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An efficient solid base catalyst from coal combustion fly ash for green synthesis of dibenzylideneacetone

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ABSTRACT

The objective of the investigation was to evaluate the catalytic efficiency of a solid base catalyst (SBC) derived from coal combustion fly ash to synthesize dibenzylideneacetone (DBA, 94% yield). The catalyst was produced using potassium hydroxide (30 wt.%) on thermally activated F-type fly ash. The physico-chemical, mineralogical and morphological characterization of the fly ash and catalyst were performed using XRF, FT-IR, BET surface area analyser, XRD and SEM-EDS. The results of such analysis revealed that the catalyst obtained was associated with strong basic hydroxyl (–OH) sites that were highly suited to produce DBA by crossed aldol condensation reaction.

Introduction

The growing dependence on coal-fired electricity generation has resulted accumulation of huge quantities of coal combustion by product—fly ash which is regarded as a problematic solid waste all over the world. It has become a threat to the environment [1]. Bulk utilization of fly ash is one of the acceptable solution to mitigate such problems. The annual generation of fly ash in India is more than 131 million metric tons, whereas only about 55% of total ash is being utilized in various applications [2]. As trace elements existing in fly ash can leach out and contaminate soil as well as surface and groundwater, their study has become important for environmental protection [3]. Fly ashes have been applied in production of glass-ceramics [4], in manufacture of bricks [5], in composite cements [6], in concrete [7], in recovery of highly valued metals [8–10], in extraction of alumina [11] and silica [12], in agriculture [13], in water and atmospheric pollution control [14], in dye removal [15] and in zeolite synthesis [16].

Coal generated fly ash, a mixture of various inorganic oxides viz. silica, alumina, ferric oxide, calcium oxide and other metal oxides (Mn_2O_3 and TiO_2) along with inert crystalline phases such as mullite, quartz and magnetite [17,18] has been used as a catalytic support in many catalytic reactions [19–21]. Previously, as a catalyst itself, fly ash has been used for H_2 production, deSO_x, deNO_x, hydrocarbon oxidation, hydrocracking, gas-phase oxidation of volatile organic compounds, aqueous-phase oxidation of organics, solid plastic pyrolysis and solvent-free organic synthesis [19]. Catalysts derived from magnetic enriched component of fly ash (ferrosphere) have been used for oxidative conversion of methane [22,23]. Fly ash supported various catalysts were also used for catalytic decomposition of ammonia [24,25], for benzylation of benzene and toluene [26] and for catalytic removal of *p*-nitrophenol in water [27]. Recently, fly ash supported various catalysts were utilized for synthesis of aryl chalcones [28], for biodiesel production by transesterification of sunflower oil with methanol [29], for production of glycerol carbonate by transesterification of glycerol with dimethyl carbonate [30,31] and for vapor phase dehydration of methanol [32].

Heterogeneous catalytic aldol and crossed-aldol condensation is a powerful tool for formation of carbon–carbon bond in many kinds of carbonyl compounds [33]. Previously, Self- and crossed-aldol condensations of ketones and aldehydes have been reported over solid base catalysts [34–37]. Recently, modified calcium oxide has been used as stable solid base catalyst for aldol condensation reaction [38].

Commercially, the base catalyzed reactions are largely performed by using homogeneous bases like NaOH, $Ca(OH)_2$, KOH etc. [39,40]. But these bases are harmful, required in excess stoichiometric amount and difficult to recover from reaction mixture. Hence, high operating costs and severe environmental issues regarding base neutralization, product separation and purification, corrosion and waste generation motivated substantial efforts toward the development of processes mediated by heterogeneous

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catalysts [40]. The solid bases were found best alternative for solving the above said problems of homogeneous bases to make the reactions more selective [40], as the type of basicity (Brønsted or Lewis basic sites) and basic strength of the solid base can be designed according to the requirement of the reactions [41]. The solid bases are also of industrial interest because of their low temperature operation, environment friendly nature and higher selectivity of required product with ease of product separation. Utilization of solid base catalysts such as hydrotalcite, MgO and KF/Al_2O_3 are well documented in literature [39]. Base catalyzed Claisen–Schmidt condensation over NaOH modified fly ash as solid base catalyst has been reported earlier [21]. Such reaction was promoted by metal oxides constituting the fly ash, although, the percentage conversion and selectivity of reaction product were quite low.

In the present investigation, the authors wish to report a new type of solid base catalyst (SBC), developed from fly ash, having catalytic efficiency comparable to other solid bases. SBC was synthesized using potassium hydroxide (30 wt.%) over thermally activated F-type fly ash. The catalyst was utilized for crossed aldol condensation of acetone with benzaldehyde to produce dibenzylideneacetone (DBA), an important compound used as a potential sunscreen component, as a medicine in treatment of oral cancer cells [42], as a ligand in organometallic chemistry [43] and as a reactant in various organic transformations [44,45]. So far the use of fly ash as a solid base catalyst to synthesize DBA is unprecedented in the literature. In this study, the effect of various reaction parameters such as catalyst-substrate weight ratio (w/w), reaction time (hours) and reaction temperature (°C) were also investigated. The catalyst was found effectively recyclable up to four cycles of synthesis, indicating its extraordinary stability, outstanding capability and that the active sites are not lixiviated in the reaction mixture. Thus the work reports an alternative pathway for utilization of solid waste fly ash by using it for developing novel, low-cost, recyclable and effective catalyst system and gives a solution to overcome the use of harmful liquid bases and other costly commercial heterogeneous catalysts for industrially important crossed aldol condensation reactions.

Experimental

Materials

Fly ash was collected from Farakka Super Thermal Power Plant, West Bengal, India. Potassium hydroxide and acetone (99.5%) were purchased from Nice Chemicals Pvt. Ltd., India. Benzaldehyde (98.5%) and chloroform (99.5%) were obtained from Fischer Scientific Ltd., UK. Methanol (99.0%) was supplied from Hi-media Chem. Ltd., India.

Methods

In order to obtain representative sample of fly ash, a systematic sampling procedure was followed. Homogenized fly ash was placed into a pan and oven-dried at 105 °C ± 0.5 °C for 24 h. Subsequently dried sample was sieved and less than 75 μm sized fraction was taken for further process. Thorough physico-chemical, mineralogical and morphological characterization were carried out using XRF (Phillips PW 2404), XRD (Windmax), FT-IR (Bruker), BET surface area analyser (ASAP 2010) and SEM-EDS (JSM-7600F).

Catalyst synthesis

The solid base catalyst (SBC) was synthesized by chemical activation of thermally activated fly ash with potassium hydroxide for which 8 g of sieved fly ash (particle size <75 μm) was washed with distilled water several times to remove dirt and impurities. It was dried and preheated for 4 h at 900 °C to remove C, S and other impurities [46], cooled down to room temperature and then transferred into a 100 ml conical flask. 66.6 ml of KOH (30 wt.%) was transferred into the conical flask and kept in a stirred reactor and refluxed at 70 °C and 1000 rpm for 10 h under constant stirring. The solid thus obtained was separated by filtration, washed several times with distilled water and finally dried at 105 °C for 4 h, followed by calcinations at 250 °C for 2.5 h.

Catalyst characterization

Fourier transform infrared (FTIR) spectrophotometer (Bruker) was used to identify the surface functional groups of the solid base catalyst (SBC) and the spectra were recorded over the range of 4000–400 cm^{-1}.

The crystalline nature and crystallite size of the samples were analyzed by X-ray diffraction study from X-ray powder diffractometer (Windmax) using Cu-*K*α radiation (λ = 1.5406 Å) at 30 kV and 15 mA and the samples were scanned in 2θ range of 0–80°. Average crystallite size was estimated from the peak broadening according to the Debye–Scherrer equation [47]:

$$B = \frac{0.9\lambda}{\beta\cos\theta}$$

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 Å for Cu-*K*α), B is the average crystallite size and θ is the angular location of the peak.

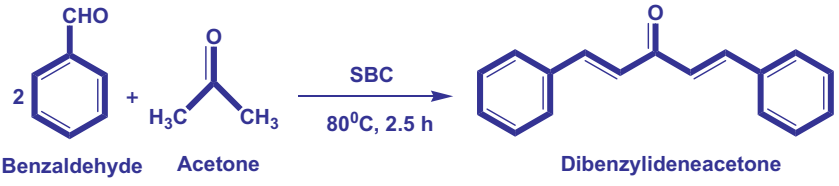
BET surface area analyser (ASAP 2010) was used to study the surface area of the synthesized catalyst by using nitrogen adsorption-desorption at 77 K by the Brunauer–Emmett–Teller (BET) method.

Field emission gun-scanning electron microscopy (JSM-7600F) was used to study surface morphology of the solid base catalyst (SBC). The elemental composition was analyzed by using an energy dispersive X-ray detector (EDS) mounted on the microscope.

Catalytic activity of synthesized catalyst

Crossed aldol condensation of acetone with benzaldehyde

The condensation of acetone with benzaldehyde (Scheme 1) was performed in liquid phase batch reactor consisting of 50 ml round bottom flask with condenser in a constant temperature oil bath with continuous magnetic stirring. A mixture of acetone (5 mmol) and benzaldehyde (10 mmol) was taken in the round



Scheme 1. Crossed Aldol condensation of acetone with benzaldehyde over solid base catalyst (SBC).