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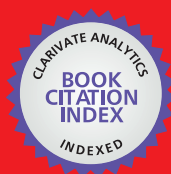
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Chapter

Transformation of Waste Coal Fly Ash into Zeolites for Environmental Applications

Henilkumar M. Lankapati, Kalpana C. Maheria and Ajay K. Dalai

Abstract

The generation of a large quantity of waste coal fly ash (CFA) *via* coal combustion process during power generation is of major concern as disposal of such huge quantity of fly ash causes serious threats to the environment. There is an exigent need to find out the proper solution for its disposal/utilization to reduce its harmful effects. The composition of waste coal fly ash mostly consists of silica and alumina. Hence, the researchers are tempted to utilize waste coal fly ash as a starting ingredient to make value-added materials like zeolites. It is anticipated that such research efforts will act as a valuable aid to reduce the disposal cost of fly ash and ultimately reduce harmful effects of fly ash to the environment. In this review, various synthesis methods to synthesize different types of zeolites from CFA, such as Zeolite-A, Zeolite-X and Zeolite-P, have been summarized and their potential for various applications such as sorption and catalysis has been explored.

Keywords: fly ash, waste utilization, zeolites, catalysis, sorption

1. Introduction

Environmental issues are the most burning issues in the world nowadays. The leading industrialist, scientists, researchers, and environmentalist around the world strive hard for the finding of the proper solution to mitigate or reduce the impact of various environmental problems. The rising issues and researches concerning around the world are (i) to reduce CO_2 levels by utilizing renewable sources as fuels and for the energy production, (ii) storage and disposal of the waste coal fly ash generated from the thermal power plants, (iii) to identify the various contaminants such as toxic/heavy metals, pesticides, petroleum hydrocarbons, which deteriorate the air, soil, and water environments, (iv) to reduce the generation of various pollutants by adopting green chemistry principles, and (v) to find out the best treatment technologies for the removal of contaminants and recovery of the precious metals or products from the waste materials or to convert the waste materials to value-added materials.

Nowadays, environmental researchers and scientists focus on the utilization of waste for the treatment of waste, that is, converting waste materials into value-added

materials such as adsorbents and catalysts and utilize them for the effective treatment of the waste. The waste coal fly ash (CFA) is generated as a byproduct during the electricity generation in thermal power plants. The CFA is considered as the harmful materials, and it is generated in a vast quantity that their disposal is so crucial and required large acre of land. The composition of waste CFA mostly consists of silica and alumina along with trace amount of other rare earth elements, which are precious. Hence, the researchers are tempted to utilize waste coal fly ash as a source of precious elements and make value-added materials such as zeolites from it. Synthesis of different types of zeolites from CFA, such as zeolite X, P, and A, is reported in the literature [1, 2].

Few studies have been undertaken for the applications of CFA-derived materials as the environmental remediation, such as, removal of phosphates and nutrients from the water [3]. Deng et al. have reported the method of converting CFA into materials like adsorbent using microwave-assisted alkali modification and utilized to adsorb Cr^{6+} metal ions from the water [4]. Appiah-Hagan et al. have modified waste CFA using freezing and thawing method and studied the adsorption efficiency of modified fly ash for the sorption of Pb^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} Cr^{3+}, and Cd^{2+} [5]. Similarly, lime-activated fly ash is utilized for the sequestration of heavy metal ions, such as Zn^{2+}, Pb^{2+}, and As^{5+} from the aqueous solution [6]. Chinh et al. have explored the potential of fly ash modified with (3-mercaptopropyl) triethoxysilane for the scavenging of Hg^{2+} ion [7]. Lathiya et al. have converted waste CFA into sulfated fly ash and applied it as a solid acid catalyst for the biodiesel production from maize acid oil [8]. These studies reveal that fly ash can be utilized efficiently for its conversion into valuable materials and may be used further for metal extraction from aqueous solution.

2. Fly ash generation and utilization

2.1 Fly ash generation

Thermal power plants are the main sources of the waste CFA generation as a byproduct of electricity generation. According to the bp (British Petroleum) statistical review of world energy 2022 (71st edition) published by British Petroleum, the generation of electricity is increased by 6.2% during the year 2021. Along the total generation of electricity, coal remains the dominant as a fuel with 36% of its share followed by natural gas (23%), hydroelectricity (15%), renewable sources (13%), nuclear energy (10%), and others (1%) as shown in **Figure 1** [9].

The last 6-year scenario of the electricity generation by fuels as shown in **Figure 2**, reveals that the coal remains dominant (approx. 36%) over all other sources since last few years [9]. The coal utilization ultimately leads to the generation of huge quantity of waste CFA, and its disposal imposes threat to the environment due to its hazardous nature. Though energy generation modes are shifting toward renewable sources, still modes of thermal energy production dominate over the renewable sources as these technologies are under development stages. Hence, the dependency on the coal for energy production is still expected to dominate significantly in the upcoming years also. This will lead to generation of significant amount of fly ash, and there is an urgent need to develop the effective utilization modes of fly ash, which are economically and environmentally viable.

In India, around 76% of total energy demand is supplied by the coal-based thermal power plants. There are more than 202 coal-based thermal power plants in India, with
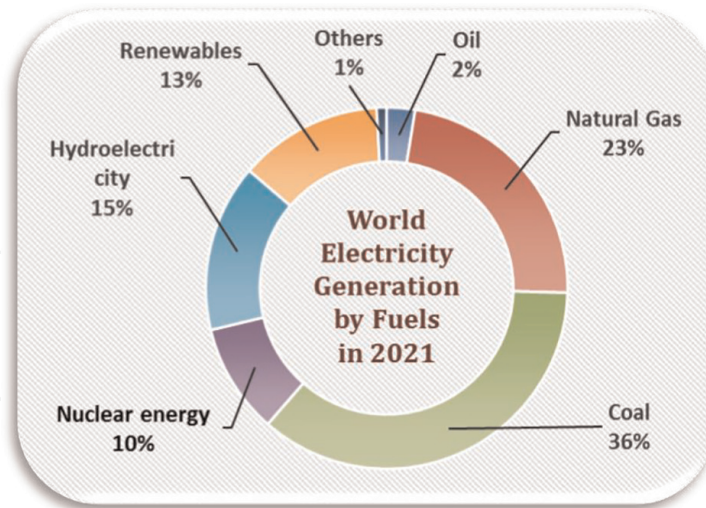
Figure 1.
World electricity generation by fuels during the year 2021 [9].
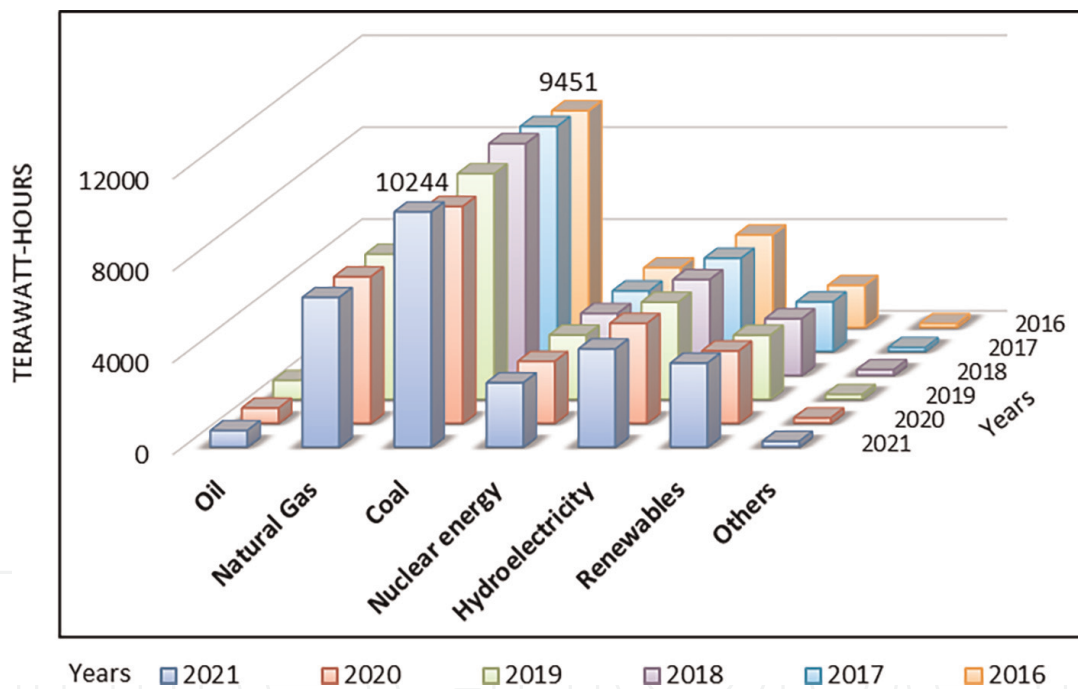

Figure 2.
Scenario of world electricity generation by fuels (terawatt-hours) from 2016 to 2021 [9].

installed capacity around 209,990 MW [10]. According to the CEA (Central Electricity Authority) report, August 2021, these power plants consume ~686 million tonnes of coal and produce ~233 million tonnes of waste CFA during the year 2020–2021. Annual fly ash generation from Indian coal power plants in last 10 years rose from 145.4 million tonnes during the year 2011–2012 to 232.6 million tonnes during the year 2020–2021, an increase of almost 60% [10].

According to the initiative implemented by Ministry of Environment, Forest and Climate Change (MoEFCC), Government of India, to utilize the 100% waste CFA, around 215 million tonnes of fly ash is utilized during the year 2020–2021, which is around 92.4% of total fly ash generation and 7.6% (~108.6 million tonnes) of fly ash
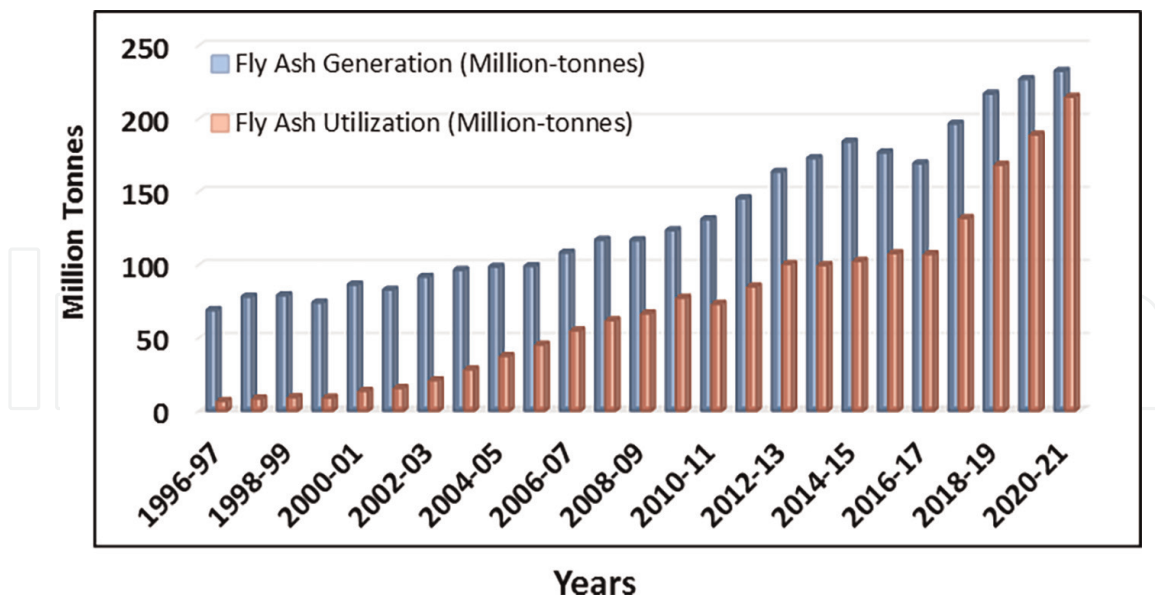
Figure 3.
Trends of CFA generation and utilization in India from 1996 to 2021 [10].

remains unutilized [10]. **Figure 3** shows the trends in fly ash generation and utilization in India from the year 1996 to 2021.

2.2 Legacy ash

The build-up of huge quantity of waste CFA by thermal power plants over decades or other terms, the fly ash stored in the ash ponds, or ash dykes by thermal power plants are considered as the legacy ash. From the CEA report, the available total quantity of legacy ash as on March 31, 2021 is 1738.19 million tonnes, which is dumped or stored at various ash dykes occupying large acre of land area surrounding the power plants [10].

According to the present practice in India, the requirement of land area for the disposal of coal fly ash by the year 2022 is estimated about 126,000 ha (approximately 0.6 ha per MW), if effective utilization will not be implemented. Even 92.4% fly ash is utilized, the land required for unutilized fly ash during the year 2020–2021 (~108.6 million tonne) would be around ~58,800 ha as per the latest reported data by CEA [10, 11].

2.3 Policy and notifications

MoEFCC, Government of India, have taken various initiatives for the protection of land to be polluted by the fly ash slurry, which is disposed into the ash dykes or ash ponds. In their effort to reduce the requirement of large acre of land, MoEFCC has issued first notification regarding the fly ash utilization on September 14, 1999, which was further amended time to time over the years, 2003, 2009, 2016, and 2021. The first notification includes the enforcement of CFA utilization for the manufacturing of bricks, tiles, blocks, and other construction-related materials, and manufacturer within 50 km radius of coal-based thermal power plant must mix at least 25% of CFA with soil by weight percentage [12].

In the first amendment, the radius of the availability of bricks/tiles manufacturers, who have to follow the notification was amended and expanded up to 100 km from

50 km. It further describes target for the waste fly ash percentages, which needs to be utilized by manufacturer as per the radius wise, up to year 2007 [13].

The amendment notification issued on November 3, 2009 provides the details of minimum quantity of fly ash, which needs to be utilized for building materials according to the category of fly ash based product. It also provides targets to the thermal power plants (those are already in operation before the date of this notification) for the utilization of fly ash in a phase manner to reach 100% utilization of fly ash, that is, starting from the date of the notification, target of 50, 60, 75, 90, and 100% for the first, second, third, fourth, and fifth, respectively, while for the newly constructed power plant, the target of achieving 50, 70, 90, and 100% fly ash utilization for the first, second, third, and fourth years, respectively, from the date of the commissioning of power plant [14].

Further, in the year 2016, the new amended notification issued in order to widen the scope of utilization and the vicinity of radius from 100 km to 300 km of the availability of manufacturers or builders needs to use the fly ash in building materials. It also stated that the cost of transportation of CFA to the manufacturers or builders within the 300 km radius shall be borne by the respective power plants and beyond 300 km, the cost shall be equally shared between the users and power plants. This notification also prescribes power stations to upload the details of stock available with them and keep updated regularly [15].

The latest notification issued on April 22, 2021, is focused on the utilization of legacy ash. According to the notification, thermal power plants need to utilize the legacy ash within 10 years from April 1, 2022 as stated in the notification [16]. The percentage utilization of legacy ash shall be based on the annual fly ah production, that is, the utilization of legacy ash should be at least 20% within 1st year; 35% within 2nd and 50% above 3rd to 10th year, from the issuance of the notification, failing to this will impose penalty as per quantity of unutilized legacy ash [16].

2.4 Fly ash utilization

Research scientists all around the world strive hard for the development of various modes of fly ash utilization in cost-effective and ecofriendly manner. Due to their immense efforts, the fly ash utilization increased steadily from the ∼6.6 million tonnes (1996–1997) up to the ∼215 million tonnes (2020–2021) [10]. **Figure 4** shows the details of the fly ash utilization in India during the year 2020–2021.

Figure 4 reveals that the considerable amount of fly ash is utilized by the cement sector, which is 25.8% of the total fly generated during the year. Then, other significant amount 15.6% of fly ash was utilized for the reclamation of low-lying area, followed by the sector of roads and flyovers, where around 15.0% of fly ash utilized. Bricks and tiles manufacturer have used about 12.9% of fly ash in 2020–2021, while ash dykes raising and filling of mining area utilized about 6.2 and 0.83%, respectively, of fly ash generated. Only 0.03% fly ash was utilized in the sector of agriculture and hydro-power sector. The quantity of fly ash remains unutilized during the year 2020–2021 was 7.59%, which is around ∼108 million tonnes [10].

Restogi et al. have studied the potential to utilize fly ash in the field of different construction area and came out with the results for the fly ash utilization with the projected level until 2030. The study revealed that concrete and cement sectors have reached their threshold limit with accommodating around 35 to 40% of total fly ash generation in the forthcoming years, while the sectors of bricks and blocks are found to be the most potential mode for the fly ash utilization, with the capacity to
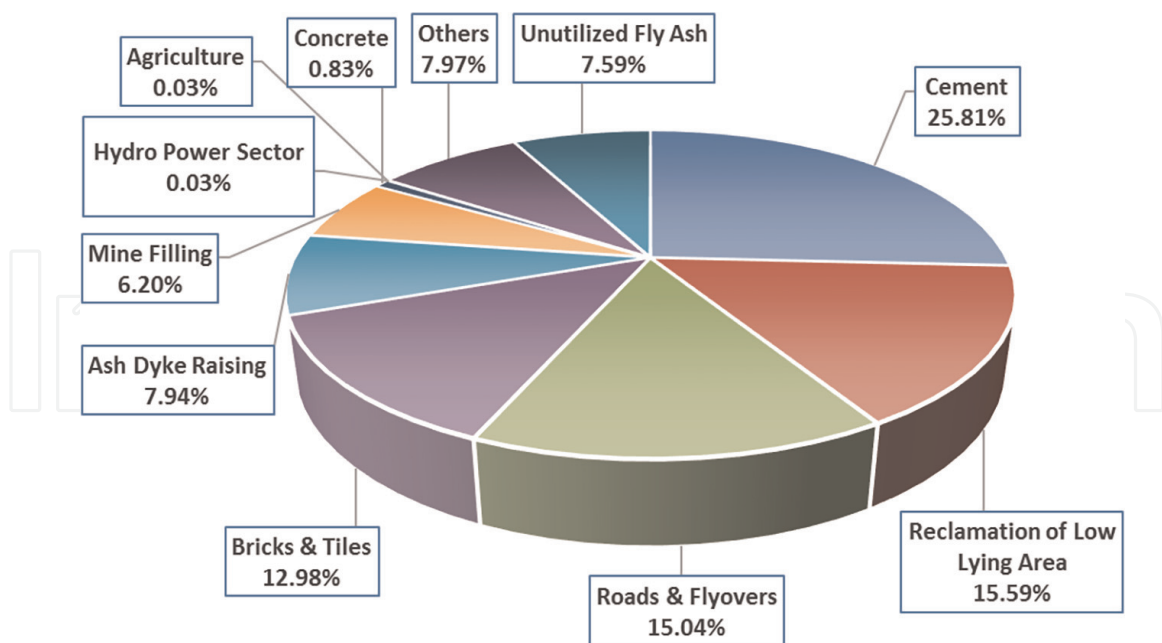
Figure 4.
Fly ash utilization in India during the year 2020–2021 as per CEA report, Aug-2021, Ministry of Power, INDIA [10].

accommodate all unutilized fly ash remaining during the year along with the potential to utilize the legacy ash within the next 15 to 20 years [17].

Though sectors such as mine filing (6.2%), reclamation of low-lying area (15.6%), ash dykes raising (7.9%), and roads and flyover (15%) consume ample amount of fly ash, it should be consider as the last option as these are still existence of threats to the environment after utilization of these modes. Hence, there is still huge quantity of fly ash available to be explored for its efficient utilization in such a manner so as to remove or reduce their harmful effects to the environment. These modes of utilization are followed by the manufacturer as the regulations have been enforced to utilize fly ash in these sectors as compulsion. If the mode of utilization that utilizes the fly ash as raw materials to produce value-added materials, then it will be utilized efficiently by the various industrialists to produce the value-added products, such as the precursor for the ceramics industries and development of ceramic membrane, for the development of adsorbents to remove toxic metals, drug impurities from the water, and development of catalysts such as zeolites for various organic transformations like methane to olefin conversion, biodiesel production, fast pyrolysis of Jatropha waste [18–25]. As fly ash consists of various elemental oxides, specifically SiO_2 and Al_2O_3, which are useful as precursors for the zeolites. Hence, intense research works have been carried out for the development of zeolites from the waste CFA [18, 26].

2.5 Properties of fly ash

The fly ash can be classified as two different types of classes (Class F and Class C) according to the ASTM C-618-3 standards, which are shown in the table below [27]:

- Class F: The fly ash produced after burning of the anthracite and bituminous type of coals. This kind of fly ash contains minimum 70% of silicon dioxide (SiO_2) plus

aluminum oxide (Al_2O_3) plus iron oxide (Fe_2O_3) along with CaO less than 10% and possesses pozzolanic properties.

• Class C: The fly ash that produced after burning of lignite or sub-bituminous type of coals. This type of fly ash contains minimum 50% of silicon dioxide (SiO_2) plus aluminum oxide (Al_2O_3) plus iron oxide (Fe_2O_3) along with lime (CaO) content more than 10% (mostly found in the range of 15 to 20%, sometimes up to 40%) and possess cementitious properties along with pozzolanic properties [27–32].

The Indian coal fly ashes with low lime content are relatively higher in concentration of oxides of silica and alumina, whereas oxides of iron contents are found lower. Due to such properties, these fly ashes require higher temperature for fusion because at lower temperature the chances of glass formation are also low. In these types of fly ashes, the silica content is found almost double than the content of alumina, whereas in high-calcium fly ashes, the oxides of silica and alumina are found almost close to each other along with the significant amount of oxides of iron with respect to the low-lime fly ashes [30]. The heterogeneity studies of the fly ashes by various methods such as sieving, sink-float, and magnetic separation suggests that the heterogeneity in fly ashes with high lime contents is found higher as more variations in the compositions are observed in such kind of fly ashes [30, 33]. The general composition of CFA from various sources is summarized in **Table 1**.

Based on physical properties of the fly ash, it could be considered as fine glass powder with the regular spherical particles sizes in range of 0.5 μm to 100 μm. Such spherical particles shapes allow them to flow and blend freely in the mixture of concrete or cement. The fly ash particles possess ball bearing effect, which provide lubricating actions in the concrete with the plastic state and thus help to decrease the dry shrinkages [11, 34]. The concrete blended with fly ash tends to resist attack of water, sea water, mild acids, and sulfates, which ultimately increases the durability of the concrete mixture and makes it suitable for coastal environment [35, 36]. The fly ash having long-lasting pozzolanic properties, which is useful to tie up free lime, thus reduces the bleed channels by decreasing the permeability of the concrete. Such properties are also useful for increasing the structural strength of the concrete mixer over a time. Due to such kind of physical properties, around 27% of the fly ashes are utilized in the concrete and cement sector [34]. But, it is believed to be at the saturation level to be more utilized in this sector and needs to be explored the utilization of fly ash in other sectors, which turns it into value-added materials.

3. Fly ash utilization for the synthesis of zeolites

3.1 Reported synthesis protocols for fly ash-derived zeolites

3.1.1 Hydrothermal synthesis method

The zeolite formation most commonly proceeds through the hydrothermal synthesis process. The crystallizations or formation of zeolites proceeds through the hydrothermal synthesis process. The various parameters, such as temperature of crystallization, pH of gel, concentration of alkaline cations, time of crystallization, reaction conditions such as static or continuous stirring mode and autogenous pressure involved during the hydrothermal process, may define the formation of specific

	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	K$_2$O	TiO$_2$	P$_2$O$_5$	MnO	SO$_3$	Na$_2$O	Others	Ref.
CFA from Thermal Power Plant India (Class F)													
	52.4	35.8	6.49	1.21	0.46	1.29	1.68	0.29	0.14	0.16	NR	0.06	[18]
South African CFA from Arnot coal power plant, Mpumalanga province (Class F)													
	59.0	28.0	5.00	4.00	1.20	0.70	1.70	0.40	NR	NR	NR	0.00	[21]
Lignite CFA collected from Serbian Thermal Power Plant (Class F)													
	59.2	22.6	6.28	7.48	2.19	1.60	NR	NR	NR	NR	0.24	0.44	[23, 24]
CFA collected from pulp and paper industries in Thailand (Class C)													
	41.4	20.0	8.40	14.10	2.30	2.00	0.60	0.40	NR	4.90	0.40	5.50	[25]
CFA produced by coal gasification process, China (Class F)													
	51.9	18.4	7.94	7.52	3.50	2.42	1.04	NR	NR	NR	1.95	5.39	[30]
CFA samples were collected from NTPC thermal power plant, West Bengal (India) (Class F)													
	47.5	27.8	5.00	1.01	NR	11.44	1.39	NR	NR	NR	NR	5.89	[31]
CFA was obtained from a power plant, China (Class F)													
	36.9	26.6	12.82	6.27	2.90	0.47	4.42	0.07	0.10	0.67	8.33	0.37	[32]
CFA of circulating fluidized bed combustion, from the Pingshuo Coal Gangue Power Plant, China (Class F)													
	40.4	34.5	4.34	7.64	1.33	0.62	1.45	NR	NR	4.28	NR	5.44	[33]
CFA was from the Anhui Province of China (Class F)													
	54.6	32.2	3.20	1.50	0.60	0.80	1.30	NR	NR	NR	0.20	5.60	[34]
CFA was from Thermal Power Plants in Bulgaria, TPP "AES Galabovo" (Class F)													
	62.1	26.6	3.87	1.97	1.40	1.18	1.73	NR	NR	0.49	0.57	0.02	[35]
CFA was collected from Mae Moh Power Plant, Lumpang provice, Thailand (Class C)													
	22.1	12.1	15.00	32.60	1.99	1.78	0.38	0.38	0.19	11.2	1.82	0.46	[36]
CFA was collected from Duvha Thermal Power Plant, Mpumalanga, South Africa (Class F)													
	46.9	31.3	2.96	4.33	0.6	0.72	1.54	0.47	0.03	0.40	NR	10.7	[37, 38]
CFA obtained from the Midong Electric Power Company Limited (China) (Class F)													
	43.4	19.8	NR	NR	NR	NR	NR	NR	NR	NR	NR	36.8	[39]
CFA used for this experiment was procured from Adhunik Power & Natural Resources Ltd., Jharkhand (Class F)													
	68.9	10.1	9.83	1.11	2.07	0.67	1.05	NR	NR	NR	6.12	0.04	[40]
CFA from was collected from Figueira Power Plant, Parana State (PR), Brazil (Class F)													
	40.9	13.5	27.2	2.60	0.31	5.00	2.60	1.40	0.11	1.40	NR	4.98	[41]
CFA was taken from a coal-fired power plant in Anhui Province, China (Class F)													
	55.8	27.7	2.92	0.88	0.40	1.23	NR	NR	NR	NR	0.66	10.4	[42]

Unit of all values: %, CFA: Coal Fly Ash, NR: Not Reported, Ref.: References.

Table 1.
Chemical composition of coal fly ash (CFA) obtained from various sources.

types of zeolites with their unique properties. The gel composition used to crystallize zeolites mainly contains the sources of hetero elements (tetravalent or trivalent elements), mainly silica and alumina, which, further, takes part in the formation of framework structure of zeolites. The gel also comprises of the sources of mineralizing agents such as OH^- and F^- along with inorganic cations, organic species, and solvent (generally water), which solubilizes the reactive elements in the gel and enables them to transfer into the growth of the zeolite crystals [37].

In hydrothermal synthesis of zeolite, homogenized well-mixed sol-gel is prepared by mixing precursors of silica and alumina, source of inorganic cations, and mineralizing agent (i.e., NaOH or KOH) along with the water as a solvent. The gel is then transferred to a teflon-coated autoclave reactor (static or agitated) and then heated for specific period of time with or without stirring [18, 37, 38]. As the hydrothermal crystallization proceeds the high temperature and autogenously generated high-pressure environment triggered, the process of crystallization and the crystal growth proceeds according to the available environment to produce zeolite product. The parameters affecting the crystallization are the concentration of alkali, temperature of crystallization, time of aging, and liquid-to-solid ratio in the reactor. If the alkalinity is too low in the gel, there may be not enough Na^+ availability too trigger the crystallinity, while, if the alkalinity is high, the dissolution of the crystal nucleus would be accelerated, which further affects the crystallization of the zeolitic product [39, 40]. The aging plays an important role in the crystallization process. Aging promotes the formation of oligosilicate ions by the polymerization of the single silicate ions available in to the sol gel, which is further utilized for the crystallization of the zeolite. The temperature of the hydrothermal synthesis is another important parameter for the efficient crystal growth of zeolite. The autogeneous pressure is dependent on the temperature and volume of the gel mixture of the autoclave reactor. High temperature of the reactor triggers the autogeneous pressure in the reaction vessels and thus accelerates the speed of the crystallization of zeolites. Different kinds of zeolite crystals are observed at different temperatures. If the temperature is too low during the process, the pressure will be less, thereby leading to reduce crystallization speed and difficulty in the formation of targeted zeolite crystals [41, 42]. Chang and Shih have synthesized zeolite A and faujasite from Class F type fly ash at low temperature (38 and 60°C, respectively), but required longer reaction time (more than 3 days) for the crystallization of Zeolite A, while at 90°C Zeolite P formation is observed [43]. On the other hand, Yoshida and Inoue have synthesized the similar zeolite at 90°C but it is observed that at the higher reaction temperature, phase of Zeolite A started to disappear and formation of Zeolite P is observed [44]. Amoni et al. have synthesized zeolite A from CFA *via* hydrothermal process after applying magnetic treatment to remove magnetic fraction and acid treatment to remove other unwanted elements [45]. Kumar and Jena have synthesized highly crystalline zeolites with pure phase of zeolites Na-P1, hydroxy sodalite, and analcime zeolites by direct hydrothermal synthesis method, with and without homogenization of the gel precursors, at 150°C temperature and 60 h (to obtain Na-P1) and 20 h (to obtain hydroxy sodalite with homogenization and Analcime without homogenization) [46].

The liquid-to-solid ratio (LSR) should be maintained in accordance with the reactor capacity to achieve desired product. The optimum LSR is useful to generate desired autogeneous pressure, which ultimately triggered the crystallization process. It is also useful to maintain Na^+ concentration and the alkalinity of the gel composition. Generally, the optimum LSR is 66% to get enough autogeneous pressure during the hydrothermal process [40, 47]. The optimum aging time helps to produce stable

silicon aluminum gel polymer, which further helps to get well-crystallized zeolite and also helps to reduce the time of crystallization. On the contrary, longer aging period may dissolve the colloidal skeleton, which affects the quality of crystallinity of the zeolites [48]. The hydrothermal synthesis methods suffer with few disadvantages such as it consumes high energy, longer reactions time, and sometimes suffering from lower crystallization efficiency [38]. Therefore, there is a need to explore other green synthesis approaches and pretreatment methods to prepare sol-gel materials before hydrothermal synthesis. The hydrothermal synthesis process is mostly followed for the zeolite crystallization, but to get targeted materials few pretreatments of the raw materials are necessary to improve the crystallization of pure zeolites.

Before the hydrothermal synthesis process, the pretreatment of the raw materials (specifically when waste CFA or other kind of waste raw materials is used as silica and alumina sources) favors the formation of the desired zeolitic materials. Such pretreatment methods involve the steps such as acid treatment of the waste CFA to remove undesired elements, that is, Fe_2O_3, CaO, MgO, K_2O, and Na_2O [49–51].

3.1.2 Alkali fusion method

The alkali fusion of the raw materials is another pretreatment method involving the fusion of the waste materials to extract maximum silica from it, which is further utilized to prepare gel composition to synthesize the zeolites *via* hydrothermal synthesis method. Fly ash is utilized as the sources of silica and alumina, which are the important starting ingredients for the synthesis of alumino-silicate or zeolite. Shigemoto et al. have introduced the pre-alkali fusion treatment prior to the hydrothermal synthesis process, to convert entire CFA particles into the zeolite [52]. The silica and alumina are present in the fly ash as the quartz and mullite phases. These phases of silica and alumina are less reactive as they are not easily soluble in the water and hence required suitable activation treatment, which weakens the bonds of silica and alumina with the oxygen available in the oxides of silica and alumina present in the fly ash [52, 53]. By applying the alkali fusion treatment, Shigemoto et al. have synthesized zeolite Na-X with 62% yield, while formation of zeolite Na-A was observed with the CFA enriched with the aluminum content [52]. Alkali fusion treatment is the method of choice for such kind of activation of fly ash, which extracts water soluble silicates and aluminates from the fly ash which further improve the crystallization of desired zeolites. Alkali fusion is carried out using NaOH and KOH classically [53, 54]. Chang et al. have established the method of alkali fusion followed by hydrothermal process as a general method to synthesize specific type of zeolites from the various fly ash sources [43]. They have converted the quartz and mullite phases of fly ashes into zeolites by melting fly ash with NaOH at 550°C. Their study reveals that the alkali fusion method followed by general hydrothermal method provides better crystallization then the simple hydrothermal process carried out without alkali fusion treatment [42, 43]. Murukutti and Jena have reported the alkali fusion treatment of fly ash that is carried out by Na_2CO_3 instead of NaOH or KOH. The use of Na_2CO_3 is cost effective with respect to the NaOH. The study reveal that when the fusion of fly ash is carried out with Na_2CO_3 or NaOH at 800°C for 2 h, fly ash transform in to the nephiline (under saturated alumino silicate), which further facilitates the crystallization of zeolites (Zeolite A at 100°C for 6 h and Zeolite X at 100°C for 8 h) through hydrothermal synthesis process, while cancrinite zeolite is formed at 100°C, with prolonged (48 h) time of hydrothermal process [53]. Park et al. have synthesized zeolite X and Y under molten condition with alkali without addition of water. The study reveal that the

crystallization could not be completely accomplished using the method of molten salt due to low temperature and insufficient contact of fly ash with the alkali (NaOH). Hence, the product formed using molten salt method was found to be irregular in their morphological shapes, which could not be identical match with the particular zeolites. The polycrystals of zeolites were very well developed when hydrothermal synthesis methods were used as compared to molten salt method. The study reveals that the alkali fusion method followed by the hydrothermal treatment is much reliable in order to obtain the zeolites selectively from fly ash [42, 55].

Though the alkaline fusion treatment followed by hydrothermal process improves the crystallization and yield of the zeolites, it also suffers with few disadvantages. Such as, when the oxides of silica and alumina are not in a sufficient amount, during the alkali fusion of fly ash the oxides of the elements other than Si and Al also mixed with the alkali melt products. These elements are hard to separate from the alkali melt product mix, which further carried out in the hydrothermal process and mixed up with the zeolite products, ultimately affect the quality of zeolite crystals. Thus, the alkali fusion method is suitable only when fly ash contains higher amount of oxides of silica and alumina. Moreover, alkali fusion treatment required higher energy consumption [56, 57].

The hydrothermal synthesis method suffers with the problems of longer reaction time and high energy requirement for the activation of Mullite and glassy phase of fly ash. Similarly, alkali fusion methods also required high temperature from 550 to 850°C [43, 53]. Even though these methods have been utilized extensively to produce highly crystallized and pure form of zeolites, however, these methods are not economically or environmentally benign as it required high temperature along with the longer time period [58]. Moreover, constructions of the large scale furnace and its operations are too expensive, it also generate solid waste and the handling of large quantity of liquid waste generated through this process is also a matter of concern as it contains most of the toxic metals dissolved from fly ash [59]. Hence, there is a need to find greener synthesis methods which are economically viable and environmentally benign. Few efforts have been reported via microwave and ultrasound assisted synthesis methods of CFA based zeolites.

3.1.3 Microwave-assisted method

Querol et al. [39] have introduced the microwave assisted method for the crystallization of zeolite from waste CFA. The quality, yield and types of the zeolites obtained using microwave assisted synthesis method and traditional experimental process have been found to be quite similar, but the activation time in the microwave assisted synthesis has been drastically reduced to 30 min instead of 24–48 h in traditional methods [39, 42]. Inada et al. have studied the mechanism of the microwave assisted synthesis and found that appropriate microwave radiation could increase the rate of crystallization, on the contrary, prolonged radiation time could inhibit the crystal formation of the zeolites [60]. The microwave assisted method provides uniform nucleation in the supersaturated gel solutions with rapid crystallization [56]. LTA zeolite has been synthesized from CFA by Behin and co-workers using microwave assisted method at low power of microwave radiation (100 to 300 W) within 10 to 30 min of shorter radiation time [61]. Makgabutlane et al. have observed that the zeolite crystallization from fly ash could not be accomplished successfully using microwave assisted synthesis, it needs to be combined with the conventional methods like alkali fusion and hydrothermal synthesis process [58].

3.1.4 Ultrasound method

As the microwave assisted synthesis method is under development stage and the traditional methods to extract the silica and alumina from fly ash suffers from severe disadvantages such as high energy consumption, longer reaction time and high temperature of fusion (550 to 800°C), the ultrasound method is also explored as alternative methods, recently, for the activation of fly ash and further crystallization of zeolites [56, 62, 63]. Ju et al. have observed that the ultrasonic waves helps to improve the efficiency of the extraction of silica from fly ash with compare to traditional methods [63]. Ojumu and co-worker have reported the ultrasonic treatment method for the activation of fly ash instead of high energy consuming method of alkali fusion method followed by hydrothermal synthesis method to produce zeolite A with a low energy requirement and shorter reaction time [64]. The synthesis induced by the ultrasonic waves shows rapid zeolite formation with significant reduced temperature of crystallization than the conventional hydrothermal synthesis process [62].

Chen et al. have reported the microwave and ultrasound collaborative activation method, which significantly improve the activation efficiency of silica and alumina from the fly ash with energy friendly treatment method [56]. The novel EU-12 nanozeolite has been synthesized from coal fly ash by the ultrasonication treatment method followed by hydrothermal synthesis process with ~76% crystallinity [65].

3.1.5 Seed assisted synthesis method

Seed assisted synthesis method is also now a days useful to get desired zeolites using the hydrothermal synthesis process [18]. Seeding is employed in so many industrial crystallization processes to improve the quality of products. Seeding offers numerous advantages such as higher production yield, reduced induction period and contributing towards controlled particle size distribution during crystallization [37]. The details regarding the effect of seeding at the molecular level are still unexplored and need more systematic study in this area. Itabashi and coworkers have studied the effect of the zeolite seeds having different types of framework structures on the crystallization process to form targeted zeolites [66]. They have suggested a working hypothesis for the seed assisted crystallization of targeted zeolites based on the composite building units (cbu) of targeted zeolites, zeolites utilized as seeding agent and unseeded sol-gels. To validate the hypothesis, synthesis of ECR-18 has been carried out using the sol-gel composition, yielded Linde W without seed, but using the calcined ECD-18 as a seeding agent in this gel, formation of pure phase of ECD-18 is observed [66]. Similarly, zeolite CIT-1 (CON type zeolite) has been synthesized using Beta type zeolite as a promising seeding agent [67].

During the synthesis of zeolite through various steps, aging is the step where the silicates and aluminates from the sol-gel mixture converts into the precursor for the crystallization of zeolites. The crystallization of zeolite then proceeds through two steps, nucleation and crystal growth. The steps involving the formation of precursor before the starting of nucleation possess high activation energies and hence considered as the induction period. The presence of seeding agent can alter the nucleation process. The crystal of seeding zeolites act as nuclei and the crystals of targeted zeolites start to grow on the active surfaces of the seeding agent. As the crystals of products started to grow, the activation energies are considered to be lower and the growth of the crystals is faster than the nucleation [37]. The equilibrium between secondary nucleation and growth of seed crystals depends upon the quantity of gel

materials, nature of the system and degree of agitation. If the seed crystals with sufficient surface area which can accommodate maximum available flux of growth species by preventing the effective solution to reach high levels of super saturation. In this condition, the most of the growth of the crystals in the system will take place on the available active area of the seeded crystals. In such case, the size and rate of growth can be controlled and predicted closely by kinetic study. If the seeded crystals with reduced surface area is added to the solution, then the natural super saturation and self-nucleation will no longer be suppressed and ultimately lead to the different kind of crystal size and type than targeted zeolites [37, 68–70].

The seed assisted methods is also explored for the OSDA (Organic Structure Directing Agent) free and ultrafast synthesis of specific type of zeolites. The zeolites obtained through OSDA free seed assisted synthesis are found well crystallized with less defects within the structure of the products than the zeolites synthesized with the OSDA. This is because the seed crystal accelerate the crystal growth and there is no need of calcination to remove OSDA, which often leads to the dealumination and resulting in the creation of defective sites [37]. Liu and coworkers have reported the ultrafast seed assisted synthesis method for the synthesis of AlPO-5 and SSZ-13, the method offers rapid crystallization of zeolites AlPO-5 (1 min) and SSZ-13 (10 min). The crystallization is carried out in tubular stainless steel reactor with fast heating in preheated oil bath. This kind of reactor can be useful for mass production with continuous operation [37, 71, 72].

Different methods that are used for the synthesis of CFA-derived zeolites along with the fly ash elemental compositions are summarized in **Table 2**.

CFA source and chemical composition	Synthesis/pretreatment methods: Reaction conditions and types of synthesized zeolites	Ref.
CFA from thermal power plant, India **(Class F)** **Chemical Composition:** SiO_2: 52.4%, Al_2O_3: 35.8% Fe_2O_3: 6.5%, CaO: 1.2%	**Aging:** Room temperature for 1 h **Seed Assisted Hydrothermal:** 170°C, 24 h, Agitated **Seeding Agent:** 5% Mordenite (with respect to silica) **Gel composition ratio:** $6Na_2O:Al_2O_3:30SiO_2:780H_2O$ **Zeolite:** Mordenite	[18]
South African CFA from Arnot coal power plant, Mpumalanga province **(Class F)** **Chemical Composition:** SiO_2: 59.0%, Al_2O_3: 28.0% Fe_2O_3: 5.0%, CaO: 4.0%	**Acid Treatment:** Conc. H_2SO_4 (extraction followed by filtration for the removal metals like Al and Fe) **Aging:** Room temperature for 2 h. **Hydrothermal:** 160°C, 72 h **Gel composition ratio:** 5.8Si: Al:1.7Na:0.9TPABr:306.9H_2O **Zeolite:** ZSM-5	[21]
CFA was obtained from the energy sector, Poland **(Class F)** **Chemical Composition:** NR	**Alkali Fusion:** with NaOH, Ratio of FA to NaOH: 0.8, Temperature: 700°C **Aging/Hydrothermal:** 700°C temp. for 6 h, static **Impregnation of Ni:** 10–15 wt% Nickel Nitrate addition at room temperature in zeolite X **Drying and calcined:** drying overnight at 105°C and calcined at 500°C for 5 h. **Zeolite:** Ni/Zeolite X	[20]
Lignite CFA collected from Serbian Thermal Power Plant **(Class F)** **Chemical Composition:**	**Acid Treatment:** 6 M HCl at 80°C for 6 h, solid-to-liquid ratio of 1:5 **Hydrothermal:** 260°C temperature for 4 h with 6.25M NaOH solution, Agitated **ES900 preparation:** Egg Shells were dried in the air for	[23, 24]

CFA source and chemical composition	Synthesis/pretreatment methods: Reaction conditions and types of synthesized zeolites	Ref.
SiO$_2$: 59.2%, Al$_2$O$_3$: 22.6% Fe$_2$O$_3$: 6.3%, CaO: 7.5%	a few days, ground into powder, calcined at 900°C at 5° C/min for 4 h. **Cao-Cancrinite preparation:** ES900 (5–10 wt%) added to 10 wt% Zeolite in alcoholic suspension and sonicated using low frequency ultrasound device for 15 min. Evaporate alcohol and drying the material overnight at 110°C, calcined at 450 to 600°C at 5°C/min heating rate for 4 h. **Zeolite:** CaO-Cancrinite zeolite	
CFA was collected from pulp and paper industries in Thailand **(Class C)** **Chemical Composition:** SiO$_2$: 41.4%, Al$_2$O$_3$: 20.0% Fe$_2$O$_3$: 8.4%, CaO: 14.1%	**Aging:** at 90°C for 3 h (with 1-3M NaOH solution) **Gel SiO$_2$/Al$_2$O$_3$ molar ratio:** 23.9 **OSDA:** Tetrapropylammonium bromide (TPABr) **Hydrothermal:** 160°C temperature for 24 h and 72 h **Dried and calcined:** dried at 100°C overnight and calcined at 540°C for 5 h to remove OSDA **Zeolite:** ZSM-5	[25]
CFA produced by coal gasification process, China **(Class F)** **Chemical Composition:** SiO$_2$: 51.9%, Al$_2$O$_3$: 18.4% Fe$_2$O$_3$: 7.9%, CaO: 7.5%	**Acid Treatment:** 10M HCl (Extraction followed by filtration to remove alkaline oxides, i.e., Fe$_2$O$_3$, CaO, Na$_2$O, K$_2$O and MgO.) **Alkali Fusion:** with NaOH for 2 h, Ratio of FA to NaOH: 0.8–1.4 g/g, Temperature: 400-700°C **Aging:** Room temperature for 12 h with stirring, after mixing with Dist. H$_2$O (5 mL/g) **Hydrothermal:** 90-110°C, 12 h, Static **Zeolite:** Zeolite Na-P1	[30]
CFA was obtained from a power plant in Datong City (Shanxi province, China). **(Class F)** **Chemical Composition:** NR	**Hydrothermal:** 95°C, 24 h **Impregnation of La:** Adding 0.23M LaCl$_3$ to the zeolite solution, stirring at 25°C for 4 h **Zeolite:** Modified Zeolite type Na–P1 (La-FA)	[71]
CFA was collected from NTPC thermal power plant, West Bengal, India **(Class F)** **Chemical Composition:** SiO$_2$: 47.5%, Al$_2$O$_3$: 27.8% Fe$_2$O$_3$: 5.0%, CaO: 1.01%	**Acid Treatment:** Conc. H$_2$SO$_4$ (Extraction followed by filtration for the removal metals like Al and Fe) **Alkali Fusion:** with Na$_2$CO$_3$ for 2 h, Ratio of FA to Na$_2$CO$_3$: 0.8–2.0 g/g, Temperature: 800°C **Aging/Homogenization:** Room temperature for 2 h with 3M NaOH. **Hydrothermal:** 100°C, 6 h, 8 h and 48 h **Gel composition ratio:** 88Na:88Al:104Si:384O:194H$_2$O (Zeolite-X), 12Na:12Al:12Si:48O:27H$_2$O (Zeolite-A) **Zeolite:** Zeolite-A and Zeolite-X	[31]
CFA was collected from NTPC thermal power plant, West Bengal, India **(Class F)** **Chemical Composition:** SiO$_2$: 47.5%, Al$_2$O$_3$: 27.8%	**Aging:** Room temperature for 48 h with 1M NaOH (LSR: 10:1) for Na-P1, Room temperature for 48 h with 5M NaOH (LSR: 10:1) for hydroxy sodalite, Room temperature for 48 h with 1-3M NaOH (LSR: 10:1) for Analcime	[31, 72]
Fe$_2$O$_3$: 5.0%, CaO: 1.01%	**Hydrothermal:** 150°C, 10-60 h (Na-P1), 150°C, 10-20 h (Hydroxy Sodalite), 200°C, 10 h (Analcime), Static **Gel composition ratio:** 2.85SiO$_2$: Al$_2$O$_3$: xNa$_2$O:199H$_2$O (x = ~1.79–8.99) **Zeolite:** Zeolite Na–P1, Hydroxy Sodalite and Analcime	

CFA source and chemical composition	Synthesis/pretreatment methods: Reaction conditions and types of synthesized zeolites	Ref.
CFA was obtained from a power plant, China. **(Class F)** **Chemical Composition:** SiO_2: 36.9%, Al_2O_3: 26.7% Fe_2O_3: 12.8%, CaO: 6.3%	**Activation of FA:** Using Microwave and Ultrasound (MU) Combined Synthesis Instrument with 4M NaOH (LSR: 20, 10, 5), at 100°C for 60 min, power 0-1000 W, ultrasound frequency 25 KHz (Activated Liquid named as: 5-MU-L, 10-MU-L and 20-MU-L, respectively as per LSR: 5, 10, 20) **Hydrothermal using microwave radiation:** 100°C, 30-60 min **Gel composition ratio:** $1Al_2O_3$: $1.17SiO_2$: $2.90Na_2O$: $277.97H_2O$ (5-MU-L), $1Al_2O_3$: $1.17SiO_2$: $4.84Na_2O$: $463.93H_2O$ (10-MU-L), $1Al_2O_3$: $1.17SiO_2$: $8.91Na_2O$: $854.43H_2O$ (20-MU-L) **Zeolite:** LTA zeolites (10-MU-75-LTA)	[32]
CFA of circulating fluidized bed combustion, from the Pingshuo Coal Gangue Power Plant in Shanxi Province, China, **(Class F)** **Chemical Composition:** SiO_2: 40.4%, Al_2O_3: 34.5% Fe_2O_3: 4.3%, CaO: 7.6%	**Acid Treatment:** 4.41M HCl (Extraction followed by filtration for the removal $CaSO_4$, CaO, Fe_2O_3, and MgO) mixing for 2 h at 90°C, LSR: 5 mL/g **OSDA:** CTAB (0.5 and 1 g/g) **Hydrothermal:** 90, 110 and 130°C, 6, 9 and 12 h, Agitated **Zeolite:** Na-P1 zeolite	[33]
CFA was from the Anhui Province of China **(Class F)** **Chemical Composition:** SiO_2: 54.6%, Al_2O_3: 32.2% Fe_2O_3: 3.2%, CaO: 1.5%	**Hydrothermal:** 170°C, 3 h, with 0.5M NaOH, LSR: 15 mL/g, Agitated **Ca/Si molar ratio:** 0.8 **Zeolite:** Zeolites-calcium silicate hydrate composite	[34]
CFA was from Thermal Power Plants in Bulgaria, TPP "AES Galabovo" **(Class F)** **Chemical Composition:** SiO_2: 62.1%, Al_2O_3: 26.6% Fe_2O_3: 3.9%, CaO: 2.0%	**Alkali Fusion:** with NaOH for 1 h, Ratio of FA to NaOH: 0.5 g/g, Temperature: 550°C **Additives:** NaCl, KCl, Na_2SiO_3 and Na_2CO_3 **Sonication:** Residue in Dist. H_2O and sonication for 15-48 min **Aging:** Room temperature for 4 h **Hydrothermal:** 90°C, 4-8 h **Zeolite:** Nanozeolite Na-X (ZFH2)	[35]
CFA was collected from Mae Moh Power Plant, Lumpang province, Thailand **(Class C)** **Chemical Composition:** SiO_2: 22.1%, Al_2O_3: 12.1% Fe_2O_3: 15.0%, CaO: 32.6%	**Acid Treatment:** 10% HCl, LSR: 25 mL/g, heated at 80°C for 1h with stirring at 300 rpm **Alkali Fusion:** with NaOH for 2 h, Ratio of FA to NaOH: 0.8–1.4 g/g, Temperature: 400–700°C **Aging:** Room temperature for 2 h **Silicate Solution (A):** FA:NaOH (1.67M) ratio: 10 mL/g, refluxed in R.B.F. at 80°C for 2h with stirring at 300 rpm **Aluminate Solution (B):** 2.4g $NaAlO_2$, 30mL NaOH (1.67M), stirred at 200 rpm for 30 min	[36]
	Aging: Solution A and B mixed on stirrer at 200 rpm for 30 min **Hydrothermal:** Mixed solution in nickel crucible and heated in hot air oven at 100°C for 340 min (5–6 h) **Zeolite:** Zeolite A (ZCF)	
CFA was collected from Duvha Thermal Power Plant, Mpumalanga, South Africa **(Class F)**	**Dissolution using Microwave radiation:** LSR (FA:2.5M NaOH): 7.5 mL/g, at 100°C, varied power (300, 600 and 900 W), and time (5, 10, and 15 min), Centrifuge to get slurry and extract.	[37, 38]

CFA source and chemical composition	Synthesis/pretreatment methods: Reaction conditions and types of synthesized zeolites	Ref.
Chemical Composition: SiO_2: 46.9%, Al_2O_3: 31.3% Fe_2O_3: 3.0%, CaO: 4.3%	**For Slurry** **Adjustment of Si/Al ratio:** with 28 mL $NaAlO_2$ Solution in 72 mL slurry (0.6 g $NaAlO_2$ + 1.2 g NaOH + 20 mL Dist. H_2O) **Hydrothermal using Microwave radiation:** at 300 and 600 W power, 10–20 min **For Extract** **Adjustment of Si/Al ratio:** with 28 mL $NaAlO_2$ Solution in 72 mL extract (0.6 g $NaAlO_2$ + 1.2 g NaOH + 20 mL Dist. H_2O) **Hydrothermal using Microwave radiation in:** at 300 and 600 W power, 10–20 min **Zeolite:** Zeolite A and Sodalite	
CFA was obtained from the Midong Electric Power Company Limited (China) **(Class F)** **Chemical Composition:** SiO_2: 43.4%, Al_2O_3: 19.8% Fe_2O_3: NR, CaO: NR	**Alkali Fusion:** with NaOH for 1 h, Ratio of FA to NaOH: 0.5 g/g, Temperature: 750°C, N_2 atmosphere **Aging:** Room temperature for 2 h (after ground and suspension of molten product in water) **Dried:** at 50°C for 12 h **Zeolite:** Carbon−Zeolite Composites (CZC)	[39]
CFA was taken from the Paiton PLTU, power plants in Indonesia **(Class** C**)** **Chemical Composition:** NR	**Dissolution:** LSR (FA:4M NaOH): 62 mL/g, stirring at 750 rpm at 100°C for 5 h **Adjustment of Si/Al ratio:** with 0.75g of $Al(NO_3)_3$ $9H_2O$ to mixture, stirring speed 750 rpm for 30 min **OSDA:** 2 g of TPABr in mixture, stirring under 100°C for 2 h **Aging:** Room temperature for 2 h. **Hydrothermal:** 160°C, 3–18 bar, 48 h **Dried and calcined:** dried at 110°C for 1 h and calcined at 550°C for 6 h to remove OSDA **Zeolite:** Zeolite obtained with Alumina was Analcime, Zeolite obtained without Alumina was ZSM-5	[73]
CFA was obtained from Adhunik Power & Natural Resources Ltd., Jharkhand. **(Class F)** **Chemical Composition:** SiO_2: 69.0%, Al_2O_3: 10.1% Fe_2O_3: 9.8%, CaO: 1.1%	**Calcination (FA):** 850°C, 90 min for the removal of unburnt carbon **Acid Treatment:** 3M HCl **Alkali Fusion:** with NaOH for 2 h, Ratio of FA to NaOH: 0.125 g/g **Ultrasonication:** at 700 W power, 20kHz, 60% amplitude for 10–30 min **Aging:** Room temperature for 24 h **Hydrothermal:** 100°C, 8 h, Static **Zeolite:** EU-12	[40]
CFA was collected from Figueira Power Plant, Parana State (PR), Brazil **(Class F)** **Chemical Composition:** SiO_2: 40.9%, Al_2O_3: 13.5% Fe_2O_3: 27.2%, CaO: 2.6%	**Hydrothermal:** 100°C, 24 h, with LSR: 8 mL/g (FA:3.5M NaOH) **Zeolite:** Hydroxy-sodalite	[41]
CFA was taken from a coal-fired power plant in Anhui Province, China **(Class F)** **Chemical Composition:** SiO_2: 55.8%, Al_2O_3: 27.7% Fe_2O_3: 2.9%, CaO: 0.9%	**Activation:** with Na_2CO_3 for 80 min, Ratio of FA to Na_2CO_3: 1 g/g, Temperature: 850°C, washed with water and filtered **Dissolution (Leaching of silicon and aluminum):** LSR (FA:2.5/3.75/**5.0** M NaOH): 1:10/15/**20** mL/g, stirring at **60**/75/90°C for 0.5/**1.0**/1.5 h and centrifuged	[42]

CFA source and chemical composition	Synthesis/pretreatment methods: Reaction conditions and types of synthesized zeolites	Ref.
	Synthesis of precipitated silica: Purging CO_2 gas into water washing solution till pH 8.00, aging at room temperature for 24 h in centrifugal tube and separate out solids, washed with water and dried at 100°C to get silica (precipitated) **Synthesis of Zeolite:** Aging of alkali leaching solution at room temperature for 24 h **Hydrothermal:** 100°C, 1/3/5 h **Zeolite:** Zeolite A and Sodalite	
CFA received from the Italian ENEL thermoelectric power plant in Cerano (Brindisi) and Fusina (Venice), Italy **(Class F)** **Chemical Composition:** SiO_2: 48.5%, Al_2O_3: 26.0% Fe_2O_3: 4.4%, CaO: 6.4%	**Alkali Fusion:** with NaOH for 1 h, Ratio of FA to NaOH: 0.83 g/g, Temperature: 550°C **Dissolution:** in artificial sea water **Hydrothermal:** incubated up to 192 h at 25°C **Zeolite:** Zeolite A (up to 96 h incubation) and Zeolite X (more than 96 h incubation)	[2, 49]

NR: Not Reported.

Table 2.
Methods for the synthesis of CFA-derived zeolites with CFA composition.

It is evident from the **Table 2** that, Zeolite Na-P, Zeolite X and Zeolite A are the most commonly synthesized zeolites from the CFA [2, 32, 41, 49, 51, 53, 56, 58, 73, 74]. It is observed that, at the lower temperature, at around, ~100°C, the conversion of CFA favors the formation of Zeolite Na-P and Zeolite A crystals [2, 32, 41, 49, 51, 53, 56, 73]. While at a high temperature, at around, ~160°C and a longer period of crystallization, CFA tends to form ZSM-5 crystals [21, 25, 75]. Formation of Analcime (in presence of high alumina contents in gel mixture) and Mordenite crystals are also observed at higher temperature of crystallization [18, 46, 53, 75]. When the significant amount of Na^+ cations are available in the gel composition, the crystallization of gel tends to form Analcime type zeolites, while at lower concentration, formation of Zeolite Na-P is observed [46, 49, 53, 75]. Zeolite A and X are crystallize even at room temperature in the presence of salt water (artificial seawater) but requires longer incubation period [2, 41]. Microwave assisted synthesis methods reduces the crystallization time for the formation of Zeolite A and Sodalite to only 10–60 min, which in conventional method takes up to few hours and sometimes up to few days [56, 58, 74]. While the use of ultrasonication during the crystallization of Nanozeolite-Na-X and EU-12 provides efficient dissolution of Si and Al within a few minutes compared to the conventional methods, thereby helping to reduce the period of hydrothermal process from few hours to only few minutes [56, 65].

4. Properties and applications of fly ash-derived zeolites

Zeolites exhibit unique properties such as higher thermal stability, high surface area and pore volume, chemical resistivity, and possess both acidic sites, Lewis and Brønsted. These properties enable zeolites to be utilized as catalysts and adsorbents in

numerous industrial processes, such as cracking of petroleum crude, trans alkylation, hydro-isomerization, methylamine synthesis, and disproportionation [76]. Zeolites exhibit excellent cation exchange capacity making it capable to be utilized in the field of environmental remediation as the adsorbents and exchangers for the successful removal of pollutants such as toxic metals, nutrients and radionuclides. For example, as shown in **Table 2**, Kumar and Jena, 2022 have synthesized Zeolite NaP1 from the waste CFA, which possess good CEC (Cation Exchange Capacity), that is, 4.2 meq. NH_4^+/g. They have evaluate its performance for the removal of Sr^{2+} and Cs^{2+} from the nuclear waste and found 92.5 and 39.3 mg/g adsorption capacities, respectively [46]. Similarly, Vichaphund et al. have synthesized ZSM-5-type zeolite from the CFA shows acidity values of 0.979 mmol NH_4^+/g and further utilized it as catalyst for the fast pyrolysis of Jatropha waste. This catalyst shows high selectivity toward aromatic hydrocarbons formation and obtained with the yields of 97.4% [25]. The synthesized zeolites (from CFA) have been explored mainly as catalyst and sorbents. **Table 3** summarizes the properties and applications of fly ash-derived zeolites.

Table 3 reveals that the BET surface area (S_{BET}) of CFA-derived zeolites synthesized *via* classical methods was found to be less, which is in the range of 7.8–117 cm^2/g. The surface area of such zeolite can be improved by employing advance technique, such as ultrasonication and microwave irradiation combined with ultrasonication. It was observed that when ultrasonication method was utilized, the formation of nano-zeolite Na-X (ZFH2) was observed, this nano-zeolite possesses high surface area (486 cm^2/g) as shown in **Table 3** [77]. Similarly, EU-12 zeolite synthesized using sonication also shows high surface area (236 cm^2/g) [65]. The combined microwave and ultrasonication technique also seems to provide high surface area zeolites, such as LTA zeolite (10-MU-75-LTA) synthesized using combined microwave-ultrasonication, was found to exhibit 442 cm^2/g surface area. The ultrasonication enhances the dissolution of silica and alumina contents from the CFA into the alkaline gel mixture, which ultimately leads to the formation of the zeolites. In addition to that during the sonication, effects of acoustic cavitation along with the collapsing of micro-bubbles in the alkaline reaction mixture additionally enhance the rate of secondary nucleation, and quicken the mass transfer and expansion in the reactive surface area by means of fragmentation of solid crystals, which further help in reducing the time and temperature for the zeolite crystallization from CFA [77–79].

5. Conclusion and future perspectives

This review addresses the environmental problems caused due to fly ash generation and its mitigation measures *via* cost-effective and ecofriendly utilization of waste fly ash. Due to the presence of considerable amount of metal oxides, mainly SiO_2 and Al_2O_3 in fly ash, it is widely accepted as precursor of choice for the zeolite synthesis. The information provided in this review will be used as a guiding tool for the selection of fly ash source and an appropriate synthetic route to follow for the synthesis of a particular zeolite of desired properties for its targeted applications. A brief exposure to various synthetic approaches has been discussed in this chapter, which is currently in practice for zeolite synthesis. In recent times, the microwave and ultrasonication methods seem promising over conventional hydrothermal methods. However, still challenges exist for their successful large-scale implementation. Further studies and research efforts are required to enhance the feasibility to transfer the technology from lab scale to industrial scale. In general, various zeolites such as ZSM-5, Zeolite A,

Fly ash source	Types of zeolites, properties and applications	Ref.
CFA from thermal power plant, India **(Class F)** **Properties:** S_{BET}: 2.9 cm^2/g Pore Volume: 0.009 cm^3/g Pore Size: 10.7 nm CEC: 0.32 meq Na$^+$/g	**Mordenite** Properties: S_{BET}: 117 cm^2/g Pore Volume: 0.20 cm^3/g Pore Size: 6.76 nm Acidity: 1.18 mmol NH$_4^+$/g CEC: 1.72 meq Na$^+$/g	[18]
	Application as Sorbent: For Pb^{2+} and Cd^{2+} removal. Removal Efficiency: 94.1% (Pb^{2+}), 88.2% (Cd^{2+}), Adsorption capacity: 20.2 mg/g (Pb^{2+}), 28.6 mg/g (Cd^{2+}) [at room temperature, Contact time: ~60 min, Dose: 10 g/L, pH: 5, Initial conc.: 0.004M (Pb^{2+}), 0.002M (Cd^{2+})]	
South African CFA from Arnot coal power plant, Mpumalanga province **(Class F)** **Properties:** NR	**ZSM-5** Properties: S_{BET}: 328 cm^2/g Pore Volume: NR Pore Size: NR Acidity: 0.31 mmol H$^+$/g	[21]
	Application as Catalyst: For methanol to olefin (MTO) conversion Propylene selectivity: 35%, Light olefin (C$_2$–C$_4$) selectivity: 66%, [Temp.: 450°C, Weight hourly space velocity (WHSV): 1.12/h, Time: 1 h]	
CFA was obtained from the energy sector, Poland **Properties:** NR	**Ni/zeolite X** Properties: S_{BET}: 190 cm^2/g Pore Volume: 0.149 cm^3/g Pore Size: 0.68 nm Acidity: 0.38 mmol H$^+$/g	[20]
	Application as Catalyst: For CO$_2$ methanation, CO$_2$ conversions: 53%, CH$_4$ selectivity: 90% [Temp.: 450°C, Gas hourly space velocity (GHSV): 12000/h]	
Lignite CFA collected from Serbian Thermal Power Plant **(Class F)** **Properties:** S_{BET}: 2.1 cm^2/g Pore Volume: 0.003 cm^3/g Pore Size: NR	**CaO-Cancrinite zeolite** Properties: S_{BET}: 14.9 cm^2/g Pore Volume: 0.06 cm^3/g Pore Size: 13.5 nm Basicity: 0.92 mmol CO$_2$/g	[23, 24]
	Application as Catalyst: For the biodiesel production, Triacylglycerols conversion: 96.5% [Temp.: 60°C, MTO ratio: 12:1, Catalyst Load: 4 wt%, Time: 2 h]	
CFA was collected from pulp and paper industries in Thailand	**ZSM-5 (Synthesized with 3M NaOH at 72 h)** Properties:	[25]
(Class C) **Properties:** NR	S_{BET}: 453 cm^2/g Pore Volume: 0.24 cm^3/g Pore Size: 3.31 nm Acidity: 0.979 mmol NH$_4^+$/g	

Fly ash source	Types of zeolites, properties and applications	Ref.
	Application as Catalyst: For the fast pyrolysis of Jatropha waste, Aromatic Hydrocarbon Yield: 97.4%, Oxygenated Compound Yield: 0.8%, N-Containing Compound Yield: 1.7%, [Temp.: 500°C, Jatropha:catalyst ratio: 1:10]	
CFA produced by coal gasification process, China **(Class F)** **Properties:** NR	**Zeolite Na-P1** Properties: S_{BET}: NR Pore Volume: NR Pore Size: NR CEC: 2.75 meq NH_4^+/g	[30]
	Application as Sorbent: For Cr^{6+} removal from water, Adsorption capacity: 17.9 mg/g [at 20°C, Contact time: 2 h, Dose: 5 g/L, pH: 3, Initial conc.: 100 mg/L]	
CFA was obtained from a power plant in Datong City (Shanxi province, China). **(Class F)** **Properties:** S_{BET}: 5.5 cm^2/g Pore Volume: 0.01 cm^3/g Pore Size: NR	**Modified Zeolite type Na–P1 (La-FA)** Properties: S_{BET}: 59.9 cm^2/g Pore Volume: 0.11 cm^3/g Pore Size: 3.9 nm	[71]
	Application as Sorbent: For phosphorous removal from water Removal Efficiency: 72.8% Adsorption capacity: 23 mg/g (pH 4), 11 mg/g (pH 8.5), [at 25°C, Contact time: 30 h, Dose: 1.0 g/L, pH: 8.5, Initial conc.: 30 mg/L]	
CFA samples were collected from NTPC thermal power plant, West Bengal (India) **(Class F)** **Properties:** S_{BET}: 4.04 cm^2/g Pore Volume: NR Pore Size: NR	**Zeolite-A (ZA) and Zeolite-X (ZX)** Properties: S_{BET}: 58.3 cm^2/g (ZA), 164.3 cm^2/g (ZX) Pore Volume: 0.071 cm^3/g (ZA), 0.054 cm^3/g (ZX) Pore Size: 5.108 nm (ZA), 4.537 nm (ZX)	[31]
	Application as Sorbent: For Sr^{2+} and Cs^{2+} removal from nuclear waste Removal Efficiency: >90% (Sr^{2+}), >50% (Cs^{2+}), Adsorption capacity: 54.1 mg/g (ZA), 53.1 mg/g (ZX) for Sr^{2+} and 95.7 mg/g (ZA), 93.1 mg/g (ZX) for Cs^{2+} [at 25°C, Contact time: 24 h, Dose: 10.0 g/L, pH: 7.0, Initial conc.: 1000 mg/L]	
CFA samples were collected from NTPC thermal power plant, West Bengal (India) **(Class F)** S_{BET}: 4.04 cm^2/g Pore Volume: NR Pore Size: NR	**Zeolite Na–P1 (ZP), Hydroxy Sodalite (ZS) and Analcime (ZA)** Properties: S_{BET}: 63 cm^2/g (ZP), 17 cm^2/g (ZS), 8 cm^2/g (ZA) Pore Volume: NR Pore Size: 8 nm (ZP), 6 nm (ZS), NR (ZA) CEC (meq NH_4^+/g): 4.2 (ZP), 0.8 (ZS), 0.6 (ZA)	[31, 72]
	Application as Sorbent: For Sr^{2+} and Cs^{2+} removal from nuclear waste Adsorption capacity: 92.5 mg/g (ZP), 43 mg/g (ZS), 11 mg/g (ZA) for Sr^{2+}, 39.3 mg/g (ZP), 15 mg/g (ZS), 0 mg/g (ZA) for Cs^{2+} [at 25°C, Contact time: 24 h, Dose: 10.0 g/L, pH: 7.0, Initial conc.: 1000 mg/L]	

Fly ash source	Types of zeolites, properties and applications	Ref.
CFA was obtained from a power plant, China. **(Class F)** **Properties:** NR	**LTA zeolites (10-MU-75-LTA)** Properties: S_{BET}: 442 cm^2/g Pore Volume: 0.30 cm^3/g Pore Size: 17-40 nm Acidity: 3.07 mmol NH$_4^+$/g	[32]
	Application as Catalyst: For the cracking of 1,3,5-tri-isopropylbenzene, Conversion: 25.40 wt% Benzene Selectivity: 11.05%, isopropyl-benzene Selectivity: 21.27%, 1,3-diisopropyl-benzene Selectivity: 16.58%, Propylene Selectivity: 51.1% [at Temp.: 300°C, Catalyst Load: 1.45 g/L]	
CFA derived from circulating fluidized bed combustion, from the Pingshuo Coal Gangue Power Plant in Shanxi Province, China. **(Class F)** **Properties:** NR	**Na-P1 zeolite** Properties: S_{BET}: 43.96 cm^2/g Pore Volume: 0.0945 cm^3/g Pore Size: 8.21 nm	[33]
	Application as Sorbent: For Pb^{2+} removal from water Removal Efficiency: 99% (at 100-300 mg/L Pb^{2+}) Adsorption capacity: 425 mg/g [at 25°C, Contact time: 60 min, Dose: 0.2 g/L, pH: 6.0, Initial conc.: 500 mg/L]	
CFA was from the Anhui Province of China **(Class F)** **Properties:**	**Zeolites-calcium silicate hydrate composite** Properties: S_{BET}: 96.5 cm^2/g	[34]
S_{BET}: 22.9 cm^2/g Pore Volume: 0.1 cm^3/g Pore Size: 8.1 nm	Pore Volume: 0.4 cm^3/g Pore Size: 9.1 nm	
	Application as Sorbent: For Pb^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+} and Cr^{3+} removal Adsorption capacity: In a single system: Pb^{2+}: 409.4 mg/g; Ni^{2+}: 222.4 mg/g; Cd^{2+}: 147.5 mg/g; Zn^{2+}: 93.2 mg/g; Cu^{2+}: 101.1 mg/g; Cr^{3+}: 157.0 mg/g In a multiple system: Pb^{2+}: 121.9 mg/g; Ni^{2+}: 4.6 mg/g; Cd^{2+}: 70.8 mg/g; Zn^{2+}: 27.5 mg/g; Cu^{2+}: 34.4 mg/g; Cr^{3+}: 9.7 mg/g [at 25°C, Contact time: 120 min, Dose: 0.5 g/L, pH: 4.5, Initial conc.: 25-400 mg/L]	
CFA was collected from Mae Moh Power Plant, Lumpang province, Thailand **(Class C)** **Properties:** S_{BET}: 1.390 cm^2/g Pore Volume: 0.006 cm^3/g Pore Size: 7.97 nm	**Zeolite A (ZCF)** Properties: S_{BET}: 10.440 cm^2/g Pore Volume: 0.030 cm^3/g Pore Size: 5.57 nm	[36]
	Application as Sorbent: For Pb^{2+} removal from water Removal Efficiency: 100% Adsorption capacity: 556 mg/g [at 25°C, Contact time: 1 h, Dose: 0.1 g/L, pH: 5.0, Initial conc.: 50 mg/L]	

Fly ash source	Types of zeolites, properties and applications	Ref.
CFA was obtained from the Midong Electric Power Company Limited (China) **(Class F)** **Properties:** S_{BET}: 11.0 cm^2/g Pore Volume: 0.03 cm^3/g Pore Size: 3.4 nm	**Carbon−Zeolite Composites (CZC)** Properties: S_{BET}: 62.5 cm^2/g Pore Volume: 0.31 cm^3/g Pore Size: 12.7 nm	[39]
	Application as Sorbent: For Pb^{2+} removal from water Adsorption capacity: 186 mg/g [at room temperature, Contact time: 40 min, Dose: 10 g/L, pH: 7.0, Initial conc.: 500 mg/L]	
CFA was obtained from Adhunik Power & Natural Resources Ltd., Jharkhand. **(Class F)** **Properties:** NR	**EU-12** Properties: S_{BET}: 236.03 cm^2/g Pore Volume: 0.273 cm^3/g	[40]
	Application as Sorbent: For Rhodamine B (RB) dye removal. Removal Efficiency: 67.32% [at room temperature, Contact time: 150 min, Dose: 1 g/L, pH: 3.0, Initial conc.: 10 mg/L]	
CFA was collected from Figueira Power Plant, Parana State (PR), Brazil **(Class F)** **Properties:** S_{BET}: 12.47 cm^2/g Pore Volume: NR Pore Size: NR	**Hydroxy-sodalite** Properties: S_{BET}: 66.12 cm^2/g Pore Volume: NR Pore Size: NR	[41]
	Application as Sorbent: For Zn^{2+} and Cd^{2+} removal Removal Efficiency: 95% (Zn^{2+}), 97% (Cd^{2+}) [at room temperature, Contact time: 20 h, Dose: 15 g/L (Zn^{2+}), 18 g/L (Cd^{2+}), pH: 6.0 (Zn^{2+}), 5.0 (Cd^{2+}), Initial conc.: 337 mg/L (Zn^{2+}), 634 mg/L (Cd^{2+})]	
CFA was collected from Duvha Thermal Power Plant, Mpumalanga, South Africa **(Class F)** **Properties:** S_{BET}: 1.19 cm^2/g Pore Volume: 0.001 cm^3/g Pore Size: NR CEC: 0.29 meq NH$_4^+$/g	**Zeolite A (ZA) and Sodalite (ZS)** Properties: S_{BET}: 29.5 cm^2/g (ZA), 7.81 cm^2/g (ZS) Pore Volume: 0.05 cm^3/g (ZA), 0.019 cm^3/g (ZS) Pore Size (nm): 6.71 nm (ZA), 8.96 nm (ZS) CEC: 3.1 meq NH$_4^+$/g (ZA), 0.98 meq NH$_4^+$/g (ZS)	[37, 38]
	Application: NR	
CFA was from Thermal Power Plants in Bulgaria, TPP "AES Galabovo" **(Class F)** **Properties:** NR	**Nanozeolite Na-X (ZFH2)** Properties: S_{BET}: 486 cm^2/g Pore Volume: 0.31 cm^3/g Pore Size: 1.39-4.18 nm Yield: 89 wt.%	[35]
	Application: NR	

NR: Not Reported.

Table 3.
Properties of zeolites derived from coal fly ash (CFA) and their applications.

Zeolite Na-P, Zeolite X, Zeolite Y, Analcime are synthesized from fly ash. However, the synthesis of other zeolites having high surface area, pore volume, high acidity, and high cation exchange capacity and thus having commercial market values such as zeolite β, Mordenite, MCM-22 can be explored *via* systematic study of different synthetic parameters and methods. Moreover, there is a need to develop a process, which is associated with minimum waste generation and providing maximum utilization of the elemental composition of fly ash by extracting elements other than Si and Al, separately such as Fe_2O_3, TiO_2, trace amount of rare earth elements. Apart from these, emphases have been put in this chapter on fly ash utilization for generation of value-added materials such as zeolites and applications of fly ash-derived zeolites in the field of catalysis and environmental remediation. Future scope exists in executing large-scale application of fly ash in waste land reclamation, floriculture, and heavy metals recovery.

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