

Synthesis, characterization and catalytic application of ordered mesoporous silica nanocomposites functionalized with chloroacetic acid (SBA-15/CA)

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ABSTRACT

In order to develop the mild acidic nanocatalyst, ordered mesoporous silica, SBA -15 was functionalized with chloroacetic acid (SBA/CA) via post synthetic grafting technique for useful acidic conversions such as Knoevenagel condensation, Biginelli synthesis and Mannich reaction. The nanocomposites were characterized by Powder X-ray Diffraction method, N₂ adsorption-desorption isotherm, ¹³C CP-MAS NMR, FT-IR, TPD and EDXRF. Very high activity and selectivity was observed for all the conversions under milder reaction conditions. Finally, the mechanism of the reaction is proposed and discussed. Copyright © 2013 VBRI press.

Keywords: Heterogeneous catalysis; chloroacetic acid; SBA-15; Knoevenagel condensation.



Amit Dubey, Associate Professor in Maulana Azad National Institute of Technology (MANIT), Govt of India-Bhopal (M.P.), is involved into the research areas of Synthesis and Characterization of Functional Nanomaterials and Nanocomposites for Advanced Application for the last fourteen years. He worked as Assistant Professor in BITS-Pilani and had pursued research in PRL-Ahmedabad, CSMCRI-Bhavnagar, KAIST-South Korea

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Introduction

Ordered silica mesoporous materials (OSM) are getting tremendous attentions during the last two to three decades compared to the microporous materials due to their remarkable properties such as high surface area, tunable pore size (2-15 nm), pore volume, flexibility to incorporate organic moieties within highly porous structures in a very systematic and designed manner with uniform dispersion of active species [1-3]. Functionalization of these materials by different organic-inorganic species can be attained easily and is advantageous for various applications such as ion-exchange, catalysis, separation technology, absorbents, chemical sensors, optical/ electronic devices and drug delivery [4-6]. The functional moieties are generally incorporated inside the silica frame work either directly by

co-condensation or post-synthetically by grafting techniques [4]. Several researchers have tailored the catalytic properties of these materials by incorporating high acidic moieties such as propylsulfonic acid, perfluoroalkylsulfonic acid, inorganic metals (Al, Ti, W) and heteropolyacids into the different silica matrix [4, 5]. However, not much attention has been paid to develop the nanomaterials having low to moderate acidity for useful organic transformations. Hence, there is a need to develop non-corrosive heterogeneous acid catalysts that can greatly improve the environmental impact of commercial products.

Heterogeneous catalysis plays an important role in modern chemical industry because of their unique properties in easier product recovery, regeneration of active sites, to overcome effluent treatment problems and environmental concerns [7]. Many heterogeneous catalysts such as zeolites [8], sulphated zirconia [9], heteropoly acids [10, 11] and functionalized ordered mesoporous materials [12] have been developed for many acids, base or redox catalyzed transformations. Microporous materials such as zeolites [2] covers the wide range of commercial acidic transformation, however, because of their smaller pore diameter and low functional group density limit their practical utilization for larger substrates. Particularly, Knoevenagel condensation is one of the most useful C–C bond forming reactions for the production of fine chemicals [13]. The products of this reaction e.g. ethyl (4*E*)-2-cyano-3-hydroxy-5-phenylpent-4-enoate have important applications in photosensitive composition and act as an intermediate for plant growth regulators [14]. Ethyl α -cyanocinnamates or phenylcinnamate's with alkoxy or hydroxyl substituents in the arenes are used in ultraviolet filters composition for protecting light-sensitive foods, wood-products, paper, dyes, fibers, plastics, cosmetics and fragrances [15-17]. According to the best of the literature, no report is available for the functionalization of chloroacetic acid inside the mesopores of SBA-15 for acid catalysis. Therefore our interest emerged to develop chloroacetic acid functionalized SBA-15 nanocomposites (SBA-15/CA) for their effective use as a nanocatalyst for Knoevenagel condensation, Biginelli synthesis and Mannich reaction. The reactions have been chosen because of the importance of their products universally. Several heterogeneous catalysts including oxides, zeolites [18], ammonia, organic amines [19], hydrotalcite in ionic liquid media [20], 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) [21], ZnCl₂ [22], CdI₂ [23], KSF montmorillonite [24] and KF-Al₂O₃ [25] have been reported for these interesting reaction but still the desired product selectivity remains an interesting concern.

Experimental

Synthesis of chloroacetic functionalized (SBA/CA)

All the chemicals were procured from Sigma Aldrich and used without further purification. The synthesis of SBA was carried out in accordance to the earlier reports using Pluronic (P123) (EO₂₀PO₇₀EO₂₀, Mw = 5800, Aldrich) as surfactant and TEOS as the silica source [26]. Chloroacetic acid was incorporated via post synthetic grafting technique into the silica framework. Typically, to 1g of SBA-15,

10ml of aminopropyltriethoxysilane (APTS) was stirred in dry toluene (20 ml) under inert atmosphere. The product SBA/APTS was filtered and exhaustively washed with ethanol in Soxhlet extractor for 24h. SBA-15 functionalized with APTS was dried under vacuum and used further for functionalization with dichloroacetic acid. Typically, 1g of SBA/APTS was mixed with 1ml of dichloroacetic acid (equivalent amount) in 15 ml of triethylamine (acts as a solvent for neutralizing HCl generated during the functionalization) and refluxed for 24h under stirring conditions. Finally chloroacetic acid functionalized SBA-15 (light brown coloured) was filtrated and washing thoroughly with dil HCl and water. No color change was observed in Ninhydrin test confirms the functionalization of SBA-15 with chloroacetic (absence of free primary amines). The sample was named as SBA/CA.

Knoevenagel condensation

The catalytic activity studies were carried out in the liquid phase. 1mmol of cinnamaldehyde and 1.2 mmol of ethylcyanoacetate were stirred at 100°C in glass reactor. The desired amount of the catalyst (10-200mg) was added to the reaction mixture under inert atmosphere and the reaction was monitored for 6-8 h. The products of the reactions were confirmed with authentic samples (prepared under homogeneous conditions) on TLC. After the completion of the reaction, the catalyst was filtered and washed with acetone. The solvent was evaporated and finally the product was isolated from the reaction mixture using ethanol and water. The solid product obtained was dried in vacuum and weighed to obtain isolated yield. The product was identified and characterized by ¹H-NMR and FT-IR (Supplementary Information).

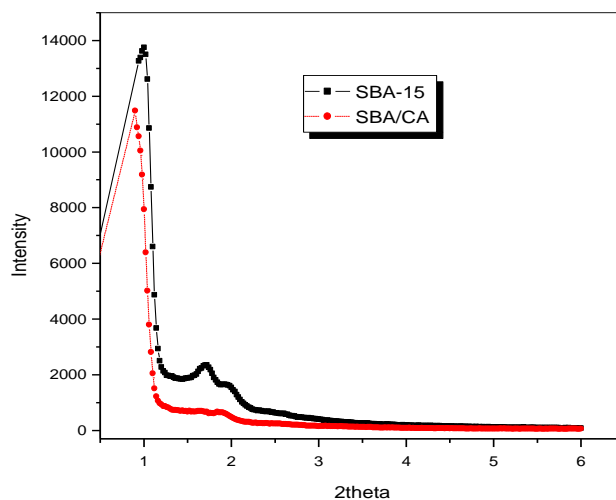


Fig. 1. PXRD pattern of SBA-15 and SBA/CA nanocomposites.

Results and discussion

PXRD studies

Powder X-Ray Diffraction (PXRD) pattern was recorded on Hecus X-Ray Systems S3 Model using Cu K α radiation ($k = 1.5404 \text{ \AA}$) from 0-10°. PXRD pattern of the samples at low angles (Fig. 1) showed the diffraction pattern similar to

Table 1. Variation of conversion of products over different samples.

Catalyst	Pore Size BJH _{Ads} (nm)	Pore volume (cm ³ /g)	Surface area (m ² /g)	^a Conversion (%)	Product selectivity (%)		^b Yield (%)
					A	B	
Blank	-	-	-	18	91	8	15
SBA-15	8.4	1.2	656	20	90	10	14
CA	-	-	-	95	75	20	65
SBA/CA	5.6	0.18	129	98	96	4	93

^aConditions: 1mmol- cinnamaldehyde, 1.2 mmol- ethylcyanoacetate, Temp- 100°C, SBA/CA catalyst-100mg.

%Conversion is based on total products formed.

^bYield (%) - is isolated yield of desired product (A)

CA -stands for chloroacetic acid

SBA-15 sample. The diffraction at (100), (110), and (200) planes can be indexed to reflections comprising of hexagonal p6 mm space group indicating that the materials possess the ordered mesoporous structure. The intensity of the base peak in SBA/CA was lowered compared to pure SBA-15 indicating that chloroacetic acid has been incorporated into the silica framework.

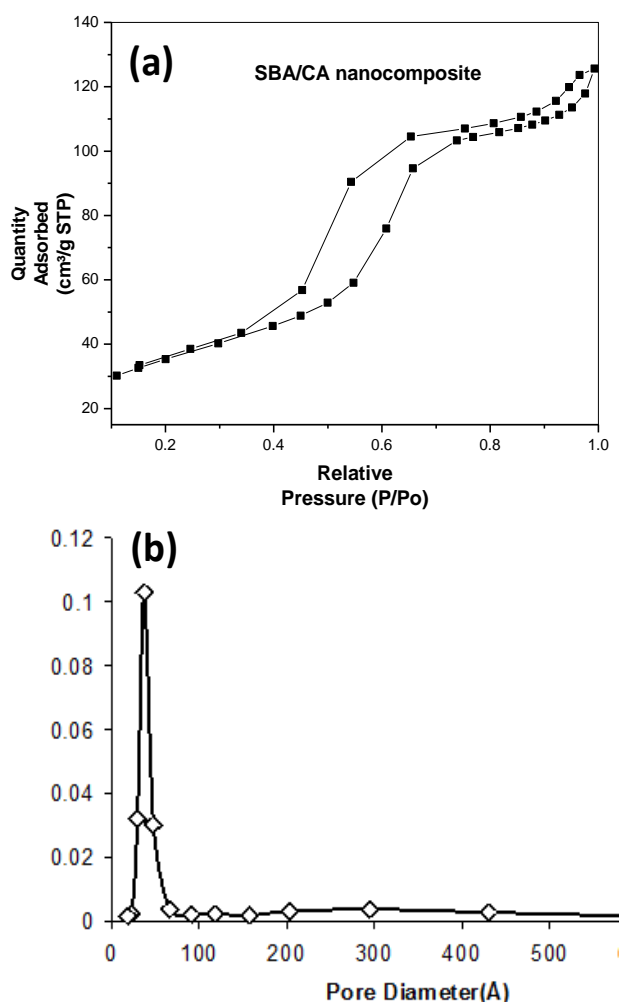


Fig. 2. N₂-adsorption-desorption isotherm (a) and pore size distribution (b) of SBA/CA nanocomposites.

N₂ sorption studies

Nitrogen adsorption-desorption isotherms were measured by using Micromeritics ASAP 2020 analyzer at -196°C. The specific surface area was calculated by the BET method and the pore size distribution was calculated by Barrett-Joyner-Halenda (BJH) method from the desorption isotherm of the sample. Before the adsorption measurements, all the samples were out gassed for 12 h at 300°C in the degas port of the adsorption analyzer. The nitrogen adsorption-desorption isotherm (Fig. 2) of the catalysts showed a type IV adsorption isotherm according to IUPAC classification [5], with a sharp capillary condensation step at relatively high pressure with an H1 hysteresis loop indicative of mesoporous nature of the samples. The shape of the isotherm is slightly tilted indicative of little strain generated during incorporation of chloroacetic acid inside the silica framework. The surface area, pore volume and pore diameter decreased with the incorporation of chloroacetic acid, indicating that the chloroacetic acid has been incorporated inside the SBA-framework (Fig. 2 and Table 1). The particle size of the SBA/CA is 46nm. All the structural parameters of the catalysts are included in Table 1.

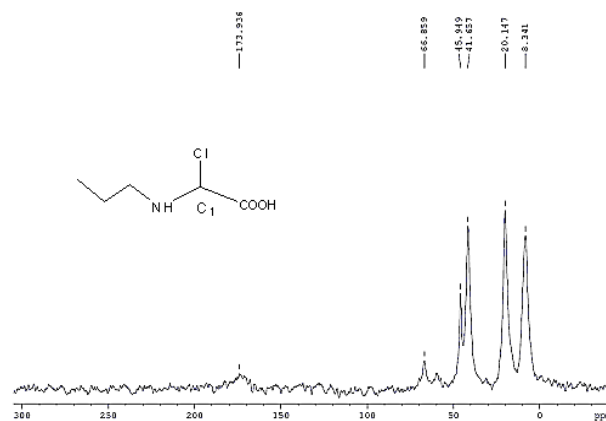


Fig. 3. ¹³C CPMAS NMR spectra of SBA/CA nanocomposites.

¹³C CP-MAS NMR

SSNMR ¹³C of samples were recorded on AV500S - 500 MHz High Resolution Multinuclear FT-NMR Spectrometer. The incorporation of chloroacetic acid into the silica framework was further confirmed by ¹³C CPMAS SS-NMR

(Fig. 3). The spectrum of SBA/CA showed five types of carbon. The peak at 173 ppm indicates the presence of deshielded carbon due to the carboxylic acid carbon. The peak at 66 ppm with low intensity indicates the presence of C_1 in chloroacetic acid group. Furthermore, the three peaks at 41, 20 and 8 ppm indicates the presence of aminopropyl group to which chloroacetic acid group is attached.

EDXRF was recorded on PANalytical Epsilon-5 EDXRF System. The amount of loading of chloroacetic acid in SBA-15 was estimated by EDXRF. The spectrum (Fig. 4, Supplementary Information) was analyzed to obtain the number of Cl $K\alpha$ counts per second and to determine the chlorine content in SBA/CA catalysts. The chlorine content present in the SBA/CA was 0.329% and is in agreement with the theoretical calculations.

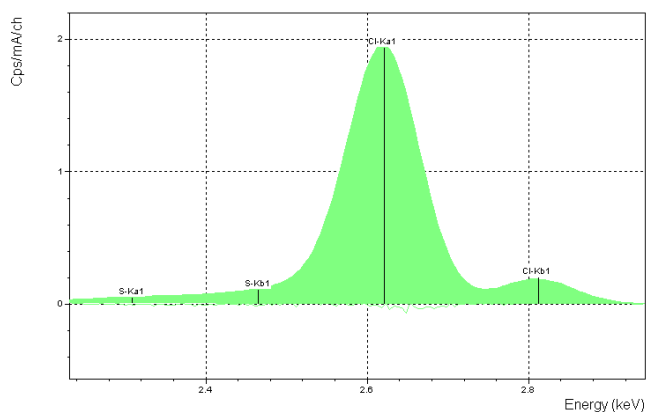


Fig. 4. EDXRF spectrum for Chlorine in SBA/CA.

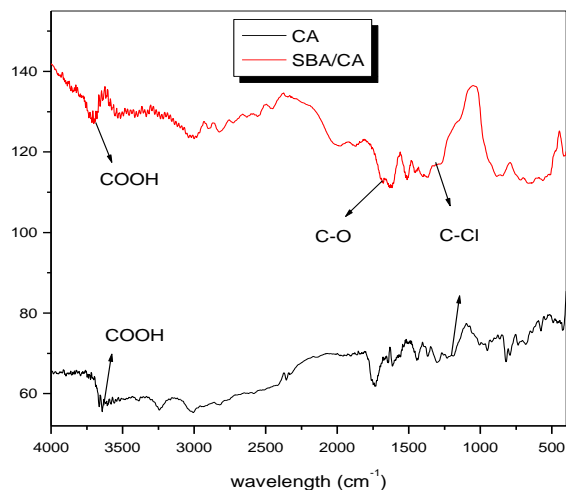


Fig. 5. FT-IR spectrum of chloroacetic acid and SBA/CA.

FT-IR studies and temperature programmed studies (NH_3 TPD)

The FT-IR spectrum (Fig. 5, Supplementary Information) of the SBA/CA showed the presence of the peak at 3604 cm^{-1} for O-H stretching in COOH group while peak at 1674 cm^{-1} indicates the presence of C-O stretching similar to chloroacetic acid (CA). Furthermore the peak at 1250 cm^{-1} confirms the presence of C-Cl stretching bond. The stretching frequencies were well correlated with neat chloroacetic acid

indicating the incorporation of acidic moiety inside the silica framework. Acidity of the catalyst was measured by TPD (NH_3) method and the number of acidic sites (Fig 6) was found to be $24.2\mu\text{mol/g}$.

Catalytic studies

The catalytic activity of SBA/CA was investigated for Knoevenagel condensation of cinnamaldehyde with ethylcyanoacetate in liquid phase (Scheme 1). The catalytic activity results showed 98% conversion with 96% selectivity of desired product (A). The catalytic activity and selectivity was also compared with chloroacetic acid (homogeneous conditions) under similar reaction conditions.

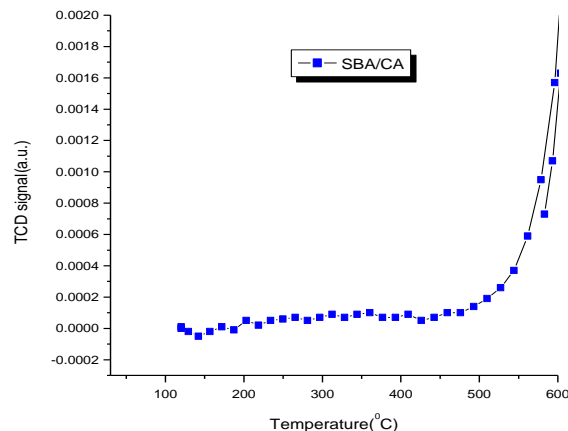
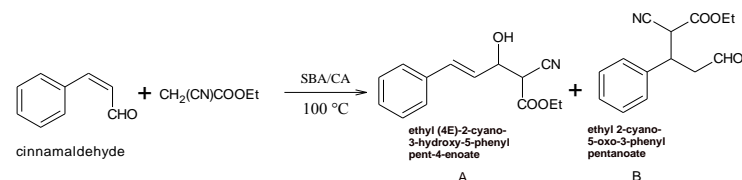


Fig. 6. Temperature Programmed Desorption (TPD) pattern of SBA/CA catalyst.



Scheme 1. Knoevenagel condensation.

No difference in the activity was observed however very low selectivity (75%) of the desired product (A) was obtained under homogeneous conditions corroborating our endeavor to heterogenize the chloroacetic acid in SBA-15. The increased product selectivity over SBA/CA is attributed to the high surface area and better dispersion of active sites on heterogenization of chloroacetic acid (Table 1). It is important to mention here that 18% activity was observed without catalysts (blank) and 20% conversion was obtained with SBA-15 catalyst indicating that more acidic centers are required for the higher conversion of reaction. The blank or with SBA-15 activity (18-20%) may be due to the high electrophilic nature of the reactant cinnamaldehyde.

Effect of the solvent

The variation of different solvents (Fig. 7) infers that the highest activity and selectivity can be obtained under solvent free conditions. Careful examination of the solvent

concludes that the conversion of the product increased with increasing polarity of the solvent. However lower activity was observed using non polar solvents. This may be due to better stabilization of transition state in polar solvents than in non-polar solvents. We believe that ethylcyanoacetate, because of its high polarity itself, may act as a solvent and stabilize the transition state in a better way to generate the desired product.

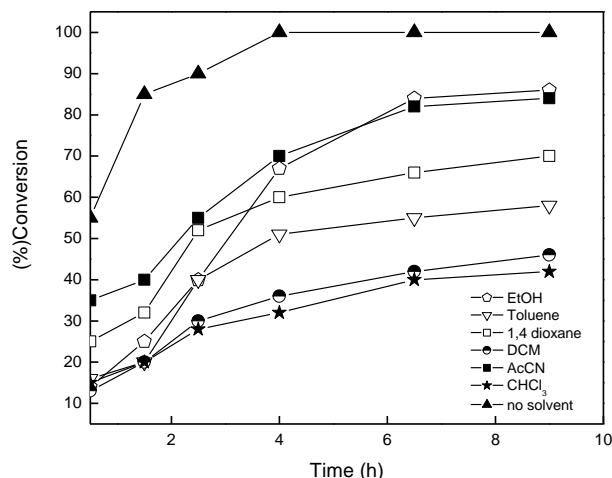


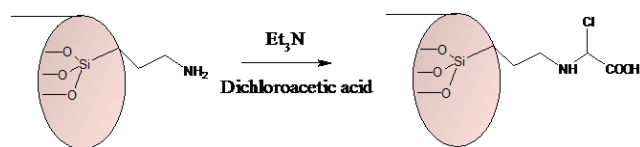
Fig. 7. Effect of different solvents on the conversion of product (A) over SBA/CA nanocomposites.

Effect of the catalyst weight

Table 2 showed the effect of catalyst weight on the conversion of product (A). The results concluded that the conversion and the selectivity of the product (A) increased with increase in the weight of the catalyst and maximum conversion can be achieved with 200mg of the catalyst within 2h. However, 100mg of the catalyst was selected for carrying out further studies.

Table 2. Effect of catalyst weight on the conversion of product (A) over SBA/CA nanocomposites.

Catalyst weight	Conversion (%)	Product selectivity (%)		Yield (%)
		A	B	
200	100 (2)	98	2	95
100	98 (3)	96	4	93
75	90	92	6	85
50	85	91	6	78
25	82	91	5	74
10	57	90	7	50



Scheme 2. Functionalization of SBA-15 with chloroacetic acid.

Effect of the reaction temperature and time on stream studies (TOS)

Fig. 8 showed the effect of temperature on the conversion and selectivity of ethyl (4*E*)-2-cyano-3-hydroxy-5-phenylpent-4-enoate (A). The results concluded that the conversion of the product (A) and the selectivity of the product increased with increase in the temperature up to 100°C and maximum conversion is achieved within 3h. Remarkable effect on product selectivity was observed at lower temperature wherein selectivity of product (A) is reduced. This may be due to the high electrophilic nature of transition state (C) at higher temperature compared to transition state (D) at lower temperature (**Scheme 2**) indicating the influence of thermodynamic vs. kinetically controlled product.

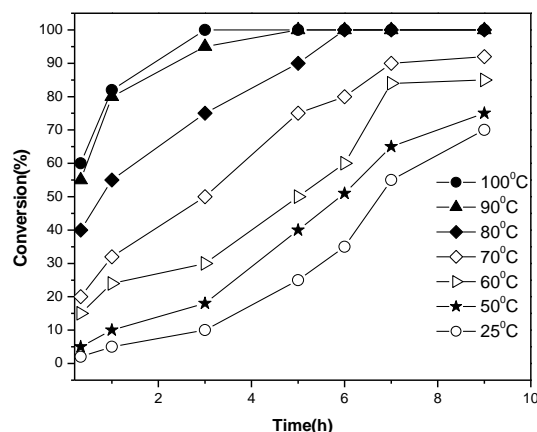
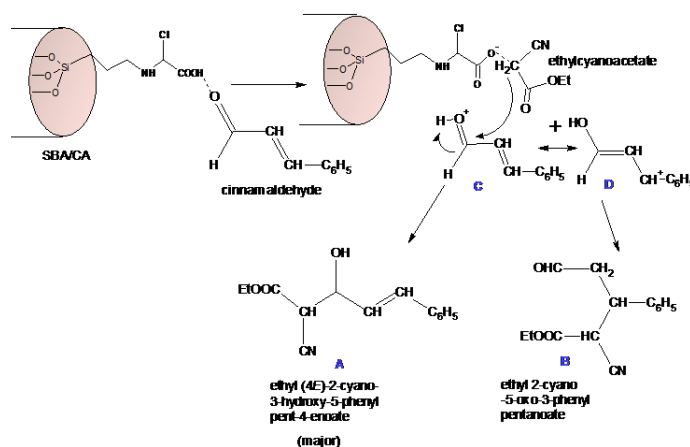


Fig. 8. Variation of reaction temperature on the conversion of product (A) over SBA/CA nanocomposites.

Time on stream studies also indicates that the total conversion increased with increase in the reaction time at all temperatures. Although maximum conversion is achieved within 3h at 100°C yet the reaction was allowed to proceed for 24h to check the formation of secondary products (either through product decomposition or inter conversions of the products). However no difference in the activity and selectivity was observed after 24h indicating the promising use of the catalyst.



Scheme 3. Plausible Mechanism of formation of products.

Table 3. Knoevenagel condensation of aromatic aldehydes with ethyl cyanoacetate using SBA/CA nanocomposites. (Conditions as in Table 1).

Reactants	Products	Conversion (%)	Yield (%)	Time (h)
		100	93	3
		96	91	4.5
		90	88	6
		95	90	5
		88	84	7

Plausible mechanism

The probable mechanism (**Scheme 3**) to achieve the desired product (A), ethyl (4*E*)-2-cyano-3-hydroxy-5-phenylpent-4-enoate, over SBA/CA is due to the formation of kinetically controlled intermediate C. The reaction proceeds via S_N2 mechanism in concerted manner wherein intermediate C subsequently reacts with deprotonated ethylcyanoacetate which further leads to the formation of product (A).

Reusability

In order to check the heterogeneity of the catalyst, a hot filtration test was carried out. The catalyst SBA/CA, after the completion of the reaction, was filtered and washed thoroughly with acetone and water. The catalyst was dried and again subjected to fresh reaction. No significant (5-8%) difference in the activity and selectivity of the product was

noted after 24h indicating the stability of the functional group in SBA/CA catalyst.

Effect of different (substituted) aldehydes

The interesting results obtained on this model reaction were extended to different substituted aldehydes (**Table 3**) having the universal utility of their products in photosensitive or ultraviolet absorbing compounds. Overall 88-96% conversion was noted with different aldehydes; however, the effect of the electronic environment could not be generalized.

Conclusion

SBA/CA catalyst with mild acidities were synthesized and characterized by standard characterization techniques. An efficient protocol for the preparation of phenylcinnamate's in liquid phase was reported with very high activity, selectivity and product yield. The catalyst was optimized

and further evaluated for the synthesis of other substituted aldehydes. We envisage a successful implementation of these SBA/CA catalysts for other acidic conversions.

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Reference

1. Taguchi, A.; Schüth, F.; *Microporous Mesoporous Mater.* **2005**, *77*, 1.
2. Li, B.; W., Guo, S.; Yuan, J.; Hu, J.; Wang, H.; Jiao, J.; *Catal.* **2008**, *253*, 212.
3. Hoffmann, F.; Cornelius, M.; Morell, J.; Fröba, M.; *Angew. Chem. Int. Ed.* **2006**, *45*, 3216.
4. Ciesla, U.; Schüth, F.; *Microporous Mesoporous Mater.* **1999**, *27*, 131.
5. Wight, A.; Davis, M.; *Chem.Rev.* **2002**, *102*, 3589.
6. Davis, M.; *Nature.* **2002**, *417*, 813.
7. Mizuno, N.; Misono, M.; *Chem. Rev.* **1998**, *98*, 199.
8. Yadav, G.; Kundu, B.; *Can.J.Chem.Eng.* **2009**, *79*, 805.
9. Garg, S.; Soni, K.; Kumaran, G.; Bal, R.; Gora-Marek, K.; Gupta, J.; Sharma, L.; Dhar, G.; *Catal. Today.* **2009**, *141*, 125.
10. Gagea, B.; Lorgouilloux, Y.; Altintas, Y.; Jacobs, P.; Martens, J.; *J. Catal.* **2009**.
11. Tsukuda, E.; Sato, S.; Takahashi, R.; Sodesawa, T.; *Catal. Commun.* **2007**, *8*, 1349.
12. Blanco-Brieva, G.; Campos-Martin, J.; de Frutos, M.; Fierro, J.; *Ind. Eng. Chem. Res.* **2008**, *47*, 8005.
13. Rong, L.; Li, X.; Wang, H.; Shi, D.; Tu, S.; Zhuang, Q.; *Synth. Commun.* **2006**, *36*.
14. Priya, K.; Buvaneswari, G.; *Mater. Res. Bull.* **2009**, *44*, 1209.
15. Teichmann, H.; Thierfelder, W.; *Ger. Patent (East).* **1978**, *129*, 959.
16. Jin, T.; Wang, X.; Liu, L.; Li, T.; *J.Chem.Res.* **2006**, *2006*, 346.
17. Corma, A.; Iborra, S.; *Adv. Catal.* **2006**, *49*, 239.
18. Reddy, T.; Varma, R.; *Tetrahedron Lett.* **1997**, *38*, 1721.
19. Texier-Boulet, F.; Foucaud, A.; *Tetrahedron Lett.* **1982**, *23*, 4927.
20. Khan, F.; Dash, J.; Satapathy, R.; Upadhyay, S.; *Tetrahedron Lett.* **2004**, *45*, 3055.
21. Muthusamy, S.; Babu, S.; Gunanathan, C.; *Synth. Commun.* **2002**, *32*, 3247.
22. Shanthan Rao, P.; Venkataratnam, R.; *Tetrahedron Lett.* **1991**, *32*, 5821.
23. Prajapati, D.; Sandhu, J.; *J. Chem. Soc., Perkin Trans.* **1993**, *1*, 739.
24. Shi, D.; Wang, X.; Yao, C.; Mu, L.; *J.Chem.Res.* **2002**, *344*.
25. Lai, S.; Martin-Aranda, R.; Yeung, K.; *Chem. Commun.* **2003**, *218*.
26. Kruk, M.; Jaroniec, M.; C, Ko.; Ryoo, R.; *Chem. Mater.* **2000**, *12* 1961.

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