Catalytic activity of copper-bis(oxazoline) grafted on mesoporous silica in enantioselective cyclopropanation

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Abstract

Chiral phenyl substituted bis(oxazoline) (PhBox) was covalently immobilized through carbamate linkers onto mesoporous silica materials. These supports were previously prepared by a sol-gel method and they exhibit different textural properties. The presence and the integrity of the bis(oxazoline) ligand was checked by ^{13}C-CP-MAS-NMR. These chiral mesoporous materials were complexed with copper (II) triflate. In spite of the different textural properties of these supports, the copper loading, determined by ICP-AES, was nearly the same (0.041-0.044 mmol Cu/g of solid). The supported Cu (II) complexes were tested as catalysts in the enantioselective cyclopropanation of styrene with ethyl diazoacetate. Enantioselectivities are consistently lower than those obtained in homogeneous phase. Different analyses point to a difficulty in the formation of the expected chelate, due to the presence of a coordinating functional group in the linker, as responsible for the loss in enantioselectivity. The textural properties of the materials do significantly affect the behavior upon recovery.

Keywords Mesoporous materials, Immobilized catalysts, Bis(oxazoline), Cyclopropanation.

Introduction

The development of new heterogeneous catalysts able to promote enantioselective organic reactions is a field of growing interest because of the important advantages of heterogeneous to homogenous catalysts, the main one being that the supported catalyst can be easily recovered and then reused [1,2]. The immobilization of chiral homogeneous catalysts on solid insoluble supports is the most common method to prepare chiral heterogeneous catalysts, and two general approaches can be used for this immobilization: the first one consists in covalently fixing the chiral ligand to the support [3,4], whereas the second one uses some non-covalent interaction between the complex and the solid support [5]. The main advantage of the covalent immobilization is to avoid the leaching of the valuable chiral ligand. As solid support, organic polymers and different kinds of silica are commonly used for the covalent attachment. Silica supported catalysts show in principle stronger mechanical resistance and a structure which is independent from the solvent used. Moreover, the restriction in the attack trajectories to the chiral complex in mesoporous solids has been the origin of interesting confinement effects on selectivity [6,7].

As chiral ligands, bis(oxazolines) are among the most versatile ones, since they form complexes with different cations and can promote a large variety of enantioselective organic reactions [8]. Their metal complexes have been immobilized on mesoporous materials through non-covalent interactions, such as hydrogen-bonding [9] and electrostatic interactions [10,11,12]. The covalent immobilization of bis(oxazoline) ligands on silica support could be achieved *in situ* by sol-gel method or by grafting on a pre-formed support. The synthesis by sol-gel process [13] presents the problem that the bis(oxazoline) ligands are sensitive to hydrolysis in aqueous acidic media, together with the possible occlusion of the ligand in non-accessible parts of the hybrid material. Regarding grafting on different silica supports, one key point is the choice of the spacer linking the bis(oxazoline) ligand and the support. A simple alkyl chain has been used, either anchoring an alkyl halide on the silica support and making it to react with a methylene bis(oxazoline) [14,15,16,17,18] or alkylating first the ligand and then grafting the modified bis(oxazoline) [19,20,21]. In other cases the spacer has functional groups, such as thioether [22,23], ether [24,25], carbamate [26,27,28] or even polyfunctional spacers prepared by click chemistry [29]. Some of those works deal with the covalent immobilization on amorphous silicas and in other examples ordered mesoporous materials are used as supports, namely

MCM41 and MCM48 [14,23], SBA15 and HMS [17,18,25], mesocellular foam silicas [19,20,21,24], and hierarchically-ordered mesocellular mesoporous silica [29].

In this work the anchoring of phenyl substituted bis(oxazoline) ligand to mesoporous silica through a carbamate linker CH_2-O-CONH-$(CH_2)_3$ is reported, used until now only to immobilize the indane [26,27] and the *tert*-butyl [28] bis(oxazolines). The catalytic performance in the cyclopropanation between styrene and ethyl diazoacetate is compared with the analogous indane derivative [30].

Experimental

Synthesis of mesoporous supports

To a solution of tetraethoxysilane (TEOS, 9.1 mL, 40 mmol) in propanol (20 mL) at the required temperature was added either acetic or propionic acid (4 mmol) and then water (4.2 mL). The final molar composition of the mixture was TEOS:propanol:H_2O:acid = 1:6.5:6:0.1. The resulting solution was stirred at the same temperature until gelification, and then for an additional period of 24 h. The resulting product was transferred into a Teflon-lined autoclave to be aged at 120 °C for 24 h, and finally it was dried at 120 °C for 24 h in an oven.

Synthesis of the chiral ligand

2,2′-Methylenebis[(4*S*)-4-phenyl-2-oxazoline] (PhBox) was synthesized by reacting (*S*)-2-phenylglycinol (10 mmol, 1.37g) with diethyl malonimidate dihydrochloride (5 mmol, 1.15 g) in dichloromethane (100 mL). After 15 hours of stirring at room temperature the resulting mixture was extracted 3 times with 100 mL of H_2O. The organic fraction was dried with $MgSO_4$ and the solvent was removed under reduced pressure to obtain a yellow liquid [31].

^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 7.26-7.20 (m, 10H), 5.22 (m, 2H), 4.67 (t, 2H), 4.11 (t, 2H), 3.51 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 162.0, 141.6, 128.6, 127.5, 126.6, 75.2, 69.7, 28.3.

After that, the ligand was functionalized in the methylene bridge by hydroxymethylation. PhBox (1 mmol, 0.308 g) was added to a solution of paraformaldehyde (2.5 mmol, 78 mg) in CH_2Cl_2 (4 mL). After that dioxane (1 mL) and water (0.2 mL) were added. Finally, a solution of triethylamine (2.96 mmol, 0.4 mL) in tetrahydrofuran (3 mL) was added dropwise for 3 hours

and the mixture was kept under stirring at room temperature. After 3 days, the solvent was evaporated under reduced pressure, CH_2Cl_2 (20 mL) was added and the solution was washed with water (3 × 20 mL). The organic phase was dried with $MgSO_4$ and the solvent was removed under reduced pressure.

^{1}H NMR (300MHz, $CDCl_3$, δ/ppm): 7.32-7.24 (m, 10H), 5.21 (m, 2H), 4.67 (t, 2H), 4.11 (t, 2H), 3.74 (m, 4H), 3.70 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 161.9, 141.6, 128.8, 127.8, 126.5, 75.0, 69.0, 67.0, 64.5.

The hydroxymethylated ligand was made react with 3-isocyanatopropyltriethoxysilane [26,27]. The hydroxymethylated ligand (1 mmol, 0.364 g) was added to a solution of dry triethylamine (3.3 mmol, 0.5 mL) in dry toluene (5 mL) under inert atmosphere. The 3-isocyanatopropyltriethoxysilane (2.2 mmol, 0.55 mL) was added dropwise for 20 min. The mixture was kept under stirring at room temperature for 48 h. The solvent was evaporated under reduced pressure and the crude reaction was used for grafting without further purification.

^{1}H NMR (300MHz, $CDCl_3$, δ/ppm): 7.98 (s, 2H), 7.32-7.24 (m, 10H), 5.23 (m, 2H), 5.01 (t, 4H), 4.67 (t, 2H), 4.11 (t, 2H), 3.78 (m, 12H); 3.13 (m,4H), 1.56 (m, 4H), 1.19(m, 18H), 0.60 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 162.2, 158.3, 142.0, 128.5, 127.4, 126.4, 75.2, 70.1, 58.1, 42.6, 36.2, 31.1, 23.4, 18.0, 7.3.

Immobilization of the ligand onto the supports

The corresponding dried silica support (500 mg) was added to a solution of functionalized PhBox (150 mg, 0.17 mmol) in anhydrous toluene (5 mL) and the resulting suspension was heated under reflux for 48h under inert atmosphere. The solid was filtered, thoroughly washed with toluene and dichloromethane, and dried under vacuum. The copper complexes were prepared by addition of $Cu(OTf)_2$ (35 mg, 0.098 mmol) to a suspension of the bis(oxazoline)-containing material (570 mg) in anhydrous methanol (2 mL). After 15 h stirring, the solid was filtered, washed with methanol and dried under vacuum.

Characterization

Nitrogen physisorption experiments were performed at 77K on an ASAP 2000 apparatus. The surface area was calculated using the BET method [32]. The pore size distribution was obtained from the desorption branch of isotherms using the BJH method [33]. ^{13}C-CP-MAS-NMR

spectra were recorded at 100.62MHz on a Bruker Avance SB 400MHz spectrometer at room temperature and magic angle spinning at 4000 Hz, with 5.2 μs excitation pulse and 5 s recycle time. Copper analysis was carried out on a Perkin-Elmer Plasma Emission spectrometer.

Cyclopropanation reaction

The solid catalyst (160 mg) was added to a solution of styrene (156 mg, 1.5 mmol) and *n*-decane (50 mg, internal standard) in anhydrous dichloromethane (2 mL). A solution of ethyl diazoacetate (171 mg, 1.5 mmol) in anhydrous dichloromethane (0.7 mL) was slowly added (2 h) with a syringe pump. The reaction was monitored by GC [34]. After total conversion of diazoacetate, the catalyst was filtered off and washed with dichloromethane (5 mL), dried under vacuum and reused under the same conditions. The enantioselectivities were determined by gas chromatography with a Cyclodex-β column. The oven temperature program is an isotherm at 125°C. The retention times for the different cyclopropanes are 28.9 min for (1S, 2R)-cyclopropane, 29.8 min for (1R, 2S)-cyclopropane, 34.3 min for (1R, 2R)-cyclopropane and 34.9 min for (1S, 2R)-cyclopropane.

Results and discussion

Synthesis and characterization of the chiral catalysts

Mesoporous silica materials were prepared by sol–gel method in propanol with a small amount of a carboxylic acid as catalyst without using any template [35]. The textural properties were determined from the N_2 adsorption–desorption isotherms, which are given in Fig.1 together with the pore size distribution. The results are gathered in Table 1.

Silica materials prepared by sol–gel show type IV N_2 isotherms with different hysteresis loop shape, indicating the formation of mesoporous materials with different pore shape. Besides, these silica materials do not present any microporosity (Table 1). When the synthesis is carried out in propanol at 35 °C with acetic acid as catalyst (material S-1), a surface area of 876 m^2/g and a main pore diameter of 35 Å were obtained. An increase in the synthesis temperature to 60°C (material S-2) produces an increase in the void volume of the solid, which favors the formation of larger pores (mean pore diameter 120 Å) and larger total pore volume (1.12 cm^3/g). When acetic acid is substituted by propionic acid (material S-3), the resulting solid exhibits

large surface area (479 m^2/g) and the highest total pore volume (1.76 cm^3/g), with a very large mean pore diameter.

Table 1 Synthesis conditions and textural properties of silica materials [a]

Solid	Catalyst	T (°C)	S_{BET} (m^2/g)	D (Å)	V_{mic} (cm^3/g)	V_p (cm^3/g)
S-1	CH_3COOH	35	876	35	0	0.77
S-2	CH_3COOH	60	609	120	0	1.12
S-3	C_2H_5COOH	60	479	289	0	1.76

[a] S_{BET}= surface area (m^2/g), D (Å) = maximum of the pore size distribution, V_{mic} = microporous volume calculated by t-plot method (cm^3/g), V_p= total pore volume at P/P_0 = 0.98.

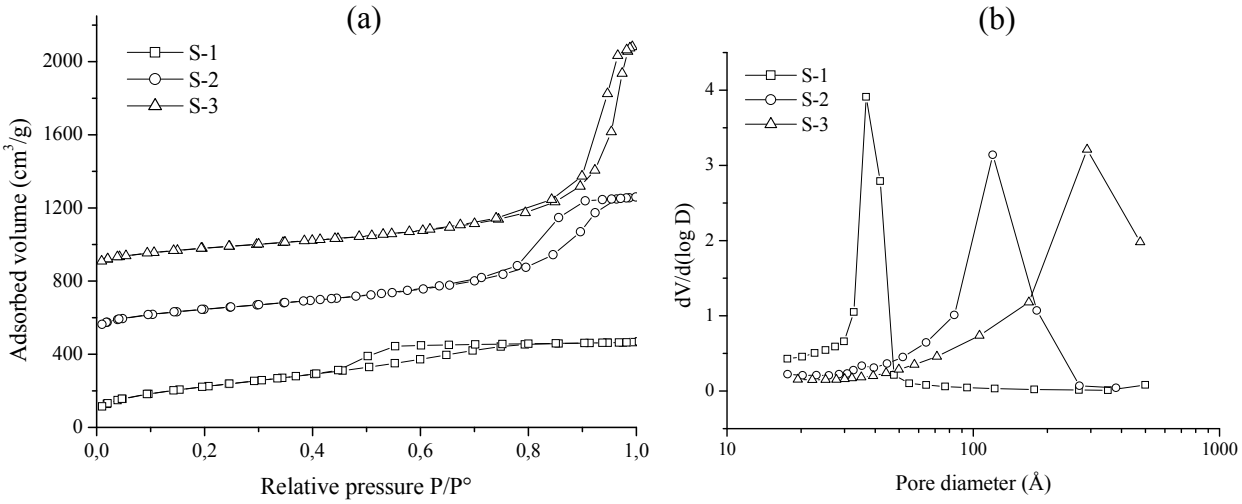
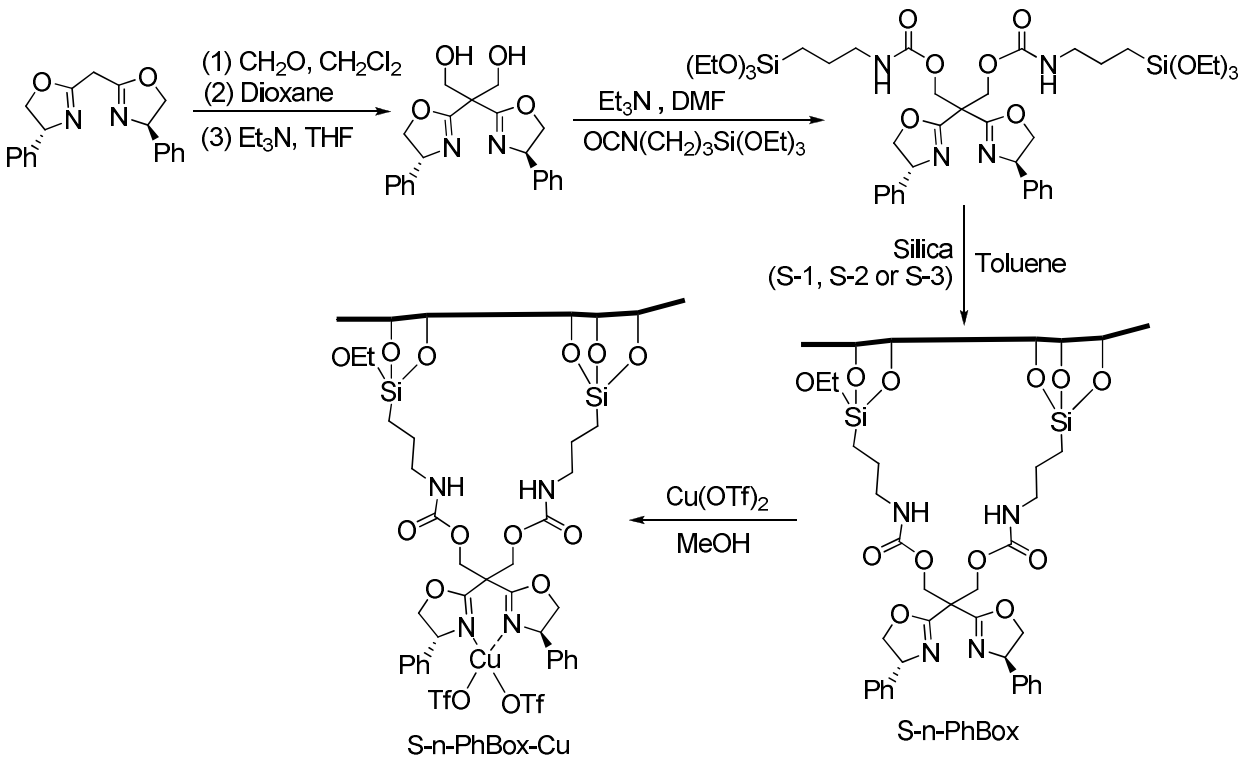


Fig 1 (a) N_2 adsorption-desorption isotherms and (b) pore size distribution of silica materials S-1, S-2 and S-3.

PhBox was functionalized with triethoxysilane groups through carbamate linkers (Scheme 1). The hydroxymethylation with paraformaldehyde was the first step followed by the reaction with 3-isocyanatopropyltriethoxysilane according to a method described in the literature [26,27]. The resulting functionalized ligand was anchored onto the different silica supports (S-1, S-2 and S-3) in toluene under reflux to obtain the materials S-1-PhBox, S-2-PhBox and S-3-PhBox. These functionalized solids were characterized by ^{13}C-CP-MAS-NMR, in order to check the presence and the integrity of the chiral ligand.



Scheme 1 Synthesis steps of the heterogeneous catalysts

The ^{13}C-CP-MAS-NMR spectra of the chiral materials S-1-PhBox, S-2-PhBox and S-3-PhBox are shown in Fig.2. All the spectra are similar, revealing the presence of the most important signals of the bis(oxazoline) ligand and the carbamate linker. All the signals were assigned to the corresponding carbons as seen in the Fig.2. The presence of residual ethoxy groups indicates the incomplete condensation of the ethoxysilane with the surface silanols.

Finally, the materials containing the chiral ligand were complexed with $Cu(OTf)_2$ in methanol (Scheme 1). These catalytic materials are labeled S-1-PhBox-Cu, S-2-PhBox-Cu and S-3-PhBox-Cu. The copper loading and the textural properties of the final catalysts were determined and they are gathered in Table 2. As can be seen the immobilization of the chiral PhBox ligand and the subsequent copper complexation produces a drop in surface area and total pore volume of the mesoporous materials S-1 to S-3, but with only a slight effect on the mean pore diameter. Copper loading in all the mesoporous chiral materials is very similar, from 0.041 to 0.044 mmol/g, in spite of the very different surface area of the three supports. Thus the highest copper surface density, 0.13 μmol/m^2, corresponds to the support with largest pores, probably due to an improved accessibility to the whole surface of the solid.

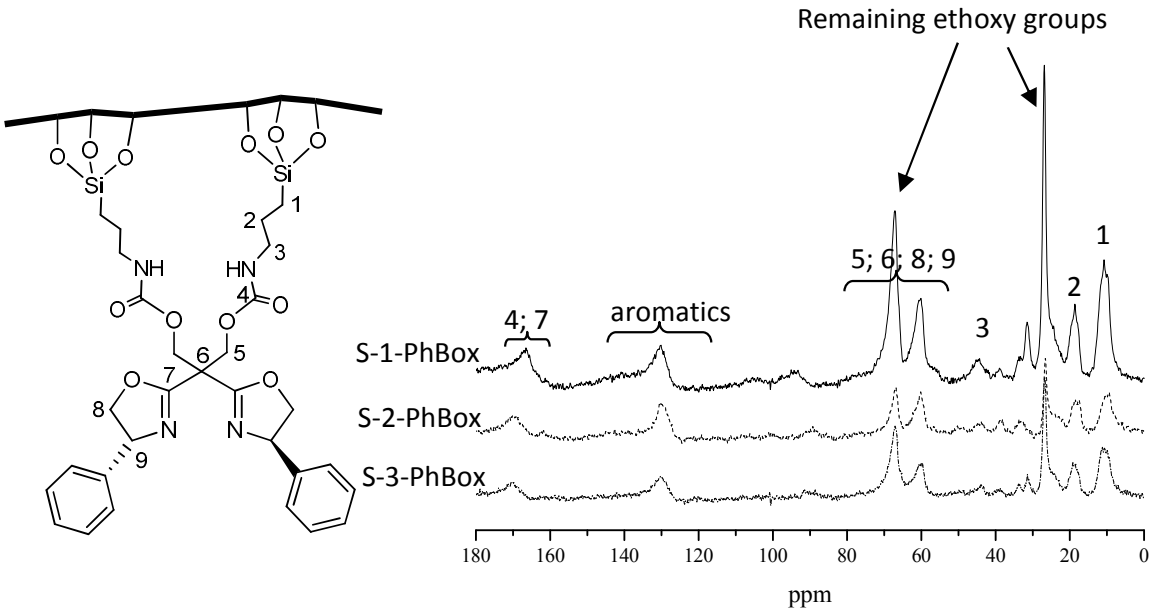


Fig. 2 ^{13}C-CP-MAS-NMR spectra of the solids S-1-PhBox, S-2-PhBox and S-3-PhBox

Table 2 Textural properties and copper content of the catalysts [a]

Catalyst	S_{BET} (m²/g)	D (Å)	V_p (cm^3/g)	Cu (mmol/g)	Cu (μmol/m²)
S-1-PhBox-Cu	583	35	0.52	0.043	0.07
S-2-PhBox-Cu	372	120	0.86	0.041	0.11
S-3-PhBox-Cu	328	278	1.16	0.044	0.13

[a] S_{BET} = surface area (m²/g), D(Å) = maximum of the pore size distribution, V_p = total pore volume at $P/P_0 = 0.98$.

The ligand functionalization of the solid and the degree of ligand complexation with copper can be estimated from the elemental analysis. The results are collected in Table 3, together with those obtained in the grafting of the indane derived bis(oxazoline) on the same supports [30]. First of all the C/N molar ratios, in the range of 7.5-7.8, are in good agreement with the theoretical value (7.25), also considering the presence of residual ethoxy groups, as shown in the NMR spectra (Fig 2). It is also worthy to note that the amount of PhBox grafted ligand, around 0.25 mmol/g, is significantly higher than in the case of indBox (around 0.18 mmol/g). This can be due to the higher flexibility of PhBox, in comparison with the polycyclic indBox, allowing an easier diffusion through the mesopores of the supports. On the contrary, the degree

of complexation is rather low. The N/Cu molar ratio is around 23 in all the three solids, whereas the theoretical ratio for a total complexation is 4. This result is also very different from those obtained with the indBox ligand. In that case the ligand complexation is not complete either, but the N/Cu molar ratio is always lower, in the range of 8.6-13.3. It can be speculated that the easiness for diffusion of the more flexible PhBox ligand allows the grafting on sites that are later on inaccessible for $Cu(OTf)_2$.

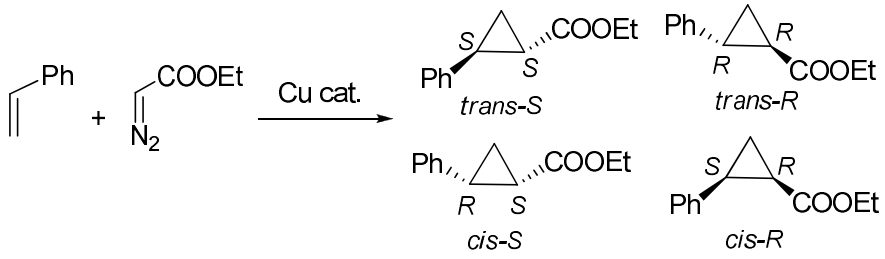
Table 3 Copper and elemental analysis of fresh and recovered catalysts [a]

Catalyst	Fresh catalyst			Recovered catalyst		
	Cu	N	C	Cu	N	C
S-1-PhBox-Cu	0.043	0.96	7.49	0.034	1.04	9.20
S-2-PhBox-Cu	0.041	1.01	7.59	0.024	0.97	9.64
S-3-PhBox-Cu	0.044	0.98	7.57	0.043	1.02	8.83
S-1-indBox-Cu[b]	0.091	0.78	8.96	0.071	0.74	12.27
S-2-indBox-Cu[b]	0.057	0.76	7.08	0.031	0.81	9.05
S-3-indBox-Cu[b]	0.061	0.72	6.86	0.025	0.64	6.70

[a] Content in mmol/g. [b] Results from ref. [30] corresponding to the catalysts with indane bis(oxazoline) on the same supports.

Results in the cyclopropanation reaction

The immobilized copper (II) complexes were tested as catalysts in the benchmark cyclopropanation reaction between styrene and ethyl diazoacetate represented in Scheme 2. The catalytic results are gathered in Table 4, together with those obtained with the analogous indane derived bis(oxazoline) ligand (indBox) grafted on the same silica supports [30].



Scheme 2 Asymmetric cyclopropanation of styrene with ethyl diazoacetate

Table 4 Results of the catalyzed cyclopropanation reactions [a]

Catalyst	Run	Yield (%)	*trans*/*cis*	%e.e. *cis*[b]	%e.e. *trans*[b]
PhBox(Me_2)-Cu[c]	1	33	68/32	51	60
Hyb-PhBox-Cu[d]	1	33	64/32	53	45
	2	30	59/41	50	43
S-1-PhBox-Cu	1	30	63/37	22	27
	2	34	63/37	2	4
S-2-PhBox-Cu	1	53	62/38	11	22
	2	45	63/37	2	9
S-3-PhBox-Cu	1	30	63/37	24	30
	2	12	62/38	6	7
indBox(Me_2)-Cu[c]	1	52	60/40	81	85
S-1-indBox-Cu[e]	1	45	56/44	52	43
	2	39	57/43	46	35
S-2-indBox-Cu[e]	1	37	57/43	52	42
	2	20	58/42	40	30
S-3-indBox-Cu[e]	1	33	56/44	57	48
	2	2	58/42	37	29

[a] Reaction conditions: Cu = 2mol%, styrene =1.5 mmol, dichloromethane (2 mL), slow addition (syringe pump, 2 h) of ethyl diazoacetate (1.5 mmol in 0.7 mL CH_2Cl_2), rt. Results determined by GC. [b] Major isomers: *trans*-*S* and *cis*-*S*. [c] Results with the homogeneous complex from ref. [34]. [d] Results from ref. [**¡Error! Marcador no definido.**] corresponding to a hybrid material prepared by sol-gel method with PhBox functionalized with a propyl linker. [e] Results from ref. [30] corresponding to the catalysts with indane bis(oxazoline) on the same supports.

The homogeneous PhBox(Me_2)-Cu complex leads to moderate enantioselectivities for both *cis* (51% e.e.) and *trans* (60% e.e.) isomers, as well as moderate yield (due to the competitive side dimerization of the diazocompound) and the typical *trans*/*cis* selectivity, close to 70/30 [36]. In the case of the immobilized catalysts, the enantioselectivities are significantly lower, 11-24% e.e. for *cis* cyclopropanes and 22-30% e.e. for *trans* cyclopropanes, with the best results

obtained with S-3-PhBox-Cu, and very close results with S-1-PhBox-Cu. With both catalysts the obtained yield is comparable to that of the homogeneous catalyst. On the contrary the lowest enantioselectivities correspond to S-2-PhBox-Cu, the catalyst leading to the highest yield, even higher than the result in solution, which seems to indicate an important contribution of copper sites uncomplexed with the immobilized ligand.

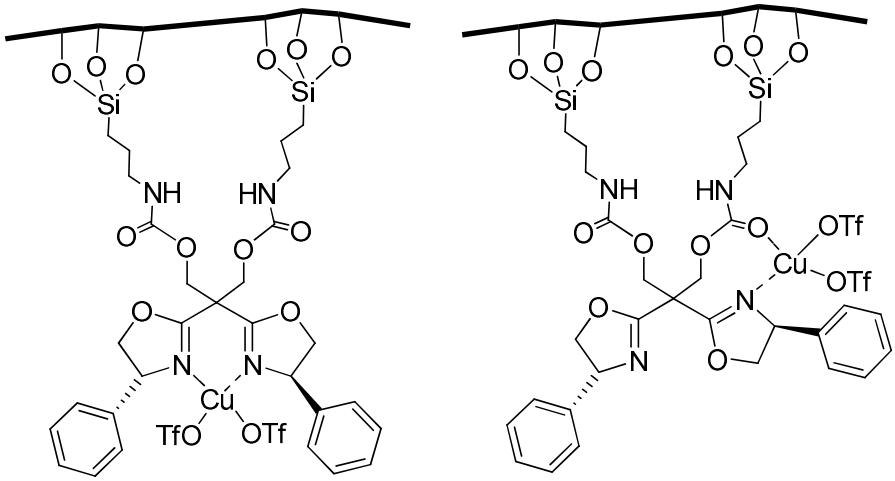


Fig. 3 Possible coordination modes for grafted PhBox: chelate mode (left) and mixed ligand-linker mode (right)

When these results are compared with those obtained with indBox (Table 4), it can be seen that the rigid ligand leads to better results in enantioselectivity, 52-57% e.e. for *cis* and 42-48% e.e. for *trans* cyclopropanes. However, a deeper inspection of the results requires the calculation of the difference in the energy of the diastereomeric transition states (ΔE_a), as this is the parameter that controls the enantioselectivity. From the relative abundances of both enantiomers it can be calculated that, in the case of PhBox, the immobilization on S1 and S3 provokes a decrease in that difference ($\Delta\Delta E_a$) of around 0.4 kcal/mol in the *cis* and 0.45-0.5 kcal/mol in the *trans* cyclopropanes. However, from the results with indBox, immobilization provokes in that case a $\Delta\Delta E_a$ of around 0.6 kcal/mol for *cis* and 0.9 kcal/mol for *trans* cyclopropanes, that is the effect of immobilization on the relative energy of the transition states is higher in the case of indBox. On the contrary, the results of PhBox grafting on different solids using a unfunctionalized propyl linker described in the literature [13,14] show that the enantioselectivity was not significantly modified with respect to the result in solution, indicating an important role of the linker in this effect. The presence of a linker functionalized with coordinating groups, and the

possible restrictions in the conformational freedom of the ligand inside the mesopores, may induce different coordination modes (Fig. 3), including one mixed ligand-linker one, whose enantioselectivity would be lower than the typical chelate mode [37,38,39]. Thus unfunctionalized propyl linker seems to be more suitable for grafting on silica supports. However, recently it has been described the grafting of PhBox with this linker on several solid supports [18], including mesoporous silicas, and in most cases the results [40] are similar to those reported here and in only one case enantioselectivities are close to those obtained in solution.

After recycling these chiral catalysts shows a drop in the enantioselectivities for both *cis* and *trans* cyclopropanes to values below 10% e.e., but the yields are similar in S-1-PhBox-Cu and S-2-PhBox-Cu, whereas the reused S-3-PhBox-Cu is much less active for cyclopropanation. This effect had been also observed in the case of supported indBox [30], in spite of being the solid with the largest pores. The analysis of the recovered catalysts (Table 3) that Cu leaching is lower in the case of PhBox than in indBox, and even null in S-3-PhBox-Cu. This result demonstrates that leaching is not the main origin of the deactivation.

The N_2 adsorption–desorption isotherms and the pore size distribution of the material S-2-PhBox-Cu before use and after the second run are given in Fig. 4. After use, the N_2 isotherm is still of type IV but the hysteresis loop has changed from H1 to H3. This suggests the modification in the shape of the pores, from pores have regular dimensions not interconnected (H1 type), to slit-shaped pores (H3 type) [41,42]. Also the pore size is reduced from 120 Å to 110 Å, with the appearance of smaller pores of about 33 Å. Besides, the surface area dropped from 372 m^2/g to 281 m^2/g, and the same trend was observed for the total pore volume, which was reduced from 0.86 cm^3/g to 0.79 cm^3/g, although it does not present any microporosity. All these results demonstrate some blockage of the pores by organic groups, in agreement with the increase in carbon content (up to 2 mmol/g, Table 3). This must be due to the presence of products or by-products (diethyl fumarate and maleate from dimerization of diazoacetate, as well as oligomers), mainly on the copper sites, which has been proposed as the main deactivation mechanism in other supported box-Cu complexes [43].

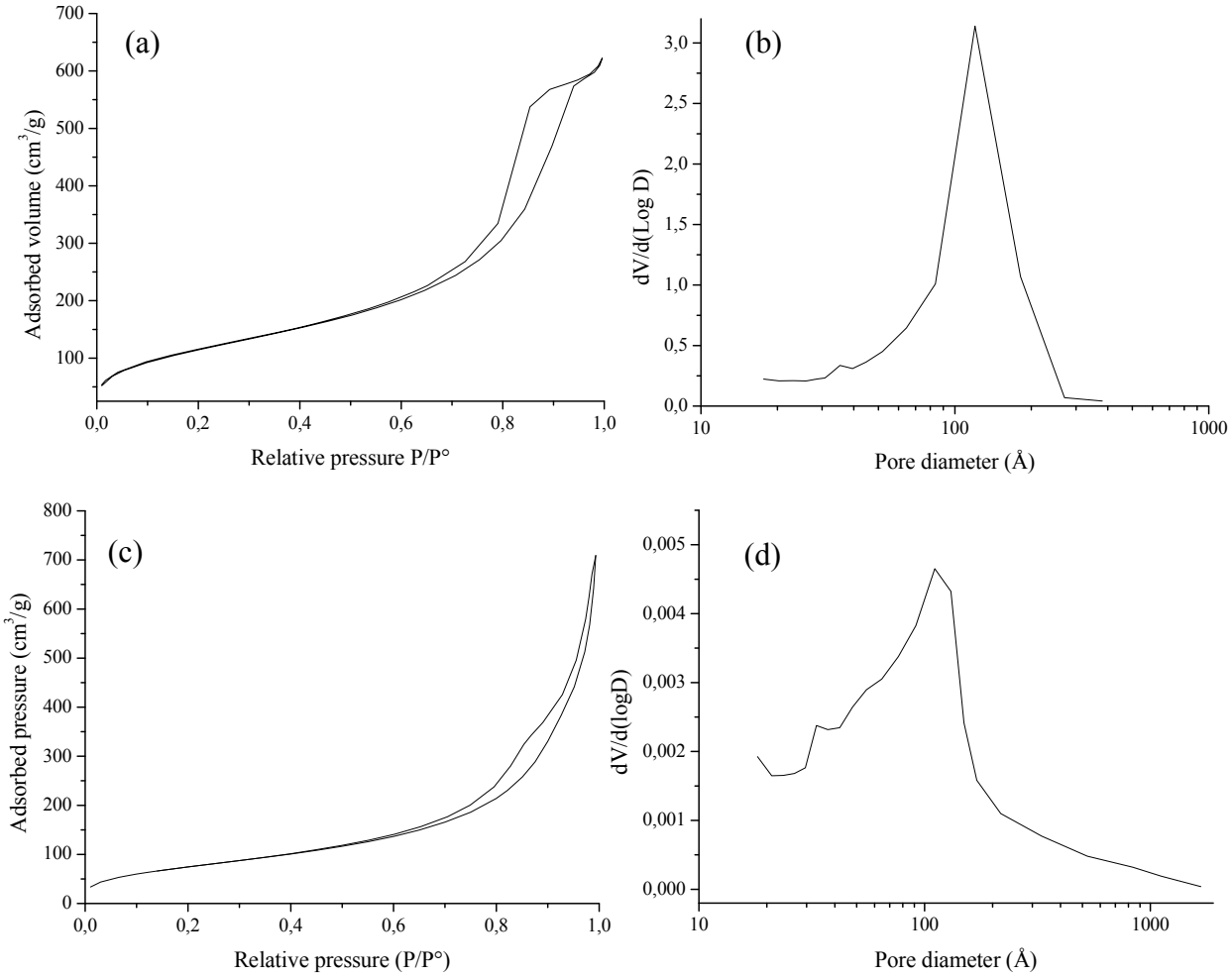


Fig. 4 N_2 adsorption–desorption isotherms and pore size distribution of S-2-PhBox-Cu before use (a, b) and after the second run (c, d).

Conclusions

A series of silica supported heterogeneous PhBox-Cu(II) catalysts have been successfully prepared by covalent immobilization on silica supports through carbamate linker. The results obtained in the cyclopropanation of styrene with ethyl diazoacetate have no apparent relationship with the textural properties of the solids. On the contrary, the drop in enantioselectivities with respect to the results in homogeneous phase parallels the behavior observed with a similar ligand indBox, and it seems to be related with the nature of the linker. The presence of coordinating functional groups in the linker, carbamate in this case, seems to be detrimental, probably in connection with a restricted conformational freedom that makes

difficult the formation of the expected chelate. On the contrary the textural properties of the material do significantly affect the deactivation, mainly due to by-products adsorption.

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