

Silica gel supported polyamine: A versatile catalyst for one pot synthesis of 2-amino-4H-chromene derivatives

R.L. Magar^a, P.B. Thorat^a, V.B. Jadhav^a, S.U. Tekale^a, S.A. Dake^a, B.R. Patil^b, R.P. Pawar^{a,*}

^a Department of Chemistry, Deogiri College, Station Road, Aurangabad 431 005, MS, India

^b Department of Chemistry, Sharda Mahavidyalaya, Parbhani 431 401, MS, India

ARTICLE INFO

Article history:

Received 19 February 2013

Received in revised form 19 March 2013

Accepted 22 March 2013

Available online xxx

Keywords:

2-Amino-4H-chromene derivatives

Active methylene compound

Malononitrile

Phenols

Polyamine

ABSTRACT

An efficient synthesis of 2-amino-4H-chromene derivatives is achieved via one pot three component coupling reaction of aromatic aldehyde, active methylene compound and activated phenol in presence of silica gel supported polyamine heterogeneous catalyst. The catalyst is easily prepared, highly stable, simple to handle and recycled for several times without significant loss of activity.

© 2013 Elsevier B.V. All rights reserved.

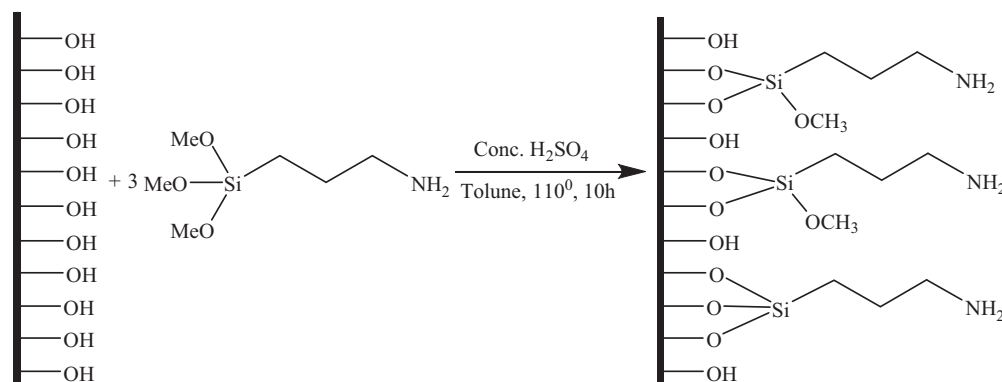
1. Introduction

Synthesis of biologically active heterocyclic compound is a thrust area for organic chemists. Among the known compounds, chromene derivatives 4H-pyrans and others possess a unique importance. Owing to their potential biological and pharmacological properties [1], Chromenes showed spasmolytic, diuretic, anticoagulant, anticancer, and antianaphylactic activity [2]. The 4H-pyran derivatives were found to exhibit anti-proliferative, cancer chemopreventive, anti-bacterial (including anti-tubercular), antitumor, hypotensive, anti-rheumatic, and antiasthmatic activities [3–10]. Among the important oxygenated heterocyclic compounds, they also showed antidepressant, antihypertensive, anti-tubulin, antiviral, antioxidative, activator of potassium channels and inhibition of phosphodiesterase IV or dihydrofolate reductase activity [11–15]. 2-Amino-chromenes are also used in cosmetics, pigments [16] and in agrochemicals [17]. 2-Amino-4H-chromenes compounds are classically synthesized by one pot three component reaction of malononitrile, aldehyde and activated phenol in organic solvents (acetonitrile, ethanol etc.) in presence of stoichiometric amounts of an organic base like piperidine [18]. Recently, other catalytic systems such as hexadecyltrimethyl ammonium bromide (HMTAB) [19], triethylbenzylammonium

chloride (TEBA) [20], rare earth perfluorooctanoate (Re(PFO)₃) [21], (S)-proline [22], amino functionalized ionic liquids [23], KF-Alumina [24] and (NH₄)HPO₄ [25] have been utilized to bring about this conversion. 2-Amino-4H-chromenes are also synthesized under microwave and ultrasound irradiations [26]. However, most of the reported methods suffer from various drawbacks such as low yield, long reaction time, harsh reaction conditions, tedious work-up procedure, complex reaction pathway and expensive catalysts. Moreover, in reported methods, catalysts are not recycled. To overcome all these drawbacks, development of efficient, mild, faster, simple, one-pot, chemoselective process for the synthesis of benzo[b]pyran is highly desirable; concerning the issues of along with higher yield of products and avoiding the environmental pollution.

In recent year, polymer supported catalyst has attracted attention of chemists from all over the world. A literature survey reports various chemical transformations under this heading. Several advantages of heterogeneous catalysis over homogeneous catalysis have been reported by different research groups. The advantages include insolubility in reaction media, catalyst recovery by simple filtration and prevent the release of any toxic chemicals. More importantly, these heterogeneous catalysts also suppressed the side reactions, including self-condensation, oligomerization, avoids complex neutralization and separation steps that needed to recover the homogeneous catalysts and better selectivity and higher yield of products. It ultimately dealt with cost and energy savings, for downstream separation and purification of product.

* Corresponding author. Tel.: +91 0240 2334577; fax: +91 0240 2334430.
E-mail address: rppawar@yahoo.com (R.P. Pawar).



Scheme 1. Synthesis of solid supported amino functionalized catalyst GN3.

The recovered solid catalyst was readily regenerated for further use. These novelties in hand accelerated considerable amount of research for the use of such catalysts.

Considering these beneficial facts, it is also diverted to use solid supported heterogeneous catalysts in organic transformations. We inspired with the findings, when Jasra et al. reported the synthesis of amino functionalized silica gel (GN3) for the adsorption of Cu (II) ion [27]. It showed that, polyamine group present in the structure having strong basic properties selectively adsorption due to Cu (II) ions. Surprisingly, literature data pointed that, such heterogeneous polyamine catalyst has not been explored in the organic transformations. Thus, it is sought to utilize the basic property of amino functionalized silica gel catalyst (GN3).

Owing to the importance of biologically active 2-amino-4H-chromenes, in the present study it is demonstrated a simple and highly efficient method for the synthesis of 2-amino-4H-chromenes by one pot three component reactions of malononitrile, aldehyde, and activated phenol in water: ethanol solvent system in the presence of silica gel supported polyamine (GN3) as heterogeneous catalyst.

2. Experimental

All the solvents were used as commercial anhydrous grade without further purification. Aluminum sheets 20 cm × 20 cm, silica gel 60 F₂₅₄, Merck grade TLC plate were used for thin layer chromatography to determine progress of reaction. The column chromatography was carried out over silica gel (80–120 mesh). Melting points were determined in open capillary tube. ¹H and ¹³C NMR spectra were recorded on Bruker 300 MHz spectrometer in CDCl₃ solvent. Mass spectra were taken on Polaris-Q Thermoscientific GC-MS.

2.1. General procedure for the synthesis of Silica gel

Silica gel was synthesized under acidic conditions. A known amount of sodium silicate solution (23.31 SiO₂%; 7.48 Na₂O %) was diluted with deionized water to obtain 12% w/v SiO₂ concentration. The slurry was added to 10.2 N H₂SO₄ solution under stirring with peristaltic pump in 12.5 min at room temperature. To adjust the SiO₂ concentration to 8% w/v it is aged for 2 h, and then kept at 100 °C for 112 h in a closed Simax glass bottle. Peristaltic pump is used to ensure uniform mixing. The silica gel thus obtained was washed with water till it was sulfate free (confirmed by BaCl₂ test). The sulfate free silica gel was dried at 100 °C in oven and further calcined at 600 °C for 6 h. Further it was cooled under vacuum and stored in a capped bottle over P₂O₅ in a desiccator.

2.2. General procedure for the synthesis of catalyst GN3

Functionalized silica was prepared by suspending the silica gel in 3-aminopropyl-trimethoxysilane (APTMS) solution using APTMS: silica gel ratios (w/w) 0.3 (1.68 mmol/g) in dry toluene (solid: liquid) 10:100 w/v). The mixture was refluxed at boiling temperature for 24 h. After completion of reaction the mixture was cooled and filtered off. The obtained solid was washed with *iso*-propanol thoroughly, and dried at 100 °C overnight. The obtained solid was designated as GN3 and used as the catalyst.

2.3. General procedure for the synthesis of 2-amino-4H-chromene derivatives

A mixture of aromatic aldehyde (1 mmol), phenol (1.2 mmol) and active methylene compound (1 mmol) was added to ethanol–water (8:2) solvent system. To this mixture, 10 wt% of silica gel polyamine catalyst was added. The reaction mixture was refluxed for appropriate time (as shown in Table 6). The progress of reaction was monitored on thin layer chromatography. After completion of reaction as indicated by TLC, reaction mixture was cooled at room temperature. The solvent was removed under vacuum to obtain crude product. The obtained crude product was purified by column chromatography using ethyl acetate/petroleum ether (1:8) as solvent system to get the desired pure compound.

3. Result and discussion

Silica gel supported polyamine catalyst was prepared by known literature process [28]. The catalyst was characterized by N₂ adsorption-desorption analysis, infrared spectroscopy, thermal analysis, elemental analysis, powder X-ray diffraction, Si solid state NMR analysis, scanning and transmission electron microscopy (Scheme 1).

3.1. Catalyst characterization

3.1.1. N₂ adsorption-desorption analysis

Silica gel and surface functionalized silica gel catalyst was characterized by N₂ adsorption at liquid N₂ temperature. Adsorption isotherms and pore size distribution curves are presented in Fig. 1. The catalyst exhibited type (IV) adsorption isotherms, characteristics of mesoporous silica [29].

Results of surface area calculated by BET (Brunauer–Emmett–Teller) method, the pore size distributions calculated by BJH (Barrett–Joyner–Halenda) method, and the total pore volume of samples are given Table 1. As expected for each functionalized silica gel, the surface area, total pore volume and pore diameter decreased as the concentration of added organo silane was

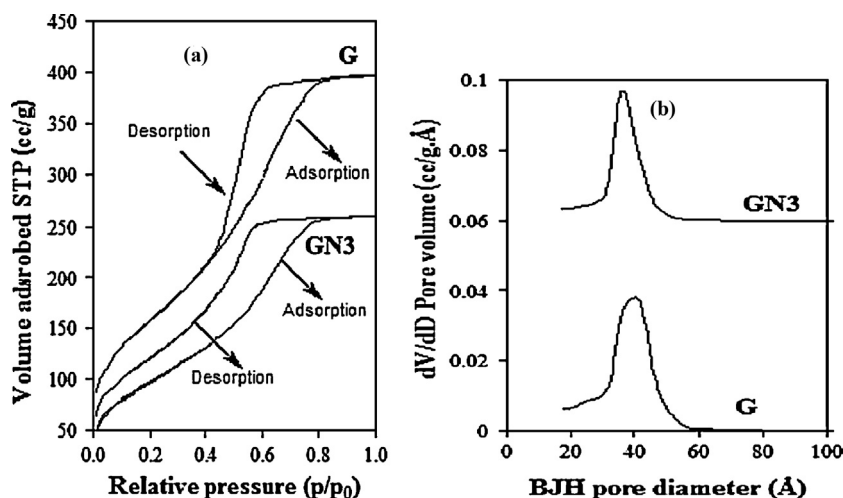


Fig. 1. (a) Nitrogen adsorption/desorption isotherms at 77 K. (b) Pore size distribution curves of silica gel (G) and aminopropyl functionalized silica gel catalyst (GN3).

Table 1

Textural properties of silica gel (G) and functionalized silica gel catalyst.

Properties	G	GN3
BET surface area (m^2/g)	575	360
Total pore volume (cm^3/g)	0.61	0.40
BJH desorption pore size ($\text{\AA}$)	47.2	35.8

increased (Table 1; Fig. 1b), such decrease in all the three properties have been reported after fictionalization of silica gels [30,31].

3.1.2. Infrared spectroscopy

The FTIR spectroscopic measurements of raw and functionalized materials were carried out using Perkin-Elmer GX spectrophotometer. The FT-IR spectra of synthesized modified polyamine samples are shown in Fig. 2. IR spectra of silica gel sample (G) before functionalization and catalyst GN3, after functionalization showed bands at 463 and 453 cm^{-1} attributed to Si–O bond rocking [30,32]. Bands at 805 and 798 cm^{-1} observed in G and GN3 respectively, assigned to Si–O–Si symmetric vibrations [33,34]. After functionalization of silica gel with aminopropyl group, new absorption peak at 1531 cm^{-1} was attributed to the presence of —NH_2 scissor of catalyst GN3 [35]. Similarly band at 1447 cm^{-1} due to —CH_2 scissor have also been observed in IR spectra of catalyst GN3 after functionalization of silica gel samples. This confirms the presence of aminopropyl group onto the surface of silica.

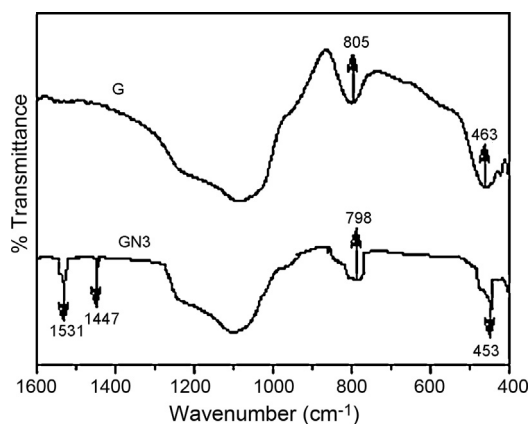


Fig. 2. Infrared spectra of silica gel (G), amino-functionalized silica gel catalyst (GN3).

3.1.3. Thermo gravimetric analysis

The stability of catalyst was determined by using thermo gravimetric analysis (TGA). Organic content of the surface modified silica gel particles, assessed by TGA are shown in Fig. 3. The samples were heated from room temperature to 850°C , at a rate of $10^\circ\text{C}/\text{min}$. Thermo gravimetric curves showed an increase in mass loss of 5.8% and 14.5% for G and GN3 respectively and results an increase in the loading of organic functional group on the surface of silica gel. For silica gel (G) weight loss occurred up to 150°C due to the loss of physically adsorbed water molecule. At higher temperature ($150\text{--}850^\circ\text{C}$) the remaining weight loss was due to the condensation of silanol groups. For GN3, an additional weight loss in temperature range of $350\text{--}650^\circ\text{C}$ was due to the decomposition of organic moiety bonded to the inorganic silica backbone [30,36]. Thus, the catalyst is found to be stable up to 300°C .

3.1.4. Elemental analysis

Elemental analysis results of functionalized silica gel samples are summarized in Table 2. The C/N ratio of sample increases with increase in amine content; it is higher than 3 for samples containing more than 12.8% amine. Almost all methoxy groups in all APTMS are reacted to form a covalent bond between the amino silane group

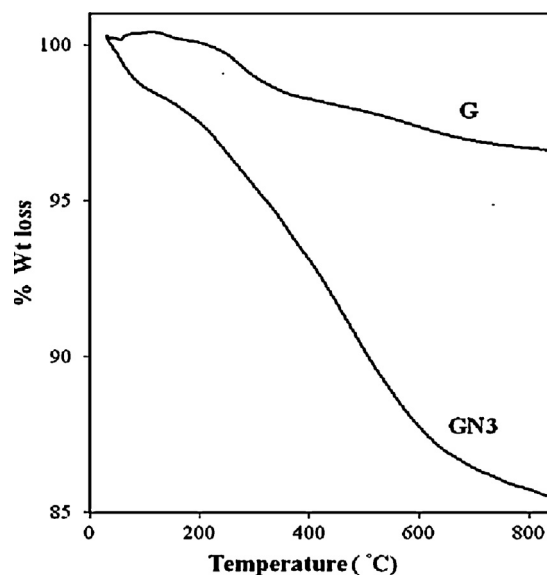
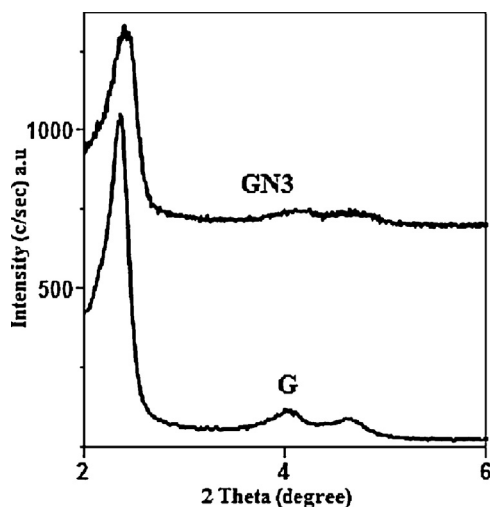


Fig. 3. TGA curves of silica gel (G), amino-functionalized silica gel catalyst (GN3).

Table 2
Elemental analysis of functionalized silica gels.

Sample	C (%)	H (%)	N (%)	C/N (M/M)	NH ₂ (mmol/g)
GN3	2.77	1.37	0.72	4.48	0.51

**Fig. 4.** PXRD patterns of silica gel G and amino functionalized silica gel GN3.**Table 3**
PXRD Patterns of parent Silica gel G and aminofunctionalized GN3.

Samples	d_{100} (Å)	a_0 (Å)	Wt (Å)
G	37.07	42.85	17.45
GN3	37.70	43.53	22.63

and silica surface and/or with neighboring aminopropyl silane moiety [32].

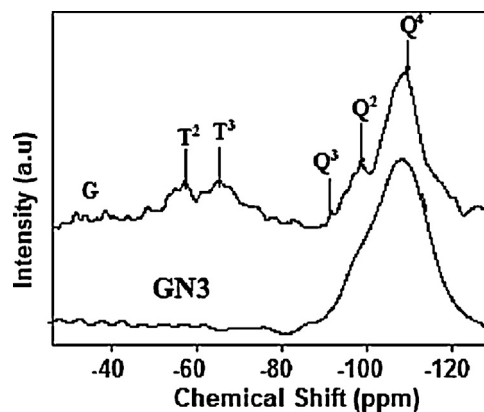
3.1.5. Powder X-ray diffraction

Powder X-ray diffraction patterns of silica gel G sample and aminopropyl functionalized silica gel are shown in Fig. 4. Powder X-ray diffraction (PXRD) patterns of functionalized silica indicate that the hexagonal structure of GN3 has been retained and showed a typical mesoporous structure with three sharp peaks corresponding to (100), (110) and (200) planes (Table 3) [32,37,38].

In Table 3, the value of d_{100} and a_0 remained almost constant with the standard deviation of 0.35, indicating that the surface modification did not result in structural properties of GN3.

3.1.6. ^{29}Si solid state NMR analysis

The ^{29}Si NMR spectra of parent silica gel (G) and functionalized silica gel (GN3) are shown in Fig. 5. Three peaks at -112 , -102 and -92 ppm are attributed to silicon in the siloxane binding environment without hydroxyl groups Q^4 [$(\text{SiO})_4\text{Si}$], isolated silanol groups Q^3 [$(\text{SiO})_3\text{Si}-\text{OH}$] and to geminal silanol groups Q^2 [$(\text{SiO})_2-\text{Si}-(\text{OH})_2$] of the silica gel. An increase in calcinations temperature from 150 to 600°C the intensity of -112 ppm signal (Q^4) increased whereas intensity of -102 ppm signal (Q^3) and -92 ppm signal (Q^2) decreased due to dehydroxylation and the formation of

**Fig. 5.** ^{29}Si MAS NMR spectra of silica gel (G), aminopropyl functionalized silica gels (GN3).

siloxane bonds ($\text{Si}-\text{O}-\text{Si}$) [39]. Area under Q^4 and Q^3 peaks were deconvoluted and results are summarized in Table 4.

The Q^4/Q^3 ratio increases with increase in temperature and indicates the decrease in $\text{Si}-\text{OH}$ group. After functionalization and broadening of Q^4 and two additional signals were observed at ~ -70 ppm due to $\text{SiR}(\text{OSi})_3$ (T^3) and ~ -60 ppm due to $\text{Si}(\text{OH})\text{R}(\text{OSi})_2$ or $\text{Si}(\text{OCH}_3)\text{R}(\text{OSi})_2$ (T^2) for the functionalized silica gel, correspond to two different environments as siloxane groups in the functionalized layers [39–41]. An increase in Q^4 peak intensity was also observed, along with a reduction in signal intensity of the Q^2 and Q^3 sites in all the functionalized silica gel samples. It indicated that the organic groups were grafted on to the surface of silica gel, and thus more Q^4 silica sites are subsequently formed.

3.1.7. Scanning and transmission electron microscopy

The morphology of organic functionalized silica materials studied using SEM and TEM technique shown in Fig. 5. The scanning electron micrograph (SEM) of the calcined GN3 (Fig. 6a) shows the agglomerates of GN3 are consisted of hexagonal-to-round shape sub-micrometer size particles. The well-ordered, hexagonal pore structure of GN3 [32,38] revealed by the high resolution transmission electron micrograph (Fig. 6b).

3.2. Catalytic activity of catalyst GN3

The synthesized material (catalyst GN3) was assessed for its activity in the synthesis of 2-amino-4-(4-chlorophenyl)-4H-chromene-3-carbonitrile. In model reaction we carried out a reaction of 4-chlorobenzaldehyde, malononitrile and phenol in presence of 10 mole% amino-functionalized silica gel catalyst (GN3) using water as solvent. It assured 2-amino-4-(4-chlorophenyl)-4H-chromene-3-carbonitrile in 34% yield successfully. For optimization of reaction conditions, a set of various experiments were performed using different parameters like solvent effect, and reusability of the catalyst. Initially, the reaction mixture was refluxed in different solvents water, acetonitrile, dimethyl sulfoxide (DMSO), chloroform, dichloromethane and ethanol.

We observed the polarity of solvent has little effect on reaction performance. Similar results were obtained in polar as well as in non-polar solvents. However, reaction performed better in

Table 4
Deconvolution analysis of ^{29}Si NMR spectra of silica gel samples treated at different temperature^a.

	Q^4	Q^3	Area of Q^4 (A1)	Area of Q^3 (A2)	% error A1	% error A2	Q^4/Q^3
G	-112	-102	17121	11673	0.874	1.304	1.467
GN3	-111	-102	23871	2036	0.456	4.432	11.73

^a Gaussian line shape was assumed for both the peaks.

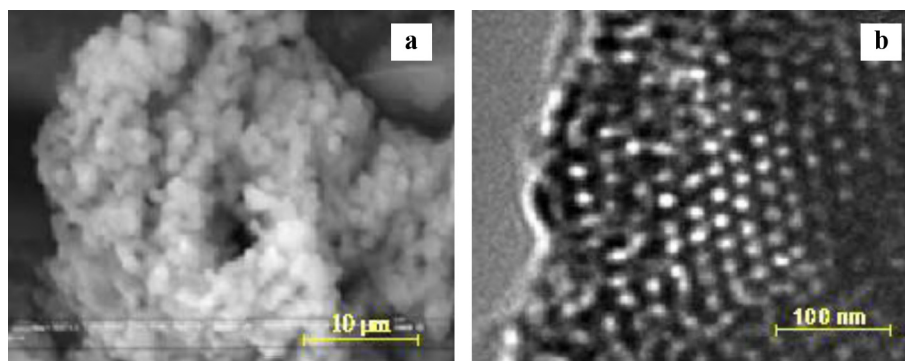


Fig. 6. Scanning electron microscopy picture of GN3 (a) Transmission electron microscopy picture of GN3(b).

ethanol solvent. In water, the reaction mixture was refluxed for 20 h to obtain the product in lower yield (Table 5, entry-1). Although acetonitrile and dimethyl sulfoxide reduced the reaction time to 12–15 h, the yield of product was not upto the satisfactory level (Table 5, entries 2 and 3). In solvent chloroform the reaction time was extended to 24 h with longed the yield amongst all the solvent used (Table 5, entry-4); whereas, reaction did not showed any progress in solvent dichloromethane even after 24 h under reflux conditions (Table 5, entry-5). Reaction performance was drastically enhanced in protic solvent ethanol, wherein the reaction completed in 4 h and excellent yield of the product was obtained 84% (Table 5,

Table 5

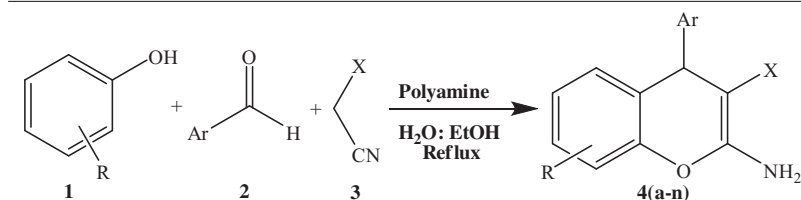
Optimization of synthesis of 2-amino-4-(4-chlorophenyl)-4H-chromene-3-carbonitrile.

Entry	Solvent	Time (h)	Yield ^a (%)
1	Water	20.00	34
2	Acetonitrile	12.00	41
3	Dimethyl sulfoxide	15.00	32
4	Chloroform	24.00	29
5	Dichloromethane	24.00	–
6	Ethanol	4.00	84
7	Ethanol–water (8:2)	2.30	94

^a Isolated yield after column chromatography.

Table 6

Synthesis of 2-amino-4H-chromene derivatives using different substrates.



Entry	R	Ar	X	Product	Time (hrs)	Yield ^a (%)	M.P. °C
1	H	4-Cl	CN	4a	2.30	94	178–180
2	H	2,4-Cl	CN	4b	2.00	89	195–197
3	H	4-NO ₂	CN	4c	3.00	90	215–217
4	H	3-NO ₂	CN	4d	3.00	93	200–202
5	H	4-F	CN	4e	2.30	95	187–189
6	H	4-Me	CN	4f	3.20	90	165–167
7	H	4-OH	CN	4g	3.00	88	167–169
8	H	3-OH	CN	4h	3.40	91	218–220
9	4-Cl	4-Cl	CN	4i	4.00	89	191–193
10	4-Cl	4-NO ₂	CN	4j	3.50	90	156–158
11	4-Cl	4-Me	CN	4m	4.00	88	222–224
12	4-Cl	3-NO ₂	COOEt	4k	4.20	91	173–175
13	4-Cl	4-F	COOEt	4l	4.40	90	181–183
14	4-Cl	4-Me	COOEt	4m	5.00	87	233–235
15	4-Cl	3-OH	COOEt	4n	5.30	86	214–216

^a Isolated yield after column chromatography.

entry-6). While experimenting on reaction conditions, surprisingly we found ethanol–water system in 8:2 combination was the most efficient solvent system for these reaction. Thus, ideal conditions were obtained for reaction. The reaction completed in less than 3 h and the yield was enhanced to 94% (Table 5, entry-7).

Finally, the optimized reaction protocol was extended to other aromatic aldehydes, phenols and active methylene compounds to check the feasibility of reaction with different substrates. Table 6 showed the results for experiment conducted with different substrate utilized. The reaction proceeds smoothly (Table 6) offering excellent yield of products successfully. Further, on replacement of malononitrile with ethylcyano-acetate; the reaction was preceded with longer reaction time. However, yield of desired compound has not shown any prominent effect. Same observation was noted with chlorophenol, and comparatively it takes more time for the completion of reaction, may be due to electron donating nature of chlorine.

Possible mechanism of 2-amino-4H-chromenes:

Based on obtained results and literature documents [42] mechanism of reaction was deduced. The proposed mechanism is depicted in Fig. 7. In the first step, the formation of intermediate I take place in situ by Knoevenagel condensation of highly active methylene compound and aldehyde. Amino functionalized silica acts as the proton scavenger to generate nucleophile. Due to the flexible [43]

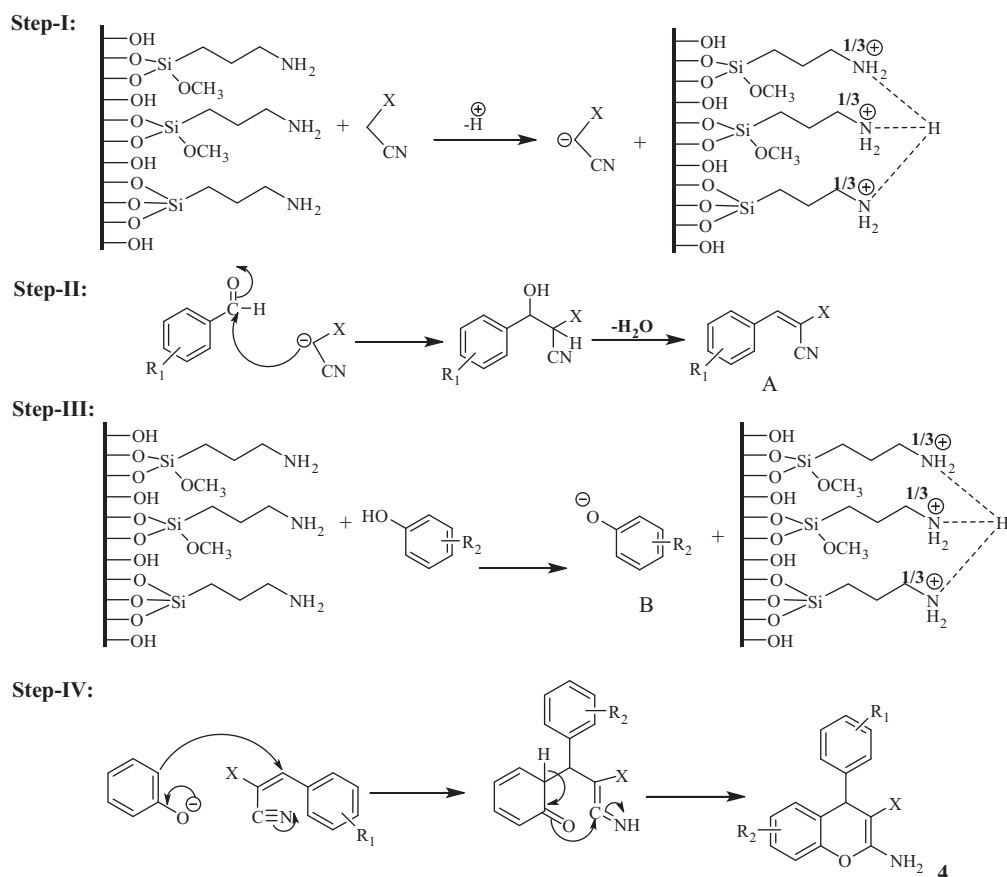


Fig. 7. Possible mechanism of 2-amino-4H-chromene derivatives using GN3 catalyst.

aminopropyl chain the abstracted proton assembled between three nitrogen atoms which strengthen the basicity of the catalyst GN3. Subsequently, in the second step catalyst GN3 abstract proton from phenol and form phenoxide ion (II) which attacks on the intermediate I and leads to a new C–C bond formation via Michael addition to produce intermediate III. Finally, after the rearrangement and tautomeric proton shift of intermediate III, 2-Amino-4H-Chromene product 4 is obtained.

Inspired from these results we moved on next task to check the reusability of heterogeneous polyamine catalyst. The catalyst was recovered by simple filtration process and after several washings with distilled water; the activated catalyst was reused to ensure its efficiency in next reaction cycles. To test this, a series of five consecutive runs for the synthesis of 4a were carried out with same catalyst and the results are shown in Table 7. In second run under similar reaction conditions, the yield obtained was decreased to 91% the catalyst from present reaction was reused after filtration, a slight decrease in activity of catalyst was observed and the yield was reduced to 88%. Further, decrease in activity could be seen in

4th and 5th reaction cycles and the yields obtained were 87 and 85 respectively.

Based on observed performance, the results demonstrate that heterogeneous polyamine catalyst is highly active, stable and recyclable upto 5th use without loss of significant activity.

4. Conclusion

In conclusion, an efficient, eco-compatible method for the synthesis of 2-amino chromene derivative by one pot multicomponent reaction from aromatic aldehyde, phenol and active methylene compounds, in presence of silica gel supported polyamine heterogeneous catalyst (GN3) has been successfully developed for the first time. Polyamine heterogeneous catalyst is highly efficient, easy to prepare and offering excellent yield of desired products. Furthermore, the catalyst is easily recovered by simple filtration, avoiding tedious work up process. The recovered catalyst is further utilized to carry the multicomponent reaction without loss of any significant activity.

Acknowledgement

The authors are thankful to the Principal Dr. P.L. More, DSM, College, Parbhani, for his encouragement during the said work.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molcata.2013.03.022>.

Table 7

Recyclability of the Heterogeneous catalyst GN3.

Entry	No. of run	Yields ^a (%)
1	Fresh	94
2	1	94
3	2	91
4	3	88
5	4	87
6	5	86

^a Isolated yield after column chromatography.

References

- [1] G.R. Green, J.M. Evans, A.K. Vong, in: A.R. Katritzky, C.W. Rees, E.F.V. Scriven (Eds.), *Comprehensive Heterocyclic Chemistry II*, vol. 5, Pergamon Press, Oxford, 1995, p. 469.
- [2] (a) W.O. Foye, *Principipi Chemico Farmaceutica*, Piccin, Padova, Italy, 1991, p. 416;
(b) L. Bonsignore, G. Loy, D. Secci, A. Calignano, *Eur. J. Med. Chem.* 28 (1993) 517.
- [3] G. Kolokythas, N. Pouli, P. Marakos, H. Pratsinis, D. Kletsas, *Eur. J. Med. Chem.* 41 (2006) 71.
- [4] M.A. Azuine, H. Tokuda, J. Takayasu, F. Enjo, T. Mukainaka, T. Konoshima, H. Nishino, G. Kapadia, *J. Pharmacol. Res.* 49 (2004) 161.
- [5] (a) S.K. Srivastava, R.P. Tripathi, R. Ramachandran, *J. Biol. Chem.* 280 (2005) 30273;
(b) H. Brotz-Oesterhelt, I. Knezevic, S. Bartel, T. Lampe, U. Warnecke-Eberz, K. Ziegelbauer, D. Habich, H. Labischinski, *J. Biol. Chem.* 278 (2003) 39435.
- [6] S. Toshiro, W. Noriko, *Eur. Pat. Appl.* EP 647445 A1 19950412 (1995).
- [7] Y. Ito, H. Kato, S. Yasuda, N. Kato, N. Iwasaki, H. Nishino, M. Takeshita, *Jpn Kokai Tokkyo Koho*, JP 06107664 A2 19940419 (1994).
- [8] K. Goto, O. Yaoka, T. Oe, *PCT Int. Appl.* WO 8401711 A1 19840510 (1984).
- [9] Y. Maruyama, K. Goto, M. Terasawa, *Ger. Offen.* DE 3010751 19810806 (1981).
- [10] K. Ukawa, T. Ishiguro, H. Kuriki, A. Nohara, *Chem. Pharm. Bull.* 33 (1985) 4432.
- [11] M. Curini, G. Cravotto, F. Epifano, G. Giannone, *Curr. Med. Chem.* 13 (2006) 199.
- [12] P. O'Kennedy, R.D. Thornes, In *Coumarins: Biology, Applications and Mode of Action*, John Wiley & Sons, Chichester, 1997.
- [13] G.P. Ellis, in: A. Weissberger, E.C. Taylor (Eds.), *The Chemistry of Heterocyclic Compounds. Chromenes, Chromanes, and Chromones*, John Wiley, New York, 1977, p. 11 (Chapter II).
- [14] G.A. Kraus, I. Kim, *J. Org. Chem.* 68 (2003) 4517.
- [15] K. Hiramoto, A. Nasuhara, K. Michiloshi, T. Kato, K. Kikugawa, *Mutat. Res.* 395 (1997) 47.
- [16] G.P. Ellis, in: A. Weissberger, E.C. Taylor (Eds.), *The Chemistry of Heterocyclic Compounds. Chromenes, Chromanes, and Chromones*, John Wiley, New York, 1977, p. 13 (Chapter II).
- [17] (a) E.A. Hafez, M.H. Elnagdi, A.A. Elagamey, F.M.A. El-Taweel, *Heterocycles* 26 (1987) 903;
(b) M.A. Sofan, F.M.A. El-Taweel, M.H. Elnagdi, *Liebigs Ann. Chem.* (1989) 935;
(c) F.M. Abdel Galil, B.Y. Riad, S.M. Sherif, M.H. Elnagdi, *Chem. Lett.* (1982) 1123.
- [18] (a) F.F. Abdel-Latif, *Indian J. Chem.* 29B (1990) 664;
(b) A.G.A. Elagamey, F.M.A. El-Taweel, *Indian J. Chem.* 29B (1990) 885;
(c) A.G.A. Elagamey, F.M.A. El-Taweel, M.N.M. Khodeir, M.A. Elnagdi, *Bull. Chem. Soc. Jpn.* 66 (1993) 464;
(d) J. Bioxham, C.P. Dell, C.W. Smith, *Heterocycles* 38 (1994) 339.
- [19] T.S. Jin, A.Q. Wang, X. Wang, J.S. Zhang, T.S. Li, *Synlett* (2004) 871.
- [20] D.Q. Shi, S. Zhang, Q.Y. Zhuang, S.J. Tu, H.W. Hu, *Chin. J. Org. Chem.* 23 (2003) 877.
- [21] L.M. Wang, J.H. Shao, H. Tian, Y.H. Wang, B. Liu, *J. Fluorine Chem.* 127 (2006) 97.
- [22] S. Balalaie, M. Bararjanian, A.M. Amani, B. Movassagh, *Synlett* (2006) 263.
- [23] Y. Peng, G. Song, *Catal. Commun.* 8 (2007) 111.
- [24] (a) X.S. Wang, D.Q. Shi, H.Z. Yu, *Synthetic Commun.* 34 (2004) 509;
(b) X.S. Wang, Z.S. Zeng, D.Q. Shi, *Chin. J. Org. Chem.* 25 (2005) 1138;
(c) X.S. Wang, D.Q. Shi, S.J. Tu, *Synthetic Commun.* 33 (2003) 119.
- [25] (a) S. Abdolmohammadia, S. Balalaie, *Tetrahedron Lett.* 48 (2007) 3299;
(b) S. Balalaie, M. Bararjanian, M. Sheik-Ahmadi, *Synthetic Commun.* 37 (2007) 1097.
- [26] (a) M. Kidwai, S. Saxena, S.S. Thukral, *Bioorg. Med. Chem. Lett.* 15 (2005) 4295;
(b) I. Devi, P.J. Bhuyan, *Tetrahedron Lett.* 45 (2004) 8625;
(c) T.S. Jin, J.C. Xiao, S.J. Wang, *Ultrason. Sonochem.* 11 (2004) 393.
- [27] V. Manu, H.M. Mody, H.C. Bajaj, R.V. Jasra, *Ind. Eng. Chem. Res.* 48 (2009) 8954.
- [28] J.G.P. Espinola, S.F. Oliveria, W.E.S. Lemus, A.G. Souza, C. Aioldi, J.C.A. Moreria, *Colloids Surf. A: Physicochem. Eng. Aspects.* 166 (2000) 45.
- [29] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, *Pure Appl. Chem.* 5 (1985) 603.
- [30] R.S.A. Machado Jr., M.G. da Fonseca, L.N.H. Arakaki, J.G.P. Espinola, S.F. Oliveira, *Talanta* 63 (2004) 317.
- [31] I.P. Blitz, J.P. Blitz, V.M. Gunko, D.J. Sheeran, *Colloids Surf. A: Physicochem. Eng. Aspects* 307 (2007) 83.
- [32] K.F. Lam, K.L. Yeung, G. McKay, *Langmuir* 22 (2006) 9632.
- [33] H. Yang, R. Xu, X. Xue, F. Li, G. Li, J. Hazard. Mater. 152 (2008) 690.
- [34] C. Lesaint, B. Lebeau, C. Marichal, J. Patarin *Microporous Mesoporous Mater.* 83 (2005) 76.
- [35] H. Yoshitake, T. Yokoi, T. Tatsumi, *Chem. Mater.* 14 (2002) 4610.
- [36] K.F. Lam, K.L. Yeung, G. McKay, *Microporous Mesoporous Mater.* 100 (2007) 191.
- [37] X.S. Zhao, G.Q. Lu, A.K. Whittaker, G.J. Millar, H.Y. Zhu, *J. Phys. Chem. B* 101 (1997) 6525.
- [38] K.Y. Ho, G. McKay, K.L. Yeung, *Langmuir* 19 (2003) 3019.
- [39] X. Wang, K.S.K. Lin, J.C.C. Chan, S. Cheng, *J. Phys. Chem. B* 109 (2005) 1763.
- [40] Z. Yan, G. Li, L. Muab, S.J. Tao, *Mater. Chem.* 16 (2006) 1717.
- [41] J.F. Diaz, K.J. Jr., F. Bedioui, V. Kurshev, L. Kevan, *Chem. Mater.* 9 (1997) 61.
- [42] (a) K.M. Parida, D. Rath, *J. Mol. Catal. A: Chem.* 310 (2009) 93–100;
(b) A. Hasaninejad, M. Shekouhy, N. Golzar, A. Zare, M.M. Doroodmand, *Appl. Catal. A* 402 (2011) 11–22;
(c) J.C. Xu, W.M. Li, H. Zheng, Y.F. Lai, P.F. Zhang, *Tetrahedron* 67 (2011) 9582–9587.
- [43] (a) T. Yokoi, Y. Kubota, T. Tatsumi, *Appl. Catal. A* 421–422 (2012) 14–37;
(b) X. Lin, G.K. Chuah, S. Jaenicke, *J. Mol. Catal. A: Chem.* 150 (1999) 287–294.