



A green and efficient solid acid catalyst from coal fly ash for Fischer esterification reaction



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ABSTRACT

A green and efficient solid acid catalyst (SAC) has been synthesized upon modification of F-type fly ash using ortho-phosphoric acid (35 wt. %). Catalyst characterization has been accomplished using different analytical techniques, such as FT-IR, XRD, SEM-EDS, and BET surface area analysis. SAC possessed excellent catalytic activity for Fischer esterification reaction between 4-aminobenzoic acid and methanol at 95 °C to produce methyl 4-aminobenzoate (MAB), an important precursor for the synthesis of pharmaceutical drugs, (±) martinelline, and (±) martinellinic acid. This investigation suggests the utilization of fly ash to develop novel solid acid catalyst system for catalyzing industrially important esterification reaction.

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Introduction

Fly ash is a coal combustion by-product, which is collected from the electrostatic precipitators in the smokestacks of coal-burning thermal power plants. Fly ash is a heterogeneous mixture of amorphous and crystalline phases with oxides of Si, Al, Ca, Fe, Mg, and Na as the predominant components along with some trace elements like B, Mo, Se, Sr, Ba, Mn, Ti, and Zr [1–3]. Every year, more than 300 billion tons of fly ash are generated all over the world [4,5] and the disposal of large amounts of fly ash has become a serious environmental problem. Only a small percentage (about 15%) of this waste is currently utilized as the construction materials, the adsorbents for gas, and water treatment or the starting material to synthesize zeolite [6–8]. Catalysts developed from a modification of fly ash have been applied in catalyzing oxidation [9], chlorination [10], Claisen–Schmidt condensation [11], Knoevenagel condensation [12], and Beckmann rearrangement [13].

Products obtained upon esterification are widely utilized as perfumery compounds [14] and drugs [15]. To effectuate valuable esterification reactions, the most frequently used catalysts are heteropoly acids [16] and homogeneous acids such as H₂SO₄,

H₃PO₄ [17]. But these acids are hazardous, corrosive, and difficult to recover from the reaction mixture. As a result, a large amount of environmentally hazardous acidic waste is produced. Replacement of traditional homogeneous Lewis and Brønsted acid catalysts by heterogeneous ones, such as solid acid catalysts like zeolites, sulfated zirconia, and acidified silica [18] represents a more eco-friendly alternative to the organic reactions. Esterification reactions of free fatty acids in sunflower oil [19] and palmitic acid with methanol [20] using solid acid catalysts are well documented in literature. Moreover, Ce/ZrO₂-TiO₂/SO₄²⁻ [21] and zinc oxide [22], supported ionic liquids [23] and cobalt oxide nanoparticles [24], sulfated Si-doped ZrO₂ [25], and zirconium-containing metal organic frameworks [26] have been used as efficient and active catalysts to perform various esterification reactions.

During acid treatment, fly ash is chemically activated upon dissolving in the acid [27]. Since most of the elements, such as alumina and iron are easily eliminated via acid leaching, the silica content of fly ash is increased by using strong acids [28]. Fly ash can be used as a catalyst and catalytic support for esterification reaction as it contains high silica content, which is associated with a significant amount of surface acidity [29].

Recently, the authors instigated an efficient solid-base catalyst from modification of coal combustion fly ash for dibenzylideneacetone synthesis [30]. In the present work, we have introduced an innovative, highly efficient, cost-effective, and regenerable solid acid catalyst (SAC) for Fischer esterification

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reaction of 4-aminobenzoic acid with methanol to produce methyl 4-aminobenzoate (MAB), an important precursor for the synthesis of pharmaceutical drugs, (\pm) martinelline, and (\pm) martinellie acid [31,32]. So far, the utilization of fly ash to synthesize MAB is unprecedented in literature. The catalyst was synthesized using o-phosphoric acid (35 wt. %) over thermally activated F-type fly ash. The mineralogical, morphological, and physicochemical characteristics of the solid acid catalyst have been investigated. The reaction conditions, such as temperature ($^{\circ}\text{C}$), time (min), catalyst to substrate weight ratio (w/w) were optimized for maximum yield (%) of the desired product.

Experimental

Materials

4-aminobenzoic acid (99.0%) has been purchased from Alfa Aesar. Ortho-phosphoric acid (85%) and Methanol (99.0%) have been obtained from Hi-media Chem. Ltd., India. Acetone (99.5%) was purchased from Nice Chemicals Pvt. Ltd., India. F-type fly ash having SiO_2 (56.4%), Al_2O_3 (29.2%), Fe_2O_3 (6.1%), TiO_2 (1.3%), K_2O (1.1%), CaO (0.6%), P_2O_5 (0.3%), MgO (0.16%), Na_2O (0.11%), MnO (0.04%), SrO (0.03%), and SO_3 (0.01%) analyzed by X-ray fluorescence spectrophotometer (Phillips PW 2404) was collected from Farakka Super Thermal Power Plant, West Bengal, India.

Methods

In a systematic sampling procedure, homogenized fly ash washed with deionised water was placed into a pan and oven-dried at $105 \pm 0.5 \text{ }^{\circ}\text{C}$ for 12 h. The dried sample was sieved and less than $45 \mu\text{m}$ sized fraction has been taken to obtain the solid acid catalyst.

Synthesis of solid acid catalyst (SAC)

The solid acid catalyst (SAC) was synthesized by acid modification of thermally activated F-type fly ash with o-phosphoric acid through reflux technique. A total of 12 g of sieved fly ash (particle size $< 45 \mu\text{m}$) and o-phosphoric acid (35 wt. %) were assimilated into 100 ml conical flask. The mixture was refluxed at $95 \text{ }^{\circ}\text{C}$ and 1200 rpm for 135 min under constant stirring. The resulting solid was separated by filtration. For removal of the leached impurities, the solid was washed with distilled water. The solid was dried at $105 \text{ }^{\circ}\text{C}$ for 6 h and thermal stabilization of acid modified fly ash was executed by calcination at $300 \text{ }^{\circ}\text{C}$ for 3 h.

Catalyst characterization

Surface functional groups of the solid acid catalyst (SAC) has been identified using fourier transform infra-red (FT-IR) spectrophotometer (Bruker) having a diffuse reflectance scanning system by mixing the sample with dried KBr in the range $400\text{--}4000 \text{ cm}^{-1}$.

X-ray powder diffractometer (Windmax) was used to analyze the crystalline nature and crystallite size of the samples by X-ray diffraction study using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 30 kV and 15 mA. The samples were scanned in a 2θ range of $0\text{--}80$ and using

Debye–Scherrer equation [33], average crystallite size was estimated.

$$B = 0.9 \lambda / \beta \cos \theta$$

where β is the broadening of the peak (measured as the full-width at half-maximum intensity, FWHM), λ is the X-ray wavelength (1.5406 \AA for Cu-K α), B is the crystallite size, and θ is the angular location of the peak.

Surface area of the synthesized catalyst was determined by the BET surface area analyzer (ASAP 2010) using nitrogen adsorption–desorption at 77 K by the Brunauer–Emmett–Teller (BET) method.

The surface morphology of the solid acid catalyst was analyzed by field-emission gun-scanning electron microscopy (JSM-7600F). An energy dispersive X-ray detector (EDS) mounted on the microscope was used to determine the elemental composition of the SAC.

Catalytic activity of solid acid catalyst

The catalytic performance of solid acid catalyst was evaluated by Fischer esterification of 4-aminobenzoic acid with methanol to produce methyl 4-aminobenzoate (MAB) in solvent-free liquid phase reaction (Scheme 1).

Fischer esterification of 4-aminobenzoic acid with methanol

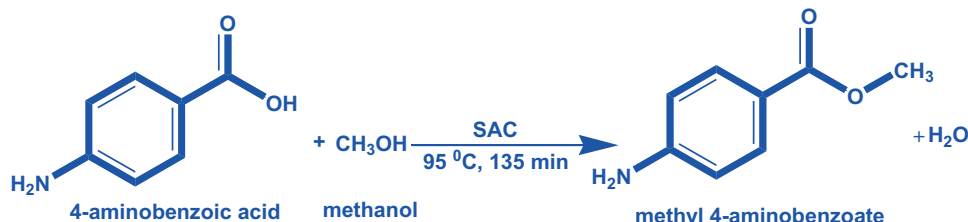
The esterification of 4-aminobenzoic acid with methanol to produce methyl 4-aminobenzoate (MAB) was performed over solid acid catalyst (SAC) in a liquid phase reflux system. The reaction mixture encompassing 4-aminobenzoic acid and methanol (molar ratio 1: 8) was dribbled into a 100 ml round bottom flask, equipped with magnetic stirrer, and condenser, drenched in a constant temperature oil bath. SAC (catalyst to substrate weight ratio = 1: 5) was engulfed in the reaction mixture. At atmospheric pressure, the heterogeneous reaction mixture was refluxed for discrete reaction times varying from 45 to 225 min. Product optimization was procured by effectuating the kinetics at variegated reaction temperatures ranging from $65\text{--}105 \text{ }^{\circ}\text{C}$. After cooling, subsequent filtration of the heterogeneous solution results in the production of crystalline solid, methyl 4-aminobenzoate. Recrystallization of the product was performed employing methanol-water system (20: 1) at room temperature. Melting point measurement, FT-IR, and ^1H NMR spectroscopic analysis confirms the formation of the product, MAB.

$$\text{Yield of MAB (\%)} = 100$$

$$\times (\text{grams of MAB obtained} / \text{grams of MAB obtained theoretically}).$$

Regeneration of SAC

With a view to make the process economic for further application, the used solid acid catalyst (SAC) was recovered by filtration from the reaction mixture. The recovered catalyst was washed with acetone and dried in oven at $105 \text{ }^{\circ}\text{C}$ for 6 h followed



Scheme 1. Fischer esterification of 4-aminobenzoic acid with methanol over solid acid catalyst (SAC).

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