

Solid acid catalyst for isobutyl propionate production from solid waste

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Abstract

This paper presents a study of the isobutanol based esterification of propionic acid with the synthesized solid acid catalyst (NAFA) at different temperature and reaction time. An efficient nano crystalline solid acid catalyst (NAFA) with crystallite size of 14 nm has been synthesized by F-type fly ash (SiO_2 and $\text{Al}_2\text{O}_3 > 70\%$) by chemical activation using concentrated HNO_3 at 110°C . The Catalyst was characterized by XRD, FT-IR, and SEM techniques. Fly ash generated catalytic material has shown sufficient catalytic activity for esterification of propionic acid and isobutyl alcohol to give isobutyl propionate, which is widely used in food and beverage industries as a rum flavor. The catalyst was completely recyclable without significant loss in activity up to four 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.

Keywords: Fly ash, Chemical activation, Acid treatment, Esterification, Eco-friendly and Isobutyl propionate (RUM).

Introduction

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.¹ Esters cover a very wide category ranging from aliphatic to aromatic with various substitutions and multifunctional groups.²

Isobutyl propionate is food spices. Mainly for the preparation of rum, strawberries and other fruits flavor. It can be synthesized by esterification of propionic acid with isobutanol using acid catalyst. Commercially this reaction was carried out using various homogeneous acid catalysts such as H_2SO_4 , HF, H_3PO_4 and other mineral acids which are environmentally hazardous, corrosive, nonreusable, poring several disadvantages in industrial processes,

produce neutralization waste and also include wasting large amount of catalyst etc.³⁻⁷

The esterification reaction have been widely investigated using several solid acids such as, nano-sized silicotungstic acid (STA) supported on zirconia embedded inside the various mesoporous silicas such as SBA-15, MCM-41 and MCM-48,^{8,9} Amberlyst-36,¹⁰ cation-exchange resin catalyst, Purolite CT-175,¹¹ ZrO_2 supported tungstophosphoric (TPA)¹² and molybdophosphoric (MPA).¹³

The present research paper elaborates an innovative support material Fly ash is selected which is a solid waste generated in power plants and being rich in silica is used in synthesizing NAFA Catalyst having wide applications in production of Isobutyl Propionate (RUM), used in food and beverage industries. This catalyst may also be explored for other esterification products to be used in synthesis of food preservatives and pharmaceutical.

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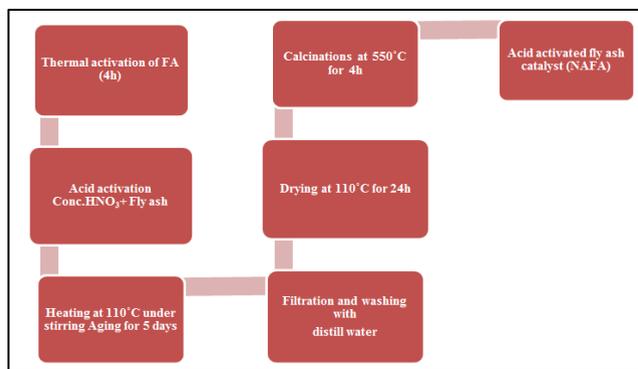
Experimental Apparatus and Methods

Raw material and reagents

HNO₃ (98%), Isobutyl alcohol (99%) was purchased from S. D. Fine Chem. Ltd. and Propanoic acid (99%) from Merck AG. The coal fly ash (Class F-type) used as solid support was collected from Tata Thermal Power Plant, Jamshedpur.

Apparatus and catalyst synthesis procedure

As received fly ash was thermally activated at 900°C for 4h to remove C, S, and other Impurities. Chemical activation was carried out by treating fly ash with concentrated nitric 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.¹⁴ The chemically activated material was thermally stabilized by calcinations at appropriate temperature for 4h in static conditions. The scheme for the preparation of NAFA catalyst is given in Scheme



Scheme 1.1: Synthesis of acid activated fly ash catalyst (NAFA) from fly ash.

Catalyst characterization techniques

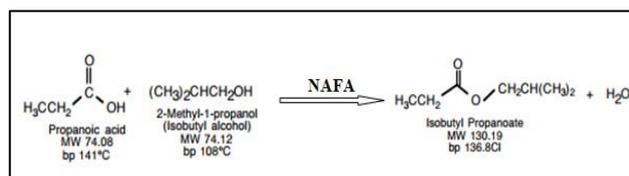
The silica content of the fly ash samples after activations were analyzed by X-ray fluorescence spectrometer (Philips PW1606). The BET surface area was measured by N₂ adsorption-desorption isotherm study at liquid nitrogen temperature (77 K) using Quantachrome NOVA 1000e surface area analyzer.

FTIR spectra of the materials were recorded in the range 550 – 4000 cm⁻¹ with a resolution of 4 cm⁻¹ using FTIR Tensor 27 Bruker with DR (Diffuse

Reflectance) accessory. The detailed imaging information about the morphology and surface texture was provided by SEM-EDX (Philips XL30 ESEM TMP). 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).

Catalytic activity of NAFA

The catalytic performance of the NAFA catalyst was evaluated by esterification of propionic acid with isobutanol (Scheme 1.2) to give Isobutyl Propionate (RUM) as test reaction in a liquid phase batch reactor.



Scheme 1.2: Esterification of propionic acid with isobutanol over NAFA catalyst.

Esterification of propionic acid with isobutanol

The esterification of propionic acid with isobutanol using NAFA catalyst was carried out in a liquid phase batch reactor. In the procedure, isobutanol and propionic acid (molar ratio of isobutanol with propionic acid = 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 activated at 550°C for 2h prior to the reaction in static air, was added in the reaction mixture. The reaction mixture was heated at required reaction temperature ranging from 110°C to 130°C for difference time from 1h to 2h. Process parameters such as reaction time, temperature, molar ratio of the reactant, weight of the catalyst and acid to alcohol molar ratio were optimized to achieve maximum conversion

After a stipulated time the reaction mixture was cooled to room temperature, acetone was added to dissolve the unreacted 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 N₂ (1.5 ml/min) as a carrier gas.¹⁵

Table:

S. No.	Substrate	Mole ratio	Product (esters)	Catalyst amount (g)	Reaction Time (h)	Temperature (°C)	% Yield
1.	Isobutanol + propionic acid	1:1	Isobutyl propionate (RUM)	0.2	2	110°C	68
		1:1		0.2	2	120°C	78
		1:1		0.2	2	130°C	88
		1:1.5		0.2	2	120°C	90
	Optimized condition	1:2		0.2	2	120°C	98
		1.5:1		0.2	2	120°C	82
		1:1.5		0.2	2	130°C	94

Catalyst Regeneration

After completion of the reaction, catalyst was filtered and washed thoroughly with acetone and dried in an oven at 110°C for 12h followed by activation at 500°C for 2h in static condition prior to the use in next reaction cycle under the similar reaction conditions.

Result and Discussion

Characterization of fly ash catalysts

The chemical composition of FA and NAFA catalyst are summarized in Table 1.1 and 1.2, which shows that after chemical activation the silica content in NAFA catalyst is greatly increased (61.9% to 84%). The BET surface area of NAFA catalyst (5.8 m²/g) is also increased as compared to FA (0.97 m²/g) while particle diameter is reduced (FA = 37.7 μm and NAFA = 3.71 μm) during chemical activation.^{16,17} The increase in silica content after activation shows the loss of other components during the chemical activation with higher concentration of HNO₃.¹⁸

Table 1.1: Chemical composition of fly ash samples before and after chemical activation.

Sample	SiO ₂ (wt%)	Al ₂ O ₃ (wt%)	Fe ₂ O ₃ (wt%)	CaO (wt%)	MgO (wt%)	TiO ₂ (wt%)	Na ₂ O (wt%)	K ₂ O (wt%)	Other element	LOI
FA	61.9	29.7	2.65	0.46	0.36	1.33	0.14	0.79	2.67	2.6
NAFA	84	11.7	1.60	0.22	0.18	0.87	0.06	0.39	0.98	1.45

Table 1.2: Physico-chemical properties of FA and NAFA catalyst

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

Powder X-ray diffraction patterns of FA (Fig. 1.1A) and NAFA catalyst (Fig. 1.1B) show the existence of crystalline phases (mullite, quartz, hematite and small amounts of magnetite) and amorphous phases.^{19,20} 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 NAFA (Fig. 1.1B) shows, that the crystallinity is decreased due to removal of most of the crystalline components present in FA, thus increasing the amorphous nature.²¹ The characteristic peaks of quartz in the NAFA are more concentrated in these fractions and indicate increment in SiO₂ concentration. The increase in quartz content leads to decrease in particle size distribution of fly ash.

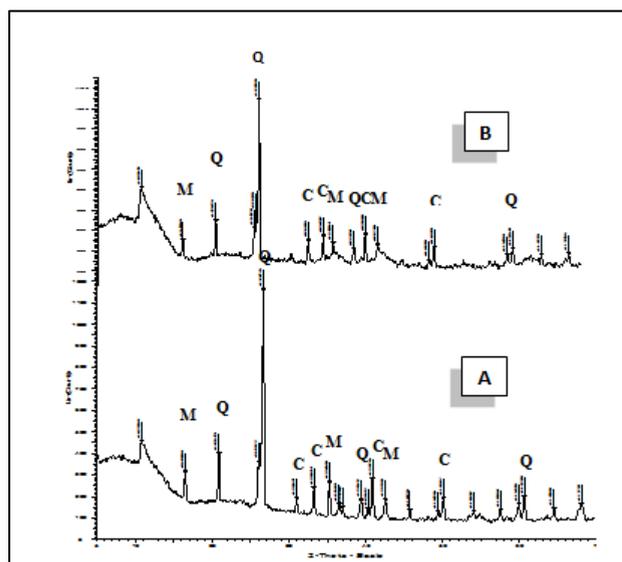


Fig. 1.1: X-ray diffraction pattern of A.) FA and B.) NAFA Catalyst

(Q = Quartz, C = Calcite, M = Mullite)

The FT-IR spectrum of FA (Fig. 1.2 (i)) 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. 1.2(ii)). 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⁻¹.²²

The increased amorphous silica is characterized in NAFA 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 NAFA, after chemical activation (Fig. 1.2(ii)), 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 HNO₃ (Fig. 1.2(ii)).²³

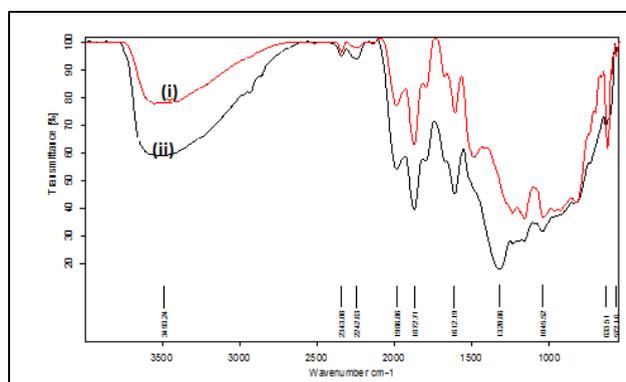


Fig. 1.2: FT-IR spectra of (i) FA and (ii) NAFA catalyst.

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. 1.3 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.^{24,25} The intensity of absorption band at 1552 cm⁻¹ assign exclusively for Brønsted acidity in NAFA catalyst due to intense hydrogen bonding at higher concentration of HNO₃.

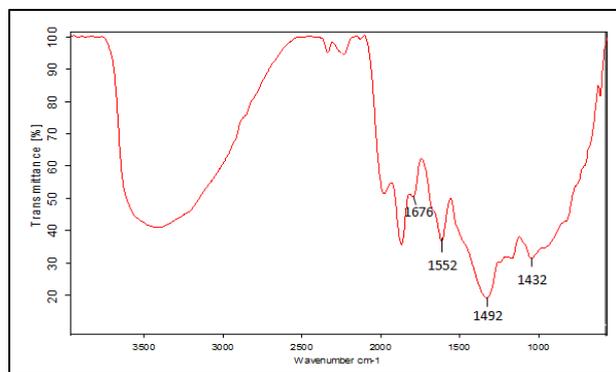


Fig. 1.3: FT-IR spectra of pyridine-adsorbed NAFA catalyst.

SEM micrograph of FA (Fig. 1.4A) 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.²⁶ After chemical activation in NAFA the crystalline and spherical particles break down into amorphous ones and get agglomerated as shown in Fig. 1.4B. 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 NAFA catalyst in Fig. 1.4B.

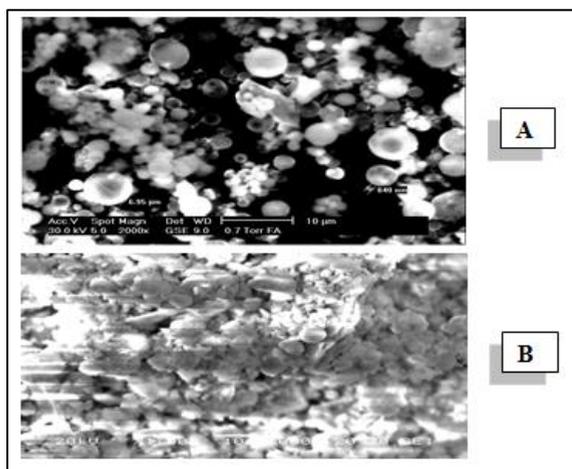


Fig. 1.4: SEM micrographs of (A) FA and (B) NAFA catalyst.

Catalytic performance of NAFA Catalyst

In order to understand the effect of activation of fly ash on surface acidity and therefore, the catalytic

activity, the catalytic performance of NAFA was evaluated for esterification reaction in single step, solvent free condition.

The catalyst NAFA was found highly active for esterification of propionic acid with isobutanol giving high yield (94%) of isobutyl propionate (RUM) after 2h. Results given in Table 1.3 show that FA did not possess any catalytic activity for studied reaction, while NAFA catalyst showed maximum activity.

Table 1.3: Catalytic activity of FA and NAFA catalyst for esterification reaction

Catalyst	% Conversion	% Yield
FA	Nil	Nil
NAFA	84	94

Conclusion

This article deals with application of fly ash supported nano crystalline solid acid catalysts (nafa) with crystallite size of 14 nm, for esterification of propionic acid and isobutanol. 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 μ m quite less than that of FA (37.7 μ m) (Table 1.2). The surface area of the catalyst is 5.80 m²/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 excellent acidic properties of synthesized catalyst have been evaluated by means of esterification of propionic acid with isobutanol to give high yield 94% of desired product isobutyl propionate (rum), which has found wide applications as in beverage industries as a rum flavor.

The catalyst was easily separated by simple filtration, regenerated and reused several times with equal efficiency, thus produces no waste and makes the process economic.

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Conflict of Interest

None.

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