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Acid Activated fly Ash, as a Novel Solid Acid Catalyst for Esterification of Acetic Acid

KEYWORDS Fly ash; Mechanical activation; Chemical activation; Acid treatment

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ABSTRACT *An efficient solid acid catalyst (AAFA) 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 HCl at 110°C. The activation of fly ash resulted in increased silica content (79%) and surface area (5.42 m^2/g) having sufficient silanol activity for esterification of n-butanol and acetic acid. The catalyst was characterized by XRD, FT-IR, and SEM techniques. The product n-butyl acetate is an important fine chemical intermediate, widely used in pharmaceutical and as flavoring agent in confectionary. 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

Acid catalyzed esterification is one of the most important industrial reactions, which are widely employed in synthetic organic process industries. Generally n-butyl esters of acetic acid are prepared under liquid phase, refluxing the reactant in the presence of small amount of concentrated H_2SO_4, HCl, HI, $AlCl_3$, BF_3, $ZnCl_2$, SbF_5 phosphoric acid and p-toluenesulfonic acid as the catalyst in homogenous systems [1]. The use of the above mentioned 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 in synthetic organic chemistry. Solid acids such as zeolites (ZSM-5), 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 for esterification reaction [2,3].

A number of solid acids such as ion exchange resin eg. Amberlyst 15, smopex-101 [4,5] , mesoporous molecular sieves like mesoporous Al-MCM-41, H-Mordenite [6] , H-beta [7] , H-ZSM-5 and HY zeolites [8,9] , solid super acids [10] and heteropolyacids (salts), lipase, sulfonic acids supported on molecular sieves, active carbon [11-13] , niobic acid and supported heteropoly acids (eg. $H_4SiW_{12}O_{40}$/ ZrO2), γ-alumina-supported vanadium oxide catalysts, sulfated zirconia and tetravalent metals acid salts [14] , hafnium (IV) and zirconium (IV) salts [15] , $Zr(SO_4)_2.4H_2$[16] and modified zirconia catalyst have also been found to be acidic in nature and catalyze esterification, alkylation and condensation reactions [17,18]. In our previous work, fly ash has been used for developing several solid acid catalysts by loading cerium triflate, sulphated zirconia and used for the synthesis of aspirin, oil of wintergreen, 3, 4-dimethoxyacetophenone (anti neoplastic) and diphenylmethane [19-21].

The present work elaborates the synthesis of AAFA catalyst to have high acidity and catalytic activity for esterification reaction to produce n-butyl acetate with high yield and purity up to five reaction cycles. This investigation brings into light the structural aspects of a solid acid which exhibit good conversion and yield of an industrially important chemical "n-butyl acetate" an important chemical intermediate, widely used in pharmaceutical and as flavoring agent in confectionary, under solvent free conditions and in low cost route.

2. Experimental methods

2.1 Materials

Class-F type fly ash was collected from Kota Thermal Power Plant, Kota (Rajasthan) HCl (98%); Acetic acid (98%) and n-butanol (99%) were purchased from S. D. Fine Chem. Ltd. and used as such.

2.2 Catalyst Synthesis

As received fly ash was ball milled (1h at room temperature) followed by thermal activation at 900°C for 4h .The chemical activation of mechanically activated fly ash (MFA) was carried out in a stirred reactor by stirring 5M aqueous solution of mineral acid (HCl) in the ratio of 1:2 (FA: HCl) for 5 days at 110°C temperature followed by washing till pH 7.0 with complete removal of soluble ionic species (Cl^-, NO_3^-, SO_4^{2-}, ClO^{4-} etc.) and drying at 110°C for 24h. The obtained solid acid catalyst (AAFA) was calcined at 500°C for 4h under static conditions in a muffle furnace.

2.3 Characterization Techniques

2.3.1. Physicochemical properties of AAFA

The silica content of the fly ash samples after mechano-chemical activations were analyzed by X-ray fluorescence spectrometer (Philips PW1606). 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°. The FT-IR study of the samples was done using FT-IR spectrophotometer (Tensor-27, Bruker, Germany) in DRS (Diffuse Reflectance Spectroscopy) system. The detailed imaging information about the morphology and surface texture of the sample was provided by SEM-EDAX (Philips XL30 ESEM TMP).

2.3.2. Catalytic activity

The esterification of n-butanol with acetic acid was performed in liquid phase batch reactor consisting of 50 ml round bottom flask with condenser in a constant temperature oil bath with magnetic stirring. A mixture of acetic acid and n-butanol (molar ratio of n-butanol and acetic acid is = 1:2) was taken in a 50 ml round bottom flask. The catalyst (substrate to catalyst ratio = 10), activated at 500°C for 2h was added in the reaction mixture. After completion of the reaction the catalyst was filtered and the product was analyzed by Gas Chromatograph.

2.3.3 Catalyst regeneration

The spent catalyst was washed with acetone, dried in oven at 110°C for 12h followed by calcinations at 500°C for 2 h and reused for next reaction cycle under similar reaction conditions as earlier.

3. Results and Discussion

3.1 Catalyst Characterization

A comparison of FA, MFA, TFA and AAFA catalyst is given in Table 1, which shows that after mechanical activation BET surface area is increased from 0.97 m^2/g to 2.57 m^2/g, which is further increased to 5.42 m^2/g after chemical activation. This result confirms that the$_2$AAFA catalyst has a higher specific surface area of 5.42 m /g than the heat-treated fly ash with 2.99 m^2/g [22, 23]. The particle diameter is reduced from 37.7 μm to 3.12 μm during milling, increased slightly (3.71 μm) after chemical activation [24]. The mechanical activation did not indicate any perceptible change in silica content of fly ash but the chemical activation increased the silica amount greatly (58% to 79%) [25].

Table 1: Physico-chemical properties of FA, MFA, TFA and AAFA catalyst.

Catalyst	Silica (Wt %)	Crystallite size (nm)	BET surface area (m^2/g)	Particle diameter (μm)
FA	58	33	0.97	37.7
MFA	59	21	2.57	3.12
TFA	70	18	2.99	3.10
AAFA	79	16	5.42	3.71

FA (Fly ash); MFA (mechanically activated fly ash); TAFA (thermally activated fly ash) and AAFA (chemically activated fly ash).

The XRD pattern of the FA showed (figure 1a) the presences of quartz, mullite, iron oxide, hematite, sulfur oxide, small amounts of magnetite [26], CaO and amorphous phases. The XRD studies of milled fly ash (figure 1b) indicate that decrease in crystallite size from 33 to 21 nm results in increased amorphous content in it but after thermal activation the crystallinity is increased slightly as indicated by higher peak intensities in Figure 1b and c. [27]. After chemical activation of thermally activated fly ash, the crystallinity is further decreased due to removal of most of the crystalline components present in FA, thus increasing the amorphous nature [28, 29].

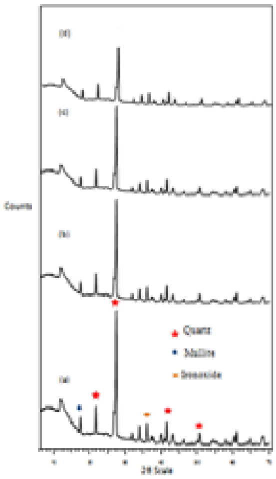

Figure 1: X-ray diffraction pattern of (a) FA (b) MFA (c) TFA and (d) AAFA catalyst.

The FT-IR spectra of FA, MFA, TFA and AAFA in Figure2a-d show broad band between 3500-3000 cm^{-1}, which is attributed to surface -OH groups of Si-OH and adsorbed water molecules on the surface. The increment in broadness after ball milling is an evidence for the breaking down of the quartz structure and formation of Si-OH groups [30]. However, FT-IR studies clearly show changes in the broadening of IR peaks corresponding to Si-O-Si asymmetric stretching vibrations indicating structural rearrangement during mechanical milling.

The FT-IR spectra of AAFA shows the tremendous increment in broadness at 3500-3000 cm^{-1} region as compared with FA,MFA and TFA which reflects strong hydrogen bonding between the hydroxyl groups due to increase in silica content and loss of significant amount of other components (Figure 2d). The increased amorphous silica in the activated fly ash can be characterized by an intense band in the range 1000-1300 cm^{-1} corresponding to the valence vibrations of the silicate oxygen skeleton. The main absorption band of the valence oscillations of the groups Si-O-Si in quartz appears with a main absorption maximum at 1162 cm^{-1} [20].

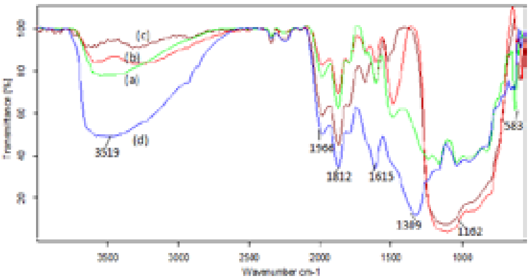

Figure 2: FT-IR of (a) FA (b) MFA (c) TFA and (d) AAFA catalyst.

SEM micrograph of the FA (Figure 3a) indicates that the most of the particles present in the fly ash are micro-particles in the shape of smooth balls (microspheres) with a relatively smooth surface grain. SEM image of MFA (Figure 3b) shows the structural break down of larger particles and increased surface roughness. The smooth spherical cenospheres are affected most resulting remarkable changes in morphology. After chemical activation with acid, rough cenospheres are transformed into agglomerations of more amorphous undefined shapes with no observation of crystal formation as seen in SEM micrographs presented in Figure 3a-d [31].

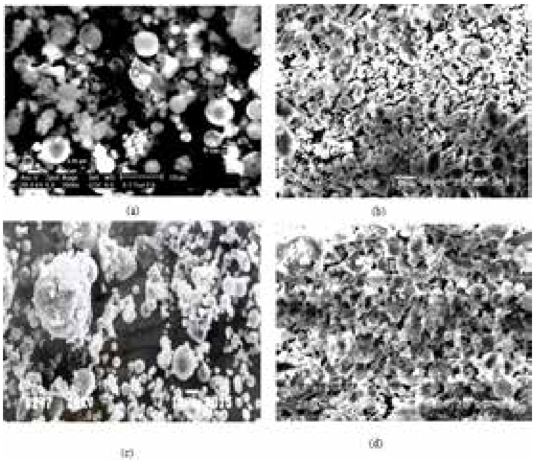

Figure 3: SEM images of (a) FA (b) MFA (c) TFA (d) AAFA.

4. Catalytic performance

To measure the catalytic performance of catalyst, esterification of acetic acid with n-butanol over AAFA was carried out at 110°C for 4h, taking n-butanol/acetic acid molar ratio 1:2 and n-butanol to catalyst weight ratio of 10. The catalyst AAFA was found highly active for esterification of acetic acid with n-butanol giving high selectivity (99.6%) and yield of n-butyl acetate after 4h under optimized conditions, whereas both FA as well as MFA did not possess any catalytic activity.

The esterification of acetic acid with n-butanol was also carried out at different temperature ranging from 90°C to 130°C for 4h to optimize the reaction temperature giving maximum conversion of n-butanol to n-butyl acetate. The result shows that the maximum conversion (87.3%) of n-butanol to n-butyl acetate is found at 110°C, which remains almost, steady till 130°C.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 catalyst was equally efficient up to five reaction cycles.

5. Conclusion

The study provides fly ash supported AAFA as an efficient solid acid catalyst possessing significant amount of acidity. The specific surface area of FA (0.97 m^2/g) was greatly enhanced after mechanical, thermal and chemical activation using HCl. AAFA catalyst possessed surface area upto 5.42 m^2/g with greater number of surface silanols responsible for surface acidity as evident by comparatively broad band at 3500-3000 cm^{-1} in FT-IR spectra.

AAFA catalyst catalyzed the esterification of acetic acid with n-butanol giving high yield of the product n-butyl acetate in heterogeneous, solvent free optimized reaction conditions. It is concluded that the mechno-chemical activation can generate sufficient activity on fly ash surface rendering its potential application in heterogeneous catalysis.

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