Effect of support properties on the performance of silica-supported bis(oxazoline)-copper chiral complexes

Fatma Fakhfakh,*‡ Leila Baraket,‡ Abdelhamid Ghorbel,‡ José M. Fraile,† Clara I. Herrerías,†
José A. Mayoral†

‡ Laboratoire de Chimie des Matériaux et Catalyse, Département de Chimie, Faculté des Sciences de Tunis, Campus universitaire, 2092 El Manar Tunis (Tunisie)
† Departamento de Química Orgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza - C.S.I.C., E-50009 Zaragoza (Spain)

E-mail: fatma.fakhfakh@gmail.com
Tel: +21698907543

Abstract

Mesoporous silica materials with different textural properties have been prepared by sol-gel synthesis under mild acidic conditions, and used as supports for chiral IndaBox ligand. After complexation with copper, these solids are catalysts for cyclopropanation reactions. Enantioselectivities in the range of 52-57% e.e. for cis cyclopropanes and 42-48% e.e. for trans cyclopropanes are obtained without any effect of the textural properties. However, these properties show an important effect on the activity and mainly on the recyclability of the catalyst. In contrast with the expected effect, solids with very large pores but low surface area lead to a significant deactivation upon recovery, whereas solids with highly developed surface area lead to the best overall results.

Keywords: immobilized catalysts; enantioselective catalysts; textural properties; mesoporous materials
1 Introduction

Organically modified silicas are interesting materials for various applications, as they combine the properties of the organic functional group with the high stability of silica. This kind of materials is very attractive for asymmetric catalysis due to the well-developed textural properties, high porosity and surface area, which should favor the accessibility to the active sites. Besides, these catalysts can be easily recycled and reused. Chiral bis(oxazoline)-metal complexes [1,2] are among the most widely studied catalysts regarding immobilization onto different supports and by different methods [3-6]. Anchoring through covalent bonds has been the most used method to immobilize bis(oxazoline) ligands on silica materials [7-13]. However, when covalent immobilization of this kind of catalysts on silica materials is achieved, the enantioselectivity results are in general worse than those obtained with the analogous homogeneous catalysts, and the optimization of this type of immobilization still remains a challenge.

Amorphous silica was used as support in the first examples of bis(oxazoline)-copper complexes immobilization described in the literature, using either thioether [14] or carbamate [15] linkers. In the first case, the immobilized complexes were not able to reproduce the high enantioselectivity obtained with the homogeneous analogues in cyclopropanation reactions. In the second one, the same effect was observed in Diels-Alder reactions, but enantioselectivity was improved by protecting the residual silanol groups by silanization with N-trimethylsilylimidazole. The role of silanols was demonstrated by the correlation between the number of free silanols and the enantioselectivity obtained with the supported catalyst [16]. The problems encountered for cyclopropanation with silica-supported catalysts seemed to be general, either in the case of immobilization of other types of complexes, such as pybox-Ru [17], or using other supports such as MCM-41, MCM-48, SBA-15, and mesocellular foam silica (MCF) [18], with bis(oxazoline) either covalently bound to the support through an alkyl
linker or simply by the presence of the support in a homogeneous reaction. The results were again improved by silanization of free silanols, with optimal yields in the case of MCF, both in cyclopropanation [19] and in Diels-Alder reactions [20]. The silica support can act as a catalyst itself and as ligand for copper, in both cases leading to non-enantioselective catalytic processes. This has been shown in the case of Diels-Alder reactions, minimization of these effects are required for an efficient catalytic process [21]. Finally, synthesis of the hybrid silica using tetraethoxysilane and a trialkoxysilane-functionalized bis(oxazoline) is another possible immobilization strategy, which has been applied with only moderate results [22].

Herein, we report the use of mesoporous silica materials, prepared by sol-gel without any template, as supports for immobilization of bis(oxazoline) ligands by anchoring, and the effect of the textural properties on the performance of the cyclopropanation reaction between styrene and ethyl diazoacetate.

2 Experimental

2.1 Synthesis of mesoporous materials (general procedure)

To a solution of tetraethoxysilane (TEOS, 9.1 ml, 40 mmol) in 20 ml of propanol 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:H2O:acid = 1:6.5:6:0.1. The resulting solution was stirred at the same temperature until gelification, and for an additional period of 24 h. The resulting product was transferred into Teflon-lined autoclave to be aged at 120 °C for 24 h, and finally it was dried at 120 °C for 24h in an oven.

2.2 Synthesis of the chiral catalysts

2,2’-Methylenebis[(3aR,8aS)-3a,8a-dihydro-8H-indeno[1,2-d]oxazole] (IndaBox) was functionalized by hydroxymethylation and reaction with 3-isocyanatopropyltriethoxysilane
following the method described by Rechavi and Lemaire [23]. The corresponding dried silica support (500 mg) was added to a solution of functionalized indaBox (150 mg, 0.17 mmol) in anhydrous toluene (5 mL) and the resulting suspension was heated under reflux for 48 h 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). The solid was filtered, washed with methanol and dried under vacuum.

2.3 Characterization

Nitrogen physisorption experiments were performed at 77K on an ASAP 2000 apparatus. The surface area was calculated using the BET method. The pore size distribution was obtained from the desorption branch of isotherms using the BJH method. ¹³C-CP-MAS-NMR spectra were recorded at 100.62 MHz 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. FTIR spectra were taken on a Nicolet Avatar FTIR from self-supported wafers treated under vacuum (< 10⁻⁴ Torr) at 50°C for 2 h. Copper analysis was carried out on a Perkin-Elmer Plasma Emission spectrometer.

2.4 Cyclopropanation reactions

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 [24]. After total conversion of diazoacetate, a second portion was slowly added in the same way. After total conversion of diazoacetate (typically 96 h), the catalyst was filtered off and washed with dichloromethane (5
mL). A third portion of diazoacetate was added to this solution to confirm the lack of catalytic activity. The solid was washed with additional dichloromethane, dried under vacuum and reused under the same conditions.

3 Results and discussion

3.1 Synthesis of mesoporous silica supports

Mesoporous silica materials were prepared by sol-gel method in propanol with a small amount of a carboxylic acid as catalyst (n_{acid}/n_{TEOS} = 0.1) without using any template [25]. Merck60 silica (M60) was used as model for a commercially available amorphous silica. The textural properties (Table 1) were determined from the N$_2$ adsorption-desorption isotherms (Figure 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 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). As can be seen in Figure 1, the hysteresis loop is broad and occurs at high relative pressure values (0.7-0.95). When acetic acid is substituted by propionic acid (material S-3), the N$_2$ isotherm of the resulting material shows a sharp adsorption step at higher relative pressure values (0.89-0.98), and the H1 hysteresis loop is very narrow. This behavior suggests the formation of uniform and large cylindrical pores. This material 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. In comparison with those solids prepared by sol-gel, Merck60 silica shows porosity values between S-1 and S-2, with lower surface area.

3.2 Synthesis and characterization of the chiral catalysts

IndaBox was functionalized with two triethoxysilane groups through carbamate linkers following the method described by Rechavi and Lemaire [23], consisting in a hydroxymethylation step with formaldehyde and subsequent reaction with 3-isocyanatopropyltriethoxysilane (Figure 2). This functionalized ligand was anchored onto the different silica supports. The effect of silanization was tested in the case of M60 silica, using N-trimethylsilylimidazole as silylating agent after IndaBox anchoring.

The elemental analysis is not a suitable method to get information about the presence of ligand on these solids, since the crude modified ligand including isocyanate molecules was immobilized without any further purification. However, these analyses were carried out in order to study the variation of C and N content between the fresh and the recovered catalysts (Table 3). In any case it can be seen that in the fresh catalysts the C/N and N/Cu ratios are always higher than the theoretical values, 7.75 and 4 respectively, showing the presence of grafted species different from the ligand, and the complexation of only a part of the immobilized ligand, probably due to lack of accessibility of some sites.

The immobilized chiral ligand was characterized by $^{13}$C-CP-MAS-NMR and FTIR spectroscopies. FTIR spectra (Figure 3) reveals the presence of a band at 1640-1650 cm$^{-1}$, characteristic of the C=N bond of the oxazoline ring, together with the skeletal bands in the 1300-1600 cm$^{-1}$ range. The bands corresponding to the aliphatic C-H bonds of both the ligand and the linker appear at 2800-3000 cm$^{-1}$. The C-H bonds of the aromatic groups present bands at 3050 cm$^{-1}$, but too weak to be detectable in the case of supported ligands due to the overlapping with the very broad band at 3000-3700 cm$^{-1}$ corresponding to hydrogen bonded silanol groups.
In the case of $^{13}$C-CP-MAS-NMR spectra (Figure 4) the most important signals of both the chiral IndaBox ligand and the linker are visible and assigned. However the spinning side bands of the aromatic carbons make difficult to detect some of the signals, such as those corresponding to the C=O and C=N groups, at around 160 ppm. These bands were detected by application of the toss (total suppression of spinning side bands) pulse sequence. Signals corresponding to remaining ethoxide groups are also clearly visible in some of the solids.

After complexation of the chiral materials by Cu(OTf)$_2$, copper loading was determined, as well as the textural properties of the final catalysts (Table 2). As can be seen the immobilization of the chiral indaBox 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. A similar result is obtained in the case of Merck60 silica, with a significant loss in surface area and pore volume. Copper loading on mesoporous materials prepared by sol-gel varies from 0.057 to 0.091 mmol/g, but the copper surface density is similar in all the cases, with values between 0.13 and 0.17 $\mu$mol/m$^2$. This result seems to indicate that the amounts of anchored ligand and complexed copper do not depend on the textural properties of the material. Probably the key factor is the surface density of silanol groups, which must be similar in all the solids prepared by analogous methods. The situation is completely different in the rest of solids, prepared by different procedures. The use of Merck60 silica leads to much lower copper content and surface density. Following the silanization method described by Rechavi and Lemaire [23] a more hydrophobic hybrid solid was obtained (M60$_\text{TMS}$-ind-Cu). In this case the copper loading is slightly higher, which together with the reduced surface area makes the copper surface density similar to that obtained in the case of mesoporous materials. Finally, a hybrid material prepared by sol-gel from the functionalized indaBox under basic conditions [22] showed a much lower surface area, corresponding probably to a non-porous solid, and hence the copper surface density is much higher than in the rest of solids.
3.3 Results in cyclopropanation reactions

The immobilized copper (II) complexes were tested as catalysts in the benchmark cyclopropanation reaction between styrene and ethyl diazoacetate represented in Figure 5. The catalytic results are gathered in table 4.

The homogeneous indaBox(Me₂)-Cu complex leads to moderately high enantioselectivities for both cis (81% e.e.) and trans (85% e.e.) isomers [26]. The hybrid material prepared by sol-gel in basic medium (Hyb-ind-Cu) was not able to reproduce these values, with enantiomeric excess of 51% and 43% for cis and trans cyclopropanes [22]. Moreover the catalyst was not recoverable with an important drop in enantioselectivity and catalytic activity. The immobilization on Merck60 silica was not efficient, and silanization showed a positive effect on activity, in agreement with previous results [19], but not on the enantioselectivity. On the contrary, the catalysts immobilized on the mesoporous materials S-1 to S-3 exhibit enantioselectivities similar to those obtained with the hybrid material, 52-57% e.e. for cis cyclopropanes, 42-48% e.e. for trans cyclopropanes, showing that anchoring is also suitable for the preparation of this type of catalysts. However, the nature of the support plays a key role on the results. Regarding yields, some significant differences can be observed, with catalytic activity in the order S-1-ind-Cu > S-2-ind-Cu > S-3-ind-Cu. The same trend is observed, with more significant differences, in the second run, even regarding enantioselectivity. The different nature of the silica surface, with different types of silanol groups and acidity, may account for the different behavior of the supports. In fact the FTIR spectra of M60-ind (Figure 3e) shows some bands at 1735 and 1750 cm⁻¹, typical zone for C=O bonds and that might come from a partial hydrolysis of the chiral indaBox ligand in the anchoring process. This problem is not present in the case of supports prepared by sol-gel, even under acidic conditions, as well as it was not detected in the hybrid material, prepared under basic conditions [22].
In the case of solids prepared by sol-gel, the textural properties affect the catalytic results (Figure 6). In the first reaction, only minor variations of enantioselectivity are observed in the whole range of surface area (40-600 m$^2$/g). This seems to indicate that the presence of carbamate groups on the linkers have a negative role on the enantioselectivity, either by additional complexation of copper or by hindrance in the correct conformation of the Box-Cu complex. The same effect has been already observed in the case of other Box ligands substituted in the central methylene bridge with bulky benzyl groups [27]. On the contrary, yield increases steadily with surface area with no effect of the pore size, showing that the smaller pores (35 Å diameter) are large enough to accommodate the starting complex and the incoming reagents. This effect is more significant in the second run. Only solids with surface area larger than 400 m$^2$/g lead to significant yields and enantioselectivity drops when surface area is lower. The importance of surface area contrasts with the role of porosity. It seems that larger pores, that presumably would allow a better accessibility to the catalytic sites, are detrimental for catalyst recycling. Several deactivation processes have been proposed in the literature for box-Cu complexes, including the coordination of by-products (diethyl maleate and fumarate) [24], decomplexation of copper [28], and formation of diazoacetate polymers [29]. In order to shed some light on the deactivation process, elemental and copper analyses of the recovered catalysts were carried out (Table 3). In all cases the copper content of the catalysts after cyclopropanation is lower than that of the fresh one. However, no activity was detected in the filtrate of the reaction, showing that copper is leached in inactive form. At the same time, an increase in the carbon content on the recovered solids S-1-ind-Cu and S-2-ind-Cu can be observed whereas the nitrogen content remains almost constant. These values may be related to the presence of diazoacetate by-products, either dimers (maleate and fumarate) or polymers, formed after the release of molecules of nitrogen. The detection of these products is not easy since NMR spectroscopy is precluded due to the paramagnetic character of Cu(II), nevertheless main FTIR bands (C=O) have been detected in other immobilized
bis(oxazoline)-copper complexes [24]. The better recoverability of S-1-ind-Cu and S-2-ind-
Cu with smaller pores and larger surface area seems to indicate that the most probable
deactivation process is the surface coverage by polymeric by-products instead of pore
blocking. In addition, the contribution of the loss of copper to the deactivation of the catalysts
must be also considered and even in a larger extent for the case of S-3-ind-Cu, whose carbon
content does not increase in the used catalyst. In any case the role of copper complexation
with diazoacetate by-products seems clear, both in poisoning the active sites and in the
leaching of inactive complexed species, with also a possible role of deposition of polymeric
materials, as shown by the large increase of carbon content in some used catalysts.

4 Conclusions

IndaBox functionalized with triethoxysilane containing linkers can be efficiently
immobilized by covalent anchoring on silica supports, prepared by sol-gel synthesis under
mild acidic conditions, with different textural (surface area and porosity) properties. The
corresponding copper complexes are catalysts for cyclopropanation reactions with reduced
enantioselectivity with respect to that obtained in solution, but probably due to the additional
substitution in the methylene bridge of the ligand, given the consistent results with the
different supports. Commercially available silica is not suitable for this type of
immobilization, probably due to its acidity. Textural properties of the solid have an influence
on yield and on the recoverability of the catalysts. The best results are obtained with solids
possessing highly developed surface area, whereas very large pores (>50 Å diameter) do not
seem to be useful for this purpose and the lower surface area leads to an important
deactivation for both activity and enantioselectivity.
Acknowledgements

This work was made possible by the generous financial support of the AECI (Agencia Española de Cooperación Internacional, projects A/5081/06 and A/8491/07), and Ministerio de Ciencia e Innovación (projects CTQ2008-05138 and Consolider Ingenio CSD2006-0003).

References

Table 1 Synthesis conditions and textural properties of silica materials

<table>
<thead>
<tr>
<th>Solid</th>
<th>Catalyst</th>
<th>T (°C)</th>
<th>$S_{\text{BET}}$ (m²/g)</th>
<th>D(Å)</th>
<th>$V_{\text{mic}}$ (cm³/g)</th>
<th>$V_p$(cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-1</td>
<td>CH₃COOH</td>
<td>35</td>
<td>876</td>
<td>35</td>
<td>0</td>
<td>0.77</td>
</tr>
<tr>
<td>S-2</td>
<td>CH₃COOH</td>
<td>60</td>
<td>609</td>
<td>120</td>
<td>0</td>
<td>1.12</td>
</tr>
<tr>
<td>S-3</td>
<td>C₂H₅COOH</td>
<td>60</td>
<td>479</td>
<td>289</td>
<td>0</td>
<td>1.76</td>
</tr>
<tr>
<td>M60</td>
<td>-</td>
<td>-</td>
<td>512</td>
<td>50</td>
<td>-</td>
<td>0.82</td>
</tr>
</tbody>
</table>

$S_{\text{BET}}$ = surface area (m²/g), $V_{\text{mic}}$ = microporous volume calculated by t-plot method (cm³/g), $V_p$ = total pore volume at P/P° = 0.98 (cm³/g), D(Å) = maximum of the pore size distribution.
Table 2 Textural properties and elemental analysis of the catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(S_{\text{BET}}) (m²/g)</th>
<th>D (Å)</th>
<th>(V_p) (cm³/g)</th>
<th>Cu (mmol/g)</th>
<th>Cu (µmol/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-1-ind-Cu</td>
<td>568</td>
<td>35</td>
<td>0.57</td>
<td>0.091</td>
<td>0.16</td>
</tr>
<tr>
<td>S-2-ind-Cu</td>
<td>418</td>
<td>120</td>
<td>0.92</td>
<td>0.057</td>
<td>0.13</td>
</tr>
<tr>
<td>S-3-ind-Cu</td>
<td>340</td>
<td>278</td>
<td>1.15</td>
<td>0.061</td>
<td>0.17</td>
</tr>
<tr>
<td>Hyb-ind-Cu(^b)</td>
<td>40</td>
<td>n.d.(^c)</td>
<td>0.14</td>
<td>0.076</td>
<td>1.90</td>
</tr>
<tr>
<td>M60-ind-Cu</td>
<td>337</td>
<td>50</td>
<td>0.52</td>
<td>0.029</td>
<td>0.09</td>
</tr>
<tr>
<td>M60(\text{TMS})-ind-Cu</td>
<td>290</td>
<td>50</td>
<td>0.41</td>
<td>0.037</td>
<td>0.13</td>
</tr>
</tbody>
</table>

\(^a\) \(S_{\text{BET}}\) = surface area (m²/g), \(V_p\) = total pore volume at P/P° = 0.98 (cm³/g), D (Å) maximum of the pore size distribution. \(^b\) Data corresponding to a hybrid material prepared by sol-gel from the modified indaBox (ref. 22). \(^c\) No maximum was observed in the distribution.

Table 3 Elemental and copper analyses of fresh and recovered catalysts

14
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Fresh catalyst</th>
<th>Recovered catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu (mmol/g)</td>
<td>N (mmol/g)</td>
</tr>
<tr>
<td>S-1-ind-Cu</td>
<td>0.091</td>
<td>0.78</td>
</tr>
<tr>
<td>S-2-ind-Cu</td>
<td>0.057</td>
<td>0.76</td>
</tr>
<tr>
<td>S-3-ind-Cu</td>
<td>0.061</td>
<td>0.72</td>
</tr>
<tr>
<td>Hyb-ind-Cu&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.076</td>
<td>1.29</td>
</tr>
<tr>
<td>M60-ind-Cu</td>
<td>0.029</td>
<td>0.91</td>
</tr>
<tr>
<td>M60&lt;sub&gt;TMS&lt;/sub&gt;-ind-Cu&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.037</td>
<td>0.91</td>
</tr>
</tbody>
</table>

<sup>a</sup> Data corresponding to a hybrid material prepared by sol-gel from the modified indaBox (ref. 22).<sup>b</sup> Analyses of N and C were carried out before protection with trimethylsilylimidazole. n.a. = not available.
Table 4 Results of the catalyzed cyclopropanation reactions\textsuperscript{a}

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Run</th>
<th>Yield (%)</th>
<th>trans/cis</th>
<th>%e.e. cis\textsuperscript{b}</th>
<th>%e.e. trans\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>IndaBox(Me\textsubscript{2})-Cu\textsuperscript{c}</td>
<td>1</td>
<td>52</td>
<td>60/40</td>
<td>81</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3</td>
<td>58/42</td>
<td>51</td>
<td>43</td>
</tr>
<tr>
<td>Hyb-ind-Cu\textsuperscript{d}</td>
<td>1</td>
<td>31</td>
<td>59/41</td>
<td>14</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3</td>
<td>59/41</td>
<td>14</td>
<td>9</td>
</tr>
<tr>
<td>M60-ind-Cu</td>
<td>1</td>
<td>2</td>
<td>68/32</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>M60\textsubscript{TMS}-ind-Cu</td>
<td>1</td>
<td>43</td>
<td>66/34</td>
<td>9</td>
<td>6</td>
</tr>
<tr>
<td>S-1-ind-Cu</td>
<td>1</td>
<td>45</td>
<td>56/44</td>
<td>52</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>39</td>
<td>57/43</td>
<td>46</td>
<td>35</td>
</tr>
<tr>
<td>S-2-ind-Cu</td>
<td>1</td>
<td>37</td>
<td>57/43</td>
<td>52</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>20</td>
<td>58/42</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td>S-3-ind-Cu</td>
<td>1</td>
<td>33</td>
<td>56/44</td>
<td>57</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>58/42</td>
<td>37</td>
<td>29</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reaction conditions: Cu = 2%, styrene =1.5mmol, dichloromethane (2.7 ml), slow addition (syringe pump, 2 h) of ethyl diazoacetate (1.5mmol), room temperature. Results determined by GC. \textsuperscript{b} Major isomers: trans-S and cis-S. \textsuperscript{c} Results from ref. 25. \textsuperscript{d} Results from ref. 22.
Figure 1 (A) N$_2$ adsorption-desorption isotherms and (B) pore size distribution of the materials used as supports.
Figure 2 Immobilization of the chiral IndaBox ligand.
Figure 3  FTIR spectra of: (a) Hydroxymethylated indaBox, (b) S-1-ind, (c) S-2-ind, (d) S-3-ind, and (e) M60-ind.
Figure 4 $^{13}$C-CP-MAS-NMR spectra of: (a) M60-ind (with toss), and (b) S-1-ind.
Figure 5 Asymmetric cyclopropanation of styrene with ethyl diazoacetate.
Figure 6 Relationship between surface area and catalytic performance: yield (squares), % e.e. *cis* (diamonds), and % e.e. *trans* (triangles) in the first run (filled symbols) and in the second one (empty symbols).