Monatshefte für Chemie 137, 627–633 (2006)
DOI 10.1007/s00706-006-0451-y

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Europium-Containing Organic Gels and Organic and Carbon Aerogels. Preparation and Initial Applications in Catalysis[#]

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Received December 12, 2005; accepted (revised) February 13, 2006

Summary. We prepared organic gels and organic and carbon aerogels doped with europium through sol–gel processes. Eu-gels were prepared by sol–gel polymerization of the potassium salt of 2,4-dihydroxybenzoic acid with formaldehyde followed by ion-exchange with $Eu(OTf)_3$. Eu–organic aerogels were obtained after CO_2 supercritical drying of the gels and Eu–carbon aerogels were obtained by pyrolysing the organic aerogels. The Eu-gels containing 12% europium proved to be efficient as recoverable catalyst in *Michael* additions.

Keywords. Lanthanoids; Catalysts; Nucleophilic additions; *Michael* reaction.

Introduction

Support or entrapment of lanthanides or lanthanide species in aerogels has been scarcely studied [1]. Thus, cerium- and lanthanum-doped SiO_2–PbO glasses have been prepared as scintillators [2] and the luminescence and photoluminescence of lanthanide-doped silica aerogels have been studied by several Chinese groups [3–6] and by *Eid et al.* in Y_2O_3 aerogels [7]. It has also been reported that rare-earth silicate aerogels produce good glasses [8, 9]. The lack of investigations is rather surprising considering the high value of lanthanide species as catalysts in a broad variety of organic reactions [10] and the interest towards metals – supported in carbon or silica – as catalysts [11].

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[#] Dedicated to Professor *Ulrich Schubert* on the occasion of his 60th birthday

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We have been interested in transition metals supported on highly porous solids as catalysts in organic reactions. Thus, in this line, we have previously reported on ferrihydrite–silica aerogel nanocomposites, which are active as catalysts in *Michael* additions [12]. In the case of carbon aerogel materials, three main strategies have been used in literature to incorporate metal species. The first consists of dissolving the metal precursor in the initial resorcinol–formaldehyde mixture. The metal source can affect the sol–gel chemistry and it can be difficult to control the pore texture. The second strategy is to deposit the metal precursor on the organic or the carbon aerogel. Finally, the third one involves the use of a resorcinol derivative containing an ion exchange moiety that can be polymerized using sol–gel techniques [13]. Following the third approach we have previously prepared Pd-doped organic and carbon aerogels that were active in the *Mizoroki-Heck* reaction [14].

Now, we used the same strategy to obtain new Eu-doped materials. This paper presents the preparation of europium loaded gels and organic and carbon aerogels, and the first trials to test those materials as catalysts in *Michael* additions.

Results and Discussion

Sol–gel processes allow to obtain solid materials by gelation rather than by crystallization or precipitation. Carbon aerogels are nanostructured carbons that can be obtained through sol–gel polycondensation of certain monomers, such as resorcinol and formaldehyde, to produce organic gels that are supercritically dried and pyrolyzed. K^+-doped gels are obtained when resorcinol is replaced with the potassium salt of 2,4-dihydroxybenzoic acid as the gel precursor. Then, in a later synthesis step, the potassium ions in the gel can be replaced with the desired metal through an ion-exchange process and the gel can be then dried and carbonized to generate metal-doped carbon aerogels. Thus, europium loaded organic gels were prepared

Table 1. Materials properties

Material	Surface area	Pore volume	Density	Metal content	C	H	S	TEM observation	XRD (tentative phase identification)
	$m^2\,g^{-1}$	$cm^3\,g^{-1}$	$g\,cm^{-3}$	%	%	%	%		
Eu-gel (1)	–	–	0.044*	12.03	39.5	3.5	2.4	particles are differentiated	amorphous
Eu-gel (2)	–	–	0.045*	–				particles are differentiated	amorphous
Eu–organic (1)	308	1.3	0.33	13.70	40.5	3.5	2.4	particles are well differentiated	amorphous
Eu–organic (2)	306	1.3	0.43	–				particles are well differentiated	amorphous
Eu–carbon (1)	497	1.2	0.53	27.3	56	0.4	1.3	particles are clearly seen	Eu_2O_2S, EuOF and $Eu_3O_2F_5$
Eu–carbon (2)	551	1.2	0.56	–				particles are clearly seen	Eu_2O_2S, EuOF and $Eu_3O_2F_5$

* Gels density was assessed by dividing the mass of the aerogels by the volume occupied by the gel therefore assuming that there has not been mass variation of the solid skeleton during the supercritical CO_2 solvent evacuation of the gels

using this methodology that ensures a homogeneous dispersion of the doping metal. The wet gels containing potassium ions were soaked in a 0.1 *M* solution of Eu(O*Tf*)$_3$ in acetone for 24 h. The procedure was repeated three times. On the basis of the elemental analysis of the obtained Eu-gel (1), the exchange of K^+ was not complete (12.0 wt% Eu and 39.5 wt% C; Eu:C = 1:41 molar ratio).

Some of the Eu-gels were then dried by solvent evacuation at CO_2 supercritical conditions. The resulting Eu–organic aerogel (1) contained a 13.7 wt% lanthanide. After pyrolysis at 1050°C Eu–carbon aerogel (1) was obtained containing 27.3 wt% europium. The metal content is almost double for the pyrolised material compared

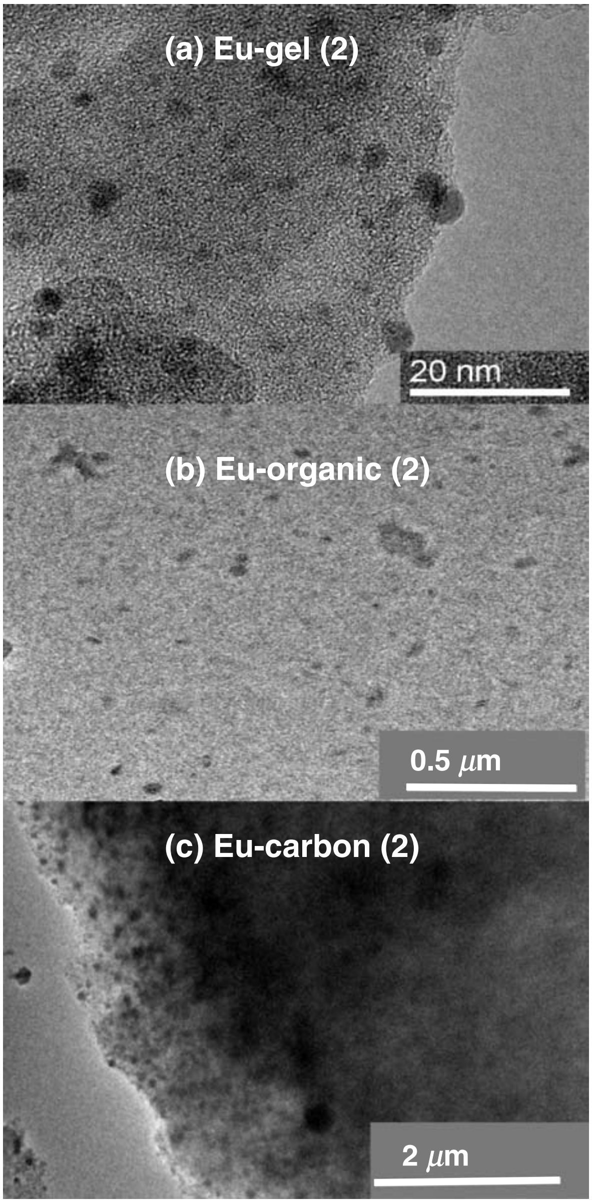


Fig. 1. TEM images of the Eu-doped materials: (a) Eu-gel, (b) Eu–organic, and (c) Eu–carbon

to the Eu-doped gel. Table 1 gathers the main characteristics of the materials under study, the labels (1) and (2) denote two different syntheses of the same material. Regarding the surface area values, this parameter increases after thermal treatment. Bulk densities were estimated by measuring the dimensions and mass of each monolithic sample. Selected bright field TEM images of the three types of materials are presented in Fig. 1. In all cases particles are distinguished from the amorphous matrix. That would explain the good catalytic performance of the Eu-gel in the reactions studied. This result differs from the one reported by *Fu et al.* [15] who did not observe nanoparticles in the organic gels or in the organic aerogels. The metallic nanoparticles were only clearly visible after pyrolysis. Powder X-ray patterns are shown in Fig. 2. Rather amorphous patterns are observed for the Eu-gel and Eu–organic samples indicating poor cristallinity of the particles seen by microscopy. In contrast, sharp peaks are evidenced for the carbon–Eu-aerogel. During the process of gel conversion into organic aerogel and finally into carbon aerogel, a change of phases took place. A tentative phase identification was done concluding that manipulations involving supercritical drying and pyrolysis convert $Eu(OTf)_3$ into a mixture of three phases corresponding to mixed oxide–sulfide, Eu_2O_2S, and oxide–fluorides, EuOF and $Eu_3O_2F_5$. In other words, mixtures of europium oxides, sulfides, and fluorides are generated.

The materials were tested as catalysts in *Michael* additions. The first report on the use of lanthanides as homogeneous catalysts in *Michael* additions was probably the one by *Scettri et al.* who reported the *Michael* addition of β-diketones and β-ketoesters to α,β-unsaturated ketones by Eu(III) chloride hexahydrate and by Eu(III) β-diketonates [16]. Since then, many other lanthanide species of La, Ce, Sm, and Yb have been studied as catalysts in conjugate additions [10a, 10b]. A remarkable example is the use of easily recoverable and reusable polystyrene-

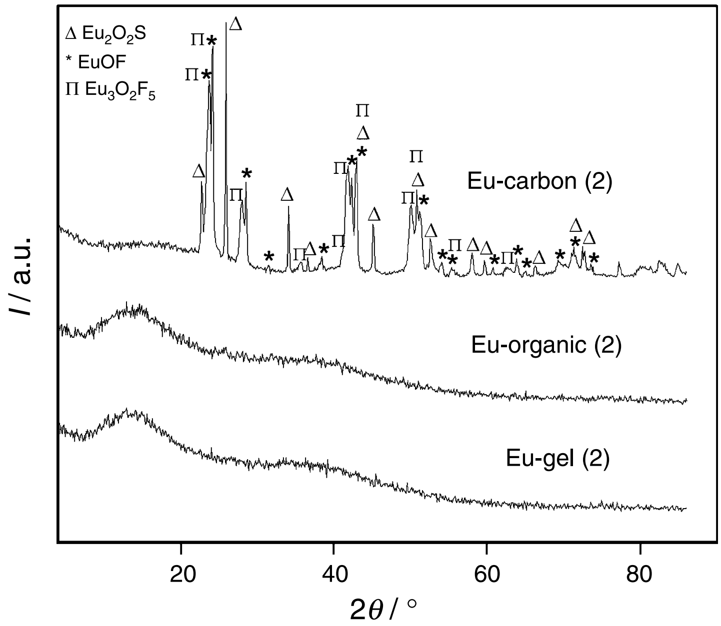


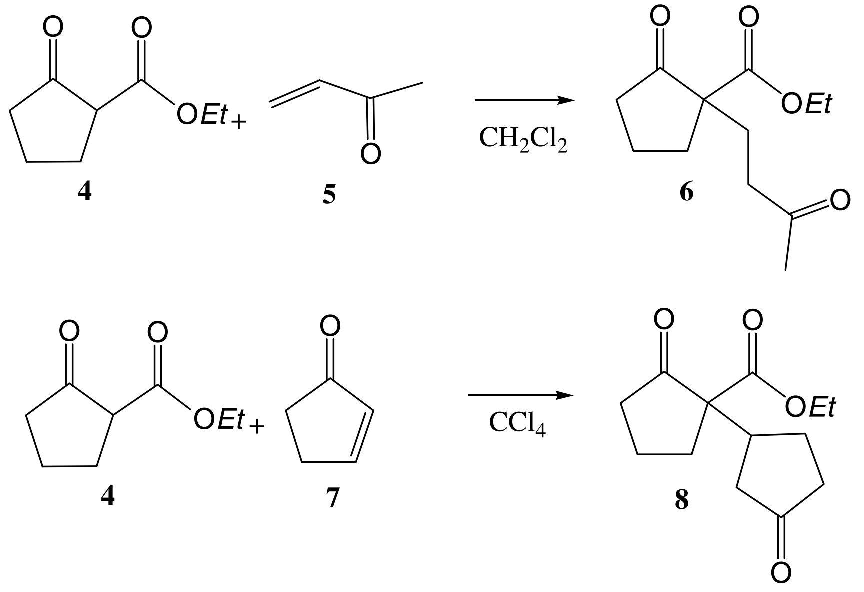
Fig. 2. XRD patterns of the Eu-doped materials

microencapsulated Sc(O*Tf*)$_3$, that has been effective to catalyze the reaction of silyl enol ethers with α,β-unsaturated carbonyl compounds [17]. As far as we know, only few examples of the use of lanthanides–silica based heterogeneous catalysts have been described: Yb(O*Tf*)$_3$ dispersed on chromatographic silica gel (Wakogel C-300), prepared by simple mixing of both reagents, was used in the reactions of β-ketoesters and α,β-unsaturated carbonyl compounds [18]; and Montmorillonite-enwrapped Sc provided an active catalyst for *Michael* reactions under aqueous or solvent free conditions [19].

We performed the reaction of ethyl 2-oxocyclopentanecarboxylate (**4**) and 2-butenone (**5**) five consecutive times using the same batch of Eu-gel (1). For all *Michael* reactions we used 3 mol% Eu with respect to the limiting reagent. The reaction of **4** and **5** was carried in dichloromethane at room temperature. The yields of pure *Michael* adduct **6** obtained in the five cycles were 99, 99, 95, 90, and 90%. The reaction times were between 4.5 and 5 h, except for the 5th run when 6 h were needed for completion of the reaction. Analysis of the reaction crude (first cycle) indicated a leaching of 0.08% of the Eu present in the gel. Curiously enough, when we have used the Eu–organic aerogel (1) we observed a slight decrease in activity and a complete consumption of the nucleophile was obtained after 8 h of reaction. The Eu–carbon aerogel (1) did not catalyze the *Michael* addition after 24 h at room temperature.

We then examined cyclopentenone (**7**) as electrophile. The reaction was carried out four consecutive times with the same batch of Eu-gel (1) and excellent yields of the pure *Michael* adduct **8** (88, 99, 98, 97%) were obtained. The reaction time slightly increased every cycle: 9, 10, 12, and 12 h. Less reactive acrylonitrile was inert in these conditions, and for ethyl acrylate the reaction was too slow for practical uses.

On the basis of elemental analysis the proportion between S/Eu was about 0.95 in the Eu-gel (1) that corresponded to one triflate anion per Eu^{3+}. This relation



Scheme 1

diminished to 0.83 in the Eu–organic aerogel (1) and finally to 0.23 after calcination, probably due to partial formation of europium oxides. This explains the decrease of activity of Eu–carbon aerogels (1) as catalyst. It is known that *Michael* additions are catalyzed by *Lewis* acids as rare-earth metal chlorides and triflates, whereas the corresponding metal oxides are inert.

In conclusion, we have prepared new Eu-doped organic gels and organic and carbon aerogels by ion-exchange methodology from the potassium salt of 2,4-dihydroxybenzoic acid and formaldehyde. This is a new approach for the incorporation of lanthanides. Moreover, the Eu-doped gels were active as catalysts in two *Michael* additions and the materials could be recovered and reused.

Experimental

Europium analyses were performed by ICP-MS analysis using a Perkin-Elmer ELAN 6000 instrument. Surface area determinations were carried out following the *BET* (*Brunauer–Emmet–Teller*) method with an ASAP-2000 surface area analyzer (Micromeritics Instruments Corp.). Elemental analyses were performed by inductively coupled plasma-mass spectroscopy (ICP-MS). The materials were characterized by X-ray diffraction (XRD) with a D500 Siemens X-ray powder diffractometer using CuKα, incident radiation. Transmission electron microscopy (TEM) observations and selected area electron diffraction patterns were performed using a JEOL-JEM-2010 microscope operating at 200 keV.

Europium loaded gels were prepared based on the methodology previously described by *Baumann et al.* [13]: A suspension of 2.9 g 2,4-dihydroxybenzoic acid (18.8 mmol) in distilled H_2O was treated with 1.3 g K_2CO_3 (9.4 mmol) under vigorous stirring. When all the acid was neutralized (0.5 h), the reaction solution became clear and then 3.0 g formaldehyde (37 wt%, 37 mmol) and 26 mg K_2CO_3 (0.19 mmol) were added. The reaction solution was poured into glass moulds that were sealed. The mixture was allowed to cure for 24 h at room temperature, and 94 h at 70°C. The K^+ doped gels were washed 4 times with acetone until H_2O was completely exchanged and then soaked in a 0.1 *M* solution of Eu(O*Tf*)$_3$ in acetone for 24 h. This procedure was repeated three times to obtain the Eu-doped gel. Finally gels were washed with acetone several times. Anal. found: C 39.5, H 3.50, Eu 12.03, S 2.40.

The Eu-doped gel was prepared in acetone, thus a slow exchange of acetone for the chlorinated solvent used in the reactions was carried out before using this material in catalysis. For some of the Eu-loaded gels the acetone was exchanged with CO_2 and the solvent was evacuated at supercritical CO_2 conditions ($T = 35°C$, $P = 130$ bar, $t = 1$ h), to obtain Eu-loaded organic aerogels (2). Anal. found: C 40.5, H 3.50, Eu 13.70, S 2.40. Pyrolysis of the Eu-doped organic aerogels was performed during 3 h at 1050°C under N_2 (2 atm), to obtain Eu–carbon aerogels (3). Anal. found: C 56.0, H 0.4, Eu 27.3, S 1.3.

Preparation of Ethyl 2-oxo-1-(3-oxobutyl)cyclopentanecarboxylate (**6**) [20]

Ethyl 2-oxocyclopentanecarboxylate (**4**, 1.2 cm^3, 7.7 mmol) and 1.9 cm^3 butenone (**5**, 22.6 mmol) were dissolved in 15 cm^3 CH_2Cl_2. Then, 0.3 g Eu-gel (1) (0.24 mmol, 3 mol%) were added to the mixture and the reaction was carried out at room temperature and mechanical stirring during 4.5 h. The solution was decanted and the gel washed several times with CH_2Cl_2. The combined extracts were evaporated and 1.7 g (100%) pure **6** were obtained. The recovered gel was used in the next preparation of **6**. The yields and times of reaction for the subsequent cycles were 99% (4.5 h), 95% (5 h), 90 (5 h), 90 (6 h). IR and ^1H NMR spectra were found to be identical with the one described in Ref. [20].

Preparation of Ethyl 2,3′-dioxobi(cyclopentane)-1-carboxylate (**8**) [21]

Ethyl 2-oxocyclopentanecarboxylate (**4**, 1.2 cm^3, 7.7 mmol) and 1.88 cm^3 2-cyclopenten-1-one (**7**, 22.6 mmol) were dissolved in 15 cm^3 CCl_4. Then, 0.3 g Eu-gel (1) (0.24 mmol, 3 mol%) were added to the mixture and the reaction was carried out at reflux of CCl_4 and mechanical stirring during 9 h. The solution was decanted and the gel washed several times with CCl_4. The combined solvent extracts were evaporated and 1.6 g (88%) pure **8** were obtained. The recovered gel was used in the next preparation of **8**. The yields and times of reaction for the subsequent cycles were 99% (10 h), 98% (12 h), 97% (12 h). IR, ^{13}C NMR, and ^{1}H NMR spectra were found to be identical with the ones described in Ref. [21].

Acknowledgements

Financial support from "Ministerio de Educación y Ciencia" (Projects BQU 2002-04002, CTQ2005-04968/BQU, and MAT2003-01052) and "DURSI-Generalitat de Catalunya" (Projects SGR 2005-00452, SGR 2001-00181, and SGR 2005-00305) is gratefully acknowledged. We thank Prof. *L. Ghosez* of the University of Louvain-la-Neuve for inspiring this line of investigations.

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