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1. Introduction

In recent years, ionic liquids have attracted significant attention as being an environmentally-friendly reaction media for their unique properties of high thermal and chemical stability, negligible vapor pressure, and selective dissolvability.1 But the high cost and difficulty in recycling limited their further applications to the industrial scale. To solve this problem, supporting or immobilizing became general concepts applied to heterogenized ILs, which is recognized as a green approach in their catalytic applications.^{2,3} Silica is usually used as an ionic liquid carrier due to its easy availability and low cost.4,5 However, the wide-range pore distribution, irregular pore shape, low pore volume and low specific surface area of silica often leads to low grafting amount of ionic liquids, high mass-transfer resistance and poor catalytic activities. To elevate the grafting amount of ionic liquids, the preparation and application of mesoporous materials for such applications have become an intensively studied hotspot in heterogeneous catalysis.

At the beginning of the 1990s, ordered mesoporous materials were discovered to reduce diffusion constraints encountered in microporous materials.⁶ Among these kinds of materials, mesoporous silicate materials such as SBA-15 have gained an increased attention owing to their interesting properties that include tunable pore sizes, stabilities and shape selectivity.⁷

Covalently anchored *n*-propyl-4-aza-1azoniabicyclo[2.2.2]octane chloride on SBA-15 as a basic nanocatalyst for the synthesis of pyran heterocyclic compounds

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In the present study, highly ordered *n*-propyl-1,4 diazoniabicycle[2.2.2]octane chloride functionalized mesoporous SBA-15, SBA-DABCO, with high surface area and narrow pore-size distribution was synthesized and characterized by TEM, SEM, FT-IR, CHN, TGA, XRD and BET. The organic-modified SBA-15 has hexagonal crystallographic order, pore diameter up to 54.2 Å, and the content of DABCO groups up to 1.38 mmol g^{-1} . The catalyst shows an environmentally benign character, which can be easily prepared, stored and recovered without obvious significant loss of activity. The synthesized basic organocatalyst provides a green and useful method for the one-pot synthesis of pyran annulated heterocyclic compounds, and especially spirooxindole pyran compounds in aqueous media. The significant features of the present protocol are simple, environmentally benign, high yields, no chromatographic separation and recyclability of the catalyst.

Besides, SBA-15 has abundant surface silanol groups, a wellorganized array of straight channels, high surface area, open pore structure and narrow pore size distribution.⁸⁻¹⁰ These advantageous characteristics made SBA-15 an attractive solid support in the field of catalysis and functional materials.^{1,11-13} The regular arrangement of uniform pores over all the porous structure is likely to ensure good accessibility to the active centers of functional groups attached to the surface and to impart fast mass transport rates. In addition, the big pore size of SBA-15 is advantageous to reaction substance transports inside pore channels and to further the process of the reaction.¹⁴

One-pot multicomponent reactions (MCRs) that convert more than two educts directly into their products, have gained considerable attention due to the atom economy and powerful bond forming efficiency in combinatorial and medicinal chemistry.15 In recent years, development of such multicomponent coupling reaction strategies in aqueous medium has been of considerable interest, as they provide simple and rapid access to a large variety of organic scaffolds through a sustainable path.¹⁶ Pyran derivatives are of considerable interest in industry as well as in academia owing to their promising biological activity such as anticoagulant, anticancer, diuretic, spasmolytic and anti-anaphylactin agents.15,16 Although a few methods with distinct advantages have been recently reported by using various catalysts, at the same time they suffer from certain drawbacks such as extended reaction times, unsatisfactory yields, high costs, harsh reaction conditions, toxic solvents and use of stoichiometric amounts of catalyst, as well as using environmentally toxic catalysts. Additionally the main



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drawback of almost existing methods is that the catalysts are decomposed under aqueous work-up conditions and their recoveries are often impossible.¹⁷ Thus, to overcome these drawbacks the development of simple and highly efficient methodologies remains desired.

Considering these facts and as a part of our ongoing interest in the synthesis of biologically relevant heterocyclic compounds,^{18–21} we attempted to design an inorganic–organic hybrid basic nanocatalyst by supporting DABCO, a type of spindle-shaped molecule with two nitrogen atoms located at both tips, on highly ordered functionalized mesoporous SBA-15. This provides a basic organocatalyst with high surface area, high accessibility of catalyst, and no leaching of active species in the reaction media. The catalytic ability of this heterogeneous basic organocatalyst is studied for the one-pot synthesis of pyran annulated heterocyclic compounds in water.

2. Experimental

2.1. General

For the direct synthesis of chloro-functionalized SBA-15, tetraethylorthosilicate (TEOS) was used as a silica source, 3-chloropropyltrimethoxysilane (CPTMS) was used as a chloropropyl group source and Pluronic P123 triblock copolymer ($EO_{20}PO_{70}EO_{20}$, MW 5800) was used as a structure-directing agent; all were supplied by Aldrich. Other chemical materials were purchased from Fluka and Merck companies and used without further purification. Products were characterized by comparison of their physical data, IR and ¹H-NMR and ¹³C-NMR spectra with known samples. NMR spectra were recorded on a Bruker Advance DPX 400 MHz instrument spectrometer using TMS as an internal standard. IR spectra were recorded on a BOMEM MB-Series 1998 FT-IR spectrometer.

The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel PolyGram SILG/UV 254 plates. The particle morphology was examined by SEM (Philips XL30 scanning electron microscope) and TEM (Zeiss-EM10C-80 kV). Nitrogen adsorption measurements were conducted at 77.4 K on a Micrometrics ASAP-2020 sorptionmeter. The specific surface area and the pore size distribution were calculated by the Brunauer–Emmett–Teller (BET) method and Barrett–Joyner–Halenda (BJH) model, respectively.

2.2. Synthesis of chloropropyl-grafted SBA-15 (SBA-Cl)

Chloropropyl-grafted SBA-15 (SBA-Cl) was prepared according to the reported method.²² Pluronic 123 (4 g) was dissolved in 125 g of 2.0 M HCl solution at room temperature. After TEOS (8.41 g, 40.41 mmol) was added, the resultant solution was equilibrated at 40 °C for prehydrolysis, and then CPTMS (1.3 g, 6.5 mmol) was slowly added into the solution. The resulting mixture was stirred at 40 °C for 20 h and reacted at 95 °C under static conditions for 24 h. The solid product was recovered by filtration and dried at room-temperature overnight. The template was removed from the as synthesized material by refluxing in 95% ethanol for 48 h (1.5 g of as-synthesized material per 400 mL of ethanol). Finally, the material was filtered, washed several times with water and ethanol, and dried at 50 $^\circ\mathrm{C}.$

2.3. Synthesis of 1,4-diazabicyclo[2.2.2]octane-SBA (SBA-DABCO)

SBA-Cl (10.0 g) was added to a flask containing 100 mL of anhydrous toluene and an excess of DABCO (1 g, 9 mmol). The reaction mixture was refluxed with stirring for 24 h. Then, the reaction mixture was cooled to room temperature, transferred to a vacuum glass filter, and washed with toluene. The SBA chemically bonded with DABCO (SBA-DABCO) was dried at 50 $^{\circ}$ C for 8 h.

2.4. Typical procedure for the preparation of spirooxindoles and pyran annulated heterocyclic compounds

A mixture of β -diketone (1 mmol), malononitrile (1 mmol), isatin or aldehyde (1 mmol) and SBA-DABCO (0.125 g) was heated at 80 °C minimum in water for 10–50 min. After complete consumption of aromatic aldehyde as judged by TLC (using *n*-hexane-ethylacetate as eluent), the reaction mixture was filtered for separation of solid product and catalyst from water. The remaining solid was washed with warm ethanol (3 × 5 mL) for separation of the product from the catalyst. Finally, the product was purified by recrystallization in hot EtOH. The desired pure product(s) was characterized by comparison of their physical data with those of known spirooxindoles and pyran annulated heterocyclic compounds.

2.5. Selected spectral data

2-Amino-5-oxo-7,7-dimethyl-spiro[(4*H*)-5,6,7,8-tetrahydrochromene-4,3'-(3'*H*)-indol]-(1'*H*)-2'-one-3-carbonitrile (**3a**): ¹H NMR (DMSO-d₆, 400 MHz): δ = 1.04 (s, 6H), 2.09 (d, 1H, *J* = 16 Hz), 2.14 (d, 1H, *J* = 16 Hz), 2.51 (d, 2H, *J* = 3.4 Hz), 6.81 (1H, d, *J* = 8.0 Hz), 6.92 (1H, t, *J* = 7.8 Hz), 7.01 (1H, d, *J* = 7.8 Hz), 7.21 (1H, t, *J* = 8.0 Hz), 7.33 (2H, br s), 10.43 (s, 1H). ¹³C NMR (DMSO-d₆, 100.6 MHz): δ = 28.1, 28.5, 32.3, 48.1, 49.9, 57.9, 110.0, 111.2, 117.8, 122.0, 124.1, 127.8, 134.8, 144.1, 157.3, 164.3, 179.2, 196.3. IR (KBr) (ν_{max} , cm⁻¹): 561, 750, 1056, 1222, 1354, 1471, 1606, 1657, 1683, 1723, 2190, 2963, 3145, 3315, 3378.

2-Amino-5-oxo-7-methyl-spiro[(3'H)-indol-3',4-4(H)-pyrano-(4,3-*b*)pyran]-(1'H)-2'-one-3-carbonitrile (**3b**): ¹H NMR (DMSOd₆, 400 MHz): δ = 2.29 (3H, s), 6.40 (1H, s), 6.83 (1H, d, *J* = 7.6 Hz), 6.92 (1H, t, *J* = 7.6 Hz), 7.13 (1H, d, *J* = 7.4 Hz), 7.17 (1H, t, *J* = 7.8 Hz), 7.52 (2H, br s), 10.62 (1H, s). ¹³C NMR (DMSO-d₆, 100.6 MHz): δ = 19.9, 47.6, 57.6, 98.5, 98.9, 110.2, 118.2, 122.5, 124.3, 129.2, 133.6, 142.6, 160.2, 160.3, 160.8, 165.1, 178.3. IR (KBr) (ν_{max} , cm⁻¹): 495, 752, 1228, 1360, 1477, 1586, 1614, 1646, 1674, 1729, 2204, 2883, 3097, 3212, 3380, 3524.

2-Amino-5-oxo-spiro[(3'*H*)-indol-3',4-4(*H*)-pyrano(3,2-*c*)chromen]-(1'*H*)-2'-one-3-carbonitrile (**3c**): ¹H NMR (DMSO-d₆, 400 MHz): $\delta = 6.91$ (1H, d, J = 7.4 Hz), 6.96 (1H, t, J = 7.8 Hz), 7.25 (2H, t, J = 7.8 Hz), 7.50 (1H, d, J = 8.6 Hz), 7.55 (1H, t, J = 7.8 Hz), 7.64 (2H, br s), 7.78 (1H, t, J = 7.8 Hz), 7.96 (1H, d, J = 7.8 Hz), 10.62 (1H, s). ¹³C NMR (DMSO-d₆, 100.6 MHz): $\delta = 50.0$, 57.9, 102.1, 110.2, 113.0, 117.3, 117.5, 122.7, 123.2, 123.9, 125.2, 130.1, 134.2, 135.2, 142.2, 151.2, 157.3, 158.4, 160.1, 178.1. IR

(KBr) $(v_{\text{max}}, \text{ cm}^{-1})$: 572, 761, 942, 1100, 1220, 1309, 1390, 1476, 1620, 1679, 1700, 1725, 2200, 2982, 3110, 3280, 3445.

4H-Naphtho[1,2-b]pyran-3-carbonitrile-2-amino-4-phenyl (Table 4, entry 1): ¹H NMR (DMSO-d₆, 400 MHz): $\delta = 4.96$ (1H, s), 6.21 (2H, br s), 7.18 (1H, d, J = 8.2 Hz), 7.16-7.41 (5H, m), 7.58-7.72 (3H, m), 7.92 (1H, d, *J* = 8.2 Hz), 8.4 (1H, d, *J* = 8.2 Hz). ¹³C NMR (DMSO-d₆, 100.6 MHz): $\delta = 59.2$, 119.1, 119.6, 120.9123.1, 125.0, 126.1, 126.7, 126.9, 127.0, 127.5, 128.1, 128.9, 133.9, 143.1, 146.1, 158.9. IR (KBr) (ν_{max} , cm⁻¹): 560, 740, 931, 1120, 1230, 1310, 1395, 1480, 1590, 1670, 2200, 3340, 3450.

4H-Naphtho[1,2-b]pyran-3-carbonitrile-2-amino-4-(4-chlorophenyl) (Table 4, entry 4): ¹H NMR (DMSO-d₆, 400 MHz): $\delta = 5.32 (1H, s), 6.89 (2H, s), 7.22 (2H, d, J = 7.6 Hz), 7.38 (2H, d, J = 7.6 Hz), 7.38 (2H, d, d, d)$ *J* = 7.6 Hz), 7.50-7.62 (3H, m), 7.89 (1H, d, *J* = 7.8 Hz), 8.25 (1H, d, J = 8.0 Hz). ¹³C NMR (DMSO-d₆, 100.6 MHz): $\delta = 55.1$, 118.6, 120.1, 120.6, 123.2, 125.1, 126.4, 127.3, 127.5, 128.6, 129.2, 131.0, 132.3, 134.2, 144.3, 146.2, 161.3. IR (KBr) (ν_{max} , cm⁻¹): 750, 807, 1105, 1185, 1379, 1405, 1574, 1603, 1637, 1663, 2201, 3195, 3318, 3478.

1H-Naphtho[2,1-b]pyran-2-carbonitrile-3-amino-1-(4-chlorophenyl) (Table 4, entry 13): ¹H NMR (DMSO-d₆, 400 MHz): $\delta = 5.01 (1H, s), 7.15 (1H, d, J = 8.4 Hz), 7.25 (2H, s), 7.35 (2H, d, d)$ *J* = 8.4 Hz), 7.41 (2H, d, *J* = 8.2 Hz), 7.45–7.62 (3H, m), 7.83 (1H, d, J = 8.0 Hz), 8.33 (1H, d, J = 8.2 Hz). ¹³C NMR (DMSO- d_6 , 100.6 MHz): $\delta = 63.1$, 113.2, 114.5, 115.2, 116.8, 124.0, 125.3, 128.1, 128.5, 128.8, 129.2, 129.4, 130.3, 131.0, 132.3, 132.5, 148.0, 158.2, 158.8. IR (KBr) (ν_{max} , cm⁻¹): 560, 740, 931, 1120, 1230, 1310, 1395, 1480, 1590, 1670, 2200, 3340, 3450.

3. **Results and discussions**

Well-ordered mesoporous chloro-functionalized SBA-15 was first synthesized by the direct incorporation of chloropropyl groups through co-condensation of TEOS and CPTMS precursors in the presence of a Pluronic P123 triblock copolymer as a supramolecular template to direct the organization of polymerizing silica. DABCO was then grafted onto the surface of the mesoporous silica by a simple nucleophilic substitution reaction. Scheme 1 shows the schematic representation of the synthetic pathway for the synthesis of

DABCO, toluene

SBA-DABCO solid base catalyst by a two-step chemical modification.

The FT-IR spectra of SBA-Cl and SBA-DABCO are shown in Fig. 1. In both materials, the typical Si-O-Si bands around 1220, 1070, 801 and 473 cm^{-1} associated with the formation of a condensed silica network are present, but weak peaks associated with noncondensed Si-OH groups in the range of 940–960 cm^{-1} were also present. The absorbance peak of the C–N with the wavelength of 1000–1200 cm^{-1} cannot generally be resolved due to its overlap with the absorbance of the Si-O-Si stretch in the same range and that of Si-CH₂-R stretch in the range 1200–1250 cm⁻¹. The weak bands located at 2950 to 2830 cm⁻¹ correspond to C-H asymmetric and symmetric stretching vibration modes, respectively. The strong peak around 1630 cm^{-1} is mainly from the bending vibration of adsorbed H₂O.²³ FT-IR spectrum of Amine-SBA-15 exhibited two bands at 2975 cm⁻¹ and 1465 cm⁻¹, assigned to the C–H stretching vibration and C-N bending vibration of the tertiary amine group, respectively. These two peaks are not observed in the spectrum of the Cl-SBA-15.24 The broad band around 3450 cm⁻¹ is due to the stretching vibration of SiO-H bond and the HO-H vibration of a water molecule adsorbed on the silica surface. The band around 1635 cm⁻¹ is also due to the bending vibration of water molecules bound to the silica matrix. SBA-Cl shows a peak at 644 cm^{-1} assigned to the C-Cl vibration. This peak is not observed for the SBA-DABCO spectrum.

The quantity of functionalized organic groups, determined from CHN elemental analysis, is presented in Table 1. The amount of DABCO is 1.38 mmol per gram in SBA-DABCO, that is 91% of propylchloride group in SBA-Cl.

The morphological features of SBA-DABCO were studied by TEM and SEM (Fig. 2 and 3). From the TEM image, the hexagonal pore structure and orderly pore arrangement could be clearly observed and confirmed the long-range, three dimensional, mesoporous ordering in this organocatalyst. Long-range order and mesoporous structure arrays were not disturbed significantly after DABCO grafting. The SEM image of catalyst also indicated a uniform particle size with hexagonal shape.

Thermal stability of samples was investigated by thermal gravimetric analysis-derivative thermogravimetric analysis (TGA-DTG) in which the observed weight loss was associated with the loss of the organic components attached to the silica



SBA-Cl

MeO

MeO-Si

MeÓ

OEt P123, HCl , EtO-Si-OEt OEt



Fig. 1 FT-IR spectra of SBA-Cl and SBA-DABCO.

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400

SBA-DABCO

SBA-CI

Materials	C (W%)	H (W%)	N (W%)
SBA-Cl	13.21	2.12	0.09
SBA-DABCO	16.36	3.38	3.86



Fig. 2 TEM image of SBA-DABCO.



Fig. 3 SEM image of SBA-DABCO.



Fig. 4 Thermal gravimetric analysis-derivative thermogravimetric analysis (TGA-DTG) of (a) SBA-Cl and (b) SBA-DABCO.



Fig. 5 Pore size distributions of SBA-Cl (a), SBA-DABCO (c) and nitrogen adsorption-desorption isotherms of SBA-Cl (b), SBA-DABCO (d).

Table 2 Specific surface area (S_{BET}), diameter pore and total pore volume

Sample	BET surface area $(m^2 g^{-1})$	Diameter (nm)	Pore volume $(cm^3 g^{-1})$
SBA-Cl	753	9.72	1.25
SBA-DABCO	290	5.42	0.70

gel. TGA-DTG curves for SBA-Cl and SBA-DABCO were shown in Fig. 4. The sample of SBA-Cl shows two and SBA-DABCO shows three distinct steps of weight loss in the combined TG-DTG curves. The curves show that the first weight loss occurs before 200 °C, which can be attributed completely to the loss of adsorbed water molecules. TGA of the samples demonstrated high thermal stability, with decomposition starting at around 300 °C under a nitrogen atmosphere. The secondary weight losses at about 380 °C and 480 °C come from the decomposition of organic substances in SBA-DABCO composites. The decomposition is complete at about 650– 700 °C to form the constituent inorganic oxides.²⁵

The mesoporous nature of the synthesized samples were studied by N_2 adsorption-desorption isotherms (Fig. 5). Nitrogen adsorption-desorption isotherms of the SBA-Cl and SBA-DABCO in Fig. 5 exhibit the typical IV adsorption (according to the IUPAC classification).²⁶ Both the isotherms present a sharp adsorption step in the P/P_0 , which implies that the materials possess a large pore size with narrow distributions. This was further confirmed by the pore size distributions calculated by the Barrett-Joyner-Halenda (BJH) method from the adsorption branches. The characteristic data on the samples are summarized in Table 2. From Table 2, we can see that the introduction of DABCO to mesoporous silica shifted the pore to a smaller diameter and decreased the surface area and pore volume.

Over the years, the fast assembly of molecular diversity utilizing multicomponent reactions (MCRs) has received a great deal of interest. MCRs are defined as one-pot processes where three or more substrates combine either simultaneously (so called tandem or domino reactions), or through a sequential addition procedure that does not require any change of solvent. MCRs are gaining more and more importance especially in the total synthesis of natural products, and medicinal heterocyclic compounds, because of their simplicity, higher yield of products, and lower reaction times.27,28 The applications of heterocyclic compounds in our life are undeniable. Tetrahydrobenzo[b]pyrans and dihydropyrano[c]chromenes have recently attracted much attention as an important class of heterocycles due to their biological and pharmacological properties, such as diuretic, anti-cancer, anticoagulant, and anti-anaphylactic activities.²⁹ Aminochromene derivatives exhibit a wide spectrum of biological activities including anticancer, antimicrobial agents, photoactive materials, and are also utilized in the synthesis of the blood anticoagulant warfarin and tacrine analogs.30



Scheme 3 Synthesis of spiro[(2-amino-3-cyano-5-oxo-5,6,7,8,tet-rahydro-4*H*-chromene)-4,30-oxindoles] by reaction of isatin (1 mmol), dimedone (1 mmol) and malononitrile (1 mmol) in water.



Scheme 2 Preparation of pyran annulated heterocyclic compounds and spirooxindole pyran compounds in water, catalyzed by SBA-DABCO.

 Table 3
 The one-pot three component reaction of isatin (1 mmol), dimedone (1 mmol), and malononitrile (1 mmol) in water

Entry	Solvent	Catalyst (g)	$T(^{\circ}C)$	Yield (%)
1	_	_	100	10
2	H_2O	_	Reflux	20
3	_	0.1	100	35
4	H_2O	0.1	Reflux	73
5	EtOH	0.1	Reflux	70
6	EtOH-H ₂ O	0.1	Reflux	70
7	CH_2Cl_2	0.1	Reflux	35
8	H_2O	0.05	Reflux	66
9	H_2O	0.125	Reflux	85
10	H_2O	0.125	80	85
11	H_2O	0.125	60	75
12	H_2O	0.125	40	68

Owing to the widespread applications of the described compounds, and in continuation of our previous research to develop green chemistry by using water as a reaction medium, herein we report the synthetic applicability of SBA-DABCO as a base catalyst for rapid and efficient preparation of pyran annulated heterocyclic compounds and spirooxindole pyran derivatives in water through a multicomponent reaction (Scheme 2).

The catalytic performance of this novel basic organocatalyst has been systematically studied in the rapid and efficient preparation of pyran annulated heterocyclic compounds and spirooxindole pyran derivatives in water through a multicomponent reaction (Scheme 2).

In the preliminary stage of investigation, we focused on a three-component process for the model reaction of isatin (1 mmol), dimedone (1 mmol) and malononitrile (1 mmol) (Scheme 3). After some experiments (Table 3), it was found that the use of 1 equiv. of malononitrile per dimedone and isatin in the presence of SBA-DABCO (0.125 g) in water at 80 °C were the best condition.

Under the optimized reaction conditions, a series of biologically interesting spirooxindole pyran derivatives were efficiently synthesized (Scheme 4) by means of three-component



Scheme 4 Synthesis of spirooxindole pyran derivatives in water, catalyzed by SBA-DABCO.



Scheme 5 The one-pot three component reaction of aldehyde (1 mmol), malononitrile (1 mmol) and α or β -naphthol (1 mmol) in water at 80 °C, catalyzed by SBA-DABCO.

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Table 4 The one-pot three component reaction of aldehyde (1 mmol), malononitrile (1 mmol) and α or β -naphthol (1 mmol) in water at 80 °C, catalyzed by SBA-DABCO

Entry	R	Naphthol	Product	Time (min)	Yield (%)
1	Н	ОН	NH ₂ CN	20	89
2	4-Me	ОН	NH ₂ CN Me	30	85
3	4-OMe	ОН	O CN OMe	30	84
4	4-Cl	ОН	NH ₂ CN	15	91
5	4-NO ₂	ОН	NH ₂ CN NO ₂	10	94
6	2-Cl	ОН	NH ₂ CN CI	20	90
7	3-Me	ОН	NH ₂ CN Me	30	86
8	3-F	OH		15	89

Entry	R	Naphthol	Product	Time (min)	Yield (%)
			NH ₂ CN F		
9	3-Cl	OH	NH ₂ CN CI	20	89
10	Н	ОН	CN NH ₂	25	87
11	4-Me	ОН	Me CN NH ₂	35	84
12	4-OMe	ОН	MeO CN NH ₂	35	84
13	4-Cl	ОН	CI CN NH ₂	20	89
14	$4 \cdot \mathrm{NO}_2$	ОН	O ₂ N CN NH ₂	15	91
15	2-Cl	ОН		25	87

Table 4 (Contd.)





characterized by FT-IR, CHN, SEM, TEM, TGA-DTG, BET and BJH. The catalytic activity of this base catalyst has been successfully applied for the one-pot synthesis of pyran annulated heterocyclic compounds, and especially spirooxindole pyran compounds in water. The promising points for the presented methodology are clean reaction profiles, short reaction times, simplicity in operation, catalyst with high catalytic activity and good recycle exploitation.

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reactions of isatin, malononitrile, and 1,3-dicarbonyl or enol compounds catalyzed by mentioned basic catalytic system in water.

To further explore the potential of this protocol for heterocyclic synthesis, we investigated one-pot three-component reactions involving malononitrile, aromatic aldehydes and α or β -naphthol compounds. To our delight, under the above optimized conditions, a variety of the desired products 4 and 5 were obtained in good yields (Scheme 5, Table 4).

The reusability of the catalyst in the reaction of isatin, dimedone and malononitrile in water at 80 $^{\circ}$ C was evaluated. In this procedure, after completion of each reaction, hot ethanol was added and the catalyst was filtered. The recovered catalyst was washed with ethanol, dried and reused (Fig. 6). The results illustrated in Fig. 6 show that the catalyst can be reused for up to ten cycles without significant loss in its activity.

4. Conclusion

In conclusion, *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride-SBA-15 (SBA-DABCO) was successfully synthesized and

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