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New hybrid silica based materials for the solid–liquid extraction of actinides

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New hybrid silica based materials containing malonamide ligands have been prepared by sol–gel hydrolysis condensation of functionalised precursors. These hybrids proved to be highly efficient extracting solids which compare favorably to related silica materials.

Sol–gel chemistry[1] has emerged as one of the most important and versatile methods for the preparation of inorganic and mixed organic–inorganic materials.[2–6] The mild reaction conditions of the sol–gel approach allow a deliberate tailoring of the material properties. Organic–inorganic hybrids exhibiting specific properties are easily prepared by incorporation of organic fragments into an inorganic network. A variety of materials can be produced according to the intrinsic properties of the organic fragment and according to the nature of the bonding interaction between the organic and the inorganic components.[2] The incorporation of functionalised Lewis bases or ligands has for example allowed the preparation of material containing metal complexes.[7,8] These heterogenised metallic species proved to be of interest as catalytic materials.[7,9]

Increasing attention is being paid to hybrid silsesquioxane gels, which are prepared by sol–gel hydrolysis condensation of organic molecules containing two or more trialkoxysilyl substituents.[10,11] These hybrids consist of a mixed three-dimensional network, where the organic fragment cross-linking siloxane chains are part of the framework. The solids are homogeneous single-phase materials and are well defined at the atomic level. Owing to the presence of a strong Si–C bond between the organic and the inorganic fragments, highly stable hybrid networks are produced in this way.

We were interested in exploring the preparation of hybrid materials with complexing properties upon hydrolysis condensation of ligands functionalised by $Si(OR)_3$ groups. These hybrids are potential new solid phase extractants. This approach is quite different from the classical immobilisation procedure of complexing agents. The sol–gel approach should allow one to adjust the ligand loading and the oxide matrix is built around the complexing moieties. The drawback of the method is that some of the ligands may not be accessible in the matrix. However, the complexing sites will be homogeneously distributed throughout the whole material and, owing to its high surface area and porosity, it should not necessarily prevent the metal from reaching the complexing site. Moreover the sol–gel approach should allow one to achieve some control and some tuning of the ligand environment.

Hybrid silica materials, which should be very stable under highly acidic conditions and under γ-irradiation, are of interest for the extraction and treatment of highly radioactive aqueous nitric wastes. We wish to report here our preliminary results on the preparation and use of new hybrid materials containing malonamide ligands and their use for solid–liquid extraction of Pu(IV) and Am(III) from aqueous wastes.[12] The malonamide ligand was chosen because it allows the extraction of actinides from highly acidic aqueous solutions.[13] Moreover the malonamide ligand contains only C, H, N, O and no undesired elements for a subsequent calcination treatment.

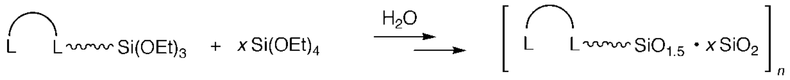
We first prepared triakoxysilyl derivatives **1–3**† according to Scheme 1. The hydrolysable triethoxysilyl groups were introduced by reaction of a γ-aminopropylsilyl reagent with ethylmalonate monoamide to give **1** or with malonyl dichloride to give **2**. The precursor **3** was obtained in two steps from *N*,*N*,*N*,*N*-tetraethylmalonamide, first by alkylation at the central carbon using allylbromide, then by hydrosilylation with triethoxysilane in the presence of platinum catalyst.[14]

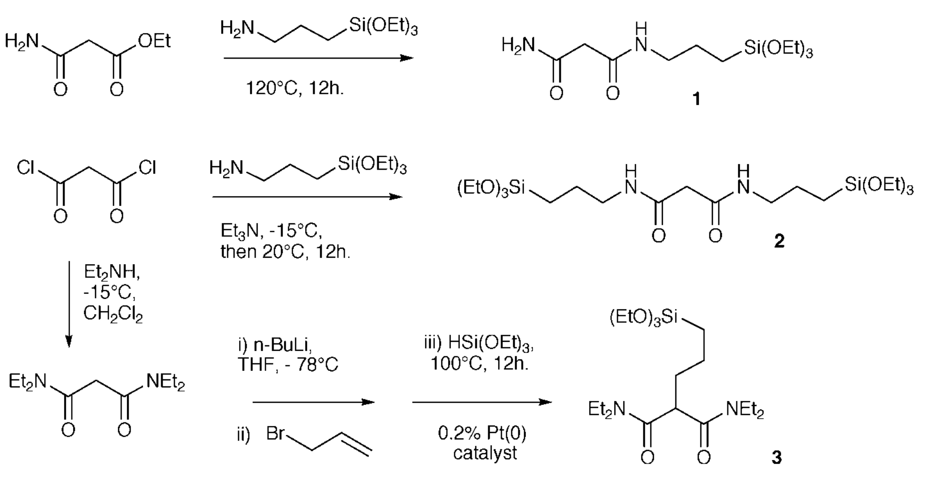
The sol–gel hydrolysis condensation of **1–3** to produce the hybrid solids **4–7** was the performed in the presence of added $Si(OEt)_4$ [eqn. (1)]. Gelation occured in 4 to 12 h in the case of precursors **1** and **3** and more slowly in the case of the disilylated precursor **2**.

The analytical and spectroscopic data‡ for the hybrid gels **4–7**, consistent with the structures presented in Fig. 1, showed the incorporation of the malonamide ligand in the solid. The ^{29}Si MAS NMR spectrum showed one set of resonances at -60 and -65 ppm for T^2: $\mathit{Si}C(OSi)_2OH$ and T^3: $\mathit{Si}C(OSi)_3$ substructures respectively, and a second set at -103 and -110 ppm corresponding to Q^3: $\mathit{Si}(OSi)_3OH$ and Q^4: $\mathit{Si}(OSi)_4$ substructures. The solid stoichiometry therefore deviates from the silsesquioxane structure represented in Fig. 1 (used here for simplification) and contained about one uncondensed OH group for two silicons in the siloxane network.

The porosity and surface properties of the materials were determined using nitrogen adsorption according to the BET method.[15] The hybrids were mesoporous materials with surface areas in the range 170–450 $m^2\ g^{-1}$ and average pore diameters in the range 40–90 Å.

The extracting properties of the solid hybrids were studied for aqueous nitric acid solutions of Pu(IV) and Am(III). Some results are given in Table 1, recorded in highly acidic medium (HNO_3: 4 to 5 $mol\ l^{-1}$). It shows the measured distribution coefficient K_d,§ which reflects at equilibrium the distribution of the metal ion between the solid phase and the aqueous liquid phase. The values of the capacity C¶ of the extracting solid are also given in Table 1 for Pu(IV). The hybrid solids here proved to be very efficient extracting solids. Quite high K_d values in the range 10^3–10^4 $ml\ g^{-1}$ were measured for Pu(IV) and values up to 250 $ml\ g^{-1}$ were found in the case of Am(III). Interestingly at


$$L\frown L\text{∿∿}Si(OEt)_3 + x\,Si(OEt)_4 \xrightarrow{H_2O} \left[L\frown L\text{∿∿}SiO_{1.5}\cdot x\,SiO_2\right]_n \quad (1)$$



Scheme 1 Synthesis of functionalised diamide precursors **1–3**.

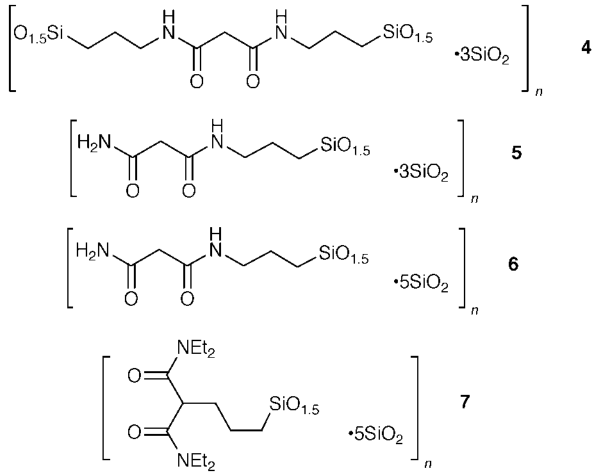
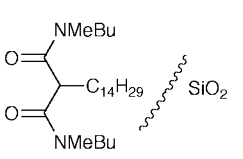
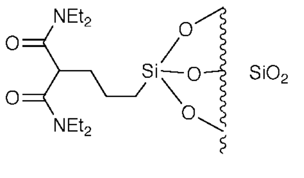


Fig. 1 Representation of hybrid gels **4–7** containing malonamide.

lower HNO_3 concentration (5×10^{-2} mol l^{-1}), the distribution coefficients are much lower (1 to 5 ml g^{-1} for Am(III)), which allows easy elution of the fixed element. When compared to gels **5–7**, gel **4**, in which the bridging amide group is linked by two functional silicon atoms, gives lower K_d values; this may be attributed to the more rigid nature of the network in gel **4**, which is less favorable for complex formation. In addition the bissilyl malonamide ligand is less likely to remain on the outer surface of the material than the monosilylated malonamide in gels **5–7**. Despite the high surface area in **4**, all the malonamide ligands may not be accessible. This is confirmed by the measured capacity values for the complexation of Pu(IV) for which the lowest value was found for gel **4**.

The hybrid materials have been compared to the related silica based materials **8** and **9** which were prepared respectively by impregnation of silica with *N*,*N*′-dimethyl-*N*,*N*′-dibutyltetradecylmalonamide[16] and by immobilising the ligand **3** at the surface of porous silica[17] according to classical procedures. It is worth noting that the hybrid materials compare favorably to immobilised malonamide on silicas **8** and **9**. It is of particular interest to compare hybrid **7** and silicas **8** and **9** which contain malonamide ligands with similar structures. Hybrid **7** gave higher distribution coefficients both for Am(III) and Pu(IV) and had a higher extracting capacity. Moreover, analysis of hybrid **7** showed a malonamide content of 1.21 mmol g^{-1} in the material, the observed capacity 0.46 mmol g^{-1} is only one third of its potential value. This means that not all complexing sites are accessible to the metal ion. The hybrid approach allows one

Table 1 Properties of hybrid gels **4–7** and immobilised malonamide ligands on SiO_2

Extracting material	Surface area/m^2 g^{-1}	Average pore diameter/Å	K_d[a] Am(III)/ ml g^{-1}	K_d[a] Pu(IV)/ ml g^{-1}	C[b] Pu(IV)/ meq g^{-1}
4	466	40	9	1030	0.19
5	176	48	56	10 300	0.59
6	342	37	23	3200	0.46
7	236	92	250	3900	0.46[c]
 **8**	300	—	9	2980	0.29[d]
 **9**	296	—	27	565	0.21[e]

[a] The measurements were performed under conditions where the metal is at a very low concentration, using 1 ml of an aqueous nitric acid solution: $[HNO_3]=4$ M, $[Am]_0=8.5 \times 10^{-5}$ M or $[Pu]_0=4.2 \times 10^{-5}$ M, and 30–50 mg of hybrid gel. [b] The capacity C was measured for an aqueous nitric acid solution of Pu(IV): $[HNO_3]=4.7$ M. [c] Malonamide content in gel **7**: 1.21 meq g^{-1}. [d] Malonamide content 0.46 meq g^{-1}. [e] Malonamide content 0.42 meq g^{-1}.

to prepare materials with much higher loading than the classical immobilisation procedure. The loading values were 0.46 and 0.42 mmol g^{-1} for silicas **8** and **9** respectively. The malonamide loading in hybrids can be increased by adjusting the ligand to Si(OEt)$_4$ ratio in eqn. (1). The capacity and distribution coefficients could be increased accordingly, leading to hybrids with a high porosity which ensures accessibility of the metal ion. Appropriate processing[1] in the sol–gel preparation of hybrids should allow one to tune the pore structure of the material. We are currently investigating the extracting properties of hybrid materials as a function of the morphology of the solid (surface area, pore size *etc.*).

Notes and references

†Selected characterisation data for precursors. **1**: ^{1}H NMR (CDCl$_3$), δ 0.59 (CH$_2$Si, 2H, t), 1.17 (CH$_3$, 9H, t), 1.55 (CH$_2$C*H*$_2$CH$_2$, 2H, m), 3.14 (CH$_2$, 2H, s), 3.18 (NHC*H*$_2$, 2H, m), 3.77 (OCH$_2$, 6H, q); ^{13}C NMR (DMSO), δ 6.8 (CH$_2$Si), 17.8 (CH$_3$), 22.1 (CH$_2$*C*H$_2$CH$_2$), 41.4 (CH$_2$NH), 42.8 (*C*H$_2$CO), 57.8 (OCH$_2$), 167.3 (CO), 169.9 (CO); ^{29}Si NMR (CDCl$_3$), δ −45.7; Analysis: Calc. for $C_{12}H_{26}N_2O_5Si$: C, 47.04; H, 8.55; N, 9.14; Found: C, 47.00; H, 8.78; N, 9.29%. **2**: ^{1}H NMR (CDCl$_3$), δ 0.61 (CH$_2$Si, 4H, t), 1.21 (CH$_3$, 18H, t), 1.62 (CH$_2$, 4H, m), 3.13 (CH$_2$CO, 2H, s), 3.21 (NCH$_2$, 4H,q), 3.78 (OCH$_2$, 12H, q), 7.26 (NH); ^{13}C NMR (CDCl$_3$), δ 7.7 (CH$_2$Si), 18.2 (OCH$_2$*C*H$_3$), 22.7 (CH$_2$(CH$_2$)$_2$), 42.0 (CH$_2$NH), 42.6 (*C*H$_2$CO), 58.5 (OCH$_2$), 167.5 (CO); ^{29}Si NMR (CDCl$_3$), δ −46.6; Analysis. Calc. for $C_{21}H_{46}N_2O_8Si_2$: C, 49.38; H, 9.08; N, 5.48; Found: C, 48.72; H, 9.09; N, 5.81%. **3**: ^{1}H NMR (CDCl$_3$), δ 0.64 (CH$_2$Si, 2H, t), 1.06 (CH$_3$, 21H, m), 1.40 (CH$_2$C*H*$_2$CH$_2$, 2H, m), 1.84 (CHC*H*$_2$, 2H, q), 3.37 (NCH$_2$, 8H, q), 3.45 (CH, 2H, t), 3.72 (OCH$_2$, 6H, q); ^{13}C NMR (CDCl$_3$), δ 10.3 (CH$_2$Si), 12.6 (N(CH$_2$*C*H$_3$)), 14.0 (N(CH$_2$*C*H$_3$)), 18.2 (OCH$_2$*C*H$_3$), 21.7 (CH$_2$*C*H$_2$CH$_2$), 32.7 (CH*C*H$_2$), 40.2 (NCH$_2$), 41.4 (NCH$_2$), 50.2 (CH$_2$), 58.2 (OCH$_2$), 168.6 (CO); ^{29}Si NMR (CDCl$_3$) δ −45.3; Analysis: Calc. for $C_{20}H_{42}N_2O_5Si$: C, 57.38; H, 10.11; N, 6.69; Found: C, 57.46; H, 9.98; N, 6.77%.

‡Selected characterisation data for hybrid gels. **4**: ^{13}C CP MAS NMR, δ 9.8, 16.9, 21.9, 42.4, 57.3, 168.4; ^{29}Si CP MAS NMR, δ −65.8 (T^3), −100.5 (Q^3), −109 (Q^4); Analysis. Found: C, 27.88; H, 4.27; N, 4.87; O, 36.98; Si, 29.97%. BET surface area 467 m^2 g^{-1}, pore volume 0.47 ml g^{-1}, average pore diameter 40 Å. **5**: ^{13}C CP MAS NMR, δ 8.7, 17.6, 28.3, 42.2, 60.1, 169.3; ^{29}Si CP MAS NMR, δ −61.2 (T^2), −65.4 (T^3), −102.8 (Q^3), −110.4 (Q^4); Analysis. Found: C, 27.7; H, 5.0; N, 5.5; O, 31.1; Si, 30.8%. BET surface area 176 m^2 g^{-1}, pore volume 0.21 ml g^{-1}, average pore diameter 48 Å. **6**: ^{13}C CP MAS NMR, δ 9.3, 17.2, 26.3, 42.2, 59.2, 170.4; ^{29}Si CP MAS NMR, δ −60.3 (T^2), −66.3 (T^3), −103.3 (Q^3), −110.2 (Q^4); Analysis. Found: C, 19.7; H, 3.7; N, 4.0; O, 39.8; Si, 32.8%. BET surface area 342 m^2 g^{-1}, pore volume 0.32 ml g^{-1}, average pore diameter 37 Å. **7**: ^{13}C CP MAS NMR, δ 13.5, 17.5, 44.2, 59.3, 170.4; ^{29}Si CP MAS NMR, δ −59.0 (T^2), −64.2 (T^3), −102.6 (Q^3), −108.9 (Q^4); Analysis. Found: C, 25.9; H, 4.75; N, 3.4; O, 38.2; Si, 27.7%. BET surface area 236 m^2 g^{-1}, pore volume 0.54 ml g^{-1}, average pore diameter 92 Å.

§The measurements were performed under conditions where the metal is at a very low concentration, using 1 ml of an aqueous nitric solution: $[HNO_3] = 4$ M, $[Am]_0 = 8.5 \times 10^{-5}$ M or $[Pu]_0 = 4.2 \times 10^{-5}$ M, and 30–50 mg of hybrid gel. At equilibrium, the extractant concentration is close to its initial value. The distribution coefficient K_d is defined as the ratio of the concentrations of the metal ion in the solid phase and in the liquid phase $K_d(\mathrm{ml\ g^{-1}}) = [L-M^{n+}]\ (\mathrm{mol\ g^{-1}})/[M^{n+}]\ (\mathrm{mol\ ml^{-1}})$. In the case of solid–liquid extraction, the distribution coefficient represents the macroscopic average of a large number of microscopic distribution coefficients related to a variety of complexing sites which are not identical in a solid material since the local (chemical, steric) environment of the ligand is not the same for all the sites in the solid. Nonetheless it shows that the distribution coefficients are dependent on the number of accessible sites per mass unit of the extracting solid.

¶The capacity C of the extracting solid is defined as the maximum quantity of metal ion which can be extracted per mass unit of material: $C\ (\mathrm{mmol\ g^{-1}}) = (n_o - n)(\mathrm{mmol})/m(\mathrm{g})$ where n_o is the initial quantity of metal ion in solution and n the remaining quantity in solution after saturation of the solid.

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