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One-pot synthesis of various 2-amino-4*H*-chromene derivatives using a highly active supported ionic liquid catalyst†

Pankaj Sharma,[a] Monika Gupta,*[a] Rajni Kant[b] and Vivek K. Gupta[b]

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In this paper, a supported ionic liquid catalyst (SILC) was synthesized by dissolving palladium acetate in [BMIM][OH] and immobilizing it on the surface of HAP. Further, it was characterized by SEM, TEM, TGA, FTIR, AAS and EDAX. This SILC was then used to synthesize various derivatives of chromenes under solvent-free conditions in excellent yields. The products obtained were characterized by ^{1}H NMR, ^{13}C NMR and mass analysis. One of the products, 2-amino-4-(3-nitrophenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile, was also characterized by single crystal X-ray crystallography.

Introduction

Recently, the growing awareness to environmental issues has focused the need for greener and more sustainable technologies in the chemical industry. Ionic liquids, which consist of cations and anions with low melting points and very low vapor pressures,[1–3] are in tremendous demand and undergoing serious growth. Many different ionic liquids have been prepared and have been successively used as solvents as well as modified catalysts. Zhang *et al.* have reviewed the recent advances in ionic liquid catalysis and expressed briefly the recent used catalytic techniques.[4] Heterogeneous catalysis is preferred in industrial processes compared to homogeneous catalysis as the extraction of product and catalyst recovery is easier in heterogeneous catalysis.[5] A catalytic system which has advantages of both homogeneous and heterogeneous catalysis can be a better option. The homogeneous catalysts in ionic liquids usually provide the advantages of high catalytic activity and good selectivity. However, their widespread use in homogeneous conditions is associated with some drawbacks such as product isolation, catalyst recovery and large amount of expensive ionic liquids are used which may cause possible toxicological concerns. The use of ionic liquids in heterogeneous form has been established to overcome these drawbacks and moreover, supported solid catalysts with ionic liquid combine the benefits of ionic liquids and heterogeneous catalysis such as designability, good solubility of catalytically active species, ease of handling, separation and recycling. In this context, ionic liquids are now widely used for immobilization of homogeneous catalysts.[6–9] Recently, ionic liquids are also used as hybrid materials called ionogels well reviewed by Bideau *et al.*[10]

Because of considerable and attractive properties of supported ionic liquid catalysis, earlier also we reported the synthesis of various compounds using these catalysts.[11–14] Here, we intend to design a catalyst combining the homogeneous nature of ionic liquid and palladium having high activity and selectivity with heterogeneous support to provide large interfacial reaction areas. The supported ionic liquid phase catalysis concept is based on a classical homogeneous catalyst that is dissolved in a thin film of ionic liquid which is further dispersed over the high internal surface of a porous support. In supported ionic liquid phase materials, the dissolved catalyst still acts microscopically as a homogeneously dissolved metal complex in its uniform ionic liquid environment while macroscopically dry solid form that can be recycled easily.

Palladium is known to catalyze many reactions and is also reported in literature to synthesize chromene derivatives.[15] The HAP support was chosen to enhance the basic nature of the catalyst and to provide heterogeneity to catalyst. Thus heterogeneous catalyst formed has its own advantages including larger interfacial reaction area, ease of product separation, cost-effective, recyclability and environment friendly.

Chromene derivatives are interesting heterocyclic compounds with numerous pharmacological and biological properties including antitumor,[16] antiallergic,[17] antimicrobial and antifungal,[18] anti-proliferative[19] and antioxidant.[20] These compounds are also involved in central nervous system activities[21] and also used in the field of biodegradable agrochemicals[22] and pigments.[23]

[a]*Department of Chemistry, University of Jammu, Jammu – 180006, India. E-mail: monika.gupta77@rediffmail.com*

[b]*Department of Physics and Electronics, University of Jammu, Jammu – 180006, India*

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There are number of methods[24–30] reported in literature for synthesis of these heterocycles using homogeneous and heterogeneous catalysts. Recently, Majumdar *et al.* published a review on catalytic synthesis of 2*H*-chromenes involving different catalysts.[15] Although these methods are effective but are associated with some drawbacks like use of high temperature, long reaction times, low yield, difficult work-up procedures and harsh reaction conditions. Savitha *et al.*[31] synthesized chromene derivatives involving complex strategy using $Pd(OAc)_2$ as catalyst with stoichiometric quantities of $CuBr_2$ and LiBr. Scheidt and coworkers[32] developed enantioselective Pd-catalyzed synthesis of 2-aryl chromenes. However, in this method besides Pd catalyst potassium carbonate, methanol, methylene chloride are used making the whole procedure complex. Mondal *et al.* have synthesized these chromene derivatives in facile way using metal-free mesoporous organocatalyst.[33] However the time taken to complete the reaction is longer and the preparation of catalyst is complex. Recently, Kundu and Bhaumik have reported the synthesis of chromenes using triazine based polymer catalyst.[34] Although this method involves recyclability and eco friendly synthesis but again the reaction time is longer. Thus, our motto was to use supported ionic liquid catalysis accompanying simple, cost effective, reusable and co-benign method, providing high yields in lesser time under solvent-free conditions.

Results and discussion

Preparation of SILC (HAP–Pd–[BMIM][OH])

[BMIM][OH] (0.78 g, 5 mmol) in methanol (5 mL) was mixed with hydroxyapatite (HAP) (5 g) in a round-bottomed flask (100 mL) and stirred at room-temperature for 10 h under inert atmosphere and then dried under reduced pressure until free flowing powder was obtained. In another round-bottomed flask (100 mL), [BMIM][OH] (1.56 g, 10 mmol) and palladium acetate (0.112 g, 0.5 mmol) were dissolved in methanol (10 mL) and stirred for 5 min. After this, hydroxyapatite pre-treated with ionic liquid was suspended in this solution and the mixture was refluxed for 10 h under inert atmosphere. Then solvent was evaporated under reduced pressure to get free flowing powder. Then, it was dried in an oven at 200 °C for 5 h. A general scheme for the preparation of the catalyst is shown in Fig. 1.

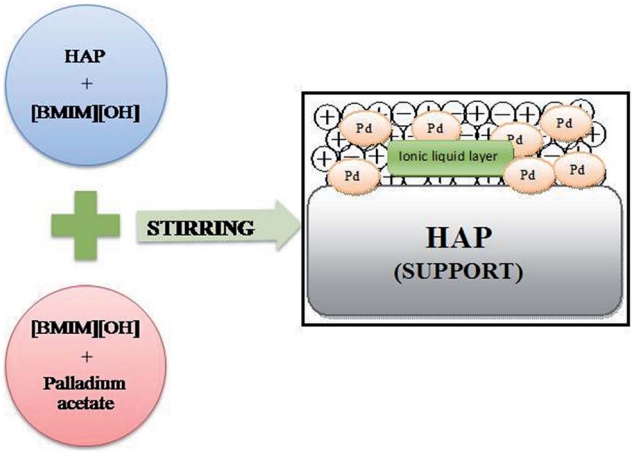


Fig. 1 Illustration of the synthesis of supported ionic liquid catalyst.

Characterization of SILC

Particle morphology and textural properties of the catalyst were studied carefully by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The surface structure of the catalyst was characterized by SEM micrographs. The views of surface are presented in Fig. 2. The SEM image of SILC showed that the catalyst is a fine homogeneous powder with porous structure. The TEM micrographs (Fig. 3) of the catalyst provided direct observation of the morphology. From TEM micrographs it looks like that Pd with ionic liquid is distributed on to the surface of HAP and there is no bulk aggregation of the Pd–IL complex and is uniformly dispersed on to the surface of HAP.

TGA-DTA analysis (Fig. 4) was employed to investigate the thermal stability of catalyst, since observed weight loss is associated with loss of components attached to the surface. The small amount of weight loss below 150 °C was attributed to desorption of physically adsorbed gases, water and minor residual solvent. However the curve gradually starts decreasing from 150 °C onwards upto 277 °C which was attributed to decomposition of alkyl chains of ionic liquid and anionic part of ionic liquid and showed sharp decline in weight upto 370 °C can be due to decomposition of cationic core of ionic liquid. The loss above 370 °C can be attributed to decomposition of HAP.

According to EDX spectrum (Fig. 5) the presence of Pd is indicated. The EDX spectrum also showed other elements including C, N, O and Ca which are present in the SILC. The amount of Pd loaded onto the surface of catalyst was determined by AAS analysis and found that 0.022 g of Pd was present per gram of the catalyst.

FTIR spectrum (Fig. 6) of supported ionic liquid phase catalyst displayed the PO_4^{3-} bands at wave numbers 1093, 1062, 601 and 569 cm^{-1}. The hydroxyl bending bands of hydroxyapatite were identified at around 3570 cm^{-1} and 624 cm^{-1} whereas the hydroxyl bands of anionic part of ionic liquid were displayed in a range from 3160–3392 cm^{-1}.

Optimization of reaction conditions

An efficient method for the preparation of chromene derivatives through the reaction of aldehydes, malononitrile and dimedone in the presence of catalytic amount of SILC as heterogeneous catalyst has been described. In a preliminarily investigation on the model reaction of 4-methoxybenzaldehyde, dimedone and malononitrile (entry 10, Table 3), it was found that the reaction could be finished in the presence of catalytic amount of SILC under solvent-free conditions at 80 °C which gave the desired product in good yield. The effect of catalyst, reaction temperature, solvent and time of the reaction was systematically investigated. In order to optimize the amount of catalyst, model reaction was carried out with different amount of catalyst. With

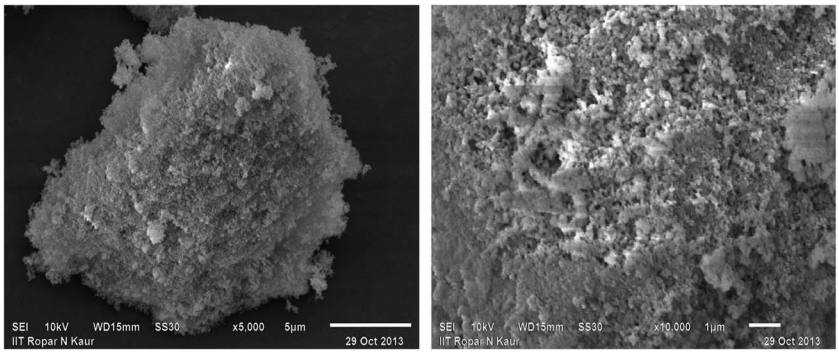


Fig. 2 SEM micrograph of SILC.

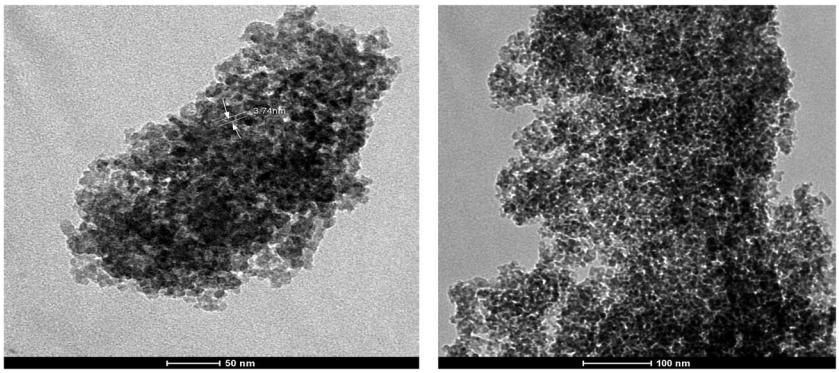


Fig. 3 TEM images of SILC.

1 mmol of each reactant, reaction with 0.025 g, 0.05 g and 0.1 g of catalyst was tried and it was found that 0.05 g of catalyst is sufficient to get the product in good yield. No significant increase in yield was observed with the increase in amount of catalyst. Thus, 0.05 g of catalyst was chosen as optimum amount to catalyze the reaction. In order to optimize the

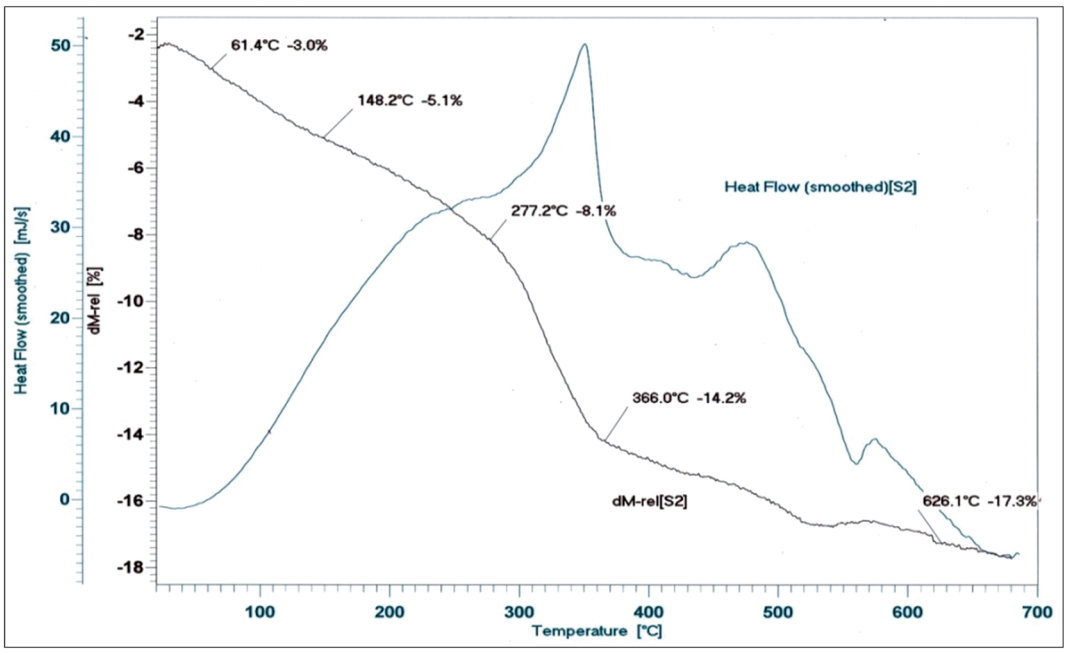


Fig. 4 TGA-DTA curve of SILC.

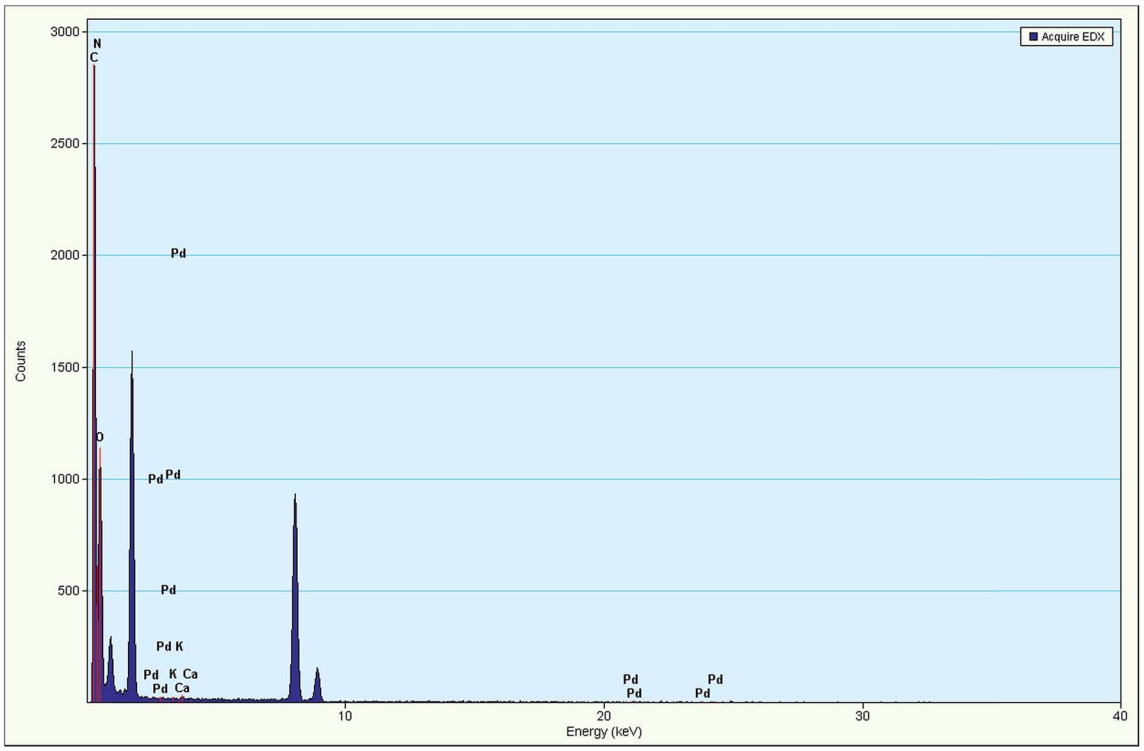


Fig. 5 EDX pattern of SILC.

temperature, model reaction was carried out at room-temperature, 40 °C, 60 °C, 80 °C and 100 °C under solvent-free conditions using SILC as catalyst and results are represented in Table 1. At room-temperature and 40 °C, lower yields of products were seen, whereas at 60 °C, 70% yield was obtained. The reaction was clean at 80 °C and afforded excellent

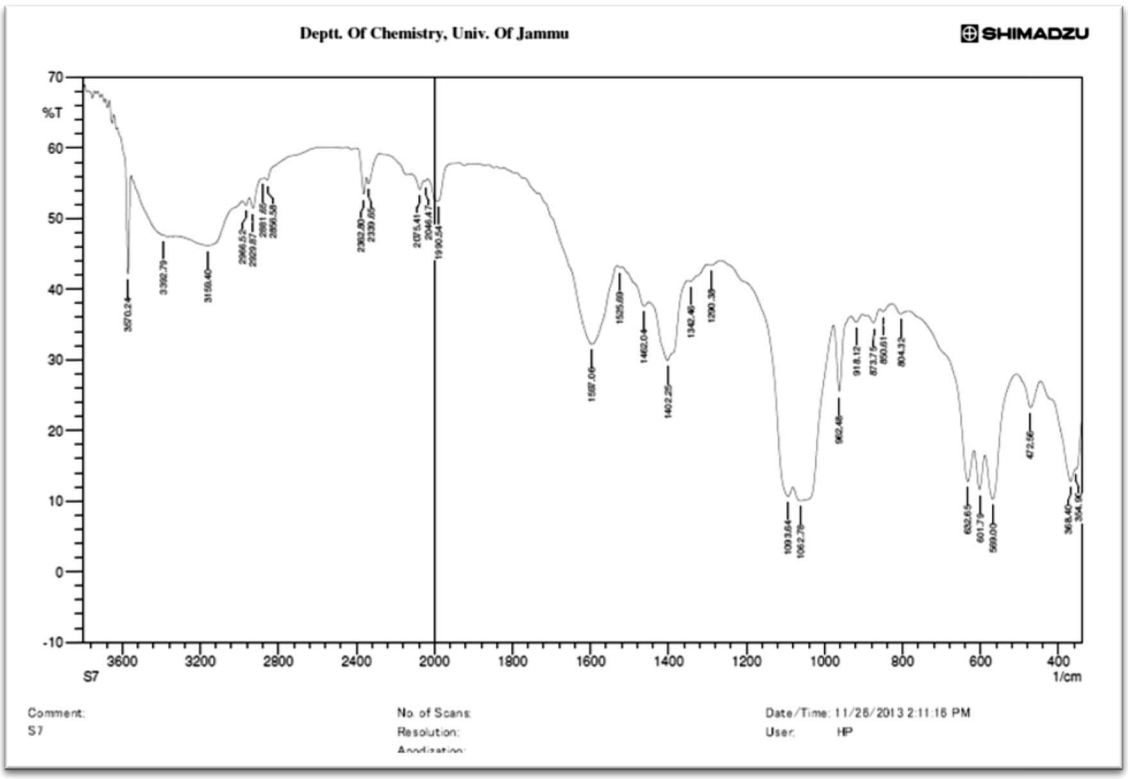


Fig. 6 FTIR spectra of SILC.

Table 1 Effect of temperature studied in the synthesis of 2-amino-4*H*-chromenes[a] under solvent-free conditions

Entry	Temperature	Time (min)	Yield[b] (%)
1	r.t.	20	20
2	40 °C	**10**	**40**
3	60 °C	**10**	**70**
4	**80 °C**	10	**96**
5	100 °C	10	96

[a] Reaction conditions; *p*-methoxybenzaldehyde (1 mmol), dimedone (1 mmol), malononitrile (1 mmol) and catalyst (0.05 g). [b] Isolated yield.

Table 2 Comparison of activity of the catalysts in the oxidation of benzyl alcohols and in the synthesis of chromene derivatives[a]

Entry	Catalyst	Time (min)	Yield[b] (%)
1	No catalyst	10	No rxn
2	HAP	10	Traces
3	HAP–$Pd(OAc)_2$	10	50
4	$Pd(OAc)_2$–IL	10	60
5	**SILC**	**10**	**96**

[a] Reaction conditions; *p*-methoxybenzaldehyde (1 mmol), dimedone (1 mmol), malononitrile (1 mmol) and catalyst (0.05 g for entries 2 and 5, 0.01 g $Pd(OAc)_2$ and 0.05 g HAP for entry 3, 0.01 g $Pd(OAc)_2$ and 0.05 g [BMIM][OH] for entry 4) and stirring at 80 °C under solvent-free conditions. [b] Isolated yield.

yield of desired product. There was no significant improvement in percentage yield of product at 100 °C. Thus, 80 °C was chosen to be best temperature for the synthesis of 2-amino-4*H*-chromenes. Further we explored the effect of different solvents on model reaction and results are presented in Fig. 7. Among various solvents used, ethanol gave reasonable yield of 70% and all other solvents were ineffective to give good yields. From the figure it was concluded that solvent-less conditions are best to carry out the synthesis of chromenes.

In order to identify the role of supported ionic liquid catalyst (SILC) as a heterogeneous catalyst, in the synthesis of chromene derivatives, the test reaction was carried out in the presence of HAP, HAP–[BMIM][OH], HAP–palladium acetate and without catalyst. Among various catalysts used, HAP was unable to carry the reaction, whereas combination of HAP with ionic liquid or palladium acetate also gave low yield but supported ionic liquid catalyst gave best results (Table 2). SILC combines the advantage of homogeneous and heterogeneous nature of the catalyst. Moreover, the supported ionic liquid catalyst can be easily recovered and recycled for several runs, thus making process cost-effective with easy work-up. So, supported ionic liquid catalyst (SILC) was used as a catalyst to catalyze the reactions.

With the optimized reaction conditions, the synthesis of chromenes was tried with range of substrates to study the scope of this method and examples are summarized in Table 3. It was observed that aromatic aldehyde bearing various functional groups on phenyl ring and heterocyclic aldehydes all yielded good amount of products. One of the product 2-amino-4-(3-nitrophenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile was characterized by single X-ray crystallography (CCDC: 1400076†) and revealed that the compound crystallizes in a triclinic crystal system with $P\bar{1}$ space group. The ORTEP view of the molecule has been shown in Fig. 8.

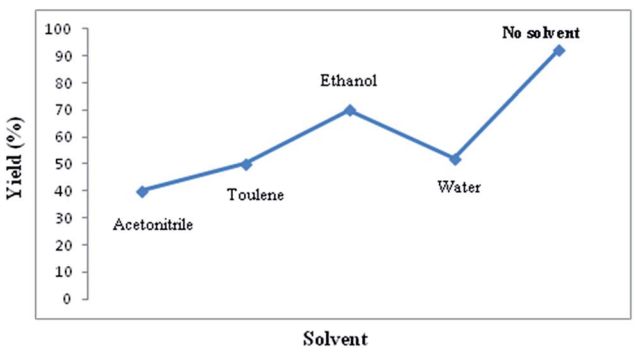


Fig. 7 Effect of different solvents studied in the synthesis of chromene derivatives.

Recyclability

Being heterogeneous in nature, the important feature of catalyst was its recyclability. To check the recyclability of SILC, a series of 7 consecutive runs for the synthesis of chromenes using 4-methoxybenzaldehyde were carried out and the results are represented in Fig. 9 which demonstrates that SILC is highly active and recyclable upto 7^{th} run with very little loss of activity.

Although, no significant change in the activity of the catalyst was observed, we performed the AAS of the catalyst after 7^{th} use to determine any change in the catalyst. We observed nearly same weight loss after 7^{th} use indicating no significant change in the structure of catalyst. Also there is negligible change from 0.022 g to 0.021 g of palladium loaded on per gram surface of the catalyst after 7 uses in both recycled catalysts as measured by AAS indicating proper interaction between ionic liquid and palladium due to polarity of ionic liquid.

Proposed mechanism for synthesis of chromenes

The plausible mechanism is shown in Fig. 10. The step 1 involves the activation of dimedone by the catalyst to attack intermediate **1**, which was formed in second step by the nucleophilic attack of activated malononitrile on aldehyde. The intermediate **2** formed undergoes cyclocondensation in the presence of catalyst to give the final product. Here, catalyst is providing larger interfacial surface area to reaction and moreover the structural and textural properties of the catalyst are strongly influenced by the presence of ionic liquid which also provide polarity to catalytic system and thus enhancing its activity. The whole catalytic system is responsible to catalyze the reaction effectively and it is quite difficult to justify the role of individual HAP, ionic liquid or palladium acetate.

Table 3 Supported ionic liquid catalyst catalyzed one-pot synthesis of 2-amino-4*H*-chromenes[a]

Entry	R	Time (min)	Yield[b] (%)	Mp/Lit. (°C)
1	C_6H_5	15	94	230–232/232–234 (ref. 35)
2	2-$NO_2C_6H_4$	20	90	235–236/234–238 (ref. 36)
3	3-$NO_2C_6H_4$	20	92	213–214/213–214 (ref. 35)
4	4-$NO_2C_6H_4$	15	95	176–178/176–177 (ref. 35)
5	2-ClC_6H_4	25	90	290–291/292–293 (ref. 37)
6	4-ClC_6H_4	15	94	212–214/212–214 (ref. 35)
7	4-FC_6H_4	15	92	199–200/198–200 (ref. 35)
8	4-BrC_6H_4	20	94	165–166/165–168 (ref. 35)
9	4-MeC_6H_4	25	90	209–210/210–215 (ref. 38)
10	4-$MeOC_6H_4$	10	96	200–202/198–200 (ref. 35)
11	4-OHC_6H_4	25	90	208–210/206–208 (ref. 35)
12	4-OH-3-$MeOC_6H_3$	30	92	228–229/230 (ref. 38)
13	2-Furyl	25	90	222–224/223–226 (ref. 35)
14	2-Thienyl	30	90	216–218/216–218 (ref. 39)
15	2,4-Dichloro-C_6H_3	25	88	194–195/192–193 (ref. 40)
16	3-OHC_6H_4	20	89	221–223/224–226 (ref. 41)
17	2-$MeOC_6H_4$	25	90	195–196/196–198 (ref. 38)

[a] Optimized reaction conditions: aldehyde (1 mmol), malononitrile (1 mmol), dimedone (1 mmol), SILC (0.05 g) and stirring at 80 °C, solvent-free. [b] Isolated yield.

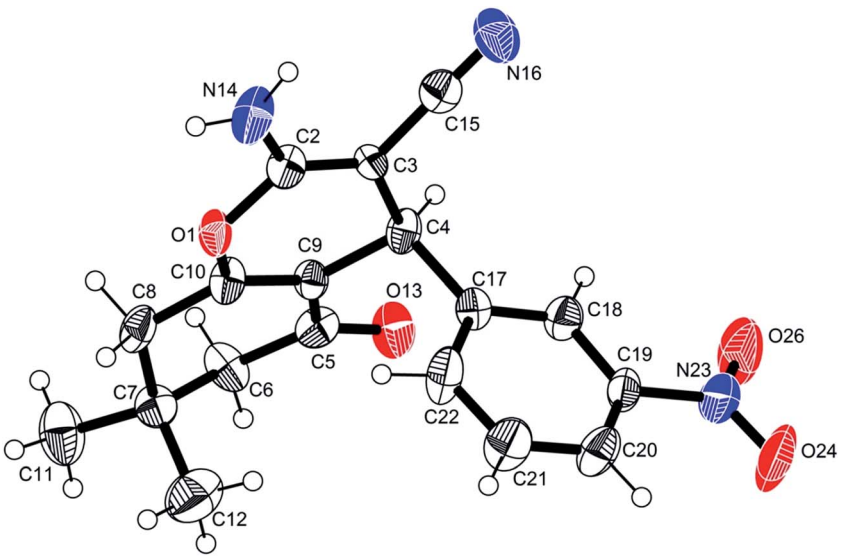


Fig. 8 The ORTEP view of 2-amino-4-(3-nitrophenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile.

Experimental

General

The chemicals used were either prepared in our laboratory or purchased from Sigma Aldrich or Merck chemical companies. The ^1H or ^{13}C NMR data were recorded in $CDCl_3$ or DMSO-d_6 on Bruker DPX 400 spectrometer. The FTIR spectra were recorded on Perkin-Elmer spectrophotometer and mass spectral data were recorded on Bruker Esquires 3000 (ESI). Thermal analysis was carried out on DTG-60 Shimadzu thermal analyzer. The amount of Pd in catalyst was determined by atomic absorption spectrometric analysis (AAS) and was performed on an Avanta-M atomic absorption spectrometer AAS. SEM was recorded on a SEM (JEOL) and TEM was recorded on a TECHNAI G^2 20 S-TWIN (FEI Netherlands). X-ray data of complex was collected on an X'calibur-Oxford Diffraction single crystal diffractometer (Department of Physics and Electronics, University of Jammu, Jammu) with CCD area-detector (graphite-monochromator, Mo-Kα radiations, $\lambda = 0.71073$ Å).

General procedure for the synthesis of 2-amino-4*H*-chromenes

SILC (0.05 g) was added to the mixture of an aldehyde (1 mmol), dimedone (1 mmol) and malononitrile (1 mmol) in a round-bottomed flask (Scheme 1). Then, the reaction was carried on a magnetic stirrer at 80 °C for the appropriate time

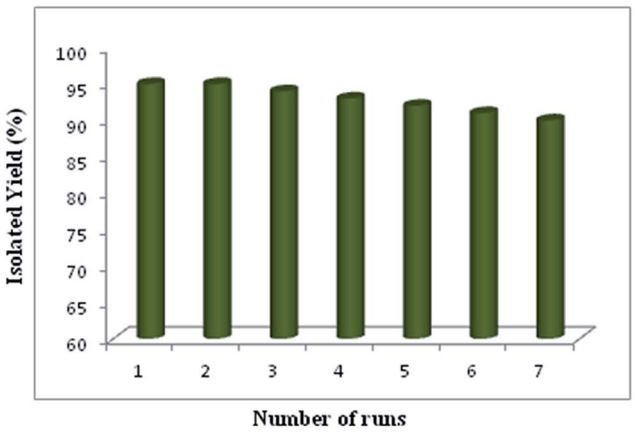
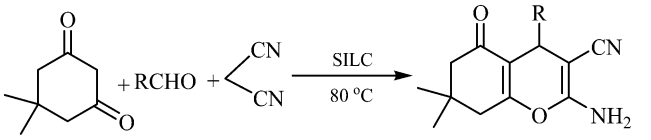


Fig. 9 Recyclability graph of the SILC for the synthesis of chromene derivatives.

as shown in Table 3. After completion of the reaction as monitored by TLC, the mixture was treated with required amount of ethylacetate and then catalyst was removed by filtration at reduced pressure and washed with hot distilled water. The filtrate was concentrated and cooled down to room temperature until solid product was formed in crystalline form. The product was filtered and crystallized from ethanol if necessary. The products were characterized with ^{1}H NMR, ^{13}C NMR and mass spectrometry.



Scheme 1 General procedure for synthesis of 2-amino-4*H*-chromenes using SILC.

Conclusion

In conclusion, we have explored the role of supported ionic liquid catalysis in the synthesis of various derivatives of chromenes. SILC was prepared by simple method using HAP and palladium acetate, and was quite efficient in synthesizing derivatives of chromenes in excellent yields under solvent-free conditions. This technique combines the most attractive features of homogeneous catalysis like high activity and selectivity with benefits of heterogeneous catalysis such as large surface area and easy product separation. Moreover it was recyclable and catalyzed the reaction in less time with simple work-up procedures and clean products were obtained. One of the product 2-amino-4-(3-nitrophenyl)-6,6,8,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile was also characterized by single crystal X-ray analysis and revealed that the compound crystallizes in a triclinic crystal system.

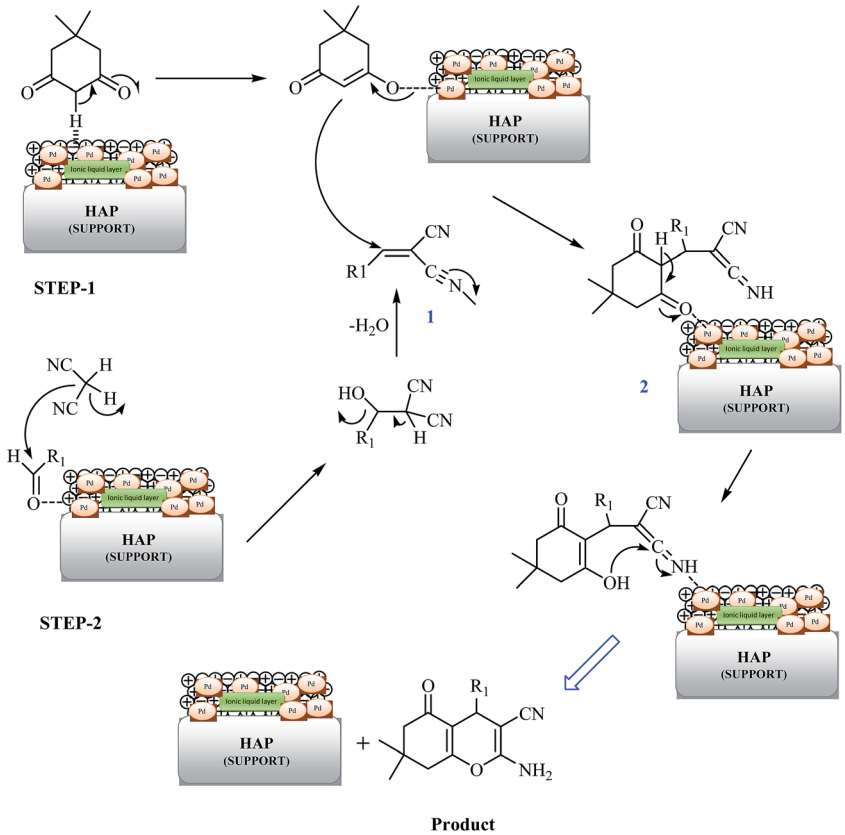


Fig. 10 Plausible mechanism for the synthesis of chromenes.

Acknowledgements

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