Ba^{2+}, while the chelating iminodiacetic acid-containing one, IRC-718, is more suited to Cu^{2+} than are the standard carboxylic-containing polymers. When necessary, a variety of other functional groups may be incorporated into emulsion and suspension polymers (see Figure 12). The choice of functional group is dictated by the characteristics of the metal to be bound as well as synthesis cost, polymer loading capacity, and the required pH stability range.

An economic consideration is the loading potential of these nanoreactors. In these atypical emulsion polymerizations, the level of functional monomer can be varied from as little as trace amounts to greater than 90% of the total polymer composition. For example, when acrylic acid is used as the functional monomer, a loading capacity of up to 11 mequiv/g of polymer is possible! In the case of platinum, this could provide a 50 wt % yield after polymer removal.

Within these robust, cross-linked polymer matrixes, chemical reactions can be carried out which cause the metallic species to precipitate within the particle. The oxidation of cerium by peroxide to form CeO_2 is a useful example. The polymer must still be pyrolyzed to harvest the inorganic materials, but this regeneration process increases the economic allure of an already enticing technology.

Since the polymers used in this study all contain oxygen, the greatest utility of this technique is in producing oxides. Nevertheless, we have successfully precipitated sulfides within the polymer matrix. Numerous groups have demonstrated exceptional control over metal−sulfide cluster formation using organic species as templates and as reagents to passivate dangling bonds.[41−44] The present study suffers from the same limitation that the nanoparticles agglomerate, if the organic species is removed.

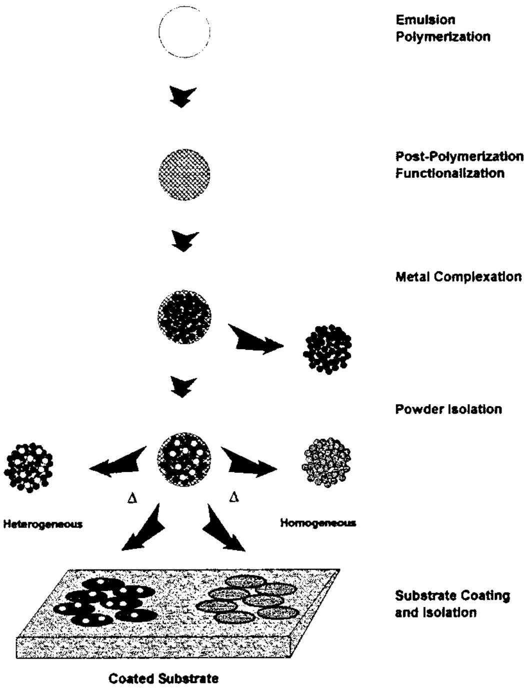

Figure 13. Process flow diagram for forming inorganic films using nanoscale reactor technology.

The number, shape, and size of the resultant inorganic materials is dependent on the nature of the polymer and the metal loading concentration. The pyrolysis of a polymer particle does not produce a single nanoparticle but rather yields a number (30−80) of aggregated particles. The ability to control the particle size and shape is critical to the formation of optical materials such as CdS, where the band gap (i.e. emission color) is tuned by the size and surface characteristics of the material. Quantum confinement effects are observed in other optical materials as well as catalytic, magnetic, and electronic materials.[45−47]

The inorganic phase is generally isolated from loaded polymer particles by simple pyrolysis. The loaded polymer can be isolated by any suitable dewatering technique such as evaporation, flocculation, ultracentrifugation, or spray drying. Removal of the polymer from the dried mass can be achieved at temperatures as low as 150 °C, depending on the choice of monomers and functionality. Remarkably little residual carbon is found (<0.1%) in these *crystalline* inorganic materials.

A powerful alternative to isolating bulk powders is the use of this nanotechnology to coat substrates. Loaded latexes can be painted, dip-coated, wash-coated or even spray pyrolyzed directly onto surfaces. If the

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polymer is removed, a fine coating of inorganic nanocrystals remains. This procedure is especially appropriate for the fabrication of catalysts.

The preparation and use of precious metal loaded emulsion polymer particles as catalysts have previously been described in the literature;[48,49] however, to our knowledge, the formation of mixed metal alloys following the polymer removal process has not been previously demonstrated. For elements that readily undergo reduction during calcination in air (e.g., the platinum group metals), our technology affords a simple method for creating strong metal support interactions which are typically formed by supporting a metal on a reducible metal oxide. We have shown that the material can be deposited directly onto catalyst supports such as 400 cell/in. cordierite honeycomb (see Figure 13). Of course, the metal-loaded polymer can be isolated as a free flowing powder and then formulated with standard catalyst washcoating techniques as well.

The benefits of this technology are diverse and substantial. Materials in aqueous media are easy to handle and have certain safety advantages. The nanoscale dimension of the polymer reactors result in intimate mixing during the metal loading process, rapid loading, and short equilibration times. Proper choice of functional groups offers selectivity and tight control over stoichiometry. Homogeneous products are formed at low reaction temperatures with reproducible, uniform particle shape and size.

Summary

Functionalized, cross-linked emulsion or suspension polymers can be used as reaction vessels for inorganic reactions. The resultant, nanometer-sized inorganic compounds can be isolated, for example, by in situ oxidation with H_2O_2, in situ precipitation with base or $(NH_4)_2S$, or pyrolysis of the loaded reactors. Alternatively, metal-loaded particles can be coated onto a variety of substrates and further treated. This technology provides unique control over stoichiometry, particle morphology, and crystalline phase. Furthermore, reaction temperatures are lower than traditional methods, due to the short diffusion path lengths. Polymeric nanoreactor technology is a versatile tool for the control and formation of inorganic materials.

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