Mo(VI) Complexes Immobilized on SBA-15 as an Efficient Catalyst for 1-Octene Epoxidation

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Abstract: SBA-15 materials were functionalized through a post-synthetic methodology with molybdenum-Schiff bases to provide catalytic activity in epoxidation reactions. Thus, glycidoxypropyl functionalities were first attached to the surface of the mesostructured silica, followed by the reaction of the immobilized oxirane groups with 2-amino propyl pyridine. This reaction allowed the obtaining of (hydroxypropyl)-2-aminomethyl pyridine ligands, directly tethered to the surface of the mesoporous silica-based SBA-15, which resulted in excellent chelating ligands to immobilize dioxo molydenum species by a reaction with $MoO_2(acac)_2$. This investigation comprises a thorough characterization of the process for building the immobilized molybdenum-Schiff base complexes, as well as the use of the obtained materials in 1-octene oxidation in the presence of organic hydroperoxides. These materials displayed high intrinsic catalytic activity in the epoxidation of 1-octene with organic hydroperoxides under a wide variety of conditions, although both the reaction solvent as well as the nature of the organic hydroperoxide, exerted a dramatic influence on the catalytic activity of these heterogeneous oxidation catalysts. Thus, whereas nonpolar solvents provided good epoxide yields with high efficiency in the use of the oxidant, polar solvents depressed the catalytic activity of the supported Mo-Schiff bases. These results have been ascribed to the competition with the solvent, when polar, for binding to the metal sites, thus avoiding the formation of the hydroperoxo-metal cycle and the epoxidation of the olefin. The catalysts presented here show good reusability with low catalytic activity decay after the first reuse.

Keywords: epoxidation; heterogeneous catalysts; molybdenum; Schiff base; tethering

1. Introduction

Alkene epoxidation is a field of both academic and industrial importance due to the versatility of the epoxides, which are key building blocks for the synthesis of numerous chemicals [1,2]. A wide variety of homogeneous catalysts based on different metals have been evaluated in this reaction, including Mo(VI) complexes, which are specially interesting due to their high inherent catalytic activity and selectivity [2,3]. Indeed, a relevant industrial example is the Halcon process, based on the formation of propylene oxide by using a soluble molybdenum complex as catalyst and tert-butylhydroperoxide (TBHP) as oxidant [4]. The heterogenization of homogeneous catalytic systems by immobilization onto solid supports makes easier catalysts recovery and recycling, improving the economic and environmental performance of the process. Numerous materials such as zeolites, polymers, amorphous and mesostructured silica, among many others, have been tested as carriers for the synthesis of molybdenum-containing heterogeneous alkene epoxidation catalysts [5,6]. Regarding to zeolites, some remarkable examples are works of Corma et al. [7] who described the synthesis of a chiral molybdenum complex anchored onto modified Y zeolite for the selective epoxidation of allylic alcohols. This Y zeolite was treated for developing, besides its typical micropores, a

supermicropore-mesopore system to facilitate the dispersion of bulky Mo species. Niederer et al. [8] evaluated the oxidation capabilities of β zeolite functionalized with molybdenum, vanadium, and titanium atoms, that were isomorphically incorporated to the zeolite framework. Their catalytic results in epoxidation of different olefins showed a clear effect of the zeolite pore size. Sakthivel et al. [9] reported the grafting of cyclopentadienyl molybdenum complexes on the surface of β and Y zeolites for cyclooctene epoxidation, obtaining high activity and epoxide selectivity. However, the comparison with homogeneous systems suggests the reaction is probably limited because of hindrances to the reactants' diffusion when using immobilized molybdenum complexes. To summarize, different molybdenum-containing zeolites have been successfully tested in the epoxidation of several olefins, but their microporous structure frequently involves mass transfer limitations.

Another promising and widely evaluated option for the immobilization of molybdenum sites has been the use of polymers as carriers. Ambroziak et al. [2], Mbeleck et al. [10], and Saha et al. [11] described the synthesis and epoxidation behavior of some Mo(VI) complexes supported on polybenzimidazole and polystyrene 2-(aminomethyl)pyridine. Catalytic results indicate that stable long-lived heterogeneous catalysts can be prepared to obtain high reaction rates and epoxide selectivity for several olefins. In a similar way, Fan et al. [6] reported the immobilization of molybdenum acetylacetonate on cross-linked polymer (divinyl benzene-allyl amine) DVB-AA, leading to an efficient heterogeneous catalyst for olefins epoxidation. However, from a practical point of view, the use of polymers as catalyst supports still presents some drawbacks mainly related to their low porosity and low chemical and mechanical stability (as compared to inorganic carriers).

An option for overcoming problems associated with zeolites (low pore size) and polymers (low porosity and stability) could be using ordered mesoporous silicas for anchoring molybdenum species. However, suitable immobilization procedures must be applied for these catalyst supports, as conventional grafting procedures on silica do not allow preserving the interaction between organic ligands and molybdenum sites, decreasing the catalytic activity or, if the silica is previously functionalized with organic binding groups, the metal loading is usually rather low [12–14]. In a previous work, we proposed a possible solution to these disadvantages by functionalizing mesostructured silicas (SBA-15) with polymer chains containing numerous molybdenum grafting points (consisting on polyglycidylmethacrylate treated with 2-aminomethyl pyridine to form the binding groups, which can coordinate to metal centers) [15]. These new catalysts combine the properties of both kinds of materials, i.e. a large number of anchoring points and the ability to control the environment of the metal sites in polymers along with the open porous structure of mesostructured materials with high surface areas. Catalytic results were very promising, but mass transfer limitations had an effect on these hybrid systems due to the fact that polymer incorporation on SBA-15 surface drastically reduced its porosity. Therefore, it seems that the best option will be a less bulky organic moiety containing numerous anchoring points (and able for tuning the molecular environment of the molybdenum centers), which must be efficiently grafted onto large surface-area silicas. Some recently reported works have been focused on this approach [3,6,16–21]. A remarkable example is the investigation of Yang et al. [3], who described the behavior of 8-quinolinol complexes of dioxo-molybdenum(VI) covalently attached onto mesoporous SBA-15 silica in epoxidation reactions. According to their results, organic ligands containing two nitrogen atoms (as electron donors) lead to more efficient and stable molybdenum sites than ligands bearing only one nitrogen. Thus, more stable coordination of the environment of active sites and less metal leaching during the epoxidation reaction are the main consequences.

Taking these facts into account and our previous experience on the modification of polyglycidylmethacrylate with 2-aminomethyl pyridine to generate stable binding sites for metal coordination, herein we present the facile synthesis, characterization, and olefin epoxidation behavior of an efficient and highly porous Mo(VI) catalyst supported onto mesostructured SBA-15 silica. Metal anchoring points on SBA-15 surface were produced by silica functionalization with (3-glycidyloxypropyl)trimethoxysilane followed by subsequent reaction with 2-aminomethyl

pyridine, opening epoxy groups and leading to a Schiff base (with two nitrogen donor atoms). Bis(acetylacetonate)dioxomolybdenum(VI) ($MoO_2(acac)_2$) was selected as metal source. The influence of different reaction variables, such as the catalyst to olefin molar ratio, the type of solvent and the type of hydroperoxide used as oxidant were evaluated in the catalytic performance assessment of these materials in 1-octene epoxidation. Likewise, a spectroscopic study of the molybdenum environment in both fresh and used catalysts was carried out to propose a detailed mechanism of the active sites performance during the epoxidation of 1-octene by using tert-butylhydroperoxide as oxidant.

2. Results and Discussion

Within this section, the main results related to the preparation of molybdenum-Schiff base-functionalized SBA-15 materials, their characterization, and their use, under a wide variety of experimental conditions, in alkene epoxidation with organic hydroperoxides, is described. Samples have been thoroughly characterized by means of different techniques, and results are described and discussed in the following section.

2.1. Characterization of Functionalized SBA-15 Materials and Mo(VI) Supported Catalyst

Table 1 summarizes the textural and physicochemical properties of the different samples obtained during each one of the steps followed in the preparation of the molybdenum-containing SBA-15-based epoxidation catalyst. All the samples display type IV N_2-adsorption-desorption isotherms (not shown) typical from SBA-15 mesostructured materials. Accordingly, the calculated values for the textural properties match fairly well with those usually reported for this type of silica-based material. However, all the evaluated parameters—surface area, mean pore size, and pore volume—experience a slight reduction with each chemical modification accomplished on the material, as a consequence of the occupation of the mesopores by the organic functionalities attached to the silica support.

Table 1. Physicochemical and textural properties of the synthesized SBA-15-type materials.

Sample	S_{BET} [1]	D_p [2]	V_p [3]	C [4]	H [4]	N [4]	Mo [5]
S1 (SBA-15 parent material)	623	77	0.97	-	-	-	-
S2 (SBA + GLY)	508	69	0.73	8.3	-	0.36	-
S3 (SBA + GLY + AMP)	463	68	0.68	6.4	1.04	0.54	-
S4 (SBA + GLY + AMP + Mo)	429	66	0.61	9.6	0.98	0.83	3.56

[1] BET surface area ($m^2 \cdot g^{-1}$); [2] Mean pore size (Å) calculated by applying the NLDFT method assuming cylindrical pore geometry; [3] Total pore volume recorded at P/P0 = 0.95; [4] Atom composition obtained by elemental analysis (wt %); [5] Determined by ICP-OES.

As for the influence of the different steps of the chemical modification of the surface of the materials, the elemental analysis confirms that the functionalization of the parent pure-silica SBA-15 material though the procedure described in Scheme 1 proceeds as it was expected. Thus, grafting of glycidoxypropyl functionalities onto the silica-based material (Sample S2) leads to the incorporation of 4.3 wt % of carbon to the mesoporous materials, whereas the attachment of the 2-aminomethyl pyridine segment (sample S3) provided some nitrogen, to yield a C:N elemental ratio of 7.2. This value corresponds closely to an amino-methyl pyridine group per glycidoxy functionality, so that the formation of the Schiff base seems to be attained almost quantitatively.
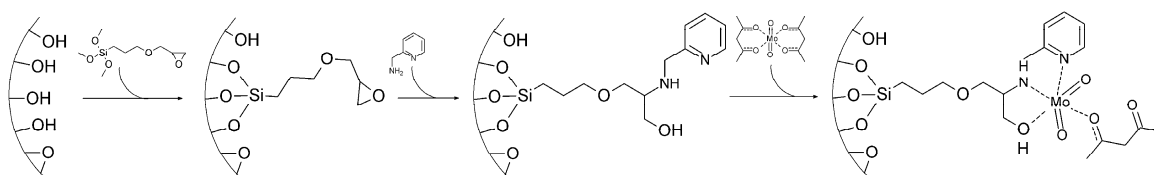
Scheme 1. Synthesis of molybdenum-functionalized epoxidation catalysts.

　　　Finally, the incorporation of molybdenum species provide a material (sample S4) showing 3.56 wt % of this metal (0.37 mmol/g), which involves a N:Mo elemental ratio of 1.9, almost that matching with that corresponding to a molybdenum site per Schiff base (N:Mo = 2).

　　　The analysis of the chemical functionalization of the surface of SBA-15 materials has been assessed by means of solid state ^{29}Si MAS-NMR and ^{13}C CP-MAS-NMR spectroscopy. Figure 1a depicts the ^{29}Si NMR recorded for samples S1 & S2, which show a different resonance envelope in their ^{29}Si NMR spectra as consequence of the presence of two different types of silicon species in these materials: Q and T silicon species. Thus, Q silicon groups are formed through condensation of the silicon precursor in three forms, depending on the Si–O–Si bridges: 4 (Q_4 species, δ = ~−110 ppm), 3 (Q_3 species, δ = ~−100 ppm) or 2 (Q_2 species, δ = ~−90 ppm), being the rest of the bondings completed with hydroxyl functionalities. T groups are related to silicon species directly bonded to carbon atoms, such as the glycidoxypropyl silane functionalities. The deconvolution of the ^{29}Si NMR spectra allows calculating the proportion of each type of silicon species. The main differences between samples S1 & S2 are related to a different proportion of silanol functionalities—higher in the pure silica sample-which are reacted with the organosilane functionality during the grafting process to create T groups, evidencing the efficiency of the first functionalization stage.
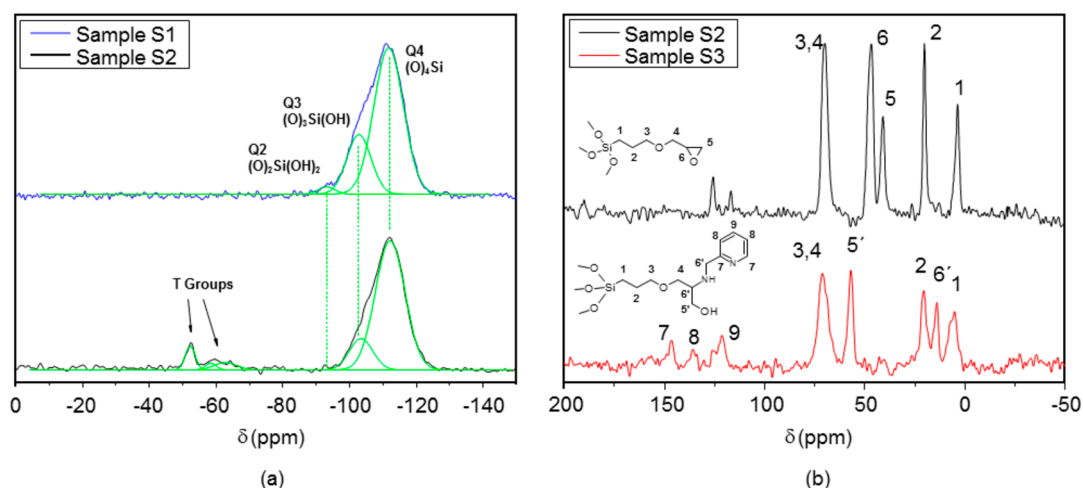

Figure 1. Solid state NMR analysis of (**a**) ^{29}Si MAS NMR and (**b**) ^{13}C CP MAS NMR.

　　　Figure 1b displays the ^{13}C MAS-CP NMR spectrum recorded for samples S2 & S3, where the different resonances attributed to the distinct carbon environments are detected, as well as their assignation. Thus, NMR spectrum recorded for sample S2 displays the characteristic signals attributable to the presence of glycidoxy-propyl functionalities. This result confirm the preservation of the oxirane ring during the grafting process, which is the key functionality to build the Schiff base to anchor molybdenum sites. The reaction of these functionalities with 2-picoline (2-aminomethyl-pyridine) leads to some additional resonances in the ^{13}C CP-MAS-NMR spectrum, which is a consequence of the attachment of the pyridine moiety to the oxirane by reaction through the primary amine group. These results confirm the right organic functionalization of the SBA-15 silica-based support to effectively build the surface-tethered Schiff base, according to Scheme 1, to serve as linkers for molybdenum redox sites.

　　　Figure 2 shows FTIR spectra of samples S1–S4 enlarged in three different regions to evaluate the most remarkable vibration signals on each sample spectrum. Thus, in the region from 4000 to 2600 cm^{-1} a clear reduction of the signal located at 3440 cm^{-1} is observed when grafting (3-glycidyloxypropyl) trimethoxysilane onto the surface of SBA-15 support (S2 vs. S1), indicating an important decrease of the hydroxyl groups population. Bands located between 3000 and 2800 cm^{-1} that can be observed for the S2, S3 and S4 samples correspond to the stretching vibration (symmetric and asymmetric) of the

C–H bonds existing in the organic functionalities incorporated on silica surface [22]. The signal found around 2980 cm^{-1} for samples S3 and S4 (but not for S2), is related to the C–H stretching of aromatic carbons that commonly appear at higher wavenumber than methylene ones [22]. So, this result seems to confirm the incorporation of the aminomethyl pyridine moiety by opening epoxy groups of S2 sample. The region from 1800 to 1400 cm^{-1} mainly shows signals corresponding to the C–H bending mode of the different carbons (mostly methylene and aromatic types). Likewise, bending vibration of amine groups (–NH$_2$ and –NH–) can also be detected here, specifically, the signal at 1575 cm^{-1} (observed for samples S3 and S4) could be attributed to these species. Water retained by siliceous materials also presents a characteristic band in this infrared zone (1630 cm^{-1}). As observed, the intensity of this band significantly decreases in S2 sample with regards to S1 because of the intensive drying process carried out before SBA-15 functionalization. Finally, a weak intense signal can be seen at 905 cm^{-1} for sample S2, a signal typically attributed to the vibration of the C–O bond of epoxy groups [15], confirming the incorporation of glycidyl species by SBA-15 functionalization. As expected, this band disappears in sample S3 where the epoxy rings have been opened by reaction with AMP.
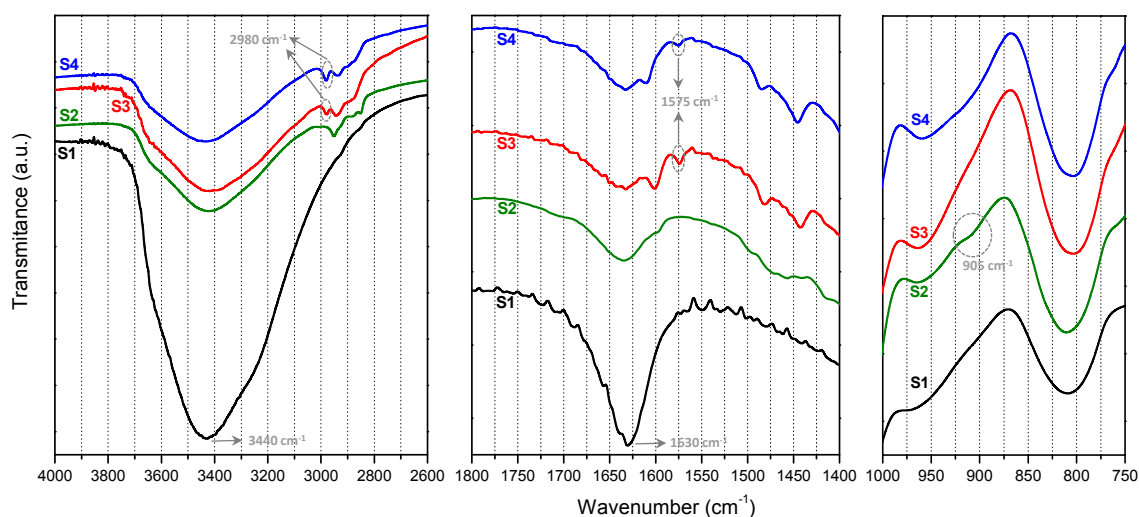
Figure 2. FTIR spectra of samples S1, S2, S3 and S4.

Figure 3 displays UV-Vis spectra of samples S2–S4. The three samples show two absorption bands located at 210 and 260 nm corresponding to silica and supported aromatic species, respectively. The presence of the band associated with aromatic species in the spectrum of the sample S2 indicates that some traces of toluene (the solvent used for GPTMS grafting) might remain on this material after the first functionalization step. For samples S3 and S4, the signal located at 260 nm is related to the presence of the aromatic ring existing in the AMP structure. Finally, the molybdenum catalyst (sample S4) shows three additional signals (as compared to sample S3) located at 220, 310 and 700 nm, which can be attributed to Mo–O bonding of isolated molybdenum species in pseudo-octahedral coordination [23], octahedral molybdenum sites of dense phase MoO$_3$ [12] and electronic transition between Mo(V) and Mo(VI) species [24], respectively. Low intensity of the signal positioned at 700 nm involves low amount of Mo(V) species in the synthesized catalyst.
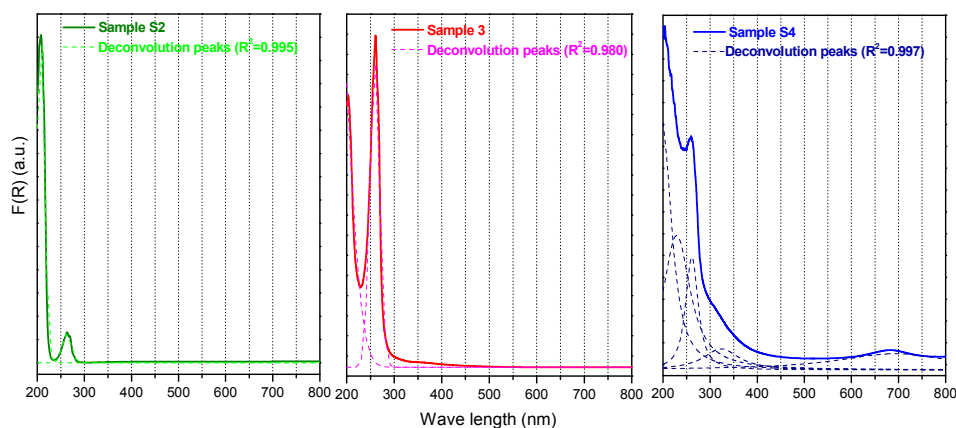
Figure 3. UV-Vis spectra of samples S2, S3 and S4.

2.2. Catalytic Performance in 1-Octene Epoxidation

2.2.1. Influence of the Catalyst Loading

The influence of the catalyst loading on the epoxidation extension of 1-octene was evaluated by testing three different molybdenum/olefin molar ratios: 1:500, 1:1000 and 1:2000, quite low, as compared to some analogue previously reported investigations. These experiments were carried out using TBHP as oxidant and isopropanol as solvent. Figure 4 shows the epoxide yield progress as a function of the reaction time for the three molybdenum/olefin ratios. Likewise, results of a blank reaction (performed without catalyst) are also displayed for comparison purposes. This result suggests the reaction requires a catalyst, as a negligible production of epoxide was obtained under these conditions. 1,2-epoxy octane was the sole product detected in the reaction media, and 1,2-epoxioctane or octanal, expected because of using silica-based catalysts, were absent, probably because of the low amount of catalyst loading. The similarity of the results obtained with 1:500 and 1:1000 ratios is remarkable; on the contrary, adding the molybdenum-based catalyst in a 1:2000 Mo to substrate molar ratio provided a substantial lower epoxide formation. Thus, we selected 1:1000 as the optimal molybdenum/olefin molar ratio for the rest of the experiments.
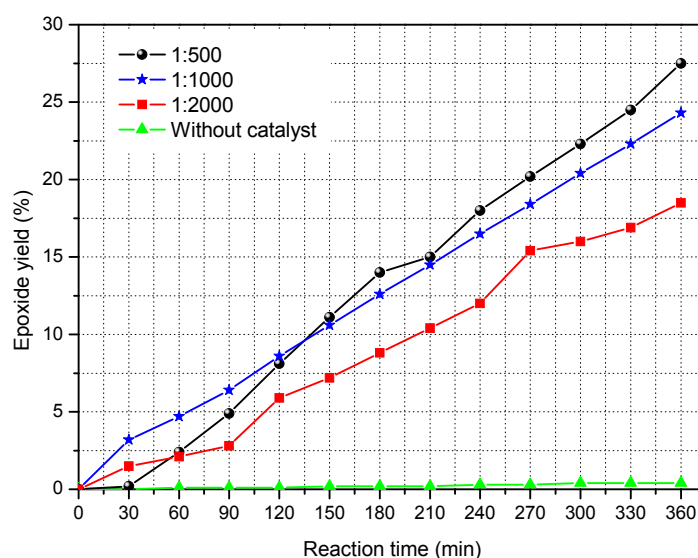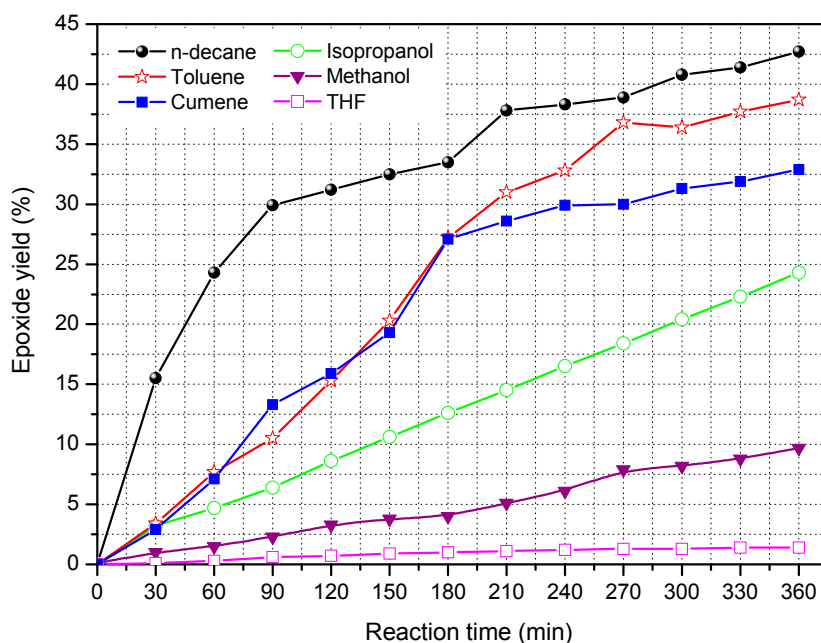

Figure 4. 1,2-epoxioctane yields obtained with different Mo/olefin molar ratios in 2-propanol (Reaction conditions: Temperature = 75 °C; tert-Butyl Hydroperoxide as oxidant; 1-octene/oxidant molar ratio of 1).

Reactions performed in 2-propanol as solvent depicted low epoxide yields even at high reaction times (Figure 4). This is probably related to the type of solvent used in these tests because of highly coordinating ligands and solvents (such as isopropanol) can compete with TBHP for binding to molybdenum sites, decreasing the overall catalytic activity [20,25] of molybdenum-based catalysts. This has prompted us to deeply analyze the influence of the epoxidation solvent on catalytic activity and products distribution, which are discussed in the following section.
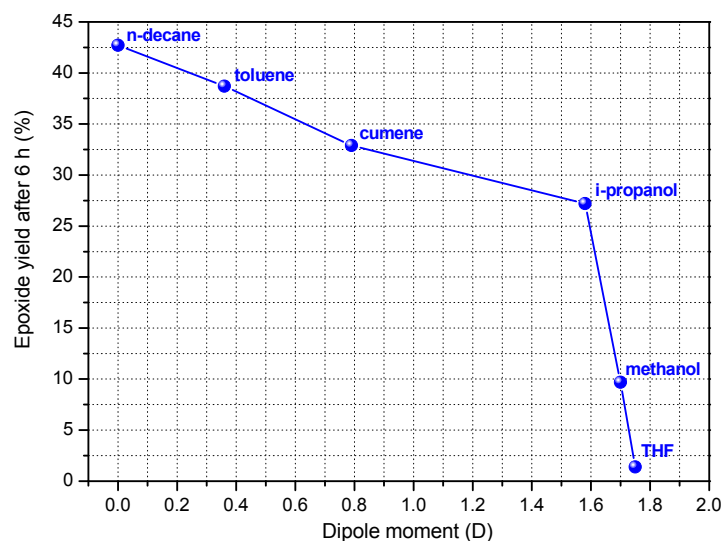
2.2.2. Influence of the Solvent

As we have previously described, the influence of the nature of the solvent was evaluated by using different conventional organic solvents: tetrahydrofuran (THF), methanol, isopropanol, isopropylbenzene (cumene), toluene, and n-decane. These compounds were selected due to their very different polarity and handling easiness. All the reactions were carried out by using a molybdenum/1-octene molar ratio of 1:1000 and TBHP as oxidant. Figure 5 displays the obtained epoxide yields in the catalytic tests carried out within these solvents (during 6 h of reaction), pointing to very remarkable differences between the different organic solvents, and suggesting that the polarity of the reagents play a major role in olefin epoxidation in presence of these catalysts.

Figure 5. 1,2-epoxioctane yields obtained in presence of different solvents (Reaction conditions: Temperature = 75 °C; TBHP as oxidant; 1-octene:oxidant molar ratio of 1; Mo:1-octene = 1:1000).

As observed, less polar solvents lead to higher 1,2-expoxioctane yields. This trend is in fairly good agreement with results obtained by Zhang et al. [25], and it is due to p-donor organic solvents capable of coordinating to molybdenum sites, hindering the coordination between these metal centers and the oxidant (TBHP), which is mandatory for the substrate epoxidation. Thus, the presence of oxygen atoms in the solvent, with an available electron pair that can effectively compete with TBHP to bind to Mo(VI) sites, involves an important inhibition of the epoxidation reaction [25,26]. Since the coordination capacity of the electron pair increases by increasing the dipole moment of the solvent molecule, there should be a relationship between this parameter and the obtained epoxide yield. Figure 6 depicts the epoxide yield values obtained after 6 h of reaction versus the dipole moment of the used solvent, confirming the connection between both parameters. A drastic decrease of the epoxide production is observed by increasing the dipole moment above 1.6 D because, in these cases, metal centers are mainly coordinated to solvent instead to TBHP molecules.

Figure 6. Relationship between 1,2-epoxioctane yield and dipole moment of the solvent (Reaction conditions: Temperature = 75 °C; TBHP as oxidant; 1-octene:oxidant = 1; Mo:1-octene = 1:1000).

The influence of the epoxidation solvent was evaluated not only on the yield towards the desired oxirane, but also on the oxidant efficiency (η_{TBHP}). This parameter is calculated as the ratio between the obtained epoxide amount and that corresponding to the converted oxidant. This calculation has been included in Equation (1). High oxidant efficiencies involve poor extension of the side reactions, not only related to the oxirane, like the ring opening of the epoxide to the diol, or its isomerization to an aldehyde [27], but also those involving the non-oxidative consumption of the oxidant, such as its thermal decomposition.

$$\eta_{TBHP}\ (\%) = (Mol)_{epoxide} / [(Mol)_{TBHP\ t\,=\,0} \cdot X_{TBHP}\,)]\,100, \tag{1}$$

Figure 7 shows the oxidant efficiency progress by increasing reaction time for all the evaluated solvents.
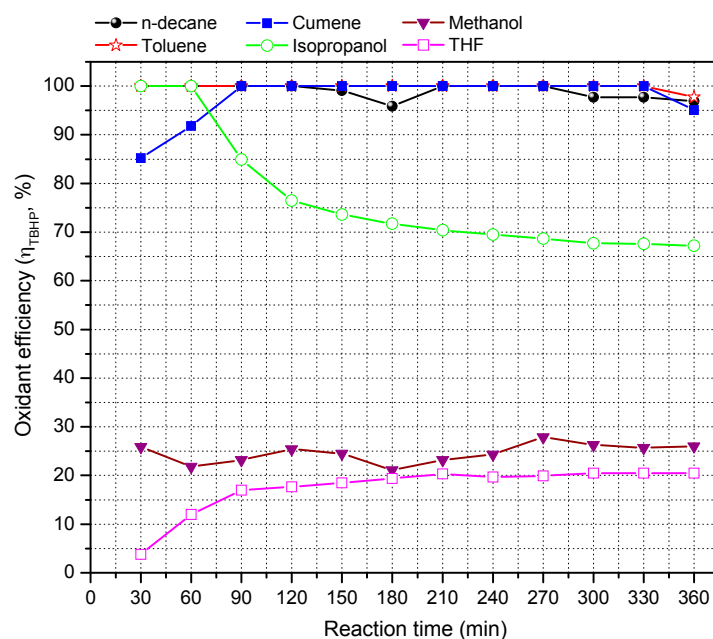
Figure 7. TBHP efficiency of 1-octene epoxidations carried out in presence of different solvents.

As observed, less polar solvents (with low dipole moment) led to very high oxidant efficiency, indicating that TBHP is exclusively converted in the epoxidation reaction. On the contrary, the use of solvents with high polarity considerably reduces the oxidant efficiency because the interaction solvent-metal prevents the coordination TBHP-Mo(VI) and, thus, the oxygen transfer from the oxidant to the olefin is jeopardized. As a general trend, oxidant efficiency values are almost constant during all the reaction time, indicating that the kind of interaction established between solvent molecules and metal centers remains unaltered throughout the evaluated process. An exception to this trend can be observed when using isopropanol as solvent, as in this case, a clear decrease of the oxidant efficiency is noted by increasing reaction time. The intermediate polarity of the isopropanol, combined with its molecular size (similar to THF but higher than methanol), probably leads to a slower coordination to Mo(VI) sites (in comparison with THF or methanol, whose interaction with the metal seems to occur at the beginning of the reaction). Consequently, the increase of the reaction time promotes isopropanol-molybdenum coordination, reducing the oxidant efficiency.

In conclusion, experimental results suggest that the best solvent for 1-octene epoxidation by using our Mo(VI) containing-SBA-15 catalyst is n-decane.

2.2.3. Influence of the Oxidant

This study was carried out by testing tert-butyl hydroperoxide (TBHP), ethylbenzyl hydroperoxide (EBHP), and isopropylbenzene hydroperoxide (usually called cumene hydroperoxide, CHP) as oxidant, using a molybdenum/1-octene molar equal to 1:1000 and n-decane as solvent. These are conventional oxidation hydroperoxides used in industry in propylene oxide production processes. Figure 8 shows the evolution of epoxide formation with the reaction time as well as the oxidant efficiency obtained after 360 min. TBHP and EBHP led to very similar results, reaching epoxide yields up to 45% in the evaluated period. Nevertheless, the use of CHP as oxidant provokes a clear reduction of both the epoxide yield and the oxidant efficiency. Some authors have previously described that CHP can be easily decomposed into acetone and phenol in presence of some vanadium, tungsten and molydenum catalytsts [28]. According to the epoxidation results, it seems to indicate this decomposition is taking place on our Mo(VI) heterogeneous catalyst leading to a poor epoxide yield. Therefore, TBHP will be the best choice to be used with this catalytic system since epoxidation results are quite similar to those obtained by using EBHP and is a much cheaper oxidant.
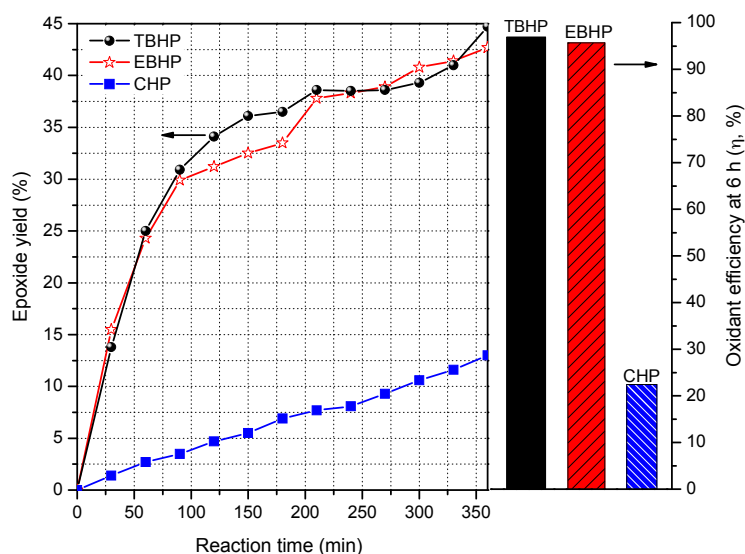
Figure 8. 1,2-epoxioctane yields and oxidant efficiency obtained with different organic hydroperoxides (Reaction conditions: Temperature = 75 °C; decane as solvent; 1-octene:oxidant = 1; Mo:1-octene = 1:1000).

2.3. Catalyst Reusability

To study the reusability of the Mo(VI) heterogeneous catalyst, the solid was properly recovered by filtration after epoxidation tests and washed with the solvent reaction at room temperature. Runs 1 and 2 were performed under the same experimental conditions: molybdenum/1-octene molar = 1:1000, decane as solvent and TBHP as oxidant. Figure 9 shows the reaction results (product yield and oxidant efficiency) obtained with both the fresh and the used catalyst, indicating that the achieved 1,2-epoxioctane yield decreases in 10% in the second use, whereas the oxidant efficiency remains almost unaltered. According to previous works [3,25] molybdenum leaching is the most probable cause to justify this catalytic activity reduction. Indeed, the metal content of the used catalyst (3.20 wt %, determined by ICP-OES) is 12% lower than the value corresponding to the fresh catalyst (3.76 wt %, see Table 1), confirming that molybdenum leaching occurs under our experimental conditions. On the other hand, high oxidant efficiency obtained for both fresh and used sample indicates that side reactions are boosted poorly by using this Mo(VI) heterogeneous catalyst.
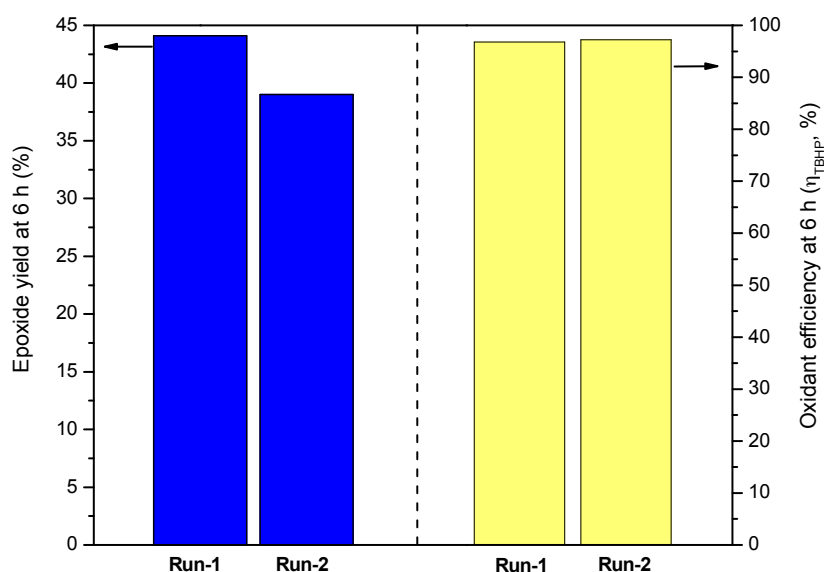
Figure 9. 1,2-epoxioctane yield and oxidant efficiency achieved with fresh (run 1) and used catalyst (run 2) (using decane as solvent, TBHP as oxidant and Mo/olefin molar ratio = 1:1000).

Finally, X-ray photoelectron spectroscopy (XPS) was employed to study the molecular environment of the active sites in the fresh and used catalyst. Figure 10 shows XPS spectra of both samples in the Mo3d (A) and O1s (B) energy regions. The Mo3d region shows well-resolved spectral lines at 231.3 and 234.4 eV, typical of the Mo3d5/2 and Mo3d3/2 spin orbit, respectively [29,30]. As observed, very similar Mo3d XPS spectra are obtained for fresh and used catalyst, indicating that molybdenum oxidation state and its coordination sphere remains unaltered during the epoxidation reaction. On the other hand, results coming from the O1s spectra show slight differences between both samples. Thus, the spectrum of the used catalyst shows three different signals: a small one located at 533.5, which can be ascribed to the presence of Mo–OH species, a very intense one located at 532.5 eV which can be attributed to the oxygen of the silica (Si–O–Si bonds existing on SBA-15 material) and a small shoulder at 530.4 eV, corresponding to oxygen atoms bonded to molybdenum sites (species Mo=O, see Scheme 1). Fresh catalyst shows these three peaks, and an additional one located at 527 eV, that is probably related to the oxygen of acac ligands coming from the molybdenum source, and which remain attached to molybdenum sites after catalyst preparation. Taking into account that the used catalyst does not present this signal and the coordination sphere of molybdenum is similar for fresh and used catalyst (as shown Mo3d XPS results), acac groups should be replaced by other oxygenated

species during the first epoxidation run. These oxygenated species should come from the oxidant, which must interact with molybdenum centers to achieve olefin epoxidation.
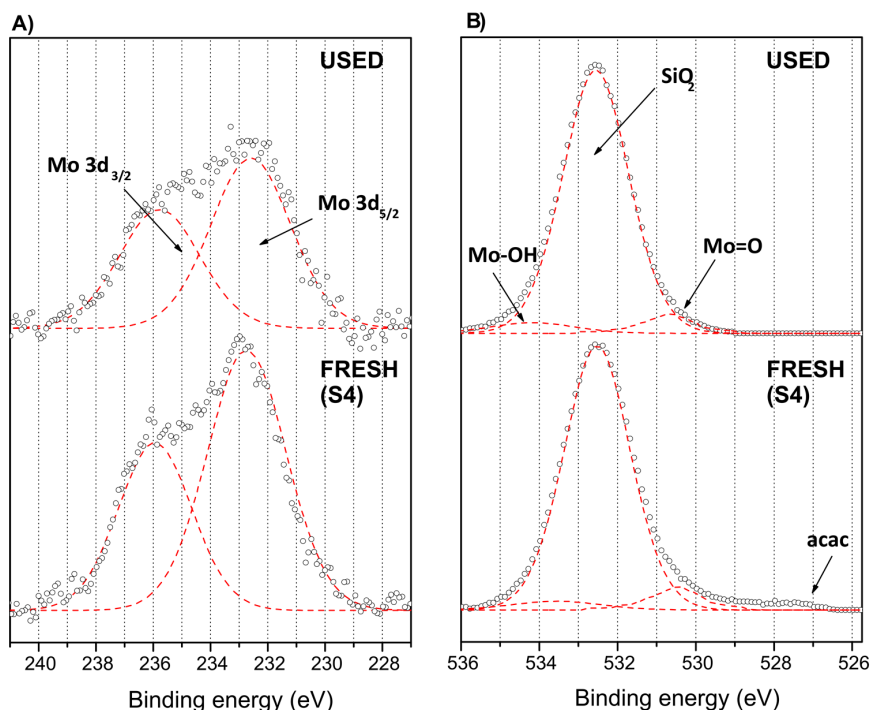
Figure 10. XPS spectra of fresh and used catalyst in the Mo3d (**A**) and O1s (**B**) energy regions.

According to the previous descriptions, Scheme 2 shows the proposed cyclic mechanism for describing the changes occurring in the environment of molybdenum sites during epoxidation runs. As observed, during the first run, the acac group is replaced by an oxidant molecule (TBHP, in this case) that interacts with the olefin substrate at the same time, thus leading to the epoxide and the corresponding alcohol (tert-butanol, in this case), which is still linked to the metal site. Then, a new oxidant molecule approaches the molybdenum, releasing the alcohol and starting the cycle again.
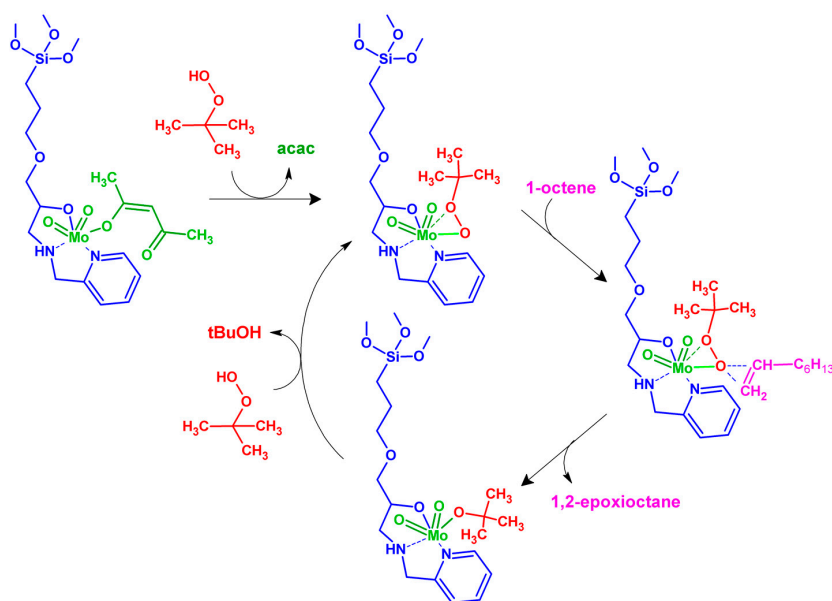
Scheme 2. Proposed cyclic mechanism of Mo(VI) catalyst for 1-octene epoxidation.

3. Materials and Methods

### 3.1. Synthesis of Mo(VI) Containing-SBA-15 Catalyst

Pure silica SBA-15 used as support for the Mo-Schiff base catalyst was synthesized according to the procedure described by Zhao et al. [31]. Pluronic P123 (PEO = 20, PPO = 70, PEO = 20, Mn = 5800, Aldrich) was used as a surfactant and tetraethyl orthosilicate (TEOS, Aldrich, St. Louis, MO, USA) as the silicon precursor. Dried silica was outgassed under vacuum conditions overnight at 150 °C. Before silica functionalization, the previously dried SBA-15 material was treated by azeotropic distillation with ethylbenzene in a Dean-Stark apparatus to ensure complete removal of water molecules. Then, sample was functionalized with (3-glycidyloxypropyl) trimethoxysilane (GPTMS, Aldrich) in under reflux and inert conditions for 8 h by using a molar GPTMS/silica ratio = 0.1. Next, the solid was recovered by filtration and intensively washed with toluene. Epoxy rings were reacted with 2-aminomethyl pyridine (AMP, 2-picolylamine, Aldrich). This stage was carried out in tetrahydrofuran under reflux and inert conditions for 24 h by using an AMP/GPTMS molar ratio = 2. Excess of AMP was removed by washing the sample with ethanol. By means of this procedure, glycidyl functionalities react with 2-picoline to form the (hydroxypropyl)-2-aminomethyl pyridine (HPAMP) ligands, which are the anchoring points to ligate and stabilize molybdenum species (see Scheme 1). The molybdenum centers were immobilized on silica surface by reaction of the HPAMP/SBA-15 material with bis(acetylacetonate)dioxomolybdenum(VI) ($MoO_2(acac)_2$, Aldrich). Typically, the HPAMP/SBA-15 material support was treated for 24 h in ethanol under reflux with one equivalent of $MoO_2(acac)_2$, relative to the amount of the previously attached HPAMP ligand. The molybdenum-containing material was then filtered off and washed with ethanol prior to vacuum drying overnight [15]. Scheme 1 summarizes the different functionalization steps carried out for the synthesis of Mo(VI) containing-SBA-15 catalyst.

3.2. Samples Characterization

The textural properties of the catalysts were assessed through N_2 adsorption-desorption experiments in a Micromeritics TriStar 3000 unit (Norcross, GA, USA). Surface area values were calculated using the BET method. Pore-size distributions were calculated through the NLDFT method using a Kernel function for cylindrical pores. Total pore volume was recorded at p/p0 = 0.985. Structural ordering was assessed by X-ray powder diffraction, using a Philips X'Pert diffractometer (Almelo, Netherlands) and irradiating the samples with the CuKα line in the 2θ angle range of 0.6°–5°, and recording the diffraction pattern with a resolution of 0.02°. FTIR spectra were collected on a Mattson Infinity spectrometer, recording the spectra in the wavelength from 4000 to 400 cm^{-1}, with a resolution of 2 cm^{-1} and collecting 64 repetitions on each analysis. UV–vis spectra (DRS) were collected under ambient conditions on a Varian Cary 500 Scan UV-VIS-NIR spectrophotometer (Santa Clara, CA, USA) in the wavelength range of 200–800 nm. X-ray photoelectron spectroscopy (XPS) analysis were carried out in a SPECS PHOIBOS 150 MCD spectrometer operating at 10^{-10} mbar, using a Mg anode (Mg Kα, 1253.6 eV). Prior to the analysis, all the samples were outgassed overnight to less than 10^{-6} Torr. Spectra were recorded with a step size of 0.1 eV at room temperature. Binding energies were referenced to 284.6 eV (C1S line). Elemental analyses were performed on an Elementar Vario EL III. Molybdenum content was determined by ICP-atomic emission spectroscopy. Single-pulse solid-state ^{29}Si MAS-NMR and ^{13}C CP-MAS-NMR spectroscopy was used to characterize the environment of the attached organic functionalities. NMR experiments were conducted at room temperature, spinning at 6 kHz, and applying a magnetic field strength of 9.4 T on a high-resolution Varian Infinity Plus 400 NMR spectrometer (Santa Clara, CA, USA) operating at a frequency of 79.41 MHz for silicon, and of 100.53 for carbon. Chemical shifts were referenced to tetramethylsilane. The spectra were recorded using a 4.5 μs π/2 pulse, a recycle delay of 15 s, and 3000 transients for silicon assays, and a 4.25 μs π/2 pulse with a repetition delay of 3 s, a contact time of 1 ms and 2000 scans for carbon.

3.3. Catalytic Tests

The catalytic activity of the molybdenum-containing hybrid SBA-15 material was assessed in the epoxidation of 1-octene (Scheme 3) under different conditions to evaluate the effect of three reaction variables: the amount of molybdenum catalyst (changing Mo/olefin molar ratio from 1:500 to 1:2000), the type of solvent (tetrahydrofuran, methanol, isopropanol, isopropylbenzene, toluene, and n-decane) and the type of hydroperoxide used as oxidant (tert-butyl hydroperoxide, ethylbenzene hydroperoxide and isopropylbenzene hydroperoxide). All the experiments were carried out in a magnetically stirred round-bottomed flask under nitrogen temperature, according to the procedure previously reported [15]. Control of the reaction temperature was performed by immersion of the flask in an oil bath kept at 75 °C. Olefin/oxidant and olefin/solvent molar ratios were 1 and 4, respectively, for all the cases.
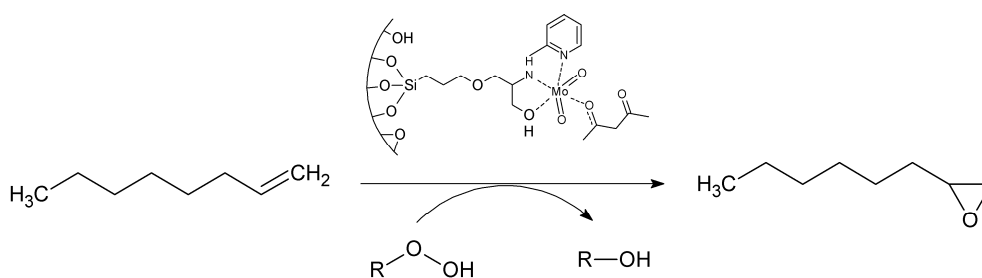
Scheme 3. Epoxidation of 1-octene.

The conversion of the hydroperoxide used as oxidant was calculated from iodometric titration. Regarding the substrate conversion and the epoxide yield, these were quantified by gas chromatography. All these parameters were used to quantify the selectivity of the catalysts in the consumption of the oxidant to form the epoxide, which can be understood as the selectivity of the hydroperoxide towards the oxirane.

The stability of the molybdenum species was assessed by estimating the leached metal fraction, by direct measurement of the molybdenum content in the used catalyst. Finally, reutilization tests were carried out with intermediate washing with the reaction solvent to avoid interferences between consecutive runs.

4. Conclusions

The functionalization of SBA-15 materials with glycidoxy-propyl functionalities, and subsequent reaction with 2-picoline, is an easy and effective way to build surface Schiff bases that are able to bind to molydenum species to form highly active, selective and stable epoxidation catalysts. These materials show quite good catalytic performance in the epoxidation of 1-octene with organic hydroperoxides in a wide variety of solvents. These materials displayed quite good inherent catalytic activity, as quite low molybdenum to substrate molar ratios (1:1000) were able to convert a large fraction of the olefin. With regards to the influence of the solvent, highly polar solvents depressed the catalytic activity of the supported Mo-Schiff bases, probably as a consequence of competition between the solvent and the oxidant for binding to the metal sites, thus avoiding the formation of the hydroperoxo-metal cycle and the epoxidation of the olefin. Finally, unlike cumene hydroperoxide, ethyl benzyl hydroperoxide and tert-butyl hydroperoxide were both able to oxidize 1-octene in a quite good extension. The poor catalytic activity of the molybdenum-based materials in presence of cumene hydroperoxide was attributed to the molybdenum-catalyzed nonoxidative decomposition of CHP into acetone and benzene. The catalysts presented here show good reusability, with low catalytic activity decay after the first reuse.

Author Contributions: All the authors have equally contributed to this research.

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