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### Mesoporous silica-functionalized dual Brønsted acidic ionic liquid as an

### efficient catalyst for thioacetalization of carbonyl compounds in water

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#### Abstract

A novel silica-functionalized dual Brønsted acidic ionic liquid (ionic liquid with two Brønsted acidic species) has been reported as a highly efficient catalyst for thioacetalization of carbonyl compounds. The reaction was efficiently performed in water as an environmentally benign solvent with good to high yields. Thermal gravimetric analysis showed that the catalyst is stable at least up to 350 °C. Furthermore, the catalyst can be recycled and reused for six runs of reaction without appreciable loss of activity. The structure of the catalyst is modelized to gain more realistic structural insight about the functionalized ionic liquid.

**Keywords**: Silica–functionalized ionic liquid; Thioacetalization; Organic reaction in water; Theoretical modeling; Density functional theory.

#### **1. Introduction**

Protecting of carbonyl groups in the form of dithioacetal is a useful method in organic synthesis [1] as they are quite stable over usual acidic and basic conditions [2,3] The dithioacetals can also be utilized as precursors of acyl anion [4] or masked methylene functions in carbon–carbon bond formations [5]. They are routinely prepared by the reaction of the carbonyl compounds with thiol precursor using either Brønsted or Lewis acids such as BF<sub>3</sub>.OEt [6], LnCl<sub>3</sub> [7], Indium triflate (In(OTf)<sub>3</sub>) [8], WCl<sub>6</sub> [9], p–toluenesulfonic acid (PTSA) [10]. Milder precursors such as lithium bromide [11] and N–bromosuccinimide (NBS) [12] have also been reported for this reaction.

The major drawbacks of the mentioned catalysts are using chlorinated organic solvents, releasing hazardous metal wastes and difficulties in catalyst separation. Recently, Brønsted acidic ionic liquids have been reported as efficient catalyst for thioacetalization [13–16]. Even though, such approaches were efficient, but homogeneous ionic liquid systems generally suffer from high viscosity of ionic liquids and requirement of large amounts of these expensive compounds. Furthermore, the ionic liquids (especially Brønsted acidic ionic liquids) have some degree of instability in the presence of air and moisture.

Immobilization of the ionic liquid on the surface of a solid support (generally silica gel) is a useful way to overcome these problems [17–19]. In these methods the homogeneous ionic liquid catalytic systems transfer into the heterogeneous processes. The supported ionic liquid catalyst can be readily used in water as a cheap, economical and environmentally benign solvent [20,21]. Herein, we wish to report a dual Brønsted acidic silica–functionalized ionic liquid catalyst for thioacetalization of carbonyl compounds in water. The study also focused on finding insight about the catalyst structure by mimicking the surface of the functionalized silica gel. Various conformers of the initial and deprotonated structures of the supported ionic liquid are explored.

The value of the  $\Delta H_{acidity}$  of the catalyst was calculated for the deprotonation reaction of the lowest energy conformers. The intra–structural hydrogen bonds (H–bonds) in the catalyst are studied in detail using natural bond orbital (NBO) [22] and the quantum theory of atoms in molecules (QTAIM) analyses [23,24].

#### 2. Results and discussion

The catalyst was prepared by the reaction of the 3–chloropropyl silica and **B** in the presence of potassium iodide (Scheme 1). The presence of the KI can facilitate the reaction between **B** and 3–chloropropyl silica via in situ formation of 3–iodopropyl silica (see electronic supplementary information for details of the experimental procedure).

#### <Scheme 1>

FT–IR spectra of pure silica, 3–chloropropyl silica and catalyst **1** are shown in Figure 1. The FT–IR analysis for the catalyst **1** shows the characteristic bands at 604 and 1177 cm<sup>-1</sup> which is attributed to the S–O and S=O stretching frequencies. The band at 1429 and 1503 cm<sup>-1</sup> belong to C=N of the imidazolium ring of the supported IL proving the successful preparation of the catalyst **1**.

#### <Figure 1>

To investigate the thermal stability, thermal gravimetric analysis (TGA) was performed for the catalyst **1** (Figure 2). The first weight loss around the 70 °C is attributed to the residual physisorbed water and/or organic solvent which were applied during the preparation of the catalyst. The largest weight loss which was occurred between 350 to nearly 500 °C is related to the decomposition of the covalently attached ionic liquid from the surface of the silica gel.

#### <Figure 2>

The performance of the catalyst **1** was investigated for thioacetalization of 4– methoxybenzaldehyde (as a sample reaction) with thiophenol in the water (Table 1). In this reaction, the corresponding thioacetal was obtained in 96% yield when 5 mol% (proton equivalent) of the catalyst **1** was applied. Encourage by this result, we then manage thioacetalization of the various available aldehydes and ketones with different thiol precursor (thiophenol, 1,2–ethanedithiol and 1,3–propanedithiol).

#### <Table 1>

As shown in Table 1, various types of aromatic aldehydes with electron–donating and electron– withdrawing groups as well as cyclohexane–1,4–dione were converted to the corresponding thioacetals in high yield. Similarly, a less reactive benzophenone was also successfully converted to the thioacetal derivative in 54% yield (Entry 11, Table 1).

The recycling experiments were also performed for the catalyst **1** in thioacetalization of 4– methoxybenzaldehyde and thiophenol at the optimized reaction condition (Entry 1, Table1). For this purpose, after the first run, the catalyst **1** was simply filtrated, washed with hexane and was subjected to another reaction with the same condition. Interestingly, it was observed that the catalyst **1** can be recovered and reused for at least five more consecutive reaction runs (Figure 3). The average yields for six runs were more than 90%, which clearly demonstrates the practical reusability of this catalyst. The small decrease in the catalytic activity may be attributed to the small leaching of the supported Brønsted acidic ionic liquid groups and/or losing the  $HSO_4^$ moieties during the reaction from the surface of the mesoporous catalyst.

#### <Figure 3>

Computational methods are fruitful ways to study the functionalized surface of the various supports [25] to gain useful information about the catalyst structure. Recently, Shanks and co-worker modelized the surface of a mesoporous propyl sulfonic acid catalyst in the form of relatively simple fixed –Si(OMe)<sub>3</sub> groups and performed the calculation for this structure [26]. However, using of relatively large cage–like structure of silica gel leads to perform more accurate mimicking of the surface of the catalyst and thus earning more reliable computational results [27–29]. In this study, we attached the acidic ionic liquid on a Si<sub>4</sub>O<sub>6</sub>H<sub>3</sub> cage–like cluster of the silicon–oxygen sequences to modelize the surface. The lowest energy conformers were selected and optimized at B3LYP/6–311++G\*\* level of calculation with the aim of finding global minimum energy structures [30]. Vibrational frequencies were calculated for the optimized geometries to ensure that each structure is the real minima. The optimized structures of the initial acid catalyst (the overall charge is zero and donated by **A**c) and their corresponding deprotonated anions (the overall charge is -1 and donated by **A**n) are shown in the best directions according to the energy in Figure 4.

#### <Figure 4>

It is worth mentioning that the sulfonic acid specie is significantly stronger acid than  $HSO_4^-$  moiety. Thus, the first deprotonation of the catalyst **1** was occurred from the sulfonic acid head group rather than  $HSO_4^-$  specie [18]. The **An1** has the lowest energy among the other anions. It is mainly stabilize by the intra–structural hydrogen bonding and electrostatic interaction.

To gain insight about the acidity, the value of the  $\Delta H_{acidity}$  of the catalyst **1** was calculated according to the literature report [31]. In order to understand the accuracy of the presented calculation method, the gas phase  $\Delta H_{acidity}$  was calculated for a known compound,

methanesulfonic acid, at B3LYP/6–311++G<sup>\*\*</sup> and the results were compared with the experimental value. The calculated value of  $\Delta H_{acidity}$  for the methanesulfonic acid is 319 kcal/mol which is in good agreement with experimental value (320.9± 2.2 kcal/mol) [32]. Next, we calculated the  $\Delta H_{acidity}$  of the catalyst **1** from the deprotonation reaction of **Ac1** to **An1** (the global minimum energy conformers). The result shows that the  $\Delta H_{acidity}$  of the catalyst **1** is 309.4 kcal/mol which is approximately 10 kcal/mol smaller (i.e. stronger acid) than methanesulfonic acid with p*K*a= –1.9.

The acidity of catalyst was also investigated measuring Hammett acidity parameter ( $H_0$ ) according to the literatures [33,34]. The Hammett acidity function expresses the acidity strength of an acid in aprotic organic solvents by the following equation:

$$H_0 = pK (\text{In})_{\text{aq}} + \log \left(\frac{[\text{In}]_{\text{s}}}{[\text{HIn}]_{\text{s}}}\right)$$

where [In] and [HIn] are concentration of the indicator and protonated indicator which can be determined by UV–vis spectrum. Concentrated sulfuric acid and methane sulfonic acid fully protonate the indicator and thus no  $H_0$  value define for these acids. The value of the  $H_0$  for the catalyst **1** measured to be 1.22 which refers to strong deprotonation potential capacity of the supported Brønsted acid ionic liquid (Table 2).

#### <Table 2>

To provide evidence about the nature of the hydrogen bonds, NBO and QTAIM analyses were performed for Ac1–4 and An1–4. In the NBO analysis, the interaction between the electron pairs of the H–bond acceptor atoms and the antibonding orbitals of the H–bonds donor is investigated as a characteristic of Hydrogen bonding. The second order perturbation stabilization energy,  $E^{(2)}$ ,

is related to the delocalization of electrons in donor–acceptor pair and was calculated from perturbation theory [22]. The higher value of  $E^{(2)}$  indicates a higher delocalization trend of electron from donor to acceptor orbitals, and thus stronger interaction. The selected values of  $E^{(2)}$ for donor–acceptor (lp– $\sigma^*$ ) interactions are listed in Table 3. Charge transfer ( $\Delta q_{CT}$ ) from donor to acceptor is another interesting result derived from the NBO analysis. Formation of H–bond leads to observed charge transfer from the donor sites to the acceptors. The value of charge transfer can be attributed to the strength of formed hydrogen bonds. As shown in Table 3, shorter H–bonds generally have higher  $\Delta q_{CT}$  values.

The nature of hydrogen bonding can also explored by QTAIM analysis. One of the useful features of this program is the topological analysis of electron density  $\rho(r)$  at the bond critical points (BCPs) of the optimized structures. The strength of a bond is described by the  $\rho(r)$  parameter which has larger values for stronger bonds. The results of the QTAIM analysis comprising the values of  $\rho(r)$  and V(r) at the BCP and the energies of the H–bonds (E<sub>H...O</sub>) are shown in Table 3.

#### <Table 3>

#### 3. Conclusion

A silica-based dual acidic ionic liquid catalyst has been prepared for thioacetalization of various carbonyl compounds in water. The catalyst showed high thermal stability and six-time recyclability without appreciable loss of activity. The advantages of the presented work over homogeneous ionic liquid system are reducing reaction cost, simple work-up procedure of the catalyst and highly accessible reactive centres on the surface of mesoporous material. The structure of the catalyst was also theoretically studied and modelized considering various

conformers to find global minimum energy of the proposed structure. This modelling gives useful insight about the structure of the catalyst in comparison of simple paper drawing structures. To the best of our knowledge this is the first example which the energetic and the r spiore.  $\Delta H_{acidity}$  of a supported ionic liquid is theoretically explored.

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#### List of Table and Figure captions

Scheme 1. Schematic illustration to preparation of the catalyst 1.

Figure 1. FT–IR spectra of pure silica, 3–chloropropyl silica and catalyst 1.

Figure 2. TGA of the catalyst 1.

**Figure 3.** Recyclability of the catalyst **1** for thioacetalization of 4–methoxybenzaldehyde with 1,2–ethanedithiol at optimized reaction condition.

**Figure 4.** The structures of **Ac1–4** and **An1–4** optimized at B3LYP/6–311++G\*\*. The lengths of the selected H–bonds are shown in Å.

**Table 1.** The data of the catalytic performance for thioacetalization of various carbonyl compounds in the reflux of the water.

**Table 2.** Comparison of Hammett acidity function ( $H_0$ ) of the catalyst **1** and other dual Brønsted acidic ionic liquid (BAIL) based catalysts.

**Table 3.** The values of the total energy, significant values of  $E^{(2)}$  (kcal/mol),  $\Delta q_{CT}$  and the results of the selected bond critical point related to the **Ac1** and **An1**.

### Scheme 1











Table 1

				$\sim$
Entry	Substrate	Product	Time (h)	Yield (%) <sup>a</sup>
1	н₃со-∕С	H <sub>3</sub> CO-	5	96
2	Н <sub>3</sub> С-СНО	H <sub>3</sub> C-	5	91
3	н <sub>3</sub> со-Сно	H <sub>3</sub> CO-	3	94
4	o= <o< td=""><td>S S S S S S</td><td>7</td><td>89</td></o<>	S S S S S S	7	89
5	Бг СНО	Br	2.5	95
6	сі————————————————————————————————————	ci-{S-S-S-S-S-S-S-S-S-S-S-S-S-S-S-S-S-S-S	3	93
7	СНО Н <sub>3</sub> С	$A_{H_3C}$ $S_{S_3}$	2	95
8	Н₃С-∕СНО	$H_3C \xrightarrow{S} S$	2	96
9	н <sub>3</sub> сс — Сно	H <sub>3</sub> CS – S	3	92
10	Сно	S_S_S_	2	85
11	o	S S	24	54



<sup>1</sup>H NMR spectra.

Table 2

			$\mathbf{\Omega}$
Entry	Catalyst	$\mathrm{H_0}^a$	Ref.
1	$H_2SO_4$	_b	
2	CH <sub>3</sub> SO <sub>3</sub> H	b	
3	Catalyst 1	1.22	This work
4	Dual BAIL	0.88	33
5	Poly(Dual BAIL)	1.83	34

<sup>*a*</sup> Condition for Hammett acidity function: solvent: CH<sub>2</sub>Cl<sub>2</sub>, indicator: 4-nitroaniline ( $pK(I)_{aq} = 0.99$ ),  $5.0 \times 10^{-4}$  mol/L. Catalyst 1:  $7.5 \times 10^{-3}$  mol/L (proton equiv.), 25 °C.

<sup>b</sup> Full protonation of indicator.

### Table 3

Structure	Total energy <sup>a</sup>	Charge transfer	r <sub>H0</sub> <sup>b</sup>	$E^{(2)}$	$\Delta q_{CT}$	BCP	$\rho(r)$	V(r)	-Е <sub>но</sub> с
Ac1	-3476.039993	lp $O_{45} \rightarrow \sigma^* H_{41} - O_{40}$	1.901	8.42	0.164	$O_{45}H_{41}-O_{40}$	0.027	-0.0214	6.71
		lp $O_{42} \rightarrow \sigma^* H_{36} - O_{35}$	1.596	36.86	0.642	$O_{42}H_{36}-O_{35}$	0.054	-0.0562	17.63
An1	-3475.549306	lp $O_4 \rightarrow \sigma^* H_{52} - O_{51}$	1.815	11.96	0.205	$O_4H_{52}-O_{51}$	0.036	-0.0324	10.17
		$lp O_{49} \rightarrow \sigma^* H_{32} - C_{30}$	2.126	5.47	0.198	$O_{49}H_{32}-C_{30}$	0.019	-0.0122	3.83

<sup>*a*</sup> The values of total energy are reported in a.u.

 $^{b}$  r <sub>H...O</sub> is the length of H–bonds which are reported in Å.

<sup>c</sup> The energy of H-bonds reported in kcal/mol which are calculated according to the following equation: E <sub>H...0</sub>= V(r)/2×627.5 [35].

. in Å . which are

### Graphical abstract



### Highlights

- Silica supported dual Brønsted acidic ionic liquid.
- Water-tolerant catalyst for thioacetalization of carbonyl compounds in water.
- Theoretical modeling of the catalyst structure.

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