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High-Gradient Magnetic Filtration of Small Particles of Ferro-, Ferri-, and Paramagnetic Catalysts and Catalyst Supports

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Diamagnetic catalyst supports—alumina, silica, carbon, phosphine-functionalized polystyrene—have been rendered ferrimagnetic by deposition of small magnetite (Fe_3O_4) particles using several different procedures. Small (<1–100 μm) particles of these materials, and of ferromagnetic (Raney nickel, cobalt on tungsten carbide), paramagnetic, and antiferromagnetic (copper chromite, manganese dioxide, cobalt molybdate nickel oxide) catalysts have been separated from suspensions in diamagnetic liquids by high-gradient magnetic filtration (HGMF) with varying degrees of efficiency. HGMF appears to have potential as a separation technique for use in a range of catalyst recovery problems to which other separation techniques are not readily applicable.

INTRODUCTION

Efficient separation of small (<100 μm) catalyst particles from liquid suspension often presents a difficult problem, particularly if high filtration rates are required and if it is important not to contaminate the recovered catalyst with diatomaceous earths or other filter aids. Very small particles commonly arise in three situations: when the catalyst is prepared *in situ* by reduction or precipitation; when attrition of larger particles occurs at a significant rate; when an initially homogeneous catalyst is precipitated during the course of a reaction. In some instances, it is possible to separate the bulk of the catalyst from the reaction mixture by conventional filtration or centrifugation, and to ignore the presence of small residual quantities of fine catalyst particles; in others, the loss of catalyst and contamination of product that result from incomplete separation of catalyst and product are unacceptable. This paper describes studies designed to explore the potential of high-gradient magnetic filtration (HGMF) as a technique for the separation of small quantities of fine catalyst particles from liquid suspension.

HGMF depends on the generation and utilization of very high magnetic field gradients (up to ca. 1 kG/μm) to collect ferro-, ferri-, antiferro-, and paramagnetic materials (*1–6*). In a representative separation, a tube loosely packed with a matrix of small-diameter filaments of a ferromagnetic material (e.g., stainless steel wool, steel sponge, or fine steel screen) is positioned between the poles of an appropriate magnet. High magnetic field gradients are generated close to these filaments in the presence of an external field, particularly when the external field is sufficient to saturate them magnetically (>14 kG) (*3*). Qualitatively, these regions of high magnetic field gradient are of approximately the same dimension as the region of the ferromagnetic filament they surround. Stainless steel wool is a particularly effective collector, because its rough and serrated edges generate local field gradients of dimension smaller than those characteristic of the mean filament diameter: these local field gradients are correspondingly more intense than those surrounding relatively smooth regions of the collector filaments. Ferro-, ferri-, and paramagnetic particles suspended in a diamagnetic fluid and passed through the magnetized matrix will experience forces which will tend to capture them in the regions of high field gradient. The efficiency with which these particles are captured depends on the relative magnitudes of the magnetic interactions that hold them in the high-gradient regions close to the matrix filaments, and of the shear forces that carry them with the flowing liquid. Unlike many filtration techniques, high-gradient magnetic filtration is more effective for small particles than for large ones: although the interaction between the particle and the gradient does not increase significantly when the particle extends outside the high-gradient region, the shear forces do increase for large particle sizes. The efficiency of high-gradient filtration is therefore greatest when the diameters of the particles and of the matrix filaments are approximately equal (*4*).

HGMF has been considered previously for mineral benefication (*5*), desulfurization of coal (*7*), separation of oil–water mixtures (*8*), removal of influenza virus from suspension (*9*), water purification (*10*), and removal of circulating boiler scale (*11*).

EXPERIMENTAL METHODS

Absolute ethanol and reagent grade acetone were used without further purification. Tetrahydrofuran (THF) was distilled from a dark purple solution containing sodium benzophenone ketyl and sodium benzophenone dianion. The iron content in the alumina–, silica–, and carbon–magnetite samples was determined by stannous ion reduction followed by permanganate titration (*12*). Additional iron analyses and carbon, hydrogen, bromine and phosphorus analyses were performed by Robertson Laboratory, Florham Park, N. J. Rhodium analyses were performed by Galbraith Laboratories, Knoxville, Tenn. All compositions are reported as weight percent. Particle sizes were estimated qualitatively by examining representative samples by optical microscopy. Gas–liquid paper chromatography analyses were carried out using a Perkin-Elmer Model 990 instrument equipped with flame ionization detectors and a disc integrator.

Materials. The alumina and silica gel used to prepare the supports were 0.05–0.20 mm, activity grade I, Woelm, obtained from Waters Associates, Inc. The carbon used was Eastman Nuchar 190-C charcoal that was cleaned with nitric acid, washed, and dried prior to use (*13*). Ferrous chloride tetrahydrate Mallinckrodt), ferric chloride hexahydrate (Baker), sodium hydroxide (Matheson, Coleman and Bell), palladium chloride (Fisher), rhodium trichloride trihydrate (Engelhard), styrene (Eastman), *para*-bromostyrene (Aldrich), divinylbenzene (Chem. Samples), benzoyl peroxide (Matheson, Coleman and Bell), bromine Mallinckrodt), boron trifluoride (Matheson Gas) and anhydrous stannic chloride (Fisher) were reagent grade and were used without further purification. Cobalt molybdate/alumina, cobalt/tungsten carbide, and nickel oxide/alumina catalysts were commercial samples obtained from Alpha Inorganics. Pharmagel fish protein for suspension polymerization was obtained from Rohm and Haas. Polystyrene–2% divinylbenzene copolymer beads (Merrifield polymer, 200–400 mesh) were obtained from Bio-Rad (Bio-Beads S-X2). Tris(triphenylphosphine)chlororhodium (I) was synthesized by the method of Osborn *et al.* (*14*) and washed thoroughly with degassed ethanol to remove excess triphenylphosphine. Kerosene-soluble and water-soluble ferrofluids—sulfactant-stabilized colloidal suspensions of magnetite having a mean particle size of approximately 5 nm (*15–19*)—were obtained from Ferrofluidics Corp., Burlington, Mass. Stainless steel wool was obtained from All Stainless Corp., Hingham, Mass., and extremely fine stainless steel yarn was obtained from Brunswick Corp., Westboro, Mass.

Preparation of alumina-, and carbon-magnetite supports. These supports were prepared by the deposition of preformed small-diameter magnetite (Fe_3O_4) particles on alumina, silica gel, or activated charcoal, and by precipitation of magnetite in the presence of these supports. Efforts to deposit the magnetite core of a ferrofluid on the supports were only partially successful. Representative procedures for each are outlined.

The preparation of a support composed of 3.7% magnetite on alumina is typical of those based on preformed magnetite. An initially colloidal suspension of magnetite (1 mmol) in water, prepared by treating 0.2 g (1 mmol) of ferrous chloride tetrahydrate and 0.54 g (2 mmol) of ferric chloride hexahydrate in 30 ml of water at 70°C with 0.5 g of sodium hydroxide (*20*), was added to 5.75 g of alumina and the water was removed on a rotary evaporator. The resulting grey powder was stirred in 50 ml of refluxing acetone for 8 hr, collected by suction filtration, and washed with 200 ml of acetone. Some magnetite was lost during the washing. The final alumina–magnetite support contained 3.7% magnetite. Alumina–, silica–, and carbon–magnetite supports containing magnetite were prepared by analogous procedures.

The precipitation of magnetite directly onto a support is illustrated by a preparation of 46% magnetite on carbon. A suspension of 4.6 g of carbon in 300 ml of water containing 2.0 g (0.01 mol) of ferrous chloride tetrahydrate and 5.4 g (0.02 mol) of ferric chloride hexahydrate at 70°C was treated with 5 g of sodium hydroxide in 50 ml of water (*20*). The carbon–magnetite support retained by magnetic filtration (*vide infra*) contained ca. 46% magnetite. This second procedure—precipitation of magnetite into the pores of the support material—was less successful than the first procedure in the preparation of supports having low loadings of magnetite: almost no magnetite appeared to be formed by this procedure when the combined quantity of ferric chloride and ferrous chloride was less than 7 wt% of the support. Deposition of preformed magnetite (*vide supra*) provided the most practical procedure for preparing magnetically responsive supports for magnetite loadings less than 7%.

Alumina, silica, and carbon supports could also be rendered magnetic by deposition of water-soluble or kerosene-soluble ferrofluids. In a typical preparation—that of ca. 3% ferrofluid on alumina—0.24 g of water-soluble ferrofluid, diluted with 8 ml of water, was added to 5.75 g of alumina in a round-bottomed flask. The water was removed on a rotary evaporator. The resulting grey solid was stirred for several hours in acetone, and collected by suction filtration. The colored supernatant contained substantial magnetite (ca. 25% of the original ferrofluid). Further washing with acetone removed only small additional quantities of ferrofluid. Although this procedure provides a method of depositing small magnetite particles on supports, the resulting materials undoubtedly contain substantial quantities of the surfactant originally used to stabilize the ferrofluid (*15–19*), and might require additional treatment—either by extraction or high-temperature oxidation—to remove this adsorbed surfactant. These preparations were not explored in detail.

Preparation of a 6% palladium on carbon–magnetite hydrogenation catalyst. The palladium catalysts were prepared using carbon–46% magnetite particles that were retained by magnetic filtration at a flow rate of 300 ml min^{-1} through the standard filtration apparatus (*vide infra*). This support (0.5 g) in 20 ml of water was treated with a solution of palladium chloride (0.05 g, 0.28 mmol) and HCl (0.12 ml) in 2 ml of water. The mixture was reduced (H_2, 50 psi, 3 hr), collected by suction filtration, washed with three 100-ml portions of water, and dried *in vacuo* to yield a 6% palladium on carbon–magnetite catalyst. Reduction of palladium chloride by basic formaldehyde (*13*) gave a catalyst of comparable activity.

A 6% palladium on carbon catalyst was prepared as a control by the literature procedure (*13*) using activated charcoal in place of carbon–magnetite.

Preparation of magnetically responsive, polymer-bound hydrogenation catalysts. Tris(triphenylphosphine)chlororhodium (I) (Wilkinson's catalyst) was the homogeneous hydrogenation catalyst used in this work. Bromination of the polystyrene–2% divinylbenzene (*21*) using boron trifluoride catalyst yielded a polymer containing bromine on 90% of the benzene rings. *Anal.* Found: Br, 41.1. Bromination using anhydrous stannic chloride as the Lewis acid (*21*) yielded a polymer containing bromine on 95% of the benzene rings. *Anal.* Found: Br, 43.1. Diphenylphosphine-substituted polystyrene beads were prepared from *para*-brominated polystyrene beads (*21*). *Anal.* Found: P, 11.5. Diphenylphosphinomethyl-substituted polystyrene beads were prepared from *para*-chloromethylated polystyrene beads (*21*). *Anal.* Found: P, 6.3. Tris(triphenylphosphine)chlororhodium(I) was anchored to the phosphine resins by the method of Pittman *et al.* (*22*). The exchange reactions failed to go to completion if any unreacted phosphine was present in the phosphine-containing resin or in the Wilkinson's catalyst. *Anal.* Found for the resin containing *para*-diphenylphosphino group (Resin I): Rh, 6.3; for the resin containing *para*-diphenylphosphinomethyl moieties (Resin II), *Anal.* Found: Rh, 6.4.

The resin beads containing the hydrogenation catalyst were rendered magnetic by treatment with freshly precipitated magnetite under an argon atmosphere. Resin beads with the hydrogenation catalyst (0.02 g) were swelled in 5 ml of degassed THF, and the excess THF was quickly removed under argon leaving only swelled catalyst. To the rapidly stirred swollen catalysts beads was added 4 ml of a degassed aqueous colloidal suspension of magnetite (*20*). The resulting mixture was stirred and dried under a stream of argon. The dark orange resin beads were resuspended and stirred in 50 ml of degassed acetone for three hours, then collected by suction filtration and dried *in vacuo*. Both resins I and II gave the same analysis for iron. *Anal.* Found for both: Fe, 0.47.

Preparation of magnetic para-bromiated polystyrene beads by suspension polymerization (resin III). Degassed water (35 ml) containing 0.35 g of Pharmagel fish protein was stirred rapidly in a 100-ml round-bottomed flask using a magnetic stirring bar. A mixture of 10 g (55 mmol) of *p*-bromostyrene, 0.142 g (1.1 mmol) of divinylbenzene, and 0.035 g of benzoyl peroxide was added. Kerosene-soluble ferrofluid (0.2 ml) was added to the resulting emulsion. This mixture was stirred vigorously for 5 hr at 80°C under argon. The resulting amorphous brown beads were triturated in water, and washed in succession with one 2-liter portion of water and five 100-ml portions of THF. These beads released less than 5% of the ferrofluid after magnetic stirring in acetone at 40°C for 5 hr. *Anal.* Found: C, 50.68; H, 4.05; Br, 41.13; Fe, 1.62. Treatment of these magnetic brominated resin beads with either butyllithium or lithium diphenylphosphide removed nearly all of the magnetite from the resin.

Apparatus and procedure for magnetic filtration. The apparatus used for magnetic filtration was a 50-ml buret having ca. 0.95 cm^2 cross-sectional area containing a loosely packed plug (ca. 0.05 g) of 00 or 0000 steel wool or stainless steel wool positioned between the poles of a magnet. Most of the magnetic filtration in this work was carried out using a small permanent magnet with a field strength of 2.5 kG; the remainder employed an electromagnet (6.9-cm pole gap) operating at 10.0 kG, or a Bitter solenoid magnet of bore diameter 5 cm operating at 34.1 kG. For magnetic filtration, ethanol or water was added to the buret until there was about 10 cm of ethanol (water) above the magnet and the steel wool. The ethanolic (aqueous) suspensions of the material to be magnetically filtered were introduced at the top of the buret and the flow rate of the suspension through the magnetized steel wool was adjusted by the stopcock on the buret. The magnetic particles collected on the strands of the steel wool could be recovered at the end of the filtration by lowering or removing the magnetic field.

Hydrogenation and magnetic recovery of catalysts. Hydrogenation by both palladium and rhodium catalysts was carried out in 40-ml centrifuge tubes equipped with magnetic stirring bars and No-air stoppers. Hydrogen was introduced into the reaction vessel by a syringe needle inserted through the No-air stopper.

Hydrogenation by palladium catalysts was carried out by adding 0.5 ml of cyclohexene to a degassed, magnetically stirred, suspension of 0.1 g of the catalyst in 10 ml of ethanol. Hydrogen gas was then introduced into the reaction vessel, and the course of the hydrogenation was followed by glpc. Magnetic recovery of the palladium catalysts was carried out following the standard procedure with a flow rate of ca. 5 ml min^{-1}. The magnetically recovered catalyst was stripped of solvent on a rotary evaporator, weighed, and reintroduced into a clean centrifuge tube for further hydrogenation.

Hydrogenation by magnetic, resin-bound, Wilkinson's catalyst (resins I and II) was carried out by swelling and stirring 0.1 g of the magnetic resin-catalyst in 10 ml of degassed methylene chloride. Cyclohexene (0.5 ml) was added to this stirred suspension, hydrogen was introduced, and the hydrogenation was followed by glpc. Magnetic recoveries of resins I and II were carried out under argon following the standard procedure with a flow rate of 5 ml min^{-1}.

RESULTS AND DISCUSSION

Preparation of ferrimagnetic catalyst supports. Four common heterogeneous catalyst supports—alumina, silica, carbon, and polystyrene–2% divinylbenzene copolymer beads containing a di- or tri-arylphosphine—have been rendered magnetic by treatment with magnetite, either as an aqueous colloidal suspension or as a ferrofluid. An important parameter in determining the utility of these supports is the tenacity with which they retain the adsorbed or occluded magnetite. Deposition of preformed magnetite from aqueous suspension seemed to be the procedure most effective in producing materials which retained their magnetite in use. After preparation, small quantities of magnetite were lost on magnetic stirring in acetone, but this loss became negligible after ca. 10 hr of stirring: at least 80% of the magnetite originally adsorbed was retained. Initial heat treatment could probably improve this performance, but was not tried. Deposition of either water-soluble or kerosene-soluble ferrofluids on the supports produced materials that lost appreciably more (10 to >50%) magnetite by prolonged magnetic stirring in an acetone suspension than the magnetic materials prepared by deposition of aqueous colloidal magnetite. The water-soluble ferrofluid adsorbed more strongly to alumina and silica supports than the kerosene-soluble ferrofluid; the two ferrofluids appeared to adsorb to a comparable degree on the resin beads. Precipitation of magnetite directly onto the support was less effective than adsorption in terms of efficiency of utilization of iron salts: Alumina, silica gel, and carbon appeared to inhibit the formation of magnetite; polystyrene beads had no effect on the formation of the magnetite, but evaporation of the aqueous phase was required to deposit the magnetite on the beads. Efforts to include magnetite in polystyrene beads by polymerization of styrene in the presence of a ferrofluid were only partially successful: although the magnetite was retained adequately in the initial preparation, it was lost on treatment with the strongly basic lithium diphenylphosphide and butyllithium used to introduce phosphine ligands. Thus, this procedure was not useful for preparing "heterogenized" metals, although it might find other applications.

Magnetic filtration. The magnetic filter used in this laboratory work was a small plug of steel wool contained in a 50-ml buret that was placed between the poles

TABLE 1

Efficiency of HGMS for Filtration of Representative Catalysts and Catalyst Supports

Catalyst or support	Description		Suspension flow rate (% retained)[b]			Magnetic field (kG)[c]
	Wt% Fe_3O_4	Size (μm)[a]	5 ml min^{-1}	60 ml min^{-1}	300 ml min^{-1}	
Raney Ni	—[d]	15	100	100	>97	2.5
Co/tungsten carbide	—[e]	20	>99	>99	>99	10
$C/Fe_3O_4/Pd$	43	40	100	100	80	2.5
$C/Fe_3O_4/Pd$[f]	43	2	100	97	78	2.5
C/Fe_3O_4	3.7	3	92	70	34	2.5
C/Fe_3O_4	3.7	<1	<50			2.5
SiO_2/Fe_3O_4	0.8	3	69	40	32	2.5
Al_2O_3/Fe_3O_4	3.5	5	88	65	30	2.5
Copper chromite	—[g]	6	>97			10.0
MnO_2	—[g]	2	40			10.0
Cobalt molybdate/Al_2O_3	—[h]	2	38	33	23	10.0
		2	79	57	37	34.1
NiO/Al_2O_3	—[i]	2	72	56	39	10.0
		2	88	79	71	34.1
Resin-catalyst/Fe_3O_4 (resin I)	0.65	35-75[j]	96	60	30	2.5
Resin-catalyst/Fe_3O_4 (resin II)	0.65	35-75[j]	90	50	20	2.5
Brominated resin/Fe_3O_4 (resin III)	2.2	40	>97	>97	80	2.5

[a] Estimated average particle size.

[b] "% Retained" is the wt% of the catalyst retained in the filter.

[c] External magnetic field strength.

[d] Raney nickel is ferromagnetic.

[e] Cobalt-coated tungsten carbide (20% w:w Co).

[f] Produced from the sample used in the immediately preceding row by grinding to reduce the average particle size.

[g] Copper chromite is paramagnetic; manganese dioxide is normally antiferromagnetic.

[h] Cobalt molybdate on alumina: 3% MoO_3.

[i] 20% NiO.

[j] Particle size range given for the commercial Bio-Beads resin used as starting material.

of a magnet. Both steel wool and stainless steel wool of varying coarseness were used as the ferromagnetic matrix of the filter. Steel wool and stainless steel wool appeared to be comparably effective as the filter material in HGMF. The apparatus used for large-scale HGMF has been described (*2*).

The behavior of a variety of catalysts and catalyst supports in magnetic filtration was determined and typical results are summarized in Table 1. External magnetic field strengths from 2.5 to 34 kG and rates of suspension flow through the filter between 5 and 300 ml min^{-1} were tested with the apparatus used. Relatively low magnetic fields were used intentionally in most of this work, because they are more economically generated, and because they provide a clearer evaluation of the limits on the technique, than do very high fields. At these relatively low magnetic fields, filtration was significantly more effective at low than at high flow rates. Only in the case of the ferromagnetic Raney nickel and cobalt/tungsten carbide is magnetic recovery of the catalyst essentially quantitative at flow rates as high as 300 ml min^{-1}. Magnetic filtration of ferrimagnetic solids (e.g., magnetite) or diamagnetic supports containing substantial ferrimagnetic material (e.g., carbon–46% magnetite) is easily accomplished at field strengths less than 5 kG and at moderately high suspension flow rates. Magnetic filtration of paramagnetic solids is more difficult. Copper chromite was retained essentially quantitatively at low flow rates; manganese dioxide, nickel oxide, or cobalt molybdate could not be quantitatively retained under any conditions we explored.

To demonstrate the utility of HGMF in recovering small particles produced by attrition from larger ones, the carbon–43% magnetite–palladium catalyst with an average particle size of 40 μm was reduced to an average particle size of 2 μm by grinding. Magnetic recovery of both the coarse and the fine particles was quantitative at low flow rates and comparable although not quantitative at faster flow rates. Magnetic stirring of particles of the 3.7% magnetite on carbon support overnight produced extremely fine particles with an average size of less than 1 μm. These particles were retained less efficiently (less than 50%) than the larger (3 μm) particles of the same support (92% retained). The observation that the recovery of this low-magnetite support is less than quantitative may reflect its magnetic properties, or it may indicate that the deposition of preformed magnetite onto the support produces a less uniform distribution through the support than does formation and precipitation of magnetite in the presence of the support.

The effect of magnetic filtration on the catalytic activity of a supported palladium hydrogenation catalyst. Reduction of palladium chloride by hydrogen in the presence of a carbon–magnetite support yielded a 6% palladium on carbon–magnetite (46%) catalyst that was catalytically active and magnetically filterable. The activity of this carbon–magnetite–palladium catalyst system in hydrogenation of cyclohexene was initially approximately 80% that a control sample of palladium on carbon, prepared using similar procedures. After 1 cycle of hydrogenation and magnetic filtration, its activity dropped to 85% of the original activity, and stayed essentially constant over 4 cycles of hydrogenation and magnetic filtration. An additional 20 cycles of magnetic filtration alone resulted in less than 10% loss of activity. The palladium–carbon control catalyst was not retained in the magnetic filter under these conditions. The activity of tris(triphenylphosphine)chlororhodium (I) immobilized in phosphinated polystyrene resins containing magnetite was 50–90% that of control samples in which no magnetite was included. These catalysts appeared to lose approximately 30% of their activity on one magnetic filtration. The origin of this loss in activity was not explored, but may simply reflect oxidation in handling the sample. Thus, it appears that the presence of magnetite does not degrade the catalyst performance in this simple hydrogenation system. Other catalyst systems, particularly those used in high-temperature oxidations, might be affected differently. The most significant implication from the observation that the Pd/C/Fe_3O_4 and Pd/C catalysts show similar activity is that the deposition of magnetite on the support does not decrease the surface area available to the palladium and accessible to the substrate in an important way.

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