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# Beyond reuse in chiral immobilized catalysis: The bis(oxazoline) case

José M. Fraile, José I. García, C.I. Herrerías, José A. Mayoral *, E. Pires, L. Salvatella

*Departamento Química Orgánica, Instituto de Ciencia de Materiales de Aragón and Instituto Universitario de Catálisis Homogénea, Universidad de Zaragoza, CSIC, E-50009 Zaragoza, Spain*

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ABSTRACT

Development of efficient immobilized chiral catalysts has been an area of increasing interest during the last decades, in spite of the excellent results obtained in some cases and the inherent advantages of heterogeneous systems, the application of these catalysts is quite limited. This is due, in part, to the fact that synthetic effort necessary to prepare them is not justified by only some reuses, furthermore some "dogmas" about these catalysts should be removed for a faster improvement in this area.

In this revision we do a critical and historical analysis of this field, taking bis(oxazoline) based catalyst as an example. We show that a deeper knowledge of the catalytic system allows improving the catalyst, so easily prepared immobilized catalysts, lead to results comparables or even better than those obtained in solution, by simply using a ligand better adapted to immobilization. Furthermore the use of the support as a "friend" cooperating in the stereodiscrimination, allows obtaining stereochemical results different from those obtained in solution, which increases the interest of these catalysts.

To sum up, the consideration of the immobilized catalyst as a joint, including the support and the comprehension of the catalytic mechanism allows the design of more efficient chiral heterogeneous systems.



## 1. Introduction

Enantioselective reactions promoted by chiral catalysts have great importance in current chemical research [1]. In this area the search for new heterogeneous catalysts able to promote enatioselective reactions has a growing interest due to the inherent advantages of heterogeneous as opposed to homogeneous catalysts [2]. The main strategy used to prepare chiral heterogeneous catalysts is the immobilization of chiral metal complexes [3], and the research in this area was directed by three kind of generally accepted "dogmas" about supported catalysts:

- Supported catalysts are less active than homogeneous ones, so that catalyst recovery is essential to improve TON.
- The best ligand in homogeneous phase will be also the best ligand in heterogeneous phase; therefore immobilization of the best homogeneous catalysts is the best option.
- The support is a necessary drawback causing undesirable interactions; as a consequence the immobilization strategy should place the catalytic sites as far as possible from the support.

In general immobilization through strong catalysts–support interactions is preferred to avoid catalyst leaching. In most of cases the catalysts is grafted by formation of a covalent bond between the chiral ligand and the support, which supposes the chemical modification of the ligands. This modification requires a synthetic effort and may have consequences on the stereochemical result of the reaction [3]. Immobilization through electrostatic interaction of charged catalysts with charged support does not need this modification; however it is limited to reactions in which the charge is maintained during all the mechanism to avoid leaching of the complex to solution.

Chiral oxazoline-based ligands (Scheme 1) are among the most popular ligands used in asymmetric catalysis because they are easily obtained from cheap amino alcohols and their complexes have been shown to be very efficient catalysts of many enantioselective organic reactions [4–6] and, as a consequence, the heterogenization of this versatile family of chiral catalysts has attracted a great deal of attention [7].

Here the use of immobilized catalysts containing bis(oxazoline) (Box) and azabis(oxazoline) (azaBox) ligands (Scheme 1) is presented in a historic way. The revision is divided into three parts, in the first one the first results are commented, trying to show the main drawbacks and limitations; in the second it is shown how to overcome these drawbacks and finally the use of the support as a source of new stereochemicals effects is discussed.

* Corresponding author.
*E-mail address:* mayoral@unizar.es (J.A. Mayoral).

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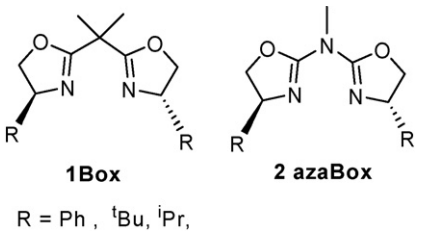
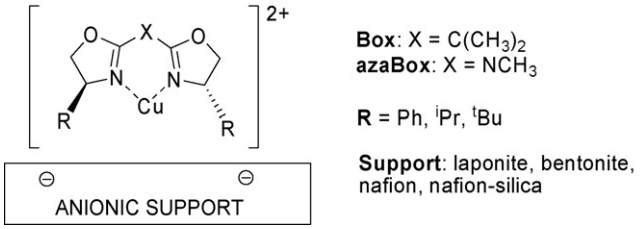



**Scheme 1.** General structure of the chiral ligands studied.




**Scheme 2.** Immobilization of Box–Cu and azaBox–Cu complexes by cationic exchange.

Along the paper cyclopropanation will be used as the benchmark reaction, although some results from other reactions will be presented to illustrate the main concepts.

## 2. Initial results

In the first works on the immobilization of these catalysts bis(oxazoline)–copper complexes were supported by cation exchange into anionic solids, such as clays, nafion or nafion–silica composites (Scheme 2).

These catalysts were tested in the benchmark cyclopropanation reaction between styrene and ethyl diazoacetate (Scheme 3) [8–14].

As a general trend the catalysts containing the ligand PhBox led to results similar to those reached in solution with yields about 35%, *trans*/*cis* selectivities about 65/35 and enantioselectivities near of 60% ee, furthermore they can be recovered and reused. It is important to note that the same enantiomers are obtained as the major product with both homogeneous and immobilized catalysts. Unfortunately, the best ligand in homogeneous phase, $^{t}$BuBox, did not exhibit similar performance when their copper complexes were immobilized onto the same supports, and only modest enantioselectivities were obtained, probably due to the leaching of ligand and the concurrence of non-enantioselective reaction. The same effect was subsequently reported with other nafion–silica supports. In this case, against a generally accepted idea, the best catalyst in solution is not the best-immobilized catalyst. A possible explanation for this behavior is the formation of non-enantioselective catalytic sites on the support. The formation of these sites, free of chiral ligand, is justified by a low constant of formation of $^{t}$BuBox–copper complex, favoring the presence of free copper during the preparation of the catalyst by cation exchange. This hypothesis was validated by adding free $^{t}$BuBox ligand to the heterogeneously catalyzed reaction. In these conditions, 91% ee in *trans*-cyclopropanes and 88% ee in *cis*-cyclopropanes was obtained [13], showing the role of complexation equilibria on the enantioselectivity. In this case the best catalyst in solution is not the best after immobilization.

The results obtained suggest that the better behavior of PhBox–Cu complexes, after immobilization, is due to a higher stability of this complex in comparison with $^{t}$BuBox ligand.

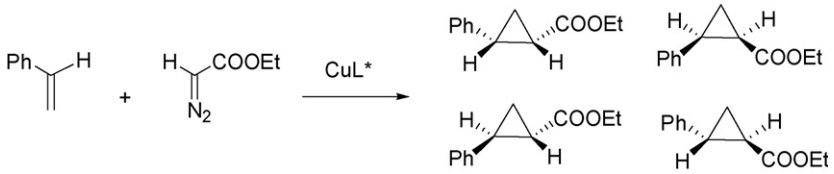
Bis(oxazoline)–Cu(II) complexes immobilized on zeolites by electrostatic interactions (Scheme 2), have been used as catalysts of enantioselective aziridination reactions (Scheme 4).

A variety of parameters, including the influence of byproducts on the reaction results has been considered. Again the best results are obtained using PhBox as the chiral ligand [15–18].

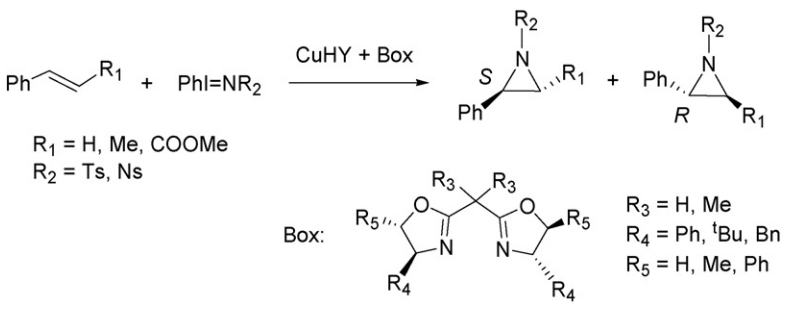
A related strategy for recovery of chiral bis(oxazoline)-derived catalysts is the use of ionic liquids coupled with an extraction of the products to an immiscible phase. This approach has been studied in the cyclopropanation reaction catalyzed by Box–copper complexes [19–21]. Using imidazolium-based ionic liquids, catalyst recovery depends again on the nature of the ligand, PhBox–$CuCl_2$ complexes are easily recovered but with $^{t}$BuBox–$CuCl_2$ enantioselectivities drop after the second recovery, even under optimal conditions.

The second main strategy for catalyst immobilization is the covalent bonding of the chiral ligand to a support. This strategy has a general applicability but requires the chemical modification of the chiral ligand.

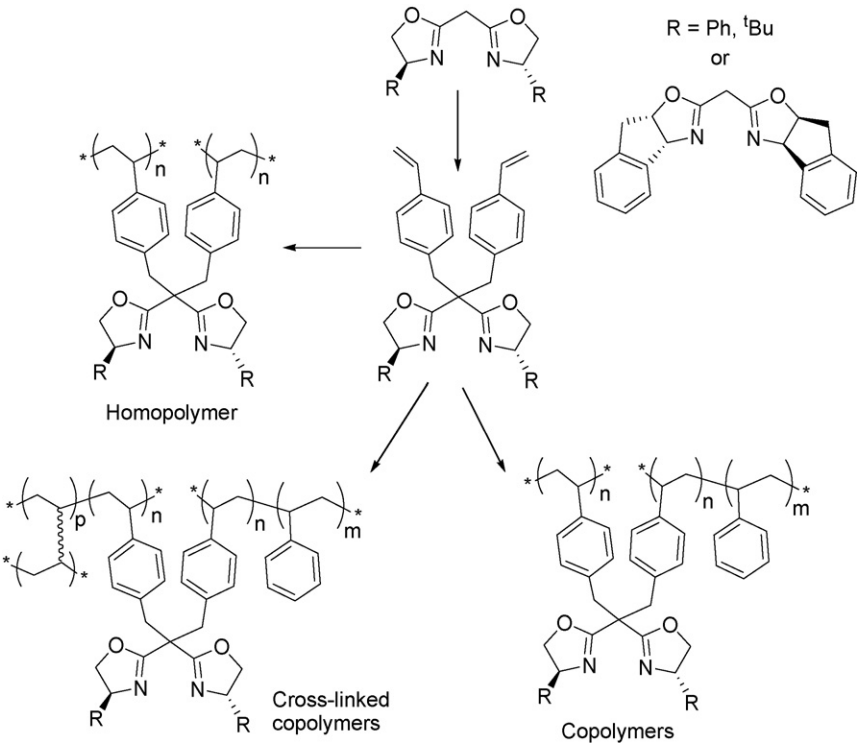
The polymerization approach, i.e. the preparation of a Box-containing monomer that is subsequently polymerized or co-



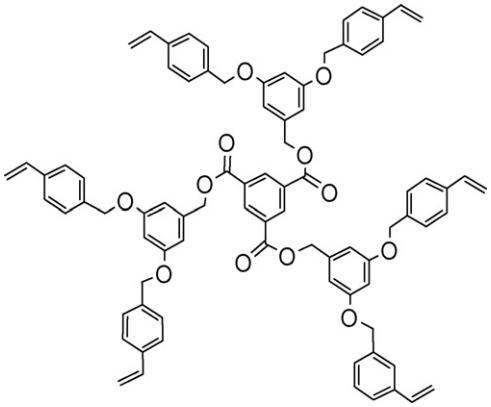

**Scheme 3.** Cyclopropanation reactions.




**Scheme 4.** Aziridination reactions with immobilized Box–Cu catalysts.



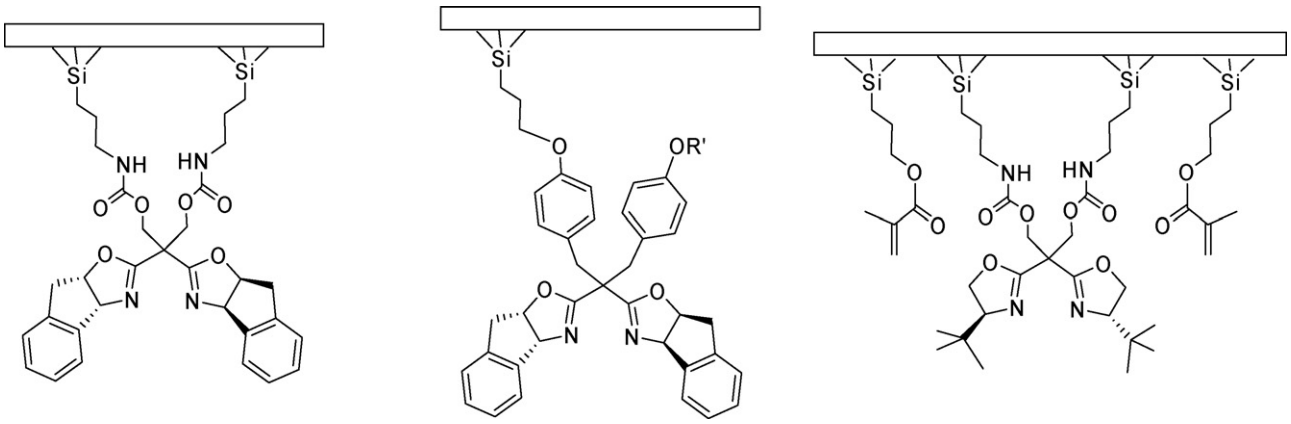

**Scheme 5.** Polymerization strategy for Box immobilization.



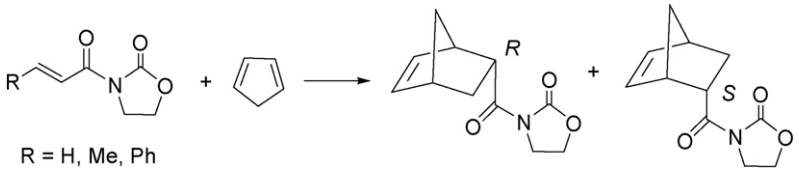
**Scheme 6.** Dendrimer used as cross-linking agent.

polymerized, was first described by Burguete et al. [30,31]. PhBox, $^{t}$BuBox and IndaBox were functionalized with vinylbenzyl groups in the Box methylene bridge, and then homo-polymerized or co-polymerized with styrene and divinylbenzene to yield macroreticular rigid polymers (Scheme 5). The best result, with moderate to good enantioselectivities in the benchmark reaction, was reported for the homopolymer. However, with the $^{t}$BuBox ligand, only ca. 70% ee could be obtained, which is due to the substitution pattern of the ligand. Thus, the dibenzylated $^{t}$BuBox led in homogeneous phase to the same enantioselectivity results. The homopolymer of the $^{t}$BuBox monomer could be reused up to five times without loss of enantioselectivity but with a slight decrease in activity [22].

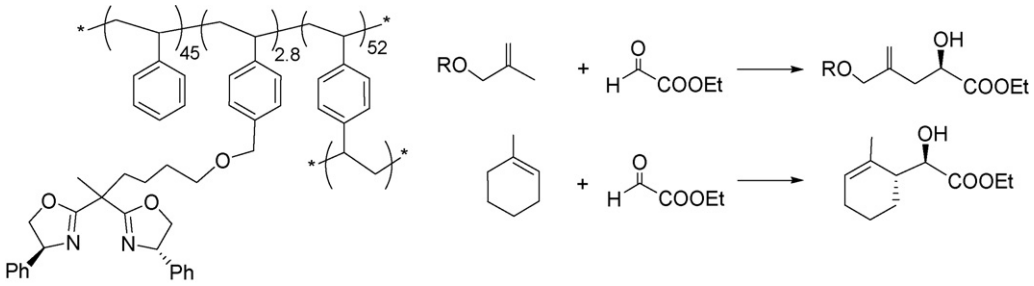
One of the drawbacks of these Box-containing polymers, even with copolymers, is that most of the chiral ligand remains in the non-accessible core of the polymer, and does not participate in the catalysis. So a small number of molecules of chiral product are produced by molecule of chiral ligand used, in spite of the high TON of the reaction. Interestingly, using a dendrimeric cross-linker



**Scheme 7.** Box ligands grafted on silica and used in Diels–Alder reactions.




**Scheme 8.** Diels–Alder reactions between cyclopentadiene and 3-acyl-oxazolidin-2-ones.




**Scheme 9.** Polymerized PhBox used in carbonyl-ene reactions.

(Scheme 6) cyclopropane/Box ratios up to 141 are reached, with similar stereoselectivity results [23]. These results show the influence of polymer morphology on reaction results.

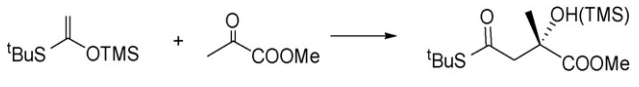
The first example of a Diels–Alder reaction catalyzed by a covalently-supported catalyst based on bis(oxazoline) ligands was reported by Rechavi and Lemaire [24,25] (Scheme 7).

Using the complex with $Cu(ClO_4)_2$ enantioselectivity, up to 92% ee at −78 °C was reached in the reaction between cyclopentadiene and 3-acryloyl-oxazolidin-2-one (Scheme 8). The catalyst was reused during four cycles. Enantioselectivities with the other dienophiles were slightly lower, 70% ee with R = Me, and 61% ee with R = Ph, in both cases at rt.

Kim and co-workers used a similar strategy [26] to immobilize the same ligand on mesocellular foam (MCF). Complexes with $Cu(OTf)_2$, were tested in the same Diels–Alder reaction (R = H, Scheme 8). Up to 75% ee was obtained at −78 °C, the decrease in enantioselectivity with regard to the homogeneous reaction was ascribed to the catalytic effect of the support, shown by the 22% yield obtained with the supported ligand, without copper salt, even at −70 °C. Other dienophiles (R = Me), and dienes, such as cyclohexadiene, led to similar or slightly worse results, between 53 and 72% ee. The best catalyst was used up to five cycles with similar enantioselectivities, but the analysis showed a considerable amount of copper leaching after each cycle.

Iwasawa and co-workers [27] have immobilized $^t$BuBox on silica (Scheme 7). The $Cu(ClO_4)_2$ complex was much more active than the homogeneous counterpart in the reaction between 3-acryloyl-oxazolidin-2-one and cyclopentadiene (R = H, Scheme 8), and at the same time the enantioselectivity was increased from 5 to 15% ee at −10 °C. When silica was silanized with 3-(trimethoxysilyl)propyl methacrylate (Scheme 7), enantioselectivity was improved up to 65% ee.

$^t$BuBox–$ZnCl_2$ has been used in [dbim][$BF_4$] (Scheme 1) as catalysts of Diels–Alder reactions (R = Me, Scheme 8) [28]. Compared with the same process in $CH_2Cl_2$, the reaction was faster and both the *endo*/*exo* selectivity and the enantioselectivity in the *endo* product were excellent (92% ee), catalyst recovery was not described.




**Scheme 10.** Mukaiyama aldol reaction.

Salvadori and co-workers have used a covalently immobilized PhBox in carbonyl-ene reactions [29]. The ligand, functionalized in the methylene bridge with one long spacer bearing a styryl, was polymerized with styrene and divinylbenzene. The resin (Scheme 9) was treated with $Cu(OTf)_2$ and used as catalyst in different carbonyl-ene reactions with ethyl glyoxylate. The catalyst was recycled 4 times with partial loss of activity, but the same enantioselectivity (90% ee). Even the catalyst was reused in different carbonyl-ene reactions with excellent results (85–95% ee), although with copper reloading. Finally the catalyst was used in a semicontinuous system.

The same resin was used in Mukaiyama aldol reactions [30] (Scheme 10). Its catalytic performance was excellent, with 90% yield and 90% ee in a first run. Ligand can be recovered but the recovery of the whole catalyst leads to a decrease in activity due to copper leaching, although the same level of selectivity is maintained. The initial activity was regained when $Cu(OTf)_2$ was reloaded.

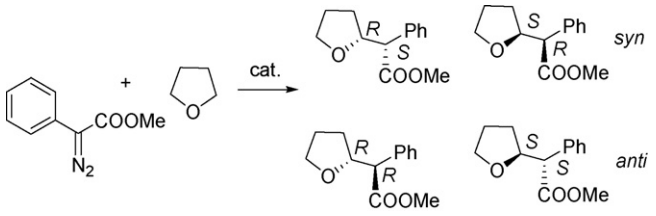
From these initial results it can be seen that immobilization of Box–Cu complexes is not free from problems. Electrostatic immobilization avoids leaching of copper, but leaching of ligand leads to the formation of non-chiral catalytic sites, free of chiral ligand. The formation of these sites gives rise to a reduction of the enantioselectivity. Covalent binding to a covalent support avoids the leaching of the ligand, but Cu leaching reduces the catalytic activity of recovered catalysts. In general more stable catalysts are obtained immobilizing PhBox, and related ligands, than immobilizing $^t$BuBox.

## 3. Improved catalysts

Most of the limitations of these immobilized catalysts are related to the low stability of the chiral complex, therefore the use of ligands able to form stronger complexes with the metals should improve the results.

Theoretical calculations and competitive catalytic experiments [32] showed that Azabis(oxazoline) (azaBox) ligands [32] (Scheme 1), with a donor nitrogen atom in the bridge, have higher coordinating ability with regard to their analogous Box.

When aza$^t$BuBox–$Cu(OTf)_2$ complex exchanged on nafion–silica is used in the benchmark cyclopropanation reaction, about 90% ee in *trans*-cyclopropanes and 84% ee in *cis*-cyclopropanes are obtained in two consecutive runs, in agreement with the stability




**Scheme 11.** Carbene insertion reaction.

of the immobilized complex. The use of other azaBox and supports corroborated these conclusions [31].

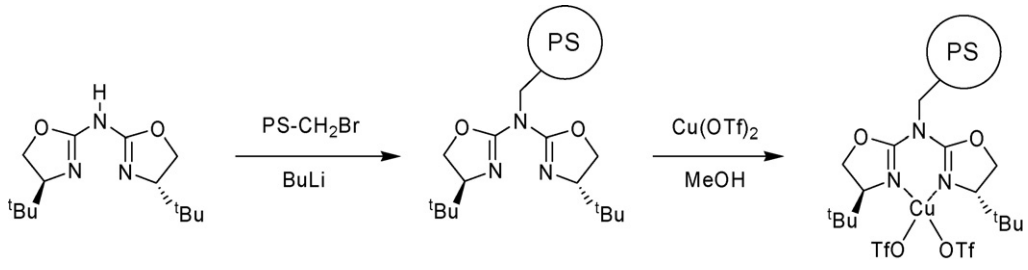
The main factor controlling the recoverability of these catalysts used in ionic liquids was again the low stability of the $^{t}$BuBox–Cu complex, leading to a lost of chiral ligand during the extraction of the products from the ionic liquid phase [emim][OTf] with *n*-hexane. Using aza$^{t}$BuBox up to eight consecutive reactions were carried out, without appreciable loss of enantioselectivity. With this highly recoverable catalytic phase, five consecutive cyclopropanation reactions using different alkenes in each recycle were carried out with excellent enantioselectivities [33].

Given the excellent behavior of the strong Box complexes, immobilized by cation exchange, in carbene–Cu mediated reactions they have being tested in reactions more difficult than cyclopropanation. The first results [34] have shown that the enantioselective C–H carbene insertion of ethyl 2-phenyl-diazoacetate on THF (Scheme 11) is efficiently catalyzed for the first time with copper complexes. Only those ligands forming strong complexes (PhBox and azaBox) lead to moderate enantioselectivities (between 40 and 60% ee). But interestingly, when the PhBox–Cu(OTf)$_2$ complex was immobilized on laponite, a more active and selective catalyst is obtained, up to 88% ee in the major *syn* product. Furthermore, the catalyst is recoverable, and can be used up to four times with the same results of yield and selectivity.

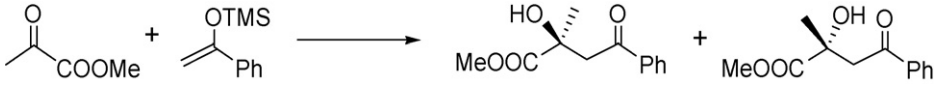
Strong complexation is also an advantage when catalysts are immobilized by grafting, in order to avoid the leaching of metal and the reduction of catalytic activity. Additionally azaBox ligands have only one link point in the bridge, which makes grafting easier. aza$^{t}$BuBox grafted to PS-DVB (Scheme 12) was used in the benchmark cyclopropanation reaction [35]. After optimizing the catalyst preparation, increasing the degree of functionalization of the resin, an excellent catalyst was obtained, able to reach high chemoselectivities (up to 94%) without excess of alkene, and excellent enantioselectivities (up to 99% ee). This catalyst is as easy to prepare as the homogeneous analogous, in both cases the ligand requires modification in a single step by alkylation of the nitrogen, the only difference is the alkylating reagent, methyl iodide in one case and brominated Merrifield resin in the other. Given that the solid catalyst leads to better chemoselectivities and similar enantioselectivties, it is a better catalyst, therefore recovery is not mandatory in this case and it should be considered as an additional advantage. In spite of this the catalyst was recovered and reused with different alkenes in each run (styrene, 1,1-diphenylethylene, α-methylstyrene and 1-hexene), keeping good chemoselectivities and enantioselectivities up to the fourth run. It is difficult to offer an explanation for this excellent behavior, it may be speculated that site isolation together with the low polarity of the support, that favors the approach to the carbene–copper intermediates of styrene, whereas makes more difficult the approach of diazoacetate, favors the cyclopropanation over the dimerization.

Analysis of the previous results had shown the limitations related to the use of Box ligands in Lewis acid promoted reactions. Again, recovery of catalysts containing PhBox or related ligands, was easier than that of catalysts containing $^{t}$BuBox. Therefore it seemed interesting to analyze the behavior of azaBox ligands in Lewis acid catalyzed reactions. In this regard azaBox–Cu(II) complexes immobilized by electrostatic interactions onto a laponite (Scheme 2) or by covalent bonding to PS-DVB (Scheme 12) were tested as catalysts of the Mukaiyama aldol reaction between methyl pyruvate and 1-phenyl-1-(trimethylsilyloxy)ethene (Scheme 13). Even the optimized systems showed a low catalytic activity; in fact they were less active than the analogous supported catalysts containing Box ligands. This activity was even lower after recovery, which was not due to leaching of Cu but to catalyst poisoning [36]. In view of the lack of copper leaching it was tested whether these sites, inactive as Lewis acids, are able to promote a reaction taking place through a completely different mechanism. The PS-DVB–aza$^{t}$BuBox–Cu catalyst, recovered after three aldol Mukaiyama reactions and leading to less than 10% yield, was tested in the benchmark cyclopropanation [37] (Scheme 3). The results (99% chemoselectivity without excess of alkene, 97% ee in *trans*-cyclopropanes and 92% ee in *cis*-cyclopropanes) were the same obtained with the fresh catalyst, showing that a catalyst deactivated for a reaction can be reused in other reactions with different mechanism. This is a new advantage of immobilized systems that can be used as true multitask catalysts.

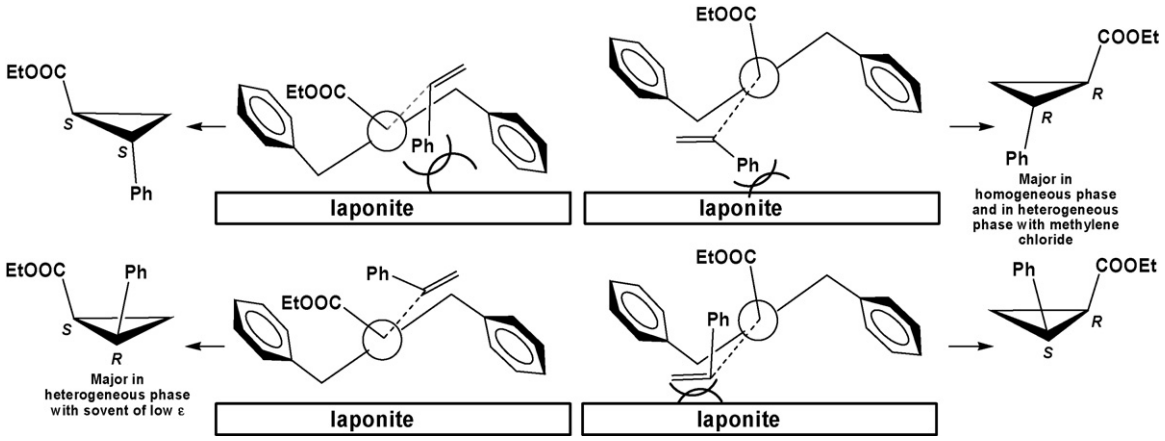
The joint of results described in this part show that immobilized catalysts can be more active and more enantioselective that their homogeneous counterparts. The use of ligands leading to strong complexes is very important to avoid leaching of ligand or metal




**Scheme 12.** Grafting of azaBox in PS-DVE.




**Scheme 13.** Mukaiyama aldol reaction.




**Scheme 14.** Support effects in the cyclopropantion reaction.

and the best copper catalysts for cyclopropanation and C–H insertion reactions has been obtained. However these strong complexes are less active in Lewis acid catalyzed reactions. As it happens in homogeneous phase it is important to select the catalyst as a function if the reaction. The reuse of the catalysts in reactions with different mechanisms increases the applicability, which is an additional bonus for supported systems.

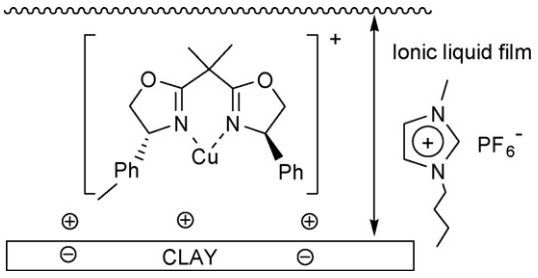
## 4. And beyond

In most of the examples commented above the support has not a decisive influence on the stereoselctivity of the reactions, in some of the examples this influence can be considered detrimental. The support can be considered, as suggested in the third dogma, as a spectator of the reaction. However the support is an important part of the catalysts, in fact it constitutes most of its mass. In view of this fact a question arises: is it possible to use the support to control the stereochemical results of the reaction?

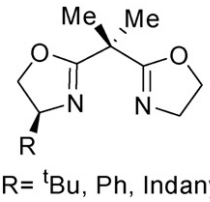
Our first observation in this point was carried out when cyclopropanation between styrene and ethyl diazoacetate was carried out in styrene as the reaction media. The use of this strategy in solution increases the chemoselectivity of the reactions and, as a consequence, the yield in cyclopropanes. When this strategy was used with the laponite immobilized PhBox–Cu complex a complete reversal of the *trans*/*cis* diastereoselectivity (31:69) was observed. Even more interestingly, the major *cis*-cyclopropane obtained has the opposite absolute configuration, with regard to homogeneous phase results. Furthermore the effect is not permanent, when the solid used in styrene is recovered and reused in methylene chloride, the "normal" stereochemical results are obtained again. This effect is not due to a particular behavior as it is also observed with other solvents with a low dielectric constant [38]. It is important to note that none of the anionic supports tested, apart from clays, displayed the behavior observed with these lamellar solids. This particular effect has been ascribed to the two-dimensional nature of the clay surface. The knowledge on the mechanism of this reaction [39,40], allowed proposing a model to explain the behavior observed. The rate determining step of the reaction is the formation of a carbene–Cu(I) complex, this intermediate reacts with styrene in the step controlling the stereochemistry. In solution the *trans*-preference is due to the steric interaction, in the *cis*-transition states, between the ester of the diazoacetate with the phenyl group of the incoming styrene. The enantioselectivity is due to the interaction between the same group and the phenyl substituent in the oxazoline ring, an interaction present in the transition states leading to the minor products. When a solvent with a low dielectric constant is used with the clay-supported catalyst, the cationic complex forms a tighter ion pair with the anionic surface, and the steric effect of the latter increases. Under these conditions the steric effect of the support surface on the incoming alkene should be considered (Scheme 14). The transition state lacking this steric interaction turns to be the most stable under these conditions, leading to the major product observed.

Supported ionic-liquid films (SILF) opens a new way to use this surface effects has been recently described for the cyclopropanation reactions using PhBox–copper catalysts [41]. In this work [bmim][$PF_6$] was supported on different clays, using decreasing amounts of IL to reduce the thickness of the film. With a small amount of IL the confinement effect, a *cis*-preference and a reversal in the absolute configuration of the major *cis*-cyclopropane are observed, pointing to a partial cation exchange of the catalytic complex, similar to that previously reported (Scheme 15).

A way to take advantage of the presence of the surface is to design tailored ligands for electrostatic immobilization that can be able to approach the surface in a more efficient way. A new family of Box ligands lacking of $C_2$-symmetry have been designed, synthesized [42] and immobilized. The study of those catalysts in cyclopropanation reactions tries to rationalize the surface effect.

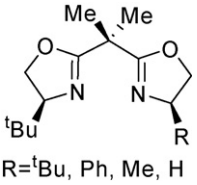



**Scheme 15.** Supported ionic liquid phase.




R= $^t$Bu, Ph, Indanyl

**Scheme 16.** Ligands lacking $C_2$-symmetry.




**Scheme 17.** Ligands lacking $C_2$-symmetric, tuning substituent volume.

Obviously the use of ligands lacking substituents in an oxazoline ring, does not lead to good enantioselectivities in homogeneous phase. But when immobilized, those ligands are able to approach the surface in such a way that *trans*/*cis* selectivities up to 9/91 with enantioselectivities for the major *cis*-cyclopropanes up to 48% are obtained [43] (Scheme 16).

The effect of tuning the volume of one of the substituents reveals how the proximity to the surface of the complex leads to the reversal in *trans*/*cis* and enantioslectivities. When decreasing R volume (R = $^t$Bu > Ph > Me > H, Scheme 17) *trans*/*cis* selectivities diminished in homogeneous phase from 72/29 to 68/32 [44]. In heterogeneous phase the effect of the surface makes *cis*/*trans* selectivities increase from 58/42 (R = $^t$Bu, Scheme 17) to 85/15 (R = H, Scheme 17) and also reversal in enantioselectivities from 2% ee with R = $^t$Bu to −48% ee with R = H are observed.

The same study is carried out with azaBox–Cu complexes and the same behavior is observed.

This surface influence has been in fact observed also in other reactions. The improved enantioselectivity in C–H insertion, using PhBox–Cu complexes immobilized in laponite (Scheme 11), can be also ascribed to a surface effect, although in this case the absolute configuration of the major product is not reversed [34]. Recently we have observed a change in the direction of the enantioselection in a Mukaiyama aldol reaction promoted by a PhBox–Cu complex immobilized into laponite [45]. Although the absolute configuration of the major product under homogeneous and heterogeneous conditions is being determined, the change is seen by the changes in the major peak in chiral HPLC.

These results show how the supports, coupled with a suitable ligand and immobilization strategy, can de used to control the stereochemical results of the reaction, leading to results complementary to those reached in solution.

## 5. Conclusions

In this revision we have tried to show that prejudices are not the best way to face chiral immobilized catalysis, the results presented allow reaching some "anti-dogma" conclusions:

- The heterogeneous catalysts may be better, both in activity and selectivity, than their homogeneous counterparts.
- The best immobilized ligand may not be the same as in solution, depending on the catalytic reaction and the immobilization method.
- The heterogeneous catalysts may give rise to products different from those obtained in solution thanks to the support effect.

To finish, non-new but frequently forgotten evidence: Combining experiments, characterization, mechanistic studies and molecular modelling is a fruitful strategy to understand the immobilized systems, as it happens with homogenous catalysts.

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