



Synthesis of two new Mo(II) organometallic catalysts immobilized on POSS for application in olefin oxidation reactions



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ABSTRACT

The purpose of this work was the preparation and characterization of two new catalysts POSS-ATZAc-[Mo(η^3 -C₃H₅)Br(CO)₂] (POSS-Mo-I) and POSS-ATZAc-[Mo(CO)₃Br₂] (POSS-Mo-II). The new heterogeneous catalysts were characterized by several techniques and used as catalysts for the epoxidation of olefins, presenting high catalytic activity. To study and optimize the syntheses of the heterogeneous catalysts, immobilization experiments of the [Mo(η^3 -C₃H₅)Br(CO)₂(NCMe)₂] and [Mo(CO)₃Br₂(NCMe)₂] organometallic complexes on the modified polyhedral oligomeric silsesquioxane were performed. The sorption properties of the modified silsesquioxane showed to be dependent of the contact time, concentration and temperature. Catalysts were tested in the epoxidation of six olefins and compared with homogeneous species [Mo(η^3 -C₃H₅)Br(CO)₂(ATZAc)] (Mo-I) and [Mo(CO)₃Br₂(ATZAc)] (Mo-II). To the best of our knowledge, this paper is the first that has reported the preparation and characterization of two new heterogeneous catalysts, as well as the comparison with homogeneous species for catalytic epoxidation of olefins.

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1. Introduction

Organometallic complexes can catalyse many reactions and are highly used in industrial processes [1]. Molybdenum(II) complexes have been used to synthesize effective catalysts for the epoxidation of olefins using *tert*-butyl hydroperoxide (TBHP) as oxidant, a process which starts with the oxidation of the precursor complex to an active species of molybdenum (VI) [2]. Attention in molybdenum complexes arises primarily from their use as (pre)catalysts or starting material for various organic transformations. One problem of the homogeneous catalysts is the difficulty of separating, recovering and recycling the catalyst.

In recent years, the demand for heterogeneous catalysts with high catalytic activity and selectivity has been increasing rapidly. Research in this area can still be considered incipient when we take into account the different combinations of chemical species to form

another with new properties. To obtain a great heterogeneous catalyst, it is necessary to choose a suitable support which has specific properties such as thermal and mechanical stability as well as prevent loss of the catalyst. A lot of attention has recently been given to the synthesis of organic-inorganic hybrid silsesquioxane with eight pendant organic molecular “arms”, which are known as polyhedral oligomer silsesquioxane (POSS). In the POSS, the cubic core is rigid with diameter 0.53 nm and a spherical radius of 1–3 nm including peripheral organic units [3].

However, to the best of our knowledge, this study is the first that has reported the preparation of a POSS functionalized with 3-amino-1,2,4-triazole-5-carboxylic acid (ATZAc) and complexes of molybdenum (II) for catalytic epoxidation of olefins.

Therefore, the objective of this work is the synthesis of two new heterogeneous catalysts POSS-ATZAc-[Mo(η^3 -C₃H₅)Br(CO)₂] (POSS-Mo-I) and POSS-ATZAc-[Mo(CO)₃Br₂] (POSS-Mo-II). POSS-Mo-I and POSS-Mo-II were tested as catalysts in the epoxidation of olefins and compared with the homogeneous catalysts [Mo(η^3 -C₃H₅)Br(CO)₂(ATZAc)] (Mo-I) and [Mo(CO)₃Br₂(ATZAc)] (Mo-II).

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2. Preparations

2.1. Synthesis of POSS-PrCl

3-Chloropropyltriethoxysilane (CPTES) (225 mL) was added to a stirred mixture of methanol (4 l) and concentrated hydrochloric acid (135 mL) under a slow continuous nitrogen purge. The reaction mixture was allowed to stir for six weeks. The resultant solution was then filtered and dried to give a white solid (POSS-PrCl) with 41% yield, according to our previous work [4]. Elemental Analysis for $\text{Si}_8\text{O}_{12}\text{C}_{24}\text{H}_{48}\text{Cl}_8$ (1036.9 g/mol): calculated C 27.77%, H 4.63%; found C 27.56%, H 4.42%. IR (KBr pellet, cm^{-1}): ν (C-H) = 2956, ν (Si-C) = 1627, ν_{as} (Si-O-Si) = 1108, ν (C-Cl) = 698. ^{13}C solid-state NMR (100.61 MHz, ppm): 10.76 (CH_2 -Si), 27.14 (CH_2 - CH_2 Si), 48.30 (CH_2 -Cl). ^{29}Si solid-state NMR (79.48 MHz, (Si-O), ppm): -68.50 (high intensity), -67.42 (low intensity). EDS (Full scale 52191 ct cursor: -0.268 (octs), keV): C, O, Si, Cl.

2.2. Synthesis of POSS-ATZAc

A solution of 3-amino-1,2,4-triazole-5-carboxylic acid (ATZAc) (49.41 g, 385.7 mmol) in anhydrous dimethylformamide (300 mL) was added over a period of 50 min to a stirred solution of POSS-PrCl (25 g, 24.11 mmol) in 300 mL of DMF. The temperature was allowed to rise to 160 °C and stirring was continued for 48 h resulting in a white solution. Ethanol was added to precipitate octa[3-amino-1,2,4-triazole-5-carboxylic acid] propyl] silsesquioxane. The precipitate was separated by filtration and washed with ethanol resulting in the POSS-ATZAc, according to our previous work [4]. The resulting product was obtained after several attempts. Elemental Analysis for $\text{Si}_8\text{O}_{28}\text{C}_{48}\text{H}_{72}\text{N}_{32}$ (1768.8 g/mol): C 32.56%, N 25.32%, H 4.07%; found C 32.49%, N 24.95%, H 4.00%. IR (KBr pellet, cm^{-1}): ν (C-H) = 2939, ν (C=O) = 1704, ν (C=N) = 1600, ν (C-N) = 1446, ν_{as} (Si-O-Si) = 1112. ^{13}C solid-state NMR (100.61 MHz, ppm): 9.64 (CH_2 -Si), 23.23 (CH_2 - CH_2 Si), 48.95 (CH_2 -N), 140.66–149.40 (aromatic ring), 155.22 (carboxylic acid group). ^{29}Si solid-state NMR (79.48 MHz, (Si-O), ppm): -66.04 (high intensity), -58.04 (low intensity). EDS (Full scale 58029 ct cursor: -0.152 (octs), keV): C, N, O, Si.

2.3. Synthesis of homogeneous species $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Br}(\text{CO})_2(\text{ATZAc})]$ (Mo-I)

The organometallic complex $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Br}(\text{CO})_2(\text{NCMe})_2]$ was prepared according to literature methods [1,5]. A solution of $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Br}(\text{CO})_2(\text{NCMe})_2]$ (2.0 g, 5.63 mmol) in ethanol (60 mL) was treated with 3-amino-1,2,4-triazole-5-carboxylic acid (ATZAc) (0.72 g, 5.63 mmol). The resulting solution was stirred for 8 h under reflux and evaporated to dryness. The solid obtained was washed with hexane and dried under vacuum (1.98 g yield) [6]. Elemental Analysis for $\text{MoC}_9\text{O}_2\text{BrN}_2\text{H}_{11}$ (354.94 g/mol): calculated C 30.42%, N 7.88%, H 3.10%, Mo 27.03%; found C 30.28%, N 7.82%, H 2.98%, Mo 26.95%. IR (KBr pellet, cm^{-1}): ν ($\text{C}\equiv\text{O}$) = 1943–1857, ν (C=O) = 1686. EDS (Full scale 22153 ct cursor: -0.348 (octs), keV): C, N, O, Br, Mo.

2.4. Synthesis of homogeneous species $[\text{Mo}(\text{CO})_3\text{Br}_2(\text{ATZAc})]$ (Mo-II)

The organometallic complex $[\text{Mo}(\text{CO})_3\text{Br}_2(\text{NCMe})_2]$ was prepared according to literature methods [1,4,5]. A solution of Mo-II (2.3 g, 5.45 mmol) in ethanol (60 mL) was treated with 3-amino-1,2,4-triazole-5-carboxylic acid (ATZAc) (0.70 g, 5.45 mmol). The resulting solution was stirred for 8 h under reflux and evaporated to dryness. The solid obtained was washed with hexane and dried

under vacuum (2.22 g of yield) [6]. Elemental Analysis for $\text{MoC}_7\text{O}_3\text{Br}_2\text{N}_2\text{H}_6$ (421.94 g/mol): calculated C 19.90%, N 6.63%, H 1.42%, Mo 22.73%; found C 19.76%, N 6.59%, H 1.31%, Mo 22.65%. IR (KBr pellet, cm^{-1}): ν ($\text{C}\equiv\text{O}$) = 1879, 1974, 204, ν (C=O) = 1679. EDS (Full scale 37854 ct cursor: -0.348 (octs), keV): C, N, O, Br, Mo.

2.5. Synthesis of heterogeneous catalyst POSS-ATZAc- $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Br}(\text{CO})_2]$ (POSS-Mo-I)

Octa[(3-amino-1,2,4-triazole-5-carboxylic acid)propyl] octa-silsesquioxane, POSS-ATZAc (2.5 g, 1.41 mmol) was added to a stirred solution of $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Br}(\text{CO})_2(\text{NCMe})_2]$ (4.00 g, 11.27 mmol) in anhydrous ethanol (50 mL) under nitrogen and the mixture was allowed to stir overnight at 80 °C. The solvent was removed by filtration; the solid that remained (yellow powder) was washed three times with anhydrous dichloromethane, and dried, giving 2.35 g of POSS-Mo-I. Elemental Analysis for $\text{Si}_8\text{O}_{36}\text{C}_{68}\text{H}_{92}\text{N}_{32}\text{Br}_4\text{Mo}_4$ (2859.36 g/mol): calculated C 28.53%, N 15.66%, H 3.21%, Mo 13.42%; found C 28.32%, N 15.19%, H 3.02%, Mo 13.15%. IR (KBr pellet, cm^{-1}): ν (C-H) = 2927, ν ($\text{C}\equiv\text{O}$) = 1938–1839, ν (C=O) = 1656, ν (C=N) = 1571, ν (C-N) = 1450, ν_{as} (Si-O-Si) = 1110. ^{13}C solid-state NMR (100.61 MHz, ppm): 8.60 (CH_2 -Si), 22.46 (CH_2 - CH_2 Si), 47.51 (CH_2 -N), 139.93–148.93 (aromatic ring), 154.53 (carboxylic acid group), 76.66, 83.92, 117.89 (allyl groups of complex). ^{29}Si solid-state NMR (79.48 MHz, (Si-O), ppm): -66.35 (high intensity), -57.14 (low intensity). EDS (Full scale 18840 ct cursor: -0.256 (octs), keV): C, N, O, Br, Si, Mo.

2.6. Synthesis of heterogeneous catalyst POSS-ATZAc- $[\text{Mo}(\text{CO})_3\text{Br}_2]$ (POSS-Mo-II)

POSS-ATZAc obtained earlier (2.5 g, 1.41 mmol) was added to a stirred solution of $[\text{Mo}(\text{CO})_3\text{Br}_2(\text{NCMe})_2]$ (4.75 g, 11.28 mmol) in anhydrous ethanol (50 mL) under nitrogen and the mixture was allowed to stir overnight at 80 °C. The solvent was removed by filtration; the solid that remained (brown powder) was washed three times with anhydrous dichloromethane, and dried, giving 2.4 g of POSS-Mo-II. Elemental Analysis for $\text{Si}_8\text{O}_{34}\text{C}_{54}\text{H}_{72}\text{N}_{32}\text{Br}_4\text{Mo}_2$ (2447.48 g/mol): calculated C 26.47%, N 18.30%, H 2.94%, Mo 7.83%; found C 26.27%, N 18.03%, H 2.66%, Mo 7.48%. IR (KBr pellet, cm^{-1}): ν (C-H) = 2927, ν ($\text{C}\equiv\text{O}$) = 1938–1839, ν (C=O) = 1656, ν (C=N) = 1571, ν (C-N) = 1450, ν_{as} (Si-O-Si) = 1110. ^{13}C solid-state NMR (100.61 MHz, ppm): 9.88 (CH_2 -Si), 22.74 (CH_2 - CH_2 Si), 48.70 (CH_2 -N), 139.94–149.40 (aromatic ring), 155.22 (carboxylic acid group). ^{29}Si solid-state NMR (79.48 MHz, (Si-O), ppm): -66.05 (high intensity), -57.45 (low intensity). EDS (Full scale 16064 ct cursor: -0.302 (octs), keV): C, N, O, Br, Si, Mo.

2.7. Study of immobilization of Mo-I and Mo-II complexes on POSS-ATZAc

For optimization of the synthesis of two new heterogeneous catalysts, reaction time, thermodynamic effect, and the amount of complexes fixed on the POSS-ATZAc were studied under air atmosphere.

2.7.1. Equilibrium time of the organometallic complexes

In this optimization, the POSS-ATZAc was thoroughly mixed into 50 mL of a solution containing each organometallic complex with concentration of 1.0×10^{-2} M in ethanol and the contact time was varied from 5 to 40 min at 70 rpm.

2.7.2. Isotherms of immobilization of the molybdenum complexes

The POSS-ATZAc was immersed in 50 mL of an ethanol solution containing each complex of concentrations between 1.0×10^{-3} to

1.0×10^{-2} M under agitation for 25 min at 25 ± 0.2 °C. The quantity of the Mo for each complex was determined by ICP-MS.

2.7.3. Thermodynamic studies of the Mo-I and Mo-II complexes

The effects of temperature on the immobilization efficiency were investigated for both complexes of molybdenum in the temperature range of 25–65 °C keeping the concentration of the complexes constant, the dose of adsorbent and the contact time.

2.8. Chromatographic parameters

The analyses were obtained through of a GC-MS (Thermo Scientific) using fused silica capillary column. The carrier gas used was the helium with constant pressure mode of 80 KPa. The heating ramp of the oven was programmed varying the temperature from 60 to 200 °C (held for 3 min) at a rate of 30 °C/min. Samples of 1.0 μ L were injected in a preheated inlet (250 °C) working in the splitless mode. The mass spectrometer was operated in the full scan mode in the range 30–350. To analyse of the conversion percentages, the proportion between diethyl ether and the olefins were calculated.

2.8.1. Catalytic studies

POSS-Mo-I and POSS-Mo-II were tested in the epoxidation of 1-octene, cyclooctene, limonene, *cis*-3-hexen-1-ol, *trans*-3-hexen-1-ol and styrene, using *tert*-butyl hydroperoxide (TBHP) as oxidant at 55 °C under nitrogen atmosphere [2,6–9] and compared with Mo-I and Mo-II. The reactions were performed in a container with magnetic stirring and under atmosphere of nitrogen (closed system) [2,6–8]. In each case, the container was loaded with catalyst/substrate/oxidant in a ratio of 1:100:200 in mmol% [2,6–8]. **Catalysts:** 0.137 mmol of POSS-Mo-I (0.10 g), POSS-Mo-II (0.175 g), Mo-I (0.055 g) and Mo-II (0.064 g); **Substrates:** 13.70 mmol of 1-Octene (1.53 g, 2.14 mL), cyclooctene (1.51 g, 1.78 mL), (S)-limonene (1.86 g, 2.20 mL), *cis*-3-hexen-1-ol (1.37 g, 1.61 mL), *trans*-3-hexen-1-ol (1.37 g, 1.67 mL) and styrene (1.42 g, 1.56 mL); dibutyl ether (internal standard) the same amount in mmol of each olefin was used and dichloromethane (CH₂Cl₂); **Oxidant:** 27.40 mmol of TBHP (5.0–6.0 M in decane) (2.47 g, 2.65 mL).

The progresses of the reactions were monitored by GC-MS analysis. The reactions were initiated with the addition of the oxidant agent (TBHP). Samples were taken every 20 min during the first 1 h and then after 2, 4, 6, 8, and 24 h of reaction. To disable the oxidant agent, manganese dioxide was added in each collected sample. The resulting suspensions were separated by filtration and an aliquot of the supernatant was injected into the GC-MS. The conversion of each substrate was evaluated by formation of their respective epoxides in a GC-MS using the previously developed methods. Epoxidation test without a metal catalyst was investigated and no catalytic activity was observed [2,6–9].

3. Results and discussion

3.1. POSS-ATZAc-[Mo(η^3 -C₃H₅)Br(CO)₂] (POSS-Mo-I) and POSS-ATZAc-[Mo(CO)₃Br₂] (POSS-Mo-II) as heterogeneous catalysts

[3-chloropropyl]-silsesquioxane (POSS-PrCl) precursor was firstly prepared by the hydrolysis of 3-chloropropyltriethoxysilane (CPTES) in methanol under acidic conditions. Next, the POSS-Cl was functionalized subsequently with ATC in a molar ratio of 1:16 resulting in a new functionalized-POSS, abbreviated as POSS-ATZAc. This new silsesquioxane was functionalized with two types of complexes of Mo²⁺ according to the optimizations performed in Section 2.3.1 to 2.3.3. The syntheses of the catalysts are shown in Scheme 1.

Based on the nitrogen elemental analysis the density of the

organofunctionalization was calculated giving a value of 4.45 mmol of (3-amino-1,2,4-triazole-5-carboxylic acid)propyl groups per gram of material POSS-ATZAc, confirming that eight (3-amino-1,2,4-triazole-5-carboxylic acid)propyl arms are linked to silsesquioxane core. The value of 13.15% of Mo suggests that four molybdenum units are bound to the POSS-ATZAc-[Mo(η^3 -C₃H₅)Br(CO)₂] (POSS-Mo-I), whereas the value of 7.48% confirming that only two molybdenum units are bound to the POSS-ATZAc-[Mo(CO)₃Br₂] (POSS-Mo-II).

In the FTIR of POSS-ATZAc the presence of the carbonyl band (C=O) suggests that the reaction between the propyl chloride arm and ATZAc ligand occurred by NH₂ group, once the amine localized in the ring has a greater stability [6,7,10–13]. The FTIR of the POSS-Mo-I and POSS-Mo-II exhibits additionally the band C≡O proving the coordination of the complexes [Mo(CO)₂] and [Mo(CO)₃] on the POSS-ATZAc. The presences of these bands are in agreement with the literature [1,4–7].

¹³C NMR of the POSS-ATZAc shows a shift of the first three peaks when compared to POSS-PrCl precursor material [14–16]. This displacement is related to the functionalization reaction with 3-amino-1,2,4-triazole-5-carboxylic acid (ATZAc). The others peaks appear due to incorporation of 3-amino-1,2,4-triazole-5-carboxylic acid, these signals are characteristic of ATZAc groups present in the structure, confirming the modifying the surface of the support. After the reaction with [Mo(η^3 -C₃H₅)Br(CO)₂(NCMe)₂] complex, the FTIR of the POSS-ATZAc-[Mo(η^3 -C₃H₅)Br(CO)₂] (POSS-Mo-I) displays three peak at over than its POSS-ATZAc precursor material. These peaks may be concerning to the allyl groups, indicating the incorporation of the complex on the functionalized-POSS [6]. On the other hand, the resonance peak of the carbonyl groups of the complex of the POSS-ATZAc-[Mo(CO)₃Br₂] catalyst are not apparent due to the absence of allyl groups [6,17].

The signals observed in the ²⁹Si NMR spectra of the synthesized compounds seem to indicate octa-substituted structures of the POSS with closed cage, which were confirmed by elemental analyses of C, H and N. On the other hand, the possibility of occurrence in much smaller percentages of isomer structures or cage expansion products such as deca- and dodecahedral silsesquioxane cages is not excluded [18,19].

Scanning electron micrographs (SEM) were performed in each steps of preparation of the heterogeneous catalysts in order to check their different morphologies. The SEM images of heterogeneous catalysts POSS-Mo-I and POSS-Mo-II are shown in Fig. 1A and B respectively.

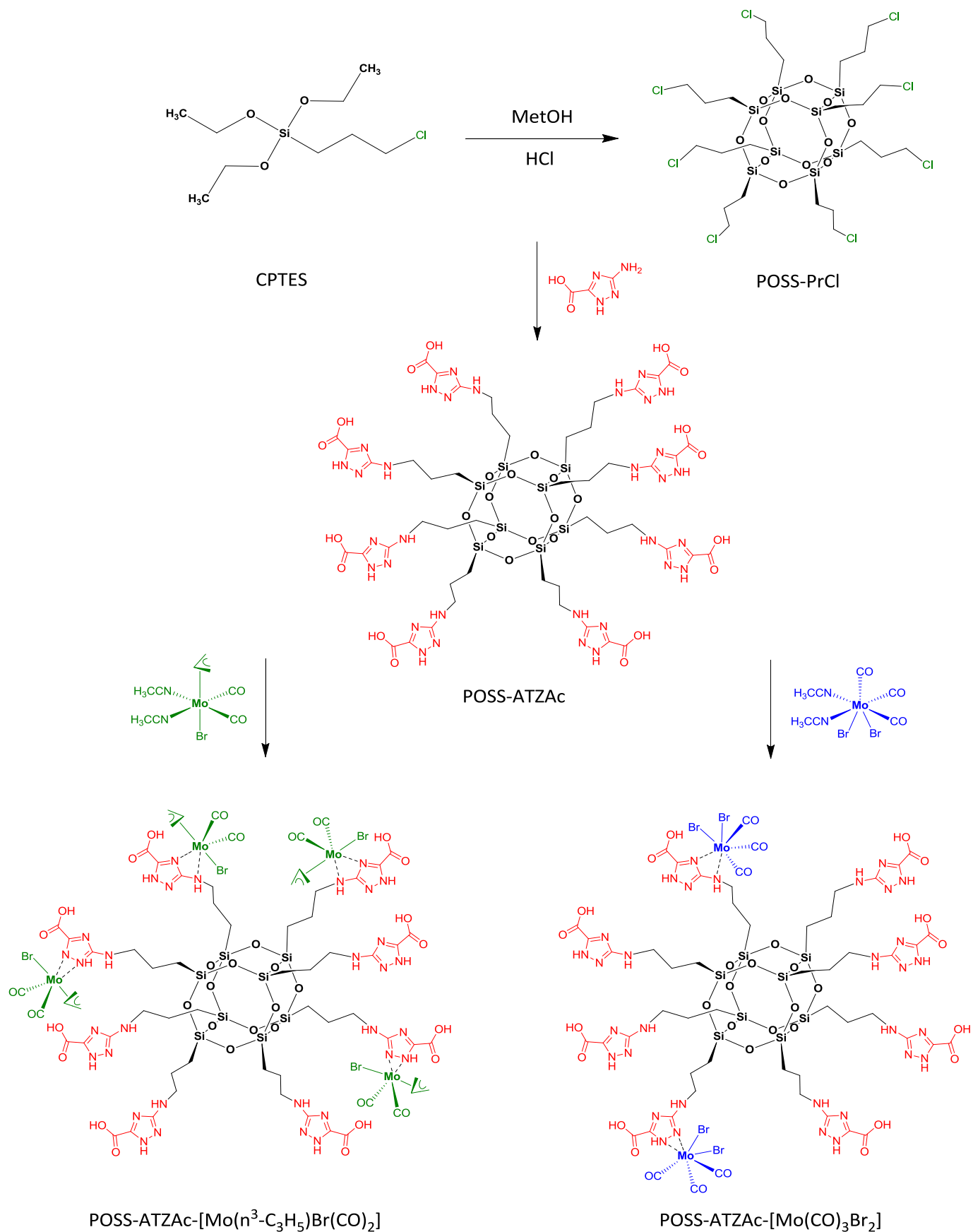
As can be seen, the images of the heterogeneous catalysts (Fig. 1A and B) present an agglomerate surface [20]. This can be beneficial when dealing with heterogeneous catalysts, since would facilitate their separation and recycling.

In addition, the crystallinity of these silsesquioxane-based compounds was evaluated using powder X-ray diffraction (XRD) techniques.

According to Fig. 2A, the X-ray diffractogram shows that the POSS-PrCl precursor material has high crystallinity, confirming its octahedral cage [18]. After the substitution with ATZAc molecules, the material acquires an amorphous nature (Fig. 2B) [21].

After the reaction with the complexes [Mo(η^3 -C₃H₅)Br(CO)₂(NCMe)₂] and [Mo(CO)₃Br₂(NCMe)₂] the X-ray spectra exhibited two major peaks at 9.54° and 21.96° (Fig. 2C) for POSS-Mo-I and at 9.36° and 21.480° (Fig. 2D) for POSS-Mo-II catalysts. The appearances of the second peak for both catalysts confirm the incorporation of organometallic complexes on the surface of the POSS-ATZAc.

The TGA curves of the POSS-Mo-I and POSS-Mo-II catalysts in Fig. 3A and 3B shows that the first mass loss occurs until 100 °C concerning the loss of physisorbed water [22] with mass loss of



Scheme 1. Synthesis of the $\text{POSS-ATZAc-}[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Br}(\text{CO})_2]$ and $\text{POSS-ATZAc-}[\text{Mo}(\text{CO})_3\text{Br}_2]$.

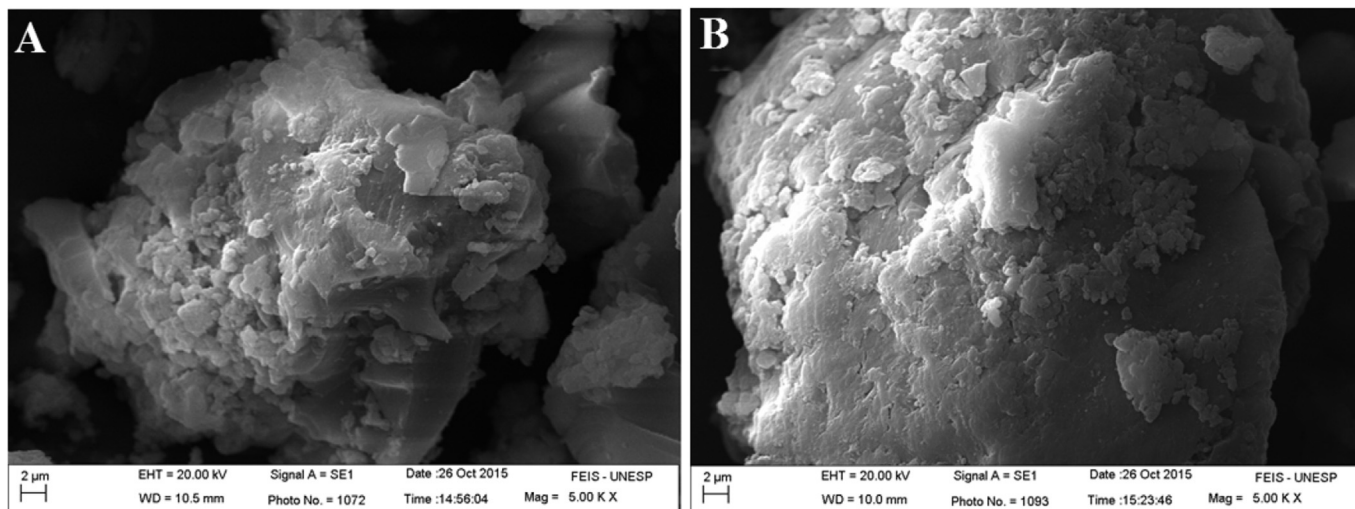


Fig. 1. SEM images of the heterogeneous catalysts POSS-Mo-I (A) and POSS-Mo-II (B).

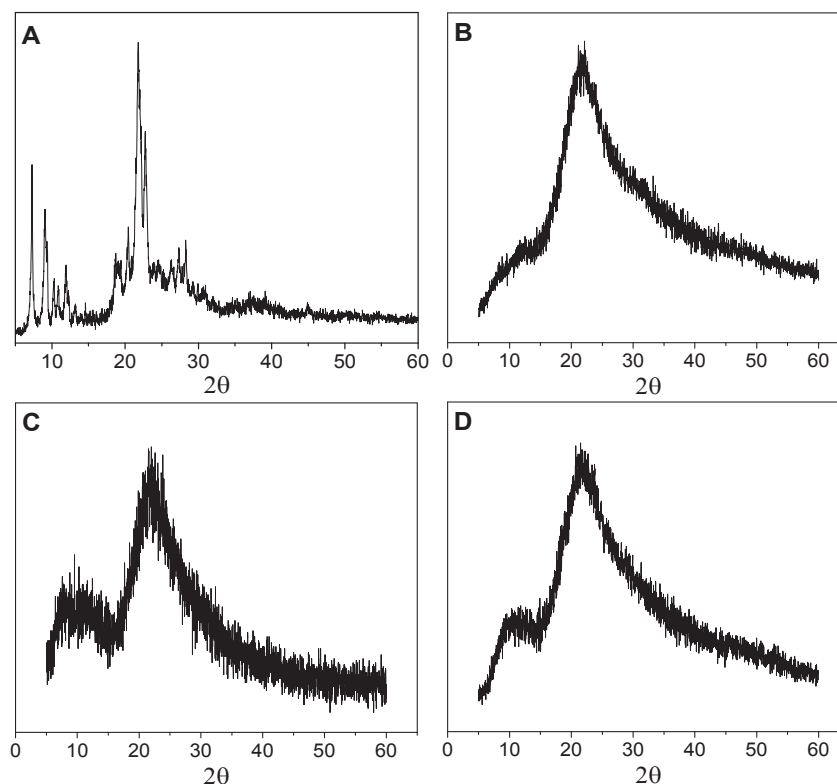


Fig. 2. X-ray diffractograms of the POSS-PrCl (A), POSS-ATZAc (B), POSS-Mo-I (C) and POSS-Mo-II (D).

6.22% for POSS-Mo-I and 4.18% for POSS-Mo-II.

The second mass loss of the heterogeneous catalysts POSS-Mo-I and POSS-Mo-II are initiated from 100 °C to about 470 °C and refers the decomposition of the 3-amino-1,2,4-triazole-5-carboxylic acid layer [22]. At this stage, the values of 34.23% for POSS-Mo-I and 38.28% for POSS-Mo-II show that the eight vertices of the POSS were functionalized with ATZAc molecules. The third mass loss occurs from 470 °C to about 550 °C. For heterogeneous catalysts are associated with the degradation of the propyl chain together with the organic groups of molybdenum complexes. The amount of mass loss for POSS-Mo-I and POSS-Mo-II was 24.94 and 24.34%

respectively. The thermal stability indicated that both catalysts could be applied under the temperature of about 200 °C.

3.2. Study of immobilization

Immobilization experiments such as adsorbent dosage, equilibrium time and immobilization isotherm have been studied to optimize the syntheses process of the two new catalysts. The adsorbent dosage on the immobilization of Mo-I and Mo-II in ethanol solution was investigated and the results were shown in Fig. 4A. As can be seen, the amount of $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)]$

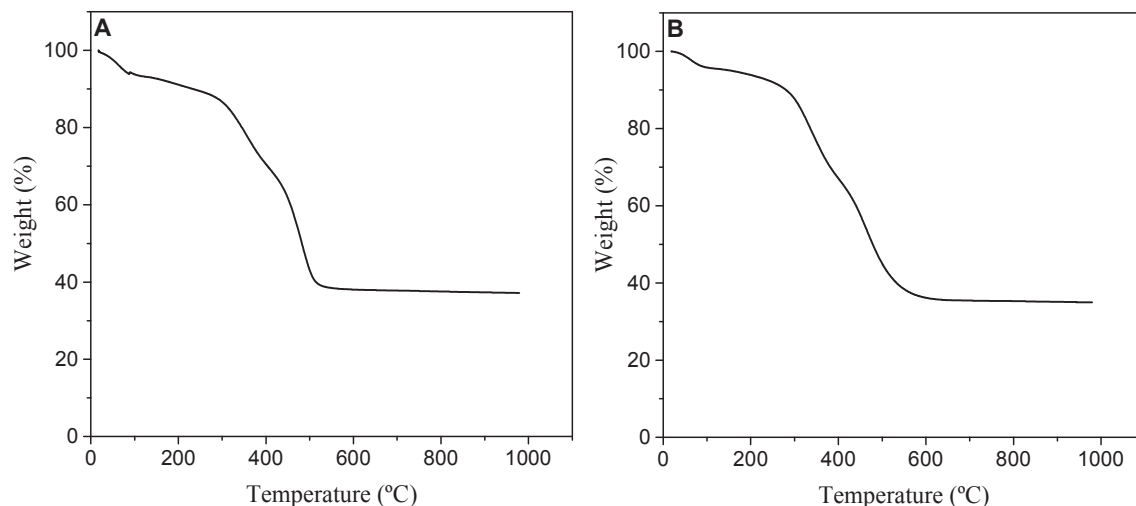


Fig. 3. Thermogravimetric curves of the POSS-Mo-I (A) and POSS-Mo-II (B) under air atmosphere.

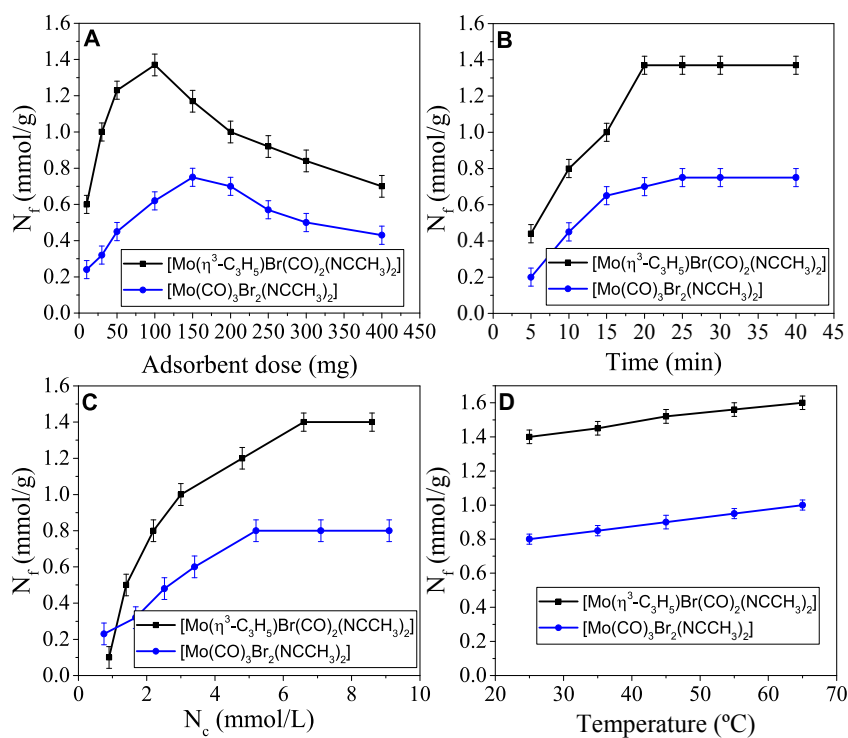


Fig. 4. Effect of dose of adsorbent (A), time of contact (B), immobilization isotherms (C) and Effect of temperature (D) in ethanol solution for $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Br}(\text{CO})_2(\text{NCMe})_2]$ and $[\text{Mo}(\text{CO})_3\text{Br}_2(\text{NCMe})_2]$ using POSS-ATZAc.

$\text{Br}(\text{CO})_2(\text{NCMe})_2]$ organometallic complex uptake increases from 0.60 mmol/g with 10 mg adsorbent up to 1.37 mmol/g with 100 mg adsorbent and from 0.24 mmol/g with 10 mg adsorbent up to 0.75 mmol/g with 150 mg adsorbent for $[\text{Mo}(\text{CO})_3\text{Br}_2(\text{NCMe})_2]$ complex. This phenomenon was likely due to increased numbers of vacant adsorption sites and increased surface area availability [23–27]. When the amounts of adsorbents were increased to 100 and 150 mg for $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Br}(\text{CO})_2(\text{NCMe})_2]$ and $[\text{Mo}(\text{CO})_3\text{Br}_2(\text{NCMe})_2]$ complexes, the adsorption amounts reached maximums. On the other hand, the immobilization capacity decreased as the adsorbent dosage increased from 100/150 mg due to reduced available surface area and reduced unoccupied active

sites.

Furthermore, large doses might result in adsorbent aggregation [24]. Similar results have been reported in the literature [23–26].

Fig. 4B shows the effects of contact time on the immobilization of POSS-ATZAc, for the complexes $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Br}(\text{CO})_2(\text{NCMe})_2]$ and $[\text{Mo}(\text{CO})_3\text{Br}_2(\text{NCMe})_2]$ at 25 °C in ethanol solution. As can be seen, the equilibrium time necessary for the immobilization of the complex $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Br}(\text{CO})_2(\text{NCMe})_2]$ was 20 min and 25 min for $[\text{Mo}(\text{CO})_3\text{Br}_2(\text{NCMe})_2]$.

The contact time has significant importance in immobilization studies. The rapid immobilization of the complexes and the equilibrium in a short period indicates the effectiveness of the support

(POSS-ATZAc).

To investigate the immobilization capacity (Fig. 4C), a concentration range of both complexes in ethanol solutions were shaken at 25 °C. The maximum value for $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Br}(\text{CO})_2(\text{NCMe})_2]$ using POSS-ATZAc was 1.40 mmol g^{-1} and 0.80 mmol g^{-1} for $[\text{Mo}(\text{CO})_3\text{Br}_2(\text{NCMe})_2]$.

Additionally, the thermodynamic study was carried out to verify the stability of the organometallic complex on the support.

The effect of the temperature on the immobilization experiments were performed at five different temperatures (25, 35, 45, 55 and 65 °C). In Fig. 4D, the immobilization process was favored by the increasing of temperature, which demonstrates that, the immobilization of the complexes is endothermic [28].

3.2.1. Applications of isotherm models

From Fig. 4C and B it was possible to apply the isotherm and kinetics models [29–31].

Langmuir and pseudo-second-order model are the best ones to describe the immobilization data of both complexes.

The theoretical data of the models that best fit the experimental data are listed in Table 1.

The Langmuir model emphasizes that the immobilization of the molybdenum complex ($[\text{Mo}(\text{CO})_3\text{Br}_2(\text{NCMe})_2]$) was in monolayers. It was also verified that the value of R_L was smaller than 1 demonstrating that the immobilization of the complex was favorable [29,30].

The parameter n greater than 1 reflects an immobilization in multi-layered (heterogeneous) of the organometallic complex $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Br}(\text{CO})_2(\text{NCMe})_2]$ [32].

The E value obtained from the D-R model [33] for immobilization of the complexes were superior than 8 kJ/mol^{-1} , in which indicates that the immobilizations of the complexes were achieved by chemisorption.

Pseudo-second order model [31] was the most appropriate to define the kinetic data for both complexes.

The negative and positive values of ΔG , ΔH and ΔS show a spontaneous nature, an endothermic process and an increased randomness for both complexes, respectively [31–33]. The temperatures of 25, 35, 45 and 55 °C showed the same behavior.

4. Activity catalytic

The activities of POSS-Mo-I, POSS-Mo-II, Mo-I and Mo-II as catalytic precursors for the epoxidation of olefins were investigated. Fig. 5 shows the epoxidation kinetics of the 1-octene, cyclooctene, (S)-limonene, *cis*-3-hexen-1-ol, *trans*-3-hexen-1-ol and styrene, using *tert*-butyl hydroperoxide (TBHP) as oxidant. Fig. 5A shows the epoxidation of each olefin by POSS-Mo-I, in which the maximum conversion rate (conversion time of the olefin to an epoxide) was achieved in a short period of time, i.e. 2 h for 1-oct and S-lim, 4 h for Cy8 and Sty. However, *cis*-3 and *trans*-3 require

a period of 6 h.

In contrast, the maximum conversion rate for Mo-I (Fig. 5B) was of 4 h for 1-oct, *cis*-3 and *trans*-3, and 2 h for Cy8, S-lim and Sty. As can be seen, the POSS-Mo-I has only one maximum conversion rate better than Mo-I for the 1-oct olefin, while that the others olefins have a better rate in the presence of the homogeneous catalyst Mo-I.

The catalysts POSS-Mo-II and Mo-II (Fig. 5C and D) do not exhibit catalytic activity for the most olefins, except for the styrene (Sty) and cyclooctene (Cy8). The maximum conversion rates for both catalysts were of 2 h for Cy8 and Sty.

Though the necessary period to produce the active species is different in each occasion, similar catalytic species are possibly formed [6,7].

Therefore, the results accessible in Table 2 show that the heterogeneous catalysts in question have a conversion and TOF slightly lower but it in general very similar to homogeneous catalysts. This is due that homogeneous catalysts have advantages over the heterogeneous, in particular greater selectivity and yield [8,34].

Nevertheless, the facility in which the heterogeneous processes products are separated and recycled, make these preferred by industry [8]. The four substrates, cyclooctene, *cis*-3-hexen-1-ol, *trans*-3-hexen-1-ol and styrene are selectively oxidized to their respective epoxide without formation of diols for all catalysts (heterogeneous and homogeneous).

However, in the oxidation of 1-octene, two products are detected and referred to as 1-octanal and 1,2-epoxyoctane (Table 3). POSS-Mo-I has a high selectivity for formation of 1,2-epoxyoctane, 92% versus 8% for the formation of 1-octanal. On the other hand, Mo-I decreases the selectivity for 90% in epoxy against 10% for 1-octanal.

No catalytic activity was detected for the POSS-Mo-II and Mo-II catalysts in the epoxidation of 1-octene, (S)-limonene, *cis*-3-hexen-1-ol and *trans*-3-hexen-1-ol.

It is known that the conversions and TOF significantly depend on the organometallic complex and the nature of the substrate, and also that the allyl complexes are more active than those of type Mo-II [6,7,17].

The single detected signal was in the epoxidation of the (S)-limonene using Mo-II, which showed a conversion (5%) and TOF very low.

The epoxidation of (S)-limonene results in the formation of several products (Table 3) and six of them were detected by GC-MS: Isomers of (+)-limonene-1,2-epoxide (Z-lim-Epox and E-lim-Epox), isomers of cyclohexen-1-ol-2-methyl-5-(1-methylethenyl) (Z-lim-OH and E-lim-OH), (1S,2S,4R) -(+)-Limonene-1,2-diol (lim(OH)₂) and dipentene dioxide (dioxide) [6,35].

(S)-limonene has a good conversion and TOF and as can be seen, there is a strong selectivity for oxidation of the double bond between carbons, yielding the Z-lim-Epox, E-lim-Epox and dioxide isomers.

Table 1

Effects of immobilization parameter: kinetics, isotherm and thermodynamics for $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Br}(\text{CO})_2(\text{NCMe})_2]$ and $[\text{Mo}(\text{CO})_3\text{Br}_2(\text{NCMe})_2]$ complexes in ethanol solutions onto POSS-ATZAc.

| $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Br}(\text{CO})_2(\text{NCMe})_2]$ N_i^{exp} mmol/g | Langmuir model | | | Pseudo-second-order model | | | Thermodynamic parameters ^a | | |
|--|-----------------------------|----------------|--------------|-----------------------------|-----------------------------|--------------|---------------------------------------|-------------------------------------|---------------------|
| | N_i^{max} (mmol/g) | R_L (L/mmol) | R^2 | N_i^{max} (mmol/g) | K_2 (min^{-1}) | R^2 | ΔG (KJ/mol) | ΔS (J/mol k^{-1}) | ΔH (KJ/mol) |
| 1.40 | 1.42 | 0.006 | 0.998 | 1.36 | 8.548 | 0.999 | -33.716 | 99.857 | 35.362 |
| $[\text{Mo}(\text{CO})_3\text{Br}_2(\text{NCMe})_2]$ N_i^{exp} mmol/g | Langmuir model | | | Pseudo-second-order model | | | Thermodynamic parameters ^a | | |
| | N_i^{max} (mmol/g) | R_L (L/mmol) | R^2 | N_i^{max} (mmol/g) | K_2 (min^{-1}) | R^2 | ΔG (KJ/mol) | ΔS (J/mol k^{-1}) | ΔH (KJ/mol) |
| 0.80 | 0.78 | 0.015 | 0.996 | 0.71 | 5.741 | 0.995 | -31.326 | 92.855 | 58.327 |

^a Temperature = 65 °C.

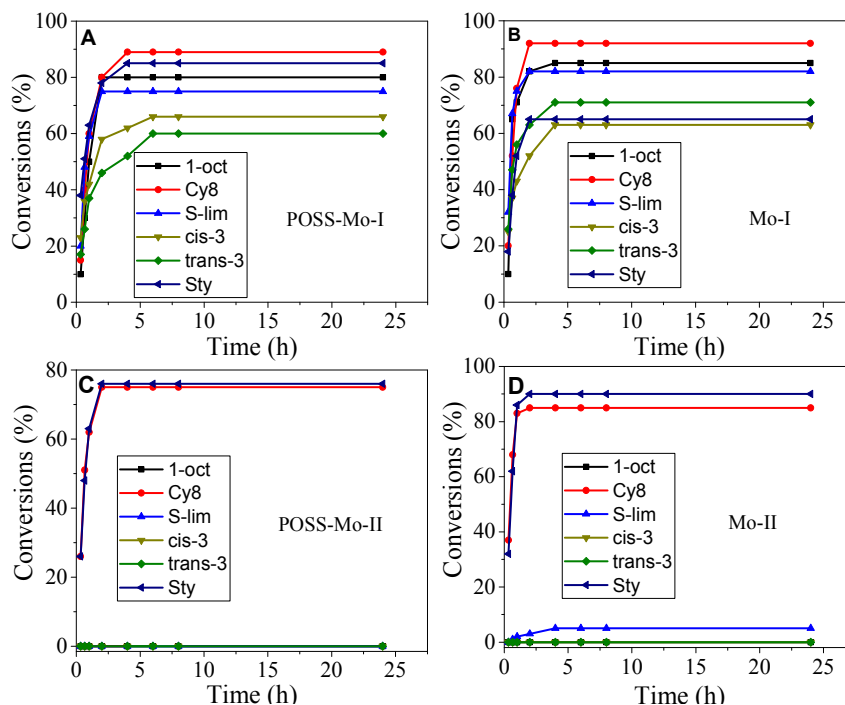


Fig. 5. Epoxidation kinetics of each olefin using heterogeneous and homogeneous catalysts.

Table 2

Conversions and Turnover Frequencies (TOF) for epoxidation of olefins in the presence of TBHP.

| Catalytic precursor | Substrate | Conversion ^a (%) | TOF ^b |
|---------------------|----------------------|-----------------------------|------------------|
| POSS-Mo-I | 1-octene | 90 | 152 |
| Mo-I | 1-octene | 85 | 176 |
| POSS-Mo-II | 1-octene | 0 | 0 |
| Mo-II | 1-octene | 0 | 0 |
| POSS-Mo-I | cyclooctene | 89 | 166 |
| Mo-I | cyclooctene | 92 | 172 |
| POSS-Mo-II | cyclooctene | 75 | 117 |
| Mo-II | cyclooctene | 85 | 123 |
| POSS-Mo-I | (S)-limonene | 75 | 149 |
| Mo-I | (S)-limonene | 82 | 158 |
| POSS-Mo-II | (S)-limonene | 0 | 0 |
| Mo-II | (S)-limonene | 5 | 10 |
| POSS-Mo-I | cis-3 ^c | 66 | 134 |
| Mo-I | cis-3 ^c | 63 | 147 |
| POSS-Mo-II | cis-3 ^c | 0 | 0 |
| Mo-II | cis-3 ^c | 0 | 0 |
| POSS-Mo-I | Trans-3 ^d | 60 | 129 |
| Mo-I | Trans-3 ^d | 71 | 137 |
| POSS-Mo-II | Trans-3 ^d | 0 | 0 |
| Mo-II | Trans-3 ^d | 0 | 0 |
| POSS-Mo-I | styrene | 85 | 130 |
| Mo-I | styrene | 65 | 142 |
| POSS-Mo-II | styrene | 76 | 80 |
| Mo-II | styrene | 90 | 76 |

^a Conversion at 24 h.

^b In units of mol (mol of Mo)⁻¹ h⁻¹.

^c Cis-3-hexen-1-ol.

^d Trans-3-hexen-1-ol.

POSS-Mo-I shows selectivity for epoxide of 87% whereas that the Mo-I increase this percentage to 95%.

Already, the Mo-II catalyst has a selectivity for epoxide of 100% (Z-lim-Epox and E-lim-Epox), but the conversion is 5%.

In the present work, the differences of reactivity between POSS-Mo-I and POSS-Mo-II catalysts may be associated with the metal

coordination sphere and nature of the ligands.

On the other hand, the unexpected better performance of the supported catalyst (POSS-Mo-I) as compared to homogeneous catalyst (Mo-I) in the cases of the 1-octene, cis-3 and styrene conversions can be attributed, at least partly, to its characteristic of being a nanosized catalyst.

Table 4 shows the comparison with other type of catalysts in the epoxidation of olefins. As can be seen, our catalysts have similar conversions or better than other types of Mo-catalysts.

5. Leaching studies

Molybdenum leaching studies were also performed by reusing the recovered POSS-Mo-I and POSS-Mo-II in five consecutive reaction cycles [17,39–41]. Before each reuse the solids were separated from the reaction solution, washed with dichloromethane and dried at 50 °C. The catalytic activity decreased slightly from the first to the second cycle, but afterwards tended to remain constant for the POSS-Mo-I and POSS-Mo-II (Table 5).

ICP-MS analysis was used to determine the percentage of molybdenum leached out into the liquid mixture during reactions. The Mo loading of the [Mo(η^3 -C₃H₅)Br(CO)₂(NCMe)₂] complex after five reaction cycles is at least 99% of the starting value for the POSS-Mo-I, whereas for POSS-Mo-II, the molybdenum loading of the [Mo(CO)₃Br₂(NCMe)₂] complex was 98.3%. The leaching of some weakly anchored molybdenum complex present in the original catalyst may account for the initial low loss of activity for both catalysts. Table 5 also shows the selectivity to epoxyoctane for the POSS-Mo-I and POSS-Mo-II until the fifth cycle and, as shown, the selectivity for both catalysts was 100% in all cycles [42]. Also, the catalytic behavior of the separated liquid was tested by addition of fresh olefin to the filtrates after each cycle. The oxidation reaction under the same reaction conditions as when the catalyst was utilized showed that the found results are the equivalent as blank experiments.

Table 3
Selectivity in the oxidation of 1-octene and (S)-Limonene.

| Catalyst | Subs. ^a | 1-Octanal ^b | 1,2-Epoxyoctane ^b | Z-Lim-Epox ^b | E-Lim-Epox ^b | Z-Lim-OH ^b | E-Lim-OH ^b | Lim-(OH) ₂ ^b | Dioxide ^b | |
|------------|--------------------|------------------------|------------------------------|-------------------------|-------------------------|-----------------------|-----------------------|------------------------------------|----------------------|---|
| POSS-Mo-I | 1-octene | 8 | 92 | | | | | | | |
| Mo-I | | 10 | 90 | | | | | | | |
| POSS-Mo-II | (S)-limonene | 0 | 0 | | | | | | | |
| Mo-II | | 0 | 0 | | | | | | | |
| POSS-Mo-I | | | | | 52 | 33 | 5 | 2 | 6 | 2 |
| Mo-I | | | | | 23 | 68 | 2 | 2 | 1 | 4 |
| POSS-Mo-II | | | | 0 | 0 | 0 | 0 | 0 | 0 | |
| Mo-II | | | | 80 | 20 | 0 | 0 | 0 | 0 | |

^a Substrate.^b Percentage (%).**Table 4**
Comparison of the conversion capacities with others types of Mo-catalysts.

| Catalysts | Olefins | Conv. ^a | Ref. |
|--|-----------|--------------------|---------------|
| Mo ^(VI) Cl ₂ O ₂ Bipy | 1-Octene | 55 | [36] |
| Mo-AFBNPs | 1-Octene | 60 | [37] |
| Mo-AMP-CuBTC | 1-Octene | 62 | [38] |
| [MoO ₂ L(EtOH)] | Cy8/1-oct | 88/64 | [39] |
| POSS-Mo-I | Cy8/1-oct | 89/90 | Present study |
| POSS-Mo-II | Cy8 | 75 | Present study |
| Mo-I | Cy8/1-oct | 92/85 | Present study |
| Mo-II | Cy8 | 85 | Present study |

^a Conversion (%).**Table 5**
Recycling studies performed over heterogeneous catalysts.

| Catalyst | Cyclooctene | |
|----------------------|----------------|----------------------------|
| | Conversion (%) | Selectivity to epoxide (%) |
| POSS-Mo-I | | |
| 1 ^o cycle | 89 | 100 ^a |
| 2 ^o cycle | 80 | 100 ^a |
| 3 ^o cycle | 80 | 100 ^a |
| 4 ^o cycle | 79 | 100 ^a |
| 5 ^o cycle | 79 | 100 ^a |
| POSS-Mo-II | | |
| 1 ^o cycle | 75 | 100 ^a |
| 2 ^o cycle | 66 | 100 ^a |
| 3 ^o cycle | 65 | 100 ^a |
| 4 ^o cycle | 65 | 100 ^a |
| 5 ^o cycle | 65 | 100 ^a |

^a Epoxyoctane.

6. Conclusions

The study of immobilization of the [Mo(η^3 -C₃H₅)Br(CO)₂(NCMe)₂] and [Mo(CO)₃Br₂(NCMe)₂] complexes was of essential importance to adjust the synthesis of the catalysts.

The results of the characterization techniques allowed attesting that the syntheses of POSS-Mo-I, POSS-Mo-II, Mo-I and Mo-II catalysts were successful.

After the immobilization of the complexes on the precursor material, no trace of the acetonitrile molecule was observed, proving its lability.

The catalyst with allyl group (POSS-Mo-I) was more effective in the epoxidation of olefins, while the POSS-Mo-II showed no catalytic activity for most substrates.

POSS-Mo-I shows a selectivity for epoxide of 100% for cyclooctene, *cis*-3-hexen-1-ol, *trans*-3-hexen-1-ol and styrene, and 92% for 1-octene and 87% for (S)-limonene.

The new catalysts are shown to have a great catalytic activity in the epoxidation of all olefins studies, but with singular attention to

cyclooctene which has 89% conversion using POSS-Mo-I and to styrene which has 76% using POSS-Mo-II.

Recycling studies performed over heterogeneous catalysts show that the conversions from the second cycle remain constant and with selectivity to epoxide of 100% for both catalysts.

The activities of the heterogeneous catalysts were similar to those of the homogeneous catalysts.

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