Journal of Nanoscience and Technology 1(1) (2015) 4–8

ISSN: 2455-0191

Contents List available at JACS Directory

Journal of Nanoscience and Technology

journal homepage: www.jacsdirectory.com/jnst


JNST

Journal of Nanoscience and Technology

2015, Volume 1, Issue 1

JACS Directory

Environmental Benign Route for the Utilization of Fly Ash as Nano-Crystalline Solid Acid Catalyst for Production of Phenyl Salicylate

S. Anita[1], A. Rani[2,*]

[1]*S.S. Jain Subodh P.G. Autonomous College, University of Rajasthan, Jaipur – 302004, Rajasthan, India.*
[2]*Department of Pure and Applied Chemistry, University of Kota, Kota - 324005, Rajasthan, India*

ARTICLE DETAILS

Article history:
Received 29 July 2015
Accepted 18 August 2015
Available online 07 September 2015

Keywords:
Fly Ash
Mechanical Activation
Chemical Activation
Acid Treatment and Ball Milling
Phenyl Salicylate (Salol)

ABSTRACT

Heterogeneous acid catalysts are active in a wide range of applications. In this paper, an overview is given of the current knowledge available about the fly ash supported solid acid catalysts and their catalytic activity in the production of phenyl salicylate. An efficient nano crystalline solid acid catalyst (AFAC) with crystallite size of 14 nm has been synthesized by mechanical and thermal activation of F-type fly ash (SiO_2 and Al_2O_3>70%) followed by chemical activation using concentrated HNO_3 at 110 °C. The activation of fly ash resulted in increased silica content (61.9% to 84%) and surface area (5.8 m^2/g) having sufficient silanol activity for esterification of phenol. The catalyst was characterized by XRD, FT-IR, and SEM techniques. Fly ash generated catalytic material has shown sufficient catalytic activity for esterification of salicylic acid and phenol to give phenyl salicylate (salol), which is used in suntan lotions as an antiseptic and pain-relieving agent. The catalyst was completely recyclable without significant loss in activity up to five reaction cycles, which confers its stability during reaction. The work reports an innovative use of solid waste fly ash as an effective solid acid catalyst.

1. Introduction

Catalytic technologies play a key role in the economic development and growth of the chemicals industry and contribute to around 20% of world GNP (gross national product). Development of heterogeneous catalysts has been a relatively recent area of research in the organic synthesis. A major emerging and challenging area of heterogeneous catalysis is that of environmental pollution control, with tightening legislation on the release of waste and toxic emissions having serious implications for the chemical industry [1]. The need for development of heterogeneous catalysts has arisen from the fact that homogeneous catalysts used for organic synthesis pose a few drawbacks. Heterogeneous catalysts offer several intrinsic advantages over their homogeneous counterparts: ease of product separation and catalyst reuse; bifunctional phenomena involving reactant activation/spillover between support and active phases; and process advantages through reactor operation in continuous flow versus batch configuration [2]. Heterogeneous catalysts are categorized as solid acid and solid base. A solid acid catalyst should possess high stability, numerous strong acid sites, large pores, a hydrophobic surface providing a favorable condition for reaction, and should also be economically viable [3]. Fly ash has been used as catalyst and catalytic support because of their, high selectivity, low permeability, smooth surface, less toxicity, environment-friendly nature and its high silica content, which helps in catalysis of various reactions and provides support to different catalytic species on the surface.

Esterification is the most widely used reaction in the organic chemical synthesizing industries because it presents a lot of applications ranging from natural product synthesis at lab scale to industrial scale production. This reaction is frequently encountered in the organic process industries due to its diverse applications of esters in a variety of industries such as pharmaceuticals intermediates, fine chemical, fragrance and flavour chemicals, plasticizers, solvents, food etc. [4]. Esters cover a very wide category ranging from aliphatic to aromatic with various substitutions and multifunctional groups [5].

Phenyl salicylate is a chemical substance, commonly known as salol, is a mild analgesic [6] and antiseptic [7], a drug based on the antibacterial activity upon hydrolysis in the small intestine. Once used in sunscreens, phenyl salicylate is now used in the manufacture of some polymers, lacquers, adhesives, waxes and polishes. It can be synthesized by esterification of salicylic acid with phenol using acid catalyst. Generally phenyl esters of salicylic acid are prepared under liquid phase, by refluxing the reactants in the presence of small amount of homogeneous catalysts e.g. concentrated H_2SO_4 [8], H_3PO_4 [9] , HCl [10] , $POCl_3$, sulfonic acid and heteropoly acid [11] and $BuSn(OH)_3$ [12]. The use of liquid acids as catalysts is undesirable from the environmental point of view as these chemicals are corrosive and generally encounter the problems of handling and transportation. Moreover reusability of the catalysts cannot be expected. For this purpose, the solid acid catalysts are employed as safe alternatives for conventional liquid acid catalysts for organic synthetic reactions [13]. Solid acids such as zeolites (ZSM-5), mixed metal oxides viz. Al_2O_3, SiO_2, ZrO_2, ZrO_2-Al_2O_3, ZrO_2-SiO_2 and their sulphated forms have been extensively studied as possible alternatives to conventional Lewis/Bronsted acid catalysts [14] for esterification reactions [15].

The present chapter reports the synthesis and application of solid acid, concentrate acid activated fly ash catalyst (AFAC). The prepared AFAC catalyst has shown effective catalytic activity towards esterification of salicylic acid with phenol to produce phenyl salicylate (salol), used in suntan lotions as an antiseptic and pain-relieving agent [16], in a single step liquid phase and solvent free reaction condition with high yield 94% and purity. Reusability of AFAC up to four production cycles makes it further more cost effective. This catalyst may also be explored for other esterification products to be used in synthesis of food preservatives, plasticizers, solvents, perfumes and pharmaceuticals.

2. Experimental Methods

2.1 Raw Material and Reagents

In this study the coal fly ash (Class F-type) used as solid support was collected from Tata Thermal Power Plant (TTPP), Jamshedpur. All chemicals HNO_3 (98%), salicylic acid (99.7%) and phenol (99%) were purchased from S. D. Fine Chem. Ltd. and were used as such.

2.2 Apparatus and Catalyst Synthesis Procedure

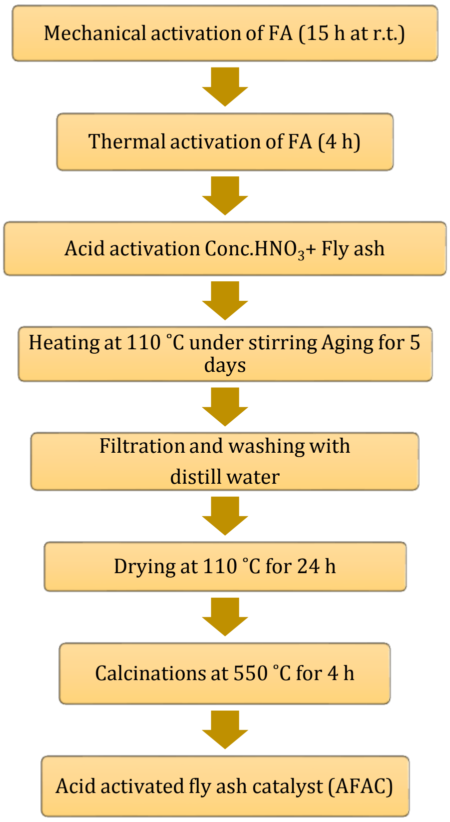
The synthesis of activated fly ash catalyst (AFAC) was carried out by mechanical activation of fly ash by wet ball milling (Retsch PM-100,

---

*Corresponding Author
Email Address: ashu.uok@gmail.com (A. Rani)

Cite this Article as: S. Anita, A. Rani, Environmental benign route for the utilization of fly ash as nano-crystalline solid acid catalyst for production of phenyl salicylate, J. Nanosci. Tech. 1(1) (2015) 4–8.

Germany, grinding jar using agate balls of 5 mm Φ ball sizes for 15 hours with 250 rpm rotation speed mill, ball to powder weight ratio (BPR) of 10:1) followed by thermal activation at 900 °C for 4 h to remove carbon, sulfur and other impurities. Chemical activation was carried out by treating fly ash with concentrated acid. The mixture was heated at 110 °C under stirring and aged for few days maintaining the temperature. After ageing, the dark pulp obtained was washed with distilled water to remove leached compounds. The pulp thus obtained was dried at 110 °C for overnight [17]. The chemically activated material was thermally stabilized by calcinations at appropriate temperature for 4 h in static conditions. The scheme for the preparation of AFAC catalyst is given in Scheme 1.



Scheme 1 Synthesis of acid activated fly ash catalyst (AFAC) from fly ash.

2.3 Catalyst Characterization

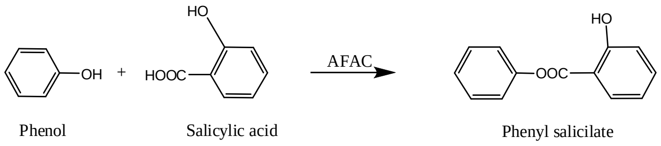
The silica content of the fly ash samples after mechano-chemical activations were analyzed by X-ray fluorescence spectrometer (Philips PW1606). The BET surface area was measured by N_2 adsorption-desorption isotherm study at liquid nitrogen temperature (77 K) using Quantachrome NOVA 1000e surface area analyzer. Powder X-ray diffraction studies were carried out by using (Philips X'pert) analytical diffractometer with monochromatic CuKα radiation (k = 1.54056 Å) in a 2θ range of 0-80°. Crystallite size of the crystalline phase was determined from the peak of maximum intensity (2θ = 26.57) by using Scherrer formula as Eq. (1) with a shape factor (K) of 0.9.

$$\text{Crystallite size} = K\lambda / W\cos\theta \qquad (1)$$

Where, W = Wb-Ws; Wb is the broadened profile width of experimental sample and Ws is the standard profile width of reference silicon sample. The FT-IR study of the samples was done using FT-IR spectrophotometer (Tensor-27, Bruker, Germany) in DRS (Diffuse Reflectance Spectroscopy) system by mixing the sample with KBr in 1:20 weight ratio. The Bronsted and Lewis acidity of the catalysts were measured by pyridine adsorbed FT-IR (Tensor-27, Bruker, Germany, with DRS. The detailed imaging information about the morphology and surface texture of the sample was provided by SEM-EDAX (Philips XL30 ESEM TMP).

2.4 Catalytic Activity of AFAC

The catalytic performance of the AFAC catalyst was evaluated by esterification of salicylic acid with phenol (Scheme 2) to give phenylsalicylate (salol) as test reaction in a liquid phase batch reactor.



Scheme 2 Esterification of salicylic acid with phenol over AFAC catalyst.

2.5 Esterification of Salicylic Acid with Phenol

The esterification of salicylic acid with phenol using AFAC was carried out in a liquid phase batch reactor. In the procedure, salicylic acid and phenol (molar ratio of salicylic acid and phenol = 1:2) were taken in a 100 mL round bottom flask, equipped with magnetic stirrer and condenser, immersed in a constant temperature oil bath. The catalyst (salicylic acid to catalyst weight ratio = 10), activated at 550 °C for 2 h prior to the reaction in static air, was added in the reaction mixture. The reaction mixture was heated at required reaction temperature ranging from 90 °C to 150 °C for difference time from 1 h to 6 h. Different reaction parameters such as molar ratio of the reactant and weight of the catalyst are also studied in order to optimize the reaction conditions to get good yield of the product. After a stipulated time the reaction mixture was cooled to room temperature, acetone was added to dissolve the unreached salicylic acid in the reaction mixture and filtered to separate out the catalyst. The product obtained was analyzed by melting point measurement, FT-IR and Gas Chromatography (Dani Master GC) having a flame ionization detector and HP-5 capillary column of 30 m length and 0.25 mm diameter, programmed oven temperature of 50-280 °C and N_2 (1.5 mL/min) as a carrier gas [18].

2.6 Catalyst Regeneration

After initial use, spent catalyst from the reaction mixture was recovered by filtration and regenerated for further use. The recovered catalyst was washed thoroughly with acetone and dried in oven at 110 °C for 12 h followed by activation at 500 °C for 2 h in static condition prior to the reaction. Thus, regenerated catalyst was used for the next reaction cycles under the similar reaction conditions.

3. Results and Discussion

3.1 Characterization of Fly Ash Catalysts

The chemical composition and physico-chemical properties of FA and AFAC catalyst are summarized in Table 1 and 2, which shows that after chemical activation the silica content in AFAC catalyst is greatly increased (61.9% to 84%). The BET surface area of AFAC catalyst (5.8 m^2/g) is also increased as compared to FA (0.97 m^2/g) while particle diameter is reduced (FA = 37.7 µm and AFAC = 3.71 µm) during chemical activation [19]. The increase in silica content after activation shows the loss of other components during the chemical activation with higher concentration of HNO_3 [20].

Table 1 Chemical composition of fly ash samples before and after chemical activation.

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	Na_2O	K_2O	Other element	LOI
	wt%									
FA	61.9	29.7	2.65	0.46	0.36	1.33	0.14	0.79	2.67	2.6
AFAC	84	11.7	1.60	0.22	0.18	0.87	0.06	0.39	0.98	1.45

Table 2 Physico-chemical properties of FA and AFAC catalyst.

Catalyst	Silica (wt%)	Crystallite size (nm)	BET surface area (m^2/g)	Particle diameter (µm)
FA	61.9	33	0.97	37.7
AFAC	84	14	5.80	3.71

Powder X-ray diffraction patterns of FA (Fig. 1A) and AFAC catalyst (Fig. 1B) show the existence of crystalline phases (mullite, quartz, hematite and small amounts of magnetite) and amorphous phases [21,22]. Quartz and aluminosilicates are found as crystals and as amorphous particles while iron rich particles exist as mixed iron oxide/aluminosilicate particles. X-ray diffraction pattern of AFAC (Fig. 1B) shows, that the crystallinity is decreased due to removal of most of the crystalline components present

Cite this Article as: S. Anita, A. Rani, Environmental benign route for the utilization of fly ash as nano-crystalline solid acid catalyst for production of phenyl salicylate, J. Nanosci. Tech. 1(1) (2015) 4–8.

in FA, thus increasing the amorphous nature [23]. The characteristic peaks of quartz in the AFAC are more concentrated in these fractions and indicate increment in SiO_2 concentration. The increase in quartz content leads to decrease in particle size distribution of fly ash.

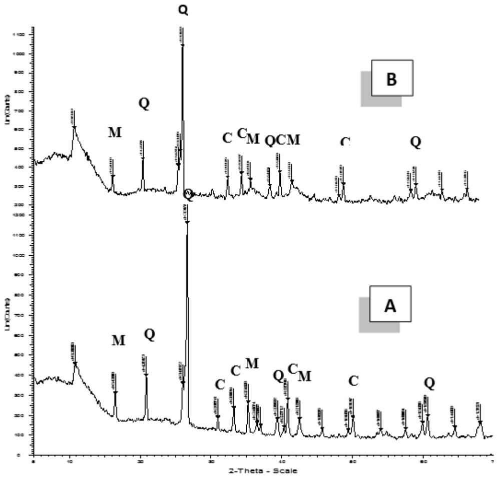


Fig. 1 X-ray diffraction pattern of A) FA and B) AFAC Catalyst (Q = Quartz, C = Calcite, M = Mullite)

The FT-IR spectrum of FA Fig. 2a shows band at 3632 cm^{-1} which is attributed to surface –OH groups of Si-OH and adsorbed water molecule on the surface. A peak at 1650 cm^{-1} in the spectra of both the samples is attributed to bending mode of water molecule. A band at 1100 cm^{-1} is corresponding to Si-O-Si asymmetric stretching which is shifted to 1155 cm^{-1} after chemical activation Fig. 2b. After chemical activation, the increase in silica content results in increase in the surface hydroxyl groups showing the broad and intense peak for hydroxyl groups at 3493.24 cm^{-1} [24]. The increased amorphous silica is characterized in AFAC catalyst by an intense band in the range 1000-1300 cm^{-1}, corresponding to the valence vibration of the silicate oxygen skeleton. The FT-IR spectrum of AFAC, after chemical activation Fig. 2b, shows a significant increase in peak intensity of the band for -OH group. FT-IR studies clearly showed changes in the intensity of IR peaks corresponding to Si-O-Si bending (572 cm^{-1}), Si-O-Si symmetric stretching (633 cm^{-1}) and T-O-Si (T = Si, Al) asymmetric stretching (1155 cm^{-1}). The peak at 1612 cm^{-1} may be attributed to the N=O stretching band in FA treated with HNO_3 Fig. 2b [25].

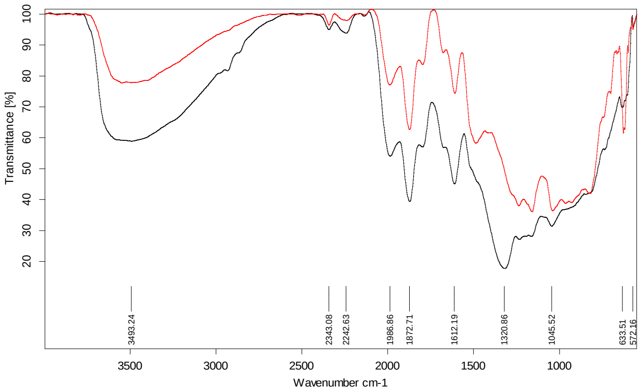


Fig. 2 FT-IR spectra of (i) FA and (ii) AFAC catalyst.

In view of learning more about the development of the type of surface acidity after chemical activation of fly ash by acid pyridine-IR studies are performed and the FT-IR spectra obtain after pyridine adsorption of dehydrated acid activated fly ash samples are presented in Fig. 3 at the magnified range of 1600-1450 cm^{-1}. The peaks observed at 1540-1552 cm^{-1} and 1480-1492 cm^{-1} for acid activated fly ash samples confirm the presence of sufficient Brønsted acidity on the surface due to formation of co-ordinated pyridine and hydrogen bonded pyridine respectively with surface silanol groups [26,27]. The intensity of absorption band at 1552 cm^{-1} assign exclusively for Brønsted acidity in AFAC catalyst due to intense hydrogen bonding at higher concentration of HNO_3.

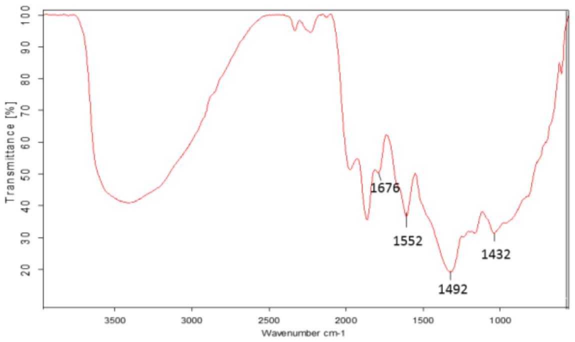


Fig. 3 FT-IR spectra of pyridine-adsorbed AFAC catalyst.

SEM micrograph of FA (Fig. 4A) indicates that the most of the particles present in the fly ash are spherical in shape with a relatively smooth surface grain consisting of quartz and also shows clusters of iron particles formed due to partial decomposition of pyrite and with dark quartz inclusions [28]. After chemical activation in AFAC the crystalline and spherical particles break down into amorphous ones and get agglomerated as shown in Fig. 4B. The absence of spherical particles in treated fly ash (as evident from the SEM) indicates high conversion of fly ash to amorphous material. The increased surface roughness after acid leaching is clearly indicated in AFAC catalyst in Fig. 4B.

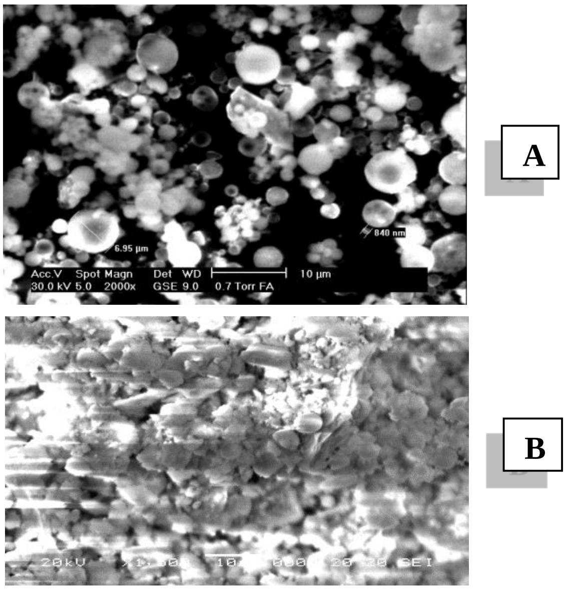


Fig. 4 SEM micrographs of (A) FA and (B) AFAC catalyst.

A typical EDX spectrum of the AFAC catalyst is given in Fig. 5, which indicates that the silica content of FA (61.9%) is greatly increased after chemical activation (84%) and content of other metal oxides are found in small proportion.

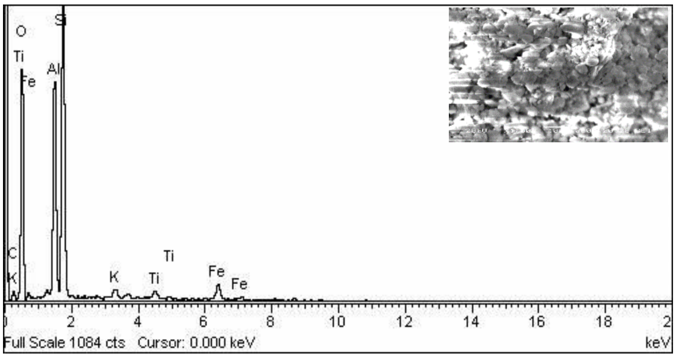


Fig. 5 EDX of AFAC catalyst.

Cite this Article as: S. Anita, A. Rani, Environmental benign route for the utilization of fly ash as nano-crystalline solid acid catalyst for production of phenyl salicylate, J. Nanosci. Tech. 1(1) (2015) 4–8.

3.2 Catalytic Performance of AFAC Catalyst

In order to understand the effect of activation of fly ash on surface acidity and therefore, the catalytic activity, the catalytic performance of AFAC was evaluated for esterification reaction in single step, solvent free condition.

The esterification of salicylic acid with phenol over AFAC was carried out at 140 °C for 4 h, taking salicylic acid/phenol molar ratio 1:2 and salicylic acid to catalyst weight ratio of 10. The esterification of salicylic acid with phenol is a Brønsted acid catalyzed reaction, the higher activity of the catalyst is attributed to higher Brønsted acidity of the catalyst developed due to increased surface hydroxyl groups. The catalyst AFAC was found highly active for esterification of salicylic acid with phenol giving high yield (94%) of phenylsalicylate after 4 h. Results given in Table 1.3 show that FA did not possess any catalytic activity for studied reaction, while AFAC catalyst showed maximum activity.

Table 3 Catalytic activity of FA and AFAC catalyst for esterificatio reaction.

Catalyst	% Conversion	%Yield
FA	Nil	Nil
AFAC	84	94

Reaction conditions: Time = 4 h; Temperature = 140 °C; molar ratio (salicylic acid / phenol = 1:2); substrate/catalyst ratio = 10; activation of NAFA catalyst = 550 °C for 2 h.

3.3 Recyclability of the catalyst

The spent catalyst from the reaction mixture was filtered, washed with acetone and regenerated at 450 °C to use for the next reaction cycles. The data in Table 4 shows that catalyst was equally efficient up to 4 reaction cycles for reaction giving similar conversion of salicylic acid in the range 84-77%. It shows that the catalyst is easily regenerated by thermal treatment without loss of catalytic activity (Fig. 6).

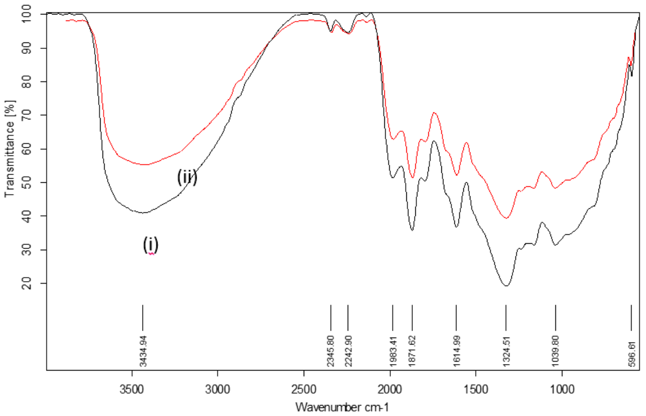


Fig. 6 FT-IR spectra of (i) fresh NAFA catalyst and (ii) regenerated AFAC catalyst.

The conversion was significantly decreased after fourth reaction cycle, which is attributed due to the deposition of carbonaceous material on the external surface of the catalyst, which may block the active sites present on the catalyst.

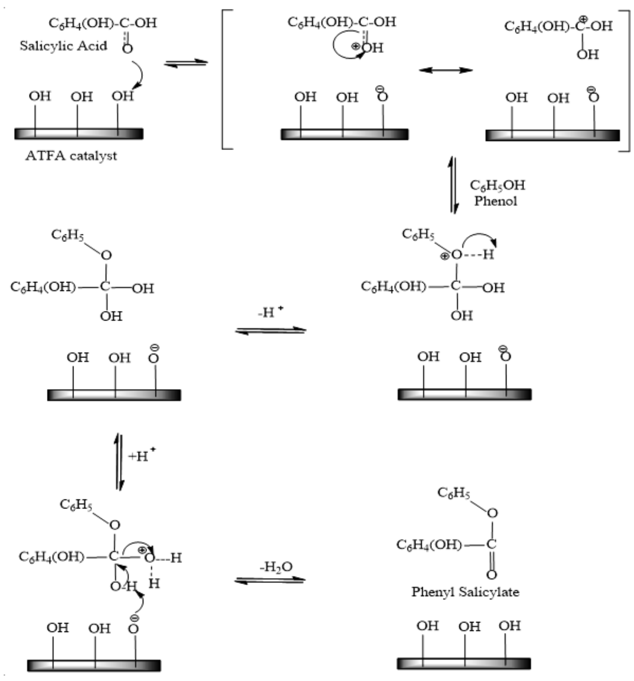
Table 4 Conversion of salicylic acid with regenerated AFAC catalyst.

Reaction cycle	%Conversion	%Yield
I	84	94
II	81	92
III	80	89
IV	77	82

Reaction conditions: substrate/catalyst = 10; Temperature = 140 °C; Time = 4 h; molar ratio = 1:2; catalyst activation = 550 °C for 2 h.

3.4 Proposed Mechanism

Esterification reaction takes place between salicylic acid and phenol, adsorbed on the acid site of catalyst, forming an electrophile by abstracting a proton from the catalyst, and then the phenol reacts with carbonium ion to form intermediate species which further gives (Scheme 3) salol, with subsequent removal of water molecule.



Scheme 3 Proposed mechanism of esterification of salicylic acid with phenol over AFAC catalyst.

4. Conclusion

This article deals with application of fly ash supported nano crystalline solid acid catalysts (AFAC) with crystallite size of 14 nm, for esterification of phenol. The process adopted for their preparation, their textural properties, thermal treatment, reuse, and leaching aspect have been discussed. The catalyst has reduced particle diameter 3.71 µm quite less than that of FA (37.7 µm). The surface area of the catalyst is 5.80 m^2/g. The chemical activation of fly ash by acid leaching resulted in increased amorphous silica content up to 84% and thus increased surface hydroxyl groups responsible for surface acidity. The prepared catalyst possessed sufficient acidity to catalyze esterification reaction between salicylic acid and phenol, which was conformed from the high yield (94%) of desired product (salol), which has wide application in medicine as internal antiseptic, in paints, waxes, varnishes etc. The solid acid catalyst should be active, selective and stable under the reaction conditions. The catalyst was recyclable up to four reaction cycles, showing that the catalyst had stable acid sites which were not lixiviated during the reaction. The industrial scale use of the catalytic material not only may give an effective partial solution for bulk utilization of waste fly ash, but also provide a low cost solvent free production of phenyl salicylate.

Acknowledgement

The authors are thankful to Dr. D.D. Phase and Er. V.K. Ahiray for SEM-EDX analysis and Mukul Gupta for XRD conducted at UGC DAE-CSR Lab Indore. XRF analysis was conducted at Punjab University, Chandigarh. The financial support was provided by Fly Ash Mission, Department of Science and Technology, New Delhi, India.

References

[1] K. Wilson, J.H. Clark, Solid acids and their use as environmentally friendly catalysts in organic synthesis, Pure Appl. Chem. 72 (2000) 1313-1319.
[2] Y.C. Sharma, B. Singh, Advancements in solid acid catalysts for eco-friendly and economically viable synthesis of biodiesel, Biofuels. Bioprod. Bioref. 5 (2011) 69-92.
[3] http://en.wikipedia.org/wiki/Acid_catalysis (Accessed on 10th June 2015)
[4] M.D. Romero, J.M. Gomez, A.G. Sanz, Study of the influence of alcohols in the synthesis of short chain esters, Chem. Eng. Trans. 24 (2011) 37-42.
[5] G.D. Yadav, M.S. Mujeebur, S. Rahnuman, Clean Technol. Environ. Policy 5 (2003) 128-135.
[6] J.A. Barberio, L.G. Gomella, S. Underwood, C.A. Beck, Nurse's Pocket Drug Guide, McGraw Hill, New York, 2010.
[7] W. Sneader, Drug discovery: A history, John Wiley and Sons, New York, 2005, pp. 358-390.
[8] S. Jansri, G. Prateerpchaikul, S.B. Ratanawilai, Acid-catalyzed esterification: a technique for reducing high free fatty acid in mixed crude palm oil, Kasetsart, J. Nat. Sci. 41 (2007) 555-560.

Cite this Article as: S. Anita, A. Rani, Environmental benign route for the utilization of fly ash as nano-crystalline solid acid catalyst for production of phenyl salicylate, J. Nanosci. Tech. 1(1) (2015) 4–8.

[9] L.L. Borer, Experiments with aspirin, J. Chem. Edu. 77 (2000) 354-355.

[10] A. Rodriguez, M. Nomen, B.W. Spur, A selective method for the preparation of aliphatic methyl esters in the presence of aromatic carboxylic acids, Tetrahed. Lett. 39 (1998) 8563-8566.

[11] Y. Peng, G. Song, Heteropoly acid catalyzed synthesis of aspirin, J. Chem. Edu. 5 (2000) 144-158.

[12] R.L.E. Furlan, E.G. Mata, O.A. Mascaretti, Butylstannonic acid catalyzed transesterification of carboxylic esters, Tetrahed. Lett. 39(16) (1998) 2257-2260.

[13] M. Shamshuddin, N. Nagaraju, Vapour phase synthesis of salol over solid acids via transesterification, J. Chem. Sci. 122 (2010) 193-201.

[14] G. Kuriakose, N. Nagaraju.Selective, Synthesis of phenyl salicylate (salol) by esterification reaction over solid acid catalysts, J. Mol. Catal. A Chem. 223 (2004) 155-159.

[15] S.Z.M. Shamshuddin, N. Nagaraju, Transesterification: salol synthesis over solid acids, Catal. Commu, 7 (2006) 593-599.

[16] M.J. Iqbal, M.A. Chaudhary, Thermodynamic study of phenyl salicylate solutions in aprotic solvents at different temperatures, J. Chem. Eng. 54(2) (2009) 338-341.

[17] C. Khatri, A. Rani, Synthesis of a nano-crystalline solid acid catalyst from fly ash and its catalytic performance, Fuel 87 (2008) 2886-2892.

[18] D. Jain, C. Khatri, A. Rani, Synthesis and characterization of novel solid base catalyst from fly ash, Fuel 90 (2011) 2083-2088.

[19] R. Kumar, S. Kumar, S.P. Mehrotra, Towards sustainable solutions for fly ash through mechanical activation, Resour. Conserv. Recyc. 52 (2007) 157-179.

[20] F. Blanco, M.P. Garcia, J. Ayala, Variationin fly ash properties with milling and acid leaching, Fuel 84 (2005) 89-96.

[21] S.O. Bada, S. Potgieter-Vermaak, Evaluation and treatment of coal fly ash for adsorption application, J. Prac. Technol. 12 (2008) 37-48.

[22] J.C. Benezet, P. Adamiec, A. Benhassaine, Relation between silico-aluminous fly ash and its coal of origin, Particuology 6 (2008) 85-92.

[23] F. Blanco, M.P. Garcia, J. Ayala, G .Mayoral, M.A. Garcia, The effect of mechanically and chemically activated fly ashes on mortar properties, Fuel 85 (2006) 2018-2026.

[24] C. Khatri, D. Jain, A. Rani, Fly ash-supported cerium triflate as an active recyclable solid acid catalyst for Friedel–Crafts acylation reaction, Fuel 89 (2010) 3853-3859.

[25] B. Samah, H. Mukhtar, S.M. Shaharun, Effect of organic and inorganic acid pretreatment on structural properties of rice husk and adsorption mechanism of phenol, Int. J. Chem. Environ. Eng. 3(3) (2012) 192-200.

[26] E.P. Parry, An infrared study of pyridine adsorbed on acidic solids characterization of surface acidity, J. Catal. 2 (1963) 371-379.

[27] Y. Du, X. Du, M.S. George, Mechanism of pyridine-catalyzed SiO_2 atomic layer deposition studied by fourier transform infrared spectroscopy, J. Phys. Chem. C 111 (2007) 219-226.

[28] B.G. Kutchko, A.G. Kim, Fly ash characterization by SEM-EDS, Fuel 85 (2006) 2537-2544.

Cite this Article as: S. Anita, A. Rani, Environmental benign route for the utilization of fly ash as nano-crystalline solid acid catalyst for production of phenyl salicylate,
J. Nanosci. Tech. 1(1) (2015) 4–8.