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Thiazolium-Based Catalysts for the Etherification of Benzylic Alcohols under Solvent-Free Conditions

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Abstract: Thiazolium and imidazolium hybrid materials were prepared by radical reactions between a mercaptopropyl-modified SBA-15 mesoporous silica and bis-vinylthiazolium or bis-vinylimidazolium dibromide salts. These hybrid materials were characterized by several techniques and were employed in the etherification reaction of 1-phenylethanol. Solvent-free conditions at 160 °C under different gas phases (oxygen, air, nitrogen and argon) were used. The thiazolium-based material displayed excellent performances. Further studies were carried out using unsupported thiazolium salts, with or without a methyl group at the C-2 position of the thiazolium moiety. These studies allowed us to propose a reaction mechanism. The supported thiazolium-based material was successfully used in the etherification reaction of two other benzylic alcohols and also in seven consecutive cycles. This work represents the first use of thiazolium-based compounds as catalysts for the etherification reaction of alcohols.

Keywords: catalysis; heterogeneous catalysis; organocatalysis; supported catalysts; synthetic methods

Introduction

The development of innovative and efficient active materials plays a central role in the field of catalysis. The design of an ideal heterogeneous catalyst should fulfill a series of requirements such as high surface area, good amount of accessible active sites, no or low diffusion limitation of reactants and products, thermal and chemical stability at selected reaction conditions. Among all the existing catalytic processes, the carbon-oxygen bond forming reaction is one of the most important transformations at both laboratory and industrial scales. Ethers are largely employed as biologically active compounds and drugs,[1] fragrances[2] and solvents. Moreover, they can find application in gasoline and diesel blends.[3,4] One of the most commonly used approaches for the preparation of ethers, the Williamson reaction,[5] presents as a major drawback the use of hard bases that can lead to the formations of salts as by-products and restrict the applicability to selected classes of ethers not containing base-sensitive functionalities.[5–7] An alternative methodology is represented by the use of Lewis acid catalysts.[8–10] The principal limitation of this synthesis protocol is represented by the decomposition of the Lewis acid caused by the water generated during the reaction. Recently, Firouzabadi and co-workers reported the etherification of different classes of alcohols using catalytic amounts of the heteropolyacid $AlPW_{12}O_{40}$.[11] Even though this catalyst is water tolerant, it was used in addition to toxic organic solvents such as the 1,2-dichloroethane. Reductive etherification from carbonyl compounds can be achieved using organosilanes and Lewis acid catalysts such as $BiCl_3$[12] or $FeCl_3$.[13] Also in this case, a large amount of acid catalyst is required due to its partial decomposition during the reaction. Very recently, Roth et al. reported a direct reductive synthesis of several ethers through a combination of organosilanes and triflic acid.[14] Although these methods are efficient, the use

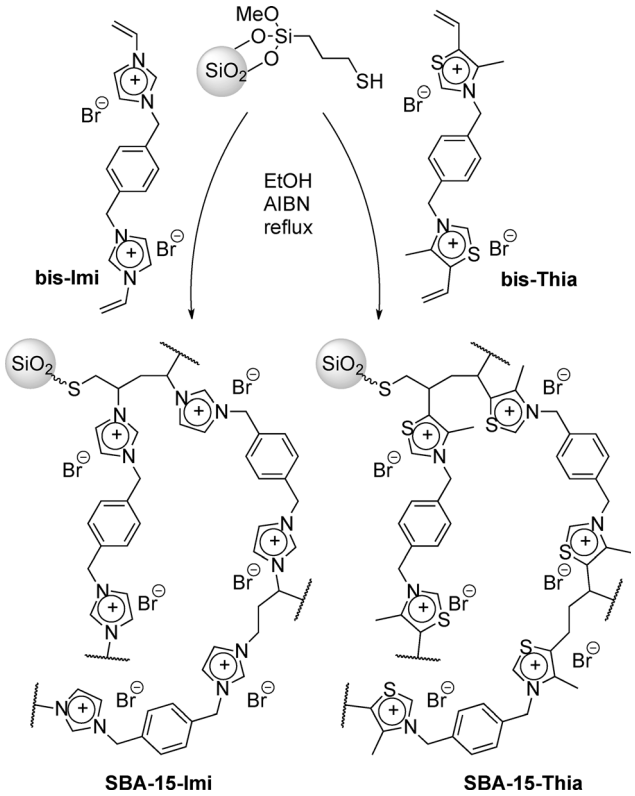
of silanes is not considered a valid alternative since some of them can release toxic SiH_4 gas.[15] Alternative routes have been investigated, for example, the use of UV irradiation,[16] dimethyl sulfoxide,[17] and phase-transfer catalysts.[18–21] Elegant catalytic methods for etherification reactions are represented by the use of transition metals.[22–26] In addition, Argouarch and co-workers reported a reductive etherification of aldehydes photocatalyzed by iron complexes.[27] Abu-Omar et al. demonstrated a direct method to prepare symmetrical and asymmetrical ethers under mild homogeneous conditions employing palladium (II) catalysts. Complexes of this metal show a high selectivity for the etherification of secondary alcohols, although they are used in combination with silver triflate.[28] Pale and co-workers investigated a series of transition metals for the formation of biphenyl methyl ethers,[29,30] using $PdCl_2$, AuCl, $CuCl_2$, $NaAuCl_4$.[31] In most of cases, the methods based on transition metal catalysts display good performances, however, the homogeneous conditions used and the elevated price of the metals limit their large-scale applications. From what is reported, it appears evident that the development of new methods to obtain a large variety of ethers, or an improvement of the existing strategies in order to increase the yield and selectivity, is still of major interest.

Ionic liquids have recently emerged as a novel class of compounds with multiple possible uses ranging from alternative "green" reaction media to the activation of molecules in catalytic reactions.[32] Supported ionic liquid phases (SILP) or supported ionic liquid-like phases (SILLP) are a class of materials that have interesting applications. These systems when compared to corresponding homogeneous ionic liquid phase show the general advantages of easy separation, recyclability, and they can be potentially applied in continuous processes.[33–35] It is worthy of note that SILP can be considered as an advanced class of heterogeneous catalysts since they combine some of the properties of the pure ionic liquids to the characteristics of a solid support. Herein, we investigate the use of supported imidazolium and thiazolium salts as catalysts for the etherification of benzylic alcohols. Recently, we have reported the synthesis and use of a new kind of SILP (or SILLP) material, the multilayered covalently-linked imidazolium salts on silica gel. These materials were employed as catalysts[36,37] or as supports for catalysts.[38–41] In the present work, we have used such an approach in order to prepare two different materials based on multilayered covalently-linked imidazolium or thiazolium salts on SBA-15 meso-structured silica. The two materials were prepared in order to study the influence of the N-heterocyclic moiety on the reaction. To the best of our knowledge, this is the first time that a multilayered covalently supported imidazolium- or thiazolium-based material has been reported as catalyst for the synthesis of ethers. In particular, the use of the thiazolium-based catalyst represents a novelty for the target reaction.

Results and Discussion

In order to study the influence of the N-heterocyclic moiety, two different materials were synthesized (Scheme 1). The syntheses of the heterogeneous organocatalysts bearing either imidazolium or thiazolium active sites (**SBA-15-Imi** and **SBA-15-Thia**, respectively) were successfully accomplished by grafting the corresponding bis-vinyl salts (**bis-Imi** or **bis-Thia**) on a thiol-functionalized SBA-15 silica (Scheme 1). The presence of the bis-vinyl functionalities allows the formation of the multilayer cross-linked organic shell *via* a well-established synthetic mechanism: one of the double bonds reacts through a thiol-ene coupling with the thiol group of the mesoporous support ensuring the covalent anchoring, and the other may undergo self-addition reactions generating the oligomeric/polymeric network. This second process is favored by the large excess of the imidazolium or thiazolium salt in the reaction mixture.

The two materials were extensively characterized by N_2 physisorption, transmission and scanning elec-



Scheme 1. Synthesis of **SBA-15-Imi** and **SBA-15-Thia**.

Table 1. BET specific surface area and cumulative pore volume of supports.

Entry	Support	BET surface area ($m^2 g^{-1}$)	Cumulative pore volume ($cm^3 g^{-1}$)	Loading of Thia or Imi[a] ($mmol g^{-1}$)
1	**SBA-15**	911	1.18	–
2	**SBA-15-SH**	675	0.86	–
3	**SBA-15-Thia**	129	0.17	2.46
4	**SBA-15-Imi**	145	0.18	2.32

[a] Loading of Thia or Imi: loading of thiazolium or imidazolium moiety, calculated by nitrogen data in elemental analysis.

tron microscopy, X-ray diffraction, ^{29}Si and ^{13}C magic angle spinning (MAS)-NMR. Nitrogen adsorption/desorption measurements, performed on all samples (Supporting Information, Figure S1 to S4), evidenced a progressive decrease of the surface area with the functionalization (see Table 1), accompanied by a reduction of the pore volume. This expected behavior can be ascribed to the coating of the silica support by the polymeric matrix and the partial filling of the mesopores. The unreacted monomers or oligomers eventually adsorbed on the surface were removed by consecutive washing with hot methanol and Soxhlet extraction of the final solids.

The transition electron microscopy (TEM) investigation evidenced the presence of the typical mesoporous structure in the SBA-15 as well as the formation of a polymeric shell covering the particles in the final solid (Supporting Information, Figure S5). Solid state ^{29}Si MAS-NMR characterization confirmed the good degree of condensation leading to the formation of Si–O–Si bonds in the SBA-15 material as well as the covalent anchoring of the 3-mercaptopropyltrimethoxysilane with the appearance of T3 and T2 signals (Figure 1a). The relative contribution of Q4/Q3 and T3/T2 species was estimated *via* deconvolution (Figure 1a, light grey line) of the original NMR signal. ^{13}C MAS-NMR spectra displayed the pattern of the imidazolium or thiazolium species. The disappearance of the signals corresponding to the terminal vinyl carbons further confirmed the absence of unreacted bis-vinyl precursors in the supported solids, although the presence of traces of adsorbed oligomers cannot be completely excluded (Figure 1b, black circle and Supporting Information, Figures S6 to S8). All these findings, combined with the exceptionally high degree of organic functionalization, quantified through combustion chemical analysis (see the Experimental Section), allow an assumption of the presence of a multilayered matrix. The two solids, **SBA-15-Imi** and **SBA-15-Thia**, display good specific surface area and high percentage of active sites, which are promising features for catalytic applications. In order to explore their activity, 1-phenylethanol was selected as model compound for the industrially relevant etherification reaction. To investigate the possible formation of oxidation by-products, the etherification reaction was initially performed in the presence of different gas phases

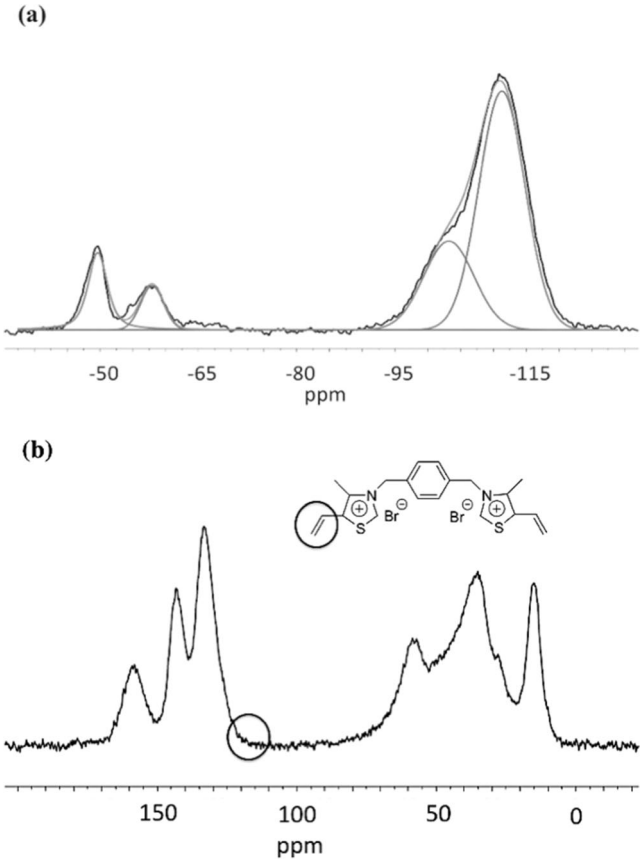


Figure 1. (a) ^{29}Si MAS-NMR spectra of **SBA-15-SH**; (b) ^{13}C MAS-NMR spectra of **SBA-15-Thia**.

(oxygen, air, nitrogen and argon) for 24 h. The results of these preliminary catalytic tests are reported in Table 2. It is worthy of note that challenging conditions in terms of substrate to catalyst weight ratio (mg alcohol/mg catalyst = 540) were used. After 24 h an almost quantitative conversion was observed using the **SBA-15-Thia** catalyst in both oxygen and air (entries 1 and 2). The selectivity toward ether was lower (73%) when the reaction was carried out under an oxygen atmosphere, acetophenone then being the main by-product. In order to understand the effect of the gas phase, the etherification was performed under an inert atmosphere.

Under a nitrogen or argon atmosphere, the conversion was much lower and an increased selectivity was observed (entries 3 and 4 in Table 2). Interestingly,

Table 2. 1-Phenylethanol etherification catalyzed by **SBA-15-Thia** or **SBA-15-Imi** materials.[a]

Entry	Support	Time [h]	Gas phase	Conv. [%][b]	Selectivity[c] [%]
1	**SBA-15-Thia**	24	O_2	93	73
2	**SBA-15-Thia**	24	air	93	86
3	**SBA-15-Thia**	24	N_2	55	93
4	**SBA-15-Thia**	24	Ar	57	91
5	**SBA-15-Imi**	24	O_2	73	38[d]
6	**SBA-15-Imi**	24	Air	48	70
7	**SBA-15-Thia**	7	O_2	92	75
8	**SBA-15-Thia**	7	air	78	88

[a] *Reaction conditions:* 1-phenylethanol (5.4 g, 44.2 mmol), **SBA-15-Thia** or **SBA-15-Imi** (10.2 mg), 160 °C, under stirring.
[b] Determined by ^{1}H NMR.
[c] Selectivity toward ether.
[d] Main by-product: acetophenone.

the analogous imidazolium-based material displayed a lower conversion and poorer selectivity evidencing that the nature of the N-heterocyclic ring has a determinant impact on the performances of the reaction (entries 1 and 2 *vs.* 5 and 6 in Table 2). In all these reactions, the main by-product was represented by acetophenone and, in some cases, by styrene which was found in the reaction mixture in lower amounts.

It is known that yield and selectivity of the etherification reaction are strongly influenced by the textural properties of the heterogeneous catalysts as well as by the nature and strength of the acid sites.[42] In our case, the distinct catalytic behavior of imidazolium- and thiazolium-based materials cannot be ascribed to relevant differences in terms of surface area, accessibility or acidity of the two solids, but rather to a different reactivity of the two heterocyclic systems.

Since the conversion under oxygen or air after 24 h was high, the reaction was monitored at a shorter reaction time (entries 7 and 8 in Table 2). As expected, the selectivity increases by decreasing the percentage of oxygen in the reaction mixture. Interestingly a lower conversion was also observed under air suggesting that the presence of oxygen has a global beneficial influence on the reaction. This trend is even more evident in Figure 2 in which are highlighted the decrease of the conversion (dark grey) and the parallel increase of the selectivity (light grey) upon lowering the initial oxygen concentration after 7 h of reaction time. A blank experiment performed in the absence of catalyst, under the same reaction conditions, revealed an extremely low conversion (6%) after 7 h with acetophenone as main product and traces of the etherification compound. Similar results were found when non-functionalized SBA-15 was used as catalyst. The kinetic profiles of the etherification under O_2, air and N_2 are shown in Figure 3. Interestingly under O_2 the maximum conversion is reached after 3 h. In the presence of air and nitrogen the reaction displayed a slower kinetic profile with a plateau that is attained after 6 h in the first case, and a linear slow increase of 1-phenylethanol conversion over time in the second.

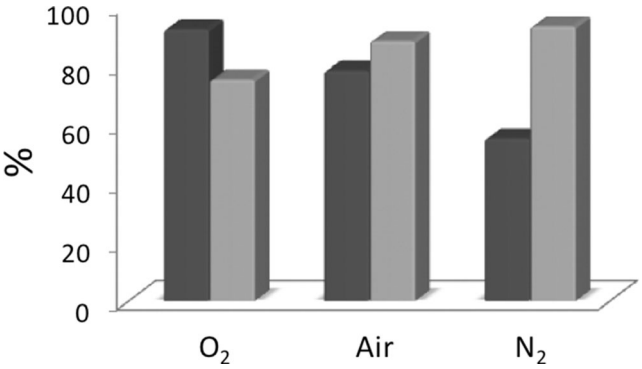


Figure 2. Conversion (dark grey) and selectivity (light grey) in the etherification reaction of 1-phenylethanol mediated by **SBA-15-Thia** after 7 h.

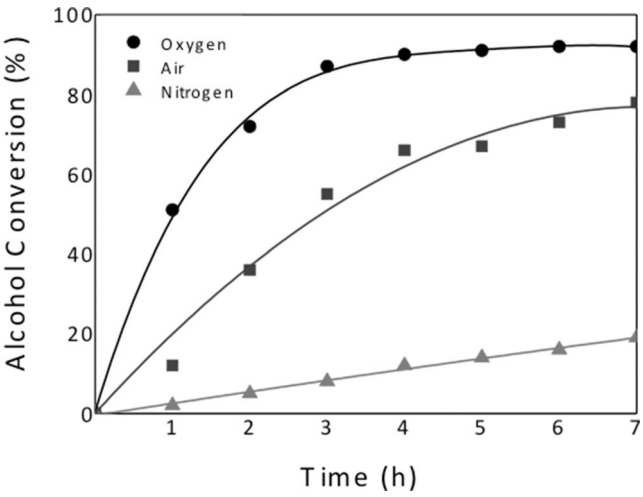


Figure 3. Conversion of 1-phenylethanol with **SBA-15-Thia** as a function of the time under oxygen, air or nitrogen atmosphere.

These results clearly evidenced an oxygen-dependent behavior of the **SBA-15-Thia**-catalyzed reaction.

Since the O_2 favors the formation of acetophenone, in order to exclude an active role of the oxidation by-product in the synthesis of the ether, the reaction was performed using an equimolecular mixture of 1-phenylethanol and deuterated acetophenone as starting materials. The presence of a partially deuterated bis(α-methylbenzyl) ether in the final products would represent evidence of the role of acetophenone as synthesis intermediate. The analysis of the mixture after 7 h reaction showed the presence of the etherification product. However, GC-MS analysis did not evidence any partially deuterated compound in the reaction mixture. This test allows us to exclude an active participation of the acetophenone in the reaction mechanism. To completely clarify the mechanism an additional test using deuterated styrene as starting materials was also performed with similar results. These findings confirmed that the three reaction products (acetophenone, ether and styrene) are formed through independent reaction routes. Motivated by the excellent catalytic results and aiming to a thorough understanding of the novel thiazolium-catalyzed reaction, we investigated the role of the hydrogen at the C-2 position. For this mechanistic study, two easily accessible thiazolium-based catalysts, to be used under homogeneous conditions, were prepared. The two salts reported in Figure 4 differ only in the presence of hydrogen (**Homo-Thia-H**) or a methyl group (**Homo-Thia-Me**) at C-2 and were prepared with the objective to simulate the proximity of the active sites in the supported heterogeneous catalyst.

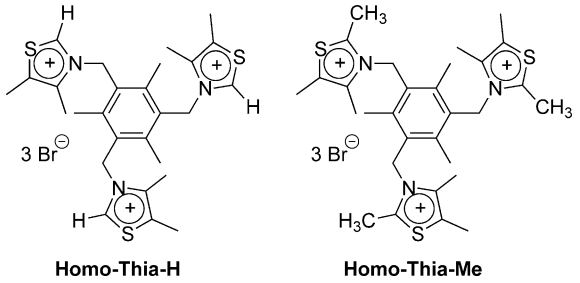


Figure 4. Structure of catalysts **Homo-Thia-H** and **Homo-Thia-Me**.

The two novel homogeneous organocatalysts (**Homo-Thia-H** and **Homo-Thia-Me**) can be prepared in high yield *via* a one-step procedure starting from the 2,4,6-tris(bromomethyl)mesitylene and the 4,5-dimethyl- or 2,4,5-trimethylthiazole, respectively (see Experimental Section and Supporting Information Figures S9 to S12). The salts were tested under the previously reported reaction conditions in both oxygen and air atmospheres (Table 3). The results of this study revealed that the methyl group has a detrimental effect on the etherification reaction. In the presence of oxygen or air the conversion of the reaction catalyzed by the **Homo-Thia-H** reach the 92% after 7 h (entries 1 and 2 in Table 3) while under the same condition the **Homo-Thia-Me** catalyst gave 80% and 24% conversion, respectively (entries 3 and 4 in Table 3). A lower selectivity was observed when the reaction was performed in oxygen (entry 3), acetophenone being the main by-product. The differences between the catalysts in terms of both yield and selectivity toward the etherification product are even more evident under air and a shorter reaction time, highlighting once more the positive influence of the high O_2 concentration (entries 5–8). After 4 h only 14% of conversion is obtained in the presence of the **Homo-Thia-Me** catalyst with a corresponding selectivity of 71% (entry 8) while a higher conversion and lower selectivity are obtained under oxygen (entry 7) where the remaining product is mainly represented by the acetophenone. These results show the key role of C-2 in the catalytic mechanism. The reduced performance of **Homo-Thia-Me** could be attributed to a negative combination of steric and electronic effects.

The kinetic profiles of the reactions performed in both air and oxygen with an analysis of the composition of the reaction mixture over time are reported in Figure 5 and Figure 6. Finally, we performed the etherification reaction of (*S*)-1-phenylethanol under

Table 3. 1-Phenylethanol etherification catalyzed by **Homo-Thia-H** or **Homo-Thia-Me**.[a]

Entry	Catalyst	Time [h]	Gas phase	Conv. [%][b]	Selectivity [%][c]
1	**Homo-Thia-H**	7	O_2	92	72
2	**Homo-Thia-H**	7	air	92	72
3	**Homo-Thia-Me**	7	O_2	80	56
4	**Homo-Thia-Me**	7	air	24	73
5	**Homo-Thia-H**	4	O_2	81	74
6	**Homo-Thia-H**	4	air	63	82
7	**Homo-Thia-Me**	4	O_2	67	51
8	**Homo-Thia-Me**	4	air	14	71

[a] *Reaction conditions:* 1-phenylethanol (5.4 g, 44.2 mmol), **Homo-Thia-H** or **Homo-Thia-Me** (10.15 mg), 160 °C.
[b] Determined by ^{1}H NMR.
[c] Selectivity toward ether.

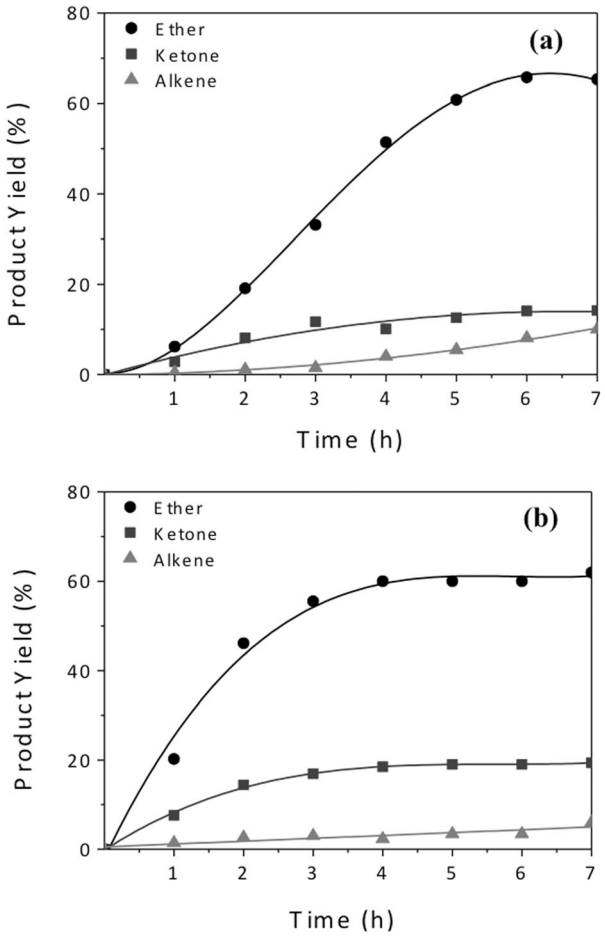


Figure 5. Kinetic profile of the reaction of 1-phenylethanol catalyzed by **Homo-Thia-H** under an air (a) and an oxygen (b) atmosphere.

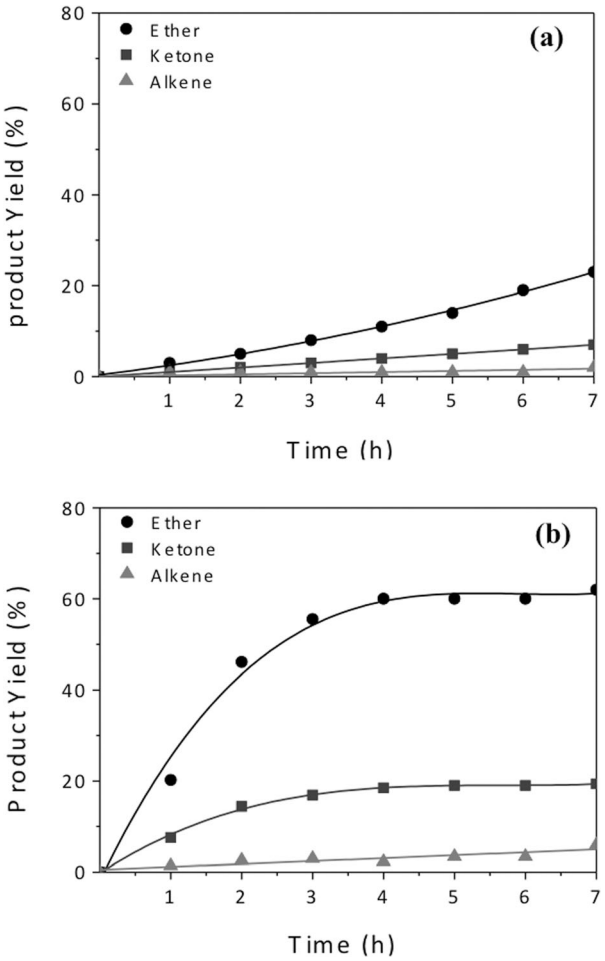
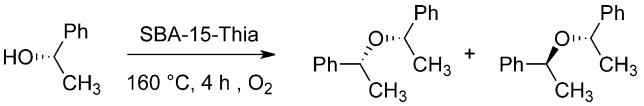


Figure 6. Kinetic profile of the reaction of 1-phenylethanol catalyzed by **Homo-Thia-Me** under an air (a) and an oxygen (b) atmosphere.

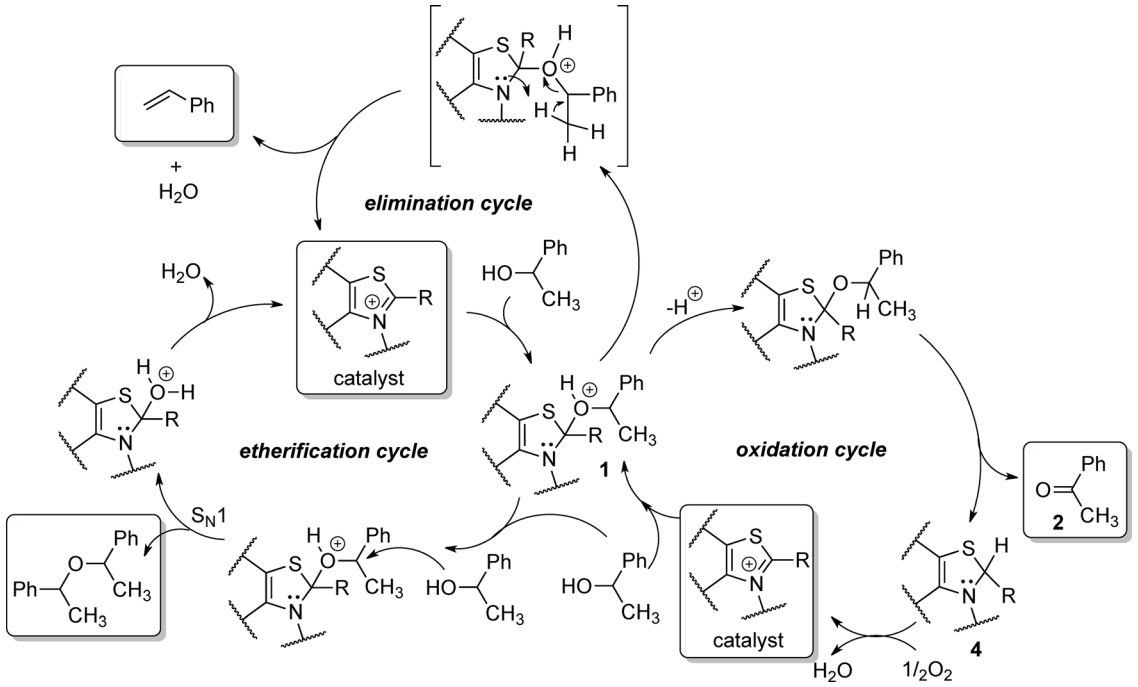
oxygen for 4 h (Scheme 2). The ^{1}H NMR spectrum showed a 60/40 ratio of the two diastereomeric ether products indicating that the reaction follows mainly an S_N1 pathway. Based on these results, a possible explanation can be found in the reactivity of the C-2 as proposed in the mechanism depicted in Scheme 3. This reaction mechanism allows us to explain the key role of the organocatalyst in the alcohol to ether transformation. It is known that the electrophilic C-2 atom may react with nucleophiles such as the hydroxide ion, amines or carbenes.[43] In our case, the nucleophilic attack of the alcohol gives the intermediate species **1**, which undergoes a nucleophilic attack by another alcohol molecule mainly *via* an S_N1 pathway.

The different reactivity observed with the imidazolium-based catalyst can be ascribed to the different reactivity of C-2 and different ability as leaving group in the etherification cycle. Formation of by-products could be also explained through the intermediate **1**. Acetophenone (**2**) could be generated *via* the oxidation cycle through a pathway which resembles the oxoammonium-based mechanism.[44] On the other side,

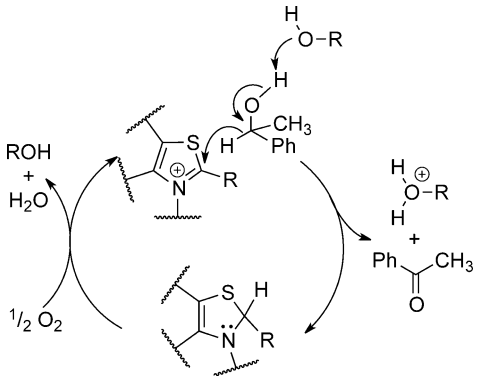


Scheme 2. Etherification reaction of (*S*)-1-phenylethanol.

the presence of styrene (**3**), may be justified by the elimination cycle. It is worthy of note that oxygen emerges as a fundamental element of the catalytic mechanism in both heterogeneous and homogeneous conditions. To justify its undeniable role, we envisaged a possible dual mechanism, similar to the one proposed by Corma and Garcia[45,46] for oxidation reactions in aerobic conditions. The O_2 could promote the elimination of hydrogen forming water and regenerating the active site of the catalyst which is engaged in the oxidation cycle and thus would be blocked for the etherification cycle otherwise. In other words it promotes the oxidation of the 2,3-dihydrothiazole ring (**4**) regenerating the thiazolium catalyst and im-



Scheme 3. Proposed etherification catalytic cycles in the presence of thiazolium-based catalyst.



Scheme 4. Oxidation of 1-phenylethanol *via* the thiazolium/thiazoline system.

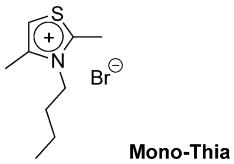


Figure 7. Structure of catalyst **Mono-Thia**.

proving, as consequence, the overall performances of the catalyst. An alternative reaction route that could allow an explanation of the formation of acetophenone as by-product would envisage a mechanism similar to the NAD^+/NADH cycle with the thiazolium moiety playing the role of the pyridinium moiety of NAD^+ and acting as a biomimetic oxidizing/reducing agent (Scheme 4).

The analysis of the results obtained with the homogenous and heterogeneous thiazolium-based catalysts (compare entry 7 in Table 2 and entry 1 in Table 3) highlight the good performances of **SBA-15-Thia** for etherification reactions. Due to the differences in the reaction conditions in terms of temperature, reaction time, nature and amount of active sites, a comparison with literature data is difficult. However, we can state that the productivity of the **SBA-15-Thia** catalyst (defined as: productivity = amount in gram of product/total amount in gram of catalyst) is one of the highest reported in the literature with a similar value after 7 h, of 338 $g_{ether}/g_{catalyst}$ for the reaction performed under oxygen and 337 $g_{ether}/g_{catalyst}$ under an air atmosphere.

In order to have a deeper understanding of the mechanism one additional catalyst, constituted by a single thiazolium unit, was prepared (Figure 7 and Supporting Information, Figures S13 and S14).

The **Mono-Thia** was tested in the etherification of 1-phenylethanol under air. After 7 h reaction a conversion of 68% was obtained. This result further proves the activity of the thiazolium moiety and evidence that **Mono-Thia** displays an intermediate catalytic behavior compared to **Homo-Thia-H** and **Homo-Thia-Me**. This finding suggests that the lower catalytic activity of the trimer catalyst (**Homo-Thia-Me**), ascribed to the presence of the methyl group at C-2, could be balanced by other effects such as the higher accessibility of the same carbon atom in the monomeric catalyst. In the evaluation of a heterogeneous catalyst, the catalytic performances related to activity

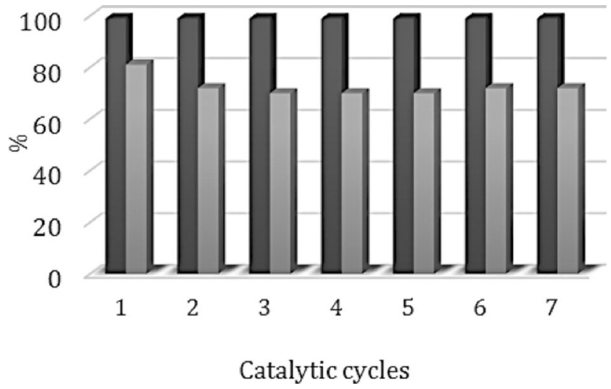


Figure 8. Conversion (dark grey) and selectivity (light grey) in multiple catalytic runs of the etherification reaction of 1-phenylethanol promoted by **SBA-15-Thia**.

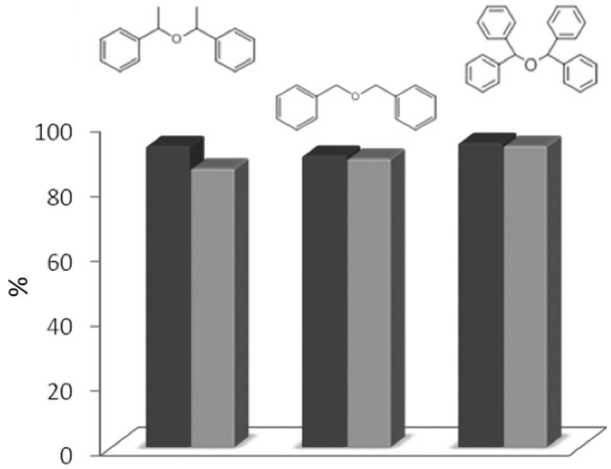


Figure 9. Conversion (dark grey) and selectivity (light grey) in the etherification reaction of 1-phenylethanol, benzyl alcohol and diphenylmethanol.

or selectivity is not the only parameter that should be taken into account. The stability under the reaction conditions should also be tested. Recycle experiments performed with the **SBA-15-Thia** highlight that the excellent catalytic performances are preserved in multiple catalytic runs (Figure 8).

In order to confirm the activity of the **SBA-15-Thia**, additional catalytic test using a primary alcohol and a more hindered secondary alcohol were performed as well (Figure 9). The ^{1}H and ^{13}C NMR spectra of the etherification compounds can be found in the Supporting Information (Figures S15 to S20). It is worthy to underline that the etherification reaction and recycle experiments were performed under solvent-free conditions. Catalytic experiments performed with non-benzylic alcohols such as 2-phenylethanol and 1-decanol gave poor conversion thus confirming that the reaction mainly proceeds through an S_N1 mechanism. The excellent catalytic performances and the stability of the material in consecutive catalytic cycles together with the straightforward preparation of the solid render **SBA-15-Thia** an extremely promising catalyst also for other possible applications.

Conclusions

Multilayered covalently supported ionic liquid-like phases were prepared through a straightforward approach. The two solids bearing an imidazolium or a thiazolium active site were extensively characterized and tested as catalysts for the etherification of 1-phenylethanol. The thiazolium-based heterogeneous catalyst displayed good catalytic performance in the etherification of benzylic alcohols with an excellent productivity ($P = 392\ g_{ether}/g_{catalyst}$) after 24 h under air. The catalyst exhibits similar productivity in the reaction performed using either benzylic alcohol or diphenylmethanol as starting material ($P = 390–394\ g_{ether}/g_{catalyst}$). Moreover, the solid preserves its activity in consecutive catalytic cycles.

The reaction mechanism was investigated using two unsupported thiazolium-based salts. This study allowed us to prove that oxygen plays an active role in the reaction, probably regenerating the catalysts. A possible triple reaction pathway was proposed to explain the formation of the etherification compound as well as the presence of the two by-products. Moreover, an additional test in the presence of enantiopure 1-phenylethanol demonstrated that the reaction follows mainly an S_N1 pathway. This study represents the first use of thiazolium-based compounds as catalysts for the etherification reaction of alcohols.

Experimental Section

Materials and Methods

1-Phenylethanol, benzyl alcohol, diphenylmethanol, 2-phenylethanol and 1-decanol were purchased from Sigma Aldrich and used without further purification. ^{1}H NMR spectroscopy and ^{13}C NMR spectroscopy were performed on JEOL 400 and Bruker 500 spectrometers, respectively. Combustion chemical analysis (C, H, N) were performed on a Thermo Finnigan-FlashEA 1112 apparatus. Transmission electron microscopy images were taken with a Philips TECNAI 10 instrument at 80 kV. MAS-^{29}Si NMR spectrum was recorded on a Bruker 500 spectrometer operating at 5.5 kHz. XRD patterns were collected with a PANalytical X′pert diffractometer with Cu K_α radiation ($k = 1.54178$ Å). Isothermal nitrogen adsorption was carried out with at 77 K with a volumetric adsorption analyzer (Micromeritics Tristar 3000) with a prior sample drying under vacuum at 120 °C.

Procedure for the Synthesis of 1,4-Bis(5-methyl-4-vinyl-thiazolium-1-methylbenzene) Bromide

In a two-necked round-bottom flask 1,4-bis-bromomethylbenzene (1.182 g, 4.48 mmol) and chloroform (3 mL) were placed. The solution was heated in an oil bath at 70 °C with magnetic stirring, under argon. A solution of 4-methyl-5-vinylthiazole (1 mL, 8.86 mmol, 2 equiv.) in chloroform (2 mL) was added drop-wise over 30 min. After 24 h, the reaction mixture was cooled down, filtered and washed several times with diethyl ether. The solid product was dried overnight in an oven at 60 °C.

1,4-Bis(5-methyl-4-vinyl-thiazolium-1-methylbenzene) bromide: Pale yellow powder, yield: 96%; mp >250 °C. ^{1}H NMR (400 MHz, D_2O): $\delta = 2.42$ (s, 6H, -CH_3), 5.63 (d, 2H, $J = 11$ Hz, *cis* CH=CH_2), 5.67 (s, 4H, Ar-CH_2-N), 5.89 (d, 2H, $J = 17.2$ Hz, *trans* CH=CH_2), 6.87 (dd, 2H, $J = 17.4$ and 11.2 Hz, CH=CH_2), 7.38 (4H, s, Ar-H), 9.67 (s, 2H, S-CH=N); ^{13}C NMR (100 MHz, D_2O): $\delta = 11.2$, 56.3, 121.9, 123.8, 129.2, 132.9, 136.5, 142.3, 155.3; IR: $\tilde{\nu}_{max} = 2985$, 1103, 1566, 1455, 672 cm^{-1}; anal. found for $C_{20}H_{22}Br_2N_2S_2$: C 44.40, H 4.29, N 5.08, S 12.44; calcd. (%): C 46.70, H 4.31, N 5.45, S 12.47.

Procedure for the Synthesis of SBA-15

Mesoporous silica material SBA-15 was prepared starting from tetraethyl orthosilicate (TEOS) as the silica source and by using the triblock copolymer poly(ethylene oxide)-poly(-propylene oxide)-poly(ethylene oxide) (EO20PO70EO20, Pluronic P123) as the template.

In a typical procedure, Pluronic P123 (11.0 g) was dissolved in an acid solution of HCl (5.99 g in 200.0 g of water). The solution was stirred overnight at 35 °C in a 500-mL closed polypropylene bottle. Afterwards, TEOS (21.80 g) was added to this solution and the mixture was stirred at the same temperature for 24 h. The milky suspension was heated to 100 °C for 24 h. The solid product was filtered off and washed with a solution of HCl (5% vol). The white solid was calcined at 550 °C for 5 h in air.

Procedure for the Synthesis of Modified Silica SBA-15

In a round-bottom flask SBA-15 (2.0 g), 3-(mercaptopropyl)trimethoxysilane (3.0 mL, 0.016 mol) and toluene (13 mL) were placed. The suspension was heated under reflux conditions for 24 h. After this time, the suspension was cooled to room temperature, filtered and washed with methanol. The white powder was dried in an oven at 80 °C overnight.

Procedure for the Synthesis of Material SBA-15-Thia

In a two-necked round-bottom flask 3-mercaptopropyl-modified SBA-15 (200 mg, SH loading 0.9 mmol g^{-1}, 0.18 mmol), bis-vinylthiazolium or -imidazolium salt (3.69 equiv.), ethanol (5.6 mL) and AIBN were placed. The suspension was degassed by bubbling argon for 30 min. The reaction mixture was heated in an oil bath at 78 °C under argon, and stirred for 20 h. After cooling to room temperature, the mixture was filtered and the solid washed with methanol in a Soxhlet system for 48 h. Then, the obtained material was dried in an oven at 40 °C overnight. Elemental analysis of **SBA-15-Thia**: N% (3.45), C% (30.23), H% (4.06), S% (8.01).

Syntheses of Homo-Thia-H, Homo-Thia-Me and Mono-Thia

Homo-Thia-H: To a solution of 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (0. 98 mmol, 400 mg, 98%) in chloroform (11.7 mL), 4,5-dimethylthiazole (3.21 mmol, 340 μL, 97%) was added and the mixture was stirred at 60 °C for 17 h. After the solvent had been evaporated the resulting residue was washed with diethyl ether (3×20 mL) and dried under reduced pressure; yield: 432 mg (60%). ^{1}H NMR (400 MHz, D_2O): $\delta = 2.1$ (s, 9H, CH_3), 2.42 (s, 9H, CH_3), 2.5 (s, 9H, CH_3), 5.52 (s, 6H, CH_2), 8.86 (s, 3H); ^{13}C NMR (100 MHz, D_2O): $\delta = 11.1$, 11.9, 15.4, 128.8, 134.8, 142.2, 143.4, 151.7, 170.8. IR (powder): $\tilde{\nu} = 3391$, 2972, 2050, 1591, 1440, 1356, 1314, 1221, 1050, 931, 820, 719, 517 cm^{-1}; anal. found for $C_{27}H_{36}Br_3N_3S_3$: C 45.01, H 5.02, N 5.48, S 13.32; calcd. (%): C 43.91, H 4.91, N 5.69, S 13.03.

Homo-Thia-Me: To a solution of 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (1.25 mmol, 500 mg) in chloroform (14.6 mL), 2,4,5-trimethylthiazole (4.087 mmol, 513 μL) was added and the mixture was stirred at 60 °C for 17 h. After the solvent had been evaporated the resulting residue was washed with diethyl ether (3×20 mL), and ethyl acetate (3×40 mL), then dried under reduced pressure; yield: 680 mg (70%). ^{1}H NMR (400 MHz, D_2O): $\delta = 2.08$ (s, 9H, -CH_3), 2.22 (s, 9H, -CH_3), 2.41 (s, 9H, -CH_3), 2.62 (s, 9H, -CH_3), 5.77 (s, 6H, -CH_2-);^{13}C NMR (100 MHz, D_2O): δ 11.2, 12.3, 16.4, 16.6, 51.7, 130.2, 130.5, 139.1, 142.6, 168.1; IR (powder): $\tilde{\nu} = 3288$, 2918, 2495, 2015, 1598, 1439, 1336, 1268, 1026, 928, 823, 743, 528 cm^{-1}; anal. found for $C_{30}H_{42}Br_3N_3S_3$: C 46.86, H 5.11, N 5.18, S 12.00; calcd. (%): C 46.16, H 5.42, N 5.38, S 12.32.

Mono-Thia: In a two-necked round-bottom flask 1-bromobutane (960 μL, 8.85 mmol, 99%) and chloroform (1.5 mL) were placed. The solution was heated in an oil bath at 70 °C with magnetic stirring, under nitrogen. A solution of 2,4-dimethylthiazole (1.0 mL, 8.86 mmol, 95%,) in chloroform (1.0 mL) was added dropwise during 10 min. After 43 h, the reaction mixture was cooled down, dried and washed with diethyl ether (3×20 mL). Then, the solid product was dried under reduced pressure. ^{1}H NMR (400 MHz, D_2O): $\delta = 0.94$ (t, 3H, -CH_3), 1.42 (m, 2H, -CH_2-CH_3), 1.77 (m, 2H,-CH_2-CH_2-CH_3), 2.53 (s, 3H, -CH_3), 2.92 (s, 3H, -CH_3), 4.31 (t, 2H, N-CH_2-), 7.53 (s, 1H, =CH-); ^{13}C NMR (100 MHz, D_2O): $\delta = 12.7$, 13.3, 15.6, 19.3, 30.1, 49.9, 116.8, 146.3, 170.8; IR (powder): $\tilde{\nu} = 3370$, 2956, 2836, 1583, 1488, 1361, 1265, 1136, 928, 846, 741, 543 cm^{-1}. anal. found for $C_9H_{16}BrNS$: C 39.19, H 6.67, N 4.99, S 11.07; calcd. (%): C 43.21, H 6.45, N 5.60, S 12.81.

Typical Procedure for the Etherification Reaction

The reaction was conducted in a two-necked round-bottom flask. Alcohol (44.2 mmol) and catalyst (10.2 mg) were stirred for 24 h at 160 °C. The suspension was then cooled down at room temperature and filtered to recover the catalyst. The mixture was analyzed by ^{1}H NMR to determine the conversion and purified by column chromatography (hexane/ethyl acetate 5:1).

Bis-methylbenzyl ether:[7] oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.40$ (d, 6H, $J = 6.8$ Hz, one diastereoisomer), 1.48 (d, 6H, $J = 6.4$ Hz, one diastereoisomer), 4.26 (q, 2H, $J = 6.8$ Hz, one diastereoisomer), 4.54 (q, 2H, $J = 6.4$ Hz, one diastereoisomer), 7.39–7.22 (m, 10H, two diastereoisomers); ^{13}C NMR (100 MHz, $CDCl_3$, two diastereoisomers): $\delta = 23.3$, 25.0, 74.6, 74.9, 126.4, 126.6, 127.4, 127.6, 128.5, 128.7, 144.4, 144.5.

Bis-benzyl ether:[14] oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 4.61 (s, 4H), 7.32–7.43 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 72.0$, 127.6, 127.7, 128.3, 138.3.

Bis(diphenyl)methyl ether:[28] oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.42$ (s, 2H), 7.25–7.40 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 79.9$, 127.1, 127.3, 128.2, 142.0.

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