Microporous and Mesoporous Materials from Natural and Inexpensive Sources

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Contents

Abstract

This chapter will attempt to describe microporous and mesoporous materials, such as zeolites, and ordered mesoporous materials, which are versatile solids that are used for the environmental remediation and energetic efficiency and the

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applications in wastewater treatment and nuclear waste, purification and separation, medicine and catalysis. These materials are constructed from tetrahedral units, TO_4 (where T is silicon and aluminum, usually), which are usually obtained from commercial sources. Furthermore, strategies and green approaches are described to contribute to the reduction of the cost production using cheaper and renewable raw materials such as rice husk, diatoms, coal ash, and clay minerals, which are potential and attractive sources of silicon and aluminum for the synthesis of zeolite and ordered mesoporous materials.

Introduction

Micro- and mesoporous materials are high-performance solids, and their pore sizes and unique structures allow interaction with atoms and ions as well as separation, processing or hosting of molecules of high scientific and technological interest. In general, porous materials must have two characteristics: many pores and pores that provide an optimized action for the performance of the material [1]. Since pores of different sizes exist, the IUPAC classified them according to their size range. Materials with pore sizes up to 50 nm are called macroporous. Materials with pore sizes between 2 and 50 nm are called mesoporous, and materials with pores sizes smaller than 2 nm are called microporous. In addition, the term nanoporous material covers materials that have pores up to 100 nm [2].

The best-known class of microporous materials is called zeolites, and the class of materials with pore sizes in the mesoporous region is called ordered mesoporous materials. The channels and cavities of these materials are able to separate molecules according to their different sizes, showing shape selectivity (molecular sieving), attractive capacity of adsorption, ionic exchange, and catalytic properties applied in environmental remediation and energy efficiency.

Both zeolites and ordered mesoporous materials are constructed from tetrahedral units (TO_4, where T is silicon and aluminum, usually), and the different spatial orientations of these units and their connections generate channels and cavities. This chapter will discuss the importance of these materials for reducing environmental problems, and how they can be synthesized via an eco-friendly synthesis using renewable, abundant, and cheap silicon and aluminum sources.

Zeolites

The term zeolites is derived from the Greek Zeo (boiling) and Lithos (stone), referring to the interesting observation made by Crönstedt of the natural mineral stilbite, the first zeolite discovered by him, which releases steam when subjected to heating in a flame [3]. Today, it is known that the effect occurred due to desorption of water, which is present inside its channels and cavities. Zeolites are crystalline materials that are composed of tetrahedral TO_4 ($T = Si$, Al, among others such as

P, Ge, Ti, Fe, Ga) interconnected by oxygen atoms. The combination of tetrahedral units of silicon (Si^{4+}) leads to a neutral structure, while the substitution of a Si^{4+} atom for an aluminum (Al^{3+}) atom causes an unbalanced charge that needs to be compensated by cations, such as Na^+, Ca^{2+}, K^+, and organic cations such as tetramethylammonium TMA^+.

Zeolites have uni-, bi-, or tridimensional channels, which can be interconnected in various ways to generate solids with higher internal surfaces compared to their external surface. These channels are occupied by water molecules, which are present during the synthesis, and by the hydrated cations, which can be removed using thermal or chemical processes. In zeolites, intracrystalline voids are maintained and, consequently, its structure. This is different from other hydrated porous materials such as $CaSO_4$ [4].

The size of the pores is what limits the ingress of ions or molecules into the intracrystalline voids of the channels and cavities. Thus, molecules that are larger than the channels and cavities cannot diffuse into zeolite. The pore opening size is dependent on the amount of bridged TO_4 units, which are also called MR (membered rings), in which the molecules or ions have access to the zeolite interior. These may have the extra-large pores (>12 MR), large (12 MR), medium (10 MR), and small (8 MR) pore, which form the pore aperture. Figure 1 shows some types of zeolitic framework structures and their pore sizes.

Each framework topology is assigned a three-letter code, which usually represents the initials of the type of framework structure, or acronyms of the university or research center where they were discovered. For example, LTA (Zeolite A) means Linde Type A, MFI (zeolite ZSM-5 and Silicalite-1) means Mobil Five, FAU (zeolites X and Y) means faujasite, and the CLO code is derived from the initials of the cloverite zeolite. Actually, there are 232 different zeolite framework codes, 67 zeolites are naturally available, and the others can be obtained via synthetic routes [5].

The way to observe zeolite construction is from their TO_4 connections. The connection of the primary units of TO_4 generates secondary building units

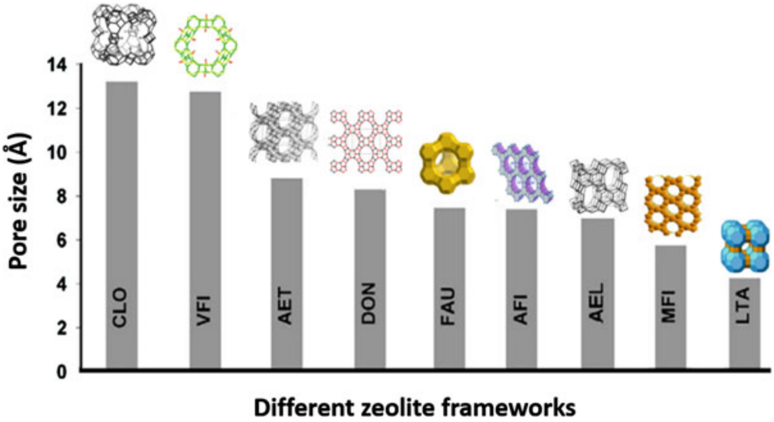

Fig. 1 Different types of zeolitic framework structures and their pore sizes

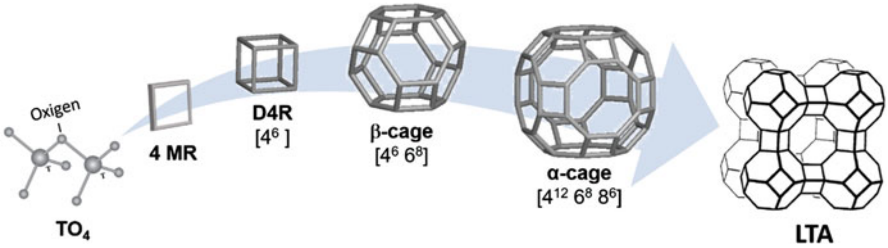

Fig. 2 Tetrahedral primary units TO_4 forming the secondary building units (SBUs) and their union for the formation of the LTA structure (zeolite A)

(SBUs), which form a polyhedral that connects until the final formation of the final zeolite structure. Figure 2 illustrates this formation, starting from the primary units of TO_4 connecting to form a 4-membered ring (4 MR). In these representations, the tetrahedron is characterized by four vertices, and oxygen atoms that connect the tetrahedron are located in the middle of each vertex. The formation of double 4-membered rings (D4R) is described in terms of their faces, in this case, six faces of four units (4^6). The β-cavity (cancrinite or sodalite cage) is formed via the union of six 4 MR and eight 6 MR (4^6 6^8). The α-cavity is formed via the union of twelve 4 MR, eight 6 MR, and six 8 MR (4^{12} 6^8 8^6). If four sodalite cages connect each other by their 4 MR faces, the zeolite sodalite (SOD, channel size of 2.6 Å) is formed. If four sodalite cages connect via D4R using their 4 MR faces, the zeolite A (LTA) is formed. This structure contains an α-cavity with an aperture of 8 MR, which allows the adsorption of molecules with sizes up to 4 Å. In zeolite A, the Si/Al ratio of 1 indicates that to balance the charges, extra cations are required, which will be distributed in the α-cage and β-cage. If these cations are close to the 8 MR window of the α-cage, they can influence the pore size. If the compensation cation is potassium, the zeolite (zeolite 3A or KA) will have its windows restricted. If the compensation cation is sodium (zeolite 4A or NaA), its small size will facilitate the entry of molecules. In contrast, when calcium (Ca^{2+}) acts as a compensating cation (zeolite 5A or CaA), it will counterbalance two charges, and the zeolite will have smaller window apertures than zeolites KA or NaA.

In general, the Si/Al ratio can determine the type of structure, which produced chemical and thermal stability, as well as the purpose of the application. Zeolites with a low Si/Al ratio, which have more aluminum in the structure (Si/Al = 1–1.5), will have a high number of charge-compensating cations and lead the material to an application such as an ion exchanger (zeolite A, X). The increase of this ratio generates zeolites with Si/Al = 2–5 (intermediates) ratios such as clinoptilolite, mordenite, and chabazite. Zeolites with Si/Al = 10–100 (high) will produce zeolites that are more thermally stable (MCM-22, ZSM-5). Zeolites with only silicon tetrahedra in their composition are called pure silica zeolites (Silicalite-1, Silicalite-2, ITQ-1, etc.) and have increased their hydrophobicity. For zeolites formed using silicon and aluminum, the exchange of compensation cations for zeolites by protons (H^+) will generate strong Brønsted sites, which are fundamental in the catalysis field [6].

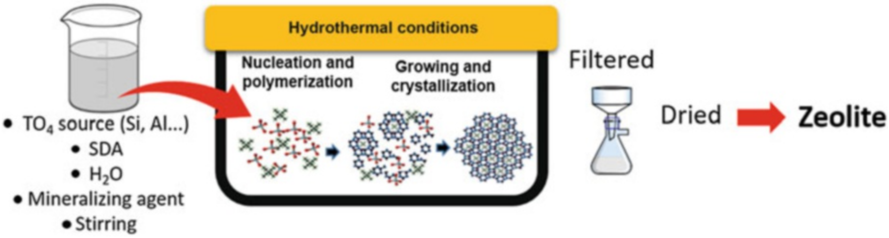

Fig. 3 An example of the synthesis procedure of zeolites under hydrothermal conditions

Zeolite formation is a complex process, and factors such as the mode of preparation, nature, and order of the added reactants and the molar composition influence the final product. Thus, it is not wrong to say that most of the zeolites obtained via synthetic routes were based on trial and error. Several mechanisms of zeolite synthesis are proposed, but they all converge on one main idea: the formation of zeolites occurs via phase transformation of the initial reactants in amorphous form into a crystalline microporous product using solution-mediated crystallization or solid transformation [7].

The reactants used for the synthesis of zeolites comprise TO_4 sources such as inorganic silica and alumina (or other heteroatom source), a mineralizing agent (OH^- or F^-) to increase the solubility of silicon and aluminum sources, a solvent such as water (hydrothermal synthesis), an organic solvent (solvothermal synthesis) or ionic liquid (ionothermal synthesis) and a structure-directing agent (SDA). Structure agents may be cations (Na^+, for example) for zeolites with a low Si/Al ratio (Zeolite A, X) or organic structure-directing agents (OSDA), such as amines and quaternary ammonium salts, which fill the void volume by inserting a less positive charge on the final solid, thus generating zeolites that contain higher amounts of silica (ZSM-5, ZSM-22, MCM-22, etc.).

The use of large organic molecules, such as OSDA, is also a strategy for obtaining zeolites with large pore sizes. For example, the zeolite ITQ-53 (germanosilicate) has a tridirectionally interconnected pore system, which is formed via 14 MR using the cation tri-tertbutylmethylphosphonium as OSDA [8]. After mixing the reactants, the gel is placed in a sealed polytetrafluoroethene PTFE-lined stainless-steel autoclave and heated to temperatures that are usually higher than 100 °C and crystallized for specified times, which may vary from hours to days or even months. At the end of the process, the material is recovered via filtration and is washed and dried, and the mass of the initial amorphous material is approximately equal to that of the zeolitic formed product. Figure 3 presents a synthesis procedure under hydrothermal conditions.

Ordered Mesoporous Materials

The ordered mesoporous materials arise from the efforts to obtain materials with larger pores, which can process larger molecules than the microporous channels of the zeolites synthesized thus far. This strategy was first developed by the Mobil

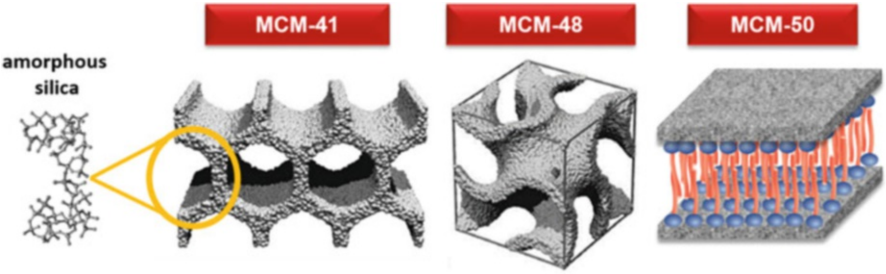

Fig. 4 Members of the M41S family. MCM-41 (hexagonal), MCM-48 (cubic), and MCM-50 (lamellar with the presence of surfactant molecules between lamellae)

group in 1992, which presented three materials synthesized from silica named MCM-41 (hexagonal), MCM-48 (cubic), and MCM-50 (lamellar) [9, 10]. These three materials belong to the M41S family (Fig. 4), and their structures are formed via amorphous silica walls.

Among the members of this group, MCM-41 received the most attention and is the most studied material; it has controllable pores between 1.5 and 20 nm, wall thicknesses of 1–1.5 nm, and a surface area of approximately 1200 $m^2\ g^{-1}$ [11]. After the discovery of M41S family, other mesoporous materials were synthesized, as observed in Fig. 5 for SBA-15 (hexagonal, which has controllable pore size from 5 to 30 nm, micropores connecting the mesoporous channels and wall thicknesses of 3–6 nm) [12], SBA-16 (cubic) [13], HMS (hexagonal) [14], KIT-6 (cubic with a mesophase similar to MCM-48) [15], MSU-X (structure with disordered channels) [16], and others. The acronyms for the mesoporous materials generally represent the research institutes that discovered these materials and/or some peculiarity of each material. For example, MCM is the acronym for a series of Mobil Composition of Matter type materials, the acronym SBA means Santa Barbara Amorphous, KIT indicates the Korea Institute of Technology, HMS means hexagonal mesoporous silica, and MSU means Michigan State University.

Like zeolites, these materials rapidly received significant interest for applications such as adsorption, catalysis, separation, and medical use such as drug release.

The synthesis of mesoporous material type M41S shares (basically) the same reactants as zeolite synthesis with one exception. The organic molecules used are surfactants with larger chain sizes such as the quaternary ammonium salt type $[C_nH_{2n+1}(C_mH_{2m+1})_3NX$ with $n = 6–22$, $m = 1–4$ and X = OH/Cl, OH, Cl, Br or $HSO_4]$. The change in the size of alkyl chain allows to control the size of the generated pore. Among the cationic surfactants, the most known and used is hexadecyltrimethylammonium bromide (CTABr). Usually, synthesis involves the dissolution of organic surfactant in the solvent (together with a basic or acidic pH), followed by the addition of a silica source (and the heteroatoms). After the stirring period at a certain temperature that permits hydrolysis and pre-condensation, the temperature can be increased and often directed toward a hydrothermal step (in autoclaves) to favor the direct condensation of silica. The synthesis of ordered

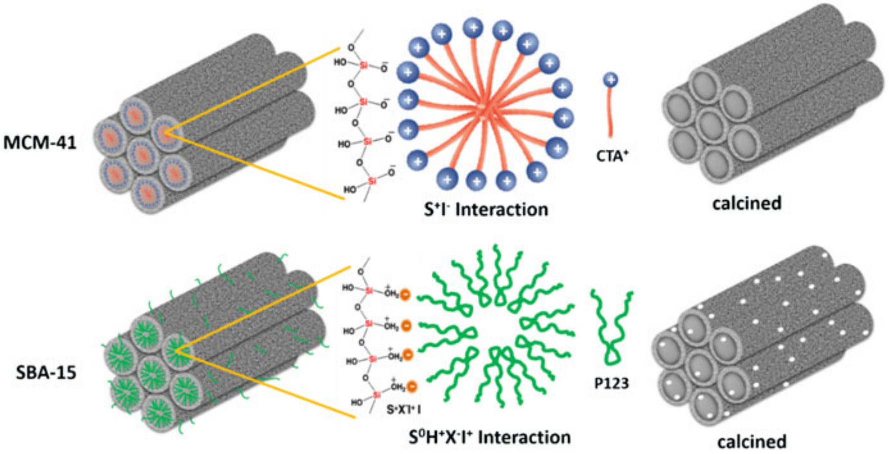

Fig. 5 Electrostatic interactions that form the ordered mesoporous material types MCM-41 and SBA-15

mesoporous materials is generally faster than the synthesis of zeolites, and the formation of materials may take from minutes to days. The main difference is because the ordered mesoporous materials depend on the electrostatic interactions between inorganic silica precursors and surfactants, which will form amorphous silica walls. In the case of zeolites, an induction time (period between the start of the reaction and the point where the crystalline product is first observed) is required for complete crystallization.

The formation of M41S mesoporous materials is based on the interactions that occur (in basic media) between positively charged species of surfactants (S^+) in the micelles and the negatively charged inorganic silica (I^-) species that form electrostatic interactions (S^+I^-), as shown in Fig. 5 for the MCM-41 case. Three mechanisms are suggested for the formation of mesoporous materials, which are called liquid crystal templating (LCT), self-assembly and cooperative self-assembly [10, 17–19].

For the ordered mesoporous material type SBA-15, the type of interaction is different. The most known triblock polymers are called Pluronic-123, poly(ethylene oxide) (PEO), and poly(propylene oxide) (PPO), which are used as surfactants. In this case, the interaction is a result of an indirect reaction between the polymer and the positively charged silica species in an acidic medium [$(S^0H^+)(X^-I^+)$]. In this case, the counter ion ($X^- = Cl^-, Br^-$) represents the strongly acidic conditions, Fig. 5. In addition, a neutral interaction (S^0I^0) can also occur, which leads to the formation of HMS and MSU-X material types. The channels of ordered mesoporous materials become accessible when the surfactants are removed via calcination or solvent extraction processes. Calcination, in addition to removing the surfactant, promotes additional condensation of the silica structure [20, 21]. The calcined SBA-15 has micropores (represented by the white dots) that connect mesoporous channels due to the PEO chains of Pluronic-123 within the silica walls. For the case of

MCM-50, which is shown in Fig. 4, calcination of the surfactant causes the collapse of silica lamellae.

Applications of Zeolites and Ordered Mesoporous Materials

Due to the properties of adsorption, ion exchange capacity, molecular sieving and acidity, zeolites and ordered mesoporous materials have applications in several areas, as follows:

Wastewater Treatment

Wastewater is usually composed of cationic pollutants, anionic compounds, organic compounds, and oils that can have toxic effects on the environment. Zeolites are versatile materials, which are used to treat these pollutants. An example of cationic pollutant is ammonia, which is derived from agricultural wastes, fertilizers, municipal factories, and sewers. Thus, when zeolite is added, it exchanges its extra-framework cations (Na^+, K^+, Ca^{2+}, usually) with NH^{4+} ions. The efficiency of zeolite (clinoptilolite) is increased when it is converted to its sodium form [22]. Many heavy metals, which are present in polluted waters that contain Ag^+, Cu^{2+}, Cd^{2+}, Cr^{3+}, Zn^{2+}, Ni^{2+}, Co^{2+}, and Pb^{2+} ions, can be treated with zeolites, which can yield better adsorption results than activated carbons in some cases [23, 24].

The mesoporous type MCM-41 and magnetic SBA-15 materials functionalized with thiol groups are also efficient in removing Hg^{2+} from wastewater, showing a 97% removal after 7 h in the case of SBA-15. In addition, the material can be separated from the solution by applying magnetic field [25, 26].

Inorganic anions, such as F^-, CN^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, ClO_4^-, CrO_4^{2-}, and $Cr_2O_7^{2-}$, are also present in large quantities in wastewater and can be removed with zeolites via ion exchange or surface modification of zeolites with surfactants. For acid anions, this removal is caused by the occlusion and adsorption of the anions in zeolite [27]. For chromate anions, a modification of the surface of zeolites with surfactants increases the adsorption of these anions [28].

Mesoporous material types MCM-41 and SBA-1 modified with amino groups are also efficient in the removal of arsenate and chromate ions. For the MCM-41 type material, the maximum adsorption capacities of CrO_4^{2-} and $HAsO_4^{2-}$ are 115.2 and 109.9 mg g^{-1}, respectively. For the SBA-1 material, the maximum adsorption capacities of CrO_4^{2-} and $HAsO_4^{2-}$ are 210.8 and 262.7 mg g^{-1}, respectively [29].

Organic dyes generated by the textile, food, and printing industries can be removed from wastewater. Zeolites can adsorb cationic dyes (methylene blue, Rhodamine B), whereas the surface modification of zeolites with surfactants also increases the removal of anionic dyes (such as Reactive Black 5, Reactive Red 239, Reactive Yellow 176). In this case, the mechanism of adsorption involves electrostatic interactions between the amine molecules (in the bilayer form) on the zeolite surface [30, 31]. The MCM-41 type mesoporous materials are also effective for the removal of Rhodamine B. The adsorption capacity of this dye, according to the authors, is related to the interaction between this dye and the MCM-41 surface [32]. The noncalcined Al-MCM-41 is also effective for the removal of Yellow Dye (Acid Yellow 49) with adsorption of 92% [33].

Nuclear Waste and Fallout

Due to the cation exchange capacity, zeolites have a certain selectivity for radionuclides (^{137}Cs, ^{90}Sr, ^{51}Cr, and ^{60}Co). Zeolites played an important role in neutralizing the effects of the Chernobyl nuclear accident in 1986. Zeolites added to the soil decreased the absorption of ^{137}Cs by plants [34]. The mordenite zeolite was added to feed contaminated ruminant, once the extra-framework cations of zeolites (Na^+, K^+, and Ca^{2+}, etc.) can be exchanged for ^{137}Cs and excreted, which decreased assimilation with their body [35]. Mixtures of zeolite A and chabazite were used to treat contaminated water containing ^{137}Cs and ^{90}Sr, and herschelite zeolite (CHA) in a sodium form was used to remove ^{137}Cs in the Fukushima nuclear accident in 2011 [36, 37]. The MCM-41-type mesoporous materials functionalized with thiol groups are also effective in removing ^{137}Cs, ^{90}Sr, and ^{60}Co in waters demonstrating a maximum adsorption capacity of 30 mg g^{-1} and selectivity of ^{137}Cs, which is greater than that of ^{90}Sr and ^{60}Co [38].

Medical

In the medical field, zeolites are applied as artificial kidneys. Due to their adsorption properties, zeolites are active for the adsorption of uremic toxins, such as urea, uric acid, creatinine, and *p*-cresol, and demonstrated that it is possible to eliminate 75% of creatinine using the mordenite zeolite in its acid form and 60% of *p*-cresol using the silicalite-1 zeolite. These results are better than those demonstrated with traditional membrane-based dialysis systems in which the elimination of creatinine and *p*-cresol is 67% and 29%, respectively [39]. It is known that zeolites with a low Si/Al ratio can adsorb water, and this property was exploited as a blood coagulation agent leading to the creation of a product that consists of a dehydrated zeolite (FAU), which is used as component of dressings that are already used in military and personal emergency [40, 41].

The ordered mesoporous materials have well defined pores, which are able to host molecules that are used for controlled drug release. MCM-41 with pore sizes of 3.6 nm was used for the controlled release of anti-inflammatory drugs such as Ibuprofen (molecular size of 15 × 6 Å) [42]. MCM-41 with pore sizes of 2.7 nm was used as the release system for Captopril (molecular size of 9 × 5.7 Å), which is a drug used to treat hypertension and heart failure [43]. SBA-15 functionalized with amino groups was used for controlled release of Gemcitabine, an anticancer drug [44].

Purification and Separation of Gases

Zeolites are used for the separation of gases. For example, lithium-exchanged chabazite zeolite can separate N_2 from air or other components of other gases such as O_2, Ar, H_2, He, Kr, Ne, and Xe. This zeolite can also separate CH_4 from other gases such as H, He, and their mixtures. In these cases, the extra-framework cations are the adsorption sites in zeolites for the weakly interacting adsorbates, and the increase in adsorptive capacity is directly related to the interaction force between the resulting adsorption sites and the adsorbate gas. Therefore, Li^+ is a small cation and favors strong interaction with the N_2 molecules inside the chabazite structure [45]. The clinoptilolite zeolite was used to improve the natural gas by separating CH_4 from N_2 [46]. The silver-exchanged mordenite separates 95% of oxygen and 5% of argon mixtures to a 99.7% oxygen purity [47]. The silver-exchanged zeolite Y (FAU) was used as a filter material in hospitals for the control of bacteria and fungi, thus increasing the internal quality of air [48]. Zeolites may also be present as oxygen concentrators for the delivery of supplemental oxygen in remote high-altitude areas, saving costs by 75% compared with oxygen cylinders [49]. MCM-41 functionalized with amino groups was used for air purification, demonstrating CO_2 selectivity in the presence of N_2, O_2, CH_4, and H_2 at low partial pressure of CO_2, which can also be applied in closed-circuit breathing systems such as air, natural gas, and H_2 purification [50]. MCM-41 was used for the adsorption of volatile organic compounds (VOCs) [51].

Catalysis

The development of synthetic FAU zeolites (zeolites X and Y) and their use on an industrial scale for the cracking of heavy petroleum fractions in FCC (Fluid Catalytic Cracking) plants in 1962 is considered one of the most important worldwide chemical processes [6]. Zeolites are more active and produce a higher gasoline yield (higher value product in an FCC plant) than the previously used amorphous silica-alumina catalysts. After 1962, within the petrochemical industry, the use of zeolites as catalysts reached other processes, such as isomerization, to increase the octanes in light gasoline, disproportionation of toluene in benzene and xylene and zeolite-based catalysts for the control of NO_x emission, and removal of sulfur from fuels [6, 52, 53]. In catalysis, zeolites represent more than 40% of the solids used in the chemical industry [54].

Several efforts have been made for the ordered mesoporous material types MCM-41 and SBA-15 that contain aluminum, which have the same characteristics of hydrothermal stability and acidity as zeolites and are mainly used in FCC. However, from the point of view of stability and catalytic behavior, these materials are more similar to amorphous materials than zeolites [55]. However, their moderate acidity may offer advantages over zeolites when used in reactions that involve large molecules (e.g., in fine chemistry, specifically during the production of acetals [56] and pyrolysis of biomass) to obtain useful products such as phenolic compounds

[57]. Due to their high surface areas, ordered mesoporous materials are used as catalyst supports of metals (e.g., Au, Pd, Au-Pd, and others) for the oxidation of VOCs, such as benzene, toluene, and *o*-xylene (BTX), and for the reforming of ethanol for hydrogen production [58].

Sources of Silicon and Aluminum Used for the Synthesis of Zeolites and Mesoporous Materials

The choice of silicon and aluminum sources for the synthesis of zeolites and mesoporous materials has a significant effect on the formation of final materials since they differ in reactivity and solubility. In general, amorphous silicon sources with higher surface areas dissolved more rapidly in the basic medium than the sources with lower surface area, and this factor directly influences the rate of nucleation and crystallization in zeolites, crystal size, and size distribution of particles.

One example of commercial silica source with a high surface area that is extensively used for the production of zeolite and ordered mesoporous silica materials is fumed silica, which is composed of submicron-sized spheres as primary particles that form branched chain-like aggregates forming agglomerates with a rough-like morphology (see Fig. 6, image a). The other commercial sources that are used for the synthesis of zeolites and ordered mesoporous materials are colloidal silica, tetramethylorthosilicate (TMOS), tetraethylorthosilicate (TEOS), silicic acid, and silicon. The sources of aluminum may be aluminum sulfate $Al_2(SO_4)_3$, aluminum nitrate $Al(NO_3)_3$, and aluminium isopropoxide $Al(O\text{-}i\text{-}Pr)_3$. These sources are not considered environmentally beneficial because they require different treatments or may generate residues at the end of their processes [59].

Within the class of inorganic sources of silicon considered environmentally beneficial, there are clay minerals (kaolin, smectite, sepiolite, palygorskite, etc.), rice husk silica, diatomite, fly coal ash, and sodium silicate, and aluminum sources include Al_2O_3, $Al(OH)_3$, clay minerals, fly coal ash, bio-waste, and sodium aluminate, which are abundant, cheap, renewable or are residues of some process types.

It is important to mention that natural or abundant sources may contain associated impurities, and a study of physicochemical properties of the raw material should be performed. For example, many raw materials that contain more stable phases (quartz, cristobalite) are difficult to dissolve, and silica may not be fully available for the synthesis. Other raw materials that contain oxides of other elements, such as Ti, Fe, and Ca, may not participate in the zeolitic structure. Other inexpensive sources have octahedral aluminum (especially in clay minerals), which has transformed into tetrahedral aluminum to be more reactive and participate in the zeolitic structure. The pretreatment (mechanical, thermic, or chemical) of raw materials will depend on silicon and aluminum sources. In general, the raw materials and their pretreatments are monitored via X-ray diffraction as a way of observing the absence or decrease of certain impurities or amorphous phases as well as the relative crystallinity after the synthesis. The elemental analyses are used for the quantification of impurities before and after each pretreatment, whereas using magic-angle

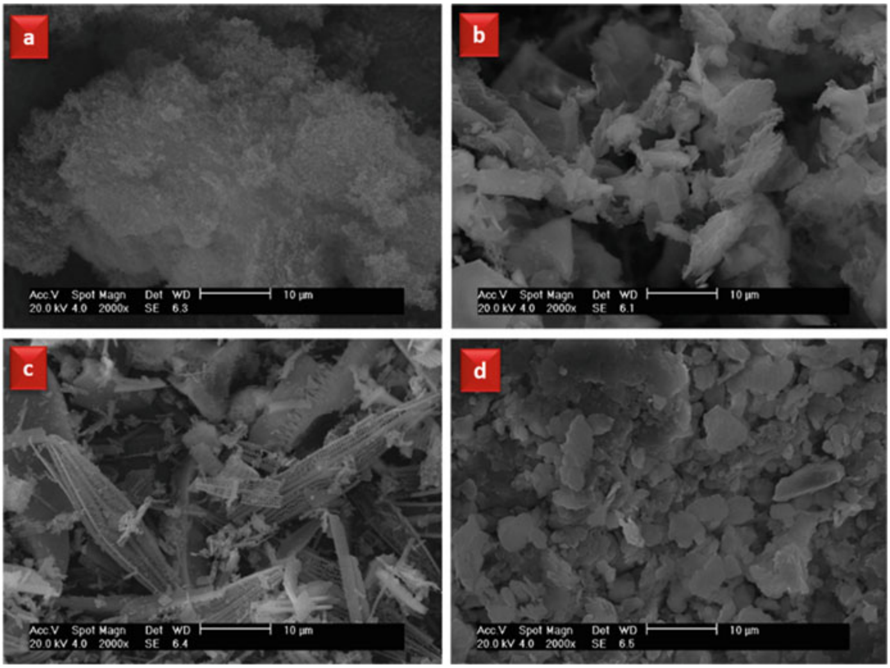

Fig. 6 Scanning electron microscopy micographs of commercial silica fumed (**a**), silica from rice husk (**b**), diatomite (**c**), and a natural smectite (**d**)

spinning nuclear magnetic resonance (^{27}Al MAS NMR), it is possible to analyze the transformation of octahedral aluminum into tetrahedral. In general, the zeolitic structure to be formed must respect the composition of the gel, and the Si/Al ratio is directly associated with this.

Silica from Rice Husk

According to the FAO (Food and Agriculture Organization), the world rice production in 2016 was 751.9 million tons [60]. Approximately 20% of this value in mass corresponds to the rice husk, which is considered the largest agro industrial waste [61]. Rice husk is composed of approximately 20% ash, and the rest is organic material (lignin, cellulose, and other organics). Approximately 95% of the ash is silica, while the remaining 5% is impurities, such as alkaline metals and carbonaceous residues, which are removed using chemical treatments (acid or basic leaching) and thermal treatments. In most cases, thermal treatments use temperatures up to 600 °C, thus generating amorphous silica of high purity, while temperatures higher than 700 °C favor the formation of crystalline silica structures such as cristobalite and tridimite [62]. Figure 6 (image b) shows the amorphous silica particles that are obtained after the thermal treatment of rice husk up to 600 °C for 4 h.

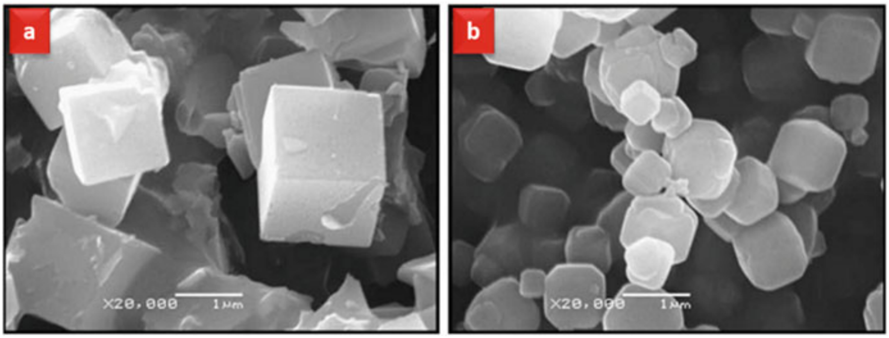

Fig. 7 Scanning electron microscopy images of zeolite A from rice husk silica (**a**) and commercial fumed silica (**b**) (Adapted from Ref. [63] with permission from Elsevier)

The results using rice husk as silica source for the synthesis of zeolite A are shown in Fig. 7, where the micrographs show zeolite A, which was synthesized using silica from rice husk calcined at 600 °C (image a), and zeolite A, which was obtained using fumed silica (image b). It was observed that the natural source of silica promotes the formation of larger crystals than the zeolite A produced using commercial silica. However, the relative crystallinity of zeolite A from rice husk and its surface area are similar to those of zeolite A obtained using commercial silica [63].

Other zeolites were synthesized using silica from rice husk such as Beta [64], NaX [65], NaY [66], ZSM-48 [67], and MCM-22 [68]. The synthesized mesoporous materials are MCM-41 (surface area of 468 $m^2\ g^{-1}$) [69], MCM-48 (1024 $m^2\ g^{-1}$) [70], SBA-15 (780 $m^2\ g^{-1}$) [71], and SBA-16 (820 $m^2\ g^{-1}$) [72].

Diatoms

Diatoms are sedimentary rocks that consist of the accumulation of carapaces of microscopic diatomaceous algae fossilized since the Precambrian period. They are mainly found in freshwater and are formed of macroporous irregular structures of hydrated amorphous silica ($SiO_2{\cdot}nH_2O$), opaline and impurities (e.g., quartz), oxides (e.g., iron, aluminum, sodium potassium, calcium, magnesium, and titanium), and organic content (Fig. 6c). Thus, the diatoms are abundant and cheap raw materials and have been used as a source of silicon and/or aluminum for the synthesis of zeolites NaA [73], Y [74], mordenite [75], and MFI [76]. In the case of the MFI-type zeolite, the diatomite was pretreated with an aqua regia solution to improve their physicochemical properties such as purity, porosity, and quartz/amorphous silica ratio. XRD patterns of synthesized zeolites with diatomite at different times are shown in Fig. 8. According to the authors, a relative crystallinity of 76% was obtained after 24 days with a yield of 82.5 wt%. In addition, SEM analysis in Fig. 8 shows the transformation of diatomite into prismatic crystals of MFI zeolite

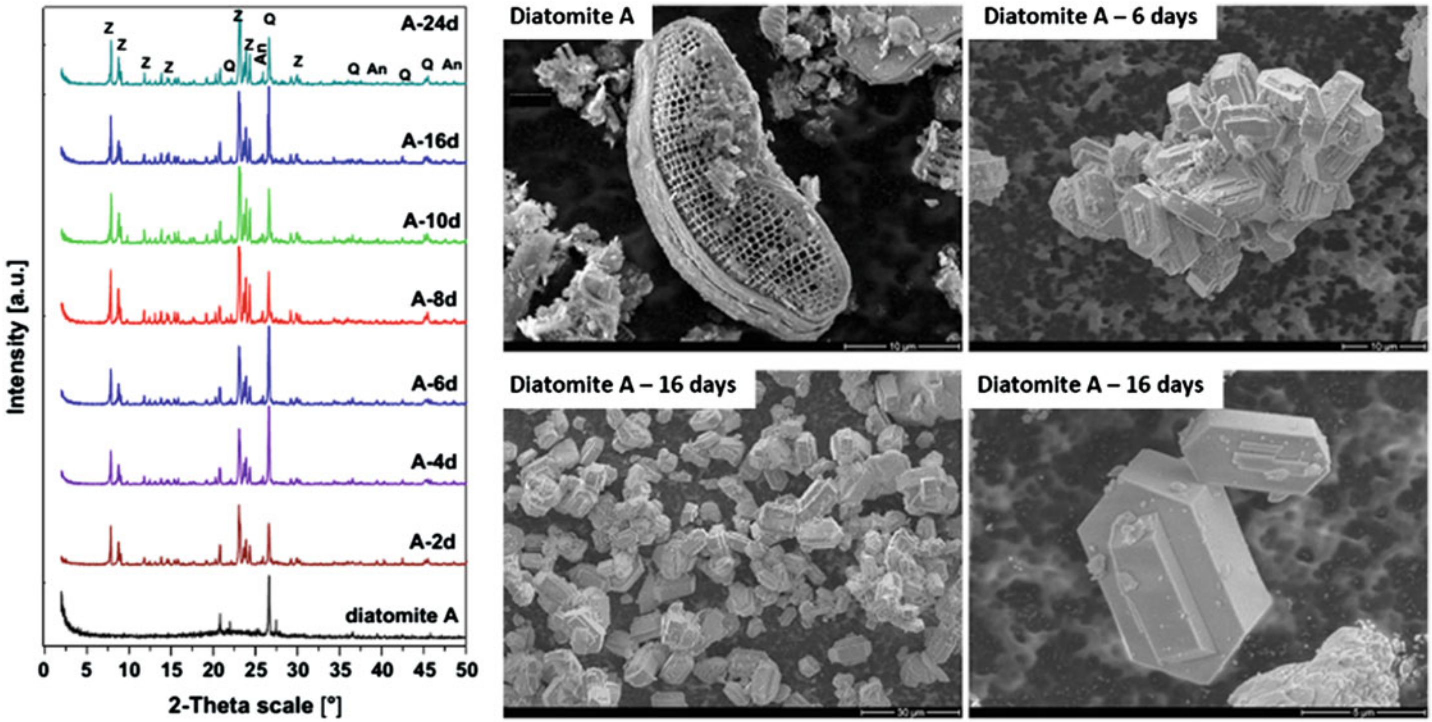

Fig. 8 XRD patterns and SEM micrographs of diatomite and synthesized MFI-type zeolite over different crystallization times (Adapted from Ref. [76] with permission from Springer)

after 6 and 24 days, and the quartz content was reduced significantly during the formation of zeolite using diatomite. In addition, the synthesis of mesoporous materials of the MCM-41 type (743 $m^2\ g^{-1}$) was also reported [77].

Clay Minerals

Smectites (Fig. 6d) are clay minerals that are considered to be lamellar oxides of the group 2:1 (two layers formed by silicon tetrahedra, and a central layer is formed by aluminum octahedra). Due to isomorphic substitutions of Si by Al in the tetrahedral layers and Al by Mg and Fe, or Mg by Li at the octahedral positions, there is an excess of negative charge in the structure, which is compensated by hydrated cations (Na^+, Ca^{2+}) between interlamellar regions. Thus, smectites can act as sources of silicon and aluminum for the synthesis of micro- and mesoporous materials. However, thermal activation at temperatures of 700–850 °C is necessary to increase its reactivity. This reactivity can be understood as the destruction of the lamellar structure of the clay to obtain the phases of $SiO_2{\cdot}Al_2O_3{\cdot}Na_2O$ and/or silicon and aluminum in amorphous and tetrahedral form, which is more reactive. The addition of fondants, such as sodium carbonate and bicarbonate, in this heat treatment step also improves the conversion of quartz to more reactive phases. For the formation of zeolites with a low Si/Al ratio such as zeolites A and X, a supplementation of aluminum is required [78].

Kaolinite is a member of clay minerals 1:1 (one layer is formed by silicon tetrahedra and one layer is aluminum octahedra) with a lamellar structure. The most reactive form of kaolin is thermally activated at temperatures between 600 °C and 800 °C and is known as “meta-kaolin.” Among the clay minerals, kaolin was more prominent in the synthesis of zeolites because they do not have compensating cations between the lamellae and have a low Si/Al ratio, similar to the zeolite A [79] and X [80]. This raw materials was used for the synthesis of other zeolites, such as P [81], Y and ZSM-5 [82], and mordenite [83]. Mesoporous material type Al-MCM-41 (494 $m^2\ g^{-1}$) has already been synthesized using clay minerals such as bentonite [84], meta-kaolin and TEOS (753 $m^2\ g^{-1}$) [85], attapulgite (1030 $m^2\ g^{-1}$) [86], halloisite (509 $m^2\ g^{-1}$) [87], and chrysotile (698 $m^2\ g^{-1}$) [88].

Recently, a new strategy called “direct synthesis” has been reported for the formation of zeolites from clay minerals (in this case, attapulgite, ATP) [89]. In this approach, no activation (high temperatures associated with acidic or basic treatments) is necessary for the destruction of clay mineral structure. This approach uses a vapor-induced transformation (VIT), where the vapor diffuses in the ATP interacting with its structure to form an MFI-type zeolite. Figure 9 shows XRD patterns and SEM micrograph of ATP and the formed ZSM-5 zeolite, where the obtained yield was 96%, and the relative crystallinity is similar to that of ZSM-5 zeolite, which is used as a reference. Other zeolite structures, such as TON, MOR, and BEA, are also obtained using this approach. This strategy provides a new green and economical route for the synthesis of zeolites from clay minerals.

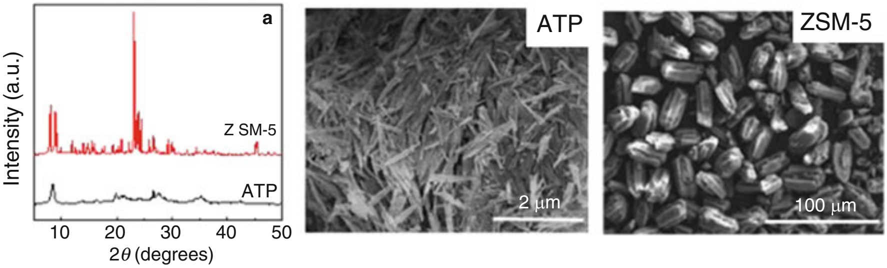

Fig. 9 XRD patterns and SEM micrographs of ZSM-5 zeolite from attapulgite using vapor-induced transformation (Adapted from Ref. [89]. Copyright 2017 American Chemical Society)

Coal Ash

Coal ash is a residue from the combustion of coal in coal-fired power plants. Large amounts of ash are produced, which can have harmful effects on the environment. The percentage of silica and alumina present in coal ash is approximately 60–70% and 16–20%, respectively. Thus, its conversion to advanced materials, such as zeolites and ordered mesoporous materials, represents an economical strategy for the reduction of environmental impact. In most cases, an alkaline fusion stage of coal ash is applied to increase silica extraction and accelerate the formation rate of the materials. The use of this residue for the synthesis of materials, such as zeolites NaP (pure), A, X, has been reported [90]. The mesoporous materials, MCM-41 and SBA-15, have already been synthesized using fly coal ash, showing surface areas of 1157 $m^2 g^{-1}$ and 483 $m^2 g^{-1}$, respectively [91, 92].

Conclusions and Further Outlook

Zeolites and ordered mesoporous materials attract significant attention due to their unique structural properties. These materials are used and modified to reach a wide range of applications related to reducing environmental problems and increasing energy efficiency. In addition, both zeolites and ordered mesoporous materials can be synthesized using renewable, abundant, and inexpensive sources of silicon and aluminum from rice husk, clay minerals, diatomite, and fly coal ash to achieve dual protection to the environment: zeolites and ordered mesoporous materials synthesized from renewable and waste sources and applied to the reduction of environmental impact. New synthesis approaches for zeolites and ordered mesoporous materials have been reported. Among these methodologies, direct synthesis via VIT using clay minerals is notable for dispensing the stages of activation (using temperatures and/or acid or basic treatments) that are commonly used. There are many silica sources, such as electronic (packaging resins) and domestic (glassware) wastes, which still represent a significant opportunity for the synthesis of zeolites and ordered mesoporous materials. In addition, inexpensive sources can be combined with other green synthesis strategies, such as the reuse of mother liquors from the synthesis, seed-assisted crystallization, microwave synthesis, free-template synthesis, and use of biosurfactants or biopolymers, to obtain microporous and mesoporous materials. It is well known that the discovery of new zeolites and mesoporous materials for advanced applications increases every day, and the use and search for inexpensive sources for their synthesis must follow in the same proportion.

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