Amino Functionalized Coal Fly Ash: A Green and Efficient Heterogeneous Solid Base Catalyst for Knoevenagel Condensation Reaction

[1,2]Dr. Nurul Alam Mazumder, [2]Dr. Ruma Rano
[1]Pandit Deendayal Upadhyaya Adarsha Mahavidyalaya, Eraligool, Karimganj, Assam, India
[2]Department of Chemistry, National Institute of Technology, Silchar, Assam, India

***Abstract*— A green and efficient solid base catalyst has been prepared upon treatment of thermally activated fly ash with 2-chloroethylamine hydrochloride. The properties of synthesized amino functionalized coal fly ash (AFCFA) were investigated using various characterization techniques such as FT-IR, XRD, FE-SEM and BET surface area analysis. AFCFA possessed excellent catalytic activity for Knoevenagel condensation reaction of benzaldehyde and diethylmalonate to produce diethyl benzalmalonate (DBM), a very important pharmaceutical intermediate. The yields of the reactions were excellent and the catalyst was easily regenerated. AFCFA could be efficiently reused for four runs without significant loss of its catalytic activity confirming high stability of the catalyst. High yields, short reaction times and solvent-free reaction conditions are the major advantages of the present method. The stability and simple recyclability without losing catalytic activity make this catalyst a good replacement to literature methods of catalyzing industrially important organic transformation.**

Keywords—Coal fly ash; 2-chloroethylamine hydrochloride; Knoevenagel condensation; solvent-free reaction.

I. INTRODUCTION

In order to produce complex and large molecules that characterize most of the fine chemicals and pharmaceutical intermediates, base catalyzed condensation and addition reactions are important [1]. Magnesium perchlorate [2], TsOH-SiO_2 [3], PhI$(OAc)_2$ [4], titanium isopropoxide/pyridine [5] and zinc chloride [6] were utilized in order to perform a variety of Knoevenagel condensation reactions. Heterogeneous solid base catalysts may replace the use of environmentally hazardous liquid organic bases like piperidine, alkali metal hydroxides and alkoxides leading to greener productions. Heterogeneous catalysts are able to suppress side reactions such as oligomerization and self-condensation resulting in better product yield and selectivity. The process also avoids the complex separation and neutralization steps required for the regeneration of the homogeneous base catalysts from the reaction mixture [7].

Knoevenagel condensation reaction is one of the well-known organic reactions to produce important intermediates of calcium antagonists and anti-hypertensive drugs [8,9]. It is the condensation of aldehydes or ketones with active methylene group compounds, catalyzed by basic sites to form C-C bond. Knoevenagel condensation reactions catalyzed by metal-organic frameworks [10] and amine functionalized MCM-41 [11] are well-reported in literature. So far the utilization of fly ash as a solid base catalyst to synthesize diethyl benzalmalonate, an important fine chemical and pharmaceutical intermediate, is unprecedented in literature. In this paper, Knoevenagel condensation reaction between benzaldehyde and diethylmalonate has been performed to produce diethyl benzalmalonate (DBM) using amino-functionalized coal fly ash (AFCFA) as solid base catalyst. AFCFA has been synthesized from thermally activated coal fly ash upon treatment with 2-chloroethylamine hydrochloride. The effects of various reaction conditions such as reaction time, temperature and catalyst-substrate weight ratio were also examined. The process provides a highly efficient pathway to utilize solid waste fly ash by developing novel, low-cost and environmental-friendly solid base catalyst system for industrially important Knoevenagel condensation reaction.

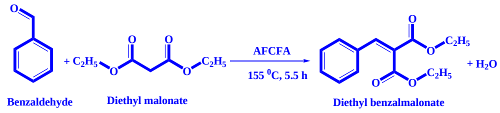
II. EXPERIMENTAL

A. *Catalyst Synthesis*

In order to remove C, S and other impurities, calcination of fly ash (5 g) was performed at 900 °C for 4 h [12]. Thermally treated fly ash was then cooled down to room temperature and kept into a 100 ml conical flask. A solution of 2-chloroethylamine hydrochloride was incorporated into the flask and the mixture was then refluxed with constant stirring for 13 h at 85 °C in a stirred reactor. After filtration, the resulting solid was washed with acetone for a number of times. The solid was then dried at 105 °C for 5 h and finally calcined at 350 °C for 3 h.

B. *Catalytic activity of AFCFA*

Under solvent free condition, Knoevenagel condensation of benzaldehyde and diethyl malonate was performed in liquid phase batch reactor over as synthesized AFCFA (Scheme 1).



Scheme 1. Knoevenagel condensation of benzaldehyde with diethylmalonate over AFCFA.

A mixture of benzaldehyde and diethyl malonate (Molar ratio 1 : 1) was introduced into a 50 ml round bottom flask equipped with a condenser and immersed in a constant temperature oil bath with continuous magnetic stirring. In the reaction mixture, AFCFA (catalyst : substrate weight ratio = 1 : 3), activated at 480 °C for 7 h prior to the reaction, was incorporated into the flask. Stirring of the reaction mixture for time ranging from 3.5 h to 5.5 h at a temperature range 115 °C to 155 °C at atmospheric pressure followed by cooling and filtration regenerates the catalyst. The product was washed with dilute HCl, aqueous $NaHCO_3$ solution, water and dried over anhydrous Na_2SO_4. It was then distilled under reduced pressure. The product obtained was confirmed by melting point measurement and ^{1}H NMR analysis.

III. Results And Discussion

A. FT-IR Analysis

In the FT-IR spectra of AFCFA (Fig. 1), bands at 1100 cm^{-1}, 797 cm^{-1} and 554 cm^{-1} are due to the asymmetric Si-O-Si stretching, symmetric Si-O-Si stretching and asymmetric Si-O-Al stretching respectively. The broad band at 3445 cm^{-1} is assigned to the stretching mode of hydroxyl groups of silanols (-Si-OH) and adsorbed water molecules on the surface. The $–NH_2$- stretching frequencies which is usually observed in the range 3600-3000 cm^{-1}, could not be observed in the spectra, as a result of overlapping of the band with that of –OH vibration groups.

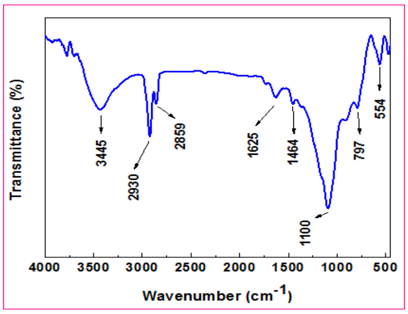


Fig. 1. FT-IR spectra of amino functionalized coal fly ash (AFCFA).

B. XRD Analysis

XRD patterns of AFCFA (Fig. 2) shows the presence of hexagonal quartz (JCPDS card no. 86-1628) and orthorhombic mullite (JCPDS card no.83-1881) as the main crystalline phases. In addition, small amount of hematite (JCPDS card no.89-2810) is also present in the catalyst.

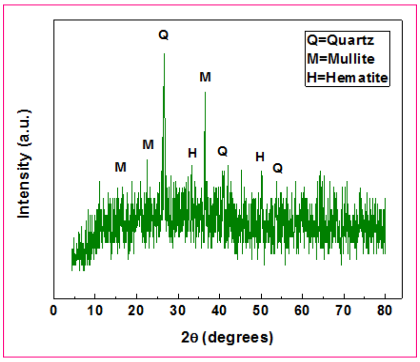


Fig. 2. XRD patterns of amino functionalized coal fly ash (AFCFA).

C. FESEM-EDS Analysis

Surface modification of the fly ash particles with amino groups resulted in irregular shapes in case of AFCFA (Fig. 3). In addition, uniformity of the spheres was lost and they were covered with different layered particles which may be due to the deposition of organic amino groups on fly ash surface.

Grafting of amino groups in AFCFA was also confirmed from the availability of C and N in EDS spectrum of the AFCFA along with other elements like Ti, O, Si, Al, C, K, Ca, Fe, Mg (Fig. 4).

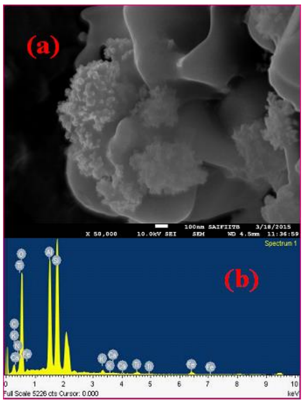


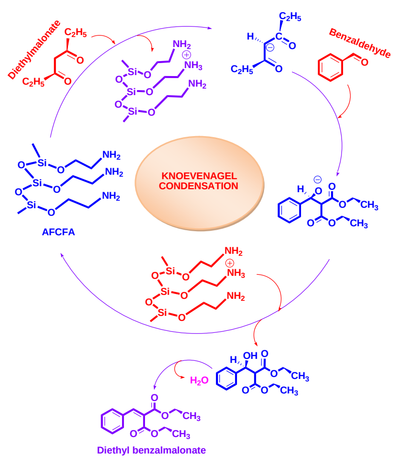
Fig. 4. (a) Scanning electron micrograph and (b) EDS spectra of amino functionalized coal fly ash (AFCFA).

D. DBM Characterization

Melting point of colourless oil (DBM), which crystallizes slowly, was obtained as 31.0 - 31.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10-1.27 (m, 6H, CH_3), 4.12-4.22 (m, 4H, OCH_2), 7.17-7.31 (m, 5H, ArH), 7.56 (s, 1H, =CH). Multiplets at δ 1.10-1.27 for $-CH_3$ protons and δ 4.12-4.22 for $-OCH_2$ protons may arise due to the presence of the protons in different environment.

E. Proposed Mechanism



Scheme 2. Mechanistic pathway for Knoevenagel condensation of benzaldehyde with diethyl malonate over AFCFA.

IV. CONCLUSION

A green and efficient solid base catalyst has been synthesized by grafting of thermally activated fly ash with amino groups. Due to the reaction of 2-chloroethylamine hydrochloride with surface silanol groups of fly ash, catalyst surface became functionalized with significant amount of amino groups. The synthesized AFCFA was associated with sufficient basisity for catalyzing the solvent free, Knoevenagel condensation reaction of benzaldehyde with diethyl malonate to produce diethyl benzalmalonate with high yield (84%). The present research work suggests a novel and cost-effective route for catalyzing industrially important reaction over solid base catalyst like AFCFA, synthesized by utilizing solid waste-fly ash.

ACKNOWLEDGMENT

The authors are grateful to Sophisticated Analytical Instrument Facility, IIT Bombay for FEG-SEM and EDS analysis.

REFERENCES

[1] M-H Shih and M-Y Yeh, "Access to the Syntheses of Sydnonyl-Substituted α,β-Unsaturated Ketones and 1,3-Dihydro-indol-2-ones by Modified Knoevenagel Reaction," Tetrahedron, vol. 59, pp. 4103-4111, 2003.

[2] G. Bartoli, M. Bosco, A. Carlone, R. Dalpozzo, and L. Sambri, "Magnesium perchlorate as efficient Lewis acid for the Knoevenagel condensation between β-diketones and aldehydes," Tetrahedron Lett., vol. 49, pp. 2555-2557, 2008.

[3] Z.N. Siddiqui and S. Tarannum, "TsOH-SiO2 as an efficient and eco-friendly catalyst for Knoevenagel condensation," Tetrahedron Lett., vol. 55, pp. 2612-2617, 2014.

[4] D. Khan, S. Mukhtar, M.A. Alsharif, M.I. Alahmdi, and N. Ahmed, "$PhI(OAc)_2$ mediated an efficient Knoevenagel reaction and their synthetic application for coumarin derivatives," Tetrahedron Lett., vol. 58, pp. 3183-3187, 2017.

[5] B.A. Robichaud and K.G. Liu, "Titanium isopropoxide/pyridine mediated Knoevenagel reactions," Tetrahedron Lett., vol. 52, pp. 6935-6938, 2011.

[6] P.S. Rao and R.V. Venkataratnam, "Zinc Chloride as a New Catalyst for Knoevenagel Condensation,"Tetrahedron Lett., vol. 32, pp. 5821-5822, 1991.

[7] X. Zhang, E.S.M. Lai, R. Martin-Aranda, and K.L. Yeung, "An investigation of Knoevenagel condensation reaction in microreactors using a new zeolite catalyst," Appl. Catal-A, vol. 261, pp. 109-118, 2004.

[8] G. Marciniak, A. Delgado, G. Leclerc, J. Velly, N. Decker, and J. Schwartz, "New 1,4-dihydropyridine derivatives combining calcium antagonism and .alpha.-adrenolytic properties," J. Med. Chem., vol. 32, pp. 1402-1407, 1989.

[9] D. Enders, S. Müller, and A.S. Demir, "Enantioselective hantzsch dihydropyridine synthesis via metalated chiral alkyl acetoacetate hydrazones," Tetrahedron Lett., vol. 29, pp. 6437-6440, 1988.

[10] A.R. Burgoyne and R. Meijboom, Knoevenagel condensation reactions catalysed by metal-organic frameworks," Catal. Lett., vol. 143, pp. 563-571, 2013.

[11] K.M. Parida and D. Rath, "Amine functionalized MCM-41: An active and reusable catalyst for Knoevenagel condensation reaction," J. Mol. Catal. A: Chem., vol. 310, pp. 93-100, 2009.

[12] M. Fan and R.C. Brown, "Comparison of the Loss-on-Ignition and Thermogravimetric Analysis Techniques in Measuring Unburned Carbon in Coal Fly Ash," Energ. Fuel, vol. 15, pp. 1414-1417, 2001.