



Synthesis and characterisation of mesoporous silica phases containing heteroatoms, and their cation exchange properties. Part 5: Cation exchange isotherms, and the measurement of radioisotope distribution coefficients, for an MCM-22 phase containing aluminium

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ABSTRACT

Cation exchange isotherms were constructed for the replacement of Na cations by Li, K, Rb, Cs, NH₄, Mg, Ca, Sr, Ba, and Al from a well characterised MCM-22 phase which contained aluminium as a heteroatom. Thermodynamic assessment of the isotherms enabled the construction of a selectivity series. Comparisons, including standard free energy values, have been drawn to similar results measured for other MCM-41 phases and some high-silica zeolites. This work additionally describes studies on the MCM-22 phase to examine its potential ability to scavenge radioisotopes from various solutions as simulants of those found in nuclear waste. The isotopes studied were 241-Am, relevant to spent nuclear fuel, and 137-Cs, 57-Co, 51-Cr, 59-Fe, 54-Mn, 89-Sr, 65-Zn present in nuclear wastes as fission products, from neutron activation in nuclear installations, and arising from medical uses.

Measurement of distribution coefficients enabled the construction of selectivity series which demonstrated the versatility of the phases to scavenge specific isotopes.

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1. Introduction

This is the final communication in a series describing the synthesis, characterisation and cation exchange properties of mesoporous phases of MCM type [1–4]. Part 2[2] of the series concentrated on a formal thermodynamic approach in which cation isotherms, for MCM-41 phases, were obtained and interpreted to provide free energy values from which a cation selectivity series was constructed.

Here a similar series of experiments have been carried out on a sodium MCM-22 phase which had been synthesised to contain an aluminium heteroatom [denoted as Al(30)MCM-22]. It was fully characterised by PXRD, MASNMR, and nitrogen porosimetry. Analysis was carried out by atomic absorption spectroscopy and thermogravimetry.

Cation isotherms have been obtained for the replacement of the sodium initially present in the solid phase by the following cations: Li⁺, K⁺, Rb⁺, Cs⁺, Ca²⁺, Sr²⁺, Mg²⁺, Ba²⁺, NH₄⁺, and Al³⁺.

The results of a thermodynamic interpretation of the isotherms were compared to similar ones from MCM-41 phases and to high-silica zeolites. The relationships of the results to the structures of the cation exchange media, and the properties of the cations involved, have been considered.

This work also examines the ability of the MCM-22 phase to scavenge trace quantities of radioisotopes from various solutions. The isotopes studied were 241-Am, for its relevance to the treatment of spent nuclear fuel (241-Am also has a wide use in smoke detectors), and 137-Cs, 57-Co, 51-Cr, 59-Fe, 54-Mn, 89-Sr, 65-Zn which are present in aqueous nuclear wastes as fission products, from neutron activation in nuclear installations, and wastes arising from medical uses.

The aqueous media studied were those used in Part 4 [4] of this series: 0.1 M NaNO₃, 0.1 M NaNO₃/NaOH, and nitric acid (0.1 and 1 M) to act as simulants for common nuclear waste streams. 57-Co uptake tests included those in the presence of complexants used in decontamination solutions.

Distribution coefficients were used to quantify the efficiency of uptake for the isotopes under the conditions defined above. The results were compared to those found for MCM-41 phases which had been synthesised with Al, B and Zn as heteroatoms and with varying pore sizes from the use of detergent templates with different chain lengths [1].

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2. Experimental

2.1. Synthesis

All chemicals were the purest available from Aldrich or Fisher Scientific and deionised water was used throughout. A solution of NaAlO₂ in NaOH was prepared and stirred until it was homogeneous. The organic template hexamethylenimine (HMI) was added and the solution again stirred to achieve homogeneity. Silica gel (60 Å) was then added and the resulting gel aged for 30 min. with gentle stirring at ambient conditions. The gel was transferred to a magnetically stirred autoclave and heated autogenously for 168 h at 423 K.

The resultant solid was recovered by gravity filtration on a sintered glass (porosity 3) funnel whilst hot, with the last portions of the supernatant being removed by applying a vacuum to the filter. This latter step minimised the hydrolysis of any unreacted silica arising in the subsequent washing by deionised water close to its boiling point on the filter.

The solids were pulled dry under vacuum and dried overnight at 303 K in a thermostatically controlled oven. Finally, the solid was ground in a mortar and pestle and stored in a polythene bottle.

The molar gel formula used was; SiO₂:0.8, Na₂O:0.50, HMI: 40.07, H₂O:0.0333 with SiO₂:Al₂O₃ = 29.97.

(Note – attempts to introduce higher amounts of aluminium into MCM-22 were unsuccessful – as were all experiments designed to incorporate boron).

2.2. Characterisation

All characterisations were carried out on calcined samples previously equilibrated in desiccators over saturated potassium chloride solution.

Elemental analyses were determined by AAS and water contents were obtained by heating to constant mass at 432 K. Thermogravimetry (MettlerTA3000) monitored the template decomposition for all materials using a heating rate 2 K/min under flowing nitrogen (10 mL/min).

PXRD analysis was carried out using a Siemens D5000 diffractometer (Cu K α , 40 mA, 40 kV, 2 θ 1–40° step size 0.02°). Porosimetry at Crosfield Limited (now PQ) Warrington, Lancs used a Micrometrics Instrument Corporation ASAP 2405.

MASNMR experiments (27-Al) were performed at Durham University, using the same conditions as before [1], on a Varian Unity Plus 300 instrument, and fitted using Systat Peakfit v4.11 software.

2.3. Construction of cation exchange isotherms

The MCM-22 phase was first isotopically labelled with 22-Na using a 2 M 22-NaOH solution which ensured that any H₃O⁺ cations arising from breakdown products from the template, or from silanol groups, were neutralised. Isotherms were constructed, using the method of isotope dilution, by placing the isotopically labelled exchangers in contact with Li, K, Rb, Cs, NH₄, Mg, Ca, Sr, Ba, and Al salt solutions and monitoring the release of 22-Na into solution from the solid phase.

Nitrate salts (AR grade or laboratory reagents of +99% purity) at total normality (T_N) = 0.15 were used throughout in contact with aliquots of 0.05 mg solid and batch factors of 200 mL/g. All radiometric measurements used a Canberra Packard 1900CA Tri-Carb LSC spectrometer with a dedicated 22-Na channel and Aquasafe 300™ scintillator solution (Zinsser Analytic). Preliminary kinetic experiments had established the times needed to reach equilibrium. Full details of the methodology used for both kinetic and equilibrium experiments have been described by Dyer et al. [5,6].

Forward and reverse binary cation exchange isotherms were obtained by plotting the measured equivalent fractions of the incoming cation in solution (A_s) and solid (A_c) phases at constant total normality (T_N) [7]. The A_c values were calculated from capacities determined by measurement of the 22-Na uptakes in the initial isotopic labeling of the MCMs (i.e. by isotope dilution).

2.4. Estimation of radioisotope distribution coefficients

2.4.1. Materials

The Al(30)MCM-22 was used throughout in its “as-synthesised” form (uncalcined) and contained both Na and H₃O⁺ cations. Calculations on pH values observed in solution compared to the radio-metrically determined cation exchange capacity suggested that these cations were present in equal proportions.

The radioisotopes were supplied by Amersham International UK (22-Na, 137-Cs, 89-Sr, 57-Co) or were those available in the University of Helsinki, Laboratory of Radiochemistry (241-Am, 51-Cr, 59-Fe, 54-Mn, 65-Zn) where some of the distribution coefficient measurements were made. All salt solutions used were nitrates of at least 99% purity dissolved in deionised water. Other chemicals were the purest available. Sodium tetraborate and tri sodium citrate were the chosen complexants.

2.4.2. Measurement of distribution coefficients (K_d)

Approximately 0.0300 g (± 0.0002 g) aliquots of the MCM were accurately weighed and brought separately into contact with 6 mL of the solutions described in Table 1 in 15 mL polypropylene centrifuge tubes.

The suspensions produced were equilibrated, end-over-end, in a mineralogical roller for 24 h, a period previously determined as that sufficient to ensure equilibrium. At the equilibrium the suspensions were centrifuged at 4000 rpm for 20 min. The supernatants were filtered through PVDF filters of pore size 0.45 μ m.

Aliquots of the equilibrium solutions were analysed for radioactivity. Small portions of the equilibrium supernatants were retained for pH analysis using a pre-calibrated Orion 720A pH meter with an Accumet semi-micro calomel electrode.

Distribution coefficients were calculated from the following:

$$K_d = (A_0 - A)/A V/m \quad (1)$$

where K_d = distribution coefficient (mL/g), A_0 = initial activity (Bq/mL), A = equilibrium activity (Bq/mL), V = volume of solution (L), m = mass of material (kg) contacted with V . All K_d measurements were in at least duplicate except when the amount of radioisotope available was limited. A full error analysis of the multiple determinations showed that they were subject to a maximum error of $\pm 10\%$.

2.4.3. Determination of radioactivity for distribution coefficient measurements

Aliquots of 4.5 mL were used to determine the gamma activities of 51-Cr, 59-Fe, 54-Mn, 65-Zn and 241-Am in a Wallac LKB 1280 Ultragamma counter. The radioisotopes 57-Co, 137-Cs, 63-Ni and

Table 1
Simulants for aqueous nuclear waste streams.

Solution	pH	Simulated waste stream
Deionised water	~6	Ground water
0.1 M HNO ₃	1	Decontamination/decommissioning waste
0.1 M NaNO ₃	~4.4	Neutralised decontamination/decommissioning waste
0.1 M NaNO ₃ /NaOH	13	Pond water or alkaline decontamination/decommissioning waste

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