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Synthesis of Organic−Inorganic Hybrid Solids with Copper Complex Framework and Their Catalytic Activity for the *S*-Arylation and the Azide−Alkyne Cycloaddition Reactions

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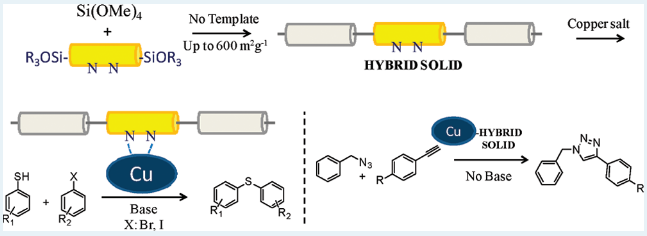
S *Supporting Information*

ABSTRACT: Two different diamines, namely, Tröger base and dimethylethylene diamine (DMEDA) functionalized with disilane groups, have been condensed with silica precursors to form mesoporous hybrid organic−inorganic materials. After introduction of copper, the Cu-diamine complexes are produced. These hybrid solids have been fully characterized and are active catalysts for the *S*-arylation of aryl iodides and bromides with thiophenols and disulfides. Additionally, the hybrids show catalytic activity for the cycloaddition reaction between azides and phenylacetylenes. The reaction conditions determine the recovery and reuse of the solid.



KEYWORDS: hybrid solid, copper, catalysis, S-arylation, Tröger Base

INTRODUCTION

Copper-diamine complexes are well-known catalytic species for Ullmann-type reactions[1] as, for instance, the coupling of aryl halides with thiols (*S*-arylation),[2] alcohols (*O*-arylation),[3] amides (amidation),[4] and phosphines (phosphination).[5] Considering the toxicity of amines, the incorporation of these complexes onto solids would be of interest to easily separate the catalyst after reaction.[6−11]

The development of molecularly designed materials can help to bridge the gap between homogeneous and heterogeneous catalysis,[12] and among these materials, porous hybrid solids represent a class of flexible and robust scaffolds for catalysis.[13,6] The possibility to combine into the same framework covalently linked organic and inorganic fragments opens the door to generate different multifunctional materials with potential catalytic applications.[14,15] These solids exhibit the advantages of conventional inorganic materials, such as high hydrothermal, structural, and mechanical stability, together with the properties of organic polymers, such as flexibility and functionality. In any case, versatile materials could in principle be prepared, lodging different active sites homogeneously distributed and stabilized in the structure.[16]

The use of suitable organic−inorganic precursors, such as bridged silsesquioxanes (also called disilanes) whose general formula is $(R'O)_3Si\text{-}R\text{-}Si(OR')_3$, has allowed the preparation of different organosiliceous materials where the organic and inorganic units are combined within the walls of a porous network.[17] Following this approach, in the past decade, numerous periodic mesoporous materials (PMOs) have been prepared by templating in the presence of surfactants, and different active sites (acid, basic, redox, or chiral) or combination of them were introduced into their framework.[18−20] This strategy has implied that the chemistry from the walls achieves more relevance than the traditional chemistry from the cavities carried out when the mesoporous materials are used as catalysts.[21,22]

Sol−gel processes are an alternative to generate interesting hybrid materials from disilanes, avoiding the use of structural directing agents (SDAs) while working under mild synthesis conditions.[23] Though it is true that the long-order organization is lost when working in the absence of SDAs, this "a priori" disadvantage could be compensated with the higher structural flexibility showed by these networks.[24] This peculiarity combined with the possibility to introduce structurally different functional groups which are homogenously distributed, isolated, stabilized, and separated at controlled distance into the framework could convert these hybrid materials into excellent multifunctional catalysts.[25] Moreover, the post-synthesis alterations carried out in the functional organic groups contained within the

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Scheme 1. Ullmann *S*-Arylation of Aryl Halides

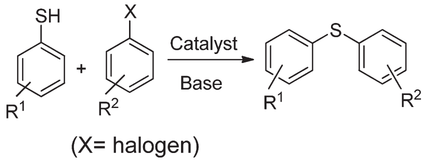
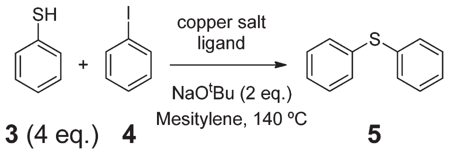


Table 1. Results for the *S*-Arylation of Thiophenol 3 with Iodobenzene 4 with Different Copper Salts and Diamines



entry	copper salt (mol %)	diamine (mol %)	ratio diamine/Cu	time (h)	**5** (%)[a]
1	CuCl (1)		∞	6	51
2	$CuCl_2$ (1)		∞	6	35
3	CuCl (1)	**1** (1)	1	6	91
4	CuCl (1)	**1** (2)	1	6	69
5	CuCl (1)	**1** (1)	1	18	99
6	CuCl (1)	**1** (2)	2	18	98
7	$CuCl_2$ (1)	**1** (1)	1	6	86
8	$CuCl_2$ (1)	**1** (1)	1	18	99
9	$CuCl_2$ (1)	**1** (2)	2	18	47
10	$CuCl_2$ (1)	**1** (6)	6	18	>99
11	CuCl (1)	**2** (2)	2	6	47
12	$CuCl_2$ (1)	**2** (2)	2	6	39
13	$CuCl_2$ (2)	**2** (4)	2	6	12
14	$CuCl_2$ (0.5)	**2** (1)	2	6	30
15	$CuCl_2$ (0.25)	**2** (0.5)	2	6	36
16	CuCl (1)	**2** (1)	1	6	53
17	$CuCl_2$ (1)	**2** (1)	1	6	60
18	$CuCl_2$ (1)	**2** (3)	3	6	88
19	$CuCl_2$ (1)	**2** (6)	6	6	53
20	$CuCl_2$ (1)	**2** (20)	20	6	52

[a] GC yield.

network could increase their catalytic possibilities. These modifications could also be associated to incorporation of stabilized metallic species by controlled interaction with the organic functional builders contained into the framework, producing finally catalysts with high activity for specific processes.[26]

This approach can be useful for heterogenizing different chelating groups, such as diamines, into the framework of hybrid porous materials which would facilitate the optimal stabilization of metallic species by interaction with promoter salts, generating finally effective heterogeneous metal-hybrid catalysts with potential applications in transition metal catalyzed cross-coupling reactions.

The Ullmann *S*-arylation[1,27,28] reaction involves the formation of biaryl sulfides from the corresponding aryl sulfides and aryl halides, in the presence of a metal catalyst, typically palladium[29] or copper[2,30−40] complexes, and a strong base in stoichiometric amount (Scheme 1). The diaryl thioethers thus formed are present in biologically active molecules and polymeric materials,[37] and copper is a preferred catalyst for environmental and economic reasons. Regarding heterogeneous catalysis, it has been reported that copper on inorganic supports can act as recyclable catalyst for the *S*-arylation of aryl iodides under microwave radiation (on hexagonal microporous silica)[38] and of aryl bromides (on alumina).[39] However, an extremely efficient copper-dimethylethylene diamine (DMEDA) has been recently reported and, to our knowledge, is the most efficient homogeneous catalytic system for the *S*-arylation.[41−43] In this case, the presence of a high excess of DMEDA as ligand (∼200 equiv with respect to copper, in optimum conditions) seems to be necessary.[42,43] This also occurs in other copper-diamine catalytic systems for the *S*-arylation, in which 4[32] and 46[34] equiv of diamine are employed. While it is true that the excess of ligand accelerates the process (ligand-accelerated catalysis)[42] and also prevents copper agglomeration,[34,42,43] it is also true that it would be desirable to avoid the use of large excess of ligands.

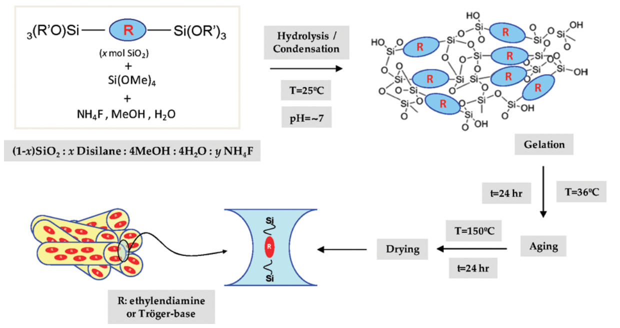
In the present work, we have synthesized different metal-hybrid catalysts following a procedure to prepare first hybrid porous organic−inorganic materials from bridged silsesquioxanes, that contain different chelating groups such as the ethylendiamine derivative (**6**) and the Tröger-base dervative (**7**),[45] and second, to generate the hybrid metallic complexes by ionic interaction of different metal salts with the chelating diamines.[46,47] After an extensive characterization to ascertain that the desired materials were indeed obtained, these materials have been used as solid catalysts for the *S*-arylation of aryl halides with thiophenols. We also show that the hybrid materials catalyze the azide-phenylacetylene cycloaddition.

■ RESULTS AND DISCUSSION

Homogeneous Catalysis. Typical catalytic systems to perform the *S*-arylation of aryl halides with thiophenol derivatives involve: a copper (I or II) salt in catalytic amount, the diamine ligand (excess 4−200 equiv), and a strong base (MO^{t}Bu, M = Li or Na; or the diamine) in stoichiometric amounts, usually in polar solvents (H_2O, DMSO, toluene) at elevated temperatures (80−130 °C). For the hybrid catalysts, the Cu/diamine (DMEDA **1** or Tröger base **2**) ratio will be ∼1:1 and solvents that do not facilitate leaching (such as methylbenzenes) must be employed. Thus, the *S*-arylation between thiophenol **3** and iodobenzene **4** was first studied in mesitylene with homogeneous metal complexes in low-coordinating form (Table 1).

Copper salts alone are able to perform the transformation in moderate yields at this catalyst loading (entries 1−2).[30] However, diamine **1** (1 equiv) is required to complete the reaction (entries 3, 5, 7−8). Curiously, when 2 equiv of **1** is added, a significant decrease in the yield of **5** is observed, regardless of the oxidation state of copper (entries 4 and 9). If the reaction time is increased (entry 6) or an excess of **2** is used (6 equiv, entry 10), the quantitative yield of **5** is restored. These results confirm[42,43] that the ratio copper/DMEDA plays a dramatic role on the catalytic activity, suggesting that some of the forms of the copper complexes are less active as catalysts for the reaction. It also explains the typical use of high excess of diamine in the literature,[42,43] since, apparently, generation of 1:2 or mixed complexes copper(II)-diamine by addition of 2 equiv of **1** leads to inactive species, either by the intrinsic nature of the catalyst or by fast agglomeration.[48] This intriguing effect also occurs for the

Scheme 2. Sol-Gel Procedure Employed to Obtain the Hybrid Catalysts, and Artistic Representation of Non-Ordered Organic-Inorganic Materials Obtained



Tröger base **2**: when 2 equiv was added to the reaction mixture (compare entries 1−2 to 11−12) the ligand was found to be inactive, and using different catalyst loadings did not improve the results (entries 13−15). In particular, an increase in the catalyst amount leads to a significant decrease in the yield of **5** (entry 13), which is than when $CuCl_2$ is used alone (entry 2). This effect is in connection with previous observations on the importance of the catalyst concentration,[34,49] which ultimately controls the agglomeration rate. Anyway, the addition of 1 or 3 equiv of **2** to $CuCl_2$ improved twice and three times the yield of **5** (compare entries 2 and 17−18), this beneficial effect not being observed for CuCl (entry 16). Finally, in contrast, high excesses of **2** do not lead to better yields of **5** (entries 19−20). With these results in hand, we can conclude that **1** and **2** (1 or 3 equiv) are both good ligands for the Cu(I) or Cu(II)-catalyzed *S*-arylation of **3** and **4** under the reaction conditions indicated in Table 1. The way of coordination with the two ligands is distinct: the mono-, di-, and tridiamine complexes can be formed by ligation of both nitrogens of the diamine **1** to the Cu cation,[50] but this way of coordination is not expected for **2** since the four-membered ring is less favorable.[31,51,52] According to the literature, a linear ligation with one of the nitrogens should occur.[51] The good catalytic activity as ligand showed by the Tröger-base **2** fits the observations that configurationally fixed Cu-diamine complexes seems to be superior as catalysts and that the basicity of the amine does not play a role.[34]

Then, we proceed to prepare the heterogeneous counterparts of these catalytic systems. Given that the isolation of the active sites seems important to control the catalytic activity of the complex Cu-diamine for the *S*-arylation, the incorporation of them onto frameworks with well-defined and separated sites should give an additional advantage compared to the homogeneous system.

Synthesis of the Hybrid Solids. Different organic−inorganic porous materials employing TMOS and variable amounts of starting silica precursors which contain ethylendiamine (DA) and Tröger-base (TB) fragments were first obtained using a NH_4F-catalyzed sol−gel route at neutral pH in absence of structural directing agents (Scheme 2).

With this approach, it was possible to introduce structurally diamine groups which are covalently bonded to inorganic units of silica to obtain the materials denoted as DA and TB, respectively. Figure 1 shows the structure of bridged silsesquioxane precursors employed in this work. The gelification process is markedly influenced by the amount of fluoride anions introduced during the synthesis, being faster the gel formation, just a few seconds, when the content of NH_4F is higher. In all cases, the presence of diamine fragments in the synthesized hybrid materials was clearly confirmed by means of elemental analyses (Table 2). Taking into account that the sol−gel method employed during the materials preparation was performed in absence of SDA molecules, the presence of analyzed carbon and nitrogen is indicative of a potential incorporation of diamine moieties into the networks from specific disilanes. Additionally, the C/N experimental molar ratios for samples DA and TB are 4.4 and among 6.4−7.2, respectively, which are near to the theoretical ratios (C/N = 4 for ethylendiamine (**1**) and C/N = 6.8 for Tröger-base (**2**)). This fact would confirm that the integrity of structural organic fragments is preserved after the sol−gel process. From elemental analyses, it is possible to estimate the organic content of the hybrid materials, being around 23 wt % for solids containing ethylendiamine groups, and varying from ~4.0 wt % to ~35.0 wt % for hybrids when the Tröger-base amount was increased.

The thermogravimetrical analyses and the corresponding derivatives (TGAs and DTAs curves) for DA and TB materials (Supporting Information, Figure S1) allow evaluating not only the amount of diamine moieties incorporated but also their hydrothermal stability. Without considering the loss of weight assigned to hydration water, the organic contents calculated from TGAs are similar to the values obtained from the CHN elemental analyses (Table 2), confirming the presence of Tröger-base and ethylendiamine functions in the hybrids. From the DTA curves, it is possible to see that the Tröger-base units are initially decomposed

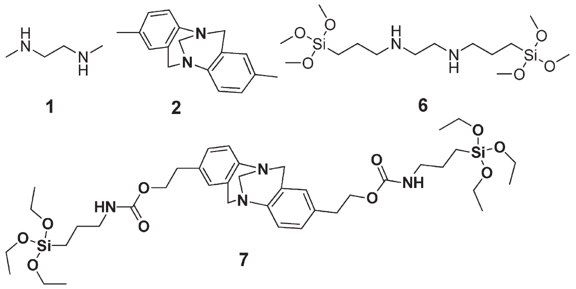


Figure 1. Structures for DMEDA (**1**), Tröger base (**2**) and the corresponding bridged silsesquioxanes used as organic−inorganic builders: bis(trimethoxysilylpropyl)ethylendiamine (**6**) and disilyl-Tröger base (**7**).

Table 2. Elemental Analyses and Organic Content of Hybrid Samples

sample[a]	%C	%N	C/N_{theor}	C/N_{exp}	% organic content[b]	% organic content[c]
DA-30-A	15.6	4.1	4.0	4.4	23.1	24.7
TB-1-A	2.2	0.4		6.4	3.9	4.2
TB-10-A	11.6	2.0		6.8	15.8	18.7
TB-10-B	12.2	2.1	6.8	6.7	16.7	17.4
TB-30-A	27.1	4.4		7.2	35.3	37.2
TB-30-B	27.7	4.8		6.7	34.7	36.4

[a] Samples denoted with (DA) or (TB) are prepared with diethylendiamine or Tröger-base precursors, respectively. The number 1, 10, or 30 correspond to percentage of SiO_2 mol introduced as disilane, and the character (A) or (B) is assigned in function if the samples are prepared using 3.13×10^{-3} or 4.70×10^{-3} of NH_4F, respectively. [b] Elemental Analysis. [c] Thermogravimetrical Analysis.

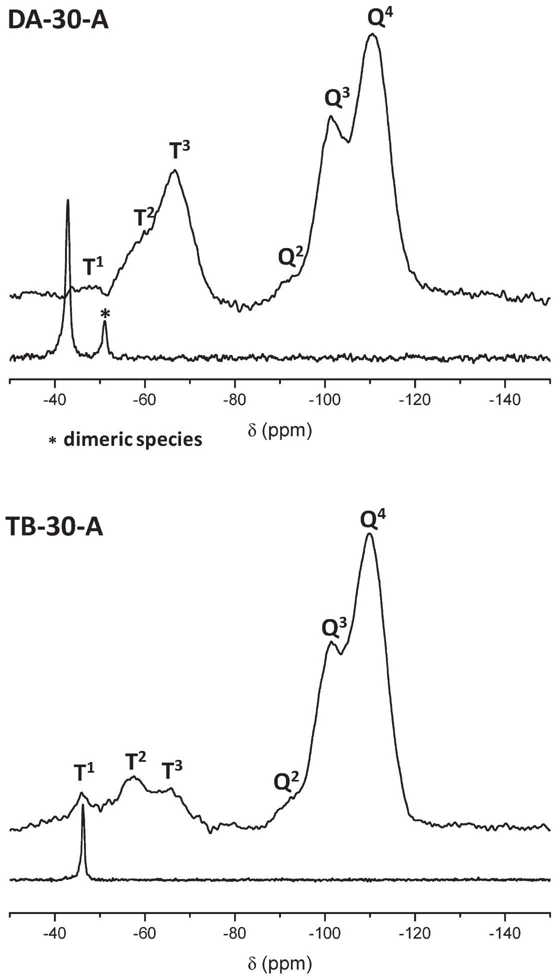


Figure 2. ^{29}Si BD/MAS NMR spectra of the samples containing structural organic fragments (top) and comparison with the respective pure disilanes (bottom). The hybrids were prepared using 3.13×10^{-3} mol of NH_4F during the synthesis.

around 300 °C, probably because of the lower stability of the tertiary amines included in the molecule, and followed by a last decomposition around 500 °C−600 °C corresponding to residual aromatic groups which normally present higher hydrothermal stability (Supporting Information, Figure S1b-d).

In the case of the ethylendiamine fragments, it is observed that the weight loss because of the decomposition of organic fragments occurs in only one step at 300 °C−400 °C (Supporting Information, Figure S1a). The higher robustness showed for the cycled tertiary amines together with the presence of aromatic rings in the molecule can explain the higher stability observed for the Tröger-base fragments.

Spectroscopic Results of the Hybrid Solids. The integrity of the diamine builders incorporated in the hybrid materials was confirmed from ^{13}C CP/MAS NMR spectra (Supporting Information, Figure S2). It was possible to observe in all cases that all carbon atoms from ethylendiamine (DA-30) and Tröger-base (TB-30) groups are unequivocably assigned in the ^{13}C NMR spectra (see the inset into the Supporting Information, Figure S2). This fact corroborates that diamine fragments remain intact as in the starting disilanes, probing the existence of Si-bonded species. The presence, in both cases, of bands corresponding to alkoxide groups present in the initial bridged silsesquioxanes confirms that the hydrolysis and polycondensation of terminal alkoxy groups was not complete during the sol−gel process.

Additionally, the ^{29}Si NMR results are necessary to corroborate unambiguously that the diamine fragments not only remain intact but they are also introduced covalently into the non-ordered porous network, linked to inorganic silica units. The ^{29}Si BD/MAS NMR spectra of DA-30 and TB-30 (Figure 2) show, in all cases, the presence of bands ranging from −50 ppm to −80 ppm which are characteristic to T-type silicon species containing a Si−C bond. Moreover, it is possible to appreciate in the spectra three bands assigned to T^1 ($C-Si(OH)_2(OSi)$), T^2 ($C-Si(OH)(OSi)_2$), and T^3 ($C-Si(OSi)_3$), which corroborate that ethylendiamine and Tröger-base groups are organosilicon species linked to inorganic silica units conforming the framework. The presence of three additional peaks at −92, −100, and −110 ppm corresponding to Q^2 ($Si(OH)_2(OSi)_2$), Q^3 ($Si(OH)(OSi)_3$), and Q^4 ($Si(OSi)_4$) units, respectively, can also be seen in the spectra (Figure 2) because of polymerization of silica units between them.

Figure 2 also shows the starting ^{29}Si NMR spectra of pure disilanes which exhibit only one peak of silicon atoms around −40 to −45 ppm. When these precursors are introduced into the framework of solids, the signal corresponding to silicon atoms bonded to diamine fragments is shifted to −50 to −80 ppm (Figure 2). However, in the case of TB-30, it is possible to observe the proximity between the signals assigned as T^1 and which correspond to pure disilane, suggesting that maybe this hybrid material could contain some Tröger-base molecules from non-condensed pure starting disilane which are occluded in the porous material.

The calculated integration of the T and Q signals from ^{29}Si BD/MAS NMR spectra (Figure 2) allows estimating the integrated intensity ratio of $T/(Q + T)$, and to evaluate the number of silicon atoms covalently bonded to diamine fragments. The results obtained show that approximately 27% and 17% of silicon atoms are functionalized by ethylendiamine and Tröger-base units, respectively. Considering that the maximal theoretical silicon functionalization corresponds to 30%, these values confirm that the effectiveness of the incorporation is higher when ethylendiamine is conforming the hybrids instead of the Tröger base.

Textural Properties of the Hybrid Solids. The type and amount of bridged silsesquioxanes, containing diamine fragments, employed as silica precursors, and the concentration of fluoride anions present during the sol−gel synthesis process are key variables to control the textural properties and pore distribution of the hybrid materials. As can be deduced from Table 3, the mesopore surface area is the most important contribution to the total surface area of the hybrid materials with an average pore diameter from 20 to 100 Å (see Figures 3 and Supporting Information, Figure S3). Specifically, the higher flexibility of ethylendiamine fragments compared with the rigidity of the Tröger-base (TB) implies that the DA materials with similar amount of organic builders than TB exhibit a larger surface area and free porous volume. It appears that the rigidity of the Tröger-base fragments does not facilitate the integration of organic species into the framework of the material. As a consequence of this, the surface area and porous volume strongly increases when the quantity of Tröger-base is lowered (see Table 3). Furthermore, the marked step observed in the isotherms of solids with flexible ethylendiamine groups (DA-30) or low content of organic in Tröger-base species (TB-1) shows that this type of non-ordered hybrid solids have a narrower pore size distribution than other

Table 3. Mean Textural Properties of Porous Hybrid Organic-Inorganic Materials

sample	surface area ($m^2\ g^{-1}$)	external surface ($m^2\ g^{-1}$)	micropore volume ($cm^3\ g^{-1}$)	total pore volume ($cm^3\ g^{-1}$)	mean pore diameter (Å)
DA-30-A	313	313	0.00	0.24	30
TB-1-A	594	594	0.00	0.45	20
TB-10-A	272	262	0.01	0.23	30
TB-10-B	197	197	0.00	0.20	30
TB-30-A	99	99	0.00	0.14	20−100
TB-30-B	3	3	0.00	0.00	

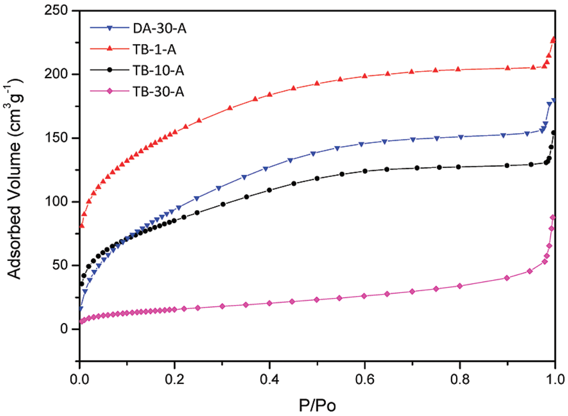


Figure 3. Nitrogen adsorption isotherms of hybrid samples prepared using 3.13×10^{-3} mol of NH_4F during the sol−gel route.

samples synthesized with higher amount of rigid organic linkers such as the Tröger base (TB-30), because of the difficulty to obtain well-structured and homogeneous materials in that case.

Additionally, it is also observed that the hybrids prepared with higher content of NH_4F catalyst during the sol−gel process (TB-10-B and TB-30-B) exhibit a more reduced porosity because gelification occurs too fast, in only few seconds, and the finally obtained porous organization was poorer and inhomogeneous.

Considering the results obtained from textural characterization, it is possible to conclude that the surface area and porosity of the hybrids are influenced not only by the type and nature of diamine builders incorporated into the framework but also by their flexibility, the organic content, and the concentration of mineralizer used in the sol−gel process.

Formation and Characterization of the Copper-Diamine Based Hybrids. The introduction of the metal into the solids was carried out by treating the different hybrid materials with a solution of the corresponding chloride salt, $CuCl_2$ or CuCl, in anhydrous acetonitrile at 60 °C for 24 h (Table 4).

ICP-AES analyses of the solids after filtration, exhaustive washings and drying showed that Cu(II) is incorporated when **6** is present in the solid but not when **6** is not present (compare entries 1 and 3). This result demonstrates that the silanol groups are not coordinating enough to retain the metal under the metal incorporation conditions, suggesting that Cu(II) is incorporated through coordination with the diamine groups. The molar ratio nitrogen/metal indicates 4 molecules of diamine per copper. Valorization with acid reveals that 40% of the total diamine groups are inaccessible. Therefore, taking into account the inherent rigidity of the solids and the possible persistence of the chloride anions, 1:1 and 1:2 metal/DMEDA complexes should be predominant. As a reference material/catalysts, Cu(II) was incorporated on silica by the incipient wetness method (entry 2).

Table 4. Metal Analyses for Different Hybrid Samples or Copper-Supported High Surface Silica after Treatment with a Solution of $CuCl_2$ or CuCl in Anhydrous Acetonitrile at 60 °C for 24 h

entry	solid	precursor	sample	metal content[a]	nitrogen/metal[b]
1	silica	$CuCl_2$		<0.01	
2[c]	silica	$CuCl_2$	Cu(II)-silica	1.18	
3	DA-30-A	$CuCl_2$	Cu(II)-DA-30-A	2.25	8.4
4	TB-1-A	$CuCl_2$	Cu(II)-TB-1-A	0.03	65.2
5	TB-10-A	$CuCl_2$	Cu(II)-TB-10-A	0.26	35.0
6	TB-10-B	$CuCl_2$	Cu(II)-TB-10-B	0.23	21.6
7	TB-30-A	$CuCl_2$	Cu(II)-TB-30-A	1.48	13.4
8	TB-30-A	CuCl	Cu(I)-TB-30-A	3.88	5.2
9	TB-30-B	$CuCl_2$	Cu(II)-TB-30-B	1.80	11.8

[a] wt %, calculated by ICP-AES. [b] Molar ratio. [c] Prepared by the incipient wetness method and calcined.

When the Tröger base derivative **7** is present, it was found that the amount of metal incorporated onto the solid is slightly less than for **6** (compare entries 3 and 7 in Table 4) and increases with the amount of **7** in the solid (compare entries 4, 5 and 7), that is, the higher the amount of Tröger base groups in the solid is, the more metal incorporation occurs. It could be expected that a decrease of the surface area would promote the formation of the complex by increasing the concentration of neighbor Tröger base groups. However, the surface area does not have any influence on the metal incorporation (compare entries 5−6 and 7, 9). Quantitative electron spin resonance (ESR) spectroscopy, using $CuSO_4$ as a reference, gives a Cu(II) content of 1.27 wt % for the Cu(II)-TB-30-A sample (entry 7 in Table 4, 1.48 wt % by ICP AES) which, within the experimental error, confirms that >90% of the Cu(II) is not reduced during the incorporation process. Remarkably, three times more Cu(I) than Cu(II) is incorporated (compare entries 7 and 8), having approximately 1 Cu atom (0.6 mmol g^{-1}) per 1.3 molecules of Tröger base groups ($N = 3.1$ mmol g^{-1}, 4 N atoms in **7**).[20] Considering the Tröger base groups that are inaccessible, a complete incorporation of Cu(I) as 1:1 complex is occurring. Following this estimation, Cu(II) may form 1:2 and 1:3 complexes, although the linear coordination metal-Tröger base, together with the inherent rigidity of the solid, will direct the complex formation to the 1:1 form.

To get more information about the form of the copper-Tröger base complex onto the hybrid solid, studies by EPR spectroscopy were carried out (Figures 4−5). The EPR spectrum of $CuCl_2$ on silica (spectrum A) is highly symmetric, consistent with octahedral copper species on the silica surface. The EPR spectrum for Cu(II)-TB-30-A (spectrum B) presents the symmetric signal

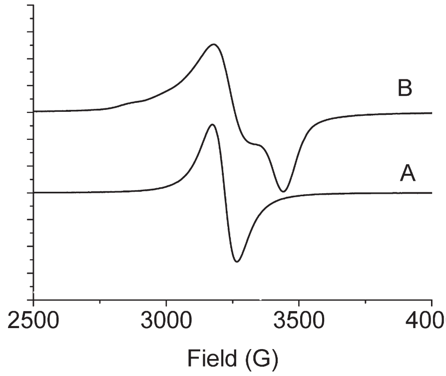


Figure 4. X-band EPR spectrum at 295 K for (a) Cu(II)-silica and (b) Cu(II)-TB-30-A.

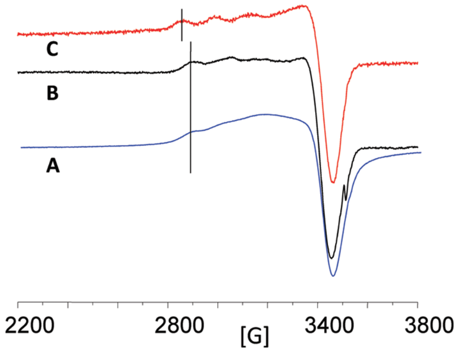
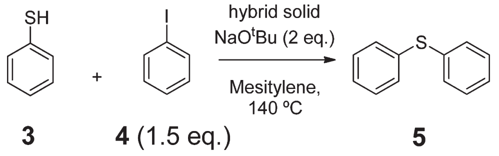


Figure 5. X-band EPR spectra at 295 K after evacuation overnight of Cu(II)-TB-30-A (**A**), Cu(II)-TB-10-A (**B**), and after evacuation for 30 min of Cu(II)-silica (**C**).

Table 5. Results for the *S*-Arylation of Thiophenol 3 with Iodobenzene 4 with Different Hybrid Solids as Catalysts



3 **4** (1.5 eq.) **5**

entry	hybrid solid	metal (mol %)	time (h)	**5** (%)[a]
1	none		24	0
2	Cu(II)-silica	2	24	0
3	Cu(II)-DA-30-A	2	24	>99
4	Cu(II)-TB-30-B	2	24	>99
5	Cu(II)-DA-30-A	1	72	35
6	Cu(II)-TB-30-B	1	24	46

[a] GC yield.

plus some anisotropy, the mononuclear axial signals corresponding to the $d_{x^2-y^2}$ electronic ground state start appearing (2800–3000 G), indicating single isolated copper-diamine complexes on the hybrid molecule.[54] These mononuclear signals are more clear when the sample is dehydrated (Supporting Information, Figure S4) and the octahedral copper species are restored after water addition.

Accordingly, the dehydrated solid Cu(II)-TB-10-A also shows the mononuclear signals but together with a broad signal of $\Delta H_{\|}$ = ~2000 G width (Supporting Information, Figure S5). This last one has no paramagnetic behavior, inferred by the fact that the intensity does not increase with the temperature. When the spectrum was recorded at 100 K for both solids Cu(II)-TB-30-A and Cu(II)-TB-10-A (Supporting Information, Figure S6), similar hyperfine signals are found with values $g_{\|}$ = 2.29 and $A_{\|}$ = 125 G.

For comparison purposes, $CuCl_2$ on silica was evacuated overnight, and no signal was observed, indicating reduction of copper, which also supports that different groups (silanols vs diamines) are coordinating the copper ion. Nevertheless, the spectra for the three solids could be compared at 295 K after a short evacuation time (Figure 5), observing the differences between the copper sites on silica and in the hybrids, and confirming that no copper was coordinated with the silanols in the hybrid material after extensive washing. Finally, the EPR spectrum of the hybrid material containing copper(I), Cu(I)-TB-30-A, was also recorded at 100 K. The stability with time of the Cu(I)-Tröger base complex when in the hybrid material was confirmed by quantitative EPR spectroscopy, since only ~1% of the total copper is detected. All these data confirm a distorted tetragonal structure for the complex in the hybrid[55,56] and, according to the correlations reported by Larsen and co-workers,[57] the values of $g_{\|}$ and $A_{\|}$ suggest that one N of the Tröger base is bound to Cu in the complex.

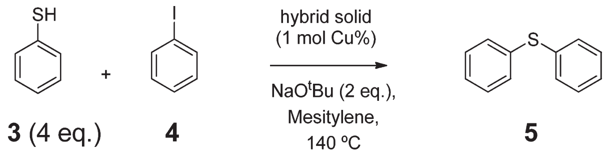
The metal-containing solids were also characterized by IR (Supporting Information, Figure S7) and DR-UV–vis spectroscopy (Supporting Information, Figure S8). The FT-IR spectra show a gradual decrease in the intensities of the Si–O band (1085 cm^{-1}) and a corresponding increase in the intensities of the aromatic bands (1497, 1540, and 1704 cm^{-1}) as the organic content increases within the hybrid materials (Supporting Information, Figure S7), confirming the stability of the solids after the copper incorporation treatment. The DR UV–vis spectra for the six copper-Tröger base hybrid materials show similar bands for all of them except for the Cu(I) material, in accordance with a different metal–ligand coordination (Supporting Information, Figure S8).

Catalytic Results for the *S*-Arylation Reaction. The different hybrid materials were used as catalysts for the *S*-arylation between thiophenol **3** and iodobenzene **4** under similar conditions to those employed in homogeneous phase (Table 5, see also Table 1).

The results show that Cu(II) on silica is inactive as catalyst while Cu(II)-DMEDA and also Cu(II)-Tröger base hybrid materials give complete conversion and selectivity at 2 mol % after 24 h (entries 1–4), the Tröger base material being slightly more active at 1 mol % (entries 5–6). To compare the catalytic activity of the different Cu(II)-Tröger base hybrid materials, kinetic experiments were carried out (Figure 6 and Table 6).

The kinetics data revealed that the catalytic activity depends on the concentration of metal complex in the solid: when the concentration is lower (Table 6, entries 1, 2 and 4, those materials presenting higher surface areas), the initial rate is higher and, in contrast, when the concentration of metal complex is higher (entries 3 and 5), the initial rates are lower (compare entries 2–3 and 4–5). Moreover, these highly loaded (30 wt % ligand) copper-diamine materials show an induction period not present in the others, after which the reaction rate undergoes a dramatic rise to finally stop abruptly again (Figure 6, lines C and D). Thus, a compromise between complex loading and surface area is needed for optimum catalytic activity, the best material

Table 6. **Initial Rate for a Series of Hybrid Solids As Catalysts**



entry	hybrid solid	metal content (wt %)	TOF (h^{-1})[a]
1	Cu(II)-TB-1-A	0.03	1.5
2	Cu(II)-TB-10-A	0.26	2.2
3	Cu(II)-TB-10-B	0.23	0.35
4[b]	Cu(II)-TB-30-A	1.48	0.7
5[b]	Cu(II)-TB-30-B	1.80	0.6

[a] GC yield. [b] After induction period.

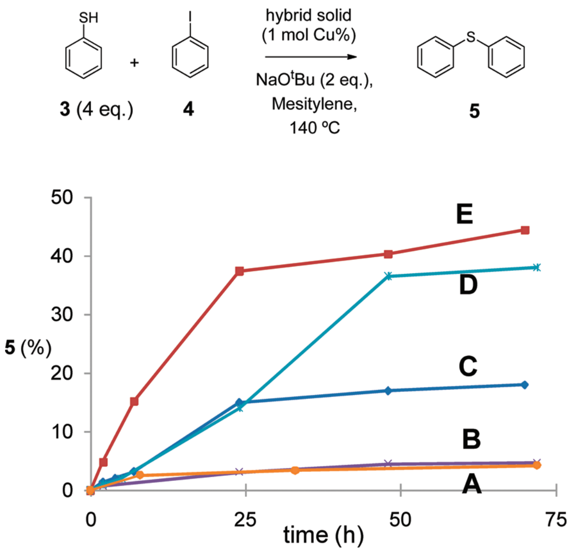


Figure 6. Plot-yield data for (A) Cu(II)-TB-1-A (4 time less catalyst), (B) Cu(II)-TB-10-B, (C) Cu(II)-TB-30-A, (D) Cu(II)-TB-30-B, and (E) Cu(II)-TB-10-A.

being that with intermediate values Cu(II)-TB-10-A (line E). The induction periods suggest that the active species is not Cu(II) but a reduced form of copper, as it occurs in Pd-catalyzed related processess,[58] and the sudden stop of the activity would correspond to the agglomeration of copper since the higher the initial loading is, the faster the deactivation of the catalyst. To check this, the kinetic behavior for the three oxidation states of Cu, (0), (I), and (II), was studied (Figure 7). The Cu(0)-TB-30-A sample was prepared by smooth reduction of Cu(II)-TB-30-A under H_2.

The Cu(I)-Tröger base complex is clearly the most active catalytic species (Figure 7, line C) while Cu(0) catalyzes to some extent (line A). Neither lines A nor C present an induction period, which suggests that these species are not pre-catalysts but the real active ones. The Cu(II) complex is only catalytically active after an induction period (line B), tentatively assigned to its reduction to Cu(I) (and finally Cu(0)). After the induction period, the reaction rate is similar to that of Cu(I), but rapidly deactivates. The relative reaction rates of Cu(I) and Cu(II) for the *S*-arylation reaction were compared to that in homogeneous phase for the corresponding Cu-Tröger base catalysts in Figure 8. The higher activity of Cu(I) compared to Cu(II) is also observed in the homogeneous phase (Figure 8, compare lines C and D), and the hybrid Cu(I)-TB-30-A shows nearly the same activity that the $CuCl_2$-Tröger base homogeneous system (compare lines B and C). With these results in hand, we proceed to study the scope of the hybrid catalysts for the *S*-arylation (Table 7).

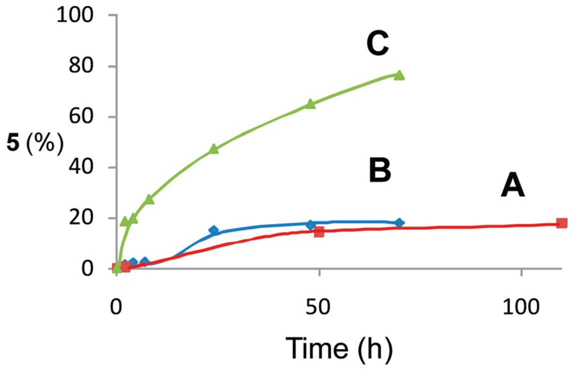


Figure 7. Plot-yield data for (A) Cu(0)-TB-30-A, (B) Cu(II)-TB-30-A, and (C) Cu(I)-TB-30-A. See Figure 6 for reaction details.

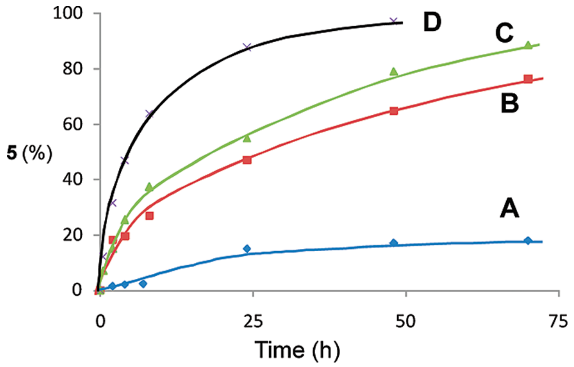
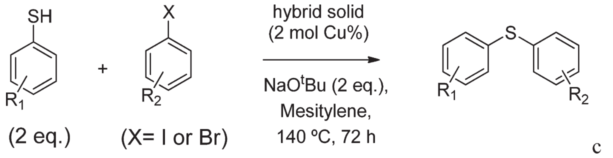


Figure 8. Plot-yield data for (A) Cu(II)-TB-30-A, (B) Cu(I)-TB-30-A, (C) $CuCl_2$-Tröger base (1:2 molar ratio), and (D) CuCl-Tröger base (1:2 molar ratio). See Figure 6 for reaction details.

The *S*-arylation of different aryl iodides proceeds in good to excellent yields (Table 7, entries 1−11) with the solids Cu(II)-DA-30-A, Cu(II)-TB-30-B, and Cu(I)-TB-30-A as catalysts. Functionalities such as ether (entries 2−3, 6 and 11), nitro (entries 3 and 4), amine (entries 6 and 7), and bromo (entry 10) are tolerated under the reaction conditions, although the substitution must be present in a particular counterpart in some cases (compare, for instance, entries 4 and 5 and entries 6, 7 and 13). Some combinations do not work so well (entries 12 and 14). Remarkably, bromoacetophenone **25** can be coupled with thiols **3** and **6** in good yields if the amount of catalyst is raised to 5 mol % (entries 15, 16, 18, and 19), although the deactivated substrate bromoanisole does not react (entry 17). An excess of catalyst leads to poorer results (compare entries 21 and 22), in accordance to the effect of the catalyst concentration commented above. It is also remarkable that thiophenol **3** can be substituted by the corresponding disulfide **26** under similar reaction conditions (entries 23 and 24). This is surprising since the use of disulfides requires the reduction to thiopenol with additional strong reductor agents, such as magnesium metal[59] or a Ni(II)−Zn(0)

Table 7. **Results for the *S*-Arylation of Different Substrates with Cu(II)-DA-30-A (*A*), Cu(II)-TB-30-B (*B*), Cu(I)-TB-30-A (*C*), or Cu(II)-TB-10-A (*D*) as Catalysts**



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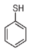
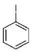
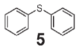
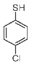
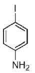
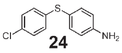
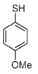
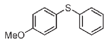
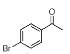
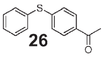
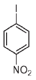
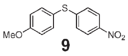
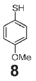
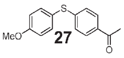
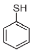
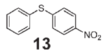
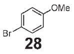
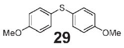
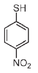
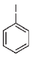
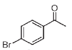
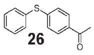
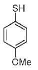
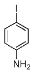
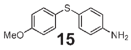
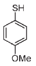
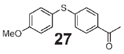
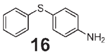
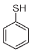
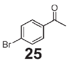
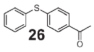
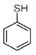
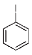
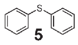
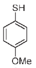
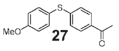
1	 3	 4	*A* (2)	 5	>99	14	 23	 14	*D* (2)	 24	20
2	 8		*A* (2)	 9	>99	15	 3	 25	*A* (5)	 26	69 [54]
3		 10	*A* (2)	 9	>99	16	 8		*A* (5)	 27	62 [61]
4	 3		*A* (2)	 13	76	17		 28	*A* (5)	 29	2
5	 12	 4	*A* (2)		N.D.	18	 3	 25	*C* (5)	 26	89
6	 8	 14	*A* (2)	 15	72	19	 8		*C* (5)	 27	81
7			*A* (2)	 16	71	20	 3	 25	*B* (5)	 26	46
8	 3	 4	*B* (2)	 5	>99	21	 8		*B* (5)	 27	60
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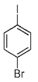
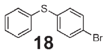
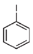
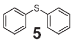
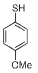
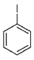
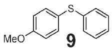
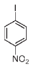
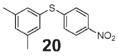
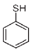
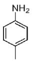
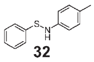
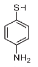
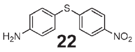
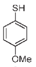
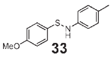
10		 17	*B* (5)	 18	75	23	Ph_2S_2 30	 4	*B* (2)	 5	88
11	 8	 4	*C* (2)	 9	>99	24			*B* (2)		4[b]
12	 19	 10	*D* (2)	 20	46	25	 3	 31	*B* (2)	 32	N.D.
13	 21		*D* (2)	 22	N.D.	26	 8		*B* (2)	 33	N.D.

[a] GC yield, between brackets isolated yields. [b] $NaHCO_3$ as base.

system.[60] We are currently investigating this intringuing result. Finally, the formation of S−N bonds was attempted[61] but, under our reaction conditions, results were fruitless (entries 25 and 26).

Leaching Studies and Recyclability of the Hybrid Solids. The possible leaching of active species from the hybrid solids to the solution under the reaction conditions was assessed in three ways: filtration in hot, analyses of the copper content in the filtrates and in the solids, and the three-phase test on silica.[58,62] First, comparison of the reaction rates with the hybrid solid as catalyst or when this is filtrated off the solution at a particular conversion will give us information about the presence of catalytically active species in solution. Kinetics experiments for two different solids are shown in Figures 9 and 10.

The filtration of the catalyst Cu(II)-TB-30-B completely stops the formation of **5**, regardless if the filtration is produced during or after the induction period (Figure 9, lines B and C). Similarly, the filtration of the catalyst Cu(II)-TB-10-A also inhibits the *S*-arylation of **4** (Figure 10). The analyses of the copper content in the filtrates by ICP AES show that ∼1% of the original content of the solids is leached out, from both solids. Therefore, it can be concluded that there is no leaching of active species under reaction conditions and the low amount of leached copper is not able to perform the reaction. In accordance, the copper content of the solids after recovery at the end of the reaction is practically the same than in the original sample. To further confirm these results, the more elaborated three-phase test was performed. In this test, an iodobenzene derivative (4-iodophenylacetyl chloride **34**) is covalently anchored to amine-functionalized high surface silica[58] as the corresponding amide. Since one of the reactants and the catalyst are in different particles, the

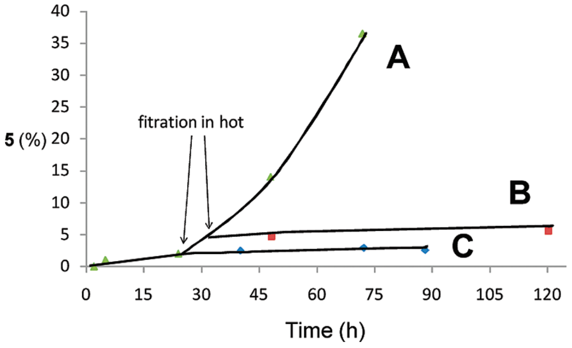


Figure 9. Plot-yield data for (A) Cu(II)-TB-30-B (Cu: 1 mol %) as catalyst, (B) after filtration of the catalyst after the induction period, and (C) after filtration of the catalyst during the induction period. For reaction conditions see Figure 6.

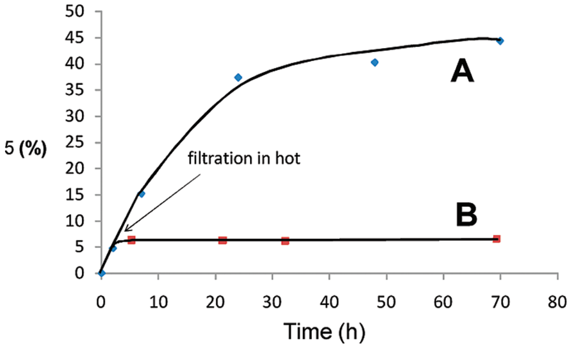


Figure 10. Plot-yield data for (A) Cu(II)-TB-10-A (Cu: 1 mol %) as catalyst and (B) after filtration in hot of the catalyst. For reaction conditions see Figure 6.

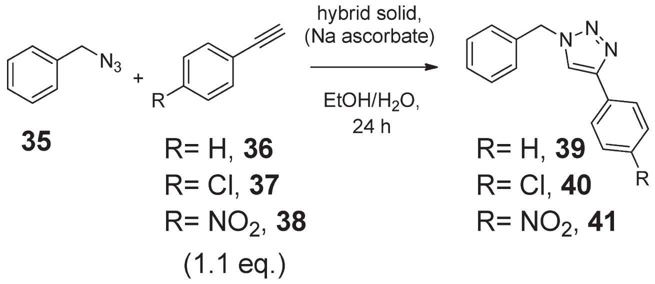
reaction will be strongly limited provided that no leaching occurs. However, if some leaching takes place, the anchored reagent will be transformed to the product to some extent. After reaction and hydrolysis of the silica, the dimer of thiophenol was the only product detected, indicating the absence of *S*-arylation by homogeneous catalysis of the leached copper.

The recyclability of the material was then tested. Unfortunately, a second use of the material leads to an important decrease in the yield of product. The EPR spectrum of the reused solids (Cu(II)-TB-materials) accounts for <2% of the original amount of Cu(II) and an important loss of the signal symmetry and a shift to higher fields are observed, which infers Cu−Cu interactions by agglomeration. This was probably due to the high pH of the reaction medium and, consequently, the possibilities of the solid catalyst were studied for another reaction, that is, the azide−alkyne cycloaddition that does not require the above experimental conditions.

Catalytic Results for the Azide−Alkyne Cycloaddition. The Cu(I)-catalyzed azide−alkyne cycloaddition is considered an example of paradigmatic reaction in sustainable chemistry, embodied in the so-called "click" chemistry reactions.[63−65] However, the recovery and recycle of the copper catalyst is not frequent.[65] Thus, different Cu-diamine hybrid solids were tested as catalysts for this reaction and, indeed, they showed catalytic activity for the cycloaddition of azide **35** to phenylacetylenes **36**−**38** (Table 8).

The corresponding products **39**−**41** were isolated in good to moderate yields after reaction and, importantly, the hybrid solid was recovered and reused without significant depletion of the catalytic activity, regardless the reaction conditions employed (entries 3−5). For instance, **39** was formed under the presence of Cu(II)-DA-30-A (Cu: 1 mol %) at room temperature (70 and 62% isolated yields, two uses) or at 60 °C (53, 34, 53, and 35% isolated yields, four uses). Interestingly, the use of sodium

Table 8. Results for Azide−Alkyne Cycloaddition between Azide 35 and Alkynes 36−38 in the Presence of Different Hybrid Solids



entry	hybrid solid	metal (mol %)	ascorbate (mol %)	*T* (°C)	alkyne	product (%)[a]
1	none			rt	**36**	<5
2	none			60	**36**	<5
3	Cu(II)-DA-30-A	1	5	rt	**36**	70[b]
4	Cu(II)-DA-30-A	1	5	60	**36**	53[c]
5	Cu(I)-TB-30-A	1		rt	**36**	29[c]
6	Cu(II)-DA-30-A	1	5	rt	**37**	29
7	Cu(II)-DA-30-A	1	5	rt	**37**	44
8	Cu(II)-DA-30-A	1	5	rt	**38**	40
9	Cu(I)-TB-30-A	1		rt	**38**	45[b]

[a] Isolated yield. [b] Reused once. [c] Reused three times.

ascorbate as reductant can be avoided by directly using a copper(I)-Tröger base supported catalyst (entry 5: 29, 21, and 28% isolated yields, three uses; also compare entries 8 and 9). An increase in the temperature does not improve the product yield (compare entries 3 and 4).

CONCLUSIONS

The formation of copper-diamine complexes by incorporation of copper in highly loaded diamine-silica hybrid materials allows producing active heterogeneous catalysts for the *S*-arylation and for the azide−alkyne cycloaddition reactions. The characterization of the materials reveals that the organic linkers containing the secondary and tertiary amines were incorporated into the network of the non-ordered organic−inorganic porous materials and that the surface areas and pore distributions indicate that these organic fragments are accessible to interact with metallic species in solution, generating the hybrid metallic catalysts. These hybrid solids are active catalysts for the *S*-arylation of aryl iodides and bromides with thiophenols and disulfides. Studies of the homogeneous catalytic system $CuCl_2$/diamine (DMEDA or Tröger base) reveal that the copper/diamine molar ratio determines the catalytic activity in high extent. In the heterogeneous system, no leaching occurs under the reaction conditions although the catalyst was severely deactivated under the reaction conditions used. However, the hybrid solids can successfully act as recyclable catalysts for other reactions such as the azide−alkyne cycloaddition. In this case, the catalyst is recovered and recycled up to four times without significant decrease in the catalytic activity. The study here reported constitutes an effective approach to heterogenize metallic and organometallic species and, considering that copper-diamine complexes are ubiquitous as catalysts in C-Heteroatom and C−C reactions, these solids are potential catalysts for low basicity-demanding reactions. Moreover, the use of Tröger base as ligand in catalysis could open the door to chiral transformations.

EXPERIMENTAL SECTION

Preparation of Disilyl-Tröger-base 7. *Synthesis of the Precursor.* Following the reported procedure,[66] 3 g of the corresponding bis-ethanol derivative of the Tröger base (6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]diazocine-2,8-diethanol) was obtained as an orange solid after column chromatography (2−10% MeOH in DCM).

*Synthesis of the Disilyl Derivative **7**.* To the previously obtained precursor (775 mg, 2.5 mmol), anhydrous 1,4-dioxane (15 mL) and 3-isocyanopropyltriethoxysilane (1.235 mL, 5 mmol) were added in a 50 mL round-bottomed flask, and the solution was placed in a pre-heated oil bath at 100 °C and magnetically stirred for 5 days under nitrogen atmosphere. After removal of the solvent under vacuum, the disilyl derivative **7** was obtained in quantitative yield as a red oil. ^{1}H NMR (δ, ppm; *J*, Hz): 6.99 (2H, d, $J = 8.2$), 6.94 (2H, dd, $J = 8.2, 1.5$), 6.69 (2H, d, $J = 1.5$), 5.07 (2H, t, $J = 5.7$), 4.59 (2H, d, $J = 16.6$), 4.20 (2H, s), 4.11 (4H, t, $J = 7.0$), 4.05 (2H, d, $J = 17.2$), 3.75 (12H, q, $J = 7.0$), 3.08 (4H, q, $J = 6.4$), 2.71 (4H, t, $J = 7.0$), 1.54 (4H, quint, $J = 7.0$), 1.16 (18H, t, $J = 7.0$), 0.60−0.51 (4H, mult). ^{13}C NMR (δ, ppm): 156.3 (C×2), 146.1 (C×2), 133.5 (C×2), 127.7 (CH×2), 127.5 (C×2), 127.0 (CH×2), 124.8 (CH×2), 66.6 (CH_2), 64.8 (CH_2×2), 58.3 (CH_2×2), 58.2 (CH_2×6), 43.1 (CH_2×2), 34.8 (CH_2×2), 23.1 (CH_2×2), 18.1 (CH_3×6), 7.4 (CH_2×2).

Synthesis of Hybrid Organosiliceous Materials. Non ordered hybrid porous materials were prepared from a starting mixture of tetramethoxysilane (TMOS) and the suitable amount of silsesquioxane ($(R'O)_3Si\text{-}R\text{-}Si(OR')_3$) as silica precursors, in methanolic solution. After total dissolution of precursors, a water solution of NH_4F was dropped into the organosilicon alkoxide solution under vigorous stirring, the pH of this mixture being close to neutrality. The final reaction slurry had the following molar composition:

$$(1-x)\mathrm{TMOS} : x(\mathrm{R'O})_3\mathrm{Si\text{-}R\text{-}Si(OR')_3} : 4\mathrm{MeOH} : 4\mathrm{H_2O} : y\mathrm{NH_4F}$$

where x corresponds to the amount, expressed in SiO_2 mol, of bridged silsesquioxane molecules added into the mixture which varied between 0.01 and 0.3 mol as a function of disilane employed, and y is 3.13×10^{-3} and 4.70×10^{-3} mol to study the influence of NH_4F amount on the gelification process. Hydrolysis and condensation of the silicon precursors was performed under vigorous stirring in a glass beaker at room temperature. Stirring was continued until gelation occurred after a few minutes. The gel formed was aged for 24 h at 36 °C, and finally dried at 150 °C for additional 24 h. The white solids obtained were exhaustively washed with ethanol and water in consecutive steps to remove the disilane molecules not covalently incorporate into the materials. In the disilanes, R is assigned to ethylendiamine and Tröger-base groups, and R′ corresponds to methyl and ethyl groups, respectively.

TMOS, NH_4F, and organic solvents were obtained from Aldrich Chemical Co. The disilane bis(trimethoxysilylpropyl)-ethylendiamine (**6**) used to introduce secondary diamines into the silicon network was provided by ABCR GmbH. The disilane named disilyl-Tröger-base (**7**), containing tertiary amines, was prepared following the procedure described above. Figure 1 shows both silsesquioxane precursors.

The different catalysts prepared in this article are denoted as DA or TB, in function of organic linkers are ethylendiamine or Tröger-base groups, respectively. The names are also followed for the percentage of SiO_2 mol incorporated as disilane in the synthesis gel (1, 10, or 30), and finally by (A) or (B), depending if 3.13×10^{-3} or 4.70×10^{-3} mol of NH_4F, respectively, is employed during the synthesis.

Preparation of Metal-Hybrid Catalysts. *Typical Reaction Procedure for Preparation of Metal-Hybrid Catalysts (Table 4, Cu(II)-DA-30-A, entry 3).* DA-30-A (1 g, 2.7 mmol N) and $CuCl_2$ (122 mg, 0.9 mmol) were placed in a 25 mL round-bottomed flask. A rubber septum was fitted, and anhydrous acetonitrile (10 mL) was added by syringe. The mixture was magnetically stirred in pre-heated oil bath at 60 °C for 24 h. After cooling, the mixture was filtered under vacuum and washed with acetonitrile (3 × 15 mL), and the solid was dried in an oven at 75 °C for 24 h.

Reaction Procedures. *Typical Reaction Procedure for the S-Arylation Reaction by Homogeneous Catalysis (Table 1, entry 3).* NaO^{t}Bu (480 mg, 5 mmol) and CuCl (2.5 mg, 1 mol %) were placed in a 25 mL round-bottomed flask. A rubber septum was fitted, and diamine **1** (2.7 μL, 1 mol %), mesitylene (5 mL), thiophenol (1.04 mL, 10 mmol), and iodobenzene (260 μL, 2,5 mmol) were added by syringe. The mixture was magnetically stirred in pre-heated oil bath at 140 °C for 6 h. After cooling, *n*-hexane (0,5 mL) was added, the liquid was passed through a microfilter syringe, and the filtrates were analyzed by GC.

Typical Reaction Procedure for the S-Arylation Reaction by Heterogeneous Catalysis (Table 5, entry 6). NaO^{t}Bu (48 mg, 0.5 mmol) and Cu(II)-TB-30-B (30 mg, 2 mol %) were placed in a 10 mL round-bottomed flask. A rubber septum was fitted, and mesitylene (0.5 mL), thiophenol (26 μL, 0.25 mmol), and iodobenzene (39 μL, 0.375 mmol) were added by syringe. The mixture was magnetically stirred in pre-heated oil bath at 140 °C for 24 h. After cooling, *n*-hexane (0,5 mL) was added, the liquid was passed through a microfilter syringe, and the filtrates were analyzed by GC.

Typical Reaction Procedure for the Azide—Alkyne Cycloaddition (Table 8). The corresponding catalyst Cu(II)-DA-30-A or Cu(I)-TB-30-A (Cu: 1 mol %) and sodium ascorbate if needed (2 mg, 5 mol %) were placed in a 10 mL round-bottomed flask, and EtOH (2 mL), bidistilled water (2 mL), benzyl azide (25 μL, 0.2 mmol), and the corresponding phenylacetylene (0.22 mmol) were added by syringe and the mixture was magnetically stirred at room temperature or in a pre-heated oil bath at 60 °C for 24 h. After cooling, product precipitated from the reaction was redissolved with acetone, and the catalyst was filtered off. The filtrates were concentrated and the product was washed with cold water and cold hexane, dried and analyzed by GC-MS. *Reuse of the solid catalyst:* after recovery, the catalyst was dried, weighed, and placed in a 10 mL round-bottomed flask for the next reaction. Then, the reagents and solvents were added as before, maintaining constant the molar ratio with respect to the catalyst.

ASSOCIATED CONTENT

S Supporting Information. Experimental procedures, additional figures, and compound characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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