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Organic–inorganic hybrid matrix doped with alkenyldiazenido complexes of molybdenum

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Abstract

New molecular systems based on conjugated groups, *trans*-[FMo(NNCHCHCHCHCHCHCH2₂CH₃)(Ph₂PCH₂CH₂PPh₂)₂][BPh₄] have been synthesized and characterized. This complex was immobilized in hybrid organic–inorganic matrix obtained by sol–gel. The hybrid matrix of these organically modified silicates, classified as *ureasil* formed by poly(oxyethylene) chains [POE, $(OCH_2CH_2)_n$] grafted to siloxane domains by means of urea cross-linkages. All of the new materials were characterized by thermal analysis (DSC), surface analysis (XPS) and spectroscopic methods (FTIR and UV/vis), to gather information on the modifications introduced by the molybdenum complex in hybrid organic–inorganic matrix, as well as on the immobilized complex integrity. The immobilization of the metal complex in the hybrid matrix has kept their integrity, although some distortions can be observed caused by steric effects imposed by the structure of hybrid matrix or/and by interactions between the metal complex and some groups of the hybrid matrix.

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1. Introduction

The development of organic–inorganic hybrid materials has been the subject of extensive research in the past decade because these systems are found to have the advantage in many fields of applications that they combine both inorganic and organic characters [1–3]. The sol–gel process has been proven to be an excellent candidate for development of the heterogeneous materials by incorporation of organometallic compounds to generate specific catalysts and nanostructured materials for potentially Green Chemistry catalytic systems, novel optical and electronic applications [4–7].

Homogeneous catalysts have uniform and well-defined reactive centers, which lead to high and reproducible selectivities. The activity and efficiency of these catalysts are generally high. However, one of the major problems is the separation of the catalyst from the reaction mixture. To solve this problem, the immobilization of metal complexes acting as homogeneous catalysts, in porous supports provides an ideal solution. Micro-

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and mesoporous materials such as zeolites, clays and mesoporous structures have been used as hosts for the encapsulation or noncovalent attachment of metal complexes [8–13]. The combination of the sol–gel method with the host–guest concept has successfully led to production of a significant multifunctional organic–inorganic framework with tunable design and appropriate characteristics for heterogeneous catalysis [7,14,15]. These systems combine many advantages of homogeneous (high activity, high selectivity and high reproducibility) and heterogeneous (easy separation and recovery of the catalysts from the reaction mixture) catalysis.

Metal transition complexes have been used as templates for the structure of host organic–inorganic 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 hybrid matrix and simultaneously have catalytic properties, the novel materials can also be used in heterogeneous catalysis [9].

Several complexes of molybdenum and tungsten with different ligands were synthesized and their electronic and structural properties studied [10–13]. Earlier work reports the heterogenization of metal transition complexes in clays materials [15],

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 $\longrightarrow \text{NHC=ONH(CH_3)CH_2[OCH(CH_3)CH_2]_a[OCH_2CH_2]_b[OCH_2CH(CH_3)]_cNHC=ONH(CH_2)_3}$

Scheme 1.

zeolites [16] and hybrid matrix [11,17], and have shown that the methodologies used for encapsulation/immobilization of the metal complexes are largely determined by the supports. The analogy between microporous solid supports and hybrid matrix obtained by sol-gel promoted us to explore the properties of the former as supports for the immobilization of metal complexes. The present work aims to assess the effect of metal complex immobilization on their physical-chemical properties and their interaction with the supports.

The hybrid matrix used in this work, designated as U(600), is an organic–inorganic network material, classified as an *ure-asil* that combines a reticulated siliceous backbone linked by short polyether-based segments. Urea bridges form the link between these two components, and the polymerization of silicate substituted terminal groups generates the inorganic network. In the reaction the organic-modified alkoxide, 3-isocyanatepropyltriethoxysilane (ICPTES), and the amine-substituted oligopoly(oxyethylene) (Jeffamine) are made to react in a mole proportion of 2 to 1 (Scheme 1).

This work reports, the effect of the concentration in the immobilization of a diazoalkene molybdenum complex, *trans*-bis-[1, 2-bis(diphenylphosphine)ethane]-fluoro-(2,4-diazoheptadiene) molybdenum of tetraphenylborate (*trans*-[FMo(NNCHCHC-HCHCHCH₂CH₃)(Ph₂PCH₂CH₂PPh₂)₂][BPh₄]), into a high molecular weight *di-ureasil* structure, U(600), which contains about 8.5 oxyethylene repeating units. The macromolecular structure is composed by oligopoly(oxyethylene) chains grafted onto a siliceous network through urea bridges [–NHC(=O)NH–] [18].

2. Experimental

2.1. Reagents and solvents

O,O'-Bis(2-aminopropyl)-polyethylene glycol-500 (Jeffamine ED-600[®], Fluka), the polyethylene oligopolymer with substituted amine terminal groups and the silicon alkoxide with a substituted isocyanate group, the 3isocyanatepropyltriethoxysilane (Aldrich) were used in the preparation of the matrix. Both of the reagents were dried under dynamic vacuum during 30 min immediately before used. All the reaction synthesis of the complex was carried out under nitrogen or argon atmosphere with the use of standard Schlenk techniques unless otherwise stated. The others chemicals, tetrahydrofuran (THF, Merck) and Et₂O were dried by distilling over sodium/benzophenone, ethanol (CH₃CH₂OH, Merck) and dichloromethane were dried by distilling over CaH₂ and stored over 4 Å molecular sieves. The complexes, *trans*-[Mo(N₂)(dppe)₂] and *trans*-[MoF(NNH₂)(dppe)₂][BF₄] were prepared by from published method [19].

2.2. Sample preparation

2.2.1. Preparation of Mo(IV) complex

The stirred solution of the complex *trans*-[MoF(NNH₂)(dppe)₂][BF₄] (0.50 g, 0.49 mmol) in 20 mL of THF solvent, was added 2,4-heptadiene-1-al (63 µL, 1.5 mmol) at room temperature. After 6 h, the resulting brown solution was filtered and hexane (4 mL) was added to the filtrate to give brown-green crystals, which were filtered off, washed with ether and hexane, and then dried, in vacuum. The product was dissolved in methanol (20 mL) and NaBPh₄ was added to the stirred solution. The complex, trans-[MoF(NNCHCHCHCHCHCH2CH3)(dppe)2][BPh4] precipitates from the reaction solution as a green solid. This was filtered off, washed with methanol $(3 \times 5 \text{ mL})$, ether $(3 \times 5 \text{ mL})$ and re-crystallized with CH₂Cl₂/Et₂O and dried in vacuum. Yield (0.36 g, 54%) Anal. found for MoFC83H78N2P4B (calcd.): C, 73.41 (73.74); H, 5.59 (5.77); N, 2.15 (2.07). NMR (CDCl₃): ¹H (300.0 MHz), § 1.1 (t, 3H, CH₃), 1.7 (m, 2H, CH₂CH₃), 2.6-3.0 (2m, 8H, PCH₂CH₂P), 4.1 (br, 1H, NCHCH), 5.3 (m, 4H, olefinic protons) and 7.0-7.5 (m, 60H, PPh₂ and BPh₄). ${}^{31}P{}^{1}H$ (121.7 MHz), δ 93.0 (s). FTIR (ν , cm⁻¹): 1545 [ν(C=N)], 1210 [ν(C=C)]. UV/vis (λ_{max}, nm): 255, 265, 272, 320 and 510. FABMS (m/z): 1033 [M⁺].

2.2.2. Preparation of hybrid matrix containing the complex

In the first stage of the synthesis the sol–gel materials, the hybrid matrix was prepared by reaction of a doubly functional amine of Jeffamine with ICPTES, to give ureapropyltriethoxysilane (*ureasil*—UPTES) [18]. Finally, different concentrations of metal complex solution (initial concentration of metal complex, 1.29×10^{-3} mol/L), were incorporated in the UPTES solution. The immobilization of the metal complex is achieved simultaneously by the hydrolysis and condensation reactions. Details of the preparation of the synthesis *ureasil* precursor (UPTES) with metal complex can be found in the authors' previous work [17]. A sample that corresponds to the pure hybrid matrix was prepared using the same methodology, but without the addition of the metal complex.

The nomenclature for the diazoalkene molybdenum complex was denoted [MoL][BPh₄] where Mo = FMo(Ph₂PCH₂CH₂PPh₂)₂ and L is a diazoalkene ligand (NNCHCHCHCHCH₂CH₃). The *ureasil* samples, have been identified by designation U(600)_n[MoL][BPh₄] where U originates from the word "urea", 600 indicates the average molecular weight of diamine used, and *n* represents the molecular ratio between the Jeffamine (the limiting reagent used in the *ureasil* synthesis) and the metal complex. Samples with n = 200 (2.16 × 10⁻³ mmol of metal complex), 250 (1.75 × 10⁻³ mmol of metal complex) and 500 (8.74 × 10⁻⁴ mmol of metal complex) were prepared. U(600) corresponds to the pure matrix. The obtained materials were a flexible, non-rigid and brittle homogeneous transparent film with brown–green coloration.

2.3. Physical measurements

Thermal analyses (DSC, differential scanning calorimetry) were carried out with a Mettler TC11 controller and a DSC20 Mettler oven equipped with a cool-



ing accessory under high purity argon supplied at a constant 50 mL min⁻¹ flow rate. Samples obtained from *ureasil* films were sealed within a 0.2 mL aluminum pan inside a preparative glovebox under argon atmosphere. All samples were subjected to a 10 °C min⁻¹ heating rate and were characterized between 25 and 350 °C.

The NMR spectra were recorded using a Varian Unity Plus spectrometer at 300 MHz, chemical shifts being given in ppm. Mass spectra (FAB) were obtained using an Analytical Fison Instruments Auto Spec VG spectrometer, using 3-nitrobenzyl alcohol as the matrix. Elemental chemical analysis was performed using a Leco CHNS-932. The FTIR spectra of free complex and *ureasil* samples were obtained from powdered samples on KBr pellets, using a Bomem MB104 spectrometer in the range 4000-500 cm⁻¹ by averaging 20 scans at a maximum resolution of 4 cm^{-1} . X-ray photoelectron spectroscopy analyses were obtained at the C.A.C.T.I. from Vigo University (Spain) in a VG Scientific ESCALAB 250iXL spectrometer using monochromatic Al Ka radiation (1486.92 eV). Reflectance UV/vis spectra of sol-gel materials were obtained from solid sample films and were recorded on a Shimadzu UV/2501PC spectrophotometer at room temperature in the range 800-200 nm using a matrix as a reference. For the free complex, the UV/vis absorption spectra were obtained from complex solution in ethanol using quartz cells.

3. Results and discussion

3.1. Synthesis and characterization of molybdenum complex

The complex of molybdenum, [*MoL*][BPh₄] (Scheme 2), was obtained by condensation of hydrazido(2-) complex, *trans*-[MoF(NNH₂)(dppe)₂][BF₄], with 2,4-heptadiene-1-al compound.

The complex has been characterized by elemental analyses, 1 H and 31 P NMR, FTIR, UV/vis and FABMS spectroscopy. The elemental analyses agree with their chemical formula, and the FABMS spectra clearly show the molecular ion M⁺. 31 P-{ 1 H} NMR spectroscopy shows a single resonance which demonstrates that the complex retains the square-planar array of P atoms about the molybdenum [20]. 1 H NMR spectrum revealed the presence of all the H of the diazoalkene ligand in similar positions for other analogous complexes of literature [21].

The infrared spectra of molybdenum complex display multiple peaks in the range $1500-650 \text{ cm}^{-1}$. These peaks are most likely associated with the diphenylphosphine ligands, $\nu(\text{PPh}_2)$ (1484, 1435, 721 and 690 cm⁻¹) and the BPh₄ anion (1052, 744 and 720 cm⁻¹) in these complexes [19]. On the other hand, the bands recorded at 1545 and 1210 cm⁻¹ are assigned to $\nu(\text{C=N})$ and $\nu(\text{C=C})$ groups of diazoalkene ligand.

In the electronic spectroscopic data of molybdenum complex, the major feature displayed by these complexes [22] is multiple bands in the range 250–300 nm and a shoulder peak in 510 nm. These absorptions are assigned to the diphenylphosphine ligands



Fig. 1. DSC thermograms: (a) U(600), (b) n = 200, (c) n = 250 and (d) n = 500.

 $(\pi - \pi^*$ transition) and diazoalkene-p π to the metal-d π charge-transfer transitions, respectively.

3.2. Characterization of materials doped with molybdenum complex

The preparation of metal complex based hybrid materials was made in two steps: (i) reaction of the alkoxysilane precursor (ICPTES) with the polyethylene oligopolymer with substituted amine terminal groups (Jeffamine ED-600, with a + c = 2.5 and b = 8.5) in a mole proportion of 2 to 1 in THF, to give the urea cross-linked organic–inorganic hybrid precursor, ureapropyltriethoxysilane, UPTES and (ii) addition to the latter precursor solution, the metal complex in THF and the solvents (ethanol and water) that would induce the hydrolysis and condensation reactions to give the xerogels.

The final *ureasil* samples obtained after the immobilization of the molybdenum complex were characterized by thermal analysis, surface analysis (XPS) and spectroscopic methods (FTIR and UV/vis).

3.2.1. Thermal analysis

For understanding the effect of molybdenum complex concentration on thermal properties of hybrid matrix, studies using (DSC) are performed. The DSC thermograms of all samples (Fig. 1) clearly show that the processes are totally amorphous in the studied temperature range.

The DSC profiles obtained for the pure matrix and *ure-asil* samples with different concentrations of metal complex shows that these materials have also a high thermal stability,

Table 1 Areas under the XPS bands in the O 1s, C 1s, Si 2p, N 1s and Mo 3d for the UREASIL samples

| Sample | XPS (atomic %) | | | | | | |
|-----------------------------------|----------------|------|-------|------|------|------|-------|
| | O 1s | C 1s | Si 2p | N 1s | F 1s | B 1s | Mo 3d |
| U(600) | 16.9 | 72.9 | 6.9 | 3.3 | _ | _ | _ |
| U(600) ₂₀₀ [MoL][BPh4] | 16.2 | 65.9 | 10.5 | 5.9 | 0.4 | 0.3 | 0.8 |
| U(600) ₂₅₀ [MoL][BPh4] | 16.6 | 65.6 | 10.7 | 5.7 | 0.4 | 0.3 | 0.7 |
| $U(600)_{500}[MoL][BPh_4]$ | 17.1 | 65.4 | 11.0 | 5.5 | 0.3 | 0.2 | 0.5 |

confirming the expected properties assigned on similar materials based on this hybrid organic–inorganic matrix [17]. For U(600), an endothermic band between 40 and 120 °C is observed which could be assigned to the evaporation of solvent molecules trapped inside the hybrid matrix. This kind of thermal process is less intense on the samples with immobilized metal complex. This difference of behaviors was observed on previous studies [17,23], and suggests that the metal complex contribute to the modification of the matrix properties resulting, in particular, on a more dense structure were less free space is available for hosting small molecules. This apparent increase of matrix cohesion may result from localized chemical interactions between atoms host matrix and metal complex.

The broad exothermic peak observed on the hybrid matrix, which is localized in the 150–200 °C region could be a result of an oxidative process involving the polyether group of the *ureasilicate* network. The presence of the metal complex apparently inhibits this oxidative process, giving to the enhancement of the material chemical stability.

At temperature higher than $250 \,^{\circ}$ C a drift on the thermogram lines towards an exothermic direction may indicate the approach of degradation of the material, and this process may be assigned to the immobilized metal complex as the extension of this process increases in intensity with increased metal complex concentration in the sample.

This behavior suggests that the presence of metal complex contribute to matrix stabilization and this is probably due to the increase of localized chemical interactions between atoms from the $[MoL][BPh_4]$ and those from the matrix structure.

3.2.2. Surface analysis

The XPS technique can provide information about the presence and distribution of molybdenum complexes in matrix as well as on the oxidation state of the metal. All samples revealed the presence of oxygen, carbon, silicon and nitrogen in their XPS resolution spectra. In low resolution XPS spectra of the U(600)_n[*MoL*][BPh₄] samples, the presence of the molybdenum, boron and fluorine, from the metal complexes were detected. The surface atomic contents obtained by the area of the relevant bands in XPS spectra are presented in Table 1.

The high resolution XPS spectra of U(600) sample shows an intense band in the C 1s region at 285.3 eV, which corresponds to aliphatic carbons, carbon atoms covalently bonded by a single bond to electronegative atoms and carbon atom from the group [–NHC(=O)NH–] of the UPTES matrix. A symmetrical band at 532.7 eV in the O 1s region was due to the oxygen single



Fig. 2. FTIR spectra in the range $2000-600 \text{ cm}^{-1}$ of: (a) U(600), (b) n = 200, (c) n = 250, (d) n = 500 and (e) $[MoL][BPh_4]$.

bonded to silicon and to carbon atoms, as well as from the double bonded oxygen of the [-NHC(=O)NH-] group (Scheme 1). The N 1s high resolution spectrum shows a symmetrical band at 400.1 eV which corresponds to the nitrogen atoms from the [-NHC(=O)NH-] group and also a symmetrical band centred at 102.5 eV is observed in the Si 2p high resolution spectrum due to the $[-(CH_2)_3-Si(O-)_3]$ groups (Scheme 1).

The XPS analysis detected the presence of the molybdenum in all *ureasil* samples. After the immobilization molybdenum complexes no significant changes were observed in the C 1s, O 1s and N 1s profile spectra. Low Mo contents at surface levels observed indicate that the outermost surface is not enriched in Mo. The metal complex is immobilized into the *ureasil* structure. The binding energy value of Mo $3d_{5/2}$ was found to be equal to 230.6 eV, which confirms that the metal is in oxidation state four, in agreement with the molybdenum coordination sphere of the complex [15].

3.2.3. Infra-red spectroscopy

The FTIR spectra of *ureasil* samples with different concentrations of metal complex and free complex in the spectral region of $2000-600 \text{ cm}^{-1}$ are presented in Fig. 2.

FTIR spectra of all samples are dominated by the typical set of intense bands assigned to the vibration of hybrid matrix U(600). The IR spectra of hosted matrix have been previous characterized [11]. Shift or broadening of these host structure-sensitive vibrations is observed upon inclusion of the complex, which provides evidence, at the molecular level, that the hybrid matrix changed upon immobilization of the molybdenum complex. For high concentrations of complex in hybrid matrix an increase of the broad band attributed to [-NHC(=O)NH-] group at 1160 cm⁻¹ was observed. The bands due to the molybdenum complex can only be observed in the regions where the hybrid matrix does not absorb, i.e. from 1050 to 800–600 cm⁻¹. The IR bands of immobilized [MoL][BPh₄] in the range 1050–600 cm⁻¹, which are assigned to the diphenylphosphine ligands and [BPh₄]⁻ anion



Fig. 3. UV/vis spectra in the range 230–400 nm of: (a) U(600), (b) n = 200, (c) n = 250, (d) n = 500 and (e) $[MoL][BPh_4]$.

occur at frequencies, which are shifted relative to those of the free complex. These observations confirm the presence of the molybdenum complex and suggest that the structure of the immobilized complex is distorted when compared with that of the structure of free complex. This is a consequence of host–guest interactions with the hybrid matrix, eventually to the matrix carbonyl oxygen atoms of the urea bridges [24]. In our previous work, with tungsten complex immobilized in the same hybrid matrix, the same behavior was observed; the complexes are distorted as a consequence of physical constraints imposed by the matrix [17]. Despite these limitations, infrared spectroscopy provide compelling evidence that the molybdenum complexes have been immobilized within hybrid organic–inorganic matrix, but failed to yield molecular information on the immobilized molybdenum species.

3.2.4. UV/vis spectroscopy

The UV/vis spectroscopy technique can provide information on the immobilized metal complexes and on the *ureasil* structure. Fig. 3 shows the electronic spectra of U(600), molybdenum complex and metal complex immobilized with different concentrations in hybrid matrix.

The electronic spectra of U(600) are very similar to those observed in sol–gel materials with similar matrices [18]. The *ureasil* samples exhibits in the range 250–300 nm, several intensity bands at $\lambda_{max} = 255$, 265 and 272 nm. These bands occur in the same range of high-energy charge-transfer band at $\lambda_{max} = 250-300$ nm for [*MoL*][BPh₄], which prevents a direct proof of the immobilization of the metal complex inside the hybrid matrix. The shoulder band at 510 nm associated to diazoalkene-p π to the metal-d π charge-transfer transitions [22] are not observed probably due to low concentration of metal complex in hybrid matrix even in the sample with higher concentration of molybdenum complex.

4. Conclusion

By combining data from the different techniques used in this work, it is possible to confirm that the immobilization of molybdenum complex occurs in hybrid organic-inorganic matrix obtained by sol-gel method. The highly transparent, flexible and amorphous films sol-gel doped with different concentration of molybdenum complex in U(600) *di-ureasil* host structure instead of poly(oxyethylene) allowed us to produce materials with improved mechanical proprieties and thermal characteristics. The analysis data suggest that the matrix *ureasil* structure exhibits host-guest interaction between the molybdenum complex and the matrix. These results confirm the interaction with macromolecular host structure and contributing to increase the cohesion and order of the resulting material.

The strategy used for the immobilization of molybdenum complexes can be extended to other metals with known catalytic properties. These novel materials may thus be used as heterogeneous catalysts, indicating that it is possible to extend the potential applications of sol–gel materials in the field of catalysis.

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77

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