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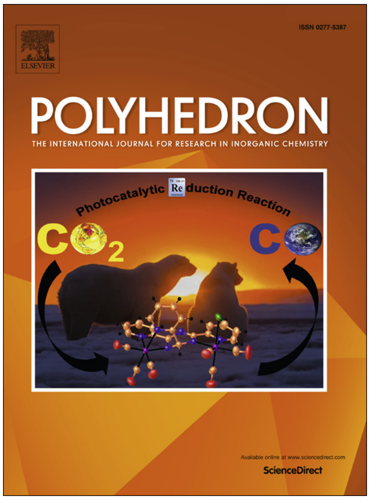

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Enantioselective cyclopropanation and aziridination catalyzed by copper(II) bis(oxazoline) anchored onto mesoporous materials

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Abstract

The preparation of multipurpose asymmetric heterogeneous catalysts based on the immobilization of expensive privileged chiral ligands onto porous supports is essential for their use in industry. The benchmark cyclopropanation of styrene has been performed using a copper(II) complex of a commercial chiral bis(oxazoline) anchored onto ordered mesoporous silica materials (including SBA-15) and their carbon replicas (including CMK-3), and for the first time, we also report on the asymmetric aziridination of styrene by anchored copper(II) bis(oxazoline). All the composites prepared were active and enantioselective in these two organic transformations. In the cyclopropanation of styrene the best heterogeneous catalyst gave higher enantioselectivities and TON than in the corresponding homogeneous phase reactions. In the aziridination of styrene the enantioselectivities for the best heterogeneous catalysts were similar to the propylated bis(oxazoline). The mesoporous silica, prepared by a straightforward one-pot procedure, was always among the best supports for the functionalized bis(oxazoline) in all the asymmetric processes studied. However its carbon replica was not a good support for the outcome of these asymmetric transformations, always yielding the lowest enantioselectivities. Once again the mesoporous materials surface properties were an important factor for the uniform distribution of the homogeneous catalyst, as well as for the course of the asymmetric organic reactions, together with the pore size. The best results presented herein are comparable to the ones reported for copper(II) bis(oxazoline) (**2**) immobilized onto other types of porous supports.

Keywords: homogeneous catalysis, heterogeneous catalysis, asymmetric catalysis, immobilization, mesoporous materials.

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1. Introduction

Enantiomerically enriched cyclic compounds are valuable building blocks in organic synthesis due to their highly regio- and stereoselective ring-opening reactions. As a large majority of organic compounds contain carbon-nitrogen bonds, aziridines are invaluable intermediates in the synthesis of pharmaceuticals and agrochemicals [1]. Cyclopropanes are also very important intermediates in organic synthesis and cyclopropane rings are often found in a variety of natural products and biologically active compounds [2]. However, the synthesis of enantiomerically enriched cyclopropanes [2] and aziridines remains a considerable challenge [1].

As catalysis is one of the fundamental pillars of green chemistry and a source of low-cost methodologies, due to its efficiency and selectivity, there is already a system that catalyzes efficiently both cyclization reactions. Copper(II/I) complexes with bis(oxazoline) ligands (Scheme 1) are versatile enantioselective and efficient homogeneous catalysts in a number of asymmetric organic transformations [3-6], including the cyclopropanation [3-7] and aziridination [8,9] of alkenes. These privileged chiral ligands are available commercially, but at high cost. Thus a heterogeneous version would be preferable due to several inherent practical advantages associated with separation, handling, stability, recovery and re-use [3-6,10]. Most reports on the heterogenization of copper(II) bis(oxazoline) are on organic polymers [3-6]. Ordered mesoporous silicas present, however, higher specific surface area, mechanical resistance, chemical robustness and thermal stability than polymers. Ordered mesoporous carbons, prepared by making use of ordered mesoporous inorganic solids as templates [11], also possess high surface areas and uniform mesopores, although accompanied by a certain amount of micropores [11,12], and are still quite unexplored as supports for homogeneous catalysts [17,18].

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In our previous work on the encapsulation copper(II) bis(oxazoline) onto zeolites [13] and also anchoring onto mesoporous silicas [14], we were attracted by the best homogeneous catalyst for the cyclopropanation of alkenes. However, as reported previously [3], when heterogenized, this copper(II) complex turned out to be very unstable, yielding low enantioselectivities and weak recyclability.

In this work, a pre-formed copper(II) complex with the commercial bis(oxazoline) **2** (Scheme 1) was anchored onto SBA-15 and its carbon replica CMK-3 using the anchoring procedure represented in Scheme 2. This immobilization procedure was already used to anchor **Cu(2)** onto mesoporous silicas, MCM-41 and MCM-48, which were highly active in the enantioselective cyclopropanation of styrene with ethyl diazoacetate with moderate enantioselectivities [15]. Another regular mesoporous silica and its carbon replica prepared in a one step pathway were also used as supports. Their efficiency and reusability as asymmetric heterogeneous catalysts in the kinetic resolution of a 1,2-diol has already been shown previously [17]. Herein the multipurpose catalytic properties of these heterogeneous catalysts will be exemplified for more reactions: (i) the benchmark asymmetric cyclopropanation of styrene at room temperature with ethyl diazoacetate (Scheme 3) and (ii) aziridination of styrene with (*N*-(*p*-tosylsulfonyl)imino)phenyliodinane (PhINTs), also at room temperature (Scheme 4). So conclusions will also be withdrawn on the effect of the mesoporous support nature on the catalytic performance and stability upon reuse of the immobilized **Cu(2)** complex for each reaction. Because we have also been investigating eventual confinement effects within the pores of materials [13,14], the **Cu(2)** complex was also heterogenized onto smaller pore hexagonal mesoporous silica (HMS).

Scheme 1 and 2

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2. Experimental Section

2.1. *Materials and solvents*

Copper(II) trifluoromethanosulfonate (copper triflate, [Cu(OTf)$_2$], 98%), (*S*)-(–)-2,2'-isopropylidenebis(4-phenyl-2-oxazoline) (**1**, 97%), 2,2′-methylenebis[(4*S*)-4-phenyl-2-oxazoline] (**2**, 97%), buthyl lithium solution 1.6 M in hexane (BuLi), 3-iodopropyltrimethoxysilane (IPS, ≥ 95.0%), triethylamine (Et$_3$N, ≥ 99%), dry tetrahydrofuran (THF, ≥ 99.9%), styrene (≥ 99%), *n*-undecane (≥ 99%), ethyldiazoacetate (EDA, ≤ 15% dichloromethane), phenylhydrazine (97%), copper(II) acetylacetonate (98%), iodobenzene diacetate (98%), *p*-toluenesulfanamide (98%), potassium hydroxide (p.a.) and potassium bromide (FT-IR grade, ≥ 99%) were purchased from Aldrich and used as received. Ethanol (p.a.) and methanol (p.a.) were from Riedel de Häen. Dichloromethane, acetonitrile, *n*-hexane, isopropanol and ethyl acetate were from Romil and were of HPLC grade. The Supplementary Data includes details for the synthesis of the aziridines and their characterization procedures.

2.2. *Physical and chemical methods*

Elemental analysis was performed in duplicate by the "Servicio de Análisis Instrumental", CACTI Vigo, Universidade de Vigo, Spain. The copper ICP-AES was performed in duplicate at the "Laboratório Central de Análises" of the University of Aveiro, Portugal. FTIR spectra were collected in the range 400-4000 cm^{-1} at room temperature using a resolution of 4 cm^{-1} and 256 scans, and were obtained by attenuated total reflectance (ATR) using a Bruker Tensor 27 spectrophotometer or as KBr pellets with a FT Mattson 7000 galaxy series spectrophotometer (carbon materials); the samples were previously dried in an oven at 100 ºC for 6 hours. Thermogravimetry coupled with Differential Scanning Calorimetry (TG-DSC) were performed under air

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flux, except for the carbon materials where a nitrogen flux was used, with a ramp of 5 °C/min in a TG-DSC apparatus, model 111 from Setaram. Nitrogen adsorption isotherms at -196 ºC were measured in an automatic apparatus (Asap 2010; Micromeritics). Before the adsorption experiments, the samples were outgassed under vacuum for 2.5 hours at 150 ºC.

2.3. Catalysis experiments

All the catalytic reactions of the prepared materials were performed in batch reactors at atmospheric pressure and with constant stirring. At the end of the reactions, the materials were isolated by vacuum filtration and then washed extensively with the appropriate solvent, dried under vacuum at 60 ºC and reused in another cycle with the same experimental procedures. In order to compare with the heterogeneous phase reactions, control experiments in the homogeneous phase were also performed using the same experimental procedures and equimolar quantities of [$Cu(OTf)_2$] plus**1**, **2** or **3**.

2.3.1. Cyclopropanation of styrene

In the experiments, typically 2.4 mmol of styrene, 0.65 mmol of *n*-undecane, 70 mg of heterogeneous catalyst in 10.0 ml of dichloromethane and 2 µl of phenylhydrazine were used (Scheme 3). Finally, 2.75 mmol of ethyldiazoacetate was added to the reaction mixture over 2 hours using a syringe pump. When the addition of ethyldiazoacetate was completed, aliquots (0.05 ml) were periodically withdrawn from the reaction mixture with a hypodermic syringe, filtered through PTFE 0.2 µm syringe filters and analyzed by GC-FID by the internal standard method. The reaction mixture was analyzed by GC-FID on a Varian 450 GC gas chromatograph equipped with a fused silica Varian Chrompack capillary column CP-Sil 8 CB Low Bleed/MS (15 m x 0.25 mm id; 0.15 µm

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film thickness), using helium as the carrier gas. The enantiomeric excesses (% ee) of the cyclopropanes (*trans*-**6** and *cis*-**6**) were determined in the same chromatograph but using a fused silica Varian Chrompack capillary column CP-Chiralsil-Dex CB (25m x 0.15 mm d.i. x 0.25 µm film thickness). Conditions used: 125 °C (40 min); injector temperature, 200 °C; detector temperature, 230 °C. The several chromatographic peaks were identified against commercially available samples and/or by GC-MS (Finnigan Trace). The absolute configuration of the major cyclopropane enantiomer was determined by performing the homogeneous phase reactions with 2,2′-methylenebis[(4*S*)-4-phenyl-2-oxazoline] (**2**) of the same configuration and comparing the results with the reported data [7,15].

2.3.2. Aziridination of styrene

Typically 0.24 mmol of (*N*-(*p*-tosylsulfonyl)imino)phenyliodinane (PhINTs, Scheme 4, see Supplementary Data) was added to 1.22 mmol of styrene and 70 mg of heterogeneous catalyst in 5.00 ml of acetonitrile and the reaction mixture was stirred for 48 hours. At the end of the reaction, the heterogeneous catalyst was recovered by filtration and the filtrate evaporated under reduced pressure. The *N*-(p-tolylsulfonyl)-2-phenylaziridine (**5**, Scheme 4) was purified by column chromatography using petroleum ether (40-60)/ethyl acetate 9:2.5 as eluent and the enantiomeric excess was determined by HPLC at 220 nm using a Chiralpak IC column (250 mm x 4.6 ID, 5µm) using 1 ml/min of *n*-heptane/isopropanol 7:3. The retention times of the (*R*)-**5** and (*S*)-**5** enantiomers (Scheme 4) were identified by comparison with those of a racemic aziridine (see Fig. A1 and A2 Supplementary Data).

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3. Results and discussion

3.1. Preparation and characterization of the materials

The anchoring of **Cu(2)** onto two ordered mesoporous silicas, SBA-15 and SPSi, as well as their carbon replicas, CMK-3 and SPC, respectively, has been described by us previously [17]. This complex was also anchored onto a mesoporous silica with a much smaller pore size, HMS, to check the effect of the material's pore size on the catalytic parameters [17]. This method has three main steps: (i) functionalization of **2**, (ii) coordination of copper(II) onto the chiral ligand **2** and (iii) anchoring onto the surface of the material (Scheme 2) [17]. Epimerization of the bis(oxazoline) does not occur upon its functionalization with trimethoxypropylsilane under strongly basic conditions, because the prepared heterogeneous catalysts have already shown moderate to high enantioselectivities in the kinetic resolution of 1,2-diol [17]. Moreover, the di-propyl functionalized bis(oxazoline) **3** showed even higher enantioselectivity in this reaction in the homogeneous phase than the original bis(oxazoline) **2**, and slightly lower than the best bis(oxazoline) **1** [17]. In order to prevent the creation of non-enantioselective active sites by direct coordination to the mesoporous silica silanols, as we found previously [14], or to the carbon oxygen groups, copper(II) coordination took place before the anchoring step (ii, Scheme 2). An eventual negative interaction between LiI and the immobilized copper(II) bis(oxazoline) complex can be also ruled out due to the efficiency of these heterogeneous catalysts in the kinetic resolution of hydrobenzoin [17]. As these materials have been extensively characterized by us, only the results from their characterization that are relevant to the catalytic experiments will be discussed; the data are summarized in Table 1.

Table 1

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Evidence for the effective anchorage of the functionalized **Cu(2)** complex was obtained by elemental analysis, copper ICP and nitrogen isotherms at 77 K. Since the molecule of **2** possesses two nitrogen atoms (Scheme 1), the chiral ligand loading was calculated based on the nitrogen content of the materials determined by elemental analysis (Table 1). Despite the lower superficial area (Table 1), curiously the mesoporous materials prepared using the one-pot procedure (SPC and SPSi) have a higher **2** loading than SBA-15 and its carbon replica, CMK-3. The SPC mesoporous carbon material has higher **2** loading than the corresponding SPSi mesoporous silica, whereas SBA-15 and CMK-3 possess similar **2** loadings (Table 1). With the exception of HMS, the amounts of copper determined by ICP-AES are lower than the ones of **2** for the materials, and they are not in line with them (Table 1). This result suggests that the constant of formation of the complex **Cu(2)** is not high and that the complexation of copper(II) by the ligand **2** is weak.

The TG-DSC shows that **Cu(2)** complex anchored onto the SPSi material decomposes more sharply and at higher temperature (365 ºC) than when anchored onto the SBA-15 and HMS mesoporous silicas (325 ºC, Fig. 1). Like already observed by us [18], this may suggest a more uniform distribution of the **Cu(2)** functionalized complex onto the SPSi mesoporous silica. Furthermore, for the SBA-15 and SPSi materials, the results of the nitrogen chemical analysis (Table 1) agree well with the TG data in Fig. 1, taking into consideration the molecular mass of the organic part of the complex and subtracting the mass loss for the initial materials. The expected mass loss due to complex oxidation in air is 11.3 and 12.6% for SBA-15 and SPSi, respectively. For the carbon replicas CMK-3 and SPC, the TG curves for the samples functionalized with **Cu(2)** (not shown, see supporting information of [17]), an inflexion in the TG curve is noticed for

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temperatures between 325 and 350 ºC, suggesting that the thermal stability of the supported complex is similar with the silica materials and with their carbon replicas.

Fig. 1

In the materials containing the anchored **Cu(2)**, besides the characteristic bands of the materials, further very low intensity bands between 2930-2850 and 1460-1400 and at 700 cm^{-1} can be seen which are due to vibrations characteristic of the ligand **2** (Figs. 2 and 3). These characteristic vibrations are generally low in intensity, due to the general low content of the bis(oxazoline) at the surface of the materials. Hence it is very difficult to detect clearly the characteristic bands of this molecule upon anchoring onto the several solid supports. However, in the **Cu(2)**@SPSi material these characteristic vibrations can be clearly observed, due to the higher ligand **2** loading than in the other materials. The characteristic strong stretching C=N vibration of the ligand **2** can be seen at 1655 cm^{-1}, which shifts to 1520 cm^{-1} upon copper(II) coordination. However it is generally masked under the O-H large bending vibration of the water adsorbed on the surface of the silica based materials, centered at about 1625 cm^{-1}. Nonetheless, in the case of SPC, it can be clearly seen at 1614 cm^{-1}, in accord with the vibration of the **Cu(2)** complex [17]. Furthermore, the low intensity band at 3746 cm^{-1}, due to the stretching of the O-H groups from the isolated silanols of the mesoporous silicas, disappeared which confirms that grafting between this group and the propylsilane functionalized **Cu(2)** has taken place according to Scheme 2 (Figs. 2 and 3) [19].

Fig.2 and 3

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The nitrogen adsorption-desorption isotherms of the materials at -196 ºC are of type IV, as expected for mesoporous materials [17,20]. According to the literature, the specific surface areas and pore volumes of the carbon replicas are higher than the respective silica templates (Table 1) [16,21]. The mesoporous size distributions of the silicas are more uniform than those of the respective replicas [17]. Upon anchoring of the **Cu(2)** complex, a decrease in the adsorption capacity is clear for all the samples, but it is more striking for the carbon replicas (Table 1). Additionally, upon anchoring, the mesopore size distributions of both the silica and replicas are not significantly changed, except for the CMK-3 material. For this solid, the relative intensities of the maxima near 8.5-10 and 4 nm are reversed after the inclusion of the complex [17]. This suggests that **Cu(2)** is essentially located in the latter pores, justifying the drastic decrease of the porous volume upon anchoring as these pores represent the highest proportion of the porosity in CMK-3, as discussed in detail elsewhere [12].

3.2. Catalysis experiments

3.2.1. Cyclopropanation of styrene

Copper(I) complexes with bis(oxazoline) ligands are efficient homogeneous catalysts in the asymmetric cyclopropanation of alkenes [3-7]. The nanostructured materials with anchored **Cu(2)** were thus tested as heterogeneous catalysts in the asymmetric cyclopropanation of styrene with ethyldiazoacetate (EDA) at room temperature (Scheme 3). EDA was added slowly to the reaction mixture over 2 hours [13,14,22-27] in order to create a local deficit of this reagent in relation to styrene. Therefore the dimerization of EDA was minimized along with the formation of diethyl maleate and diethyl fumarate. Cu(II) was also reduced to Cu(I) by phenylhydrazine prior to the asymmetric cyclopropanation of styrene.

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Scheme 3 and Table 2

The results obtained with these materials are compiled in Table 2 and it can be seen that they are active in the cyclopropanation of styrene, with moderate to low enantioselectivities. The order of the values for this parameter is: SPSi > CMK-3 ≈ SBA-15 > HMS > SPC. Hence the ordered mesoporous silica SPSi gives rise to the most enantioselective heterogeneous catalyst, with % ee(*cis*-**4**) and % ee(*trans*-**4**) of 42 and 47, respectively, which are higher than in the homogeneous phase reaction run under the same experimental conditions and using the same amount of **2+Cu**, or even the best **1+Cu** (0.2% mol, Table 2). The corresponding carbon replica yields the least enantioselective heterogeneous catalyst, with % ee(*cis*-**4**) and % ee(*trans*-**4**) of 10. The values for SBA-15 and its carbon replica are similar and are slightly above 20% for both *trans*-**4** and *cis*-**4** diastereoisomers. Taking into consideration only the silica mesoporous materials and since the reactions with these materials possess similar Cu mol% (Table 2), it can be concluded that the lowest enantioselectivity values were obtained for the material with the lowest pore size and catalyst density [17]. Nonetheless, the **Cu(2)**@HMS heterogeneous catalyst possesses more copper than bis(oxazoline) ligand **2**. Thus lowering of the enantioselectivity may have occurred through non-enantioselective cyclopropanation involving only copper. Therefore the positive effects on the enantioselection of the immobilized **Cu(2)** catalyst can only be observed using the SPSi material. This cannot be fully attributed to the propylation of the bridge bis(oxazoline) carbon atom (Scheme 2) as the homogeneous reaction with **1+Cu** (0.2% mol, Table 2) gives similar enantioselectivities as the one performed with **2+Cu** (0.2% mol, Table 2). The use of the other mesoporous silicas, SBA-15 and HMS,

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leads to a decrease in the enantioselectivity when compared to the homogeneous phase reaction, run using the same amount of Cu and with the same experimental conditions.

We have already found that the surface acidity of these mesoporous materials is an important parameter in the asymmetric cyclopropanation of styrene by anchored copper(II) aza-bis(oxazoline). The least acidic materials (SPSi and CMK-3) yielded the most enantioselective heterogeneous catalysts [18]. This is also the case for the present heterogeneous catalysts with the anchored commercial copper(II) bis(oxazoline) on SPSi and CMK-3, although the heterogeneous catalysts bearing the CMK-3 support is not as enantioselective as the one with the SPSi support. As the **Cu(2)**@SPSi heterogeneous catalyst also possesses a more uniform distribution of the anchored copper(II) bis(oxazoline) when compared to the other mesoporous materials (Fig. 1), it may be an important factor for the course of the asymmetric cyclopropanation, together with the lowest support acidity [18].

On the other hand, the immobilization of the **Cu(2)** catalyst on these mesoporous silica materials leads to better styrene conversions and TON than the homogeneous phase reactions (0.2% mol Cu). The order for the styrene conversions is CMK-3 > SBA-15 ≈ SPC > SPSi > HMS, which agrees well with the materials copper contents (Table 1). The heterogeneous catalysts with the mesoporous carbons as supports convert more styrene than with their corresponding silica templates, which must be due to their higher copper contents (Table 1). The TON of the heterogeneous phase reactions are high and are in the order: SBA-15 > SPSi > SPC > CMK-3 > HMS. Thus it can be concluded that the ordered mesoporous silicas SBA-15 and SPSi yield more active heterogeneous catalysts than when the corresponding mesoporous carbon replicas are used as homogeneous catalyst supports. This could be due to the effect of the type of matrix support, i.e. carbon *vs* silica, and also due to the pore size of the materials, since the

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ordered mesoporous carbon possess a pore size of 4 nm, whereas their silica templates possess pore sizes around 7 nm. The latter is sustained by the fact that the **Cu(2)** catalyst supported onto the HMS mesoporous silica, with a pore size of 2.5 nm (Table 1), is the least active heterogeneous catalyst (Table 2). It is noteworthy that the **4** *trans*/*cis* ratios for all the heterogeneous catalysts (1.8-1.6) are lower than the ones for the homogeneous phase reactions (2.3).

Although a deficit of EDA was used in the catalytic experiments of a reported heterogenized **Cu(2)** complex onto MCM-41 and MCM-48 mesoporous silicas with 3 nm pores [15], it showed slightly higher enantioselectivities and yields than the present best **Cu(2)**@SPSi heterogeneous catalyst. Also using also a deficit of EDA and a similar homogeneous complex, CuPh$_2$Box, immobilized onto mesoporous TUD-1 through non-covalent interactions, lower enantioselectivities and yields were obtained than the results reported herein [22]. For a **Cu(1)** complex exchanged into a clay, higher enantioselectivities and yields were obtained using regular mesoporous materials as supports under similar experimental conditions [23]. In comparison with our previous attempts to immobilize the best homogeneous catalyst, **Cu(1)** [13,14], better enantioselectivities were achieved with **Cu(2)** and SBA-15. This is in accordance with previous reports that the best homogeneous catalyst (ligand) will not always give the best heterogenized catalyst [3].

Heterogenization of a chiral homogeneous catalyst may increase stability upon single site isolation on a porous material, but the main aim of their immobilization is easy separation from the reaction media at the end of the reaction and the possibility of further use in more catalytic cycles. Hence the nanostructured materials were reused in two more successive catalytic cycles after filtration from the solution, washing with dichloromethane and drying. The results are also compiled in Table 2 and it can be

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concluded that most of the materials deactivate upon reuse. This has been attributed to the low stability of the chiral complex under the cyclopropanation reaction conditions, because the bis(oxazoline) ligands are only bidentate and thus heterogeneous catalyst deactivation is also highly dependent on the nature of the chiral ligand used [3]. However the carbon materials present a much sharper loss of enantioselectivity upon reuse than the mesoporous silicas. Moreover, the FTIR spectra of the heterogeneous catalysts at the end of the recycling experiments (Fig.2) show a very intense band at around 1726 cm^{-1}. This band is typical of the carbonyl moiety in an ester group, as can be confirmed in Fig.2.f, which represents the spectra of the reagent EDA and the products styrene cyclopropane and the by-products diethyl fumarate and diethyl maleate. The vibration of the carbonyl band in the recycled heterogeneous catalysts is closer to that of styrene cyclopropane and the diethyl maleate and diethyl fumarate by-products, formed from EDA dimerization. Therefore, as observed by us previously, with the presence of more nitrogen and carbon (EA) on the recycled catalysts [13], catalyst poisoning through strong adsorption of the products cannot be ruled out, as it would also justify the lowering of the catalytic activity of the heterogenized catalysts upon reuse [24,26]. Ligand degradation has also been reported [28].

Nevertheless, the TON of the reused heterogeneous catalysts is still generally higher or comparable to the homogeneous phase reaction run with a comparable amount of **Cu(2)**. Deactivation upon reuse was also observed in the **Cu(2)** catalyst anchored onto MCM-41 and MCM-48 [15], CuPh$_2$Box immobilized onto a mesoporous TUD-1 through non-covalent interactions [22] and **Cu(1)** catalyst exchanged into clays [23]. It is also commonly observed for other copper bis(oxazoline) catalysts immobilized onto mesoporous silica materials [3,14,27]. Only when immobilized onto siliceous mesocellular foam, which possesses ultra-large pores of 25 nm, do these commercial

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systems present high enantioselectivity, activity and excellent recyclability [24,25]. It is noteworthy, however, that these catalytic studies were always performed using 2% mol of Cu in relation to the substrate [24,25], double than the necessary amount in homogeneous phase reactions [7], whereas in ours catalytic experiments the Cu and **2** contents were between 0.2-0.5% and 0.1-0.8% mol, respectively.

3.2.2. Aziridination of styrene

Evans *et al.* also reported in 1991 that copper(II) bis(oxazoline) complexes acted as homogeneous catalysts for the enantioselective aziridination of alkenes at room temperature, with a maximum 63% ee for the industrially important and challenging styrene [8,9]. There are a few reports on asymmetric heterogeneous aziridination, just by bis(oxazoline) ligands added to the reaction mixture containing copper exchanged zeolites [29-33] and copper(II) bis(oxazoline) immobilized by electrostatic interactions onto clays, silica Nafion nanocomposite and silica-CF_2SO_3H [34]. However it was recently reported that the enantioselectivities of some of the aziridines obtained with the former copper exchanged zeolites were higher than reality due to the enrichment in one of the enantiomers as the racemate precipitated in *n*-hexane rich eluents [35]. There are no reports on the asymmetric heterogeneous aziridination by anchored copper(II) bis(oxazoline) complexes. The previous experience for the preparation of efficient heterogeneous catalysts for the aziridination of styrene [19,36] prompted us to test the prepared heterogeneous catalysts in this reaction as well (Scheme 3). The results are compiled in Table 3, which were obtained after an initial analytical method development with the styrene aziridine racemate and *n*-hexane free eluent (see Fig.A1 and A2 of the Supplementary Data for the HPLC chromatograms) [35].

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Scheme 3 and Table 3

All the materials prepared were active in the aziridination of styrene with moderate yields (6-33%) and low enantioselectivities (7-20%). The order of the enantioselectivities were: SBA-15 (20) ≈ SPSi (19) > CMK-3 (14) > HMS (10) > SPC (7). Therefore, like in the kinetic resolution/monobenzoylation of 1,2-diphenyl-1,2-ethanediol [17], the mesoporous silicas bearing 7 nm mesopores yield the most enantioselective heterogeneous catalysts [17], whereas **Cu(2)**@HMS, with a smaller pore size, yields lower enantioselectivity. So, definitely, smaller mesopores in the silicas are detrimental for the course of these asymmetric organic transformations by anchored copper(II) bis(oxazoline). The maximum enantioselectivity achieved is similar to the homogeneous phase reaction run with the copper(II) complex with bis-propylated bis(oxazoline) **3** (Scheme 1) [17] that mimics the anchored bis(oxazoline) **2** (Scheme 2). Looking at the homogeneous phase reactions performed with ligands **1**, **2** and **3** (Scheme 1 and Table 3), it may be concluded that, under the experimental conditions used, **Cu(2)** is more enantioselective than **Cu(1)** and **Cu(3)**. Hence contrary to what has been observed for kinetic resolution/monobenzoylation of 1,2-diphenyl-1,2-ethanediol, the propylation of **2** upon anchoring onto the mesoporous materials (Scheme 3) has a detrimental effect on the enantioselection capacity of the anchored **Cu(2)** complex in the aziridination of styrene. Despite 48 hours being allowed for the heterogeneous phase reactions to take place, the yields were lower than with the corresponding homogeneous phase reactions under similar experimental conditions. This may be due to the dissolution of the solid nitrogen source PhINTs limiting step and the heterogeneous nature of the catalyst making the formation of the intermediate species difficult. Nevertheless, **Cu(2)**@HMS is the most active catalyst (TON 15), followed by

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Cu(2)@SBA-15 (10) and **Cu(2)**@SPSi (8); the least active heterogeneous catalysts are both mesoporous carbons as supports, **Cu(2)**@CMK-3 (4) and **Cu(2)**@SPC (2). The best enantioselectivities presented herein are comparable to **Cu(1)** immobilized by electrostatic interactions onto silica-Nafion nanocomposite (21%) and slightly lower than **Cu(1)** immobilized using the same process onto clays (25%) and silica-CF_2SO_3H (26%) [34]. The yields reported herein are nevertheless much lower than these catalysts (58-75%). Recycling experiments were not performed for these heterogeneous catalysts, with electrostatic immobilization being highly susceptible to leaching.

Upon recycling of our **Cu(2)** anchored onto several mesoporous materials, a decrease in the activity and enantioselectivity is observed upon reuse, with the exception of **Cu(2)**@SPC and **Cu(2)**@SPSi; this last one nevertheless showing a small decrease in enantioselectivity. The FTIR spectra of the reused mesoporous silicas are similar to the original heterogeneous catalyst, but the mesoporous carbon shows a new band, which might suggest ligand degradation under the aziridination conditions (Fig.3).

4. CONCLUSIONS

Multipurpose asymmetric heterogeneous catalysts based on the anchoring of a copper(II) complex with a commercial chiral bis(oxazoline) (**Cu(2)**) onto ordered silica mesoporous materials and their carbon replicas were prepared. All the composites were active and enantioselective in (1) the benchmark asymmetric cyclopropanation of styrene with low to moderate enantioselectivities (TON 78-96, 10-42% ee*cis* and 10-47% ee*trans*) and (2), for the first time, the less studied aziridination of styrene with low yields and enantioselectivities (6-33% yield and 7-20% *ee*). Furthermore, higher enantioselectivity and activity than in the homogeneous phase was obtained with **Cu(2)**@SPSi for the cyclopropanation of styrene, suggesting that propylation of **2** is

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beneficial to the course of the reaction and the surface properties of this support. These results are in accordance with what we observed previously in the cyclopropanation of styrene by immobilized copper(II) aza-bis(oxazoline) [18]. In the aziridination of styrene the maximum enantioselectivity obtained was similar to the homogeneously catalyzed reaction with the bis-propylated bis(oxazoline) **3** (Scheme 1), which mimics the immobilized bis(oxazoline) **2**. Moreover, for all the reactions the ordered mesoporous silicas SBA-15 and SPSi yield generally more active heterogeneous catalysts than when the corresponding mesoporous carbon replicas are used as homogeneous catalyst supports. This could be due to the effect of the type of matrix support, i.e. carbon *vs* silica but, apparently, for the type of enantioselective reactions studied in the present work, more uniform mesopore size distributions of the silica materials are revealed to be a more relevant factor than, for instance, the total pore volume. Among the silica materials, the heterogeneous catalysts with smaller mesopores (HMS) showed much lower enantioselectivities.

The **Cu(2)**@SPSi heterogeneous catalyst can be recycled for the aziridination of styrene, with almost quantitative recovery, by simple filtration. For the cyclopropanation of styrene a noticeable deactivation upon reuse of the heterogeneous catalysts is observed, probably due to the combination of the reported low stability of the copper(II) bis(oxazoline) complexes and competing deactivating process by binding of by-products[1]. However, the TON remains generally higher than the corresponding homogeneous phase cyclopropanation reaction. Generally, the carbon materials present a sharper loss of enantioselectivity upon reuse than the mesoporous silicas. Therefore the ordered mesoporous silicas are better supports for the **Cu(2)** homogeneous catalyst than the ordered carbon materials.

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With this work we were able to show that a copper(II) complex of an expensive commercial bis(oxazoline) anchored onto a mesoporous silica (SPSi), prepared using a simple one-pot procedure, is a stable heterogeneous catalyst for at least two asymmetric organic transformations, as well as the kinetic resolution/monobenzoylation of 1,2-diphenyl-1,2-ethanediol [17]. As in the kinetic resolution of 1,2-diphenyl-1,2-ethanediol we could recycle and reuse one of the heterogeneous catalysts for 4 consecutive cycles without significant loss of activity, enantioselectivity or selectivity [17]. We can also conclude that the stability of these heterogeneous catalysts on reuse is highly dependent on the reaction experimental conditions.

Acknowledgements

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Appendix

SupplementaryData: synthesis of the PhINTs, racemic aziridine and HPLC chromatograms.

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Table 1

Chemical and textural characteristics of the materials.

Sample	**Concentration (µmol/g)**		**Cu/2**	**Textural properties**	
	Cu[a]	**2**[b]		A_{BET} **(m^2/g)**	V_{total} **(cm^3/g)**
SBA-15				756	0.99
CMK-3				1396	1.26
SPSi				571	0.84
SPC				1140	1.23
HMS				994	0.72
Cu(2)@SBA-15	101	187	0.5	556	0.79
Cu(2)@CMK-3	175	180	1.0	529	0.65
Cu(2)@SPSi	74	209	0.4	404	0.62
Cu(2)@SPC	104	277	0.4	719	0.75
Cu(2)@HMS	80	46	1.7	667	0.50

[a] Determined by ICP-AES, media of duplicate analyze [17].

[b] Determined by elemental analysis from the nitrogen content, media of duplicate analyze [17].

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Table 2

Benchmark cyclopropanation of styrene with **Cu(2)** anchored onto various porous supports and in the homogeneous phase (Scheme 3).[a]

	t(h)	**Run**	**%mol**[b]		**%C**[c]	**4**	**% ee**[e]		**TON**[f]
			Cu	**Box**		***trans/cis***[d]	***cis-4***	***trans-4***	
1+[Cu(OTf)$_2$]	24	1st	0.2	0.2	16	2.5	31	42	84
2+[Cu(OTf)$_2$]	24	1st	0.2	0.2	8	2.3	31	38	41
2+[Cu(OTf)$_2$]	24	1st	0.5	0.5	49	2.3	41	51	99
2+[Cu(OTf)$_2$]	3	1st	1.0	1.0	58	2.3	36	51	57
Cu(2)@SBA-15	24	1st	0.3	0.5	28	1.8	21	22	96
	24	2nd	0.2	0.5	16	1.9	10	9	66
	24	3rd	0.2	0.4	6	1.8	18	18	33
Cu(2)@CMK-3	24	1st	0.5	0.5	41	1.6	22	23	82
	24	2nd	0.4	0.4	24	1.8	5	5	56
	24	3rd	0.4	0.4	10	2.0	2	2	29
Cu(2)@SPSi	24	1st	0.2	0.6	22	1.8	42	47	93
	24	2nd	0.2	0.5	7	1.7	25	25	38
	24	3rd	0.2	0.5	10	2.0	17	18	58
Cu(2)@SPC	24	1st	0.3	0.8	27	1.7	10	10	90
	24	2nd	0.3	0.8	22	1.7	3	3	70
	24	3rd	0.3	0.7	19	1.9	2	3	67
Cu(2)@HMS	24	1st	0.2	0.1	19	1.7	13	14	78
	24	2nd	0.2	0.1	9	1.6	12	10	38
	24	3rd	0.2	0.1	15	1.5	12	5	66

[a] Reactions performed at room temperature using 2.40 mmol styrene, 0.65 mmol *n*-undecane (internal standard), 70 mg of (*S*,*S*)-Cu(2)@MM heterogeneous catalyst or (*S*,*S*)-Cu(2) or (*R*,*R*)-Cu(2) homogeneous catalysts, 2 µl phenylhydrazine and 2.75 mmol of EDA in 10.0 ml of CH_2Cl_2.

[b] % of copper and Box ligand in the catalyst in relation to styrene (see Table 1); for the recycling experiments corrected for the loss of heterogeneous catalyst weight, after filtration and drying.

[c] Conversion of styrene determined by CG-FID.

[d] Ratio *trans/cis* for **4**.

[e] *Cis*-**4** and *trans*-**4**enantiomeric excesses determined by chiral GC-FID.

[f] TON = moles of styrene converted/moles of Cu.

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Table 3

Aziridination of styrene with **Cu(2)** anchored onto various porous supports and in the homogeneous phase (Scheme 4).[a]

	t(h)	**Run**	**%mol**[b]		**5**	**% ee**[d]	**TON**[e]
			Cu	**Box**	**%yield**[c]		
(*R*,*R*)-1+$[\mathrm{Cu(OTf)_2}]$	2	1st	1.9	2.1	40	18 (*S*)	4
(*R*,*R*)-1+$[\mathrm{Cu(OTf)_2}]$	48	1st	0.4	0.4	71	24 (*S*)	32
(*S*,*S*)-2+$[\mathrm{Cu(OTf)_2}]$	48	1st	0.6	0.6	66	31 (*R*)	22
(*S*,*S*)-3+$[\mathrm{Cu(OTf)_2}]$	48	1st	0.5	0.8	60	21 (*R*)	24
Cu(2)@SBA-15	48	1st	0.6	1.1	30	20 (*R*)	10
	48	2nd	0.5	0.9	21	7 (*R*)	8
Cu(2)@CMK-3	48	1st	1.0	1.0	18	14 (*R*)	4
	48	2nd	1.0	1.0	13	11 (*R*)	3
Cu(2)@SPSi	48	1st	0.4	1.2	18	19 (*R*)	8
	48	2nd	0.4	1.1	20	12 (*R*)	10
Cu(2)@SPC	48	1st	0.6	1.6	6	7 (*R*)	2
	48	2nd	0.5	1.4	5	10 (*R*)	2
Cu(2)@HMS	48	1st	0.4	0.3	33	10 (*R*)	15
	48	2nd	0.5	0.3	14	2 (*R*)	6

[a] Reactions performed at room temperature using 1.22 mmol of styrene, 70 mg of heterogeneous catalyst and 0.24 mmol of PhINTs in 5.00 ml of acetonitrile.

[b] % of copper and Box ligand (Scheme 1) in the catalyst in relation to styrene (see Table 1); for the recycling experiments corrected for the loss of heterogeneous catalyst weight, after filtration and drying.

[c] Isolated yield of **5** aziridine.

[d] Enantiomeric excess of **5** aziridine and configuration of the major enantiomer in brackets (Scheme 4), determined by HPLC.

[e] TON = moles of aziridine **5** /moles of Cu.

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Figures Captions

Scheme 1	Bis(oxazoline) ligands (**1**) Me_2PhBox, (**2**) PhBox and (**3**) Pr_2PhBox.
Scheme 2	Anchoring procedure for the **Cu(2)** complex.
Scheme 3	Cyclopropanation of styrene with ethyldiazoacetate.
Scheme 4	Aziridination of styrene with PhINTs.
Fig.1	Thermo analysis curves for silica based samples. Solid lines for thermogravimetric data (TG) and broken lines for Differential Scanning Calorimetry (DSC) data.
Fig.2	FTIR spectra (KBr pellets) of the heterogeneous catalysts before and after cyclopropanation of styrene reactions: (a) SBA-15, (b) CMK-3, (c) SPSi, (d) SPC and (e) HMS materials and (f) reagents and products (Scheme 3).
Fig.3	FTIR spectra (ATR silicas and KBr pellets carbon materials) of the heterogeneous catalysts before and after aziridination of styrene reactions: (a) SBA-15, (b) CMK-3, (c) SPSi, (d) SPC and (e) HMS materials and (f) PhINTs and styrene aziridine (**5**) (Scheme 4).

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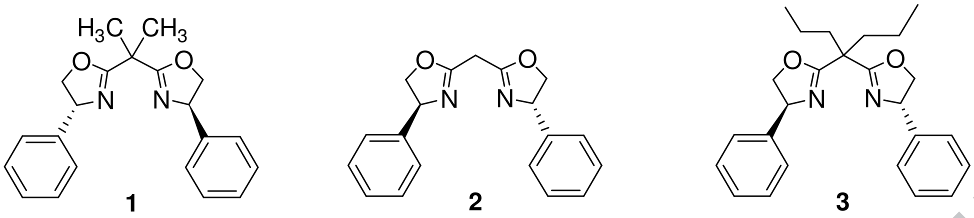
Scheme 1



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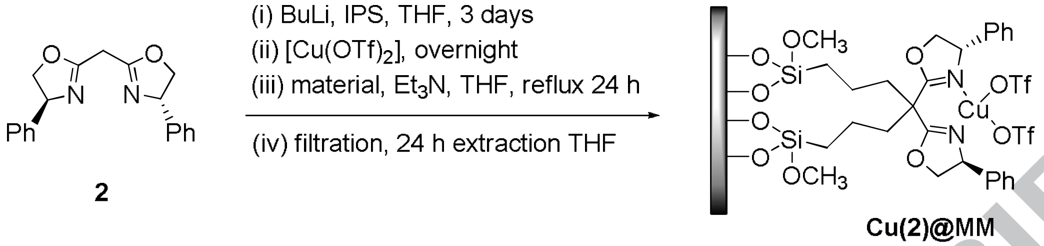
Scheme 2



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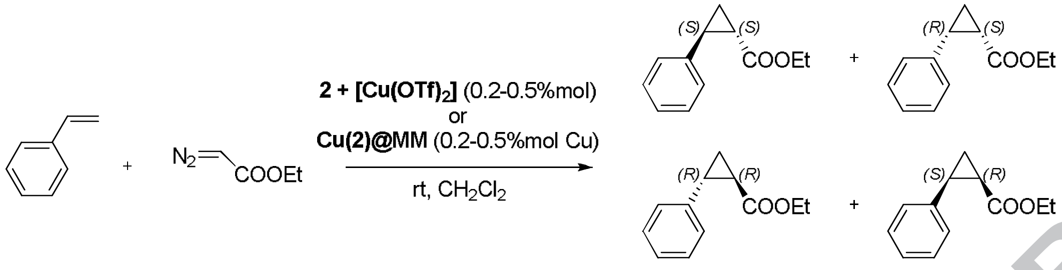
Scheme 3



trans-**4** *cis*-**4**

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Scheme 4

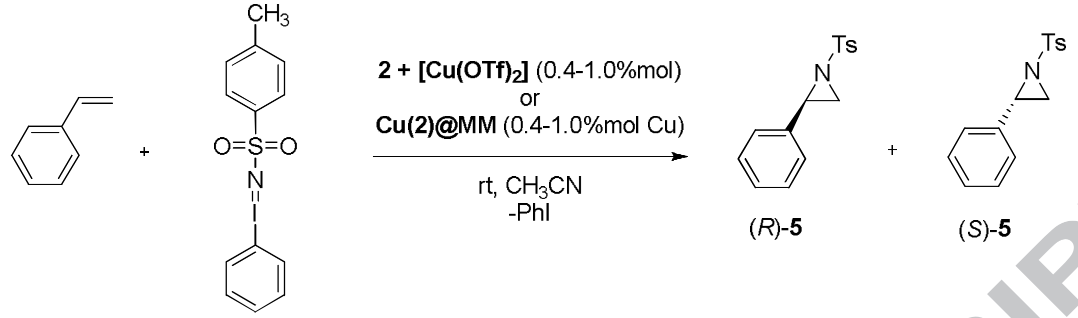

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Fig.1

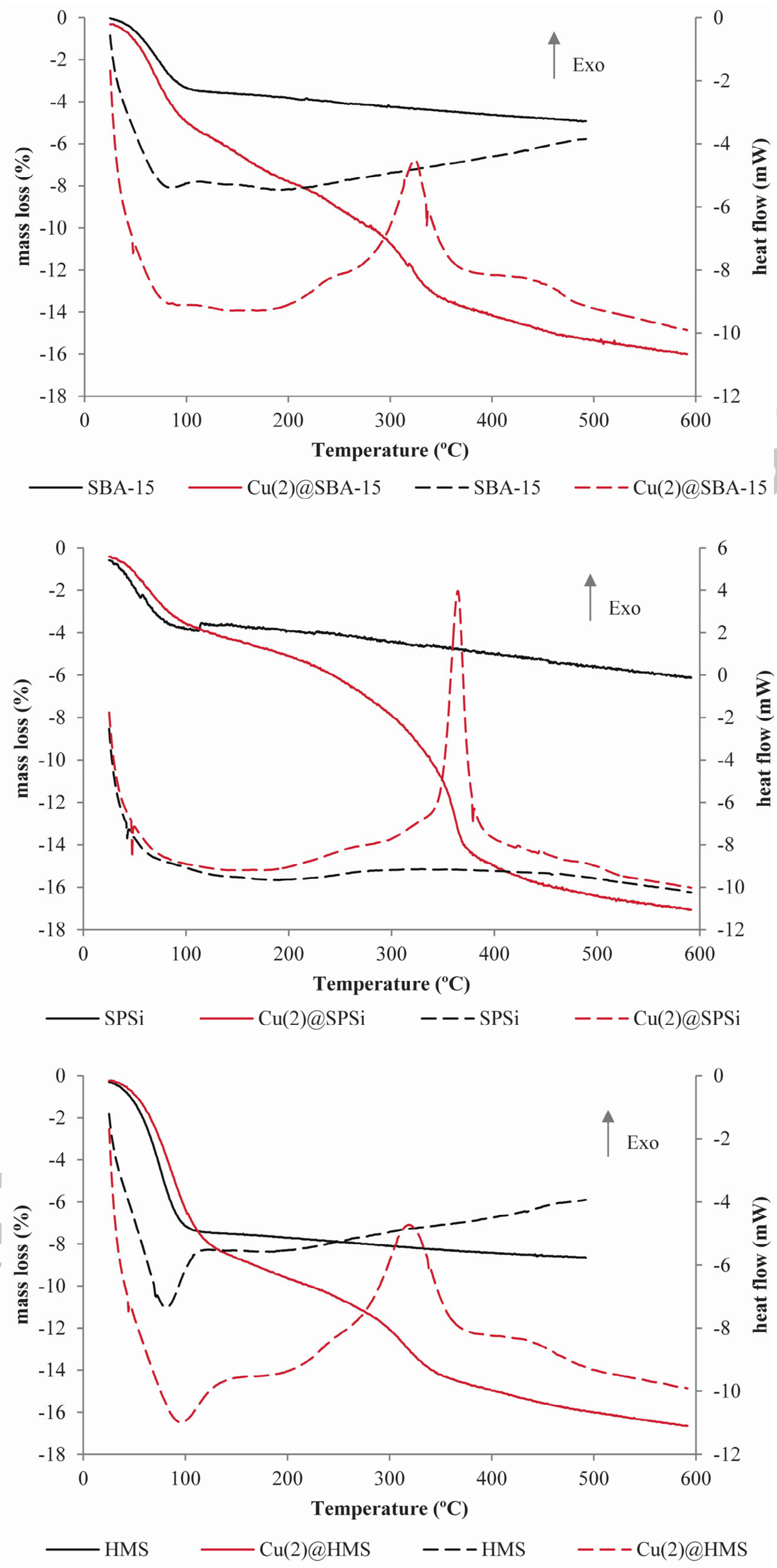

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Fig. 2

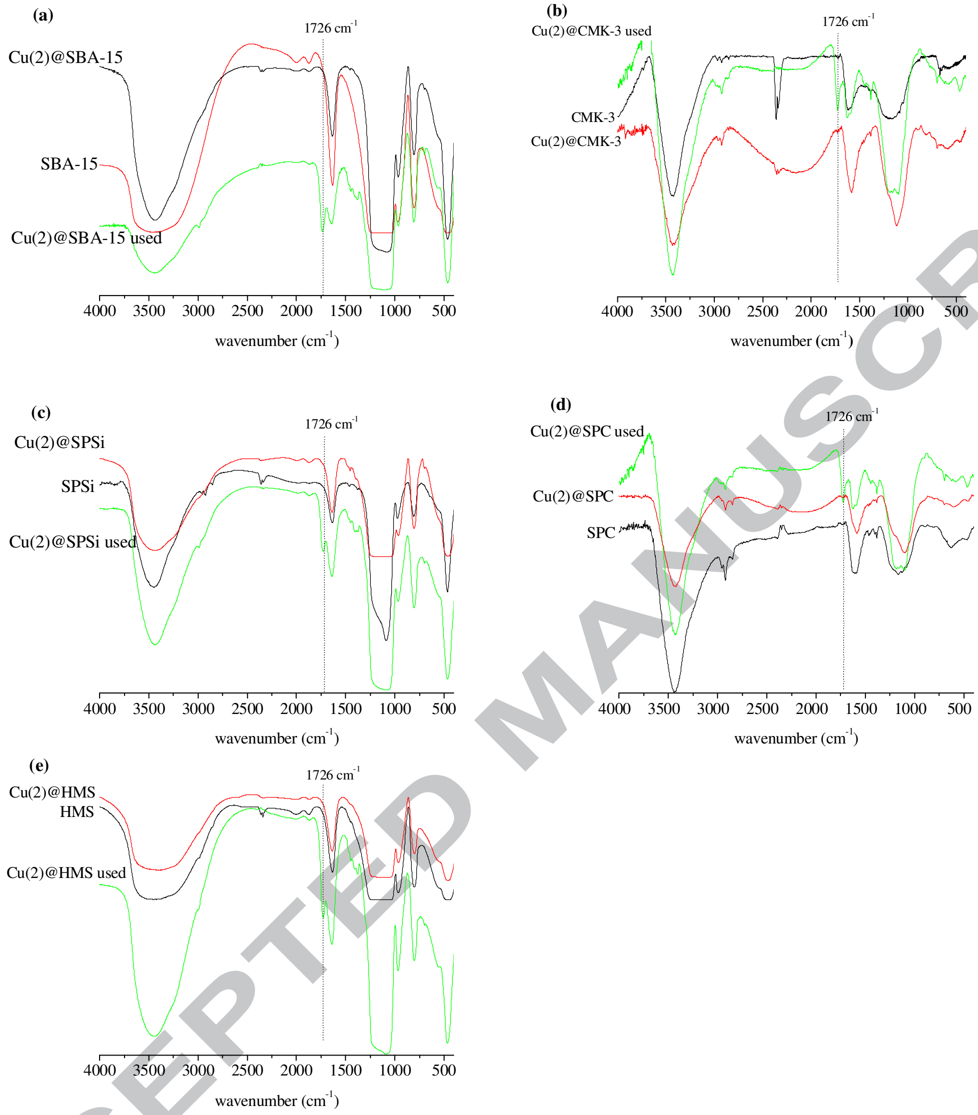

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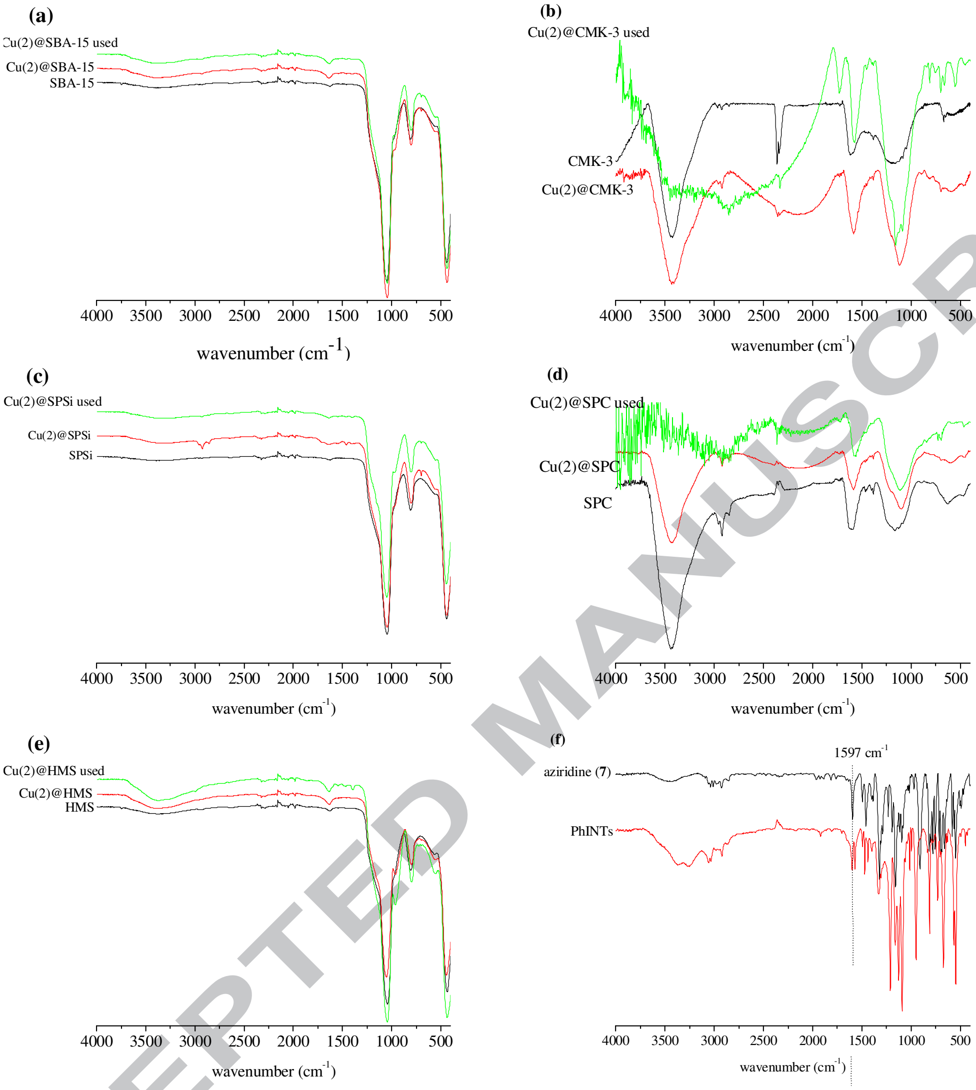
Fig. 3



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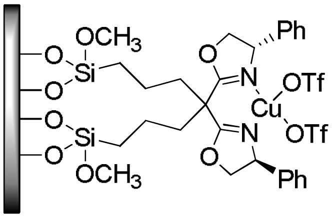
Graphical Abstract



The preparation of multipurpose asymmetric heterogeneous catalysts based on anchored expensive privileged chiral ligands onto porous supports is of great interest. The asymmetric cyclopropanation and aziridination of styrene were performed using a copper(II) complex with a commercial chiral bis(oxazoline) anchored onto ordered mesoporous silica materials and their carbon replicas.

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