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Dioxomolybdenum(VI) Epoxidation Catalyst Supported on Mesoporous Silica Containing Phosphane Oxide Groups

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A new mesoporous hybrid material (denoted LP-TEPPPO-Mo) has been prepared by tethering [MoO_2Cl_2] onto mesoporous silica previously functionalised with phosphane oxide spacer ligands. The LP-TEPPPO-Mo material was tested in the liquid-phase epoxidation of olefins [*cis*-cyclooctene, (*R*)-(+)-limonene, *trans*-2-octene and 1-octene] with *t*BuOOH, at 55 °C, and without a co-solvent, giving at least 90 % selectivity to the corresponding epoxide at 36–77 % conversion: in the case of limonene, regioselectivity favours the epoxidation of the endocyclic double bond, giving mainly 1,2-epoxy-*p*-menth-8-ene. The catalytic system based on a liquid–liquid biphasic system containing the homogeneous complex [$MoCl_2(O)_2\{OP(CH_2CH_3)(Ph)_2\}_2$] dissolved in the ionic liquid 1-butyl-4-methylpyridinium tetrafluoroborate leads to lower epoxide selectivity (91 % at 64 % conversion) in the reaction of cyclooctene in comparison to that observed for LP-TEPPPO-Mo (100 % at 87 % conversion). The reused solid–liquid and liquid–liquid biphasic catalytic systems show partial loss of catalytic activity.

Introduction

Heterogeneous catalytic epoxidation is a topic of great interest in the field of catalysis due to significant industrial interest.[1–4] In the heterogenisation of homogeneous catalysts for liquid-phase reactions, covalent host–guest interactions are desirable in terms of catalyst stability. The group of Thiel reported that oxodiperoxomolybdenum(VI) species supported on mesoporous silicon-containing hybrid materials may possess high stability against leaching of the active species into the liquid phase during the epoxidation of cyclooctene with *tert*-butyl hydroperoxide (*t*BuOOH).[5–9] Molybdenum(VI) complexes possessing the [MoO_2Cl_2] core are effective catalysts for the selective epoxidation of olefins with the use of *t*BuOOH as the mono-oxygen source[10–18] and have been supported on ordered mesoporous MCM-41 or MCM-48 supports via two different approaches using organosilanes: direct grafting (denoted G-method) or tethering (or indirect grafting, denoted T-method).[19–21] The G-method involves the preparation of complexes of the type [MoO_2Cl_2L], where L is one bidentate or two monodentate Lewis base ligands possessing at least one trialkoxysilyl pending group, which reacts with the silica surface to form covalent Si–O–Si bonds. The T-method generally involves the initial preparation of silica functionalised with N-donor spacer ligands, followed by ligand exchange of the precursor [$MoO_2Cl_2S_2$], where S is a solvent molecule (e.g., tetrahydrofuran or acetonitrile), with the spacer ligands. In the case of the T-method, steric constraints and/or diffusion limitations during the catalyst immobilisation step may be less important than in the case of the G-method and allow greater metal loadings to be reached. The coordination chemistry of Mo^{VI} with phosphane oxide and phosphonate ligands is interesting, as these compounds can be easily synthesised in good yields and are relatively stable under atmospheric conditions.[22–27]

In this work, a new mesostructured hybrid material, denoted LP-TEPPPO-Mo, has been prepared via the T-method, by introducing [MoO_2Cl_2] into a mesoporous silica functionalised with phosphane oxide spacer ligands. Merckle and Blümel have previously reported that for the phosphane $Ph_2P(CH_2)_3Si(OEt)_3$ (TEPPP) immobilised on different oxide supports (MgO, TiO_2, Al_2O_3 and SiO_2), SiO_2 is the most favourable support with respect to stability towards ligand leaching.[28] The LP-TEPPPO-Mo material was tested as a catalyst in the epoxidation of *cis*-cyclooctene, (*R*)-(+)-limonene, *trans*-2-octene and 1-octene with *t*BuOOH, at 55 °C, without a co-solvent. For comparison, the complex [$MoCl_2(O)_2\{OP(CH_2CH_3)(Ph)_2\}_2$] (**1**) was tested without a co-solvent or under liquid–liquid biphasic conditions using an ionic liquid.

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Results and Discussion

Preparation and Characterisation of the Catalysts

Mesostructured LP-TEPPPO-Mo

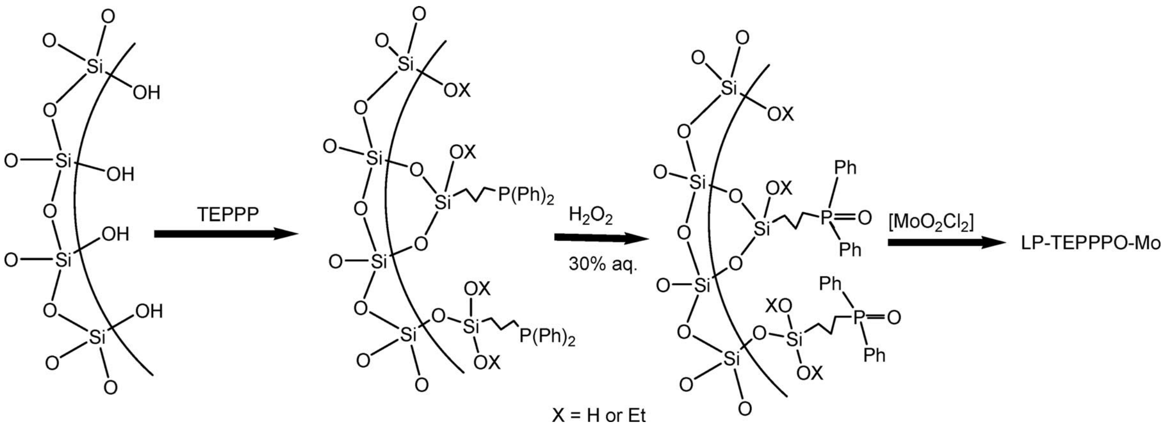
The supported catalyst LP-TEPPPO-Mo was prepared from a large pore mesoporous silica (LP) by using the T-method (Scheme 1). In a first step, phosphane pendant groups were introduced to the LP by treating the latter with an excess amount of the (diphenylphosphanyl)propyltriethoxysilane precursor (TEPPP). An oxidising treatment was applied to transform the surface phosphane groups into phosphane oxide groups, and finally, the metal precursor [MoO_2Cl_2] was introduced. The resultant material, denoted LP-TEPPPO-Mo, possesses 0.17 mmol/g of Mo and a P/Mo mol ratio of 1.8.

The powder XRD patterns of the pristine LP, LP-TEPPPO and LP-TEPPPO-Mo materials (not shown) display broad diffractions in the range $2\theta = 0.5–4°$, indicating poor long-range order. The three materials exhibit irreversible type IV nitrogen adsorption–desorption isotherms (characteristic of mesoporous solids) with capillary condensation steps in the relative pressure range of 0.65–0.84 (Figure S1, Supporting Information). The grafting of organosilane onto LP leads to a significant decrease in S_{BET} and V_{p}. On the basis of the estimated van der Waals molecular volume for TEPPPO (ca. 400 Å^3)[29] one could expect a V_{p} value of ca. 1.59 $cm^3 g^{-1}$ for LP-TEPPPO, which is slightly higher than the value calculated from the nitrogen isotherm (1.33 $cm^3 g^{-1}$; Table S1, Supporting Information). Possibly a fraction of the organic ligands is located at the pore entrances, leading to partial pore blockage. Upon treatment of LP-TEPPPO with [MoO_2Cl_2], the values of S_{BET} and V_{p} further decrease, albeit to a smaller extent than that observed for the organosilane grafting step. The pore-size distribution curves are rather broad with a maximum (d_{p}) at ca. 11.5 nm, which is consistent with the XRD data.

The ^{29}Si CP MAS and MAS NMR spectra of the pristine LP material (not shown) display the typical Q^n resonances [$Q^n = Si(OSi)_n(OH)_{4-n}$] of a pure silica material. In the ^{29}Si CP MAS and MAS NMR spectra of the LP-TEPPPO and LP-TEPPPO-Mo materials, mainly Q^n species can be observed (Figure S2, Supporting Information). The T^m ^{29}Si [$T^m = RSi(OSi)_m(OH)_{3-m}$] environments are not clearly observed (usually in the range –69 to 87 ppm) most likely due to their low quantity. The ^{13}C CP MAS NMR spectra of the LP-TEPPPO and LP-TEPPPO-Mo materials (Figure S3, Supporting Information) display a signal at δ = 130 ppm corresponding to the phenyl group of the phosphane ligand, and the resonances at δ = 61.2, 29.2 and 14.0 ppm can be assigned to the methylene groups (in the order from left to right) in the $P\mathit{C}H_2\mathit{C}H_2\mathit{C}H_2Si$ groups. The presence of reminiscent ethoxy groups is not clear due to the possible overlapping of the peaks assigned to these groups (expectedly $\delta \approx 16$ and 57 ppm for the $\mathit{C}H_3$ and $\mathit{C}H_2$, respectively) with the peak at δ = 14.0 ppm (associated to $PCH_2CH_2\mathit{C}H_2Si$) and the spinning side band at $\delta \approx$ 58.5 ppm. The ^{31}P (CP) MAS spectra of the LP-TEPPPO and LP-TEPPPO-Mo materials revealed the presence of the phosphane oxide specie at δ = 39.0 ppm (Figure S4, Supporting Information). A second peak at δ = 22 ppm may be related to a P^V species of the type $(EtO)_3Si(CH_2)_3(Ph)_2\mathit{P}$-(-O-[$SiO_2$])$_2$ formed in a side reaction of the phosphane precursor with the silica surface.[30] The phosphorus atom in these groups is expectedly not available for coordination with molybdenum and may be located in the vicinity of surface silanol groups, which is supported by the increase in the relative intensity of the peak at δ = 22 pm relative to that at δ = 39.0 ppm when cross polarisation is applied. Hence, the effective P/Mo molar ratio involved in the complexation reaction may be less than 1.8.

Catalytic Epoxidation of Olefins

The catalytic performance of LP-TEPPPO-Mo was investigated in the epoxidation of *cis*-cyclooctene with *t*BuOOH, at 55 °C, without a co-solvent. Control experiments were performed by using LP or LP-TEPPPO (without Mo): LP gives 5% conversion after 24 h and cyclooctene oxide is the only product, whereas LP-TEPPPO gives 29% conversion at 24 h with 61% epoxide selectivity



Scheme 1. Preparation of LP-TEPPPO-Mo by using the T-method.

(cyclooctane-1,2-diol was the only byproduct; Table 1). The LP-TEPPPO-Mo catalyst leads to significant improvements in the reaction rate and epoxide selectivity in relation to those of LP-TEPPPO: the initial TOF calculated for a 10 min reaction is 648 mol$\,$mol$_{\text{Mo}}$$\,$h^{-1} and after 24 h conversion reaches 87% with 100% epoxide selectivity. In the case of complex **1**, the initial TOF is 519 mol$\,$mol$_{\text{Mo}}$$\,$h^{-1}, which is comparable to that observed for LP-TEPPPO-Mo, and quantitative epoxide yield is reached at 24 h. For complex **1** and LP-TEPPPO-Mo, iodometric titrations indicated that *t*BuOOH is essentially consumed in the olefin epoxidation process. The epoxide yields at 24 h are comparable with those reported in the literature for several micelle-templated mesoporous silica-supported complexes of the type [MoO_2Cl_2L] or [$CpMo(CO)_3(X)$] (Cp = cyclopentadienyl ligand; X = methyl, siloxane) possessing a –$Si(OEt)_3$ moiety on the L, Cp or X ligand.[7] The kinetic curve for LP-TEPPPO-Mo is comparable to that of MCM-41-supported [$MoO(O)_2L$] complexes, used as a catalyst in the same reaction.[8,9]

The LP-TEPPPO-Mo catalyst was further tested in the reactions of (*R*)-(+)-limonene, 1-octene and *trans*-2-octene with *t*BuOOH, at 55 °C, without a co-solvent (Table 1). A comparative study for 1-octene and *trans*-2-octene indicates that the latter substrate is more reactive than the former (epoxide yield at 4 h is 9 and 45% for 1-octene and 2-octene, respectively). These results suggest that more-substituted (electron richer) olefins tend to be more reactive than less-substituted ones, which is congruent with the mechanistic considerations reported in the literature for the epoxidation of olefins with *t*BuOOH in the presence of pseudo-octahedral complexes possessing the [MoO_2]$^{2+}$ moiety and organic Lewis base N,O,S ligands,[31–34] and for Mimoun-type peroxo complexes of the type [$MoO(O_2)_2\{OP(CH_3)_3\}$] (R = H, alkyl).[35] The reaction of (*R*)-(+)-limonene gives mainly 1,2-epoxy-*p*-menth-8-ene (denoted P1) formed in 72% yield at 4 h: byproducts include mainly 1,2–8,9-diepoxy-*p*-menthane (P2), *p*-menta-1,8-dien-7-ol and 4-isopropyl-1-methylcyclohexane-1,2-diol. The molar ratio P1/P2 at 90% conversion (at 24 h reaction) is 5.7, indicating that regioselectivity favours the epoxidation of the endocyclic C1–C2 double bond.

To assess the homo/heterogeneous nature of the catalytic reaction in the presence of LP-TEPPPO-Mo, a leaching test was performed by filtering off the reaction solution after 30 min through a 0.2 µm PVDF w/GMF Whatman membrane, at 55 °C, and leaving it to react for 150 min. No increase in olefin conversion was observed after the filtration step, in contrast to that observed in the presence of LP-TEPPPO-Mo, suggesting that the catalytic reaction is heterogeneous in nature. The FTIR spectra of fresh and recovered solids were identical (not shown). The LP-TEPPPO-Mo was reused twice at 55 °C (Figure 1). Epoxide selectivity is always 100%, although the catalytic activity decreases in consecutive runs: conversion at 24 h is 87, 77 and 73% for runs 1, 2 and 3, respectively. After the recycling runs, the solid was separated from the reaction mixture by centrifugation, thoroughly washed with *n*-hexane and dried at room temperature overnight. ICP-AES analyses (experimental error of 5%) of the recovered solid indicated reductions in the initial P and Mo contents (mmol$\,$g^{-1}) of 16 and 17%, respectively. These results together with those obtained for the leaching test, suggest that the leached species are inactive and/or leaching of active species does not occur to a measurable extent in the initial stage (at least 30 min) of the catalytic reaction. On the basis of the characterisation studies, the LP-TEPPPO-Mo material may possess a diversity of surface species because (i) grafting of the organosilane precursor onto the mesoporous silica may give mono-, di- and tripodal surface species; (ii) molybdenum species with different Mo/P mol ratios may be formed; (iii) the molybdenum precursor may react with surface organosilane groups or with silanols to give species that are susceptible to metal leaching.[36] Leaching of Mo and P may be attributed to certain populations of the respective surface species.

Merckle and Blümel have previously reported that TEPPP immobilised on silica surfaces may be partially detached in polar/protic medium.[28] The group of Thiel reported for molybdenum(VI) complexes supported on silicon-containing materials that catalyst stability towards leaching phenomena may be improved by (i) decreasing the concentration of surface silanol groups (with concomitant increase in the surface hydrophobicity) by silanisation[8,9] or

Table 1. Reaction of olefins with *t*BuOOH in the presence of complex **1** or LP-TEPPPO-Mo at 55 °C.

Olefin	Catalyst	Conversion[a] (%)	Epoxide selectivity[b] (%)
cis-Cyclooctene	LP-TEPPPO-Mo	57/87 (39/77)[c]	100/100 (100/100)[c]
	LP-TEPPPO	20/29	61/61
	LP	–/5	–/100
	Complex **1**	96/100	100/100
	Complex **1**/[BMPy][BF_4]	52/64 (36/67)[c]	91/91 (100/100)[c]
(*R*)-(+)-Limonene	LP-TEPPPO-Mo	77/90	90/80[d]
1-Octene	LP-TEPPPO-Mo	9/36	100/100
trans-2-Octene	LP-TEPPPO-Mo	45/65	100/100

[a] Olefin conversion at 4 h/24 h without a co-solvent unless specified in the "Catalyst" column. [b] Selectivity to the corresponding epoxide at 4 h/24 h (1,2-epoxy-*p*-menth-8-ene in the case of limonene). [c] Catalytic results for the second reaction run. [d] Byproducts include 1,2–8,9-diepoxy-*p*-menthane formed in 2%/14% selectivity at 4 h/24 h, respectively.

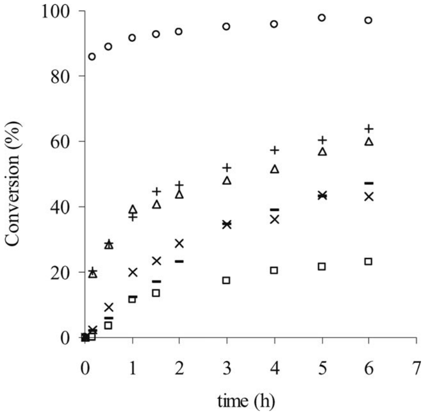


Figure 1. Reaction of *cis*-cyclooctene with *t*BuOOH at 55 °C without co-solvent in the presence of complex **1** (○), LP-TEPPPO (□), LP-TEPPPO-Mo [run 1 (+); run 2 (–)] or using the complex **1**/[BMPy][BF$_4$] liquid–liquid biphasic system [run 1 (Δ); run 2 (×)].

(ii) preparing hybrid mesoporous materials by the co-condensation of an organosilane (ligand) precursor with silica reagents (e.g., tetraalkoxysilanes).[5,6]

An alternative approach for facilitating the recycling of the homogeneous catalysts is to dissolve the complex in an appropriate ionic liquid (IL) to give a biphasic liquid–liquid (L-L) system where the catalyst is dissolved in the IL phase. The catalytic performance of complex **1** was further investigated in the reaction of *cis*-cyclooctene with *t*BuOOH by using the IL 1-butyl-4-methylpyridinium tetrafluoroborate ([BMPy][BF$_4$]) at 55 °C. The choice of this IL resides in the fact that it is (i) readily available and relatively cheap, (ii) dissolves the metal complex and (iii) although it solubilises *t*BuOOH, it is immiscible with the olefin. Under these reaction conditions, the main product is cyclooctene oxide and cyclooctane-1,2-diol is the only byproduct, which is most likely formed through ring opening of the epoxide: although epoxide selectivity decreases from 100% at 29% conversion to 91% at 44–64% conversion, selectivity to the diol increases proportionally. The reaction is slower (initial TOF = 120 mol mol$_{\mathrm{Mo}}$ h^{-1}; conversion at 24 h = 64%) and less selective to the epoxide than that observed for complex **1** without a co-solvent (initial TOF = 519 mol mol$_{\mathrm{Mo}}$ h^{-1}; 100% epoxide yield at 24 h), under similar reaction conditions (Table 1, Figure 1). Possibly mass transfer limitations exist in the case of the biphasic L-L system and/or the nature of the active metal species present in the ionic and neutral reaction media are different.

The products of the cyclooctene reaction were extracted after a 24 h-run by using *n*-hexane (immiscible with the IL), and the resulting catalyst/[BMPy][BF$_4$] mixture was reused in a second run. The olefin and oxidant were added to the catalyst/[BMPy][BF$_4$] mixture in the same amounts as those used for the first run, and the reaction was monitored for 24 h at 55 °C. In contrast to that observed for the first run, in the second run the epoxide is the only product until 68% conversion (reached at 24 h; Table 1, Figure 1). The reaction is slower in the second run, although the conversion after 24 h is similar for both runs. Possibly, the nature and amount of active species are different in the two runs and/or a fraction of active metal species is extracted with the products in the workup procedures.

Conclusions

A mesostructured hybrid material (denoted LP-TEPPPO-Mo) has been prepared by introducing [MoO$_2$Cl$_2$] into a mesoporous silica functionalised with phosphane oxide spacer ligands. The hybrid support (LP-TEPPPO) possesses mainly two types of P species: phosphane oxide pendant groups of the type Si(CH$_2$)$_3$(Ph)$_2$P=O and possibly (EtO)$_3$Si(CH$_2$)$_3$(Ph)$_2$*P*(-O-[SiO$_2$])$_2$. The latter are expectedly not available for complexation with the molybdenum(VI) precursor. The LP-TEPPPO-Mo material was tested as a catalyst in the liquid-phase epoxidation of olefins [*cis*-cyclooctene, (*R*)-(+)-limonene, *trans*-2-octene and 1-octene] with *t*BuOOH at 55 °C and without a co-solvent: the respective epoxides were obtained in relatively high yields (e.g., 72% 1,2-epoxy-*p*-menth-8-ene in the limonene reaction at 24 h with regioselectivity favouring the epoxidation of the endocyclic double bond). A disadvantage of this catalyst is the occurrence of Mo and P leaching during catalysis and a concomitant decrease in catalytic activity in recycling runs. These results may be related to the presence of a diversity of surface groups in LP-TEPPPO-Mo. Improvements in catalyst stability may be accomplished by preparing a uniform, single-site mesostructured catalyst using alternative synthesis methodologies, such as organosilane templated-co-condensation of TEPPP with another organic precursor in an attempt to improve the dispersion and stability of the P surface groups towards leaching and minimise the amount of silanol groups (reactive with the metal precursor to give different metal species that are susceptible to leaching[36]).

The catalytic system based on a liquid–liquid biphasic system containing the homogeneous complex [MoCl$_2$(O)$_2$-$\{$OP(CH$_2$CH$_3$)(Ph)$_2\}_2$] dissolved in the ionic liquid 1-butyl-4-methylpyridinium tetrafluoroborate and used in the reaction of cyclooctene does not lead to major improvements in terms of catalyst recyclability and epoxide selectivity is lower in comparison to that observed for LP-TEPPPO-Mo.

Experimental Section

Materials and Characterisation Techniques: Starting reagents were acquired from Aldrich and commercially dried solvents from Acros Organics and used as received. The catalysts were prepared by using standard Schlenk techniques under a nitrogen atmosphere.

Powder X-ray diffraction (PXRD) data were collected with a Philips X′Pert MPD diffractometer (Cu-K_α X-radiation, λ = 1.54060 Å) fitted with a graphite monochromator and a flat plate sample holder, in a Bragg–Brentano *para*-focusing optics configuration. Samples were step-scanned in 0.02° 2θ steps with a counting time of 2 s per step. Nitrogen adsorption isotherms at –196 °C were measured by using a Gemini 2375 Micromeritics Instrument (Eng. M. C. Costa, University of Aveiro). The mesostructured materials were pretreated at 150 °C prior to analysis. Microanalyses for C and H were carried out at the Department of Chemistry, University of Aveiro (M. M. Marques). The P and Mo contents were determined by ICP-AES at the Central Laboratory for Analysis, University of Aveiro (L. Carvalho). Infrared spectra (KBr pellets) were measured by using a Mattson 7000 FT spectrometer. ^{13}C, ^{29}Si and ^{31}P solid-state NMR spectra were recorded at 100.62, 79.49 and 161.98 MHz, respectively, with a (9.4-T) Bruker Avance 400P spectrometer. ^{29}Si MAS NMR spectra were recorded with 40° pulses, spinning rates 5.0–5.5 kHz and 60-s recycle delays. ^{29}Si CP MAS NMR spectra were recorded with 4-μs 1H 90° pulses, 8 ms contact time, a spinning rate of 5 kHz and 4-s recycle delays. For ^{31}P MAS NMR spectra were recorded with 45° pulses, spinning rate of 15 kHz, ^{1}H decoupling and a 60 s recycle delay. Chemical shifts are quoted in parts per million from phosphoric acid (85%). ^{13}C CP MAS NMR spectra were recorded with 4.5-μs 1H 90° pulses, 2 ms contact time, a spinning rate of 7 kHz and 4-s recycle delays. Chemical shifts are quoted in ppm from TMS. ^{13}C spectra were also recorded in the solid state at 125.76 MHz with a Bruker Avance 500 spectrometer.

Preparation of the Catalysts

$[\mathrm{MoCl_2(O)_2\{OP(CH_2CH_3)(Ph)_2\}_2}]$ (1): Complex **1** was synthesised by following a procedure similar to that described in the literature by Hursthouse et al.:[37] Ethyldiphenylphosphane oxide (0.500 g, 2.17 mmol) was added to $[\mathrm{MoO_2Cl_2}]$ (0.200 g, 1.00 mmol) in dichloromethane (5 mL), under a nitrogen atmosphere. The solution was stirred for 2 h and then left at 5 °C for 8 d, giving a solid containing colourless transparent crystals (yield: 99%). The solid was separated by filtration, washed with *n*-hexane and dried at room temperature. $\mathrm{C_{28}H_{30}Cl_2MoO_4P_2}$ (659.33): calcd. C 51.01, H 4.59; found C 50.28, H 4.66. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, room temperature): δ = 7.30–7.76 (m, 10 H, Ph), 2.45 (9, $^{3}J_{\mathrm{H,H}}$ = 6.00 Hz, 4 H, $\mathrm{P}C\mathrm{H_2}$-), 1.13 (t, $^{3}J_{\mathrm{H,H}}$ = 6.00 Hz, 6 H, $\mathrm{-CH_2}C\mathrm{H_3}$) ppm. ^{31}P NMR (300 MHz, $\mathrm{CDCl_3}$, room temperature): δ = 49 ppm. IR (KBr pellets): $\tilde{\nu}$ = 901, 944 ($\nu_{\mathrm{Mo=O}}$); 1173, 1146 ($\nu_{\mathrm{P=O}}$); 321 ($\nu_{\mathrm{Mo-Cl}}$); 3057 [$\nu_{\mathrm{(C-H)Ph}}$]; 1232–1482 [$\nu_{\mathrm{(C-C)Ph}}$]; 1238 [$\delta_{\mathrm{p(CH)}}$]; 1030 [$\nu_{\mathrm{s(CC)}}$]; 719 [$\delta_{\mathrm{op(CH)}}$] cm^{-1}.

Mesoporous Silica-Supported Molybdenum(VI) Complex (LP-TEPPPO-Mo): The (diphenylphosphanyl)propyltriethoxysilane precursor (TEPPP) was prepared by a modified literature procedure:[38,39] Potassium diphenylphosphide (0.5 M in THF, 20 mL) was added dropwise to a solution of 1-chloro-3-(triethoxysilyl)propane (2.40 mL, 0.01 mol) in THF (20 mL). The mixture was stirred for 3 h at 15 °C and left at room temperature overnight. The workup of the reactions consisted of the evaporation of THF, addition of pentane to precipitate the salt and dissolution of the products. After filtration and evaporation of pentane, the resulting yellow oil was distilled under reduced pressure (1 Torr) at 240 °C. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, room temperature): δ = 7.20–7.33 (m, 10 H, Ph), 3.79 (q, $^{3}J_{\mathrm{H,H}}$ = 7.06 Hz, 6 H, $\mathrm{O}C\mathrm{H_2CH_3}$), 2.06 (t, $^{3}J_{\mathrm{H,H}}$ = 7.70 Hz, 2 H, $\mathrm{P}C\mathrm{H_2}$-), 1.44–1.57 (m, 2 H, $\mathrm{CH_2}C\mathrm{H_2CH_2}$), 1.10 (t, $^{3}J_{\mathrm{H,H}}$ = 7.06 Hz, 9 H, $\mathrm{OCH_2}C\mathrm{H_3}$), 0.74 (t, $^{3}J_{\mathrm{H,H}}$ = 7.93 Hz, 2 H, -$C\mathrm{H_2Si}$) ppm. ^{31}P NMR (300 MHz, $\mathrm{CDCl_3}$, room temperature): δ = –16.8 ppm. IR (KBr pellets): $\tilde{\nu}$ = 3051 [$\nu_{\mathrm{(C-H)Ph}}$], 1363–1481 [$\nu_{\mathrm{(C-C)Ph}}$], 1294 [$\delta_{\mathrm{p(CH)}}$], 696 [$\delta_{\mathrm{op(CH)}}$], 1074 ($\nu_{\mathrm{Si-O}}$) cm^{-1}.

An excess amount of TEPPP ligand dissolved in dichloromethane was added to dehydrated LP (0.400 g, prepared as in references[40,41]), and the mixture was heated at reflux and stirred for 48 h. The white solid was separated and washed with dichloromethane (3 × 10 mL). The material was treated with 30% aqueous $\mathrm{H_2O_2}$ according to the procedure reported in the literature, giving LP-TEPPPO.[42] ^{29}Si (CP) MAS NMR (ppm from TMS): δ = –91.2, –102.6 (br., Q^3), –111.2 (br., Q^4) ppm. ^{13}C CP MAS NMR (ppm from TMS): δ = 130 (Ph), 61.2 (P-$C\mathrm{H_2}$-), 29.2 ($\mathrm{-CH_2}C\mathrm{H_2CH_2}$-), 14.0 (-$C\mathrm{H_2Si}$) ppm. ^{31}P (CP) MAS NMR (ppm from $\mathrm{H_3PO_4}$, 85%): δ = 39 [$\mathrm{(Ph)_2P(O)(CH_2)_3Si{\equiv}O\text{-}(SiO_2)}$], 22 $\{\mathrm{(EtO)_3Si(CH_2)_3(Ph)_2}P\mathrm{[\text{-}O\text{-}(SiO_2)]_2}\}$ ppm.

For anchoring the $[\mathrm{MoO_2Cl_2}]$ complex, a solution of $[\mathrm{MoO_2Cl_2}]$ (0.0601 g, 3.022×10^{-4} mol) dissolved in dichloromethane (5 mL) was added to LP-TEPPPO (0.186 g), and the mixture was stirred overnight at room temperature. The light-green solid in suspension was separated by filtration, washed with dichloromethane and dried in vacuo, giving LP-TEPPPO-Mo (0.17 mmol/g of Mo and a P/Mo mol ratio of 1.8). ^{29}Si (CP) MAS NMR (ppm from TMS): δ = –91.2, –102.6 (br., Q^3), –111.2 (br., Q^4) ppm. ^{13}C CP MAS NMR (ppm from TMS): δ = 130 (Ph), 61.2 (P-$C\mathrm{H_2}$-), 29.2 ($\mathrm{-CH_2}C\mathrm{H_2}$-$\mathrm{CH_2}$-), 14.0 (-$C\mathrm{H_2Si}$) ppm. ^{31}P (CP) MAS NMR (ppm from $\mathrm{H_3PO_4}$, 85%): δ = 39 $\{\mathrm{(Ph)_2P(O)(CH_2)_3Si{\equiv}O\text{-}[SiO_2]}\}$, 22 $\{\mathrm{(EtO)_3\text{-}Si(CH_2)_3(Ph)_2}P\mathrm{[\text{-}O\text{-}(SiO_2)]_2}\}$.

Catalytic Reactions: The liquid-phase olefin epoxidation reactions were carried out in air and autogenous pressure, in batch microreactors equipped with a magnetic stirrer and a sampling valve, and immersed in an oil bath heated at 55 °C. Typically, the reaction vessels were loaded with the olefin (1.8 mmol), *t*BuOOH (5.5 M in decane; 2.75 mmol) and complex **1** (18 μmol) or LP-TEPPPO-Mo (4.8 mg, 4.3 μmol Mo). The reactions were carried out without a co-solvent in the case of LP-TEPPPO-Mo and complex **1** or by using the ionic liquid 1-butyl-4-methylpyridinium tetrafluoroborate ([BMPy][$\mathrm{BF_4}$], 0.1 mL) in the case of complex **1**.

The course of the reactions was monitored by using a Varian 3900 GC equipped with a capillary column (SPB-5, 20 m × 0.25 mm) and a flame ionisation detector. For quantification of the products, nonane or undecane were used as internal standards added after the reaction. The reaction products were identified by GC–MS [Trace GC 2000 Series (Thermo Quest CE Instruments) – DSQ II (Thermo Scientific)], using He as the carrier gas.

Supporting Information (see footnote on the first page of this article): Parameters for the LP related materials; nitrogen adsorption–desorption isotherms and pore-size distribution curves for LP, LP-TEPPPO and LP-TEPPPO-Mo; ^{29}Si CP MAS and MAS NMR spectra of LP-TEPPPO and LP-TEPPPO-Mo; ^{13}C CP MAS NMR spectra of LP-TEPPPO and LP-TEPPPO-Mo; ^{31}P CP MAS and MAS NMR spectra of LP-TEPPPO HM and LP-TEPPPO-Mo.

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