Catal Lett
DOI 10.1007/s10562-013-1190-4

Nano Fibrous Silica Sulphuric Acid as an Efficient Catalyst for the Synthesis of β-Enaminone

Zeba N. Siddiqui · Kulsum Khan · Nayeem Ahmed

Received: 28 October 2013 / Accepted: 25 December 2013

Abstract Synthesis of KCC-1 silica sulphuric acid as a new catalyst has been reported. The catalyst was characterized using XRD, SEM, TEM, BET, FT-IR, TGA-DTA, and EDX analysis. The catalytic activity was evaluated for the synthesis of enaminones under solvent-free conditions. The catalyst was easily recovered and reused up to seven cycles with slight loss of activity. The attractive features of this protocol are low amount of catalyst loading, short reaction time, mild reaction conditions, good to excellent yield of the products, easy handling of the catalyst and simple operational procedure.

Keywords KCC-1-SA · β-Enaminones · Solvent-free condition

1 Introduction

Nanocatalysis adds greenness to chemical process through higher activity with less amount of catalysts. It also avoids drastic reaction conditions and increases energy efficiency and selectivity, which reduces by-products and allows to perform chemical reactions in a selective manner with the least possible consumption of substances [1]. This, in turn, improves atom economy and waste prevention. Nanosilica functionalized by incorporating organic and inorganic functional groups within their mesopores are of great interest for their use as heterogeneous catalysts. Various mesoporous silica compounds such as SBA, MCM and FSM that have been functionalized by sulfonic acid groups offer simpler, less costly, more reactive and more environmentally benign alternatives than their homogeneous counterparts [2–6]. While these differently functionalised nanosilica provide large specific surface areas [7, 8], but their surface accessibility could become an issue limiting their applications in certain cases, since any molecule involved in adsorption or reaction have to travel through a long pathway and therefore the actual surface area may not be fully utilized. To overcome this problem, we have used high-surface area fibrous SiO_2 spheres with much more open porosity for the synthesis of sulphuric acid functionalised nanosilica. These SiO_2 spheres (KCC-1) with a very large specific surface area have promising applications as catalyst supports, where diffusion is no longer a limiting step in heterogeneous catalysis. The high surface area of KCC-1 is attributable to fibres and not to pores, which dramatically increase its accessibility of active sites [9]. Moreover, this material exhibits excellent physical properties, including a fibrous surface morphology, good thermal, hydrothermal and mechanical stability. Therefore, it has been used as a support for many catalysts in organic transformations [10–14]. However, so far synthesis of β-enaminones using sulphuric acid modified nano fibrous silica as catalyst has not been studied.

The β-enaminones having the general formula of –NH–CH=CH–$(CH_2)_x$–C=O are bioactive compounds used as key intermediates for the synthesis of various heterocyclic and naturally occurring alkaloids [15–17]. The conventional approach for the preparation of β-enaminones and β-enamino esters is by direct condensation of 1,3-dicarbonyl compounds with amines in refluxing aromatic solvents with azeotropic removal of water. A variety of catalysts such as B_2O_3/Al_2O_3 [18], $SbCl_3/SiO_2$ [19], $HClO_4/SiO_2$ [20], P_2O_5/SiO_2 [21], silica chloride [22], sulfamic acid [23], L-proline [24], phosphotungstic acid

---

Z. N. Siddiqui (✉) · K. Khan · N. Ahmed
Department of Chemistry, Aligarh Muslim University,
Aligarh 202002, India
e-mail: siddiqui_zeba@yahoo.co.in

[25], and Ag [26] or Cu nanoparticles [27] and Ga(OTf)$_3$ [28] have been used to promote this transformation. Previous investigations required prolonged reaction times, use of hazardous reagents, tedious workup procedures, rigorous reaction conditions, unsatisfactory yields, low selectivity, or the use of toxic solvents which limit these methods to small-scale synthesis. Therefore, there is a need for development of more efficient and eco-friendly catalysts for the synthesis of enaminones. In the present work, we have developed a mild route to synthesize β-enaminones under solvent free conditions taking into consideration the green principle of chemistry.

2 Experimental

2.1 Materials

All reagents were purchased from Merck and Aldrich and used without further purification. All yields refer to isolated products after purification. Products were characterized by comparison of melting points with authentic samples. Melting points were taken in Riechert Thermover instrument and are uncorrected. The IR spectra were recorded on Perkin Elmer RXI spectrometer. All of the compounds were solid and solid state IR spectra were recorded using the KBr disk technique.

2.2 Catalyst Synthesis

2.2.1 Fibrous Nano Silica Support KCC-1 is Synthesized According to the Reported Procedure [9]

2.2.1.1 Synthesis of Catalyst Fibrous Nano Silica Sulfuric Acid (KCC-1-SA) KCC-1 (1.0 g) was dispersed in CH_2C1_2 (10 mL) in a flask. Chlorosulfonic acid (8 mmol) was dissolved in CH_2C1_2 (10 mL) and added to KCC-1 silica suspension through a constant-pressure dropping funnel under stirring, over a period of 30 min at room temperature. After the addition was completed, the mixture was stirred for another 30 min at room temperature. The brown solid was collected by filtration and washed with ether (50 mL). Finally it was dried at room temperature.

2.3 H^+ Ion concentration Determination of the Catalyst

H^+ ion concentration of the catalyst was determined by back titration analysis of KCC-1-SA. NaOH solution (20 mL, 0.1 M) was added to the catalyst (100 mg) in an Erlenmeyer flask. This solution was stirred for 10 min. Excess amount of the base was neutralized by addition of HCl solution (0.1 M) to the equivalence point of titration.

2.4 Catalytic Activity Determination

A mixture of primary aromatic amine (1 mmol), 1,3-dicarbonyl compound (1 mmol), and the catalyst KCC-1-SA (5 mg) was taken in a 25 mL round bottom flask. This reaction mixture was stirred at 80 °C and the progress of reaction was monitored by TLC after every 30 s, till the completion of the reaction. After completion of the reaction, ethyl acetate was added to the reaction mixture and the catalyst was filtered off. The solvent of the filtrate was evaporated and the crude product purified by recrystallization from appropriate solvent. The products obtained were identified by IR and comparing the melting points with authentic samples. The filtered catalyst was washed with ethyl acetate and acetone, dried at 110 °C for 2 h and used for the next catalytic cycle.

3 Results and Discussion

3.1 Amount of Acid Loading

In order to find most efficient and recyclable nanosilica bonded sulphuric acid a series of KCC-1 bonded sulphuric acid with different acid loading x mmol ($x = 4, 6, 8, 10$) in 1 g of KCC-1 were prepared according to the Scheme 1. The effect of acid loading on the model reaction using aniline and acetylacetone as model substrates was studied (Fig. 1). It was found that catalyst with 8 mmol of acid loading performed most efficiently.

3.2 Structure and Morphology of the KCC-1-SA

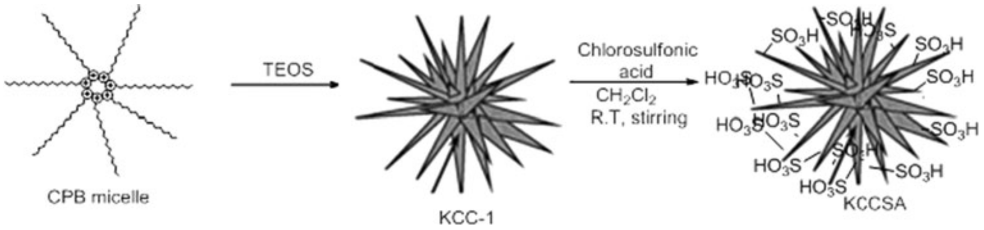
To gather insight about the surface area, pore volume, pore diameter and morphology of KCC-1-SA catalyst with 8 mmol of acid loading, different analyses were performed such as N_2 adsorption analysis, powder X-ray diffraction, transmission electron microscopy (TEM), EDX, thermogravimetric analysis and FTIR spectroscopy.

3.2.1 H^+ Ion Concentration of the Catalyst

The amount of H^+ in KCC-1-SA with 8 mmol of acid loading was calculated through back titration and was calculated to be 9 mmol H^+/g.

3.2.2 XRD

X-ray diffractograms (XRD) of the samples were recorded in the 2θ range of 0–80° with scan rate of 4°/min on a Rigaku Minifax X-ray diffractometer with Ni-filtered Cu Kα radiation at a wavelength of 1.54060 Å. Diffraction peak at around $2\theta = 22°$ (Fig. 2) was characteristic of



Scheme 1 Preparation of fibrous nano silica sulphuric acid (KCC-1-SA)

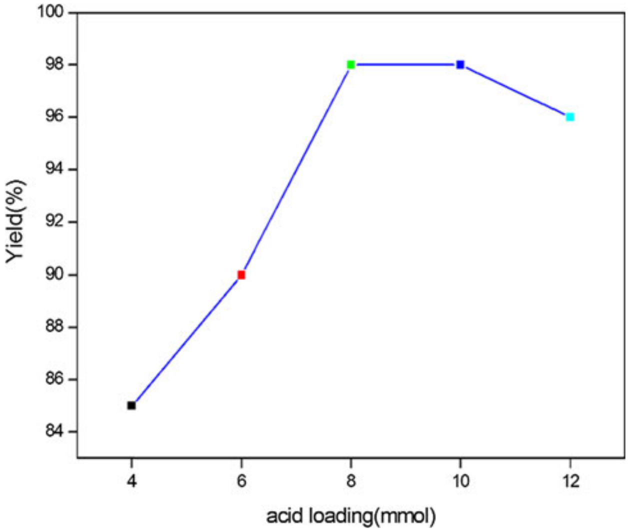


Fig. 1 Effect of acid loading on KCC-1 for catalysing model reaction

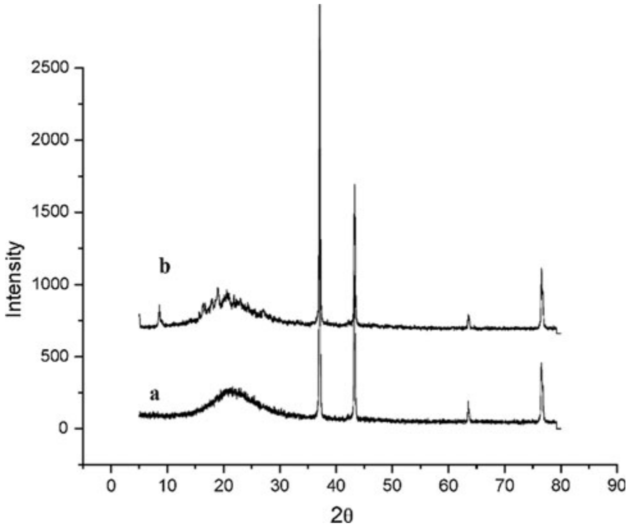


Fig. 2 XRD (*a*) KCC-1-SA (*b*) recovered catalyst

silica. Moreover, the XRD peaks of KCC-1-SA and recovered catalysts showed the same positions with different intensities.

3.2.3 FTIR

The FT-IR spectrum of the catalyst (Fig. 3) showed broad antisymmetric Si–O–Si stretching from 1,200 to 1,000 cm^{-1} and symmetric Si–O–Si stretching near 800 cm^{-1} for SiO_2. For sulfonic acid functional group, the absorption range of the O=S=O asymmetric and symmetric stretching modes were present at 1,110–1,240 and 1,020–1,080 cm^{-1} respectively, and that of the S–O stretching mode at 600–700 cm^{-1} respectively. The spectrum also exhibited overlapping of asymmetric and symmetric stretching bands of SO_2 with Si–O–Si stretching bands in the silica sulfuric acid catalyst whereas broad OH stretching absorption were present at 3,500 $cm^{-1.}$

3.2.4 SEM and TEM Images

Scanning electron microscopy (SEM) image of KCC-1 (Fig. 4a) revealed that the material consisted of colloidal spheres. Close inspection of TEM image of KCC-1 (Fig. 4b) showed that the material possessed dendrimers which were arranged in 3D to form spheres of diameter 100–500 nm.

TEM images (Fig. 5) of KCC-1 after functionalization with chlorosulfonic acid showed that dendrimeric fibers were intact arranged in three dimensions to form spheres with diameters 150–500 nm. Thus, functionalization did not alter the basic morphology of the KCC-1.

3.2.5 EDX

The EDX spectrum of KCC-1-SA (Fig. 6), showed the peaks for S, Si and O confirming the formation of expected catalytic system.

3.2.6 Thermogravimetric Analysis

TGA and DTA data were obtained with DSC-60 Shimadzu instrument. DTA and TGA analysis were performed in the temperature range of 0–600 °C at a constant heating rate of 20 °C/min in the nitrogen atmosphere. The TGA curve furnished information about the thermal stability of loaded

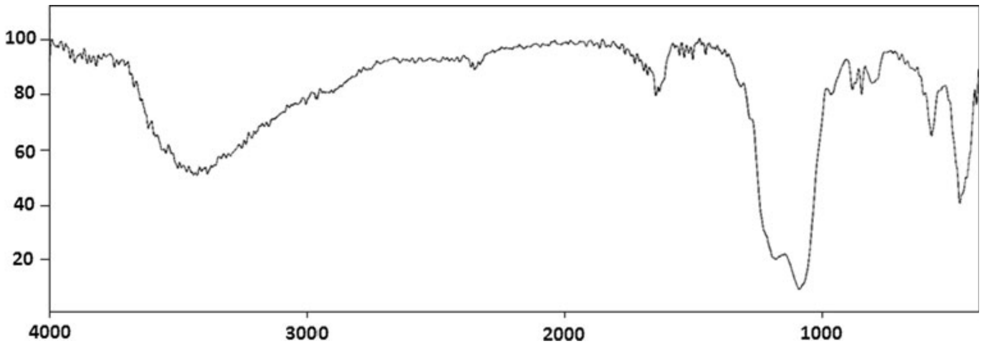


Fig. 3 FT-IR spectra of fibrous - silica sulfuric acid (KCC-1-SA)

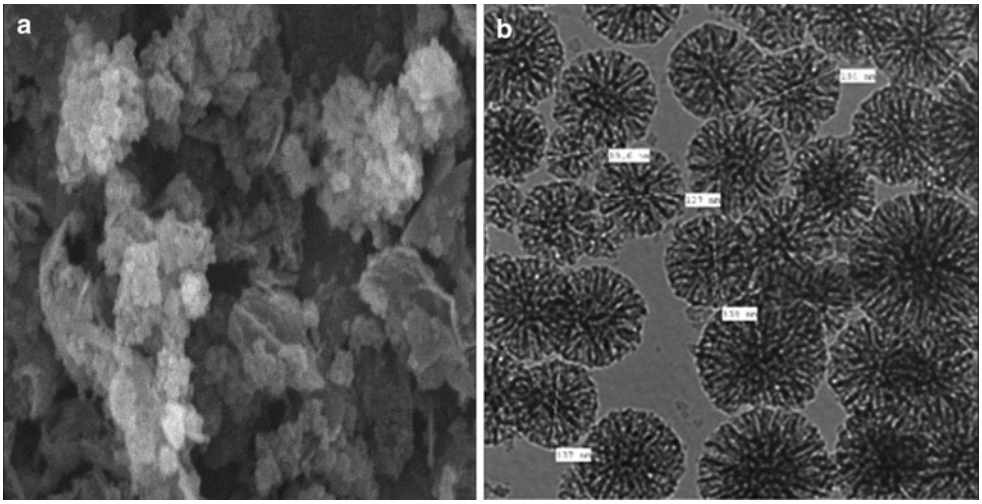


Fig. 4 SEM and TEM images of KCC-1

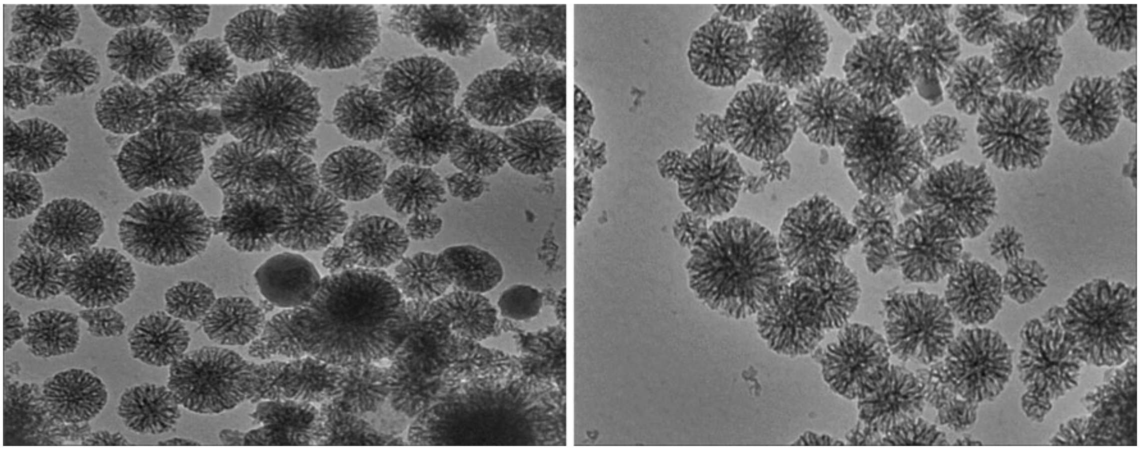


Fig. 5 TEM images of KCC-1-SA

sulphuric acid on silica. TG (Fig. 7) curve indicated two-stage decomposition. The weight loss of about 30 % around 76 °C can be attributed to the loss of surface physisorbed water. A further weight loss of about 28 % at 225 °C was due to decomposition of the SO_3H group bonded to KCC-1. DTA measurement also confirmed the loss of physiosorbed water and SO_3 group (Fig. 7).

3.2.7 BET Surface Area Analysis

The surface area of KCC-1 and KCC-1-SA were obtained by Brunauer–Emmett–Teller (BET) method, which employed nitrogen adsorption at different pressures at the liquid nitrogen temperature (77 K). The surface area of KCC-1 (Fig. 8) was found to be 386.16 m^2/g [10–14].

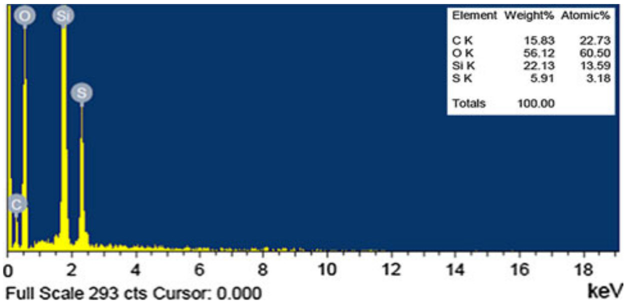


Fig. 6 EDX spectra of fibrous-silica sulfuric acid (KCC-1-SA)

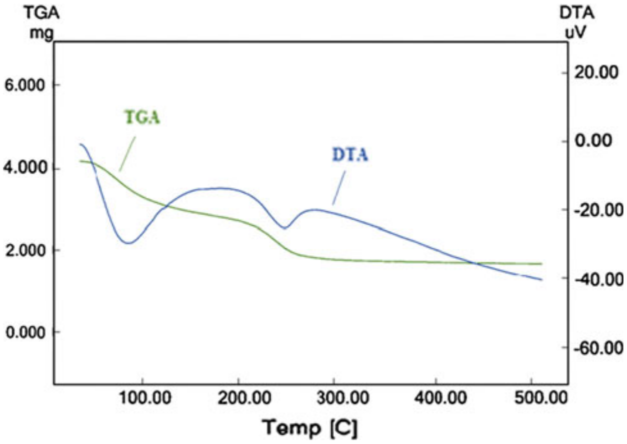


Fig. 7 TG and DTG analysis of the KCC-1-SA

After functionalization of KCC-1 the surface area reduced to 91.21 m^2/g (Fig. 9). The reduction in surface area was due to encapsulation of dendrimeric fibres of silica (KCC-1) by SO_3H groups. The pore size distributions were also obtained from these adsorption isotherms by employing Barrett–Joyner–Halenda (BJH) method. The total pore volume was estimated from the amount of nitrogen adsorbed at the highest relative pressure. Pore volume and pore diameter were found to be 0.1155 cc/g and 25 Å respectively. Shape of N_2 adsorption–desorption isotherm (Fig. 9) was a typical type IV isotherm [14]. Large N_2 uptakes and hysteresis at the relative pressure near 1.0 was due to fibrous morphology of silica nanoparticles. Due to this fibrous nature of the nanosilica there was easy accessibility of surface area hence increasing the activity of the catalyst.

3.3 Catalytic Activity of KCC-1-SA

After characterizations of sulphuric acid functionalized KCC-1, experiments were performed to optimize the reaction conditions for synthesis of β-enaminones from 1,3-dicarbonyl compounds and primary amines (Scheme 2). In our preliminary experiments, we investigated the optimization of reaction conditions regarding the solvent, amount of catalyst and temperature of the reaction. For this purpose, aniline and acetylacetone were chosen as model substrates for the synthesis of representative compound **4a**.

3.4 Effect of Solvents on Catalysis

To study the effect of solvent on the reaction, we performed the reaction using model substrates and 5 mg of KCC-1-SA as catalyst in different solvents (Table 1) under reflux conditions. In MeOH, EtOH and $(CH_3)_2CHOH$ (Table 1, entry 1, 2 and 3), the reaction took longer time (1.2–2 h) with moderate yield of the products whereas in water (Table 1, entry 4), the product was obtained in low yield (25 % yield) only after 2.5 h. In CH_3CN (Table 1, entry 5) lower yield of the product was obtained with long reaction time. Conducting the reaction in THF and $C_6H_5CH_3$ (Table 1, entry 6, 7), again only trace amount of the product was obtained. However, when the model reaction was carried out under solvent free conditions (Table 1, entry 8) there was significant increase in the yield of the product in shorter time period. Thus, it is concluded that solvent-free condition is the best condition for the synthesis of enaminones.

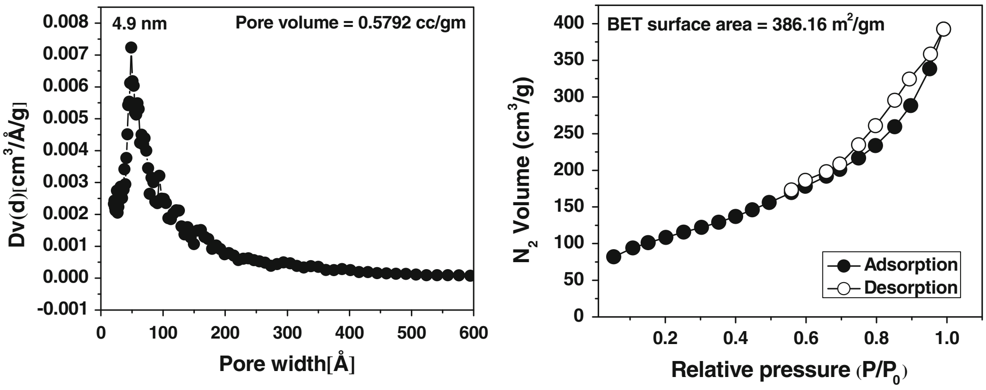


Fig. 8 N_2 adsorption–desorption isotherm of KCC-1

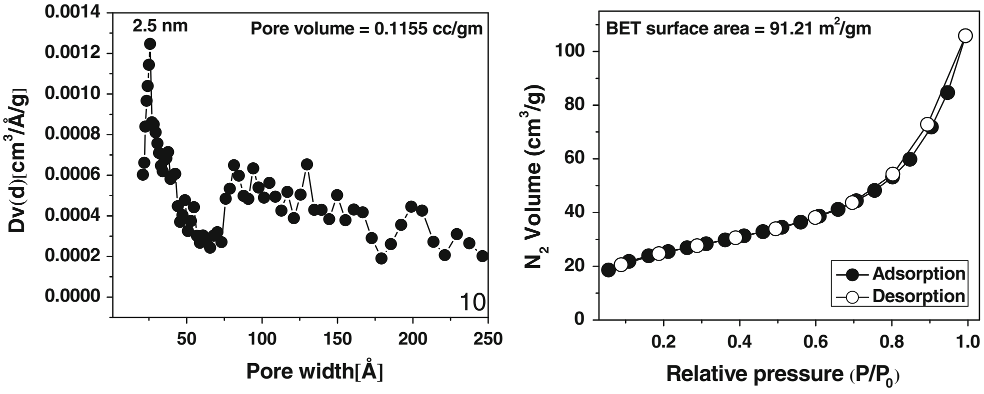
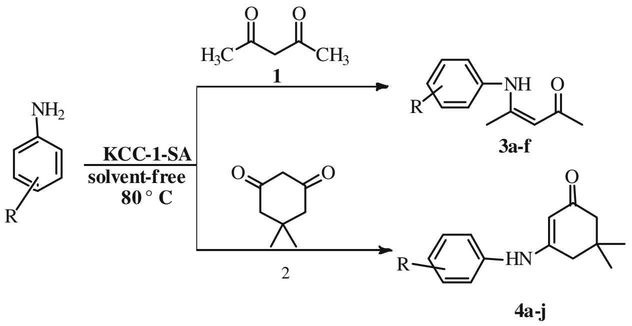


Fig. 9 N_2 adsorption–desorption isotherm of KCC-1-SA



R= H, p-OMe, p-NO_2, m-NO_2, p-Cl, p-OH, p-CH_3,

Scheme 2 Synthesis of β-enaminones

Table 1 Effect of various solvents on the model reaction

S. No.	Solvent	Temperature	Time (min)[a]	Yield (%)[b]
1.	MeOH	Reflux	1.5 h	68
2.	EtOH	Reflux	1.2 h	71
3.	$(CH_3)_2CHOH$	Reflux	2 h	57
4.	H_2O	Reflux	2.5 h	25
5.	CH_3CN	Reflux	3 h	41
6.	THF	Reflux	4 h	Trace
7.	$C_6H_5CH_3$	Reflux	4.5 h	Trace
8.	Solvent-free	80 °C	2	98

Model reaction: 1 mmol acetyl acetone and 1 mmol aniline

[a] Reaction progress monitored by TLC

[b] Isolated yield

3.5 Effect of Temperature on Catalysis

To get optimum temperature, the model reaction was carried out at different temperatures (Fig. 10). The yield of product increased when the reaction temperature was raised from room temperature to 80 °C. However, no increase in the yield of product was observed when the reaction temperature was raised from 80 to 110 °C. Therefore, all further reactions were carried out at 80 °C.

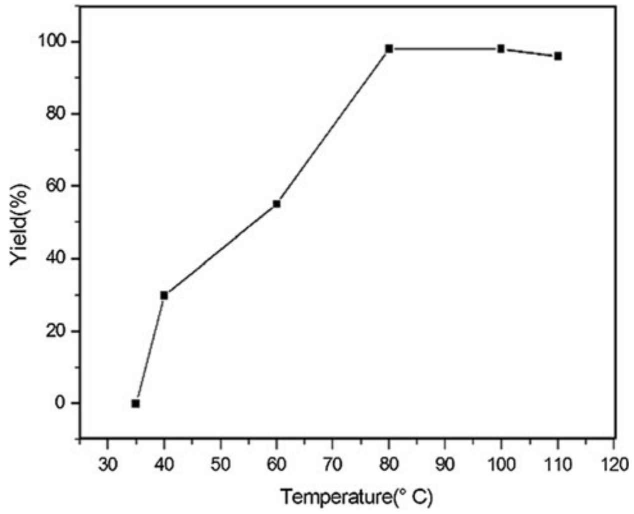


Fig. 10 The effect of temperature on the model reaction

Table 2 Effect of catalyst loading on the synthesis of model reaction

S. No.	Amount of catalyst	Time (min)[a]	Yield (%)[b]
1.	–	2	–
2.	2	2	70
3.	5	2	98
4.	10	2	98
5.	15	2	98
6.	20	2	98

Model reaction: 1 mmol acetyl acetone and 1 mmol aniline

[a] Reaction progress monitored by TLC

[b] Isolated yield

3.6 Effect of Catalyst Loading

Effect of amount of catalyst on model reaction was investigated to get the optimum concentration of catalyst.

Table 3 KCC-1-SA catalyzed synthesis of β-enaminones

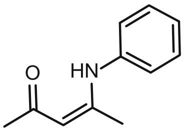
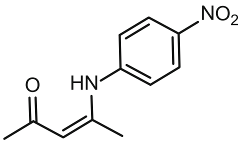
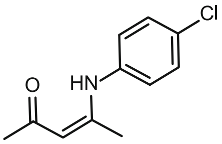
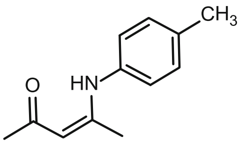
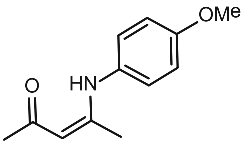
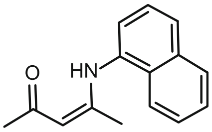
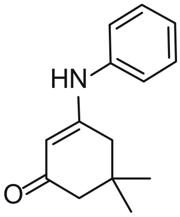
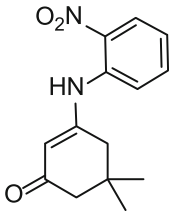
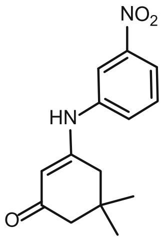
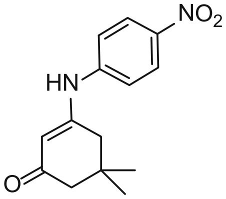
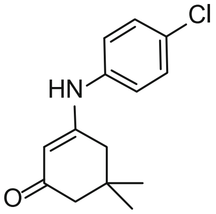
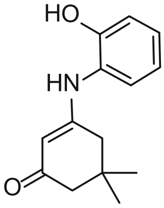
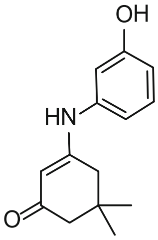
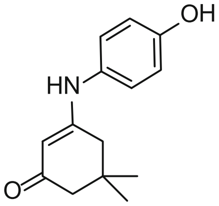
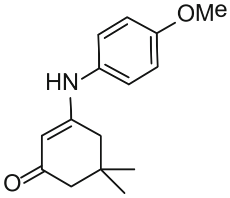
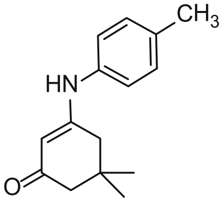
S. No.	Products	Time (min)[a]	Yield (%)[b]	M.P Observed (°C)[c]
4a.		2	98	45–46 [29]
4b.		2	97	144–146 [30]
4c.		3	95	60–62 [29]
4d.		2	96	58–59 [29]
4e.		1	98	41–43 [18]
4f.		4	92	61–63 [31]
5a.		1	99	184–186 [31]
5b.		4	94	163–164 [31]
5c.		3	94	174–175 [31]

Table 3 continued

S. No.	Products	Time (min)[a]	Yield (%)[b]	M.P Observed (°C)[c]
5d.		2	96	246–247 [31]
5e.		3	92	209–210 [31]
5f.		4	91	236–237 [31]
5g.		3	92	221–224 [31]
5h.		2	94	250–251 [31]
5i.		1	97	192–194 [31]
5j.		2	97	203–204 [31]

[a] Reaction progress monitored by TLC

[b] Isolated yield

[c] Reference for melting point of products

Table 4 Comparison of the efficiency of KCC-1-SA for synthesis of 4a

S. No.	Catalyst	Amount of catalyst	Time[a]	Yield[b]	Ref.
1.	$HClO_4$-SiO_2/ solvent-free	50 mg/mol	14 min	98	[20]
2.	Silica chloride/ solvent-free	10 % (w/w)	5 min	91	[22]
3.	$Fe(HSO_4)_3\cdot SiO_2$/ solvent free	25 mol%	7 min	89	[32]
4.	Silica sulfuric acid/ solvent-free	0.4 g	10 min	89	[33]
5.	L-Proline/solvent-free	5 mol%	4 h	85	[24]
6.	Ag nanoparticles/ MeOH	20 mol%	8 h	90	[26]
7.	Cu nanoparticles/ MeOH	10 mol%	2.5 h	92	[27]
8.	KCC-1-SA	5 mg	2 min	98	Present work

Reaction conditions: acetyl acetone (1 mmol), aniline (1 mmol) and catalyst

[a] Reaction progress monitored by TLC

[b] Isolated yield

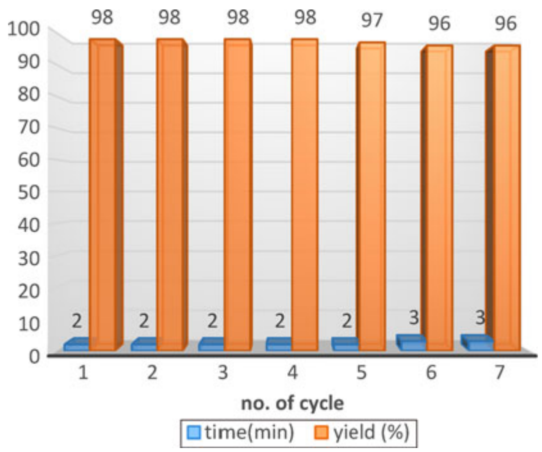


Fig. 11 The reusability of the catalyst in the synthesis β-enaminones

For this purpose model reaction was carried out using 2, 5, 10, 15 and 20 mg (Table 2 entry 1, 2, 3, 4, 5 and 6) of KCC-1-SA at 80 °C under solvent-free conditions. The product was obtained in 0, 70, 98, 98, 98 and 98 % yield, respectively. Thus it is concluded that 5 mg of the catalyst is sufficient for the best result. Therefore, all reactions were carried out at 80 °C in the presence of 5 mg of KCC-1-SA under solvent-free conditions.

3.7 Synthetic Application of KCC-1-SA

Using these optimized reaction conditions, the scope and efficiency of this approach was explored for the synthesis of β-enaminones using different amines and different 1,3-dicarbonyl compounds. The obtained results are summarized in Table 3. The products obtained were confirmed by comparing its melting point with authentic samples.

To show the superiority of KCC-1-SA, the model reaction was also carried out in the presence of other heterogeneous catalysts including nanocatalysts. The data of comparative study is summarized in Table 4. As we can see (Table 4 entry 1–4) that in silica based heterogeneous catalysts, excellent yield of products were obtained with relatively shorter time period but amount of catalyst required as compared to our catalyst is higher. When we carried out the reaction in L-proline (Table 4, entry 5) under solvent-free conditions good yield of products were obtained with prolonged reaction time. We also carried out the model reaction using nanocatalysts such as Ag and Cu (Table 4 entry 6, 7). These catalyst took very long time period ranging from 2.5 to 8 h for completion of reaction with an additional requirement of solvents. Thus it can be concluded that KCC-1-SA (Table 4, entry 8) is the best catalyst as it took only 2 min for completion of reaction with excellent yield of product. Moreover only 5 mg of catalyst is required. This enhanced activity was explained by the excellent accessibility of these sites due to the open and flexible fibrous structure of KCC-1 which helped substrates to easily penetrate and interact with acidic sites and, in turn, accelerated the overall reactions.

3.7.1 *Recycling Study*

The reusability of the catalyst is a significant advantage particularly for commercial applications. Thus, the recovery and reusability of the catalyst were also investigated (Fig. 11). After the completion of the reaction, products were extracted by ethyl acetate and the recovered catalyst was washed with ethyl acetate and then with acetone and dried in oven at 110 °C for 2 h. The recovered catalyst was reused at least seven times without any appreciable decrease in yield.

4 Conclusion

In conclusion we have developed an efficient protocol for the preparation β-enaminones. The reactions are carried out under thermal solvent-free conditions within few minutes yielding corresponding products with excellent yields. The requirement of catalyst is also very low. The methodology is environmentally benign as compared to H_2SO_4 with respect to the amount, hazard and reaction conditions. The catalyst could be successfully recovered and is recyclable up to seven cycles without significant loss in activity.

Acknowledgments The authors are thankful to the SAP scheme (DRS-I) from the University Grants Commission, New Delhi. One of the authors KK is thankful to UGC for providing financial assistance in the form of MANF[No.F.40-3(M/S)/2009(SA-III/MANF)]. Authors are also thankful to Centre of nanotechnology, Department of Applied Physics, AMU, for providing powder XRD, University Sophisticated Instrument Facility (USIF), AMU, Aligarh for providing SEM, TEM facilities and SAIF Punjab University, Chandigarh for providing NMR and Mass spectra.

References

1. Gladysz JA (2001) Pure Appl Chem 73:1319
2. Rhijn WMV, Vos DED, Sels BF, Bossaert WD, Jacobs PA (1998) Chem Commun 317
3. Das D, Lee JF, Cheng SF (2001) Chem Commun 2178
4. Wilson K, Lee AF, Macquarrie DJ, Clark JH (2002) Appl Catal A 228:127
5. Shimizu K, Hayashi E, Hatamachi T, Kodama T, Higuchi T, Satsuma A, Kitayama Y (2005) J Catal 231:131
6. Bossaert WD, Vos DED, Rhijn WMV, Bullen J, Grobet PJ, Jacobs PA (1999) J Catal 182:156
7. Kresge CT, Leonowicz ME, Roth WJ, Vartuli JC, Beck JS (1992) Nature 359:710
8. Zhao DY, Feng JL, Huo QS, Melosh N, Fredrickson GH, Chmelka BF, Stucky GD (1998) Science 279:548
9. Polshettiwar V, Cha D, Zhang XX, Basset JM (2010) Angew Chem Int Ed 49:9652
10. Polshettiwar V, Thivolle-Cazat J, Taoufik M, Stoffelbach F, Norsic S, Basset JM (2011) Angew Chem Int Ed 50:2747
11. Fihri A, Bouhrara M, Patil U, Cha D, Saih Y, Polshettiwar V (2012) ACS Catal 2:1425
12. Fihri A, Cha D, Bouhrara M, Almana N, Polshettiwar V (2012) Chem Sus Chem 5:85
13. Patil U, Fihri A, Emwas AH, Polshettiwar V (2012) Chem Sci 3:2224
14. Bouhrara M, Ranga C, Fihri A, Shaikh RR, Sarawade P, Emwas A, Hedhili MN, Polshettiwar V (2013) ACS Sustain Chem Eng 1:1192
15. Greenhill JV (1977) Chem Soc Rev 6:277
16. Li G, Watson K, Buckheit RW, Zhang Y (2007) Org Lett 9:2043
17. White JD, Lhle DC (2006) Org Lett 8:1081
18. Chen JX, Zhang CF, Gao WX, Jin HL, Ding JC, Wu HY (2010) J Braz Chem Soc 21:1552
19. Zhang LF, Yang ST (2009) Russ J Org Chem 45:18
20. Das B, Venkateswarlu K, Majhi A, Reddy MR, Reddy KN, Rao YK, Ravikumar K, Sridhar B (2006) J Mol Catal A 246:276
21. Mohammadizadeh MR, Hasaninejad A, Bahramzadeh M, Khanjarlou ZS (2009) Synth Commun 39:1152
22. Gholap AR, Chakor NS, Daniel T, Lahoti RJ, Srinivasan KV (2007) J Mol Catal A 245:37
23. Wang L, Lu XH, An LT, Zou JP (2009) Chin J Chem 27:1353
24. Dhiman K, Adinath M, Alakananda H (2008) Chin J Chem 26:1545
25. Li GC (2007) J Chem Res 696
26. Bhatte KD, Tambade PJ, Dhake KP, Bhanage BM (2010) Catal Commun 11:1233
27. Kidwai M, Bhardwaj S, Mishra NK, Bansal V, Kumar A, Mozumdar S (2009) Catal Commun 10:1514
28. Chen Jiuxi, Yang Xiaoliang, Liu Miaochang, Huayue Wu, Ding Jinchang, Weike Su (2009) Synth Commun 39:4180
29. Zhang ZH, Song LM (2005) J Chem Res 817
30. Zhang ZH, Yin L, Wang YM (2006) Adv Synth Catal 348:184
31. Greenhill JV (1976) J Chem Soc Perkin Trans 1:2207
32. Eshghi H, Seyedi SM, Safaei E, Vakili M, Farhadipour A, Bayat-Mokhtari M (2012) J Mol Catal A 363:430
33. Hasaninejad A, Zare A, Mohammadizadeh MR, Shekouhy M, Moosavi-Zare AR (2010) E-J of Chem 7:1546