

Complexation of crystal-like mesoporous phenylene-silica with $\text{Cr}(\text{CO})_3$ and catalytic performance in the oxidation of cyclooctene

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ABSTRACT

Chromium carbonyl complexes were incorporated into a molecularly ordered mesoporous phenylene-silica by reaction with $\text{Cr}(\text{CO})_6$ in refluxing 1,2-dichloroethane (DCE). The modified material with a chromium loading of 0.07 mmol g^{-1} was characterised by powder X-ray diffraction, N_2 adsorption, thermogravimetric analysis (TGA), FT-IR, ^{13}C and ^{29}Si MAS NMR spectroscopies. TGA under air indicated that thermal decarbonylation between 250 and 350°C preceded the Cr-promoted decomposition and release of organic fragments at a lower temperature (onset ca. 380°C) than that registered for the phenylene-silica precursor (onset ca. 550°C). The catalytic performance of the modified phenylene-silica was evaluated in the oxidation of *cis*-cyclooctene at 55°C with *tert*-butylhydroperoxide (TBHP) as the oxidant and DCE as the co-solvent. The main product was the epoxide, formed in 83% yield after 24 h, with 2-cycloocten-1-one being the main by-product. Although the activity of the catalyst decreased after the first recycle, possibly due to partial chromium leaching, it remained nearly the same thereafter, and leaching tests indicated that the catalytic reaction was essentially heterogeneous in nature. Tests carried out using a radical scavenger indicated that the reaction of the olefin with TBHP may involve both free radical and non-radical reaction mechanisms.

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1. Introduction

Arene chromium tricarbonyl complexes have been widely used as selective catalysts for numerous organic transformations [1], such as the 1,4-hydrogenation of conjugated dienes to monoenes [2], the hydrogenation of alkynes to (*Z*)-alkenes [3], the hydrogenation of α,β -unsaturated carbonyl compounds to saturated analogues [3], and room temperature cycloaddition reactions [4]. The immobilisation of these complexes on inorganic oxides or polymeric supports is of special interest, not just to prepare more practical catalysts for the above reactions, but also to prepare heterogeneous catalysts for alkene polymerisation [5]. For example, the adsorption of $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ on alumina or silica-alumina gives sub-carbonyl species which are active as ethene polymerisation catalysts [6]. Various arene chromium tricarbonyl complexes have been encapsulated within the supercages of faujasite zeolites, either directly by adsorption of the preformed complex or indirectly by adsorption of $\text{Cr}(\text{CO})_6$ (to give surface tricarbonyl species, $\text{Cr}(\text{CO})_3(\text{O}_2)_3$) followed by adsorption of the arene [7]. In

an alternative approach, $\{\eta^6\text{-(organosilyl)arene}\}\text{Cr}(\text{CO})_3$ species were covalently linked to silica supports by condensation reactions of alkoxy-silane-functionalised complexes with the reactive SiOH groups on the silica gel surfaces [8]. Preliminary catalytic tests for the polymerisation of phenylacetylene indicated that only a ladder intermediate was formed, the formation of the final poly(phenylacetylene) not being detected.

Several research groups have sought the immobilisation of arene chromium tricarbonyl complexes where the aromatic ligand is integrated into a silica or metal-organic network [5c,9]. The organosilica materials are generally prepared by a sol-gel process involving the hydrolysis and polycondensation of substituted alkoxy-silanes containing nonhydrolysable Si-C bonds. There are two routes for the incorporation of the organometallic complexes: route A, one-pot reaction using $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ containing one, two or three $\text{Si}(\text{OR})_3$ groups [5c,9a,9b]; route B, hydrolysis of the organoalkoxy-silane precursor followed by complexation [9a]. Route A generally ensures a better homogeneity of the complexed metal throughout the polymer, and also allows the co-polymerisation of metal-bound and metal-free molecular precursors [5c]. For route B, the hydrolysis-polycondensation of $\text{C}_6\text{H}_5\text{Si}(\text{OR})_3$ leads to a solid in which most of the organic groups are located at the surface and readily react with $\text{Cr}(\text{CO})_6$ to give

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anchored (η^6 -arene)Cr(CO)₃ complexes [9a]. In contrast, the use of 1,4-bis(trialkoxysilyl)benzene gives a phenylene-bridged hybrid silsesquioxane in which most of the organic groups are located inside the solid rather than at the surface, and are therefore not accessible for chemical reaction [9a]. An important development in this field was the surfactant-mediated synthesis of periodic mesoporous phenylene-silica materials with crystal-like pore walls [10]. These materials possess hexagonal arrays of uniform mesopores and surface structures with alternating hydrophobic phenylene and hydrophilic silica layers. Kamegawa et al. reported the incorporation of arenetricarbonyl complexes [$-C_6H_4M(CO)_3-$, M=Cr, Mo] by treatment of a crystal-like phenylene-silica with Cr(CO)₆ or Mo(CO)₆ vapour, achieving complexation of 15% of the phenylene groups [11].

In recent work we found that the liquid phase deposition of Mo(CO)₆ onto crystal-like mesoporous phenylene-silica gave immobilised arene molybdenum tricarbonyl complexes with metal loadings between 1.5 and 5.9 wt.% depending on the reaction conditions [12]. These materials exhibit promising performance in liquid phase catalytic olefin epoxidation. We have now extended this study to chromium and report on the performance of a Cr-containing material as a pre-catalyst for the oxidation of *cis*-cyclooctene at 55 °C, using *tert*-butylhydroperoxide (TBHP) as the oxidant.

2. Experimental

2.1. Materials and methods

All air sensitive operations were carried out using standard Schlenk techniques under a nitrogen atmosphere. Octadecyltrimethylammonium bromide (ODTMA) and Cr(CO)₆ were obtained from Aldrich and used as received. Solvents were dried by standard procedures, distilled under nitrogen and stored over 4 Å molecular sieves. 1,4-Bis(triethoxysilyl)benzene (BTEB) was prepared by a Barbier–Grignard reaction and purified by distillation under reduced pressure [10b,13]. The benzene-silica PMO with a crystal-like wall structure (PMO-ph) was prepared exactly as described previously, under basic conditions using ODTMA as the structure directing agent and BTEB as the silica source [10b]. The surfactant was removed from the as-synthesised material by solvent extraction with an acidic solution. Powder XRD (*hkl* in parentheses): 2θ (°) = 1.88 (100 overlapping with 110 and 200), 11.60, 23.40, 35.40; d_{100} = 47.0 Å; $a = 2d_{100}/\sqrt{3} = 54.3$ Å.

Microanalyses for C and H, and ICP-AES determination of Cr were performed at the University of Aveiro. The N₂ adsorption isotherm was measured at –196 °C using a Gemini 2375 Micromeritics Instrument (Eng. M.C. Costa, University of Aveiro). A pre-treatment at 150 °C was applied prior to analysis. Thermogravimetric analyses (TGA) were carried out under air using a Shimadzu TGA-50 system, with a heating rate of 5 °C min⁻¹. Powder XRD data were collected on a Philips X'Pert MPD diffractometer (Cu K α X-radiation, $\lambda = 1.54060$ 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. IR spectra were obtained using a FT-IR Mattson-7000 infrared spectrophotometer with 2 cm⁻¹ resolution. Attenuated total reflectance (ATR) spectra were measured on the same instrument equipped with a Specac Golden Gate Mk II ATR accessory having a diamond top-plate and KRS-5 focusing lenses. Solid-state magic-angle spinning (MAS) NMR spectra were recorded at 79.49 MHz for ²⁹Si and 125.76 MHz for ¹³C on Bruker Avance 400 and 500 spectrometers, respectively. ²⁹Si MAS NMR spectra were recorded with 40° pulses, a spinning rate of 5.0 kHz, and 60 s recycle delays. ¹³C CP MAS NMR spectra were recorded

with 4.5 μ s ¹H 90° pulses, a contact time of 2 ms, spinning rates of 7.0 and 9.0 kHz, and 4 s recycle delays.

2.2. Preparation of PMO-phCr(CO)₃

Physisorbed water was removed from PMO-ph (1.0 g) by heating the material at 120 °C under reduced pressure for 2 h. A suspension of Cr(CO)₆ (0.50 g, 2.27 mmol) in 1,2-dichloroethane (15 mL) was then added to a suspension of PMO-ph in 1,2-dichloroethane (15 mL). After refluxing the mixture for 12 h, the solution was filtered off and the solid washed with CH₂Cl₂ (3 × 20 mL), and vacuum-dried (first cycle). A further two cycles were performed using freshly prepared suspensions of Cr(CO)₆ in 1,2-dichloroethane. Elemental analysis found: (after first cycle) C 37.82, H 3.08, Cr 0.14%; (after second cycle) C 37.15, H 3.19, Cr 0.26%; (after third cycle) C 37.61, H 3.15, Cr 0.35%. Data from type IV N₂ sorption isotherm: BET specific surface area ($p/p_0 = 0.01-0.1$) = 639 m² g⁻¹, specific total pore volume = 0.6 cm³ g⁻¹, pore width (taken from the maximum of the pore size distribution curve calculated using the BJH method) = 3.7 nm. IR (KBr, cm⁻¹): 3434s, 3062m, 3015m, 1978w, 1935m, 1830w, 1636m, 1385m, 1160vs, 1101sh, 1077vs, 1020sh, 922m, 809m, 756m, 559sv, 520s, 432m, 388m.

2.3. Catalytic studies

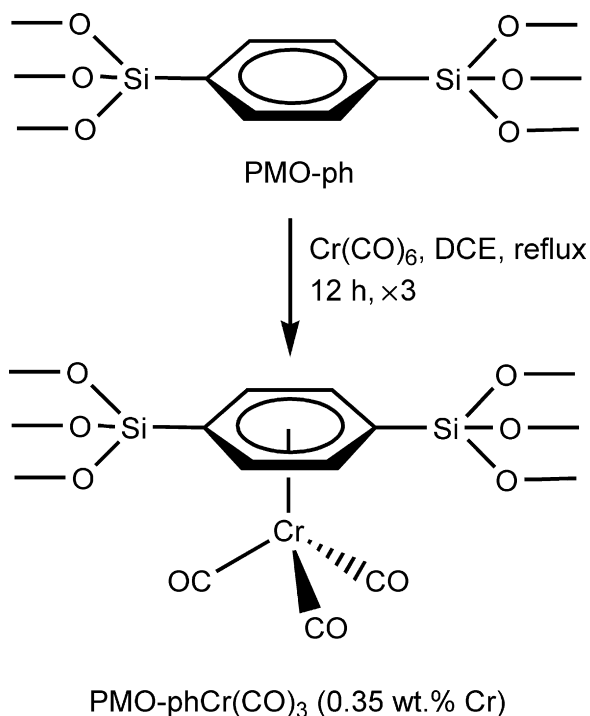
The liquid phase catalytic epoxidation reactions were carried out with magnetic stirring under air (atmospheric pressure) in closed borosilicate reaction vessels (5 mL capacity), which were immersed in a thermostatted oil bath (55 °C). The reaction vessel was loaded with Cr(CO)₆ (3.3 μ mol) or PMO-phCr(CO)₃ (50 mg, corresponding to 3.3 μ mol of chromium), *cis*-cyclooctene (1.7 mmol), TBHP (2.7 mmol, 5.5 M in decane) and 1,2-dichloroethane (2 mL). In order to avoid the photodissociation of the carbonyl ligands (which could occur by interaction with reagents or solvent [14]), the catalytic tests were carried out in the dark. The reaction courses were monitored using a Varian 3800 GC equipped with a flame ionisation detector and a DB-5 column (30 m × 0.53 mm), with hydrogen as the carrier gas.

3. Results and discussion

3.1. Catalyst preparation and characterisation

Mesoporous phenylene-silica with crystal-like pore walls (PMO-ph) was treated with a mixture of Cr(CO)₆ and 1,2-dichloroethane (DCE) under reflux for 12 h (Scheme 1). The solid was then filtered, washed with DCE, and vacuum-dried, giving a pale yellow material with a chromium content of 0.14 wt.% (0.03 mmol g⁻¹). A similar treatment of PMO-ph with Mo(CO)₆ gave a material with a much higher metal loading of 5.9 wt.% (0.6 mmol g⁻¹) [12]. In an attempt to boost the chromium loading, the recovered solid was subjected to two more treatments with Cr(CO)₆ and DCE, which resulted in the final derivatised PMO (PMO-phCr(CO)₃) with a chromium content of 0.35 wt.%.

Fig. 1 shows the powder XRD patterns of PMO-ph and PMO-phCr(CO)₃. The pattern of PMO-ph contains one strong low-angle peak at 47.0 Å, which is assigned to the (100) reflection of a two-dimensional hexagonal symmetry (*p6mm*) lattice with a lattice constant $a = 54.8$ Å. The broad, weak shoulder on this peak toward higher angles (3–4° 2θ) comprises the overlapping (110) and (200) reflections. In addition to the low-angle peaks, three medium-range reflections at 7.6, 3.8 and 2.5 Å are observed, which arise from the molecular-scale periodicity in the PMO-ph pore walls along the channel direction [10]. The pattern for PMO-phCr(CO)₃ is practically identical, which indicates retention of the mesoporous structure as well as the molecular-scale periodicity.



Scheme 1. Preparation of PMO-phCr(CO)₃.

The material PMO-phCr(CO)₃ was further characterised by FT-IR, solid-state ²⁹Si and ¹³C MAS NMR spectroscopies. The ²⁹Si MAS NMR spectrum (Fig. 2) is similar to that for PMO-ph, exhibiting peaks at about -79.5 and -70.1 ppm attributed to T³ and T² organosilica species [T^m = RSi(OSi)_m(OH)_{3-m}], respectively [10b]. The relative intensity of the peaks shows that the dominant silicon species is T³, which is consistent with a high degree of condensation. Accordingly, virtually no signal around -60 ppm is present, indicating that the proportion of T¹ sites is no higher than about 5%. The absence of SiO₄ species in the range of -110 to -90 ppm confirms that no Si-C bond cleavage took place during the chem-

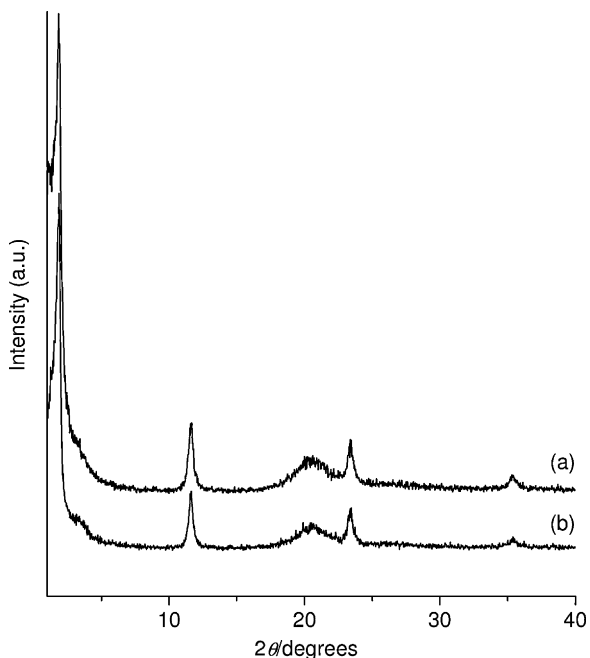


Fig. 1. Powder XRD patterns of PMO-ph (a) and PMO-phCr(CO)₃ (b).

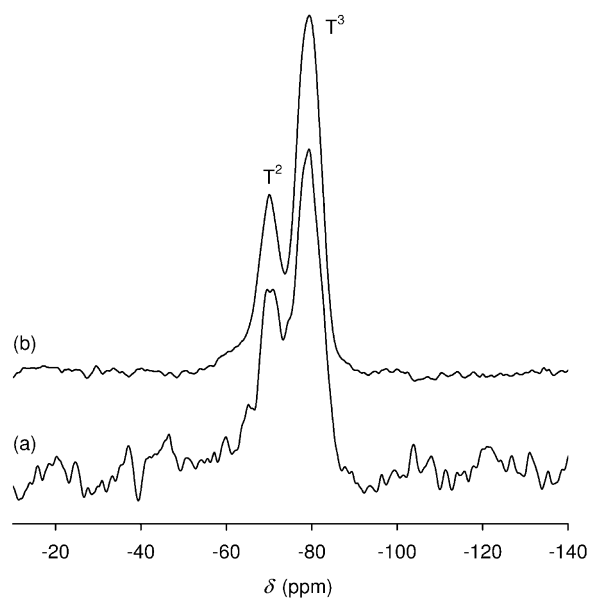


Fig. 2. Solid-state ²⁹Si MAS NMR spectra of PMO-ph (a) and PMO-phCr(CO)₃ (b).

ical modification. The ¹³C CP MAS NMR spectrum (Fig. 3) displays a single peak at 133.5 ppm for the benzene ring carbon atoms, in agreement with that observed for PMO-ph. The absence of resonances for aromatic carbon atoms complexed with Cr(CO)₃ (expected ca. 95 ppm) or CO ligands (expected ca. 230 ppm) can be attributed to the low chromium loading. PMO-ph and PMO-phCr(CO)₃ exhibit IR bands in the range of 400–1700 cm⁻¹ very similar to those described by Hoffmann et al. for a benzene-bridged PMO prepared using BTEB as the precursor [15]. Toward higher frequencies the spectra display absorption bands assigned to combination modes originating from the aromatic groups (1830 and 1935 cm⁻¹) [16], ν_{CH} (3015 and 3062 cm⁻¹) and ν_{OH} of hydrogen-bonded silanol groups (3200–3800 cm⁻¹). A very weak band at 1978 cm⁻¹ (absent for PMO-ph) is assigned to the A₁ vibrational mode involving carbonyl groups of Cr(CO)₃ units (Fig. 4) [5b,8,9a,9b,11].

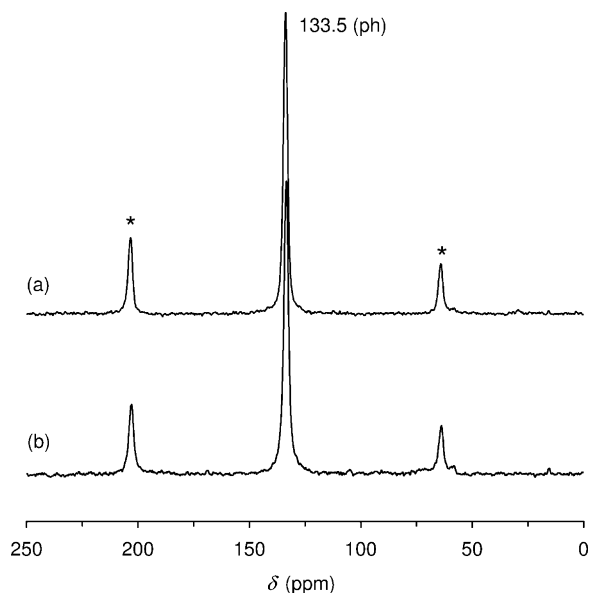


Fig. 3. Solid-state ¹³C CP MAS NMR spectra of PMO-ph (a) and PMO-phCr(CO)₃ (b). Spinning sidebands are labeled with asterisks.

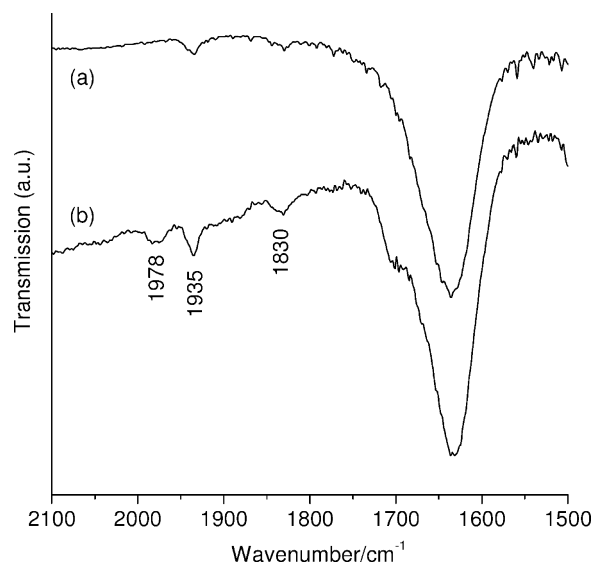


Fig. 4. FT-IR spectra in the range of 1500–2100 cm^{-1} for PMO-ph (a) and PMO-phCr(CO)₃ (b).

Thermogravimetric analysis of PMO-ph under air shows a weight loss of 8.0% below 100 °C due to desorption of physisorbed water (Fig. 5). A second weight loss takes place above 550 °C and corresponds to the decomposition and release of organic fragments from the pore wall. The TGA curve for PMO-phCr(CO)₃ shows a small weight loss of 2.7% extending from room temperature to 150 °C, a second weight loss of 1.4% between 250 and 350 °C, and full decomposition above 380 °C. The second step with a peak temperature of 325 °C in the derivative thermogravimetric curve can be assigned to the escape of carbon monoxide, and is in agreement with that reported for hybrid organic-inorganic silica gels prepared by the hydrolytic sol-gel polymerisation of pure arene Cr(CO)₃ precursors containing one, two, or three Si(OMe)₃ groups [9b]. Taking into account a “background” loss of at least 0.5% in the range of 250–350 °C, the actual weight loss due to the removal of CO is less than 0.9%, which is close to the calculated value of 0.6% based on the Cr content of 0.35 wt.%. Despite the low metal loading, the supported Cr species generated by thermal decarbonylation appear to promote the early decomposition and release of organic fragments from the pore wall.

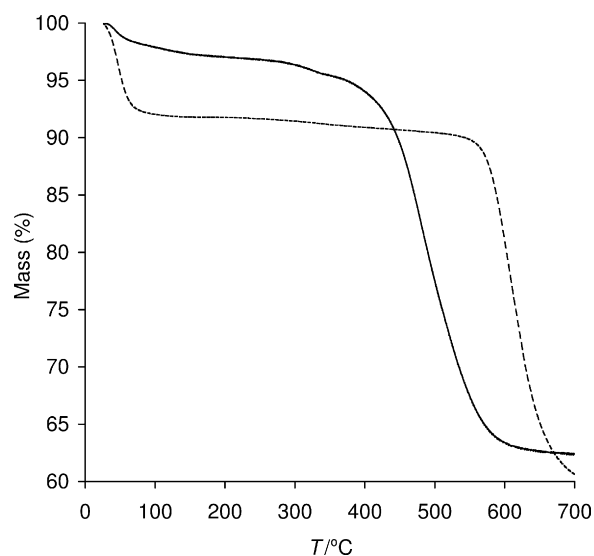


Fig. 5. TGA curves of PMO-ph (---) and PMO-phCr(CO)₃ (—).

Table 1
Reaction of *cis*-cyclooctene with TBHP at 55 °C catalysed by PMO-phCr(CO)₃.

| Solvent | Conversion at 6 h/24 h (%) | Epoxide selectivity at 6 h/24 h (%) |
|--------------------|----------------------------|-------------------------------------|
| DCE | 50/88 | 100/94 |
| <i>n</i> -Hexane | 44/70 | 100/93 |
| Toluene | 43/64 | 100/100 |
| Without co-solvent | 71/85 | 91/90 |

3.2. Catalytic oxidation of *cis*-cyclooctene

The reaction of *cis*-cyclooctene (Cy8) with TBHP at 55 °C, using DCE as the co-solvent and PMO-phCr(CO)₃ as the pre-catalyst (Cr: Cy8: TBHP molar ratio = 0.2:100:159), gave conversions of 50%/88% at 6 h/24 h, and 1,2-epoxycyclooctane was formed with 100%/94% selectivity (Table 1, Fig. 6). 2-Cycloocten-1-one was the main by-product. When the same reaction was carried out using PMO-phMo(CO)₃ containing 1.5 wt.% Mo (Mo: Cy8: TBHP molar ratio = 1:100:154), the epoxide was obtained in quantitative yield within 1 h [12]. The formation of epoxides and enones as main products was previously reported for chromium-catalysed oxidation of Δ^5 -steroids with TBHP using CH₂Cl₂ as the solvent [17]. The reaction in the absence of PMO-phCr(CO)₃ or in the presence of PMO-ph, under similar reaction conditions, was very sluggish, giving conversions at 6 h/24 h of 2%/4% and 2%/7%, respectively (Fig. 6). Hence, for the reaction carried out using PMO-phCr(CO)₃, the catalytically active species contain chromium. When the material possessing 0.26 wt.% Cr was used instead of PMO-phCr(CO)₃ (0.35 wt.% Cr), under similar reaction conditions (identical Cr: Cy8: TBHP molar ratios), conversion and epoxide selectivity at 24 h were 86% and 97%, respectively, which are similar to the results obtained for PMO-phCr(CO)₃ with the higher metal loading (88% and 94%, respectively). Hence, it may be beneficial to increase the amount of supported metal species to reduce costs associated with the catalyst preparation (by using a lower amount of the PMO support).

When the reaction of *cis*-cyclooctene was carried out under nitrogen instead of atmospheric air, no decrease in reaction rate was observed, suggesting that TBHP is the oxidant involved in the (ep)oxidation. Iodometric titration carried out for the reaction of TBHP (without Cy8), under similar reaction conditions, gave 83%

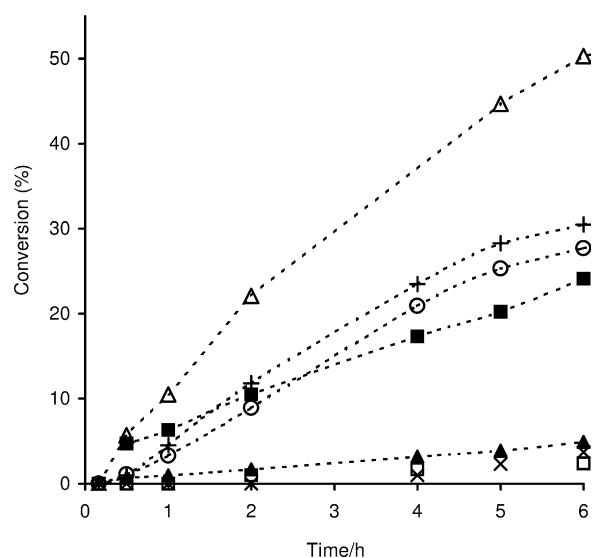


Fig. 6. Reaction of *cis*-cyclooctene with TBHP at 55 °C using PMO-phCr(CO)₃ as the pre-catalyst (Δ run 1, + run 2, \circ run 3), PMO-ph (\square) and Cr(CO)₆ (\times). The results of the leaching tests LT-run1 (\blacksquare) and LT-run3 (\blacktriangle) are also shown. DCE was used as the co-solvent for all reactions. The dotted lines are visual guides.

conversion at 5 h, suggesting that the “non-productive” decomposition of TBHP during the catalytic oxidation of Cy8 may be significant and therefore affect the overall reaction rate. It may be beneficial to carry out the reaction under semi-batch mode to avoid the “non-productive” decomposition of TBHP.

When the precursor $\text{Cr}(\text{CO})_6$ was used instead of $\text{PMO-phCr}(\text{CO})_3$ (with the same equivalent amount of chromium), the reaction of *cis*-cyclooctene was rather sluggish, giving 4%/18% conversion at 6 h/24 h. Possibly, the dissolved precursor decomposed into less active/inactive metal species, accounting for the slower reaction in comparison to that observed for $\text{PMO-phCr}(\text{CO})_3$ (under the applied oxidising conditions, the metal species on the PMO support may possess enhanced stability in comparison to those present in homogeneous phase).

After the first run using $\text{PMO-phCr}(\text{CO})_3$, the catalyst was separated from the reaction mixture by centrifugation, washed three times with *n*-hexane, dried at room temperature, and used in a second run. The reaction rate (based on conversions at 6 h/24 h) decreased significantly from the first to the second run, possibly due to partial metal leaching during the reaction (Fig. 6); ICP-AES analysis indicated 20% metal leaching. When the solid was recovered and used in a third run, only a minor decrease in the reaction rate was observed (compared with the second run, Fig. 6); conversions after 24 h were 69% for run 2 and 68% for run 3. In all three consecutive batch runs the epoxide was the main product, and 2-cycloocten-1-one was a minor by-product formed in less than 5% yield at 24 h. To assess the homo/heterogeneous nature of the catalytic reaction, leaching tests (LT) were performed for the fresh catalyst (denoted LT-run1) and the solid recovered after the second run (LT-run3). The LT were performed by separating the solid phases from the reaction mixtures (runs 1 and 3) after 30 min by filtration at the reaction temperature of 55 °C through a 0.2 μm PVDF w/GMF Whatman membrane. The filtrates were then allowed to react at the same temperature for a further 5.5 h. The increases in conversion between 30 min and 6 h were 19% for LT-run1 and 4% for LT-run3, compared with 45% for run 1 and 27% for run 3 carried out without filtration, and 2% for the reaction carried out without catalyst. These results suggest that the catalytic reaction in run 1 takes place in heterogeneous and homogeneous phases (possibly due to partial metal leaching), and in subsequent runs the catalytic reaction is essentially heterogeneous in nature.

The ATR FT-IR spectrum of the solid recovered after the third reaction run was similar to that for $\text{PMO-phCr}(\text{CO})_3$ except that the ν_{CO} band at 1978 cm^{-1} was absent, indicating that decarbonylation of the supported metal species took place. An induction period of at least 10 min is observed for runs 1 and 2, which may be partly due to the relatively slow formation of active oxidising species (expected to involve primary decarbonylation, at least during run 1). Possibly, TBHP interacts with zero valent chromium centres to give high valent oxometal intermediates that are responsible for the transfer of the oxygen atom to the olefin. The oxygen transfer may be effected by electron transfer, radical, carbocation or metallaoxetane formation, or a combination of these mechanisms [18]. GC-MS analysis of the reaction mixture for $\text{PMO-phCr}(\text{CO})_3$ showed the presence of di-*tert*-butylperoxide, which is formed by the decomposition of TBHP into chain initiating alkoxy and alkyl peroxy radicals in one-electron transfer processes. When the reaction of *cis*-cyclooctene with TBHP was carried out in the presence of $\text{PMO-phCr}(\text{CO})_3$ using equimolar amounts of TBHP and a radical scavenger (2,6-di-*tert*-butyl-4-methylphenol, denoted RS), the *cis*-cyclooctene reaction was slower than without RS (suggesting the formation of free radical intermediates), although it still took place to a significant extent, giving 11%/47% conversion at 6 h/24 h, with the epoxide being the only product. Two reaction mechanisms for *cis*-cyclooctene oxidation may be involved: (A) free radical chain process (possibly responsible for allylic oxidation of *cis*-cyclooctene

to the corresponding enone, which was not detected when using RS), and (B) oxometal pathways responsible for the epoxidation of *cis*-cyclooctene to the corresponding epoxide (the only product formed when using RS). Taking into consideration that epoxide selectivity is at least 94% until 88% conversion, it seems that the heterolytic pathways are preferred for the reaction of *cis*-cyclooctene using $\text{PMO-phCr}(\text{CO})_3$ as the pre-catalyst. Similar mechanistic considerations have been reported in the literature for the reaction of olefins with TBHP in the presence of CrO_3 and mono/bidentate pyridines: the allylic oxidation of the olefin and the decomposition of TBHP were reported to be free radical reactions, while the epoxidation reaction was considered to be dependent on the formation of a TBHP- CrO_3 complex [18c]. In the case of (A) the chain reaction may take place in the liquid bulk, which may contribute to the very small increase in conversion between 30 min and 6 h for LT-run3 (free radicals formed prior to catalyst filtration).

The reaction of *cis*-cyclooctene with TBHP using $\text{PMO-phCr}(\text{CO})_3$ as the pre-catalyst was further investigated using toluene or *n*-hexane as the co-solvent instead of DCE, or using no co-solvent (Table 1). After 6 h the latter system gave the highest conversion of 71% (cf. 43–50% for the other systems), which rose to 85% after 24 h (cf. 88% for DCE, 64% for toluene and 70% for *n*-hexane). The absence of dilution effects when no co-solvent is added may account for the higher conversion at 6 h. Of the co-solvents studied, DCE gives the best results, which may be partly due to the higher solvent polarity: a balance is required taking into consideration the surface polarity of the PMO supported catalyst and the quite different polarities of the reagents. No significant effects on product distribution were observed with or without a co-solvent: the epoxide was always the only product at 6 h reaction and after 24 h epoxide selectivity was at least 93%.

4. Conclusions

Mesoporous phenylene-silica with molecule-scale periodicity in the pore walls can be modified with chromium carbonyl species by the liquid phase deposition of $\text{Cr}(\text{CO})_6$. Elemental analysis indicated a metal loading of about 0.07 mmol g^{-1} , which is about one order of magnitude lower than that previously achieved using $\text{Mo}(\text{CO})_6$ under similar conditions. The reason(s) for the different degrees of functionalisation are unclear at present. Attempts to prepare $\text{PMO-phCr}(\text{CO})_3$ materials with higher loadings by one-pot reactions using alkoxy-silane-functionalised complexes have so far been unsuccessful, mainly due to phase separation or to the disintegration of incorporated $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes during surfactant removal. The characterisation of the supported Cr species in $\text{PMO-phCr}(\text{CO})_3$ is complicated by the low loading. Nevertheless, the FT-IR and TGA data are consistent with the presence of chromium tricarbonyl complexes. The modified material promotes the epoxidation of *cis*-cyclooctene with TBHP, leading to a much faster reaction than that achieved using the hexacarbonyl precursor in homogeneous phase. Recycling and leaching tests for fresh and used catalysts suggest that active chromium species retained on the PMO support are largely responsible for the epoxidation reaction in recycling runs. Decarbonylation of supported complexes takes place and it is postulated (on the basis of tests using a radical scavenger) that the reaction of the olefin with TBHP may involve a combination of free radical and non-radical reaction mechanisms, with the latter possibly being responsible for the formation of the epoxide.

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