Review

Synthesis and Environmental Applications of Nanoporous Materials Derived from Coal Fly Ash

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Abstract: Coal fly ash (CFA) is the primary solid waste generated by the coal-fired industry, and the predominant treatment methods include accumulation, landfill, and the production of cement-based building materials. However, the availability of these methods is relatively limited, and there is a need for technological upgrades. The extensive accumulation not only leads to environmental pollution but also has detrimental effects on human health. With its loose structure and main chemical components of Al₂O₃ and SiO₂, CFA is conducive to the synthesis of promising nanoporous materials for applications in adsorption. The use of CFA as a raw material can significantly reduce preparation costs, improve comprehensive utilization efficiency, and manufacture more valuable products, aligning with the current strategy of sustainable development. Currently, the most widely used synthesis method is hydrothermal synthesis. This review focuses on the principles, methods, and influencing factors of synthesis, with particular emphasis on CFA-based mesoporous silica, zeolites, and metal–organic frameworks (MOFs), which have not been systematically reviewed previously. The quality of these synthesized nanoporous materials can be finely adjusted through the synthesis process. A comparison of the advantages and disadvantages of each process will be made, and the impact of the synthesis conditions on the synthetic products will be analyzed. Additionally, a brief discussion on the latest research advances in their applications in adsorption will be provided. Finally, relevant challenges and issues have been proposed.

Keywords: solid waste; coal fly ash; nanoporous materials; metal–organic frameworks; environmental remediation

1. Introduction

As the primary solid waste generated by thermal power plants, CFA is released along with the flue gas during the combustion of coal, potentially contributing to the formation of haze [1,2]. Currently, global CFA emissions are substantial, with China and India together accounting for approximately half of the global emissions [3,4]. By the end of 2018, China’s CFA output had exceeded 550 million tons, and due to insufficient utilization, the accumulated volume of CFA has continued to increase [5].

Currently, 25% of the comprehensive utilization of CFA is primarily adopted by the cement industry in China, with 18% allocated for low-end buildings, 10% for concrete, and 3% for mine backfilling and paving. Additionally, approximately 35% of the 200 million tons of CFA are in a state of shelving [5]. Therefore, there is an urgent need to increase research efforts to enhance the comprehensive utilization of CFA. CFA is characterized by a loose and porous aggregate of spherical particles ranging from 1 to 100 μm, primarily composed of quartz, mullite, magnetite, hematite, and other amorphous components [6,7].
Nanoporous materials refer to a class of solid materials with unique microstructures characterized by pore sizes below 100 nm [8,9]. These materials have found applications in adsorption, separation, energy storage, catalysis, and biology, and hold significant potential for further development. As per the classification by the International Union of Pure and Applied Chemistry (IUPAC), porous materials are categorized into microporous, mesoporous, and mesoporous materials based on pore sizes, which are defined as less than 2 nm, greater than 50 nm, and 2–50 nm, respectively [10].

Zeolite molecular sieves are among the most common nanoporous materials, characterized by a crystalline structure primarily composed of silicate and aluminosilicate, with a clearly defined three-dimensional tetrahedral skeleton. Due to the high content of amorphous aluminosilicate glass in CFA, which shares an effective composition structure with zeolite molecular sieves, CFA can be transformed into higher value-added zeolite molecular sieve products or other nanoporous materials [11]. As of November 2023, the International Zeolite Association (IZA) has documented 255 zeolite molecular sieves with different topologies. Among these structures, zeolite A, zeolite X, zeolite Y, and ZSM-type nanoporous materials exhibit good structural stability and are primarily utilized in the synthesis of high-performance catalysts [12]. Natural zeolite is constrained by limited resources, complex pore size, and channel structure, which restricts its application. In contrast, CFA offers the advantages of low cost and controllable morphology, enabling it to serve as a substitute for natural zeolite in the synthesis of zeolite molecular sieves, thus playing a vital role in the preparation of nanoporous materials.

In the 1960s, the first generation of zeolite molecular sieves was developed, including zeolites A, X, Y, and M. They were widely used as catalysts and garnered significant attention in the petrochemical and oil refining field. During the 1970s, the second generation of zeolite molecular sieves emerged, primarily characterized by new structural nanoporous materials such as ZSM-5. The catalysts synthesized using these materials exhibited higher activity and selectivity, were less prone to carbonization, and demonstrated good stability. ZSM-5 nanoporous material is distinguished by its high silicon content and a three-dimensional cross-shaped straight channel structure. Subsequently, in the 1990s, mesoporous molecular sieves came into existence, exemplified by the M41S series nanoporous materials and SBA series mesoporous materials [13]. Presently, the primary types of nanoporous materials synthesized using CFA include zeolites A, X, Y, P, ZSM-5, M41S series, SBA-n series, etc.

The utilization of the synthesis process varies depending on the specific synthetic products. Currently, the primary synthesis methods for nanoporous materials include the alkali melting method and the hydrothermal technique. Among these, the hydrothermal technique is particularly noteworthy for its ease of operation and cost-effectiveness, leading to its widespread application in synthesis. This method involves adding a certain proportion of reaction precursors into a closed reactor containing an aqueous solution, where the reactants dissolve and undergo reactions under high temperature and pressure conditions. By adjusting the reaction parameters, various products can be obtained [14]. The products synthesized using this technique possess several advantages, including high purity, high crystallinity, uniform particle size distribution, strong stability, and certain selectivity [15], making it a highly effective method for synthesizing nanoporous materials.

In general, the emissions resulting from coal combustion-derived CFA have serious environmental implications. Due to its high silicon and aluminum content, CFA can be utilized to produce higher value-added nanoporous materials, such as zeolite molecular sieves, mesoporous silicas, and MOFs, presenting significant prospects for development. Several outstanding reviews on the use of CFA-derived porous materials have been published. These encompass the synthesis of nanoporous materials from CFA and other solid wastes [16], the use of CFA-based porous materials as catalysts [17], the development of CFA-derived porous adsorbents [18], the recycling of CFA for mesoporous silicas [19], and the synthesis of zeolites from CFA for environmental applications [3]. However, there is a
pressing need for a systematic and updated review focusing on a diverse range of nanoporous materials, particularly the emerging MOFs, derived from CFA for environmental applications. This article aims to summarize the latest developments in synthesizing various nanoporous materials from CFA and provide a detailed discussion of their environmental applications (refer to Figure 1). Additionally, the conclusions and future prospects will be emphasized.

Figure 1. The schematic of CFA-based nanoporous materials for environmental applications.

This review paper provides an overview of the environmental hazards that coal fly ash (CFA) may cause at present, along with the proposed solutions to these hazards. Compared to the simplistic use of CFA as a mineral aggregate for constructing materials, the profitable recovery of Si and Al from CFA as a fundamental ingredient for creating recycled nanoporous materials is a significantly high value-added approach. Next, the article describes and summarizes the widely accepted reaction mechanism for the conversion of nanoporous materials by CFA (Section 2.1); the methods for synthesizing CFA-based nanoporous materials that are presently available (Section 2.2), and the factors influencing the nucleation and growth of nanoporous materials (Section 2.3) are subsequently classified and introduced; following this, we classify the research concerning the prosperous production of three typical nanoporous materials from CFA (Section 2.4), namely CFA-based zeolites (CFAZ), mesoporous silica, and metal-organic frameworks (MOFs). Finally, we provide a review of the research related to the application of CFA-based nanoporous materials for the removal of VOCs (Section 3.1), organics (Section 3.2), metal ions (Section 3.3), fluoride ions (Section 3.4), and other inorganic ions (Section 3.5). Finally, we will conclude this article with a concise overview of the challenges and issues faced in current research as well as a promising vision for the future of CFA-based nanoporous materials.

2. Synthesis of CFA-Based Nanoporous Materials

According to recent research on the preparation of nanoporous materials from CFA, production is continually being updated and improved [3]. In addition to the traditional hydrothermal synthesis method [14,15,20] and the alkali melting method [21], several new synthesis methods have emerged, including the supercritical hydrothermal technique [22–24], the microwave heating [25–27], the ultrasonic method [28], and the dialysis
method [29]. Notably, a range of new synthesis methods based on the traditional hydrothermal method have shown continuous improvement, which will be discussed in the following section.

2.1. Synthesis Principle

Numerous methodologies exist for synthesizing nanoporous materials with CFA, each generally adhering to similar synthesis principles. These primarily involve the preparation of precursors, dissolution, and the polymerization of aluminosilicates. Currently, it is understood that the formation mechanisms of molecular sieve nanoporous materials primarily encompass solution-mediated hydrogel, solid hydrogel, and dual phase transformation mechanisms.

2.1.1. Solid Hydrogel Transformation Mechanism

In the 1960s, Breck et al. [30] utilized X-ray diffraction technology to monitor the crystallization of zeolite molecular sieves and initially proposed a “solid hydrogel transformation mechanism” based on their research findings. During the process of zeolite molecular sieve crystallization, silicate and silicic acid radicals polymerize into an initial amorphous silicate gel. The solid phase of the gel does not dissolve, and the resulting liquid gel does not directly contribute to the growth of the crystallization nucleation. A large number of related studies have provided experimental evidence for the solid phase conversion mechanism, and some excellent reviews have been published discussing the mechanism of solid hydrogel transformation [31,32].

2.1.2. Solution-Mediated Hydrogel Transformation Mechanism

In 1966, Kerr et al. [33] first proposed the solution-mediated hydrogel transformation mechanism during the investigation of the crystallization process of zeolite A. According to this theory, the formation of molecular sieve crystals involves the dissolution of aluminosilicate gels in an alkaline solution, followed by nucleation and growth. Liu et al. [34] conducted a systematic investigation into the effects of Na+ and K+ on the nucleation and growth kinetics of ZSM-5. They observed, for the first time, that different ions lead to the crystallization of the same gel along different transformation mechanisms (solid hydrogel transformation mechanism or solution-mediated hydrogel transformation mechanism). This suggests the existence of various formation mechanisms in crystal nucleation, influenced by the surrounding environment.

2.1.3. Dual Phase Transformation Mechanism

The crystallization process of nanoporous materials has been the subject of debate, particularly regarding the dispute between solid hydrogel and liquid transformation mechanisms. In the early 1980s, researchers proposed a two-phase transformation mechanism that integrates the characteristics of both solid hydrogel and solution-mediated hydrogel transformation mechanisms. Both mechanisms are observed during the synthesis of molecular sieves, occurring simultaneously in the middle and late stages of the crystallization reaction. Different reaction systems and stages of the reaction emphasize distinct reaction mechanisms. Matlob et al. [35] employed the microwave radiation method to synthesize zeolite NaA and subsequently analyzed it using inductively coupled plasma-optical emission spectroscopy and response surface methodology. Their findings indicated that the zeolite underwent conversion from the solid state of the precursor, thus supporting this theory.

2.2. Synthesis Methods

Currently, the primary valuable utilization of CFA is the production of nanoporous materials. There are numerous methods for synthesizing nanoporous materials using CFA, with the most advanced techniques being conventional hydrothermal methods and
alkali melting activations. Among these, several new synthesis methods based on the traditional hydrothermal method have been continuously improved, enabling the synthesis of nanoporous materials of higher quality.

2.2.1. Traditional Hydrothermal Synthesis

The essence of the hydrothermal synthesis technique is the reactant reacts in the aqueous solution with high temperature and pressure. In an alkaline environment, the silicon and aluminum in the CFA are leached and transformed into an aluminosilicate gel. Under specific temperature and pressure conditions, this gel can be used to synthesize various types of nanoporous materials. The traditional hydrothermal synthesis technique encompasses both one-step and two-step synthesis methods.

(1) One-step method

The one-step hydrothermal technique is a type of traditional hydrothermal method that has gained more attention in current research. The one-pot method lacks pretreatment, and the metallic components in the fly ash are dissolved and retained in the slurry during the hydrothermal reaction, resulting in the synthesis of typically only zeolite-based nanoporous materials via this method. Na-P1 zeolite [36,37], Na-X zeolite [38], and K-CHA zeolite [39] have been successfully synthesized by the one-pot method. The presence of many inert components in the fly ash may give rise to the development of unfavorable impurities (e.g., hydroxyl sodalite) [40], insufficient crystallinity of the product, defects such as poor crystallinity, and detrimental impacts on the pore structure of the product and ion exchange properties [41]. Therefore, it is necessary to ensure high alkalinity and reaction temperatures while also ensuring long reaction times.

(2) Two-step method

The CFA is uniformly dispersed in an alkaline solution using this method. By detecting the Si/Al ratio in the precursor and adjusting it through the addition of Si and Al sources to match the synthesis conditions of different types of zeolites. The final products can be obtained through crystallization reaction, washing, and drying procedures.

Wang et al. [20] synthesized artificial zeolite using a two-step hydrothermal method. Initially, they extracted the silico-aluminum component from the CFA raw material, followed by converting the alkali-silica component in the CFA into soluble metasilicate and aluminate hydrates to produce nanoporous materials. Hollman et al. [42] used the two-step method to synthesize zeolite P1, X, and A (Figure 2), and the highly pure Na-P1 and zeolite Na-X were obtained, i.e., above 95 wt.%. The silicon and aluminum ions of the waste liquid were fully used in the first step, which greatly improved the total conversion rate of CFA. While the addition of silicon and aluminum salts can yield excellent products, it also leads to increased production costs. Iqbal and colleagues [43] successfully synthesized a pure and single-phase Na-A zeolite from fly ash through a two-step hydrothermal process that implemented a temperature step. The specific surface area of the synthesized zeolite phase was 122 m² g⁻¹, significantly surpassing that of commercial Na-A zeolite (36.3 m² g⁻¹). Castillo et al. [44], Wang et al. [45], and Yuan et al. [46] employed a comparable strategy to extract the sodium silicate-enriched solution using a two-step process, initially removing impurities such as iron and calcium ions. Subsequently, hexagonal mesoporous silica (HMS), mesoporous silica nanospheres (MSN), and mesoporous silica (CFA-MS) were obtained via hydrothermal reaction with an additional templating agent. Notably, the specific surface area of HMS, MSN, and CFA-MS can reach 281.7, 693, and 497 m² g⁻¹ respectively.
Based on the synthesis results, the equipment used in traditional hydrothermal synthesis is simple and the operation is convenient, making it a popular method for preparing nanoporous materials. The conventional hydrothermal technique typically requires higher alkalinity, temperature, and reaction time to ensure product purity and pore structure [47]. While this method is easy to operate and suitable for scaling up, it imposes more stringent requirements on reaction conditions.

2.2.2. Modified Hydrothermal Methods

The synthesis of CFA nanoporous materials is predominantly carried out using the conventional hydrothermal synthesis method. However, this approach encounters challenges related to product purity, prolonged reaction cycles, limited reproducibility, and underutilization of reactants. In order to address these issues, researchers have focused on integrating conventional hydrothermal techniques with alternative methods to enhance the synthesis process. These methods include microwave-assisted synthesis, seed induction techniques, and supercritical hydrothermal synthesis, among others.

(1) Microwave radiation method

The microwave radiation method employs microwave technology to heat and synthesize materials in the CFA crystallization reaction. Gao’s [25] findings suggested that the product synthesized without microwave radiation under identical conditions had lower purity and more ambiguous features. The main synthesis process involves batching and grinding the raw materials, using microwave-assisted technology for microwave crystallization, and after washing, drying, and other operations, the corresponding nanoporous material products were obtained. Fukasawa et al. [26] utilized microwave radiation technology to convert CFA into zeolite nanoporous material and compared the crystalline zeolite synthesis rate with the oil bath heating method, which revealed that microwave heating did not alter the process of crystallization, as shown in Figure 3. The larger zeolite crystal formation rate in the microwave method can be attributed to the localized heating caused by microwave radiation. Behin et al. [48] achieved the successful synthesis of NaA zeolite via the microwave hydrothermal technique. The application of microwave power resulted in an increase in the crystallinity and yield of NaA zeolite. This method produced a specific surface area of 42.43 m² g⁻¹ with a maximum pore size distribution of 9.4 nm.

The production of porous materials through the microwave hydrothermal method typically accelerates the crystal formation rate and boosts product purity [3]. Nevertheless, challenges such as low overall crystallinity and inadequate conversion rates of high-
quality crystals persist, necessitating further optimization of experimental conditions in future studies.

Figure 3. SEM of zeolite crystals synthesized by (a) oil-bath heating and (b) microwave radiation. (c) Schematic diagram of CFAZ synthesis by oil-bath and microwave heating. (a–c) Permitted from ref. [26]. Copyright (2018) Elsevier.

(2) Seed induction method

In the process of preparing nanoporous materials using the CFA alkali melted hydrothermal synthesis method, the critical factor is the formation of aluminosilicate gel. The formation of aluminosilicate crystals involves the induction, nucleation, and crystal growth phases. The seed induction method involves adding seeds to the mixed raw materials to induce the acceleration of crystal growth, thus achieving a shortened reaction period. This method is to introduce the desired seed into the mixture of CFA and alkali, mix it uniformly, and then react at a lower temperature, then this target product can be obtained through filtration, washing, drying, and other operations [49].

In the 1990s, LaRosa et al. [49] employed CFA for synthesizing zeolite and discovered that the addition of specific seed crystals to the reaction raw materials, such as natural zeolite, can orient the reaction in a specific direction, significantly reducing the reaction cycle while achieving higher synthesis purity and crystallinity. It should be noted that not all zeolite species can be employed as crystalline agents in zeolite synthesis. In the study of LaRosa et al. [49], the addition of natural zeolites such as clinoptilolite, chabazite, erionite, and mordenite did not prove effective under identical conditions. Conversely, the inclusion of phillipsite resulted in the formation of Na-P zeolites. Zhao et al. [50] used aluminosilicate-gel slurry as a source of seed added to the synthesis of zeolite to prepare high-purity zeolite-Y in a directed manner. Li et al. [51] used CFA for alkali treatment and added 13X type zeolite as seed crystals to induce the synthesis of zeolite X, and explored the ammonia removal performance of X-type molecular sieves synthesized under differ-
ent reaction conditions. The addition of a small amount of 13X molecular sieve seed crystals effectively guided the production of molecular sieves and prevented the generation of other zeolite phases. Under optimal synthesis conditions with a 10 h crystallization time, the maximum removal rate of NH$_4^+$ in the sewage of the zeolite synthesized with CFA is approximately 70.2%, providing a new preparation method for NH$_4^+$ adsorption material. Wang et al. [52] synthesized Cu-SSZ-13 in different routes. They supplemented Si sources, organic structure-directing agents (OSDAs), and SSZ-13 seed (Figure 4). The diameter of the zeolite prepared by adding seed crystals was smaller than that of the zeolite prepared by only adding a silicon source, but the Cu content was lower compared to other routes.

The addition of seed crystals during the zeolite synthesis process typically reduces the crystallization period and promotes the formation of specific zeolite species in a controlled manner, thus enhancing their purity. The seed induction method offers several advantages over other methods, but further mechanistic studies are required to establish the connection between the introduced crystalline species and the type of products synthesized in a directed manner, the induction mechanism of which has not yet been clearly elucidated.

(3) Supercritical hydrothermal technique

The supercritical hydrothermal technique is a novel composite method derived from the combination of hydrothermal synthesis technology and supercritical fluid technology. Supercritical water, with both temperature and pressure exceeding 374 °C (the critical temperature) and 22.01 MPa (the critical pressure), exhibits a density and solvation capacity comparable to that of liquids [53]. It has the ability to dissolve many solids or high-boiling substances, similar to general liquid solvents. Moreover, its viscosity and diffusion coefficient resemble those of gases [54]. The chemical and physics features of water near the critical point are highly sensitive to temperature and pressure. In a supercritical environment, reactions can be manipulated by controlling the pressure. This offers the advantage of enhancing the solubility of reactants and products, as well as eliminating the
limitations of interphase mass transfer on the reaction rate [54,55]. The properties of the fluid can be adjusted by pressure without changing its chemical composition. In addition, the zero surface tension makes it easy to dissolve into porous substances [53].

Currently, the supercritical hydrothermal method is frequently employed for the synthesis of nanomaterials [56]. Wang et al. conducted a study on the synthesis of sodalite and cancrinite in a supercritical hydrothermal environment, focusing on the impact of CFA type, solid-liquid proportion during reaction, and time-interfering factors for nanoporous materials [24]. The researchers successfully synthesized zeolites using this method within a 5 min reaction time. It was observed that as the concentration of NaOH increases, the zeolite species transition from cancrinite to sodalite. Compared to the conventional hydrothermal technique, this approach offers enhanced crystallinity, accelerated reaction rates, and relatively simple controllability. Zhao et al. [22] synthesized CFA zeolite in an alkali fusion-supercritical hydrothermal method. The supercritical hydrothermal synthesis method enabled the production of cancrinite within just 1 min, exhibiting high crystallinity and demonstrating significant enhancement in reaction rates under supercritical water conditions. The supercritical hydrothermal technique can substantially accelerate the speed of zeolite synthesis. However, the current study still has certain shortcomings, such as fewer types of synthesized zeolites, an incomplete understanding of influencing factors, and an unclear synthesis mechanism that requires further elucidation.

(4) Steric hindrance method

The method of introducing steric hindrance involves adding specific groups to regulate the growth of crystal. The added steric hindrance agent contains special groups, such as amide groups, which exhibit a strong affinity with polar molecules and other groups. In the synthesis process, the silicon source and aluminum source of the raw materials undergo decomposition polymerization to form a precursor. The added steric hindrance agent and the precursor of the reactant undergo a self-crosslinking reaction, thereby playing a role of steric hindrance and regulating the synthesis of nanoporous materials [57]. Bonaccorsi et al. [58] found that incorporating organic additives into the molecular sieve manufacturing can play a role in steric hindrance, alter the nucleation and growth velocity of the molecular sieve, and lead to the enhancement of molecular sieve control. Kang [57] synthesized the ZSM-5 molecular sieve with polyethylene glycol (PEG), polyvinylpyrrolidone (PVP), and triethanolamine (TEA) as a steric hindrance agent (Figure 5). Adding a steric hindrance agent can shorten the nucleation and induction, whilst simultaneously enhancing the crystallization rate. The synthesized ZSM-5 molecular sieve with the presence of PVP exhibits a reduction in particle size, a rise in specific surface area (from 375 to 423 m² g⁻¹) and pore volume (from 0.21 to 0.12 cm³ g⁻¹), as well as a more uniform distribution of aluminum, that is, a better distribution of active centers. Steric hindrance can affect the crystalline nucleation process of zeolites through steric hindrance agents, possibly through complexation (e.g., TEA) as well as adsorption. Steric hindrance agents tend to reduce the grain size of molecular sieves, increase the growth rate, and may have an effect on the characteristic crystalline surface of the material.
Figure 5. SEM image of ZSM-5 molecular sieve synthesized by different types of steric hindrance agents: (a) PVP, (b) PEG, (c) TEA, and (d) Original. (a–d) Permitted from ref. [57]. Copyright (2018) Elsevier.

Research indicates that this method is able to effectively control the growth process of nanoporous materials and yield products with improved performance. Nonetheless, despite its shorter development time, the associated technology has not yet been fully developed and implemented in practical production.

According to the above article, the basic process of various synthetic methods is summarized, and the advantages and drawbacks of their individual methodologies as well as the type of nanoporous materials are summarized in Table 1.

Table 1. Summary of merits and demerits for different synthesis processes.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Type of Nanoporous Materials</th>
<th>References</th>
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<tbody>
<tr>
<td>One-step hydrothermal method</td>
<td>simple process and low cost</td>
<td>high alkalinity, long reaction time, low product purity, and more by-products</td>
<td>Na-P1 [36,37]</td>
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<td>Na-X [38]</td>
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<tr>
<td>Two-step hydrothermal method</td>
<td>higher product purity, less impurities</td>
<td>high alkalinity, long reaction time, complex operation and high cost</td>
<td>Na-P1 [42,59,60]</td>
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<td></td>
<td></td>
<td>Na-A [20,42,43,61]</td>
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<td></td>
<td>Na-X [42]</td>
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<tr>
<td>Microwave radiation method</td>
<td>simple process, short reaction time and high crystallization rate</td>
<td>low crystallinity, lack of mechanism of action high cost</td>
<td>Mesoporous silica [44–46]</td>
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<td>Na-P1 [62]</td>
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<td>Na-A [25,48,63]</td>
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<td>Phillipsite [26,64]</td>
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<tr>
<td>Seed induction method</td>
<td>high product purity, mild reaction conditions, short time</td>
<td>lack of mechanism of action, more by-products, complex operation</td>
<td>Na-P1 [49]</td>
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<td>Cu-SSZ-13 [52]</td>
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</table>
2.3. Preparation Factors

The properties and types of synthesized nanoporous materials from CFA can be determined or altered by different reaction conditions during the synthesis process. Among these, the most influential conditions include Si/Al ratio, alkalinity, crystallization time, and crystallization temperature.

2.3.1. Silicon–Aluminum Ratio

The impact of the Si/Al ratio on nanoporous materials derived from CFA primarily manifests in two aspects. Firstly, variations in the intrinsic silicon–aluminum ratio of specific CFA lead to the production of distinct nanoporous materials. A lower silicon–aluminum ratio is generally conducive to the synthesis of zeolite A molecular sieves, while the formation of zeolite Y and zeolite P molecular sieves necessitates relatively higher silicon–aluminum ratios. Secondly, altering the silicon–aluminum ratio within the reaction system by introducing additional silicon or aluminum results in the creation of diverse nanoporous materials. Based on the experimental results obtained by Dai [65], it was observed that at a high silicon–aluminum ratio, the crystallization process occurred rapidly and zeolite P molecular sieves could be formed. On the other hand, when the sample has a low silicon–aluminum ratio, the crystallization time is dependent on the alkalinity of the reaction. If a high level of basicity is present, a zeolite X molecular sieve is formed, whereas a zeolite P molecular sieve is formed with low basicity.

2.3.2. Alkalinity

With a constant Si/Al, the type of nanoporous material synthesized is influenced by the alkalinity of the reaction system. The alkali in the reaction system is mainly used to control the state of the silicate anion and the equilibrium state of each component in the reactant so that the reactant can generate a specific nanoporous material under certain conditions [66]. Therefore, nanoporous materials synthesized with different alkalinity are also diverse. In Dai’s experiment [65], only the alkalinity range of a certain fixed nanoporous material, the greater the alkalinity, the shorter the crystallization time. When the alkalinity increases, the zeolite P molecular sieves will transform into zeolite X molecular sieves, and as the crystallization time increases, the crystal crystallization effect of the zeolite X molecular sieves can be improved. Moreover, as the reaction time is prolonged, lower alkalinity seems to be more advantageous for the generation of molecular sieves.

Generally, the type of nanoporous material products can be regulated by modulating the pH, as diverse nanoporous materials exhibit sensitivity to the pH levels during synthesis. For instance, SBA-15 is usually synthesized under acidic conditions, and MCM-41 is synthesized under alkaline conditions.

2.3.3. Crystallization Time

The duration of crystallization significantly impacts the synthesis of nanoporous materials. The duration of crystallization typically exhibits a direct correlation with the degree of crystallinity, but when the crystallization time is too long, it will damage the crystal structure or cause a transformation reaction. So, there is an optimal reaction crystallization time [67]. At the onset of the crystallization reaction, fewer silicon–aluminum reactants are activated, leading to an incomplete crystallization process. Consequently, numerous
uncrystallized sodium aluminosilicate sol mixtures persist within the system. Extending the crystallization duration continuously activates the properties of the Si-Al compound, thereby increasing crystallinity. However, there exists an optimal crystallization time. Beyond this point, when the reaction time surpasses the optimal duration, the crystallinity of the reactants begins to decrease.

2.3.4. Reaction Temperature

The preparation of nanoporous materials from CFA is significantly impacted by the reaction temperature. The reaction temperature is also another important factor in the synthesis of nanoporous materials from CFA. In the crystallization process of nanoporous materials, the main factor that controls nucleation at the crystallization is temperature which mainly limits the growth rate of crystal nucleation [67,68]. In theory, a higher temperature can accelerate the formation of crystal nuclei, by raising the temperature, the reaction of crystallization can be diminished, so the decrease in crystallinity will slow down the crystallization rate. However, when the temperature is too high, impurity crystals will appear and the crystallinity will decrease, which is not conducive to the growth of crystals, and the energy consumption will increase. Therefore, there is an optimal crystallization temperature.

2.4. Synthetic Nanoporous Materials from CFA

Based on the previous discussion, despite being a coal-based solid waste, CFA has the potential to serve as a source of Si and Al for the synthesis of nanoporous materials, owing to its excellent Si–Al contents. This section provides a summary of relevant research and categorizes the synthesized nanoporous materials based on their type, including zeolites, mesoporous silica, and MOFs. The focus here is on the structural and porous properties of nanoporous materials derived from fly ash.

2.4.1. Zeolite

Zeolites make excellent adsorbents and catalysts because of their significant specific surface area, pore size, molecular sieving properties, and acidity, so the synthesis of zeolites using CFA is a valuable method to treat this solid waste. Höller [69] first reported the mineral phase transformation behavior of CFA after hydrothermal treatment in NaOH medium in 1985, after which the successful synthesis of various types of CFAZ was reported, which provided a new way for the comprehensive management of CFA. The hydrothermal technique is a well-established technique for synthesizing zeolites. This method has successfully produced NaP [70], NaP1 [59], and NaA [71] zeolites with promising results. In pace with progressive research, many improvements have been employed to optimize the synthesis of CFAZ. For instance, Iqbal et al. [43] improved the conventional two-step hydrothermal method by performing a 12 h induction before the second hydrothermal reaction, which favors the formation of primary and secondary gels and is more conducive to the formation of single-crystal 4A zeolites. The zeolite synthesized by this method has a single crystalline phase with 82% crystallinity and a well-defined cubic structure as well as smaller particle size compared to the 75% crystallinity of reference zeolite, and the BET analysis shows that the specific surface area (122 m² g⁻¹) is three times greater than the reference zeolite.

The synthesis of high-purity zeolite nanocrystals using CFA is a challenging task that typically takes several days to complete, even with conventional alkali activation methods. In order to address this challenge, Sivalingam et al. [28] succeeded in obtaining NaX zeolites with good crystallinity through ultrasonic hydrothermal premelting of seven different CFAs for the purpose of metal ion adsorption (specifically zinc, copper, cadmium, lead, nickel, calcium, and magnesium divalent ions) as well as dye adsorption. After just 20 min of ultrasonication, the synthetic NaX zeolite exhibited a spherical hollow morphology, with nano-sized grains, smaller than those found in commercial NaX zeolite (which
are on a micrometer scale). The high-purity zeolite synthesized by this method showed excellent adsorption of Pd$^{2+}$ and crystalline violet (maximum adsorption of 171.23 and 149.36 mg g$^{-1}$, respectively). This performance surpasses that of the low-cost adsorbents developed in the same period. Zhang et al. [72] prepared NaP zeolite by graded extraction and found that different sodium salts were used to replace NaOH to avoid the dissolution of crystals by excessive alkalinity. Finally, it was found that the addition of NaBr was able to obtain purer NaP zeolites with good morphology, and Zhang also examined how the inclusion of organic steric hindrance PEG could impede the aggregation of precursors and decelerate the growth of crystals, which was conducive to the generation of zeolite crystals with small particle size and high dispersity, and that NaP zeolites with the inclusion of organic steric hindrance (CyOH) had the largest specific surface areas and corresponded to the highest Zn(II) adsorption. Four different zeolites were prepared using CFA by Park et al. [73]. They initially screened the CFA to obtain non-magnetic CFA. Subsequently, the non-magnetic zeolites were pretreated using milder acetic acid, followed by alkali melt activation. Ultrasonication was then applied to the activated precursor, and the zeolites were induced to crystallize through a hydration reaction. XRD analysis revealed a greater removal of quartz and mullite phases from the zeolite products synthesized via this method. Additionally, it was observed that with an extended crystallization time, NaA zeolite and NaX zeolite transformed into a more stable HS zeolite. Furthermore, CFAZ with good crystallinity can be efficiently synthesized using a template-free low-temperature induction method, graded treatment method, and solvent-free method.

2.4.2. Mesoporous Silica

Mesoporous silica has garnered considerable attention in academic research due to its well-organized pore structure, varied mesopore shapes, facile regulation of pore composition and properties, and ease of modification. Since 1992, when Mobil first synthesized mesoporous silica using templating agents, researchers have been able to manipulate the morphology of mesoporous materials and fabricate materials with specific sizes and morphologies [13]. At present, the preparation of mesoporous silica primarily adopts the sol–gel technique, and the use of templating agents as well as high-purity silicon sources make it difficult to reduce the synthesis cost, which limits the development of mesoporous silica. The primary constituents of CFA consist of SiO$_2$ and Al$_2$O$_3$, with SiO$_2$ comprising approximately 60–70 weight percent, and previous studies for the synthesis of mesoporous silica have shown that mesoporous silica is not sensitive to the type of silica source, which provides a feasible solution for the resource utilization of CFA. As early as 1999 Chang et al. [74] had successfully made mesoporous silica MCM-41 from CFA, which they synthesized using a molten CFA solution as well as cetyltrimethylammonium bromide (CTAB) as the raw material, proving that even if the raw material contains a large number of impurities, it can still be used to produce mesoporous silica, which opens up the way to subsequent research.

However, controlling the composition and homogeneity of precursors is challenging when synthesizing mesoporous SiO$_2$ on a large scale via the sol–gel process, the composition and homogeneity of the precursors are difficult to effectively control, which also hinders the development of an industrialized process for the preparation of mesoporous silica [75]. To address this challenge, Li et al. [76] proposed to successfully prepare and synthesize mesoporous silica from CFA by controlled acid leaching. They incorporated various influencing parameters into a new parameter termed reaction intensity, to precisely characterize their contribution to pore formation. As reaction intensity increased, the pore structure evolved from none to V-shaped pores, followed by slit pores, and eventually cylindrical pores. The pore characteristics of mesoporous silica produced via the acid impregnation rival those obtained using the sol–gel technique, which provides a new idea for reusing CFA and synthesizing mesoporous silica on a large scale.

The CFA produced in some areas contains a large amount of aluminum (up to 55%), and although there are mature production lines to extract aluminum resources from CFA
on a large scale, the large amount of silica-rich waste streams contained in the waste streams has become an urgent problem. To solve this problem and improve the resource utilization efficiency of CFA, Wang et al. [45] simulated the extraction of alumina from CFA and prepared mesoporous silica materials from the resulting desilication waste solution. MSN exhibited superior hydrothermal stability, cyano-distribution, and specific surface area than ISM. Then they compared mesoporous silica produced in non-homogeneous and homogeneous systems. Results demonstrated that the MSN had better hydrothermal stability, cyano-distribution, and specific surface area than ISM. The specific surface area and pore volume of MSN were 693 m\(^2\) g\(^{-1}\) and 0.594 cm\(^3\) g\(^{-1}\), respectively, indicating MSN’s efficacy in treating actual wastewater from battery factories. Wang et al. [77] produced amidoxime-functionalized mesoporous silica nanospheres (ami-MSN) from CFA through a modified non-homogeneous system. These were then employed in the adsorptive elimination of U(VI). The ami-MSN possessed a surface area of up to 676 m\(^2\) g\(^{-1}\) and achieved an adsorption level of U(VI) of up to 263.85 mg g\(^{-1}\). Ju et al. [78] combined a silicon extraction process with a porous material synthesis process to fully utilize the amorphous and crystallized phases of silicon in CFA. As a result, ordered mesoporous silica was synthesized without excess residue. The silicon-extracted efficiency increase to almost 100% from 31.75%. The mesoporous silica synthesized demonstrates a meticulously arranged pore structure, which yields a specific surface area of 663.87 m\(^2\) and a pore volume of 0.41 cm\(^3\) g\(^{-1}\), alongside an average pore size of 2.73 nm.

In addition to effectively utilizing inexpensive silica sources in CFA and thus reducing the cost of synthesizing mesoporous silica, reducing or not using expensive templating agents is also a viable approach. Ju’s group [79] also prepared mesoporous silica powders using a green method that utilized CO\(_2\) as a precipitant and template. The powders had a specific surface area of 355.45 m\(^2\) g\(^{-1}\), a pore volume of 0.73 cm\(^3\) g\(^{-1}\), and an average pore size of 7.67 nm. After calculation, 285 kg of mesoporous silica can be synthesized from 1 ton of CFA, 1.02 tons of crude Na:CO\(_2\) could also be produced, resulting in the recycling of CFA and the fixation and storage of approximately 433 kg of CO\(_2\), as well as the production of high-value mesoporous silica materials.

2.4.3. MOFs

In recent times, MOFs have emerged at the forefront of extensively researched and rapidly developing nanoporous materials. Extensive research has demonstrated the potential of MOFs as functional materials in numerous fields, including adsorption, gas storage, drug conveyance, and photoelectrocatalysis. However, the high production cost of MOFs remains one of the biggest challenges for their commercialization [80]. The extraction of terephthalic acid (H:BDC) and other organic ligands from used polyethylene terephthalate (PET) bottles as a viable source of organic ligands for MOF synthesis was realized as early as 2016 [81]. However, it was not until 2021 that Rambau et al. [82] synthesized Al-MOFs with fumaric acid for the first time using a solution of metal ions extracted from CFA was utilized as the metal source for MOF synthesis, which provided a new way to add value to CFA and control the cost of MOFs synthesis. CFA-FumMOF synthesized using inexpensive metal sources was almost similar to commercial Al-FumMOF, and the specific surface area of CFA-FumMOF (1236 m\(^2\) g\(^{-1}\)) was comparable to that of commercial Al-FumMOF (1266 m\(^2\) g\(^{-1}\)). On the basis of this study, Rambau’s group used the synthesized CFA-FumMOF for capacitor electrode materials. The resulting materials scored an impressive specific quantity capacity value of 9.88 mAh g\(^{-1}\), while the specific capacitance of the derivatized carbon material prepared with CFA-FumMOF as precursor displayed a significant value of 306.59 F g\(^{-1}\) under the same conditions, providing a feasible path for high-value reuse of solid wastes [83]. Yuan’s group [84] prepared MIL-53(Al) by employing high alumina coal fly ash (HFAA) and its sintered product obtained by alkali melt activation reacted with terephthalic acid in a one-pot process, respectively, and proposed the concept of ecological MOFs (eco-MOF). The synthesized eco-MIL-53(Al) maintained a
firm backbone at 500 °C. The surface area and pore volume of eco-MIL-53(Al) treated with hydrochloric acid can reach 16.3 m² g⁻¹ and 0.075 cm³ g⁻¹, respectively.

Considerable developments have been made in CFA-based nanoporous materials, including the synthesis of various types of zeolites, mesoporous silica, and even the emerging MOFs from fly ash. However, the CFA-based nanoporous materials in these studies exhibit inferior pore structure and weaker properties in comparison to the pure materials prepared using traditional methods. For instance, according to literature, conventional NaX zeolite can adsorb Pb²⁺ and crystal violet up to 491 [85] and 227.27 mg g⁻¹ [86] correspondingly, whereas CFA-based NaX zeolite exhibited an adsorption capacity of 171.23 and 149.36 mg g⁻¹ for Pb²⁺ and crystal violet [28]. The zeolite Y synthesized from high-purity raw materials had a specific surface area of 680.6 m² g⁻¹, whereas the specific surface area of the CFA-based zeolite Y decreased to 386.9 m² g⁻¹. Furthermore, the zeolite Y synthesized from fly ash yielded an 18.2% lower acetone adsorption capacity compared to the conventionally synthesized zeolite Y [87]. As demonstrated in Table 2, this decline in performance is also widespread for both CFA-based mesoporous silica and MOFs. The reduction in the specific surface area of nanoporous materials is a significant factor in their decreased adsorption. This could be attributed to the existence of impurity components in the precursor solution obtained from fly ash, which hinders the formation of the pore structure. In the future, it is imperative to enhance the pore structure and practical application properties of CFA-based nanoporous materials.

Table 2. Summary statistics of the type of nanoporous materials and their porosity parameters and adsorption capacity.

<table>
<thead>
<tr>
<th>Types of Nanoporous Materials</th>
<th>Specific Surface Area (m² g⁻¹)</th>
<th>Pore Volume (cm³ g⁻¹)</th>
<th>Pore Size (nm)</th>
<th>Adsorbate</th>
<th>Adsorption Capacity (mg g⁻¹)</th>
<th>Reference</th>
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<td>[43]</td>
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<tr>
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<td>[86]</td>
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<tr>
<td>Conventional zeolite Y</td>
<td>680.6</td>
<td>0.3558</td>
<td>2.11</td>
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<td>NaP-RAW</td>
<td>26.8</td>
<td>0.01503</td>
<td>3.856</td>
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<td>NaP-AMP</td>
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<td>0.01648</td>
<td>3.623</td>
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<td>NaP-PEG</td>
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<td>FAU-type zeolites</td>
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<td>NaP1</td>
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<td>[59]</td>
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<td>Conventional NaP1</td>
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<td>Mesoporous silica</td>
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<td>2–10</td>
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<td>Conventional MCM-41</td>
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<td>Mesoporous silica</td>
<td>MOFs</td>
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<td></td>
<td>676</td>
<td>0.619</td>
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<td>263.85 [77]</td>
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<tr>
<td></td>
<td>663.87</td>
<td>0.41</td>
<td>2.73</td>
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<td>CFA-FumMOF</td>
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<td></td>
<td>MB</td>
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<tr>
<td>MIL-53(Al)</td>
<td>16.3</td>
<td>0.075</td>
<td>1.8</td>
<td>MB</td>
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<tr>
<td>Conventional MIL-53(Al)</td>
<td>39.6</td>
<td>0.059</td>
<td></td>
<td>MB</td>
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</tr>
</tbody>
</table>

3. Environmental Applications of CFA-Based Nanoporous Materials

The entire life cycle of CFA-based nanoporous material systems comprises production, utilization, and recycling. The production process involves the following steps: initially, the coal-fired industry generates the primary solid waste, fly ash. Subsequently, CFA-based nanoporous materials are predominantly prepared through alkali melting and hydrothermal methods. These CFA-based nanoporous materials can be mainly utilized for the adsorption of pollutants. Ultimately, valuable by-products from the synthesis process of CFA-based nanoporous materials can be reclaimed through physical and chemical methods [94,95]. In Figure 6, it is evident that CFA-based nanoporous materials represent an environmentally friendly solution for effectively addressing the issue of fly ash accumulation. Their efficient utilization contributes significantly to mitigating environmental pollution concerns. Moreover, the environmental impact stemming from their production process has been successfully addressed through recycling [96].

![Figure 6](image_url)

**Figure 6.** The CFA-based nanoporous materials throughout their life cycle.

The following content offers a concise analysis of the preparation, utilization, and end-of-life costs associated with CFA-based nanoporous materials. The preparation cost encompasses raw material acquisition, material transportation, and equipment expenses. The utilization cost involves regular inspections and repairs, while the end-of-life cost pertains to the management and recycling of scrapped items.

The total life cycle cost of CFA-based nanoporous materials is obtained as shown in Formula (1):

\[
C = C_{internal} + C_{external}
\]

where \(C_{internal}\) and \(C_{external}\) refer to internal and external costs, respectively.
\[ C_{\text{internal}} = MC + TC \]  
(2)

where \( MC \) refers to the raw material cost, while \( TC \) refers to the transportation cost. The \( MC \) includes the raw material CFA expenses, with the \( MC \) of CFA amounting to only 61.83 USD per ton [97]. As a large amount of solid waste generated by coal-fired factories, fly ash has a relatively low price and can usually be obtained at a lower or even zero cost. Therefore, overall, the purchase cost of raw materials is reduced [98,99].

\[ TC = TP \times M \]  
(3)

where \( TP \) refers to the transportation price per unit mass of raw materials, and \( M \) refers to the weight of raw materials. \( TC \) can be cut down by shortening the distance between the factory site for producing nanoporous materials and coal-fired factories. Utilizing CFA as a raw material for production can help reduce the demand for nanoporous materials made from other carbon-intensive sources. This, in turn, reduces the carbon footprint associated with the production and transportation of these materials. Therefore, \( C_{\text{internal}} \) will be very low [100].

The external cost includes waste generation and end-of-life costs (the cost of managing and recycling scrap items). The use of CFA in the production of nanoporous materials can bring environmental benefits as it reduces the demand for natural resources and minimizes waste generation. In terms of environmental impact, the utilization of CFA helps to reduce greenhouse gas emissions and \( C_{\text{external}} \) will also be very low.

Overall, the economic analysis of nanoporous materials derived from CFA highlights their potential as cost-effective and environmentally friendly materials.

CFA-based nanoporous materials have special pore structures making them suitable for sewage treatment, flue gas decontamination, soil remediation, and the like. Next, the applications of CFA-based nanoporous materials in adsorption will be introduced.

Due to their significant specific surface area and porous structures, CFA-based nanoporous materials have excellent adsorption performance and can adsorb harmful substances in solid, liquid, and gaseous states. They have good selective adsorption and efficient ion exchange properties. The adsorbates can be classified into two broad categories: gaseous pollutants and waterborne contaminants.

3.1. Removal of VOCs

According to the definition of the World Health Organization, volatile organic compounds (VOCs) generally refer to organic compounds with boiling points ranging from 50–260 °C [101]. These substances are extensively present in the air, water, soil, and other environmental media and have biological toxicities that pose a major hazard to human health [102]. Both zeolite and activated carbon are effective VOC adsorbents. However, activated carbon presents challenges as it is highly flammable and hydrophilic during the adsorption process, making it unsuitable for absorbing complex and variable industrial organic gases. On the other hand, zeolite may provide better adsorption performance, as shown in Figure 7 [15]. To demonstrate this, Zhu et al. [15] synthesized zeolite X with a BET-specific surface area of 990.3 m² g⁻¹ using CFA. It was discovered that zeolite X had a higher adsorption capacity than activated carbon and also demonstrated better stability. Zhu et al. [103] investigated the adsorption performance of 13X molecular sieves on VOCs prepared from CFA and found that although the adsorption rate of the 13X molecular sieve was slower than activated carbon, its adsorption capacity was higher. Moreover, a higher polarity of VOC molecules improved the adsorption capacity.
3.2. Removal of Organics

In addition, CFA nanoporous materials can also remove organic pollutants in water. Yuan et al. [46] used CFA to fabricate mesoporous silica to adsorb methylene blue in water, resulting in an augmented adsorption capacity over time. Under the ideal adsorption conditions, the experimental maximum adsorption capacity achieved was 316.8 mg g\(^{-1}\), which is higher than the mesoporous silica prepared in the conventional way. Oliveira et al. [104] employed CFA to synthesize microporous and mesoporous silica under different pH conditions and used it to adsorb parabens. Figure 8 exhibits the adsorption impact of the materials and pore parameters. The adsorption capacity of mesoporous silica differed depending on the molecular weight of parabens. The zeolite synthesized at a pH of 7 achieved a maximum BET-specific surface area of 396 m\(^2\) g\(^{-1}\). Yuan et al. prepared MIL-53(Al) by employing HAF A and its sintered product obtained by alkali melt activation. The adsorption capacity of this material for MB is 28.80 mg g\(^{-1}\). In comparison to pure MIL-53(Al) synthesized through conventional techniques for MB, eco-MOF exhibited a certain degree of decrease in both specific surface area and adsorption capacity (52.9% for specific surface, 65.9% for adsorption capacity) [93]. This could stem from the impurity of eco-MOF and the low conversion rate of MOFs.
3.3. Removal of Metal Ions

Human production activities emit a large amount of pollutants, and it is difficult for the ecosystem to completely degrade these pollutants. However, water is a valuable and essential resource, and a significant cause of its scarcity is the severe degradation of water quality due to pollution. As cheap adsorbents, CFA-based nanoporous materials have great potential in water treatment applications.

After various levels of physical and chemical precipitation treatments, the content of pollutants in water bodies can be reduced. However, the ionization balance and trace amounts are among the factors that may impede such reductions, and it is difficult to completely remove toxic or radioactive pollutants in water. Nanoporous adsorbents can be used for advanced wastewater depth treatment owing to their changeable and steerable pore structures and excellent specific surface areas [45]. He et al. [105] prepared zeolite A derived from CFA using a hydrothermal technique to adsorb Ni²⁺ in wastewater. The surface area of the synthesized zeolite enhanced from 1.21 m² g⁻¹ to 90.04 m² g⁻¹, and under optimal adsorption conditions, the Ni²⁺ adsorption rate could reach 94% (Figure 9).
Figure 9. SEM images of (a) CFA and (b) zeolite. (c) The impact of sorption time on adsorption of Ni^{2+} by zeolite and CFA. (a-c) Permitted from ref [105]. Copyright (2020) Elsevier.

Tuanov et al. [106] synthesized zeolite using local CFA samples from Brazil and used it to treat heavy metal mercury ions from water. The conversion rate of the synthesized zeolite reached 78%, the specific surface area exceeded 58 m^2 g^{-1}, and the adsorption rate of heavy metal mercury ions was twice that of CFA raw materials. Ma et al. [107] used CFA to synthesize nanoporous materials to adsorb copper-containing wastewater, and the synthesized materials with an optimized process had a copper ion adsorption rate as high as 93.3%. Sewage treatment is an important application field of CFA nanoporous materials. Scholars at home and abroad have done more research in this area and have developed a variety of products with good adsorption properties. Lankapati et al. [108] used a seed induction hydrothermal synthetic method to synthesize mordenite-type zeolite, and at room temperature (298 K), the maximum absorption rates for Pb^{2+} and Cd^{2+} are 94.1% and 88.2%, respectively. Wang et al. [77] used CFA to synthesize mesoporous silica nanoparticles (ami-MSN) to adsorb U^{6+}. Due to the robust bond formation between the uranyl ion and the oxygen/nitrogen atom within the amidoxime moiety, the highest adsorption rate can reach 98.9% as shown in Figure 10.

Figure 10. (a) Adsorption kinetics and (b) the sorption isotherms of U(VI) onto ami-MSN, (c) schematic demonstrating complexation between ami-MSN and UO_{2}^{2+} [77]. Copyright (2018) Elsevier.

3.4. Removal of Fluoride

Fluoride ion pollution is currently recognized as a serious issue, the appropriate amount of fluoride can prevent dental diseases, but fluoride content exceeding a certain limit will hurt the human body. Fluoride ion pollution of water bodies mainly comes from the natural geological conditions of pollution and man-made industrial production emissions of pollution (Figure 11).
Adsorption is a well-established water treatment technology that adsorbs fluoride by utilizing interactions on the surface of the adsorbent. With the importance of national sustainable green development, the use of solid wastes to prepare fluoride removal agents due to the adsorbent preparation cost can be greatly reduced, has become a new trend, such as the use of CFA, coal cinders, oil shale, etc. Among them, Panda et al. [109] synthesized NaP1 zeolite using NaOH treatment of CFA. The synthesized zeolite had more pores and pore channels on the surface (56.14 m² g⁻¹) and subsequently, Panda and colleagues modified the obtained zeolite together with calcium chloride to remove fluoride from water through adsorption. Chen et al. [110] used an in situ coating strategy to synthesize aluminum hydroxide-coated zeolite (AHZ) originating from CFA to study the adsorption mechanism for fluoride. AHZ has a fast fluoride removal rate, strong resistance to anionic interference, and adsorption of fluoride through hydroxyl exchange on the surface, and material achieved 18.12 mg g⁻¹ (the maximum adsorption capacity). Yang et al. [111] synthesized La-modified zeolite (LMZ) using CFA, where the adsorption of fluoride was enhanced on zeolite by substituting hydroxyl groups and bonding with La-modified on the zeolite surface, with an adsorption capacity up to 141.5 mg g⁻¹. The adsorption of F⁻ by LMZ was highly selective and easy to desorb, and the large adsorption capacity was still maintained after five adsorption cycles. In a separate study, Song et al. [112] synthesized MOF (Zr)-MOF (Ce) with varying Ce:Zr molar ratios, and the findings demonstrated outstanding performance in removing fluoride (Figure 12e). Similarly, Wang et al. [113] prepared a MOF fluoride removal adsorbent, MIL-96(Al), using 0.1 and 0.2 mol L⁻¹ NaOH solutions for regeneration. The OH⁻ was exchanged with F⁻ on the adsorbent, transferring fluorine to the NaOH to remove F⁻. The increase in solution concentration contributed to the exchange rate. Furthermore, MIL-96(Al) exhibited good adsorption performance after regeneration and demonstrated potential as a new type of fluoride removal adsorbent (Figure 12f). Although MOFs are a potential fluoride ion adsorbent of interest owing to their high porosity surface area and stability, their high synthetic cost limits their application [114]. Therefore, in the future, synthesizing MOFs from solid waste and using them to adsorb fluoride ions could be an inexpensive and efficient method for purifying fluoride-containing water.
3.5. Removal of Other Inorganics

CFA-based nanoporous materials can remove many kinds of inorganic pollutants in water. Chen et al. [11] synthesized zeolite X (from 0.15 to 270 m² g⁻¹), which increased almost two thousand times, displaying the adsorption capacity of ammonia nitrogen of 138.89 mg g⁻¹ (Figure 13). Mokgehle et al. [115] removed sulphates from acid mine drainage (AMD) using CFA hydrothermally treated zeolites. The surface area of the obtained zeolite was 3.141 m² g⁻¹, its anion selectivity decreased in the following order $\text{SO}_4^{2-} > \text{NO}_2^- > \text{Br}^- > \text{NO}_3^- > \text{Cl}^-$, and the removal of $\text{SO}_4^{2-}$ was up to 73.0%.

![Figure 12. SEM images of (a) MIL-53 (Fe), (b) UIO-66, (c) AP-UIO-66, and (d) MOF-235. (e) The fluorine removal efficiency of adsorbents with different Ce:Zr molar ratios of MOF(Zr)-on-MOF(Ce) and (e) fluorine removal efficiency of adsorbents with different Ce:Zr molar ratios of MOF(Zr)-on-MOF(Ce). (a-d) Permitted from ref [114]. Copyright (2021) Elsevier. (e) Permitted from ref. [112]. Copyright (2024) Elsevier. (f) Permitted from ref. [113]. Copyright (2019) Hindawi.](image)

![Figure 13. The influence factors (a) adsorbent dosage, (b) contact time, and (c) pH value on the ammonia nitrogen removal efficiency [116]. Copyright (2018) Springer Nature.](image)
yield of the desired products (shown in Table 2). The use of CFA-based nanoporous materials to support special particles to make functional materials can greatly increase its value. In particular, the use of CFA to synthesize nanoporous materials-based membranes, balls, fibers, or their assemblies can be used in many special fields. In addition, it is necessary to continue to increase the research work on the use of CFA nanoporous materials as insulation materials or storage materials to enrich their applications.

4. Conclusions

By the employment of CFA as a raw material, varieties of nanoporous materials including zeolite A, X, Y, P, ZSM-5 microporous materials, M41S, SBA-n series of mesoporous materials, and MOFs can be synthesized. Various types of nanoporous materials have their intrinsic characteristics and possess excellent performance in environmental remediation.

Besides the conventional hydrothermal synthesis technology, a variety of new composite hydrothermal methods have been developed, such as the use of microwave radiation, seed induction, supercritical water, and steric hindrance agents. Through effectively controlling the manufacturing conditions, such as crystallization time, alkalinity, temperature, and the Si/Al ratio, nanoporous materials with optimal properties and performance can be obtained. At present, there have been comprehensive studies on synthesizing zeolites and mesoporous silica from CFA. It is worth noting that Al-based MOFs from CFA have been reported and demonstrated excellent performance in environmental remediation, which will arouse great interest in the materials community.

The synthesis of nanoporous materials with CFA as a starting material possesses cost advantages, solves the accumulation of solid waste, and produces nanoporous materials with promising applications which, thus, has certain environmental and economic benefits. The conversion of CFA to nanoporous materials has good application and research prospects and brings new economic benefits while in line with the sustainability development strategy. Nevertheless, there remain numerous issues and challenges that must be addressed, including the need to maintain harsh reaction conditions in the traditional hydrothermal method to ensure the purity of the product, the reaction mechanism of modified hydrothermal methods that need to be investigated in depth, and the inadequacy of the textural properties and performance of the nanoporous materials converted from CFA due to the presence of impurities, et al. With the development of the research, the synthesis technologies will be continuously improved and optimized, and the CFA-based nanoporous will serve as a unique platform to resolve environmental issues.

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Abbreviations

AMD  Acid mine drainage
AHZ  Aluminum hydroxide-coated zeolite
Ami-MSN  Amidoxime-functionalized-MSN
BET  Brunauer–Emmett–Teller
CFA  Coal fly ash
CFAZ  Coal fly ash-based zeolite
CTAB  Cetyltrimethylammonium bromide
HAFA  High alumina coal fly ash
HBDC  Terephthalic acid
HMS  Hexagonal mesoporous silica
IUPAC  International Union of Pure and Applied Chemistry
IZA  International Zeolite Association
LMZ  La-modified zeolite
MC  Raw material cost
MOFs  Metal organic frameworks
MSN  Mesoporous silica nanospheres
OSDAS  Organic structure-directing agents
PEG  Polyethylene glycol
PET  Polyethylene terephthalate
PVP  Polyvinylpyrrolidone
SEM  Scanning electron microscope
TC  Transportation cost
TEA  Triethanolamine
VOCs  Volatile organic compounds
XRD  X-ray diffraction

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