



Bio-waste originated, heterogeneous catalysts based on pomegranate peel for Knoevenagel condensation: a green approach

Monika Sujit Chavan¹ · Sonali Suryawanshi¹ · Arjun Kumbhar²

Received: 28 March 2023 / Accepted: 17 May 2023
© Akadémiai Kiadó, Budapest, Hungary 2023

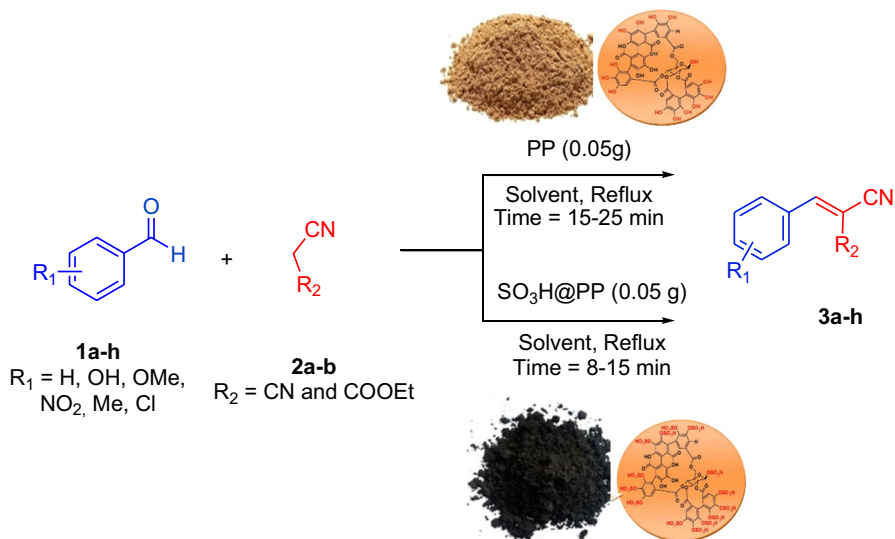
Abstract

A bio-waste-originated heterogeneous solid acid catalyst ($\text{SO}_3\text{H@PP}$) was easily prepared from cheap and easily available pomegranate peel (PP). The catalyst was characterized by IR, FE-SEM, XRD and EDX techniques. The prepared catalyst was efficiently applied for the Knoevenagel condensation of the various aromatic aldehydes and active methylene compounds (malononitrile and ethyl cyanoacetate) in water and EtOH at reflux conditions. The products were obtained with good to excellent yields. The catalysts were easily recovered by simple filtration and reused at least five times with a slight decrease in product yields. A bio-waste origin, easy availability, inexpensive, easy recovery and reusability are the prominent features of the reported catalysts. Cleaner reaction conditions, simple experimental and work-up procedures are the conspicuous features of this protocol.

Extended author information available on the last page of the article

Published online: 12 June 2023

Graphical abstract



Keywords Pomegranate peel · Sulfonic acid supported pomegranate peel · Bio-based catalyst · Knoevenagel condensation

Introduction

Green chemistry and sustainability aim to develop a cleaner and environmentally friendly pathway to reduce the use of hazardous reagents, solvents auxiliaries, harsh and prolonged reaction conditions as well as expensive catalysts. Green chemistry tackles the environmental risk caused by toxic, volatile, hazardous reagents and solvents and their impact on living things. In recent years, the chemist is much more aware of sustainable organic synthesis using both environmentally and economically benign acceptable reagents, renewable catalysts, safer solvents, atom-efficient methods and energy-efficient technologies. Recently, bio-based synthetic processes involving the use of renewable catalysts and solvents attracted much attention due to their numerous advantages. The selection of such bio-based catalysts with excellent atom economy plays a vital role in organic transformations. Numerous environmentally friendly, bio-based catalysts have been reported for different organic transformations [1–16].

The Knoevenagel condensation is an important carbon–carbon bond-forming reaction involving aromatic aldehydes condensation with active methylene compounds. The α , β -unsaturated products formed by Knoevenagel condensation are extensively used as intermediates in the manufacture of important pharmaceuticals, perfumes, cosmetics, polymers, natural products, and therapeutic drugs [17–22]. Numerous homogeneous and heterogeneous catalysts have been

reported for Knoevenagel condensation such as $\text{H}_3\text{PW}_{12}\text{O}_4$ [23], TiCl_4 [24], UiO-66-NH_2 [25], ZnCl_2 [26], Cu-HPA [27], MgF_2 [28], InX_3 [29], $\text{HClO}_4\text{-SiO}_2$ [30], $\text{K}_7\text{HfNb}_6\text{O}_{19}\cdot 13\text{H}_2\text{O}$ [31], Ni-SiO_2 [32], $\text{PS-[MeIm]Cl-XAlCl}_3$ [33], PCN-222-Co@TpPa-1 [34], surfactants [35], amine or ammonium salt [36], $\text{SA-DETA-Fe}_3\text{O}_4$ [37], $\text{SO}_4^{2-}/\text{ZnO}_2$ [38], Cu-PMA Cu-PMA [39], USY Zeolite [40], $\text{AlPO}_4\text{-Al}_2\text{O}_3$ [41], $\text{LaCl}_3\cdot 7\text{H}_2\text{O}$ [42], Mn salen complex [43].

In recent years different natural materials have been used for many organic transformations. *Punica granatum* commonly known as a pomegranate is an edible fruit-bearing deciduous shrub in the family Lythraceae. *Punica granatum* name is derived from *Pomum* means apple and *granatus* mean grainy. Peels, fruit, seeds, flowers, and leaves of *P. granatum* are enriched in various biologically important compounds. Its extracts exhibit potent anti-oxidant, antimicrobial, antiviral, anticarcinogenic, anticancer, and antimutagenic properties [44–48]. The byproduct formed during the food processing of pomegranates like juice, jam, oil, and wine is peels of pomegranate. The peels of pomegranate are even though rich in numerous photochemical and responsible for health benefits [49].

Though various homogeneous and heterogeneous catalysts have been employed for Knoevenagel condensation, still inexpensive and ecofriendly protocol is a valid exercise. These past reports exhibit various drawbacks such as less solubility of catalyst, metal leaching, harsh reaction conditions and toxic organic solvent. These current procedures can be improved by more efficient, environmentally friendly, cleaner reaction conditions. Therefore, in continuation of our current interest in the design of green protocols by using bio-catalysts for organic transformations [50–53]. Herein we report the simple, efficient, environmentally friendly protocol for Knoevenagel condensation of aromatic aldehydes with active methylene compounds catalyzed by pomegranate peel (PP) and sulfonic acid-supported pomegranate peel ($\text{SO}_3\text{H@PP}$). The catalysts were characterized by IR, FE-SEM, XRD, and EDX techniques. The PP worked in the water, while $\text{SO}_3\text{H@PP}$ worked in ethanol at reflux conditions. Moreover, both catalysts were easily recovered by simple filtration and reused at least five times with a slight decrease in the product yields.

Experimental

General remarks

All chemical reagents and solvents were purchased from Thomas Baker and were used as received. The NMR spectra were recorded on a Bruker AC spectrometer using tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) are expressed in parts per million (ppm) values with TMS as an internal reference and coupling constants (J) are expressed in hertz (Hz). Mass spectra were recorded on an Agilent gas chromatograph mass spectrometer. The FT-IR spectra were measured on Jasco FT/IR-4600 type A. The size and morphology of the pomegranate peel powder and $\text{SO}_3\text{H@PP}$ were observed by using the FESEM of MIRA3 TESCAN microscope with an accelerating voltage of 10 kV.

Preparation of PP catalyst

Fresh pomegranate was purchased from a local market. Its peel was separated using a table knife and washed with a copious amount of distilled water to remove surface impurities and dirt. The pomegranate peel was dried for 2 days in the oven. The resultant dried PP was pulverized twice (Grinding plate: 6 mm followed by 1 mm plate). The obtained fine powder was again dried for 24 h at 60 °C in an oven.

Synthesis of SO₃H@PP catalyst

The pomegranate peel powder (6.0 g) was taken in a 100 mL round bottom flask containing dichloromethane (20 mL). Then chlorosulfonic acid (2.33 g) was added dropwise at 0 °C with continuous stirring. The resulting reaction mixture was then stirred for 60 min at 0 °C. The obtained black-colored product was filtered under vacuum, washed with diethyl ether (3 × 5 mL), dried in the oven, and further pulverized to get the desired catalyst SO₃H@PP as a fine powder.

General procedure of Knoevenagel condensation

In an oven-dried Schlenk flask, equipped with a magnetic stir bar and condenser containing water or ethanol (2.5 mL) added malononitrile/ethyl cyanoacetate (1 mmol), aromatic aldehyde (1.0 mmol), PP or SO₃H@PP catalyst (0.05 g). The reaction mixture was stirred in an oil bath at reflux. After the complete consumption of starting materials as analyzed by TLC, the reaction mixture was cooled to room temperature. The ethanol was poured into the flask and filtered to remove the catalyst. The ethanol was removed under vacuum to give the crude product which was further purified by recrystallization to afford pure α , β -unsaturated product.

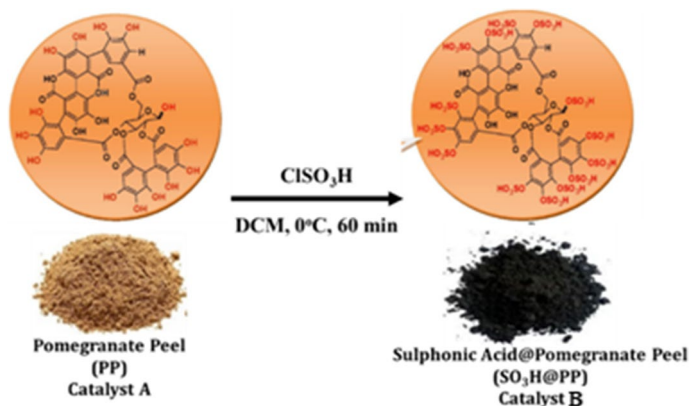
Representative spectral data of representative compounds (3a)

Mp: 84–85 °C, ¹H NMR (400 MHz, CDCl₃) δ (ppm): δ 7.45 (t, J =7.5 Hz, 2H, ArH), 7.54 (t, J =7.50 Hz, 1H, ArH), 7.76 (s, 1 H, C=CH), 7.95 (d, J =7.5 Hz, 2H, ArH); ¹³C NMR (75 MHz, CDCl₃) δ : 193.6, 146.3, 136.9, 127.0, 128.3, 125.8, 114.4, 51.2, 42.3, 35.4, 32.6, 27.0; IR (KBr, cm⁻¹) ν : 28–3100, 2226, 1700, 1611. The spectroscopic data of 3a was in good agreement with that reported in the literature.

Results and discussion

Preparation of PP and SO₃H@PP catalysts

The peel was separated from fresh pomegranate and washed with distilled water to remove surface impurities and dirt. The pomegranate peel was dried for 2 days in the oven. The resultant dried pomegranate peel (PP, Catalyst A) was pulverized twice



Scheme 1 Preparation of pomegranate peel (PP) and $\text{SO}_3\text{H@PP}$ catalysts

(grinding plate: 6 mm followed by 1 mm plate) and again dried for 24 h at 60 °C in an oven. The $\text{SO}_3\text{H@PP}$ catalyst was prepared by a procedure as described in the literature [54]. The hydroxyl groups present in the PP are replaced with sulfonic acid groups by reacting with chlorosulfonic acid in dichloromethane at 0 °C. The $\text{SO}_3\text{H@PP}$ product obtained was filtered under vacuum and washed with diethyl ether (3×5 mL), dried in the oven and further pulverized to get the targeted $\text{SO}_3\text{H@PP}$ (*Catalyst B*) as a fine black powder (Scheme 1).

The characterization of PP and $\text{SO}_3\text{H@PP}$ catalysts

The prepared PP and $\text{SO}_3\text{H@PP}$ catalysts were characterized by different characterization techniques such as IR, FE-SEM, EDX, and XRD techniques.

In the FT-IR spectrum (Fig. 1a) of PP, the broad spectrum of O–H groups was displayed around 3000–3500 cm^{-1} . The FT-IR spectrum $\text{SO}_3\text{H@PP}$ (Fig. 1b) showed the peaks at 1195 cm^{-1} , 1021 cm^{-1} for asymmetric and symmetric stretching of SO_2 , 1445 cm^{-1} for S=O stretching, 674 cm^{-1} for S–O symmetric stretching, and 880 cm^{-1} for S–OH bending. IR spectrum also displayed characteristic broad peaks at 3323 cm^{-1} due to OH stretching of SO_3H .

Scanning electron microscopy (SEM) was studied to determine the surface morphology of PP and $\text{SO}_3\text{H@PP}$ catalysts. The SEM images (Fig. 2a and b) proved irregular morphology of PP as well as $\text{SO}_3\text{H@PP}$ having different particle sizes.

The elemental analysis was also done by energy-dispersive X-ray analysis (EDX) of both catalysts (Fig. 3a and b). The EDX analysis of PP indicates carbon(C) and oxygen (O) as the major elements while $\text{SO}_3\text{H@PP}$ revealed sulfur(S) with carbon(C) and oxygen (O). The presence of sulfur in EDX analysis of $\text{SO}_3\text{H@PP}$ supports the immobilization of sulfonic acid groups on pomegranate peel.

The X-ray diffraction (XRD) pattern of pomegranate peel and modified pomegranate peel shows weak sharp peaks at 21.43°, 28.11°, and 30.75° (Fig. 4a and b). The crystallite size of PP and $\text{SO}_3\text{H@PP}$ were calculated using the Debye–Scherrer formula $D = K\lambda / (\beta \cos \theta)$, where K is the Scherrer constant (0.9), the X-ray

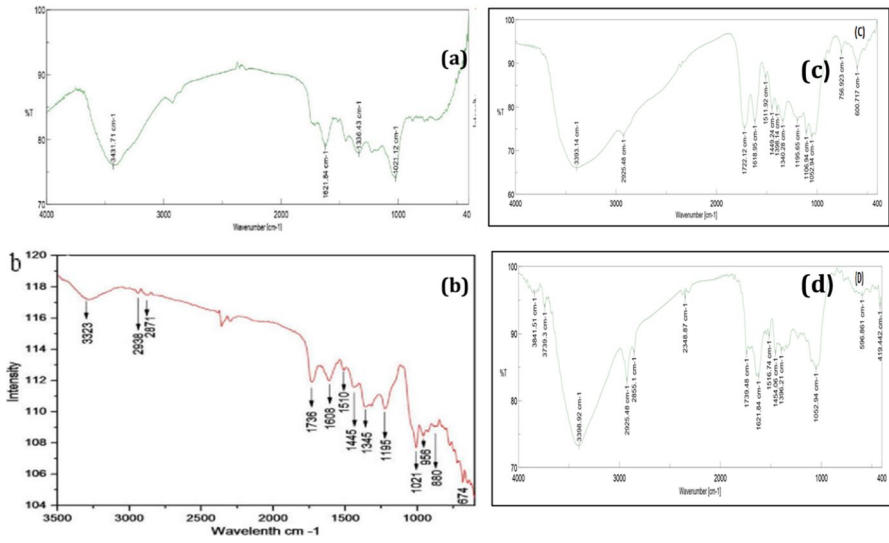


Fig. 1 The FT-IR spectrum of fresh **a** PP, **b** SO₃H@PP, and reused **c** PP, **d** SO₃H@PP catalysts

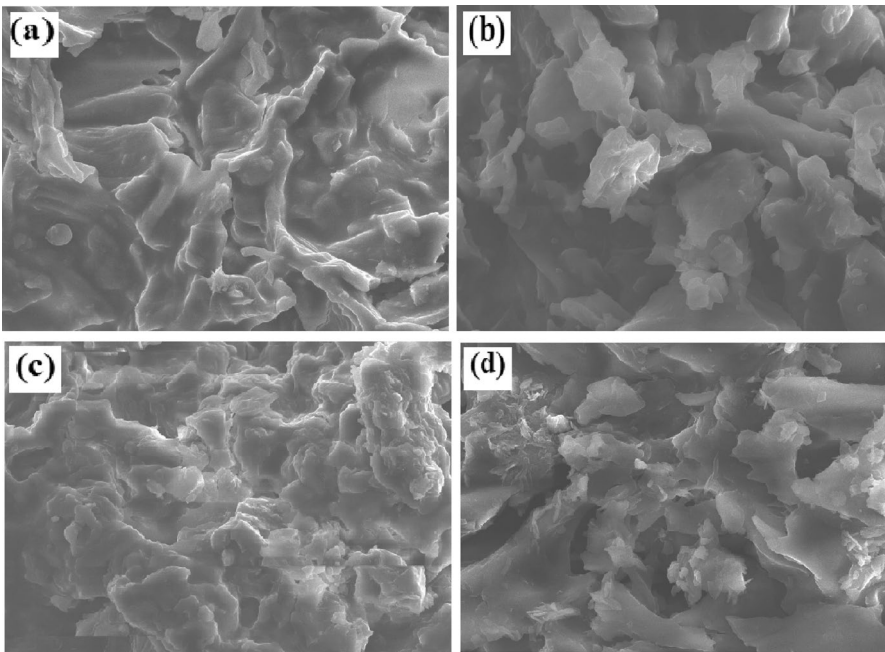


Fig. 2 SEM images (10 μm) of fresh **a** PP, **b** SO₃H@PP, and reused **c** PP, **d** SO₃H@PP catalysts

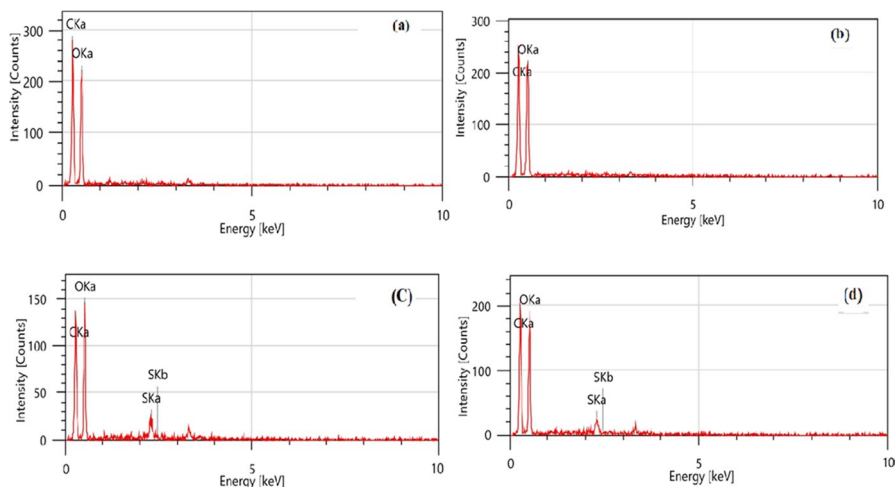


Fig. 3 EDX spectra of fresh **a** PP, **b** SO₃H@PP and reused **c** PP, **d** SO₃H@PP catalysts

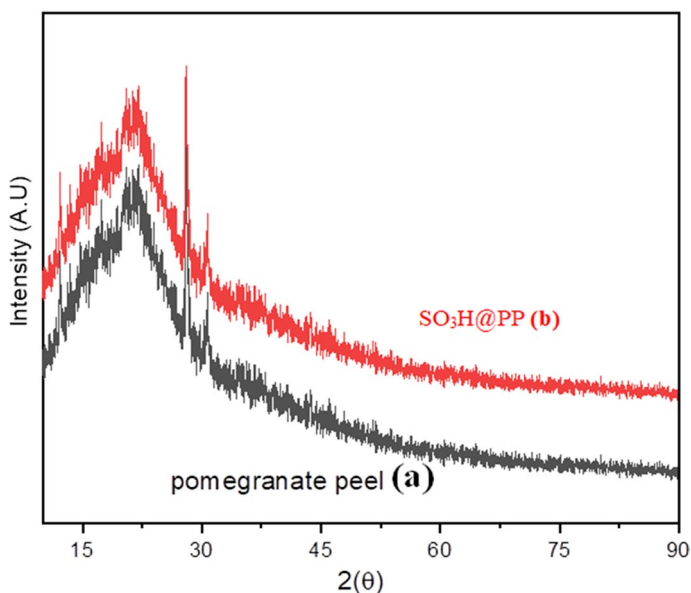
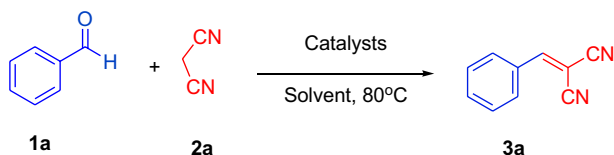


Fig. 4 XRD spectrum of (a) PP and (b) SO₃H@PP catalysts

wavelength ($\lambda=0.154$ nm), β the peak width of half-maximum (FWHM), and q is the Bragg diffraction angle. The interplanar distance was calculated via the Bragg equation: $dhkl = \lambda / (2 \sin q)$. The crystal dimensions from various diffraction lines using the Scherrer equation of PP and SO₃H@PP were found to be in the nanometer range 18 nm and 16 nm.



Scheme 2 Knoevenagel condensation catalyzed by PP and SO₃H@PP catalysts

Table 1 Effect of solvents in Knoevenagel condensation of benzaldehyde and malononitrile

Entry	Solvent	Temperature (°C)	PP		SO ₃ H@PP	
			Time (min)	Yield ^a (%)	Time (min)	Yield ^a (%)
1	THF	Reflux	20	45	20	50
2	DCM	Reflux	20	48	20	56
3	Chloroform	Reflux	20	53	20	60
4	Acetonitrile	Reflux	20	58	20	66
5	Toluene	Reflux	20	59	20	68
6	EDC	Reflux	20	49	20	59
7	Methanol	Reflux	20	69	20	70
8	Ethanol	Reflux	20	81	20	92
9	Water	Reflux	20	89	20	88
10	Water + Ethanol	Reflux	20	80	20	85

Reaction condition: Benzaldehyde (1 mmol), malononitrile (1 mmol), catalyst PP/SO₃H@PP (0.05 g), solvent (3 mL) at reflux

^aIsolated yields

PP and SO₃H@PP catalyzed Knoevenagel condensation

We initially investigated the optimum reaction conditions by reacting benzaldehyde (1.0 mmol) and malononitrile (1 mmol) as model reaction partners (Scheme 2).

Initially, we carried out solvent optimization by doing the model reaction in various organic solvents at reflux conditions in the presence of PP or SO₃H@PP catalysts (Table 1). It was observed that, though the condensation reaction occurs in solvents like THF, DCM, chloroform, acetonitrile, toluene, methanol, water and ethanol. The yield of the reactions was moderate (Table 1, entries 1–7). On the other hand, the PP was highly efficient in the water, while the SO₃H@PP worked well in ethanol (Table 1, entries 8 and 9).

We further optimized the catalyst loading by carrying the model reaction using different quantities of catalysts (Table 2). It was observed that changing the quantity of catalysts changes the yields of the desired product. It was found that 0.05 g of catalysts afforded the desired product with 89% and 92% yields.

Next, we evaluated the effectiveness of both catalysts for Knoevenagel condensation by reacting a series of aryl aldehydes (1a–h) with malononitrile (2a)

Table 2 Effect of catalyst loading in Knoevenagel condensation of benzaldehyde and malononitrile

Entry	Amount of catalyst (g)	PP		SO ₃ H@PP	
		Time (min.)	Yield ^a (%)	Time (min.)	Yield ^a (%)
1	0.01	20	55	20	59
2	0.02	20	59	20	63
3	0.03	20	60	20	70
4	0.04	20	73	20	84
5	0.05	20	89	20	92
6	0.1	20	89	20	92

Reaction condition: Benzaldehyde (1 mmol), malononitrile (1 mmol), catalyst PP/SO₃H@PP (0.01–0.1 g), solvent (3 mL) at reflux

^aIsolated yields

and ethyl cyanoacetate (2b) under optimal reaction conditions. The results of this study are tabulated in Table 3. It was observed that all the aromatic aldehydes underwent condensation reactions with active methylene compounds efficiently to afford a wide range of α , β -unsaturated compounds. The reaction time and yield of α , β -unsaturated compounds vary with the electron-donating and electron-withdrawing substituents on aryl aldehydes.

Mechanism

The plausible mechanism for the SO₃H@PP catalyzed synthesis of **3a** is depicted in Scheme 3. The carbonyl group of aldehydes is activated via protonation by SO₃H@PP followed by an attack of active methylene compound to form adduct (A). Adduct A eliminates the water molecule and delivers the desired product **3a**.

Catalyst reusability

The recovery and reusability of the catalyst are significant aspects of green organic transformations. The reusability of both the catalysts was investigated for the model reaction (Fig. 5). After the completion of the reaction, the catalyst was easily separated by simple filtration and reused at least five times without significant loss in the yield of product. The slight loss in catalytic activity was studied by analyzing recovered catalysts by IR, and SEM–EDX analysis (Figs. 1, 2, 3). The decrease in activity may be due to slight change in morphology as observed by SEM analysis. Another reason is the blocking of active sites of catalysts by some organic compounds.

Compared to the efficiency of PP and SO₃H@PP catalysts, the present protocol is more efficient than the reported methods concerning time (Table 4).

Table 3 Knoevenagel condensation of aryl aldehydes with malononitrile/ethyl cyanoacetate catalyzed by PP and SO₃H@PP





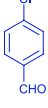

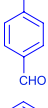

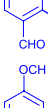

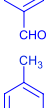



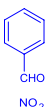

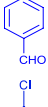

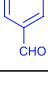



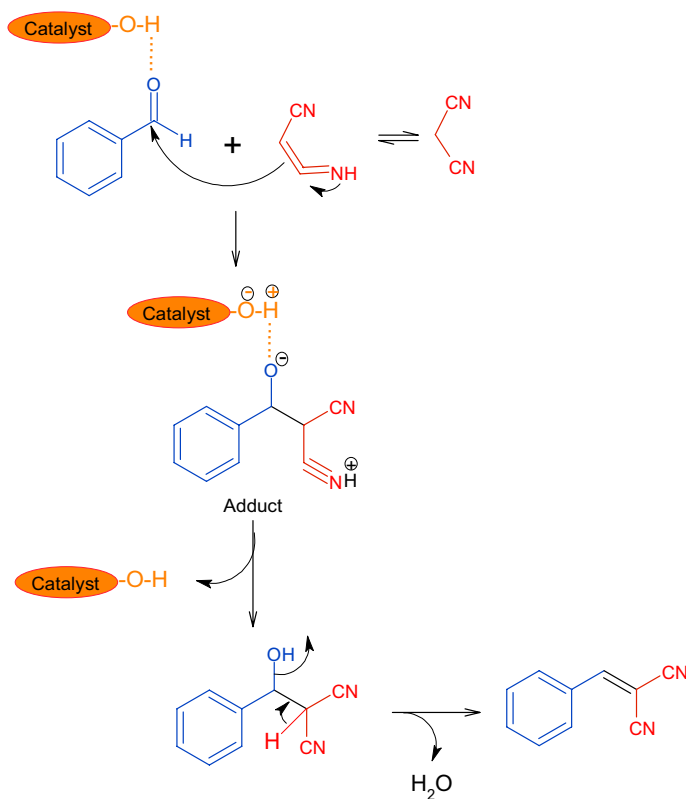
Entry	1a-h	2a-b	PP		SO ₃ H@PP	
			Time (min)	Yield ^a (%)	Time (min)	Yield ^a (%)
1			20	89	10	92
2			16	91	8	94
3			15	85	9	90
4			15	84	10	90
5			22	81	10	84
6			25	80	14	83
7			23	87	12	89
8			20	85	11	88
9			21	85	15	89
10			18	88	9	91
11			20	84	10	90

Table 3 (continued)

Reaction condition: ARYL aldehyde (1 mmol), malononitrile/ethyl cyanoacetate (1 mmol), PP/SO₃H@PP (0.05 g), Solvent (3 mL) at Reflux

^aIsolated yields



Scheme 3 Plausible mechanism for SO₃H@PP catalyzed synthesis of **3a**

Conclusion

In conclusion, we elaborated a new, simple, efficient, and environmentally friendly protocol for the Knoevenagel condensation by implementing pomegranate peel (PP) and SO₃H@PP catalysts as an economical, non-toxic and bio-waste-originated catalyst. The SO₃H@PP catalyst was revealed to be a more effective heterogeneous catalyst than PP for condensation of aryl aldehyde and active methylene compound concerning time and yields. The catalysts can be easily recovered and reused at least five times without significant loss in efficiency. A bio-waste origin, easy availability, economical, Easy recovery, and reusability are the prominent features of the reported catalyst. Cleaner reaction conditions,

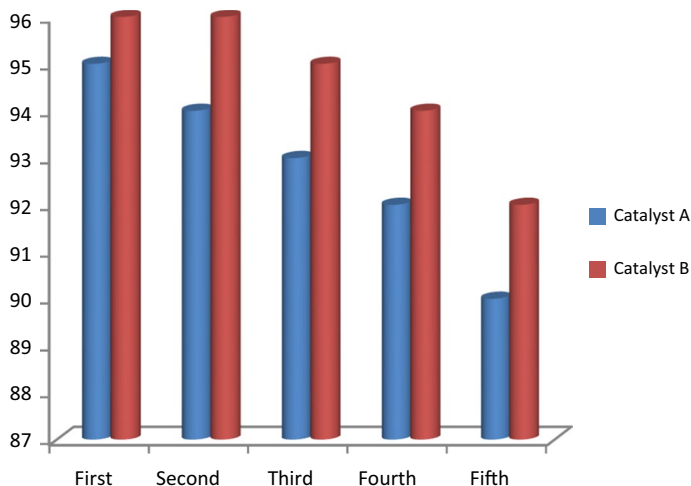


Fig. 5 Reusability of catalysts in Knoevenagel condensation reaction

Table 4 Comparison of the efficiency of PP and SO₃H@PP with reported catalysts

Entry	Catalyst	Reaction condition	Time	Yield (%)	References
1	Pomegranate peel (PP)	Water, reflux	20 min	89	Present work
2	SO ₃ H@PP	Ethanol, reflux	10 min	92	
3	H ₃ PW ₁₂ O ₄	Reflux	15 min	91	[23]
4	SO ₄ ⁻² /ZrO ₂	heat	2 h	88	[38]
5	Cu-PMA	Solvent free/70 °C	40 min	98	[39]
6	USY Zeolite	Benzene/reflux	12 h	92	[40]
7	AlPO ₄ -Al ₂ O ₃	RT	1 h	80	[41]
8	LaCl ₃ ·7H ₂ O	80 °C	1 h	95	[42]
9	Mn salen complex	Toluene	1 h	100	[43]

simple experimental and work-up procedures, inexpensive, and the reusability of the catalyst are the conspicuous feature of this protocol.

Dataavailability Not applicable.

References

- Misra K, Maity HS, Chanda S, Nag A (2012) *J Mol Catal B Enzym* 82:92–95
- Shameli K, Ahmad MB, Shabanzadeh P, Jaffar Al-Mulla EA, Zamanian A, Abdollahi Y, Jazayeri SD, Eili M, Jalilian FA, Haroun RZ (2014) *Res Chem Intermed* 40:1313–1325
- Pore S, Rashinkar G, Mote K, Salunkhe R (2010) *Chem Biodivers* 7:1796–1800
- Adrom B, Maghsoodlou MT, Lashkari M, Hazeri N, Doostmohammadi R (2016) *Synth React Inorg Met Org Chem* 46:423–427

5. Morbale ST, Jadhav SD, Deshmukh MB, Patil SS (2015) *RSC Adv* 5:84610–84620
6. Vekariya RH, Patel KD, Patel HD (2016) *Res Chem Intermed* 42:7559–7579
7. Patil MA, Ubale PA, Karhale SS, Helavi VB (2017) *Der Chemica Sinica* 8:198–205
8. Fonseca AM, Monte FJQ, Oliveira MCF, Mattos MC, Cordell GA, Braz-Filho R, Lemos TLG (2009) *J Mol Catal B Enzym* 57:78–82
9. Shafqat SS, Khan AA, Khan MA, Salleh SF, Jamaludin MS, Cem PS (2017) *Asian J Chem* 29:261–266
10. Pal R (2016) *Int J Green Chem Biopro* 6:13–16
11. Azeri N, Doostmohammadi R, Adrom B, Lashkari M, Maghsoodlou MT (2016) *Chem J Mold* 11:68–73
12. Xie B, Yang J, Yang Q, Zhejiang J (2012) *Univ Sci B* 13:248–253
13. Phukan K, Devi N (2012) *Int J Chem Tech Researc* 4:203–207
14. Leyva E, Moctezuma E, Diaz MDS, Carrillo Gonzalez OH (2012) *Rev Latinoam Quim* 40:140–147
15. Pramanik PT, Pathan AH (2014) *Res J Pharm Biol Chem Sci* 5:444–449
16. Fiorito S, Teddeo VA, Genovese S, Epifano F (2016) *Tetrahedron Lett* 57:475–479
17. Knoevenagel L (1998) *Ber* 31:258
18. Yu N, Aramini JM, Germann MW, Huang Z (2000) *Tetrahedron Lett* 41:6993–6996
19. Bigi F, Chesini L, Maggi R, Sartori G (1999) *J Org Chem* 64:1033–1035
20. Liang F, Pu YJ, Kurata T, Kido J, Nishide H (2005) *Polymer* 46:3767–3775
21. Tietze LF, Rackelmann N (2004) *Pure Appl Chem* 76:196
22. Kraus A, Krolski ME (1986) *J Org Chem* 51:3347
23. Hossien A, Oskooie Heravi MM, Derikvand F, Khorasani M (2006) *Synth Commun* 36:2819–2823
24. Green B, Crane RI, Khaidem IS, Leighton RS, Newaz SS, Smyser TE (2002) *J Org Chem* 50:640–644
25. Panchenko VN, Matrosova MM, Jeon J, Jun JW, Timofeeva MN, Jhung SH (2014) *J Catal* 316:251–259
26. Shanthan RP, Venkataratnam RV (1991) *Tetrahedron Lett* 32:5821–5822
27. Viswanadham B, Pedadal J, Friedrich HB, Singh S (2016) *Catal Lett* 146:1470–1477
28. Kumbhare RM, Sridhar M (2008) *Catal Commun* 9:403
29. Ogiwara Y, Takahashi K, Kitazawa T, Sakai N (2015) *J Org Chem* 80:3101–3110
30. Bartoli G, Beleggia R, Giuli S, Giuliani A, Marcantoni E, Massaccesi M, Paletti M (2006) *Tetrahedron Lett* 47:6501
31. Xu Q, Niu Y, Wang G, Li Y, Zhao Y, Singh V, Niu J, Wang J (2018) *Mol Catal* 453:93–99
32. Pullabhotla VSRR, Rahman A, Jonnalagadda SB (2009) *Catal Commun* 10:365–369
33. Boroujeni KP, Jafarinasab M (2012) *Chin Chem Lett* 23:1067–1070
34. Gao M, Qi M, Liu L, Han Z (2019) *Chem Commun* 55:6377–6380
35. Bennazha J, Zahouilly M, Boukhari A, Hol EA (2003) *J Mol Catal A: Chem* 202:247–252
36. Schijndel JV, Canalle LA, Molendijk D, Meuldijk J (2017) *Green Chem Lett Rev* 10:404–411
37. Shiri L, Narimani H, Kazemi M (2017) *Appl Organometal Chem* 32:1–13
38. Reddy BM, Patil MK, Rao KN, Reddy GK (2006) *J Mol Catal A Chem* 258:302–307
39. Viswanadham B, Pedada J, Friedrich HB, Singh S (2016) *Catal Lett* 146:1470–1477
40. Wang QL, Ma YD, Zuo BJ (1997) *Synth Commun* 27:4107–4110
41. Cabello JA, Campelo JM, Garcia A, Luna D, Marians JM (1984) *J Org Chem* 49:5195–5197
42. Narsaiaha AV, Nagaiah K (2003) *Synth Commun* 33:3825–3832
43. Kantam ML, Bharathi B (1998) *Catal Lett* 55:235–237
44. Seeram NP, Adams LS, Henning SM, Niu Y, Zhang Y, Nair MG, Heber D (2005) *J Nut Biochem* 16:360–367
45. Reddy MK, Gupta SK, Jacob MR, Khan SI, Ferreira D (2007) *Planta Med* 73:461–467
46. Kotwal GJ (2008) *Vaccine* 26:3055–3058
47. Bell C, Hawthorne S (2008) *J Pharm Pharmacol* 60:139–144
48. Negi PS, Jayaprakash GK, Jena BS (2003) *Food Chem* 80:393–397
49. Kahramanoglu I, Usanmaz S (2001) *Pomegranate production and marketing*. CRC Press, Boca Raton
50. Karhale S, Patil M, Rashinkar G, Helavi V (2017) *Res Chem Intermed* 43:7073–7086
51. Patil M, Karhale S, Kudale A, Kumbhar A, More S, Helavi V (2019) *Curr Sci* 116:936–942
52. Patil M, Karhale S, Ubale P, Helavi V (2017) *Der Pharma Chemica* 9:28–32

53. Patil M, Karhale S, Bhenki C, Kumbhar A, Helavi V (2020) *React Kinet Mech Catal* 130:993–1007
54. Sadeghi B, Bouslik M, Shishehbore MR (2015) *J Iran Chem Soc* 12:1801–1808

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.

Authors and Affiliations

Monika Sujit Chavan¹  · Sonali Suryawanshi¹ · Arjun Kumbhar²

✉ Monika Sujit Chavan
monikapatilchavan@gmail.com

¹ Department of Chemistry, Sanjay Ghodawat University, Kolhapur, Maharashtra 416118, India

² Department of Chemistry, Vivekanand College, Kolhapur, Maharashtra 426003, India