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Immobilization of Mo(IV) complex in hybrid matrix obtained via sol-gel technique

C. Marques^a, A.M. Sousa^a, C. Freire^b, I.C. Neves^{a,*}, A.M. Fonseca^a, C.J.R. Silva^a

^aIBQF/Departamento de Química, Escola de Ciências, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal ^bCEQUP/Departamento de Química, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal

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Abstract

A molybdenum(IV) complex, *trans*-bis-[1,2-bis(diphenylphosphino)ethane]-fluoro-(diazopropano)-molybdenum tetraphenylborate, $[MoF(DIAZO)(dpp)_2][BPh_4]$, was prepared and immobilized in a hybrid matrix synthesized by the sol-gel process. The host matrix, designated as U(500), is an organic-inorganic network material, classed as ureasil, that combines a reticulated siliceous backbone linked by short polyether-based segments. Urea bridges make the link between these two components, and the polymerization of silicate substituted terminal groups generates the inorganic network. The free Mo(IV) complex and all new materials were characterized by spectroscopic techniques (FT-IR and UV–Vis) and thermal analysis (DSC). The ionic conductivity of the resulting material was also studied. The results indicate that immobilized Mo(IV) complex has kept its solid-state structure, although there is evidence of inter-molecular interactions between the Mo(IV) complex and some groups/atoms of the hybrid host matrix. © 2003 Elsevier B.V. All rights reserved.

Keywords: Molybdenum(IV) complex; Complex immobilization; Sol-gel; Conductivity; FTIR

1. Introduction

The preparation of solid-state materials via sol-gel processing is an important and successful method for preparing new materials with enhanced properties, such as non-linear optics properties, high ionic conductivities or containing dispersed nano-particles, for application in several fields such as lens coating and electronics [1-3].

The chemistry of the sol-gel method was initially based in metal alkoxides, $M(OR)_4$, where M stands for a metal atom (Si, Ti, etc.) and OR for an alkoxy group $-OC_nH_{2n+1}$. The reactivity of the metal alkoxides, the properties of the solvent used, the catalysts present and the properties of the reactive media (such as temperature and pH) have a strong influence on the kinetics of the process and control the structure and morphology of the resulting material.

In earlier work, the sol-gel process involved the hydrolysis of the alkoxide group [4]

$$(OR)_{3}M-OR + H_{2}O \rightarrow (OR)_{3}M-OH + ROH$$
(1)

after which polycondensation reactions took place. These latter reactions can occur by two possible mechanisms, either by a condensation reaction with the formation of an oxygen bridge (oxolation),

$$(OR)_{3}M-OH + XO-M(OR)_{3} \rightarrow (OR)_{3}M-O-M(OR)_{3} + XOH \quad (X = H \text{ or alkyl group})$$
(2)

by the formation of a hydroxo bridge (olation), or as an addition reaction

$$(OR)_{3}M-OH + HO-M(OR)_{3} \rightarrow (OR)_{3}M-(OH)_{2}-M(OR)_{3}$$
(3)

The propagation of the polymerization process promotes the size increase of the polymeric structure and the extent of branch formation, giving this structure a fractal dimension. The final product is a gel where the polymeric particles can trap solvents, molecules, colloidal solutions or other particles.

Sol-gel syntheses are attractive because they offer a lower processing temperature with high homogeneity and purity of the resulting materials and the possibility of various forming processes. The materials can exhibit important physical properties, in particular: (i) high surface

^{*}Corresponding author. Tel.: +351-253-604-386; fax: +351-253-678-983.

E-mail address: ineves@quimica.uminho.pt (I.C. Neves).

area; (ii) accessibility of molecular reactants to the nanoscale domains throughout the aerogel via rapid mass transport through the continuous volume of mesopores; (iii) stabilization of nanoscale matter to coalescence or agglomeration; and (iv) low densities, together with a high thermal and chemical stability [5].

More recently, sol-gel methods have been used as a new route to prepare organic-inorganic hybrid materials. One of the steps in the preparation of these materials includes the formation of a urea bridge between the diamine and the substituted group of the organic-modified alkoxide; an example of the preparation of one type of organic-inorganic hybrid material is presented in Scheme 1. In the reaction, the organic-modified alkoxide (represented in the scheme as ICPTES) and the amine-substituted oligopolyoxyethylene (Jeffamine, ED-600[®]) are made to react in a mole proportion of 2 to 1.

The hybrid materials have also been used in combination with transition metal complexes. Metal complexes have been used as templates for the structure of host inorganic–organic matrix, inducing the formation of interaction with localized atoms of the macromolecular host structure and increasing the cohesion and order of the resulting material. On the other hand, if the complexes keep their structure inside the host matrix and simultaneously have catalytic properties, the novel materials can also be used in heterogeneous catalysis. Hence, sol–gel techniques can be taken as a new route for the heterogenization of molecular catalysts.

This paper describes the immobilization of a diazoalkane complex of molybdenum(IV), *trans*-bis-[1,2-bis-(diphenylphosphino)ethane]-fluoro-(diazopropano)-molybdenum tetraphenylborate (Scheme 2), in a hybrid inorganic–organic matrix material prepared by sol–gel technique. The macromolecular structure is composed of oligopolyoxyethylene chains grafted onto a siliceous net-



Scheme 2. Molecular structure of the complex *trans*- $[MoF(NN=CHCH_3)(dppe)_2][BPh_4].$

work through urea bridges (-NHC(=O)NH-). These materials have been classed as ureasilicates [6].

The new material obtained, an amorphous and transparent monolith, was characterized by infrared (DRIFT) and UV–visible (UV–Vis) spectroscopy, thermal analysis (DSC) and total ionic conductivity. The data indicate that the Mo(IV) complex *trans*-bis-[1,2-bis(diphenylphosphino)ethane]-fluoro-(diazopropano)-molybdenum tetraphenylborate, [MoF(NN=CHCH₂CH₃)(dppe)₂][BPh₄], has been immobilized inside the matrix, although there is evidence for inter-molecular interactions between the Mo(IV) complex and some groups/atoms of the hybrid host matrix.

2. Experimental

2.1. Reagents and solvents

A polyethylene oligopolymer with substituted amine terminal groups, available commercially under the trade name of Jeffamine ED-600[®] (Fluka) and a silicon alkoxide

ICPTES



2 (Et-O)₃ - Si (CH₂)₃ - N=C=O

UPTES

Scheme 1. Synthesis of the ureasil precursor (ureapropyltriethoxysilane, UPTES).

with a substituted isocyanate group, the 3-isocyanatepropyltriethoxysilane (ICPTES, Aldrich), were used in the preparation of the matrix. Both reagents were dried under dynamic vacuum for 6 h at room temperature. Ethanol and tetrahydrofuran (both from Merck) were used as received and stored over molecular sieves. High purity water (k > 18M Ω) obtained by a purification system (Barnstead E-Pure) was used in all experiments.

All experiments in the preparation of Mo(IV) complex were carried out under an inert atmosphere of argon using Schlenk techniques. The solvents from Merck were freshly distilled from appropriate drying agents under dinitrogen before use.

2.2. Preparation of Mo(IV) complex

The complex trans- $[MoF(NN=CHCH_2CH_3)(dppe)_2][BPh_4]$ was prepared by dissolving the precursor complex trans-[MoF(NNH₂)(dppe)₂][BF₄], previously prepared by a literature method (0.45 g, 0.44 mmol) [7] in dichloromethane (10 ml) at room temperature. An excess of propionaldehyde (100 µl, 1.5 mmol) was added and the reaction mixture stirred overnight. During this period, the solution color changed from red to brown-green. The solution was filtered and ethyl ether (10 ml) was added to the filtrate and a green solid was obtained. The product was dissolved in methanol (20 ml), and an excess of NaBPh₄ (Merck) was added to induce the precipitation of the product *trans*- $[MoF(NN=CHCH_2CH_3)(dppe)_2][BPh_4]$. The complex was filtered, washed with methanol (2×5) ml), hexane $(2 \times \sim 5 \text{ ml})$ and dried under vacuum for several hours.

trans-[MoF(NN=CHCH₂CH₃)(dppe)₂][BPh₄]: yield (73%) found (calc. for MoFC₇₉H₇₆N₂P₄B): C, 72.6 (72.8); H, 5.6 (5.8); N, 2.1 (2.2). NMR (CDCl₃): ¹H NMR (300.0 MHz δ, ppm); δ =0.5 (t, 3H, CH₃), 1.2 (m, 2H, CH₂CH₃), 2.6–2.8 (2 m, 8H, PCH₂CH₂P), 5.1 (t, 1H, NCHCH₂) and 6.8–7.6 (m, 60H, PPh₂ and BPh₄). ³¹P-{¹H} (121.7 MHz), δ 97.5 (s). FTIR (ν/cm^{-1}): 1523 [ν (C=N)]. This band is characteristic of diazoalkane complexes confirming that the metal have the oxidation state four [8–10].

2.3. Preparation of hybrid matrix containing the Mo(IV) complex

The matrix was prepared by reaction of a doubly functional amine, O,O'-bis(2-aminopropyl)-polyethylene glycol-500, (Jeffamine ED-600[®]), with 3-isocyanatepropyltriethoxysilane (ICPTES), to give ureapropyltriethoxysilane (UPTES) (Scheme 1) [6]. The synthesis was performed in a fume cupboard, and was started by drying the two reagents under dynamic vacuum for 6 h at room temperature. A stoichiometric proportion of 1 mol of Jeffamine (1.00 ml, 1.75 mmol) to 2 mol of ICPTES (0.87

ml, 3.50 mmol) was dissolved in tetrahydrofuran (THF, 1 ml) previously dried under dynamic vacuum for 6 h at room temperature. The solution was stirred in a sealed glass flask for 30 min. The completion of the reaction was monitored by infrared spectroscopy using the extinction of the strong band at 2277 cm⁻¹, assigned to the stretching vibration of the R_3 -Si-(CH₂)₃-NCO group [11].

Mo(IV) complex, trans-[MoF(NN=CHCH₂CH₃)(dppe)₂][BPh₄] (0.60 mg), was dissolved in a mixture of 2.4 ml of ethanol and 2.0 ml of THF by using an ultrasound bath for 10 min. After complete dissolution, 360 μ l of water was added.

The latter solution was added to the UPTES solution and the mixture was stirred for 10 min, and then poured in two Teflon[®] moulds, covered with Parafilm[®] and left in a fume cupboard for 24 h. When the gelification had begun, which took ≥ 2 days, the mould was transferred to an oven equipped with a gas re-circulation system, through a column containing dried type 4A (Fluka) molecular sieves, for a period of 7 days at 70 °C. The obtained material was a yellow flexible and brittle homogeneous transparent film.

The ureasil samples, which corresponded to the pure matrix, are denominated as U(500). Using the same nomenclature the prepared material containing the immobilized Mo(IV) complex, [MoF(DIAZO)(dppe)₂][BPh₄], is denominated as $U(500)_n$ [MoF(DIAZO)(dppe)₂][BPh₄] where n = 3434represents the molecular ratio between the Jeffamine (the limiting reagent used in the ureasil synthesis) and the Mo(IV) complex.

2.4. Characterization

The total ionic conductivity of the solid samples was determined by an impedance spectroscopy technique and was carried out under a dry argon atmosphere, within high-integrity gloveboxes containing argon. The measurements were carried out using a Frequency Response Analyser (Solartron 1250) and an Electrochemical Interface (Solatron 1286) controlled by a PC computer. The conductivity data were extracted from complex plane impedance plots analysis using an suitable program. Impedance measurements were made using a sine wave function, in a frequency range between 65 kHz and 0.1 Hz, at open circuit potential.

The cell and the procedure used are described in the literature [12]. A thin film of the prepared material (~230 μ m) was placed between two gold electrodes discs ($\phi = 13$ mm and 100 μ m thickness) in a home-made cell support and heated for 6 h at a constant temperature of 60 °C. The cell was dried overnight and the conductivity measurements were performed at between 25 and 100 °C, in intervals of 15 °C.

Thespecificconductivityof $[MoF(DIAZO)(dppe)_2][BPh_4]$ complex(0.60 mg)in amixture of 2.4 ml of ethanol, 2.0 ml of THF and 360 µl of

water was measured using a Philips PW 9527 Digital Conductivity Meter.

Disk sections were removed from ureasil films and sealed within 20- μ l aluminium differential scanning calorimeter (DSC) pans inside a preparative glovebox. The purge gas used in throughout the analysis was high purity argon supplied at a 20 ml min⁻¹ flow rate. Thermal analysis was carried out with a Mettler TC11 controller and a DSC20 Mettler oven equipped with a cooling accessory. All samples were subjected to a 5 °C min⁻¹ heating rate and were characterized between 25 and 350 °C.

Room temperature FTIR spectra of free complex and sol-gel materials were obtained from powered samples without dilution in a Bomem MB104 spectrometer, using a reflectance (DRIFT) cell. The spectra were collected over the range 4000–400 cm⁻¹, by averaging 20 scans at a maximum resolution of 8 cm⁻¹. The reflectance spectra were calculated as the ratio (*R*) of sample reflectance to that of background and expressed as $f(R) = (1 - R)^2/2R$, the Kubelka-Munk function.

Reflectance UV–Vis spectra of free complex and sol– gel materials were obtained from powered samples and were recorded on a Shimadzu UV/3101PC spectrophotometer at room temperature in the range 1500–200 nm using MgO as reference.

3. Results and discussion

3.1. Ionic conductivity

The ionic conductivity of the $[MoF(DIAZO)(dppe)_2][BPh_4]$ complex in a $CH_3CH_2OH/THF/H_2O$ solution is 0.383×10^{-6} S cm⁻¹ (k=0.91 cm⁻¹), which indicates that the free complex in solution behaves as a 1:1 electrolyte [13]. This result suggests that Mo(IV) complex added to the ureasils solution is largely dissociated in the Mo(IV) complex cation and BPh₄ anion.

Fig. 1 depicts the logarithm of the total ionic conductivity as a function of the inverse of absolute temperature, for the matrix, U(500), and the prepared material containing the Mo(IV) complex, $U(500)_n$ [MoF(DIAZO)(dppe)_2][BPh_4]. In both materials the variation of the logarithm of conductivity with 1/Tshows a similar curved shape described as Vogel-Tamman-Fulcher (VTF) behavior, which is typical of amorphous ion-conductive polymeric materials [14–16]. This behavior was previously observed in sol–gel materials with similar matrix [6], containing highly soluble salts.

As observed, the pure matrix shows a conductivity which is two orders of magnitude greater than that exhibited by the films of the material containing the Mo(IV) complex.

The ionic conductivity is the sum of all mobile charged species (charge-carriers) contributions: their concentration,

Fig. 1. Temperature dependence of ionic conductivity of U(500) and $U(500)_n[MoF(DIAZO)(dppe)_2][BPh_4]$.

individual mobility and charge. However, there are several mechanisms that can be responsible for the decrease of conductivity. Ion-ion interactions will produce the formation of ionic pairs, which contribute to reduce the concentration of free mobile charges, although the electrostatic nature of these interactions could result in the formation of transient form species. Such interactions will promote the reduction of the ionic mobility, as the free ions will be subject to the electrical field of other ionic species. Another mechanism that can contribute to the decrease of conductivity is ion-molecule interactions, which can involve, in particular, hydrogen cations and BPh_4 anions. These interactions will induce the formation of chemical bonds or dipole-ion interactions, which produce the same effects on concentration of the free ionic species, as that referred to for ion-ion interactions.

In the pure matrix, U(500), the ionic conductivity is assigned to the most efficient charge carrier present in the material, the free protons. As in the metal complex based material, a significant decrease in the total conductivity is observed, it can be proposed that strong chemical interaction between the charge-carriers (free protons) with atoms or groups present either in polymer chain or in the Mo(IV) complex, may be responsible for the observed behavior. Interaction between free protons and NN atoms of the DIAZO group of Mo(IV) complex and formation of ionic pairs between free protons and BPh₄⁻ ions are two different factors which may contribute to the decrease of the conductivity of the matrix by incorporation of Mo(IV) BPh₄ salt.





3.2. Thermal analysis

The thermograms of free complex, $U(500)_n[MoF(DIAZO)(dppe)_2][BPh_4]$ material and hybrid matrix U(500) are presented in Fig. 2. The most significant feature observed in the DSC curve of the free complex is the wide exothermic peak around 380 °C, attributed to the decomposition of the complex.

DSC curves of the pure matrix, U(500) ($T_{\text{onset}} = 347 \text{ °C}$), and that of metal complex based material ($T_{\text{onset}} = 310 \text{ °C}$) are very similar. In both materials a broad endothermic peak is observed at $\geq 90 \text{ °C}$, which is often assigned to the evaporation of water and ethanol molecules [6]. At higher temperatures, between 180 and 200 °C, an exothermic peak is observed, which can be assigned to the reorganization of partial fused oxyethylene chains.

DSC curves indicate that both materials are clearly largely amorphous and the incorporation of the complex in the hybrid host does not modify the morphology of the matrix. Moreover, the presence of the complex [MoF(DIAZO)(dppe)₂][BPh₄] in the matrix causes a slight reduction in the decomposition temperature of the material: the pure matrix is thermally stable up to 350 °C, whereas in the presence of the Mo(IV) the onset temperature is \sim 325 °C.

3.3. FTIR spectroscopy

The infrared spectra of free complex, $U(500)_n$ [MoF(DIAZO)(dppe)₂][BPh₄] and the hybrid matrix U(500) in the spectral region 2000 to 500 cm⁻¹ are shown in Fig. 3.

The spectrum of the free complex is dominated by the bands characteristic of diphenylphosphine ligands (1480, 1435, 735 and 695 cm⁻¹) and the BPh₄ anion (1412, 744 and 720 cm⁻¹) [17]. Other important bands are observed at 1523 cm⁻¹, which is assigned to ν (C=N), and the weak band at 1190 cm⁻¹ is assigned to ν (N–N) of the DIAZO group.

The spectra of the sol-gel materials are dominated by bands due to the hybrid matrix U(500): the strongest band at 1160 cm⁻¹ is attributed to N-CO-N stretching and in the spectral region between 1050 and 800 cm⁻¹ are observed bands corresponding to the vibration modes associated with the matrix. Others bands are summarized



Fig. 3. Infrared spectra of [MoF(DIAZO)(dppe)₂][BPh₄], U(500)_n[MoF(DIAZO)(dppe)₂][BPh₄] and U(500).

Table 1 Selected IR band locations (cm⁻¹) and assignments for the matrix [U(500)]

Wavenumber (cm ⁻¹)	Designation		
3000-3500 (m, br)	R-CO-NH- stretching vibrations		
2900–2940 (S, br)	CH asymmetric stretching vibrations		
2850–2870 (S, br)	CH symmetric stretching vibrations		
1640–1670 (m, br)	C=O asymmetric stretching vibration		
1560 (m)	N-H deformation and symmetric stretching of C=O		
1500 (s)	Si-CH, stretching vibration		
1450 (m)	CH deformation		
1350 (m)	CH ₂ groups of the (CH ₂ CH ₂ O) units of the diamine		
1260 (m, br)	Si-OCH ₂ CH ₃ stretching vibration		
1050 (s, br)	CH ₂ rocking to C-C and C-O stretching vibrations and asymmetric stretching of Si-O-Si		
960 (s)	Asymmetric stretching of Si-OH		
750–800 (s)	Symmetric stretching of Si-O-Si		

br, broad; m, medium; s, small; S, strong.

in Table 1 [18–21]. As no change in the matrix bands was observed after immobilization of the complex, we suppose that the complex has promoted no significant variation on the structure of the matrix.

New low intensity bands due to the Mo(IV) complex are observed superimposed upon those of the matrix after immobilization of the complex. When compared to those of the free complex, there is a shift of the phosphine bands at 1435 and 1480 cm⁻¹ upwards to 1448 and 1498 cm⁻¹, respectively, and the band at 1523 cm⁻¹ characteristic of C=N stretching vibration, shifts upwards to 1531 cm⁻¹. The presence of these bands indicates that metal complex has been immobilized in the hybrid host and primarily has kept its integrity.

The frequency shift observed in the bands of the complex upon immobilization can be attributed to: (i) the presence of a small distortion on the complex; or (ii) interactions between the hybrid matrix and the ether oxygens of the polyethylene chain segments of the hybrid matrix and the Mo(IV) metal ion; and/or (iii) the protonation of NN atoms of the DIAZO group.

3.4. UV–Vis spectroscopy

Room temperature electronic spectrum of $[MoF(DIAZO)(dppe)_2][BPh_4]$ exhibits two intense, high energy bands at $\lambda_{max} = 380$ and 470 nm and a less intense broad band at $\lambda_{max} = 650-700$ nm. The spectrum is analogous to those observed for Mo(IV) complexes with similar coordination sphere as described in the literature [22,23]. The two bands of higher energy are assigned to metal–

Table 2Electronic spectral data for the samples

ligand charge transfer transitions, $d_{\pi}(MoIV) \rightarrow \pi^{*}(LD)$ (LD=DIAZO ligand), and the broad band at lower energy to d-d transitions.

Electronic data for hybrid matrix U(500), $U(500)_{\mu}$ [MoF(DIAZO)(dppe)₂][BPh₄] and the free complex are summarized in Table 2. No electronic bands due to the complex could be detected in $U(500)_n$ [MoF(DIAZO)(dppe)₂][BPh₄], probably due to the low concentration of the complex in the matrix.

4. Conclusion

This paper explores a new approach to the heterogenization of a Mo(IV) complex in hybrid organic–inorganic materials, classed as ureasils. The complex has been immobilized successfully by the sol–gel technique and the resulting material was obtained as amorphous transparent thermally stable monoliths. Combination of all techniques suggests that the immobilization process does not affect morphology and structure of the matrix. However, there is some evidence for host–guest interaction between the Mo(IV) complex and the matrix, which only affects the geometry of the complex to a small extent.

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Samples	$\lambda_{\rm max}$ (nm)					
U(500) $U(500)_{n}[MoF(DIAZO)(dppe)_{2}][BPh_{4}]$ $[MoF(DIAZO)(dppe)_{2}][BPh_{4}]$	250 ^a 250 ^a	300 ^a 300 ^a	380 ^ª	470 ^ª	670 ^t	

^a $d_{\pi} - \pi^*$ electronic transitions.

^b d–d electronic transitions.

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