

Magnetic Filtration of Small Heterogeneous Catalyst Particles. Preparation of Ferrimagnetic Catalyst Supports

High-gradient magnetic separation (HGMS) provides a very effective method of removing small (1–100 μ) particles of certain heterogeneous catalysts from reaction mixtures. The preparations of magnetically responsive carbon-, silica-, and alumina-magnetite supports are described, and the behavior of these supports in magnetic filtration is summarized.

Large-scale processes involving heterogeneous catalysis often require that the recovery of catalyst from product be very efficient, both to minimize loss of expensive catalyst components and to avoid contamination of products with catalyst. Large catalyst pellets can normally be retained in reactors or separated from products by conventional filtration or centrifugation techniques. The recovery of small catalyst particles—either used intentionally or formed by attrition from larger particles—is presently inefficient and expensive. Here we wish to report a general technique for the preparation of magnetically responsive, ferrimagnetic, supported heterogeneous catalysts, and to illustrate the usefulness of high-gradient magnetic separation (HGMS) techniques for separating these as well as ferromagnetic and certain paramagnetic catalyst particles from suspension.

Ferro-, ferri-, and paramagnetic solids suspended in a diamagnetic liquid move in a magnetic field gradient toward regions of high magnetic field. The magnetic force acting on a particle is proportional, *inter alia*, to the magnitude of the gradient. HGMS depends on techniques, developed at the M.I.T. National Magnet Laboratory, which permit the generation of very high magnetic field gradients using very simple apparatus (Kolm et al., 1971; Kolm, 1972; Oberteuffer, 1973, 1974; Kelland, 1973; deLatour, 1973; Trindade and Kolm, 1973; Warren et al., 1969; Kaiser et al., 1971). Typically, in the small-scale experiments carried out in this work, separations were carried out using a 50-ml buret containing a loosely packed plug (ca. 0.05 g) of 00 or 0000 steel wool, positioned between the poles of a magnet having 2.5–10-kG field strength. Large magnetic field gradients are generated close to the steel wool strands by their magnetization, and these high gradient regions act as efficient "collectors" for magnetic particles suspended in a liquid that is passed through the plug.

Magnetic filtration of ferromagnetic and ferrimagnetic solids (e.g., Raney nickel and magnetite, *vide infra*) is easily accomplished at field strengths less than 5 kG. Magnetic filtration of paramagnetic solids is more difficult: very intense magnetic field gradients, moderately large paramagnetic susceptibilities, and a matching of the diameters of the particles and the steel wool strands is required (Oberteuffer, 1974). Using field strengths sufficient to saturate steel (≥ 12 kG), gradients as great as 1 kG/ μ may be generated in a HGMS filter, if the strands of the steel wool are sufficiently fine: these gradients will trap many paramagnetic particles. Magnetic particles collected during a magnetic filtration are easily released at its conclusion by lowering the field.

HGMS is peculiar among filtration techniques in being more effective for small particles than for large ones: qualitatively, the most efficient separations occur for particles whose size matches the dimensions of the regions of high magnetic field gradient in the filter. For such particles, HGMS is probably the most efficient filtration technique known. For example, magnetite particles having diameters

between $<1 \mu$ and 60 μ can be completely separated from an aqueous suspension flowing at 100 ml/min through a $0.95 \text{ cm}^2 \times 2 \text{ cm}$ 0000 steel wool collector in a 2.65-kG field.

A representative magnetically responsive heterogeneous catalyst was prepared by precipitating fine particles of magnetite (Fe_3O_4) into the pores of activated charcoal and using this modified charcoal as the support for a palladium hydrogenation catalyst. A suspension of 4.6 g of charcoal (Eastman Nuchar C 190-N) in 300 ml of water containing 2.0 g (0.01 mol) of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 5.4 g (0.02 mol) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ at 70° was treated with 5 g of NaOH in 50 ml of water (Craik and Griffiths, 1958). The resulting finely divided black solid was separated, resuspended in ethanol (80 ml), and filtered twice magnetically using the apparatus described previously at a field strength of 2.65 kG. The material passing through the filter was discarded, and the material retained in the second filtration was collected and dried. Analysis of this material indicated that it contained approximately 47% by weight Fe_3O_4 , and had an average particle size of 40 μ (measured qualitatively using optical microscopy). Carbon, silica gel, or alumina supports with low magnetite loadings were prepared by deposition of preformed suspension of magnetite onto the supports. For example, 0.5 mmol of Fe_3O_4 prepared by treating 0.5 mmol of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 1.0 mmol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 20 ml of water at 70° with 0.25 g of NaOH in 5 ml of water was added to 11.5 g of carbon, and the water was removed by evaporation. The resulting 4% Fe_3O_4 -carbon was ground to a fine powder (average particle size ca. 3 μ), washed with saturated aqueous NH_4Cl solution and water, and dried. Our experience in magnetic filtration of these supports is summarized in Table I. In this table, supports that separate completely ($>95\%$) using 00 or 0000 steel wool, high flow rates, and low fields are indicated by ++; those for which complete separations are possible, but which require high fields and low flow rates, by +; those for which only partial separation was achieved, even with the best conditions used, by -; and those for which no filtration took place by --. Thus, for example, the C/ Fe_3O_4 /Pd catalyst was quantitatively retained at flow rates of $\leq 5 \text{ ml min}^{-1}$, $>97\%$ retained at 60 ml min^{-1} , and 78% retained at 300 ml min^{-1} using 0000 steel wool in a 2.65-kG field. Under the same conditions the 4% Fe_3O_4 -carbon support was 92% retained at flow rates of $<5 \text{ ml min}^{-1}$, 70% retained at 60 ml min^{-1} , and 34% retained at 300 ml min^{-1} .

An aqueous suspension of 0.5 g of the C/ Fe_3O_4 (46%) support in 20 ml of water was treated with a solution of PdCl_2 (0.05 g, 0.03 mmol) and HCl (0.12 ml) in 2 ml of water, reduced (H_2 , 50 psi, 3 hr), collected, washed with water, and dried. The activity of this C/ Fe_3O_4 /Pd catalyst system in hydrogenation of cyclohexene was initially approximately 80% that of a control sample of Pd/C, prepared using similar procedures. After one cycle of hydrogenation and magnetic filtration, the activity dropped to 85% of the original activity, and stayed essentially constant over four cycles of hydrogenation and magnetic filtration. An

Table I. Efficiency of HGMS for Filtration of Representative Catalysts and Catalyst Supports

Catalyst or support	Description		Separation characteristics		
	Wt % Fe ₃ O ₄	Size, μ	Ease ^b	% Re-tained ^c	Field, kG ^d
Raney Ni	<i>e</i>	15	++	100	2.5
C/Fe ₃ O ₄ /Pd	46	40	++	100	2.5
C/Fe ₃ O ₄ /Pd	46	2	++	100	2.5
C/Fe ₃ O ₄	4	40	++	>97	10
SiO ₂ /Fe ₃ O ₄	4	3	++	>97	10
Al ₂ O ₃ /Fe ₃ O ₄	4	3	++	>97	10
Copper chromite	<i>f</i>	6	+	>97	10
Manganese dioxide	<i>f</i>	2	—	>30	10
C	Diamagnetic	2	—	0	10
SiO ₂	Diamagnetic	2	—	0	10
Al ₂ O ₃	Diamagnetic	2	—	0	10

^a Estimated average particle size. ^b A qualitative estimate of the efficiency of the filtration: see the text for a discussion. ^c "% Retained" is the weight % of the catalyst retained in the filter. ^d External magnetic field strength. ^e Raney nickel is ferromagnetic with permeability estimated to be that of nickel metal: $\mu = 250-300$ (Kersten, 1931, 1951). ^f Copper chromite and manganese dioxide are paramagnetic. The paramagnetic susceptibility, χ , of the latter is approximately 2280×10^6 cgs (Föex, 1957).

additional 20 cycles of magnetic filtration alone resulted in <10% loss of activity. The Pd/C control catalyst is not retained in the magnetic filter under these conditions.

To demonstrate the utility of HGMS in recovering small particles produced by attrition from larger ones, this C/Fe₃O₄/Pd catalyst was reduced to an average particle size of 2 μ by grinding. Magnetic recovery of these particles was quantitative under the same conditions used to recover the larger ones.

The applicability of HGMS in recovering other types of magnetically responsive catalysts was explored briefly. A ferromagnetic catalyst (Raney nickel) separated, as expected, very easily. The effectiveness of filtration of paramagnetic catalyst was lower, and depended on the magnetic

susceptibility of the catalyst. Copper chromite separated quantitatively, how be it at low flow rates, at 10 kG external field; manganese dioxide could not be completely retained in the filter under any conditions we explored.

High gradient magnetic separation has the potential to provide a useful filtration method for a wide range of catalyst types: naturally ferromagnetic, ferrimagnetic, and moderately or strongly paramagnetic materials, and normally diamagnetic catalysts modified to be ferro-, ferri, or paramagnetic. Its unique aptitude for separations involving small (<100 μ) particles suggests utility for a range of catalyst recovery problems to which no other filtration technique is easily applicable. The utility of those catalyst systems that require incorporation of magnetite or other ferri- or ferromagnetic components to be separable is clearly determined in part by the influence of these components on the activity of the catalyst.

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