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Agglomerated carbon based phases for anion exchange chromatography

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ABSTRACT

Carbon-clad zirconia particles have been converted into ion exchange media through addition of charged latexes after covalent modification of the carbon surface. A variety of methodologies were investigated to introduce a negative charge to the carbon surface in the form of either sulfonate or oxygen containing functionalities (e.g. hydroxyl or carboxylate). Short analytical sized columns (35 mm × 4 mm I.D.) were packed with modified 2 μm nonporous carbon clad zirconia. Addition of the latex particles after the initial packing produced almost double the efficiency for the system compared to adding the latexes before packing. The optimized system could separate mixtures of common inorganic anions with efficiencies greater than of 41,000 plates/m and retention reproducibility of <2% RSD.

1. Introduction

Agglomerated materials for IC were first reported and patented by Small and Stevens in 1975 [1–3]. These phases revolutionized the analysis of inorganic anions such as fluoride, chloride, nitrate and sulfate. The early agglomerated phases were based on 15–40 μm polystyrene divinylbenzene particles whose surface were made anionic by sulfonation. To make the phases anion-exchanging, polycationic latexes were electrostatically bound to the anionic surface. The quaternary amine functionality of the latexes act as the anion exchange sites. Since latexes can be made easily, cheaply and homogeneously in large scale, this insures that reproducible columns can readily be manufactured [4]. Agglomerated columns provide higher efficiencies than microporous exchangers due to reduced resistance to mass transfer [5].

Although more than 25 years have elapsed since the original patent, agglomerated polymeric particle based ion exchangers still comprise a significant portion of the stationary phases used in modern IC. Other polymer and latex compositions have been introduced to modify selectivity [5–7]. Also, the cross-linking within the polymer core particle has been increased from 2–5% to ≥50% to increase the mechanical strength of the particles and reduce their swelling in organic solvents [8]. This increased mechanical strength has enabled reduction of the agglomerated particle size to 7 μm to improve efficiency. However, such particles are still much larger and of lower efficiency than the silica-based chromatographic particles used in RPLC and other HPLC modes (2–5 μm). Thus, IC columns are long (≥15 cm) compared to RPLC, resulting in slower speed of separation.

Standard silica based stationary phases typically have greater efficiency and mechanically stability than polymers for small molecules. To convert silica bonded phases into ion exchange phases, columns can be dynamically coated with cationic [9] and amphoteric [10] surfactants. However, the columns are typically greater than 15 cm in length, resulting in analysis times of ≥30 min. In contrast, Pelletier and Lucy separated 7 ions in less than 1 min using a 1.3 cm × 4.6 mm I.D. column coated with the cationic surfacatant didodecyldimethylammonium bromide (DDAB) [11]. As particle size is proportional to efficiency as governed by the van Deemter equation [12], 1.8 μm C_{18}-silica particles were utilized to increase efficiency, and thus reduce the length of the column needed to separate the analytes. A very short column (≤2 cm) was also required to maintain an operating pressure that a regular HPLC pump could handle (<4.1×10^4 kPa, 6000 psi). To reduce the backpressure requirements, separations have also been performed on surfactant coated silica monoliths in both the capillary [13,14] and analytical formats [15–18].

Although surfactants provide a cheap and easily prepared dynamic coating, surfactant coated columns require a significant break-in period and experience gradual losses in column capacity [19]. Also, organic additives cannot be added to the eluent since they can remove the surfactant from the column.

As an alternative to charged surfactants, ionic polymers [20] and ionic latexes [21,22] have been added to silica media to create IC columns. The combination of the silica backbone with latexes yields highly efficient separations, with a quick start-up time and highly reproducible retentions. However, silica column degrade at high pH (>8) due to silica dissolution [23]. As a result, silica based columns

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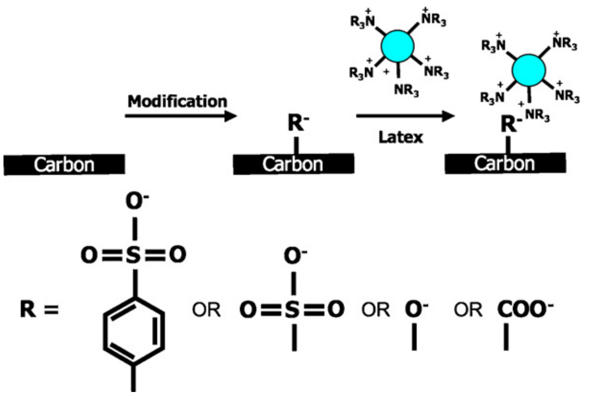

Fig. 1. Preparation of agglomerated phases for IC using carbon-clad zirconia.

are limited to weak organic acid eluents that produce higher backgrounds and yield poorer detection limits than IC eluents such as carbonate/bicarbonate and hydroxide.

Carbon-clad zirconia is a phase that is mechanically strong and that allows the use of eluents that span the entire pH range (0–14). Our lab has demonstrated the use of surfactant coatings on carbon based particles [24]. Pure carbon packings lacked mechanical strength [24], although this instability may have derived from poor column packing by the manufacturer [25]. However, carbon-clad zirconia was shown to be a promising new support for IC. Surfactant coatings provided good separations, but experienced long break-in times and gradual capacity loss. Covalent introduction of arylamine anion exchange sites to carbon-clad zirconia phases yielded stable retention in IC, but were incompatible with hydroxide eluents and exhibited low capacity [26].

Herein agglomerated phases are explored as a means of introducing ion exchange characteristics to carbon-clad zirconia. The first step in preparing an agglomerated carbon clad zirconia is to introduce a negatively charged functionality (R^-) onto the carbon surface (Fig. 1). Diazonium chemistry and other techniques are explored. Positively charged latexes are then added to convert the particles into agglomerated anion exchangers (Fig. 1).

2. Experimental

2.1. Materials and reagents

Methanol (Fisher Scientific, Ottawa, ON, Canada) and tetrahydrofuran (EMD Chemicals, Gibbstown, NJ, USA) were of HPLC grade. Dichloromethane (Fisher) and chloroform (Fisher) were of Optima grade. Pyridine (Fisher) and 1,2-dichloroethane (Fisher) were of analytical grade. Anhydrous ethanol (Fisher), concentrated nitric acid (Caledon Chemicals, Georgetown, ON, Canada), chlorosulfonic acid (99%, Sigma–Aldrich, Oakville, ON, Canada), sulfanilic acid monohydrate (Sigma–Aldrich) and potassium permanganate (Sigma–Aldrich) were used as received. All water was 18 MΩ nanopure water (Nanopure Water System, Barnstead, Chicago, IL, USA) and was filtered through 0.22 μ nylon membrane filters (Millipore, Bedford, MA, USA) prior to use. All non-aqueous solvents were filtered through 0.2 μm Fluoropore filters (Millipore). All inorganic chemicals were reagent grade or better. Iodide (BDH, Toronto, ON, Canada), sulfate (BDH), nitrite (99.9+%, Sigma–Aldrich), bromide (Sigma–Aldrich), fluoride (Sigma–Aldrich), chloride (EMD) and nitrate (EMD) were used as their sodium salts. Molecular sieves (8–12 mesh, Acros Organics, NJ, USA) were heated to 250 °C in a moisture free oven overnight prior to use. A suspension of latex particles (polyvinylbenzylammonium-divinylbenzene, AS12A, Dionex, Sunnyvale, CA, USA) was used as received.

Carbon-clad zirconia particles (3 μm, porous (30 m^2/g, batch #65-175 and #69-119); 2 μm, non-porous (0.7 m^2/g, batch #70-250); ZirChrom, Anoka, MN, USA) were used as received. The carbon-clad zirconia particles were kept in their original container in a desiccator until just prior to use. The 3 μm carbon-clad zirconia particles were from batch #65-175, used unless otherwise stated.

2.2. Reaction vessel cleaning

Glass vials (28 mm × 57 mm, Fisher) used to contain the modification reactions were cleaned with piranha (1 part 30% H_2O_2, 3 parts sulfuric acid), rinsed with an abundance of filtered 18 MΩ nanopure water, dried in a moisture free oven (≥140 °C), and allowed to cool before use. A new, clean vial with a new screw cap top was used for every modification. The reactions involving nitric acid used 200 mL round-bottom flasks, cleaned with copious amounts of water, ethanol and methanol, dried in a moisture free oven, and allowed to cool before use.

2.3. Diazonium modification of carbon-clad zirconia

Carbon-clad zirconia was modified using *in situ* generated diazonium ions as described previously [26]. In brief, sulfanilic acid and two equivalents of HCl were dissolved in 8 mL of 36% ethanol and sonicated for 10 min. Then, 0.1 g of carbon-clad zirconia particles and a magnetic stir bar were added. The contents of the vial were stirred, sonicated for 10 min, and the vial placed into a 60 °C oil bath with stirring. An equivalence of an aqueous sodium nitrite solution was added dropwise over 1 min, darkening the solution yellow and producing bubbles (**Caution**: nitrogen gas is evolved rapidly). The vial was capped and the contents of the vial were allowed to react. The vial was then placed on an ice bath. The particles were collected on a 0.22 μm nylon filter and washed with a series of solvents ranging in polarity – specifically water, ethanol, THF, acetone, methanol and then with various water/methanol blends. Washing continued until the filtrate was clear and colorless. The particles were transferred to a clean vial and rotovapped. The vial was placed into a sonic bath for a few seconds to free the particles from the vial walls prior to being sent for analysis. Scale up of the synthesis was accomplished by increasing the solvent and reaction components 20-fold, with care taken during the sodium nitrite addition.

2.4. Chlorosulfonic acid modification of carbon-clad zirconia

A known amount of carbon-clad zirconia (0.1 or 2.0 g) was added to a cleaned vial containing a stir bar and 10 mL of either chloroform, dichloromethane, 1,2-dichloroethane or pyridine. The vial was then sonicated for 10 min and stirred for 20 min. A known amount of chlorosulfonic acid (0.1–0.5 mL) was added slowly using a syringe (**Caution**: chlorosulfonic acid reacts violently with water). The reaction was allowed to proceed for a set period of time (15 min to 30 h). The particles were collected on a 0.2 μm Fluoropore filter and washed with the reaction solvent, water, water/methanol blends, ethanol, THF and acetone. The particles were periodically agitated with fine streams of solvent during filtration. If the filter became stained during filtration, the particles were transferred to another Fluoropore filter and rinsed with methanol and water. Washing continued until the filtrate was clear and colorless. The particles were transferred into a clean vial using methanol, sonicated, decanted, and then placed on a rotovap (35 °C) to remove residual methanol. To ensure the particles were free from the vial walls, the vial was sonicated for a few seconds before particles were sent for analysis. Scale up of the synthesis was accomplished by increasing the solvent and reaction