Thiazolium-based catalysts for the etherification of benzylic alcohols under solvent-free conditions

UNIVERSITÀ DEGLI STUDI DI PALERMO

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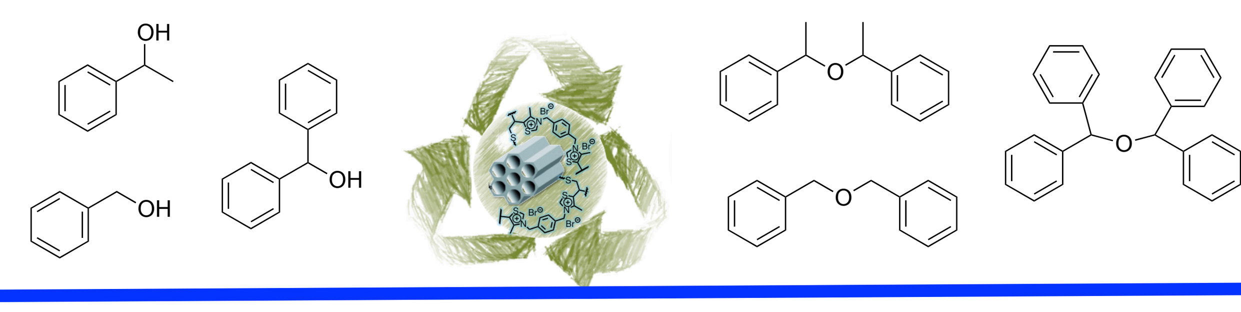
I. INTRODUCTION:

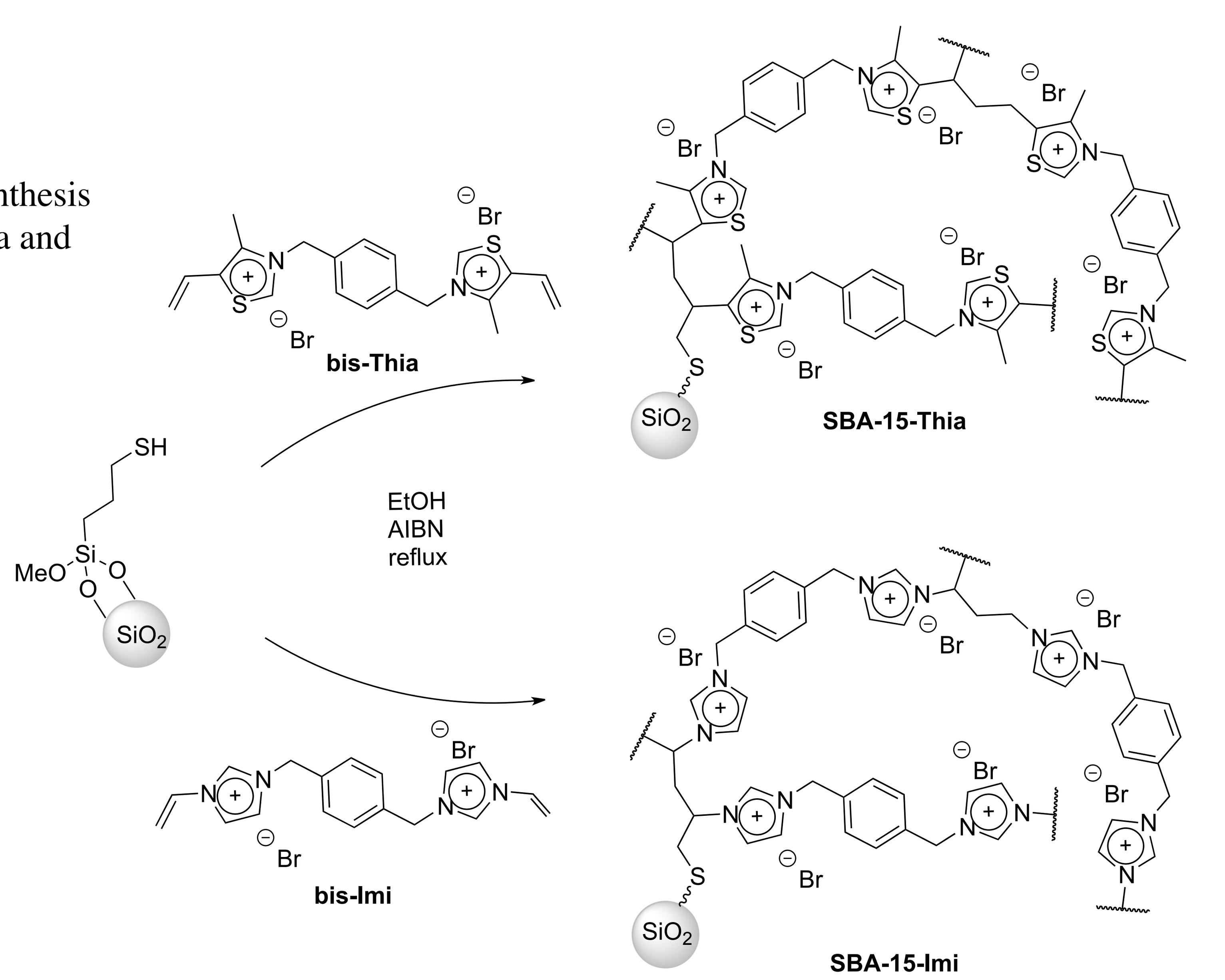
Etherification reaction is one of the most important transformations in organic synthesis and industrial processes. Ethers are largely employed as solvents, fragrance precursor and diesel blends.[1] Several methods are reported for the preparations of ethers from alcohols, but not without limitations. A variety of catalysts based on Lewis acids are employed for etherification reaction, also in presence of organosilanes. In most of the cases, the methods based on transition metal catalysts display good performances, however the homogeneous conditions used represent a major drawback for industrial applications.[2] Ionic liquids recently emerged as a novel class of compounds with multiple possible uses from alternative "green" reaction media to active molecules in catalytic reactions. Supported ionic liquid-like phase (SILLP) are a class of materials that have interesting applications in heterogeneous catalysis.[3] In this work a novel class of thiazolium based supported ionic liquid phase is reported for etherification of benzylic alcohols under solvent-free conditions, showing excellent performances.[4]

AIM: In the present work we present a thiazolium based supported ionic liquid phase as efficient catalyst for the etherification reaction.



II. SYNTHETIC STRATEGY AND CHARACTERISATION

Procedure: Synthesis of SBA-15-Thia and SBA-15-Imi.



Entry	Support	BET Surface Area ($m^2\ g^{-1}$)	Cumulative pore Volume ($cm^3\ g^{-1}$)	Loading of Thia or Imi ($mmol\ g^{-1}$) [a]
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

Table 1: BET surface area and cumulative pore volume of support SBA-15 and supports fonctionalized (SBA-15-SH, SBA-15-Thia and SBA-15-Imi). [a] Loading of thiazolium or imidazolium moiety, calculated by nitrogen data in elemental analysis, show an high degree of organic functionalization.

^{29}Si and ^{13}C NMR spectra (500 MHz)

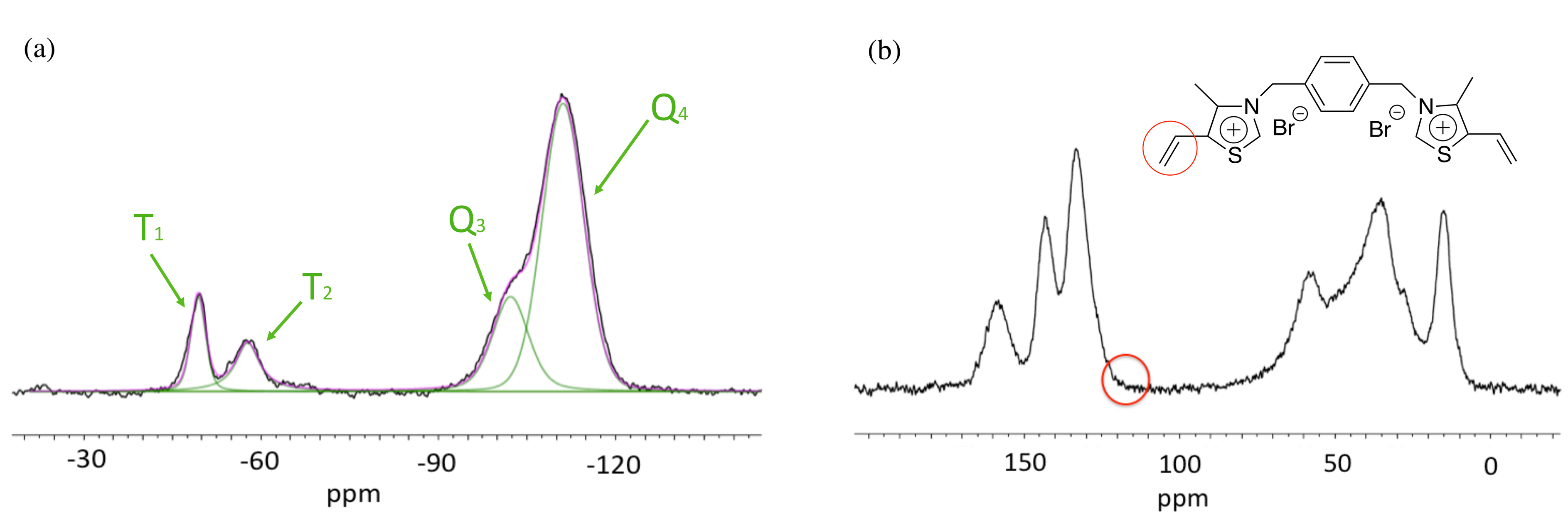
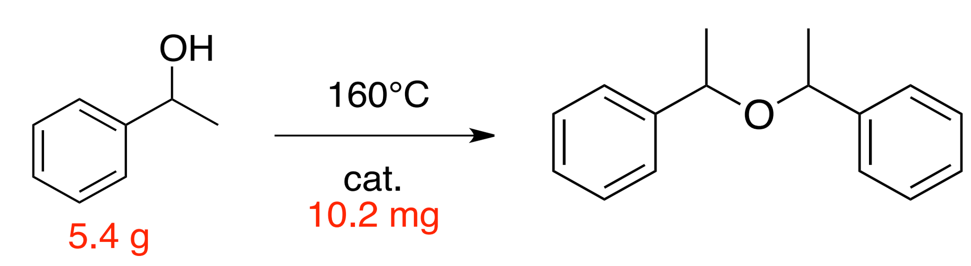


Figure 1: ^{29}Si-NMR spectrum in the solid state of SBA-15-SH (left, a); ^{13}C-MAS-NMR spectrum in the solid state of SBA-15-Thia (right, b). In ^{13}C-MAS NMR data the absence of the signals corrisponding to vinylic carbons confirms the absence of unreacted bis-vinyl precursors in the supported solid,

III. CATALYTIC TESTS



Procedure: Investigation of reaction conditions with SBA-15-Thia and SBA-15-Imi.

Entry	Support	Time (h)	Gas phase	Conversion (%)[a]	Selectivity (%)[b]
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[c]
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

Table 2: Reaction condition: 1-phenylethanol (5.4 g, 44.2 mmol), **SBA-15-Thia** o **SBA-15-Imi** (10.2 mg), 160 °C, under stirring. [a] Determined by ^{1}H NMR. [b] Selectivity toward ether. [c] Main by-product: acetophenone

Catalytic Study with SBA-15-Thia

Conversion in function of the time

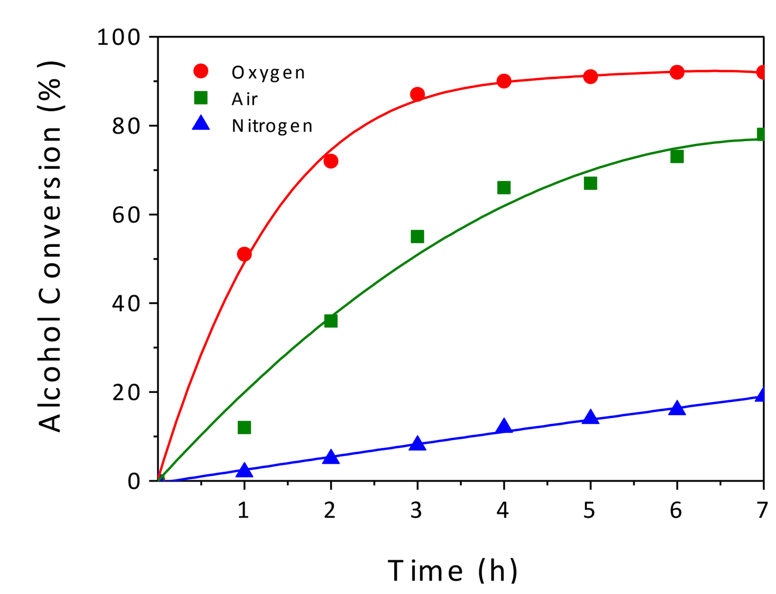


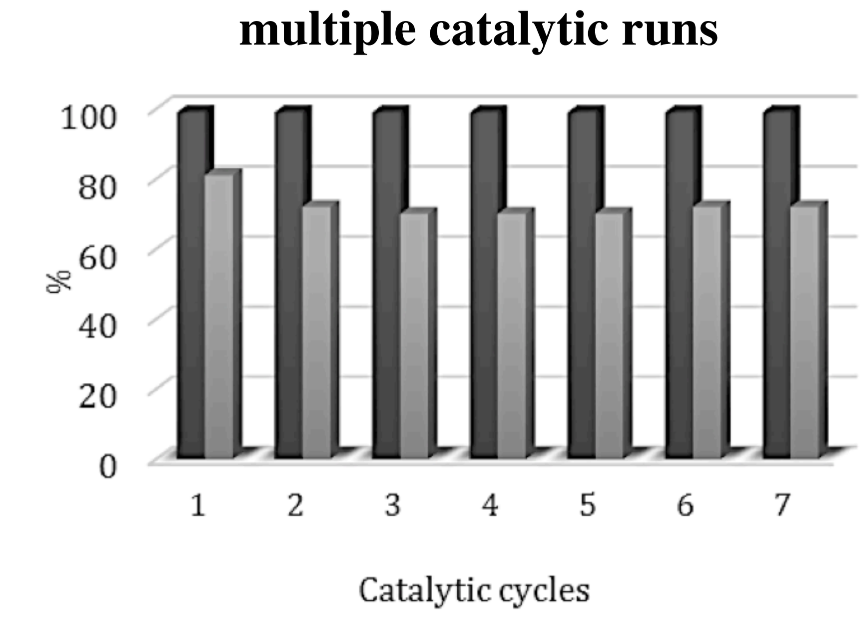
Figure 2: Conversion of 1-phenylethanol with SBA-15-Thia as function of the time in oxygen (red), air (green) and nitrogen (blue) atmosphere.

Oxygen dependent behavior of the SBA-15-Thia catalysed reaction

Productivity ($g_{ether}/g_{catalyst}$): 392 (Air, 24 h)

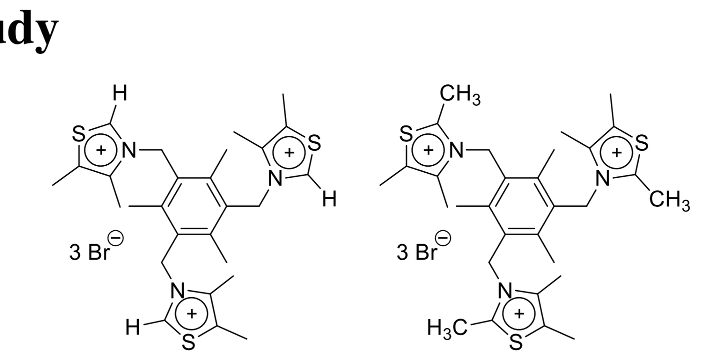
SBA-15-Thia was tested with primary alcohol and more hindered secondary alcohol (as benzylic alcohol and diphenylmethanol) showing excellent results in term of conversion and selectivity.

Conversion and Selectivity in multiple catalytic runs



Mechanicistic study

We investigated the role of the hydrogen at C2 position with two thiazolium based catalysts in homogeneous condition (Homo-Thia-H and Homo-Thia-Me) obtaining reduced performance with Homo-Thia-Me.



IV. CONCLUSION:

Thiazolium and imidazolium hybrid materials (**SBA-15-Thia** and **SBA-15-Imi**) were prepared and tested as catalysts for the etherification of 1-phenylethanol. The SBA-15-Thia displayed an excellent catalytic performance, also with others benzyl alcohols. The results allow proving that oxygen play an active role in the reaction probably regenerating the catalysts. A mechanistic study in homogeneous conditions was also performed. This study represents the first use of thiazolium-based compounds as catalysts for the etherification reaction of alcohols.

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