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Graphical Abstract

Synthesis of the 3D-network polymer supported Bronsted acid ionic liquid based on calix[4]resorcinarene *via* two post-functionalization steps: Highly efficient and recyclable acid catalyst for the preparation of symmetrical bisamides

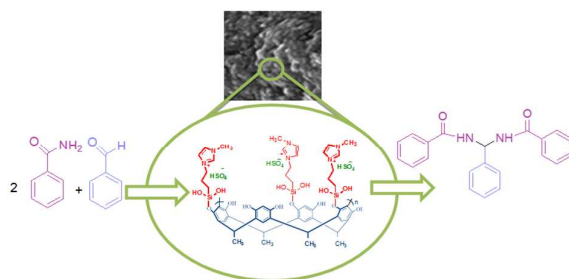
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We report a straightforward route for the synthesis of novel functional polymer bearing ionic liquid arms as an efficient and green acidic catalyst for the preparation of symmetrical bisamides.



Synthesis of the 3D-network polymer supported Bronsted acid ionic liquid based on calix[4]resorcinarene *via* two post-functionalization steps: Highly efficient and recyclable acid catalyst for the preparation of symmetrical bisamides

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Abstract

In this work, for the first time, 3D-network polymer supported Bronsted acid ionic liquid was synthesized *via* two post-functionalization steps. Initially, the active homogeneous catalyst is chemically immobilized onto the polymeric support based on calix[4]resorcinarene through silylation of hydroxyl groups to form cationic polymer that contains imidazolium moieties. The formation of this cationic polymer was confirmed by elemental analysis, scanning electron microscopy (SEM), thermal gravimetric analysis (TGA) and derivative thermogravimetric (DTG). Subsequently, HSO₄ anion was incorporated into the polymer along the imidazolium pendant groups *via* the well-known ion exchange reaction. Elemental analysis data revealed that cationic polymer was conveniently loaded with desired Bronsted acid anion. Therefore, it provides a novel heterogeneous acid catalyst for achieving synthetic goals.

The immobilized acidic ionic liquid effectively catalyzed the one-pot synthesis of symmetrical bisamides by multicomponent condensation of two moles of amides with aldehydes. Interestingly, the catalyst exhibited high turnover number (TON) and turnover frequency (TOF), which were even comparable with that of H₂SO₄.

The unique features of this catalyst such as superior thermal stability, recyclability, excellent catalytic activity in terms of yield and reaction time, high turnover number and turnover frequency, will be potentially important for its applications in industry.

Keywords: Polymer supported Bronsted acid ionic liquid; Polymeric support based on calix[4]resorcinarene, Two post-functionalization steps, Symmetrical bisamides.

1. Introduction

Ionic liquids including the Lewis and the Bronsted acid anion have been proved to be efficient catalysts for various reactions.¹ However, unendurable viscosity, high cost, tedious purification procedure of the product, moisture sensitivity and decomposition of some ionic liquids under normal atmospheric conditions, restricted their widespread practical applications to the industrial scale.² In order to solve this problem, immobilized ionic liquid catalysts which combine the advantageous characteristics of ionic liquids, inorganic acids and solid acids had been proposed.³

In this context, the grafting of strong acidic ionic liquids (ILs) onto inorganic materials, such as mesoporous silicas and zeolites, has received considerable attention.⁴ However, the hydrophilic inorganic networks of the supports largely affect their catalytic activities due to water, usually a by-product in many acid catalyzed reactions, which easily co-adsorbs near the acidic sites, further leading to the partial deactivation or leaching of the active sites.⁵ Moreover, the presence of organic halides containing cations usually results in the destroying of the inorganic supports, which largely constrains their wide applications.⁶

Compared with inorganic supports, polymers showed adjustable hydrophobicity and good stability for various acids. These features coupled with their biodegradability and green natures, make polymeric supports attractive materials to organic and industrial chemists.

However, some of these polymeric supports suffer from one or more defects in their synthetic or functionalization routes and properties, including long reaction times, multiple steps synthetic route, functionalization *via* copolymerization or further post-polymerization under harsh reaction condition, the use of expensive catalysts, solubility in various solvents, low thermal and/or chemical stability. Hence, in the main stream of the current interest, developing and applying new supports for the heterogeneous type catalytic system, which may quickly be moved from the laboratory to the green industrial plant, have received increasing attention.

It seems that the 3D-network polymer based on calix[4]resorcinarene can be a good candidate as support materials for heterogeneous catalysis, because of ease of preparation and unique properties such as good dispersion of active sites, versatile chemical modification (acylation, alkylation and silylation of hydroxyl group and nucleophilic aromatic substitution on the aromatic ring), straightforward functionalization route *via* post-functionalization without undergoing copolymerization or further post-polymerization, porous surface (pore radius from approximately 100 to 500 nm), high thermal and chemical stability.⁷

To the best of our knowledge, despite its convenient properties and significant potential for functionalization under mild reaction conditions without the use of acidic or basic catalyst, there have been no reports on the immobilization of acidic ionic liquid onto this polymeric structure.

Up to now, some immobilization processes for acidic ILs onto solid support have been designed. Among them, synthesis of functionalized cationic polymer *via* covalently anchored ILs onto polymeric backbone, which could be converted to acidic form by facile ion exchange reaction, has generated much interest.

Quaternary ammoniums (QAs) have been the most widely studied as cationic groups for functionalization of various polymers. However, the environmental issue concerning the use of highly volatile reagents such as trimethyl amine for introduction of these QAs limits their large scale synthesis and applications.

To overcome this limitation, alkyl imidazolium has recently been incorporated into polymers as cationic moieties due to their low volatility, excellent thermal and chemical stabilities.⁸

Hence, it would be reasonable to survey the immobilization of acidic ionic liquid containing imidazolium moieties onto the 3D-network polymer based on calix[4]resorcinarene as a promising solid support which can be used as an efficient acidic catalyst in chemical reaction for construction of valuable target molecules.

Exceptional properties of amide bond offer many vital roles to amide derivatives, such as biochemicals, structural subunit of polymers, and stable synthetic intermediates in chemistry and materials science.⁹ Among a large variety of compounds containing amide bond, bisamides are one of the important amide derivatives which have been used as versatile intermediates in the synthesis of

biologically active compounds such as amidoalkyl.¹⁰ They were also applied as the ligands in the Ullmann coupling reactions.¹¹ Moreover, they are of considerable interest in the synthesis of pharmacological materials such as peptidomimetic compounds.¹²

Due to the aforementioned chemical and pharmacological significance, a great deal of efforts has been drawn to develop new and efficient synthetic routes to their generation in recent years. Although these methods are effective, they suffer from some drawbacks such as long reaction time, multiple steps, the use of expensive catalyst, special care in handling and storing the catalyst, laborious workup and purification steps. Consequently, the development of more convenient, economical and eco-friendly protocol that uses an efficient and reusable catalyst is highly desired.

Having the above points in mind, as part of our continuing efforts to develop high performance and environmentally friendly procedures for various important reactions and transformations¹³ and our new interest in the application of the 3D-network porous polymer based on calix[4]resorcinarene for the preparation of biologically important molecules,⁷ herein, we report for the first time, the functionalization of polymeric calix[4]resorcinarene *via* covalently anchored acidic ionic liquid and the investigation of its efficiency as solid acid for the synthesis of bisamide derivatives through the one-pot reaction of various aldehydes with aliphatic and aromatic amides.

2. Experimental

2.1. General

Chemicals were purchased from Fluka, Merck and Aldrich chemical companies and used without further purification. Products were characterized by physical data, IR, ¹H NMR and ¹³C NMR spectra. IR spectra were obtained on a Bomem MB:102 FT-IR spectrophotometer. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker spectrometer at 400 MHz and 100 MHz, respectively, in CDCl₃ or dimethyl sulfoxide (DMSO) with tetramethylsilane as an internal standard. Elemental analyses were performed at a Thermo Finnigan Flash EA 1112 CHNS-Analyzer. The polymer morphology was examined by SEM (LEO-1455VP). Thermal stability of the functionalized polymer was investigated by NETZSCH STA 409 PC/PG under nitrogen atmosphere (rate of N₂ ≈ 1 Lit/h).

Monitoring of the reactions and the purity determination of the products were accomplished by TLC on silica gel PolyGram SILG/UV 254 plates.

2.2. *Synthesis of calix[4]resorcinarene (1)*

Calix[4]resorcinarene was prepared according to the literature procedures.¹⁴

2.3. *Synthesis of the 3D-network polymer based on calix[4]resorcinarene (2)*

The desired polymer was synthesized by adding 42 mmol of formaldehyde to 14 mmol of the prepared calix[4]resorcinarene dissolved in 40 mL NaOH solution (10%) at room temperature. The resultant mixture was heated to 90 °C and kept at 90 °C for 20 h. Next, the excess alkali was washed out of the gel formed with cold water. The gel was allowed to stand at 100 °C for 1 h. Then, the gel was transformed to the H form by treatment with the 0.1 M HCl solution. The resulting solid was dried at 100 °C for 10 h.¹⁵

2.4. *Synthesis of novel functionalized polymer (3) through one-step chemical modification*

The synthesized polymer (1.0 g), 3-chloropropyltrimethoxysilane (3.4 g, 16 mmol) and an excess of methyl imidazole (25 mmol) were added to a round bottom flask containing 10 mL H₂O/EtOH at room temperature. The reaction mixture was heated to 90 °C and kept at 90 °C for 20 h. The desired cationic polymer was collected by filtration and washed with deionized water several times before drying at 80 °C.

2.5. *Determination of the amount of grafted cationic moieties onto polymer*

The amount of grafted cationic moieties onto polymer was achieved by elemental analysis. The amount of grafted imidazolium moieties was generally found to be 2.5 mmol per gram of the dry cationic polymer.

2.6. *Preparation of polymer-supported acidic catalyst 4*

The dried cationic polymer (1.0 g) was suspended in 10 mL CH_2Cl_2 . During vigorous stirring, 3.5 mmol of concentrated H_2SO_4 (98%) was introduced drop by drop at 0 °C. Then the mixture was warm up to room temperature and was refluxed for 48 h. The desired catalyst was collected by filtration and washed with deionized water several times.

2.7. Determination of the capacity of the polymer-supported catalyst

The capacity of the polymer-supported catalyst was achieved by elemental analysis. The capacity was generally found to be 0.906 mmol H^+ per gram of the dry polymer-supported catalyst **4**.

2.8. General procedure for the synthesis of bisamide derivatives (5)

To a mixture of aldehyde (1 mmol) and amide (2 mmol) in toluene (5 mL) was added 0.08 g catalyst. The resulting mixture was stirred under reflux condition, after completion of the reaction (TLC monitoring), a white viscous solid was obtained. The mixture was cooled and the solvent was removed by filtration. Then hot ethanol (10 mL) was added to the residue and the catalyst was separated by filtration. Evaporation of ethanol under reduced pressure gave the products which were purified by recrystallization in a suitable solvent (ethanol or acetone).

2.9. Recycling of catalyst 4

The multicomponent reaction of 1 mmol benzaldehyde and 2 mmol benzamide in toluene as a model reaction was studied. When the reaction was completed, the mixture was cooled and the solvent was removed by filtration. Then hot ethanol was added to dissolve the product. The solid catalyst was filtered off, washed with hot ethanol and dried under vacuum after each cycle, and then reused for the next reaction.

3. Results and discussion

As stated earlier, the search for more efficient catalytic systems that might combine the advantages of both homogeneous and heterogeneous catalysis is one of the most exciting challenges of modern

chemistry. Considering this fact, we have chosen the immobilization of Bronsted acidic ionic liquid (1-methyl-3-(trimethoxysilylpropyl) imidazolium hydrogensulfate) [pmim]HSO₄ onto the 3D-network polymer based on calix[4]resorcinarene *via* two post-functionalization steps. The first step consists of the synthesis of novel cationic polymer *via* immobilization of IL ([pmim]Cl) onto polymeric backbone and the second step consists of [pmim]Cl transformation into [pmim]HSO₄ by ion exchange reaction.

To achieve this objective, the 3D-network polymer **2** was prepared by the reaction of resorcinol and acetaldehyde, followed by polycondensation of calix[4]resorcinarene **1** with formaldehyde,¹⁴⁻¹⁵ the synthesis steps are depicted in Scheme 1.

The structure of compound **1** was established unambiguously from spectroscopic (IR, ¹H NMR, ¹³C NMR) data (See Supplementary Material). Formation of polymer **2** was also confirmed and characterized by atomic force microscopy (AFM), X-ray diffraction (XRD) and scanning electron microscope (SEM)⁷ (Available in Supplementary Material).

<Scheme 1>

Subsequently, in the first step of post-functionalization, the prepared polymer **2** was treated with 1-methyl imidazole and (3-chloropropyl) trimethoxysilane in water/ethanol to undergo a condensation reaction, yielding cationic polymer **3** in one-step modification reaction (Scheme 2). The loading amount of the cationic moieties on polymer was determined by elemental analysis. The nitrogen analysis of supported IL **3** (N, 7%) indicates that 2.5 mmol of imidazolium moieties was grafted onto the surface of per 1 g of the polymer. The formation of **3** was also confirmed by SEM, TG and DTG analysis.

<Scheme 2>

In order to gain insight into the morphology of the synthesized polymer **3**, scanning electron microscopy was used (Fig 1).

<Fig. 1>

Since the cationic polymer **3** shows smaller pores (about 97 nm in diameter) than polymer **2** (300 nm in diameter, See Supplementary Materials), it can be concluded that ILs are successfully grafted to the polymeric backbones.

The stability of the functionalized polymer **3** was determined by thermo-gravimetric analysis at a heating rate of 10 °C per minute under nitrogen atmosphere (Fig. 2). The TG curve indicates an initial weight loss of 8.46% up to 100 °C due to the adsorbed water and organic solvent in polymeric support which is common in the cases of immobilized catalysts onto organic or inorganic supports.¹⁶ Complete loss of the IL chains is seen in the range of 300–469 °C. Weight loss in the temperature range of 500–1100 °C can be assigned to the decomposition of the polymeric support. Meanwhile, the peak in the DTG curve shows that decomposition of the IL chains mainly occurred in two steps at 395 and 430 °C which can be attributed to the decompositions of the imidazolium moieties and propylsilane linkers, respectively. Thus, the TGA and DTG curves also convey the obvious information that IL chains are successfully grafted to the polymeric backbones.

<Fig. 2>

After characterization of **3**, in the second step of post-functionalization, the resulting cationic polymer was further reacted with H₂SO₄ in dichloromethane to form the corresponding 3D-network polymer-supported acidic catalyst **4** (Scheme 3).

<Scheme 3>

The sulfur content of the catalyst, measured by CHNS analysis, showed the value of about 2.9%. Based on this value, the amount of HSO₄ anions which were supported on the polymer is about 0.906 mmol per gram polymer. This result gave us confidence that, the imidazolium side chains and polymeric backbones are completely stable under acidic conditions.

It is noteworthy that, this polymeric support showed more potential for covalently anchored acidic ionic liquids in comparison with some previous solid supports reported in literature.¹⁷ Moreover, the synthesized polymer supported acid catalyst (**4**) is effectively insoluble in various solvents, including H₂O, CH₃OH, EtOH, DMSO, DMF, CH₃CN, CH₂Cl₂ and CHCl₃. These features render it suitable for conducting chemical transformations in various reaction media as an efficient heterogeneous acid catalyst.

In this regard, owing to the widespread applications of bisamide derivatives, we decided to investigate the synthetic applicability of **4** as an acid catalyst for rapid and efficient construction of bisamide derivatives through multicomponent reaction.

To develop suitable reaction conditions, the reaction of 2 mmol benzamide with 1 mmol benzaldehyde was chosen as a model reaction (Scheme 4) and parameters such as solvent and amount of catalyst (**4**) were examined in detail.

<Scheme 4>

The solvent optimization revealed that the solubility of both substrate and product play an important role in the process. It was found that the reactivity, the ease of work-up using filtration, the high yield and the purity of product could meet together when the substrate was well soluble and the product could precipitate.¹⁸ Thus the tetrahydrofuran, acetone, acetonitrile and ethyl acetate failed to obtain a homogeneous solution at the first stage, diminishing the yield and purity of the final product (Entry 2-5, Table 1). To our surprise, among the solvents investigated, boiling toluene boosted the yield to 80% (Entry 6, Table 1), due to its perfect solubility for substrate and insolubility for product.

The reaction was also evaluated in the presence of various amount of catalyst. The results showed that 0.08 g of catalyst efficiently catalyzed the reaction to give desired product (**5**) (Entry 7, Table 1). It was also found that increasing or decreasing the amount of catalyst not only improves the reaction times but also reduces the yield of the desired product significantly (Entry 6 & 8, respectively, Table 1). This may be rationalized by considering the fact that small amounts of acidic catalyst could not activate the aldehyde effectively and the large amounts of it inactive the amide *via* its protonation. Thus the reaction of 2 mmol benzamide with 1 mmol benzaldehyde in the presence of 0.08 g catalyst in refluxing toluene was chosen as the optimized reaction conditions.

<Table 1>

To confirm the catalyst efficiency, further experiments were carried out. Initially, in a control experiment, we carried out the model reaction in absence of any catalyst. In this case only a trace amount of product was detected after 6 h (Entry 9, Table 1).

Next, the model reaction was examined in the presence of H₂SO₄. As shown in Table 1, the yield of *N,N'*-phenylidene bisamide (**5**) was much higher with solid protic acid (**4**) than with sulfuric acid (Entry 7&10, respectively, Table 1).

The superiority of this solid analog of sulfuric acid to commercial sulfuric acid is attributed to its porosity. The adsorption of substrate on the surface of the functionalized polymer based on hydrophobic interaction between substrates and polymeric backbone could increase local concentration of substrates around the active sites of the polymer and effectively promoting the reaction. These observations clearly highlight the existence of synergistic effect between cavities of polymeric support and immobilized acidic ILs in obtaining high catalytic activities.

These results encouraged us to demonstrate the efficiency and the applicability of the present acid-catalyzed multicomponent reaction. For this purpose, the optimized reaction conditions were applied to a variety of aldehydes containing electron-withdrawing or electron-donating groups. Representative results of this synthetic modification are listed in Table 2.

Both electron-rich and electron-deficient aldehyde gave the *N,N'*-arylidene bisamide in good to excellent yields (Entry A-F, Table 2).

In order to further expand the scope of this catalytic system, acetamide was treated with variety of aldehydes and successfully converted to their corresponding bisamide (Entry G-L, Table 2).

<Table 2>

All products were identified by comparing their physical and spectral data with those of authentic samples.¹⁹

It is noteworthy that, the formation of **5 A-F** by this method are of considerable interest since this is the first attempt to the synthesis of these privileged compounds in the presence of polymer supported Bronsted acid ionic liquid as an efficient solid acid catalyst.

On the basis of the results obtained above, a possible mechanism for the sequence of events is shown in Scheme 5. It seems that initially, solid acid catalyst **4** activates the carbonyl group of aldehyde for reaction with amide to form a hemiamidal intermediate (**6**). Subsequently, elimination of water from **6**, forms *N*-acyliminium intermediate (**7**) which then is converted to desired product **5** through nucleophilic reaction with another molecule of amide.

<Scheme 5>

It is well-known that the reusability, turnover numbers (TON) and turnover frequencies (TOF) of a catalytic system are the key factors that determine whether it has the potential applications in industry. Considering this fact, in order to test the catalyst reusability, the reaction of 2 mmol benzamide with 1 mmol benzaldehyde was carried out under optimal reaction conditions. After completion of each reaction, hot ethanol was added and the catalyst was filtered. The recovered catalyst was washed with ethanol, dried and reused. The results illustrated in Fig. 3 showed that the catalyst can be reused for up to five cycles without significant loss in its activity. This result indicates that the catalyst was very stable and could endure this reaction's conditions without decomposition or leaching of active species in the reaction media.

<Fig. 3>

Next, the catalytic performances as TON and TOF of this reusable analog of sulfuric acid were compared with commercial available sulfuric acid for the model reaction under optimized conditions (Entry 1&2, Table 3). The results show much superiority of catalyst **4** to H₂SO₄.

In order to show the merit of this novel catalyst, Table 3 compares our results obtained from the model reaction in the presence of catalyst **4** with the results reported in literature. It can be seen that, heterogeneous catalyst **4** exhibited significantly higher turnover number and turnover frequency than those reported for other catalytic systems (Entry 3-5, Table 3).

<Table 3>

Based on these results, we expect that this catalyst **4** will be a suitable alternative to the existing acid catalyst in laboratory and industrial applications.

4. Conclusion

Bronsted acid ionic liquid has been immobilized onto the 3D-network polymer based on calix[4]resorcinarene to form novel heterogeneous solid acid catalyst. The synthesized catalyst shows remarkably and somewhat extraordinary catalytic activity for the synthesis of bisamide derivatives. This catalyst is even more reactive than the homogeneous strong acid (H₂SO₄) under the same

reaction conditions. Porosity of polymeric support and covalently anchored acidic ionic liquid might indeed provide a synergistic means of the efficient approach of the starting materials to acidic sites, enough space for the preparation of product and suitable hydrophobicity to drive out the water formed during the reaction from the support.

Catalyst **4** which possesses a combination of a stable and hydrophobic polymeric support, strong acid strength, excellent catalytic activity and good recyclability in acid catalyzed reactions, will open a new way for the synthesis of novel and efficient heterogeneous acid catalysts *via* modification of the 3D-network polymer based on calix[4]resorcinarene. Unique properties, such as uniform reaction site and significant potential for functionalization, allow one to optimize the properties of this polymer for immobilization of desired catalyst *via* post-functionalizations without undergoing copolymerizations or further post-polymerization modifications.

Thus, this study suggests that the 3D-network polymer based on calix[4]resorcinarene can be used as an important and versatile green solid support for a variety of acid catalysts.

Acknowledgments

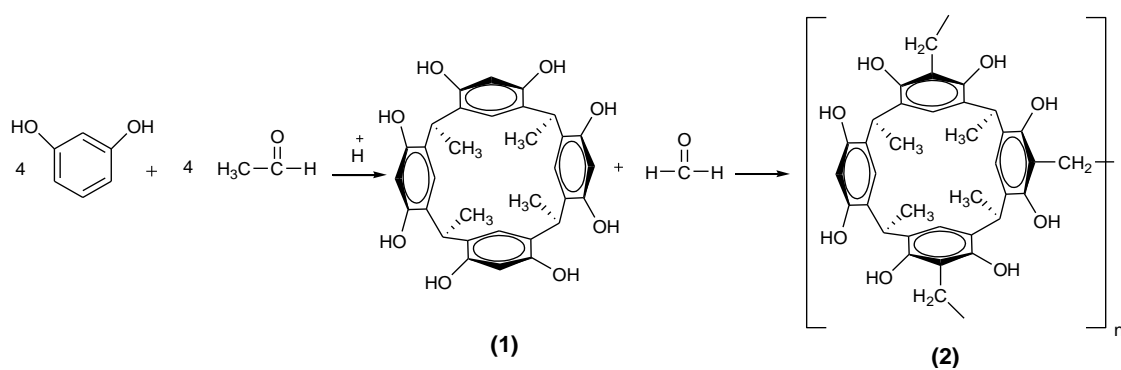
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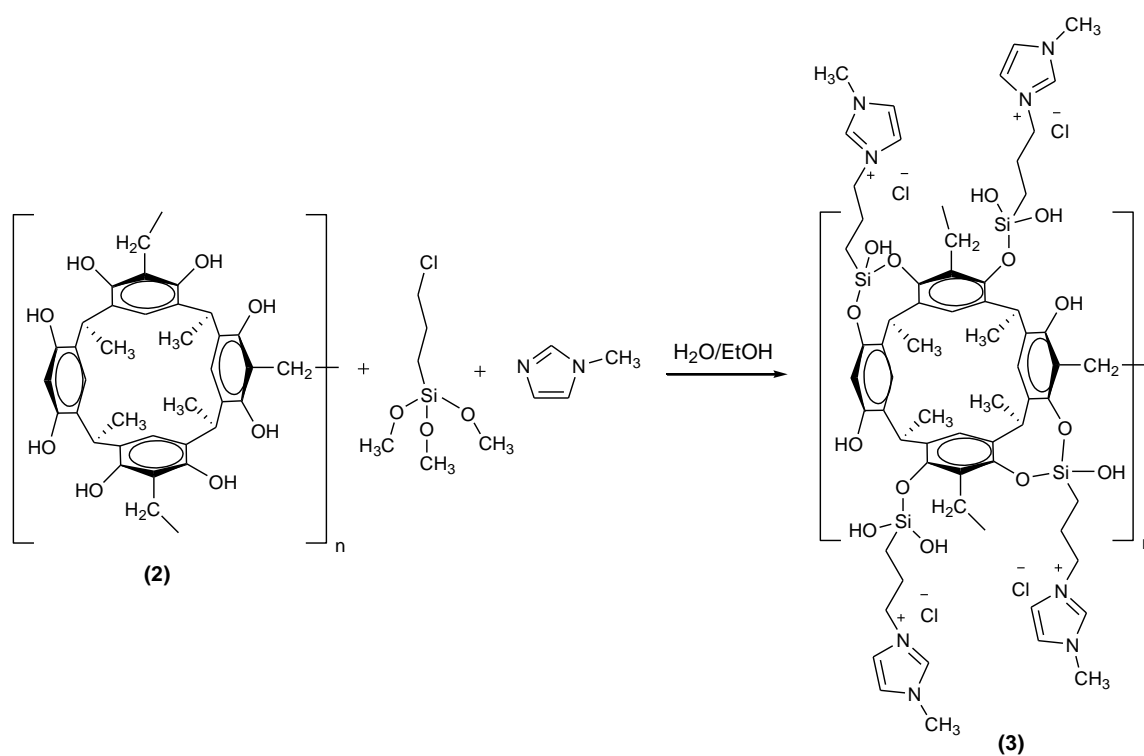
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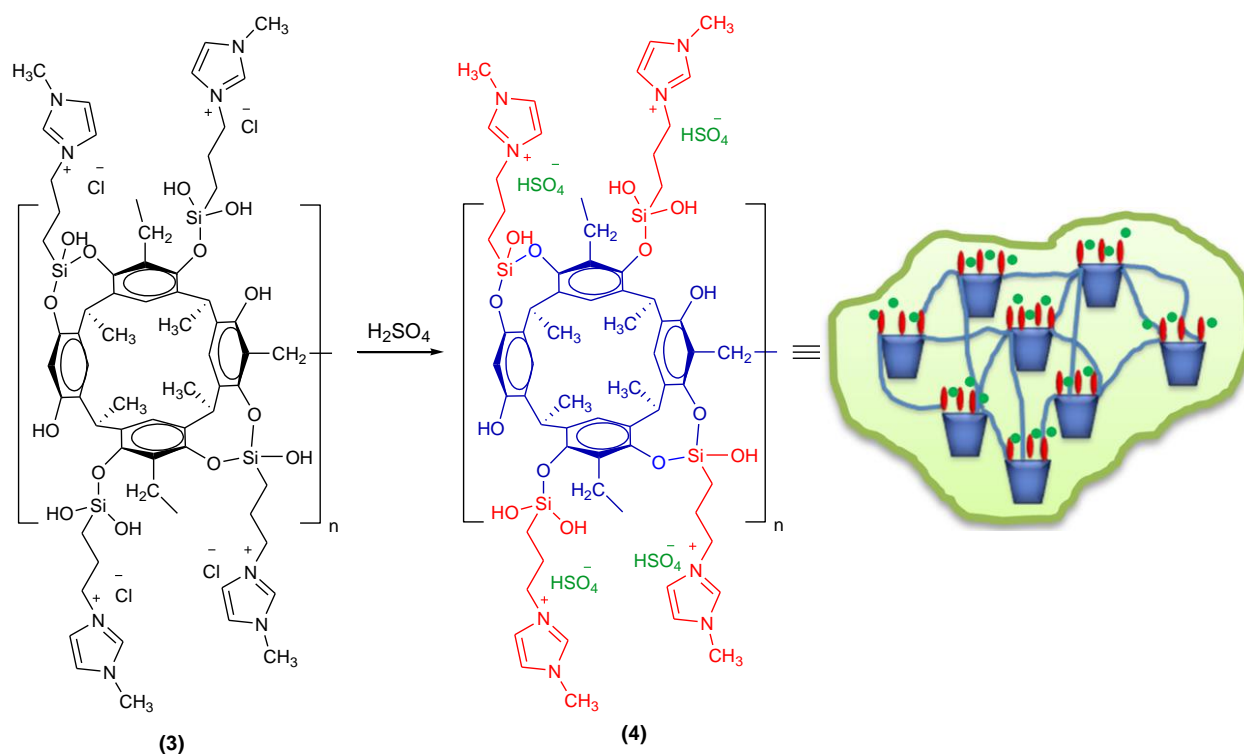
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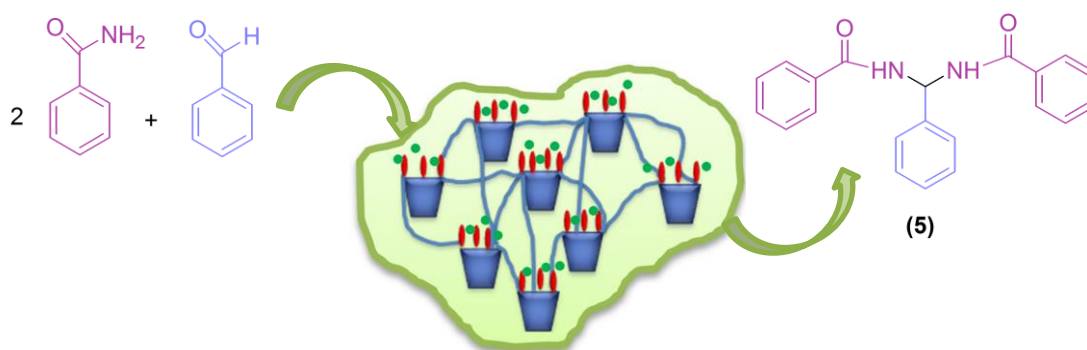
Scheme 1 Synthesis of calix[4]resorcinarene (1) and the 3D-network polymer (2).



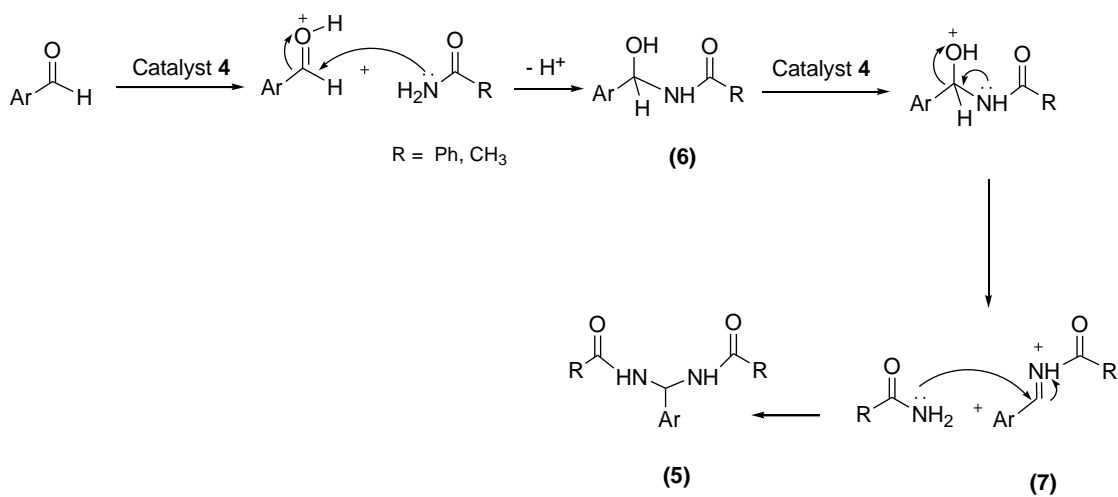
Scheme 2 Synthesis of cationic polymer (3) containing imidazolium moieties through one-step chemical modification of (2).



Scheme 3 Synthesis of polymer supported Bronsted acid ionic liquid (4).



Scheme 4 The reaction of model compounds with polymer supported catalyst.



Scheme 5 The proposed mechanism.

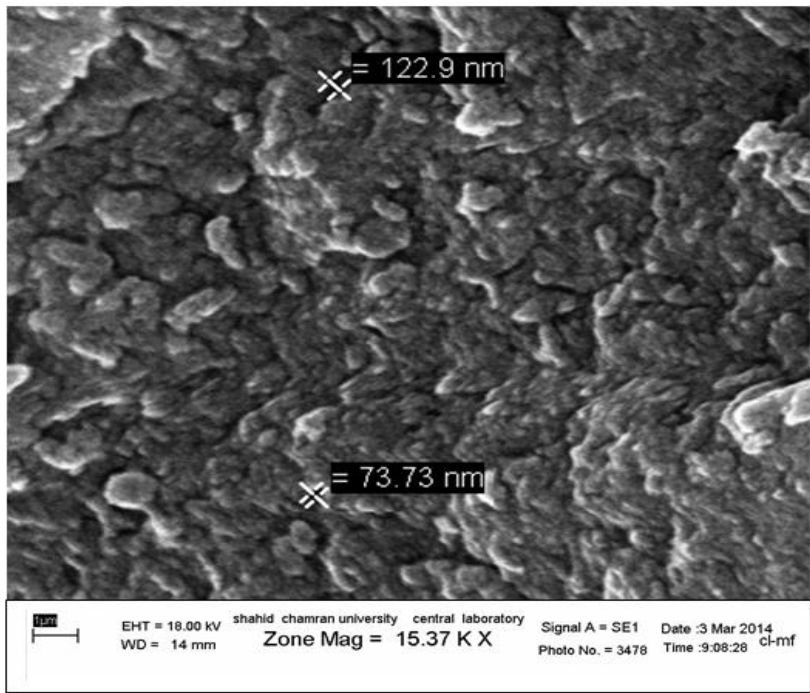


Fig. 1 SEM image of synthesized polymer 3.

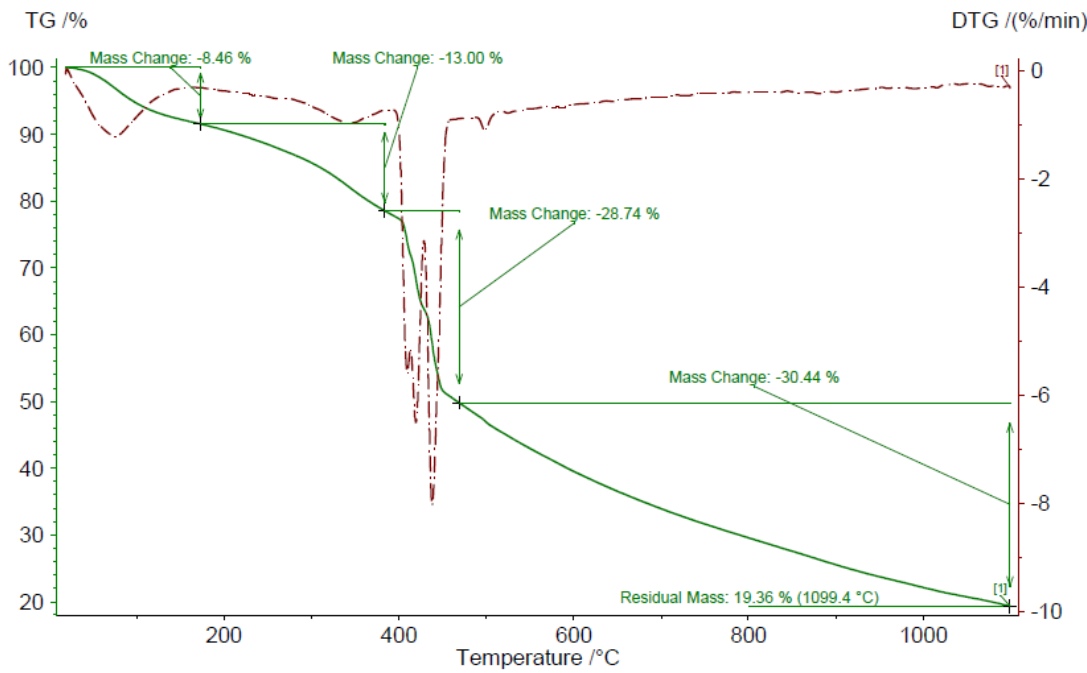


Fig. 2 TGA and DTG curves of cationic polymer 3.

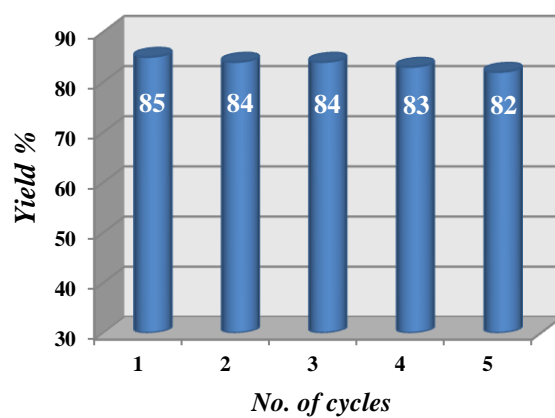
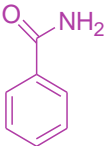
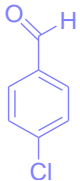
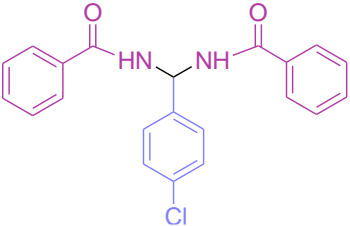
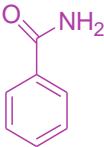
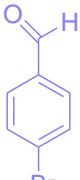
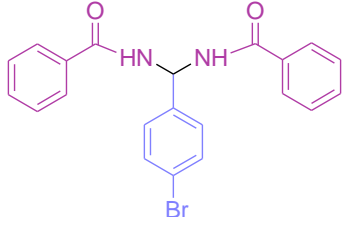
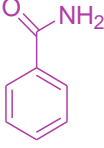
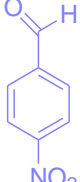
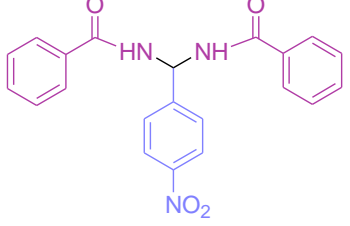
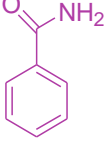
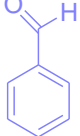
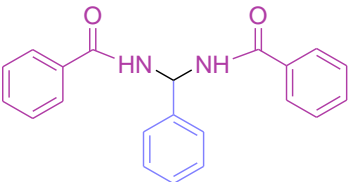
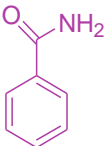
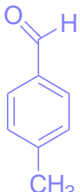
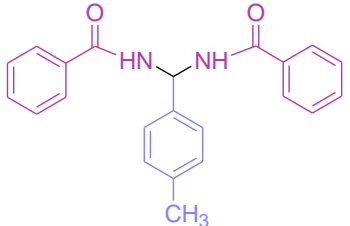


Fig. 3 Recyclability of catalyst.

Table 1 Optimization of the reaction conditions

Entry	Solvent	Catalyst	Amount of catalyst (g) / mmol H ⁺	Time	Yield (%)
1	None	4	0.1 / 0.092	6h	0
2	THF	4	0.1 / 0.092	6h	5
3	Acetone	4	0.1 / 0.092	6h	15
4	Acetonitrile	4	0.1 / 0.092	6h	13
5	Ethyl acetate	4	0.1 / 0.092	6h	20
6	Toluene	4	0.1 / 0.092	30 min	80
7	Toluene	4	0.08 / 0.074	30 min	85
8	Toluene	4	0.07 / 0.065	30 min	78
9	Toluene	None	-	6 h	10
10	Toluene	H ₂ SO ₄	0.004 / 0.074	60 min	50

Table 2 Synthesis of bisamides catalyzed by polymer supported catalyst **4**

Entry	Amide	Aldehyde	Product 5	Time (min)	Yield (%)	mp (°C)
A				25	83	258-261
B				30	84	260-262
C				20	91	265-267
D				30	85	237-238
E				30	87	241-244

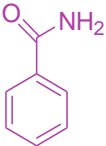
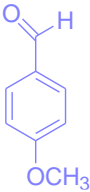
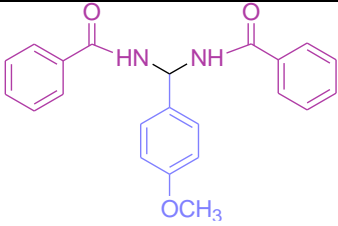
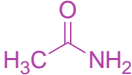
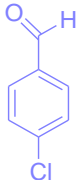
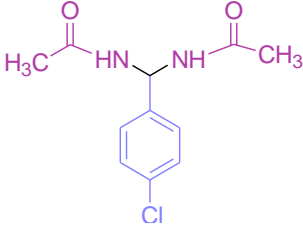
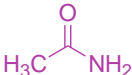
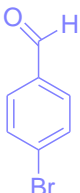
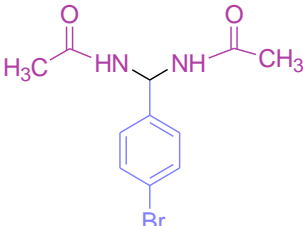
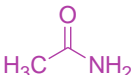
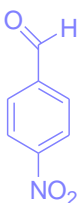
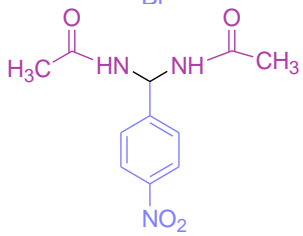
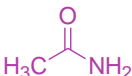
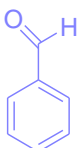
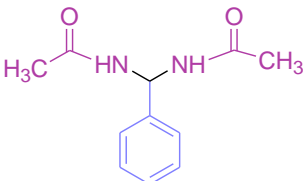
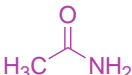
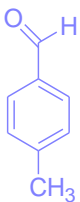
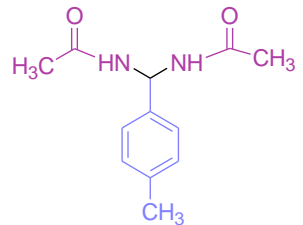
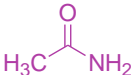
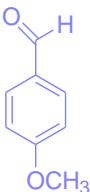
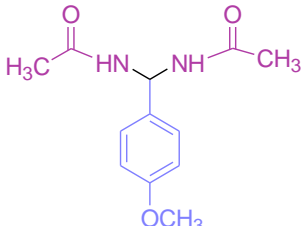
F				50	80	225-227
G				35	83	254-257
H				30	90	269-271
I				25	92	271-273
J				50	80	233-236
K				35	92	270-273
L				50	79	216-219

Table 3 Comparison of the catalytic performance of catalyst **4** with H₂SO₄, MSA ^a, SSA ^b and SBSSANPs ^c

Entry	Catalyst	Acid capacity	Yield (%)	Time (min)	TON	TOF	Ref
1	4	0.074 mmol H ⁺ per 0.08 g	85	30	1148	38.26	Present work
2	H ₂ SO ₄	0.074 mmol H ⁺ per 0.004 g	50	60	676	11.26	Present work
3	MSA	0.2 mmol H ⁺ per 0.029 g	91	30	455	15.2	[19 d]
4	SSA	0.125 mmol H ⁺ per 0.05 g	90	30	720	24	[19 d]
5	SBSSANPs	0.096 mmol H ⁺ per 0.08 g	93	240	969	4.04	[19 a]

^a Molybdate Sulfuric Acid^b Silica Sulfuric Acid^c Silica-Bonded S-Sulfonic Acid Nanoparticles