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Research paper

New heterogeneous catalysts with Mo(II) intercalated in layered double hydroxides

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ABSTRACT

The Mo(II) complexes $[MoX_2(CO)_3(BDC)]$ (X = I, Br; H₂BDC = 2,2'-bipyridine-5,5'-dicarboxylic acid) were immobilized by intercalation in two layered double hydroxides (LDH), containing Zn/Al (synthesized) and Mg/Al (commercial), as shown by infrared and ¹³C solid state NMR spectroscopies, and X-ray powder diffraction. Their catalytic activity was studied in olefin oxidation, using as oxidant *tert*-butylhydroperoxide (tbhp), and was compared with the activity of the related $[MoX_2(CO)_3(bpy)]$ complexes (bpy = 2,2'bipyridine). *cis*-Cyclooctene, styrene, 1-octene, *trans*-hex-3-en-1-ol, and *R*-(+)-limonene were the substrates tested. All the catalyst showed in average a high selectivity toward the epoxide of each substrate (above 90%, except for styrene), with variable conversions, but none of the heterogeneous catalysts proved to be more active than the homogeneous ones. The same or higher activity in a second catalytic run, as observed in most reactions, suggests a good recycling capability.

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1. Introduction

Catalysis plays a crucial role in addressing environmental challenges, since catalysts modify reaction mechanisms, allowing them to occur in milder conditions, with larger yield and selectivity. Homogeneous catalysts are more likely to achieve such results, but in general they lack an easy route for product separation and catalyst regeneration. These ideas pointed toward the design of heterogeneous catalysts able to exhibit the best of both types, namely associating the reactivity of a molecular species with the easy extraction of the products and recovery of the active catalyst [1,2].

This can be done by immobilizing a well-defined catalyst in a material with a large surface area, by means of a strong bond, either covalent or electrostatic, to avoid its loss [3–5]. Clays, in particular layered double hydroxides (LDH), are porous solids with two dimensional spaces between charged layers of hydroxides of mixed cations [6,7]. Varying their composition, it is possible to obtain positively charged layers where negatively charged species may intercalate. A very common class derives from magnesium

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http://dx.doi.org/10.1016/j.ica.2016.07.030 0020-1693/© 2016 Elsevier B.V. All rights reserved. hydroxide and the layers consist of edge-sharing octahedral Mg $(OH)_6$ motifs. Substitution of part of Mg²⁺ by Al³⁺ requires the introduction of anions to balance charges. Other M²⁺ dications, such as Zn²⁺ and Ni²⁺, may replace Mg²⁺ in the cationic layer, while Al³⁺ may be substituted by other M³⁺ trications (Al³⁺, Cr³⁺, Ga³) in a general composition $[M_{1-x}^{2+}M_x^{3+}(OH)_2][A^{m-}]_{x/m} \cdot nH_2O$. The x value defines the proportion between the two types of cations and controls the inter layer space, which may also be occupied, besides anions, by water molecules [8–10]. These anionic clays may be easily functionalized by exchanging the anions, either directly or, when starting from the carbonate containing clays, by calcination followed by rehydration by a solution containing the new anion. Calcination leads to the collapse of the layered structure, which is reestablished by intercalation of the new anion, usually modifying the distance between layers [8–11]. It is also possible to synthesize directly clays with the ions that have been chosen to be present in the final clay [12,13]. The intercalated anion may contain donor atoms able to bind metal centers, thus opening the way to the introduction of a catalyst or catalyst precursor in the structure. We have used this methodology to obtain new heterogeneous catalysts for polymerization and olefin epoxidation [14–17]. Other authors have reported a variety of catalytic reactions taking place in similar clays functionalized with active metal centers [18]. Mo(II) complexes of two large families, $[Mo(\eta^3-C_3H_5)X(CO)_2(L)_2]$ [19,20] and $[MoI_2(CO)_3(L)_2]$ [21],



where L or $(L)_2$ represent mono- or bidentate nitrogen ligands, showed significant activity as catalyst precursors in olefin epoxidation [22]. Their immobilization in porous materials, namely derived from MCM-41, led to improvement of their catalytic properties, for several L ligands, as reviewed recently [23].

In this work, we describe the catalytic behavior of an immobilized complex similar to $[MoI_2(CO)_3(bpy)]$ (bpy = 2,2'-bipyridyl), where the bpy ligand had to be modified in order to functionalize the LDH materials. For this purpose, two carboxylate substituents were introduced in the 4,4' positions (H₂BDC), so that the dianion might intercalate in an anionic clay, leaving the diamine functionality available for coordination to the metal (Scheme 1). Two different clays, with Al³⁺ and Zn²⁺ or Mg²⁺, as M³⁺ and M²⁺, respectively, were chosen as supports.

2. Experimental

2.1. General

All reagents, including the Mg/Al clay (LDH_{Mg/Al}-CO₃), were obtained from Aldrich and used as received. Commercial grade solvents were dried and deoxygenated by standard procedures (dichloromethane, dimethylformamide (dmf) over calcium hydride), distilled under nitrogen, and kept over 4 Å molecular sieves. The Zn/Al clay (LDH_{Zn/Al}-CO₃) was synthesized by the methodology previously described [24]. [Mo(CO)₃X₂(NCMe)₂] [21] and [Mo(CO)₃X₂(bpy)] (1) (X = I₂, Br₂) [25] were prepared by reported procedures.

2.2. Catalysts characterization

FTIR spectra were obtained by Diffuse Reflectance (DRIFT) measurements on a Nicolet 6700 in the 400-4000 cm⁻¹ range with 4 cm⁻¹ resolution. Solid state ¹³C NMR measurements were performed at room temperature on a Tecmag Redstone/Bruker 300 WB spectrometer operating at 75.47 MHz. Samples (\sim 200 mg) were packed into 7 mm o.d. zirconia rotors, equipped with Kel-F caps. The standard magic angle spinning (MAS) cross polarization-dipolar decoupling RF pulse sequence (CP-DD) was used under about 4 kHz spinning rate. ¹³C spectra were recorded with 2 ms contact time, 90° RF pulses of around 4 µs, 4 s recycling delay and a number of scans higher than 900. The Hartmann-Hahn condition was optimized using glycine; it was also the external reference to set the chemical shift scale (¹³CO at 176.03 ppm). Powder XRD measurements were taken on a Philips Analytical PW 3050/60 X'Pert PRO (theta/2 theta) equipped with X'Celerator detector and with automatic data acquisition (X'Pert Data Collector (v2.0b) software), using a monochromatized Cu-Ka radiation as incident beam, 40 kV-30 mA. TGA studies were performed using a Netzsch F3 Jupiter system in ISIS, Neutron & Muon Source on Rutherford Appleton Laboratory. The measurements were done in the 300-1073 K temperature range using a heating rate of 10 K min⁻¹ under N₂ atmosphere. Microanalyses for CHN and Mo quantitation were performed at CACTI, University of Vigo. CHN analyses were performed on a Fisons EA 1108; Mo quantification

was performed on a Perkin Elmer Optima 4300DV using In as internal standard.

2.3. Catalytic epoxidation of materials

The materials were tested in epoxidation of olefins and alcohols, namely cis-cyclooctene, styrene, R-(+)-limonene, 1-octene and trans-hex-3-en-1-ol, using tert-butylhydroperoxide (tbhp) as oxidant (5.5 M in n-decane). The catalytic oxidation tests were carried out at 398 K, using toluene as solvent. The reactions occurred under air in a reaction vessel equipped with a magnetic stirrer and a condenser. In a typical experiment, the vessel was loaded with olefin or alcohol (100 mol%), oxidant (200 mol%) and 3 mL of solvent. The final volume of the reaction was ca. 6 mL. The addition of the oxidant determined the initial time of the reaction. Conversion, product yields and stereochemistry were monitored by sampling periodically and analyzing the products on a Shimadzu QP2010-Plus GC/MS system and a capillary column (Teknokroma TRB-5MS, TRB-1MS or Restek Rt-BDEXsm) operating in the linear velocity mode. Recycling tests were carried out as described above using the recycled materials as catalyst; conversion and product yields were monitored as described above. After each cycle (24 h) the catalyst was filtered, washed which CH₂Cl₂ several times and dried prior to reuse in a new catalytic cycle.

2.4. Synthesis of materials and catalysts

2.4.1. Synthesis of $LDH_{M/Al}$ materials-BDC (M = Zn, Mg)

A mixture of H_2BDC (7.30 mmol) in deionized type II water (20 mL) with KOH (14.6 mmol) was stirred until complete solubilization. This solution was then added to a suspension of the LDH (LDH_{Zn/AI} or LDH_{Mg/AI}) clay (1.00 g) in freshly distilled dmf (25 mL) at 343 K, and the reaction mixture was stirred at the same temperature for 48 h.

All the manipulations were carried out under a dry N_2 atmosphere to prevent the uptake of carbonate anions. The resulting materials were then filtered off, washed with deionized type II water (3 × 20 mL), and dried in a desiccator under vacuum.

2.4.1.1. LDH_{Zn/AI}-BDC. Elemental analysis (%): found C 18.27, H 3.41, N 2.27.

DRIFT (KBr v/cm⁻¹): 3385 (vs), 2963 (vs), 1619 (vs), 1403 (vs), 1262 (vs), 1024 (vs), 801 (s).

XRD (20, planes): 4.85 (003), 8.962 (006), 12.12 (009).

2.4.1.2. LDH_{Mg/Al}-BDC. Elemental analysis (%): found C 14.58 H 4.17 N 2.71.

DRIFT (KBr v/cm⁻¹): 3400 (vs), 1601 (s), 1539 (m), 1389 (s), 776 (s).

XRD (20, planes): 4.71 (003), 9.83 (006), 13.80 (009).

2.4.2. Synthesis of LDH materials-BDC-MoX₂

 $[Mo(CO)_3X_2(NCMe)_2]$ (0.3 g) was added to a suspension of $LDH_{M/Al}$ -BDC (0.75 g) in dichloromethane (10 mL). The slurry was stirred under a N₂ atmosphere, at room temperature, for 24 h.



Scheme 1. 2,2'-Bipyridine and derivatives.

The resulting material was then filtered off, and dried in a desiccator under vacuum.

2.4.2.1. LDH_{Zn/AF}-BDC-MoI₂. Elemental analysis (%): found C 10.51, H 1.14, N 1.89, Mo 7.00.

DRIFT (KBr v/cm⁻¹): 3446 (vs), 1954 (m), 1620 (vs), 1558 (s), 1385 (vs), 1041 (vs).

XRD (20, planes): 4.83 (003), 8.96 (006), 12.11 (009).

*2.4.2.2. LDH*_{Zn/Al}-*BDC*-*MoBr*₂. Elemental analysis (%): found C 17.71, H 1.76, N 0.57, Mo 8.02.

DRIFT (KBr v/cm⁻¹): 3421 (vs), 1977 (m), 1909 (m), 1843 (m), 1832 (s), 1615 (vs), 1386 (vs), 970 (vs).

XRD (20, planes): 4.78 (003), 8.79 (006), 12.08 (009).

2.4.2.3. LDH_{Mg/AI}-BDC-MoI₂. Elemental analysis (%): found C 8.30, H 2.72, N 1.70, Mo 7.07.

DRIFT (KBr v/cm⁻¹): 3431 (vs), 2963 (s), 2013 (s), 1889 (vs), 1661 (vs), 1554 (s), 1389 (vs), 1261 (s), 1100 (vs), 775 (s).

XRD (2*θ*, planes): 3.77 (003), 9.59 (006), 13.79 (009).

*2.4.2.4. LDH*_{Mg/AI}-*BDC-MoBr*₂. Elemental analysis (%): found C 9.67, H 3.21, N 1.93, Mo 5.39.

DRIFT (KBr v/cm⁻¹): 3436 (vs), 1950 (m), 1900 (m), 1609 (vs), 1400 (vs), 1050 (s).

XRD (20, planes): 3.89 (003), 10.06 (006), 14.08 (009).

3. Results and discussion

3.1. Synthesis and characterization

New heterogeneous metal catalysts were obtained from two clay-based hybrid materials after immobilization of the anion of 2,2'-bipyridine-5,5'-dicarboxylic acid (H₂DBC) and further reaction with a Mo(II) precursor, as shown in Scheme 2. The first material, LDH_{Zn/Al} was synthesized by the co-precipitation method as reported, leading to the carbonate clay (LDH_{Zn/Al}-CO₃). The carbonate ions were exchanged with chloride anions yielding LDH_{Zn/Al}-Cl,

and finally chloride was exchanged with hydroxyl anions. Although this procedure is lengthy, further ion exchange to prepare the organic-LDH materials becomes easier to conduct. Therefore, introduction of the BDC dianionic ligand is achieved by ion exchange of the OH⁻ anions, in the presence of KOH, according to a published protocol [24], yielding the LDH_{Zn/Al}-BDC material. Based on the N-content from elemental analysis, the loaded amount of ligand is estimated as 0.81 mmol g⁻¹ in LDH_{Zn/Al}-BDC. Also, reaction with [Mo(CO)₃X₂(NCMe)₂] (X = I, Br) afforded the new LDH_{Zn/Al}-BDC-MoX₂ (X = I, Br) hybrid materials.

The second material was obtained from the commercial LDH_{Mg/} _{Al} layered material. It was calcined at 823 K during 5 h, before the intercalation experiments, to eliminate carbonate anions in the interlayer region. This calcination leads to the collapse of the layers, but the reconstruction of the intergallery space is forced by the intercalation of the dianionic ligand BDC in dmf, at 343 K [14,26]. The composite materials LDH_{Mg/Al}-BDC, containing the BDC anions in the interlayer space, were prepared as described previously, leading to the new LDH_{Mg/Al}-BDC-MoX₂ (X = I, Br) hybrid materials (Scheme 2) [14]. Based on the N-content from the elemental analysis, the loading of ligand is 0.97 mmol g⁻¹ in LDH_{Mg/Al}-BDC, and the loading of molybdenum is 7.07 wt.% corresponding to 0.74 mmol_{Mo} g⁻¹ for the I containing material, and 5.39 wt.% corresponding to 0.56 mmol_{Mo} g⁻¹ for the Br one.

The powder XRD patterns of LDH_{Zn/Al}-BDC, LDH_{Zn/Al}-BDC-Mol₂, and LDH_{Zn/Al}-BDC-MoBr₂ (Fig. 1) exhibit a series of well-resolved Bragg reflections in the range 3–70°, which can be indexed to the hexagonal layered LDH structure having rhombohedral symmetry [27]. Peaks from zincite (ZnO) and Zn/Al-CO₃ impurities were also observed as shown in Fig. 1. In addition, the relatively sharp and symmetric shapes of the diffraction peaks strongly suggest that all synthesized materials are highly crystalline, and have a small particle size.

In the LDH_{Zn/Al}-BDC material, some intense peaks arising from basal reflections *001* at low 2 θ angles allow direct estimation of the basal spacing to the plane *003* which is equal to the thickness of one lamella of the brucite structure (ca. 4.8 Å) plus the thickness of the interlayer region. In the case of the parent materials the *003*



Scheme 2. Schematic representation of the immobilization procedure.

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Fig. 1. XRD powder patterns of $LDH_{Zn/AI}$ -BDC, $LDH_{Zn/AI}$ -BDC-Mol₂, and $LDH_{Zn/AI}$ -BDC-MoBr₂ materials. * denotes a peak arising from $LDH_{Zn/AI}$ -CO₃ and # peaks from zincite (ZnO).

reflections are located at 2θ values of 4.85° , corresponding to an interlayer spacing of 18.2 Å [11]. These values suggest that BDC is in a tilted vertical arrangement. Caution should prevail in this analysis, however, as the interlayer arrangement depends on many other factors (humidity and temperature conditions) which were not accounted for. For LDH_{Mg/AI}-BDC and LDH_{Mg/AI}-BDC-MoX₂ (X = I, Br) materials, the 003 reflections are located at 2θ values of 4.56° , corresponding to an interlayer spacing of 19.4 Å. The gallery heights for the Zn/Al materials after intercalation of the organometallic moieties, LDH_{Zn/AI}-BDC-MoX₂ (X = I, Br), are 18.3 Å and 18.5 Å, respectively, according to powder XRD. For the Mg/AI materials, LDH_{Mg/AI}-BDC-MoX₂ (X = I, Br), the gallery heights are 22.8 Å and 21.8 Å, respectively, suggesting the same arrangement of the ligand in the gallery.

Diffuse reflectance infrared spectroscopy (DRIFT) was used to characterize the hybrid materials. The LDH_{Zn/Al}-OH and LDH_{Mg/Al}-CO₃ host materials show a FTIR spectrum similar to that of other materials of the same type. The high frequency region $(4000-2000 \text{ cm}^{-1})$ is dominated by broad bands of the O–H stretching modes of weakly hydrogen bonded water molecules and layer hydroxyl groups at about 3400 cm⁻¹. Other strong and broad peaks associated with the O-H group are observed between ~ 1650 and 1400 cm^{-1} . The derivatized material LDH_{Zn/} Al-BDC resulting from exchange of OH with BDC anions showed new bands in the vibrational spectra. Well defined peaks at \sim 1403 and \sim 1558 cm⁻¹ can be assigned to the symmetric and antisymmetric CO stretching of the carboxylate groups [28]. One peak at 1619 cm⁻¹ is most likely associated with the vC=Nstretching mode of the pyridyl ring but is overlapping other modes from the material still present despite the lower content of water in the interlayer region.

The same peaks characteristic of the ligand are present in the spectra of the Mo(II) containing materials, with minimal shifts. However, several new peaks centered around 2000 cm⁻¹ can be assigned to the vC=O stretching modes of the carbonyls ligands of the immobilized complexes, the strongest being observed at 1954 cm⁻¹ for LDH_{Zn/Al}-BDC-MoI₂ and 1977, 1909, and 1843 cm⁻¹ for LDH_{Zn/Al}-BDC-MoBr₂. The number of peaks results from the three CO groups of the Mo(CO)₃X₂(BDC) (X = I, Br) fragment intercalated in LDH material and the coexistence of several isomers for each species. The reported vC=O frequencies for the parent complex [MoI₂(CO)₃(bpy)] [25] are 2035, 1960, and 1912 are cm⁻¹ and suggest very small changes upon introducing the carboxylate substituents and intercalating. Similar results were obtained for the LDH_{Mg/Al} materials.

The ¹³C CP MAS NMR spectra of the lamellar materials LDH_{Zn/Al}-BDC, LDH_{Zn/Al}-BDC-MoI₂ and LDH_{Zn/Al}-BDC-MoBr₂ (Fig. 2) exhibit several resonances in the 120 < δ < 190 ppm range assigned to car-



Fig. 2. Solid state NMR of LDH_{zn/AI-BDC, LDH_{zn/AI-BDC-Mol_2} and LDH_{zn/AI-BDC-MoBr_2} materials. \ast indicates spinning sidebands.

bon atoms of the aromatic moiety of BDC, and signals at δ ca. 190.0 ppm, 187.7 ppm and 190.4 ppm, for LDH_{Zn/Al}-BDC, LDH_{Zn/Al}-BDC-MoI₂ and LDH_{Zn/Al}-BDC-MoBr₂, respectively, assigned to the carboxylate carbon atoms, which are clearly detected in both spectra of the materials. This result indicates that the deprotonated ligand is inside the interlamellar space of LDH_{Zn/Al} materials. The signals observed for material LDH_{Zn/Al}-BDC, at δ = 189.9 ppm assigned to the COO⁻ resonance, and at 148.7, 140.8, 133.4 and 131.9 ppm to the resonances of the phenyl ring of the BDC ligand, are similar to those found in solution for the H₂BDC ligand.

The carbon atoms of the aromatic phenyl ring of material $LDH_{Zn/Al}$ -BDC-MoI₂ were identified by resonances at 150.9, 145.4, 125.8 and 122.9 ppm, and for $LDH_{Zn/Al}$ -BDC-MoBr₂ the same signals were observed at 148.7, 131.8, 125.6, and 121.1 ppm. $LDH_{Mg/Al}$ derivatized materials led to similar results, the COO⁻ group resonances being observed at 180.4, 181.6 and 193.4 ppm, for $LDH_{Zn/Al}$ -BDC, $LDH_{Zn/Al}$ -BDC-MoBr₂ and $LDH_{Zn/Al}$ -BDC-MoI₂, respectively.

Fig. 3 depicts the thermogravimetric analyses (TGA) of the synthesized clay materials $LDH_{Zn/Al}$, $LDH_{Zn/Al}$ -BDC, $LDH_{Zn/Al}$ -BDC-Mol₂ and $LDH_{Zn/Al}$ -BDC-MoBr₂. All materials show some high temperature mass loss due to dehydroxylation of the clay structure. Both $LDH_{Zn/Al}$ -BDC-Mol₂ and $LDH_{Zn/Al}$ -BDC-MoBr₂ materials experience mass losses (less pronounced in the latter) corresponding to physisorbed water until 478 K. Taking into account the high temperature mass loss observed in $LDH_{Zn/Al}$ due to dehydroxylation, this

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Fig. 3. TGA profiles of $LDH_{Zn/Al},\ LDH_{Zn/Al}\text{-}BDC\text{-}Mol_2$ and $LDH_{Zn/Al}\text{-}BDC\text{-}MoBr_2$ materials.

leaves a net weight loss of 50.9% in the LDH_{Zn/Al}-BDC-Mol₂ material, which can be assigned to the loss of the ligands and metal center. This corresponds to 0.75 mmol g⁻¹ of the immobilized complex inside the clay material (LDH_{Zn/Al}). Similar results obtained for the LDH_{Zn/Al}-BDC-MoBr₂ material showed a total mass loss of ligand and metal center of 33.5%, corresponding to 0.58 mmol g⁻¹ of the organic and metallic counterpart inside the clay material. The LDH_{Mg/Al} clay materials exhibited the same kind of trends.

3.2. Catalysis

The derivatized materials, $LDH_{Zn/AI}$ -BDC-MoI₂ and $LDH_{Zn/AI}$ -BDC-MoBr₂, $LDH_{Mg/AI}$ -BDC-MoI₂ and $LDH_{Mg/AI}$ -BDC-MoBr₂, were tested as catalyst precursors for the epoxidation of several substrates, and the activity of the complexes [MoBr₂(CO)₃(bpy)] and [MoI₂(CO)₃(bpy)] was also tested in order to compare the performance of homogeneous vs. heterogeneous systems. Two sets of substrates were studied. The first one comprises simple olefins, such as *cis*-cyclooctene (cy8), styrene (sty) and 1-octene (1-oct), while the second one includes multifunctional olefins, namely, *trans*-hex-3-en-1-ol (trans) and *R*-(+)-limonene (*R*-lim). Unless otherwise stated, all reactions were carried out using *tert*-butylhydroperoxide (tbhp) as oxygen donor, in toluene as solvent at 383 K Some attention was given to the stereoselectivity in the oxidation of *R*-(+)-limonene, the presence of enantiomers/diastereomers in the catalysis products being detected using a chiral GC column.

Scheme 3. Substrates studied: *cis*-cyclooctene (cy8), styrene (sty), 1-octene (1-oct), *trans*-hex-3-en-1-ol (trans), and *R*-(+)-limonene (*R*-lim) and the epoxides detected.

Table 1

Conversion and selectivity in the olefin epoxidation catalyzed by $[MoI_2(CO)_3(bpy)]$ and $[MoBr_2(CO)_3(bpy)]$ complexes, and materials $LDH_{Zn/AI}$ -BDC-MoI₂ and $LDH_{Zn/AI}$ -BDC-MoBr₂, $LDH_{Mg/AI}$ -BDC-MoI₂ and $LDH_{Mg/AI}$ -BDC-MoBr₂.

Substrate	Entry	Catalysts	Conv.% ^{a,b}	Select.% ^c
су8	1 2 3 4 5 6	[MoI ₂ (CO) ₃ (bpy)] [MoBr ₂ (CO) ₃ (bpy)] LDH _{Zn/AI} -BDC-MoI ₂ LDH _{Zn/AI} -BDC-MoBr ₂ LDH _{Mg/AI} -BDC-MoI ₂ LDH _{Mg/AI} -BDC-MoBr ₂	89 100 68/98 ^d 50/98 ^d 30/70 ^d 100/100 ^d	100 100/100 ^d 100/100 ^d 100/100 ^d 100/100 ^d
sty	7	[MoI ₂ (CO) ₃ (bpy)]	100	56
	8	[MoBr ₂ (CO) ₃ (bpy)]	99	11
	9	LDH _{Zn/AI} -BDC-MoI ₂	92/100 ^d	79/75 ^{d,e}
	10	LDH _{Zn/AI} -BDC-MoBr ₂	77/96 ^d	70/60 ^{d,e}
	11	LDH _{Mg/AI} -BDC-MoI ₂	77/77 ^d	83/78 ^{d,e}
	12	LDH _{Mg/AI} -BDC-MoBr ₂	100/100 ^d	78/83 ^{d,e}
1-oct	13	[MoI ₂ (CO) ₃ (bpy)]	46	100
	14	[MoBr ₂ (CO) ₃ (bpy)]	99	100
	15	LDH _{Zn/AI} -BDC-MoI ₂	40/34 ^d	99/99 ^d
	16	LDH _{Zn/AI} -BDC-MoBr ₂	33/58 ^d	100/100 ^d
	17	LDH _{Mg/AI} -BDC-MoI ₂	45/55 ^d	100/100 ^d
	18	LDH _{Mg/AI} -BDC-MoBr ₂	97/83 ^d	100/100 ^d
trans	19 20 21 22 23 24	[Mol ₂ (CO) ₃ (bpy)] [MoBr ₂ (CO) ₃ (bpy)] LDH _{Zn/Al} -BDC-Mol ₂ LDH _{Zn/Al} -BDC-MoBr ₂ LDH _{Mg/Al} -BDC-Mol ₂ LDH _{Mg/Al} -BDC-MoBr ₂	91 100 96/97 ^d 96/100 ^d 100/100 ^d 72/100 ^d	100 100/100 ^d 95/97 ^d 100/100 ^d 100/100 ^d
R-lim	25	[Mol ₂ (CO) ₃ (bpy)]	100	99
	26	[MoBr ₂ (CO) ₃ (bpy)]	100	96
	27	LDH _{Zn/Al} -BDC-Mol ₂	63/86 ^d	90/90 ^d
	28	LDH _{Zn/Al} -BDC-MoBr ₂	83/80 ^d	93/92 ^d
	29	LDH _{Mg/Al} -BDC-Mol ₂	25/63 ^d	82/89 ^d
	30	LDH _{Mg/Al} -BDC-MoBr ₂	100/100 ^d	93/97 ^d

^a All reactions were carried out in the presence of 200 mol% oxidant (tbhp), 1 mol % of Mo catalyst and 100 mol% of substrate.

^b Calculated after 24 h, unless otherwise stated.

^c Calculated as "Yield of epoxide"/"Conversion" × 100%.

d 1 run/2 run.

^e Benzaldehyde formed as by-product.

The substrates and the major oxidation product are shown in Scheme 3.

In the epoxidation of *cis*-cyclooctene, all materials and complexes catalyzed selectively the oxidation of the substrate to the corresponding epoxide, without formation of any by-products (Table 1, entries 1–6), with yields of the corresponding epoxide between 30 and 100%. The maximum yield (100%) was obtained with the [MoBr₂(CO)₃(bpy)] complex and the LDH_{Mg/Al}-BDC-MoBr₂ material (Table 1, entries 2 and 6).

Styrene conversion was very efficient for all the tested catalysts. Both homogeneous and heterogeneous catalysts reached very high conversion yields for styrene, 77% being the lowest value found (Table 1, entries 11 and 12). The selectivity for the epoxide is low (11% and 56% after 24 h), respectively, when the complexes [MoBr₂(CO)₃(bpy)] and [MoI₂(CO)₃(bpy)] are the catalysts. Benzaldehyde was the other product formed, being the major product when using [MoBr₂(CO)₃(bpy)]. As reported before [17], styrene oxide yield reaches a maximum after ca. 2 h of reaction, decreasing swiftly afterwards as it converts into benzaldehyde. This product interconversion proceeds through an oxidative cleavage mechanism from over-oxidation of styrene epoxide. The heterogeneous catalysts lead to a striking difference in epoxide selectivity (Table 1, entries 9-12). All of them display epoxide selectivity in the range 60-83% after 24 h reaction time. This is a remarkable achievement, since in all cases high substrate conversion is also observed, showing that the use of the clays is beneficial for this particular process. In addition, these results evidence how the same catalyst can tune

Table 2

Selectivity toward R-(+)-limonene-1,2-epoxide in the R-(+)-limonene epoxidation catalyzed by [MoI₂(CO)₃(bpy)] and [MoBr₂(CO)₃(bpy)] complexes, and materials LDH_{Zn/Al}-BDC-MoI₂ and LDH_{Zn/Al}-BDC-MoBr₂, LDH_{Mg/Al}-BDC-MoI₂ and LDH_{Mg/Al}-BDC-MoBr₂

Catalyst	Isomer ^a		
	cis (%)	trans ^b (%)	
[MoI ₂ (CO) ₃ (bpy)]	19	81	
[MoBr ₂ (CO) ₃ (bpy)]	16	84	
LDH _{Zn/Al} -BDC-MoI ₂	51/51 [°]	49/49	
LDH _{Zn/Al} -BDC-MoBr ₂	52/53	48/47	
LDH _{Mg/Al} -BDC-MoI ₂	55/51	45/49	
LDH _{Mg/Al} -BDC-MoBr ₂	48/64	52/36	

^a Enantiomeric ratios.

^b See Scheme 3.

^c 1 run/2 run.

product selectivity, depending on whether it is homogeneous (yielding benzaldehyde) or heterogeneous (yielding styrene oxide), which is a remarkable achievement.

1-Octene is a bit harsher for the catalysts, as it is an unbranched terminal olefin and therefore harder to oxidize. In fact, all catalysts display overall lower substrate conversion values for this olefin than for all the other ones. Despite this, epoxide selectivity is kept at 100% throughout the tests (only one catalyst at 99%), which is an excellent attainment. trans-Hex-3-en-1-ol is an alcohol and therefore a sensitive substrate, making the results once more worth of note in what concerns both substrate conversion and product selectivity. Indeed, the present catalysts were found to yield the epoxide with outstanding selectivity, with values at 100% except for entry 22 (95%). This shows that the catalytic systems reported here are specific for the epoxidation of the C=C bond and do not affect the alcohol moiety to yield, eventually, the aldehyde product.

The *R*-(+)-limonene substrate has two unsaturated C=C bonds, meaning that two different epoxides, the endo- and exo-cyclic isomers, can be formed. The former was the only epoxide observed in all tests (Table 1, entries 25–30) with selectivity above 82%, which is excellent. These results were accompanied by very high substrate conversion rates, reaching 100% for the complexes and one of the materials (entries 25, 26, 30). They are still high for two other material (63% and 83%, entries 27 and 28), and only the $LDH_{Mg/Al}$ -BDC-MoI₂ material evidences a low activity (entry 29).

Stereoselectivity was also assessed for the R-(+)-limonene-1,2epoxide product. As evidenced in Table 2, there are relevant differences between homogeneous and heterogeneous catalysts. While the former show a clear trend to yield more selectively the trans diastereomer, in the heterogeneous counterparts there is no defined preference with all catalysts yielding both diastereomers roughly in a 50/50 ratio. This result is not surprising. Even though some isomers of the Mo(II) complexes might induce chirality, the active species obtained after oxidation should not.

The recyclability of the heterogeneous catalysts was evaluated for all substrates (Tables 1 and 2). In many reactions the catalysts performance was better (or similar) in the second run than in the first. This may be related to the activation of the catalyst, which may reach its optimal conditions in the second run [23]. Indeed, the Mo(II) catalyst precursor undergoes an initial oxidation step. Interestingly, the difference is more evident in the substrate conversion than in the selectivity.

4. Conclusions

Several techniques, namely infra-red and ¹³C solid state NMR spectroscopy, X-ray powder diffraction, indicated that the Mo(II) complexes $[MoX_2(CO)_3(BDC)]$ (X = I, Br; H₂BDC = 2,2'-bipyridine-5,5'-dicarboxylic acid) were intercalated in LDH materials, affording four new clays containing molybdenum, LDH_{Zn/AI}-BDC-MoI₂ and LDH_{Zn/Al}-BDC-MoBr₂, LDH_{Mg/Al}-BDC-MoI₂ and LDH_{Mg/Al}-BDC-MoBr₂. All of these heterogeneous catalysts were active in the oxidation of cis-cyclooctene, styrene, 1-octene, trans-hex-3-en-1-ol, and R-(+)-limonene in the presence of *tert*-butylhydroperoxide, the activity being kept or increased in a second catalytic run. On the other hand, their performance was similar to that of the homogeneous similar systems studied. As more relevant conclusions, it can be said that the four materials showed an unusually high selectivity toward the styrene epoxide (above 70%) with high conversions, and also a high selectivity toward the 1-octene epoxide (99-100%) with variable conversions (33-97%).

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