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Review article

Porous catalysts fabricated from coal fly ash as cost-effective alternatives for industrial applications: A review

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A B S T R A C T

Coal fly ash (CFA) -an industrial solid waste- has tremendous potential to be used as a starting material for development of valuable porous catalysts and adsorbents because of its silicon and aluminum content. Among various products fabricated from CFA by chemical synthesis process, CFA-based porous catalysts have recently gained remarkable interest among researchers. Each CFA–based catalyst has different properties, the most important of which is the ion exchange capability that depends on the chemical composition and structure of the synthesized product. Studies proved that CFA-based compounds can be used as catalysts/photocatalysts in different environmental processes such as degradation of pollutants. Chemical conversion reactions and synthesis of fine chemicals are among other applications, in which CFA is used as substrate for developing different catalysts. In this review paper, CFA-based catalysts have been classified based on their properties and applications. Methods of characterizations including kinetics and isotherm models are discussed. Furthermore, the effect of several parameters including reaction time, reaction temperature, and the ratio of active compounds to CFA substrate on chemical reactions catalyzed by CFA-based catalysts are discussed. This review paper reveals that CFA-based catalysts are highly efficient compounds not only for application in environmental pollution remediation processes, but also in achieving comparable results in chemical conversion reactions for synthesizing fine chemicals. It can be concluded that CFA as a solid waste should be considered as a low-cost source of alumino-silicate that is a promising candidate for developing inexpensive methods of manufacturing highly efficient and eco-friendly porous catalysts for a wide array of applications.

1. Introduction

Catalysts based on porous materials are considered as an important category of catalysts applicable in many environmentally friendly processes as well as for production of a wide array of fine chemicals. Highly porous structure, large surface area and tunable pore size are the main characteristics of porous catalyst including aluminosilicate compounds. Because of these unique characteristics, porous aluminosilicate are widely used as adsorbents, catalysts, catalyst supports, sensors, filters, thermal insulators and electrodes [1]. The increasing demand for porous materials has led to more research on using inexpensive materials as alternatives with comparative efficiencies. Many trails for the synthesis of these materials were accomplished targeting specific applications [2]. A renowned category of the porous materials are zeolitic aluminosilicates with highly crystalline frameworks capable of adsorbing different reactants and products. Generally speaking, in order to synthesize zeolites, various pure chemical sources of silicon and aluminum such as sodium silicate (a.k.a. water glass), tetraethyl orthosilicate (TEOS), alkoxysilanes as Si sources and sodium aluminate, and aluminum isopropoxide as Al sources has been used [3]. High manufacturing costs of using these Si and AL precursors is still a major concern that needs to be addressed properly.

Coal fly ash (CFA)- a solid waste produced in thermal power plants as a result of coal combustion- is one of cost effective materials that can be used as a source of silica and alumina. In order to lower air pollution caused by coal-fired power plant, CFA is separated from gas flue in smokestacks by precipitators. It is recognized as an alumino-silicate mineral rich in aluminum and silica with Ca, Fe, and Na as the

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prevailing elements and certain elements like B, Mo, S, and Se which are defined as heterogeneous compounds of crystalline and amorphous materials [4,5]. On the other hand, worldwide production of electricity by coal-fired power plants is around 37% [6].

According to a paper published in 2012 [7], annual worldwide generation of CFA is 750 million tons. Furthermore, in some countries like China, the rate of CFA production by electric power plants is increasing annually. The global average utilization of CFA is estimated to be close to 25% (39% in the US and 47% in Europe) [7]. The high rate of CFA production leads to a serious disposal problem resulting a global environmental concern. Therefore, worldwide research on using CFA as an inexpensive starting material (source of Si and Al) for manufacturing a wide array of value-added products is growing rapidly [8,9].

For many years now, researchers are around the world are trying to develop new and cost effective CFA-based porous compounds as adsorbents and catalysts These products can not only be used as adsorbents in different environmental remediation process such as soil conditioning and water treatment, but also in various chemical reactions as catalysts to accelerate synthesis of fine chemicals. CFA-based porous materials have large specific surface area and higher surface energy that can result in higher performance. Unique characteristics of CFA-based porous materials make them suitable substrate for development of a wide array of acidic and basic catalysts [10,11]. Currently however, one of the main industrial applications of CFA is in construction industry including CFA-based geopolymer pastes and mortars [12]. Using CFA as starting material for manufacturing porous catalyst reduces the cost of bulk production of catalysts because it can replace commercially used expensive supports such as SiO_2, TiO_2, ZrO_2 and Al_2O_3. In order to develop selective catalytic materials for various applications such as acylation reactions [13,14], benzylation [15], oil of wintergreen, [16] some types of condensation reactions [17,18] studied under liquid phase conditions, catalytic combustion of methane [19–22], syngas production [23] and photo-degradation of RB [24], addition of proper catalyst promoters and conducting suitable activation process is necessary. These can be achieved though suitable morphological and mineralogical modifications of CFA-based catalysts.

CFA-based catalysts have been used in many reactions including but not limited to: de-sulfurization, de-nitrification, production of H_2, pyrolysis of solid plastic, synthesis of organic solvents, and a variety of reactions regarding organic compound oxidation in aqueous and gas phases such as hydro cracking reactions [25]. Using different preparation methods, CFA cenospheres can be converted into catalyst substrates with characteristics very similar to some of commercially available silica-based catalyst substrates. Researchers have paid particular attention to CFA-based catalysts for industrial chemical reactions including but not limited to oxidation [26,27], chlorination [28], condensation [29], benzene and toluene benzylation [15], NOx reduction [30], glycerol hydrogenolysis [31], transesterification [33], ammonia decomposition [34], Fischer-Tropsch [35], Beckmann rearrangement [36], synthesis of aspirin [37], methanol to olefins (MTO) reaction [38], pyrolysis of the wastes [39], as well synthesis of aryl chalcones [40], and 2-mercaptobenzothiazole derivatives using a microwave-assisted technique [41]. Almost all the reported CFA-based catalysts are effective and can be recycled. It seems CFA-based catalysts can result high conversion and selectivity rates for several significant organic transformation reactions under solvent free conditions.

Several activation (modification) process of CFA-based catalysts have been reported. Researchers enhanced silica amount and nanocrystalline nature of CFA-based catalysts using silanols groups. The applied modification increased surface active sites with higher reactivity for different chemical sections. Incipient wetness impregnation is one of the techniques that being used to modify CFA-based catalysts with metal promoters. A synthesized CFA-supported vanadia (FAV) catalysts are found to have an effective metal support interaction and stability at high calcinations and reaction temperatures [42]. The developed FAV was then used as catalysts in conversion reactions of toluene to benzaldehyde and benzoic acid with partial oxidation under optimized temperature and pressure in a vapor phase micro-reactor. The monolayer vanadia species remained dominant on the activated CFA support responsible for high conversion under the optimized reaction conditions [42]. CFA nano-catalysts- as renewable sources- are another category of CFA-based catalysts that are used for environmental pollution control. They are categorized as green products with significant advantages such as excellent efficiency due to high catalytic activity, cost-effectiveness, and eco-friendly because of good selectivity and their potential for being regenerated and recovered [43]. Chemical and thermal activation processes are used to develop CAF-based nanocrystalline catalyst. Khatri et al. [16] reported that the generated acidic properties of catalyst surfaces could be attributed to OH groups.

In fact, the key questions in this ground, such as the type, structure, and acid strength of the acid sites on the catalysts are still unanswered [16]. Nickel supported-CFA catalysts were synthesized by Wang et al., under chemical treatment for syngas production in CO_2 reforming process of methane [45,46]. Nickel ions had special transition abilities during catalytic oxidation reaction which led to higher removal efficiencies of organic and inorganic pollutants from wastewater streams. In another study, oxidation degradation of phenol in aqueous phase was accomplished by Saeed et al. using synthesized nickel hydroxide catalyst with complete assessments of catalytic activities [44]. The authors also examined the catalytic ozonation method for degradation of pollutants in aqueous phase and claimed that this method had advantages of higher efficiency, being eco-friendly, and availability in both homogeneous and heterogeneous form which overall made it appropriate for wastewater treatment [44].

Advanced oxidation process is one the most important methods of mitigation organic pollutants from wastewaters. Materials with high photo-catalytic properties are suitable candidates in this process. CFA photo-catalysts are strong oxidizing agents; for instance, radical species with high reactive specifications due to hydroxyl groups are proper choices for degradation of large molecules like dyes. The decolonization of dyes such as Azo, orange (II), orange (VI), and reactive black (VI) were conducted efficiently by several types of powerful catalytic composites, synthesized from CFA cenospheres and buoyant metal mixtures [48]. The catalytic composition of F class CFA and potassium were used to produce methyl ester – a type of biodiesel – from sunflower oil through transesterification reaction [49]. In addition, one type of CFA zeolite demonstrated promising catalytic yield when treating heavy oil residues during cracking reactions [50]. Another type of recyclable CFA catalyst prepared from CFA and calcium oxide mixture was applied in Knoevenagel condensation reaction [18]; however, it was not economic because of using reagent grade $CaCO_3$ to gain CaO.

To the best of the authors' knowledge, to date, there is not any review article to review CFA-based catalystsCFA. This review paper discusses the catalytic aspects of CFA-based catalysts in chemical reactions. The possibility of using waste CFA as a catalyst support in producing in expensive and highly efficient catalysts will be discusses. In addition, the significant properties of CFA catalysts such as their structure, texture, surface area, and reusability as well as their performance are discussed. The physicochemical characteristics of solid CFA catalysts and parameters such as reaction time, reaction temperature, and catalyst to substrate mass ratio affecting the optimum conversion yield (%) of the desired products are evaluated. In addition, the dominant kinetics and isotherm models applied to compare the performance of CFA-based catalysts are studied. Many published reports show that catalysts synthesized by CFA are economical, efficient, and environmentally friendly compared with commercially available catalysts.

2. Coal fly ash hazards

Nowadays, CFA disposal is one of the main environmental concerns of coal-fired power plants. The inappropriate disposal of CFA in open