

## Review

# Applications of Zeolites in Sustainable Chemistry

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To face the global sustainability issues arising from rapid industry development and population increase, many efforts have been made to develop new materials and technologies toward renewable energy and environmental improvement. Zeolites are a family of crystalline materials with orderly distributed micropores in molecular dimensions. As the most important solid catalysts used in traditional petrochemical industries, zeolites are also finding promising applications in many sustainable processes given their unique shape selectivity, adsorption and ion-exchange capability, high hydrothermal stability, tunable acidity and polarity, and low production costs. In this review, we present the state-of-the-art applications of zeolites as potential solutions to the sustainability issues, including biomass conversion, fuel cells, thermal energy storage, CO<sub>2</sub> capture and conversion, air-pollution remediation, and water purification, etc.

## INTRODUCTION

Sustainability involves broad content across ecology, economics, politics, and culture. In brief, sustainability represents a state of society where living conditions and resources continue to meet human needs without undermining the integrity and stability of the natural systems.<sup>1</sup> Global industrial and economic development over the past century has largely relied on combustion of non-renewable fossil fuels, such as petroleum, coal, and natural gas, which are also harmful to our environment because of the release of a large amount of CO<sub>2</sub>. Meanwhile, industrial processes and human activities have produced various hazardous gases, such as NO, NO<sub>2</sub>, NH<sub>3</sub>, and volatile organic compounds, and liquid wastes containing heavy metals and radionuclides, which have posed serious threats to the environment and human health. Therefore, establishing eco-friendly and cost-effective processes to achieve renewable energy sources and environmental improvement is currently one of the most urgent issues for the sustainable development of our society.

Zeolites are traditionally referred to as a family of open-framework aluminosilicate materials consisting of orderly distributed micropores in molecular dimensions. The frameworks of zeolites are built from the connections of corner-sharing TO<sub>4</sub> tetrahedra ("T" denotes tetrahedrally coordinated Si, Al, or P, etc.), and different ways of tetrahedra connection lead to a diversity of zeolite framework types based on various compositions.<sup>2</sup> To date, 235 distinct zeolite framework types have been identified in natural or synthetic zeolites, each of which has been assigned a three-letter code by the International Zeolite Association (Figure 1).<sup>3</sup> The frameworks of zeolites can be decomposed into rings of different sizes, which correspond to the pore opening windows of zeolites. According to their largest pore windows, zeolites can be categorized into small-pore ( $\leq 8$ -ring), medium-pore (10-ring), large-pore (12-ring), and extra-large-pore zeolites ( $> 12$ -ring). The negative charges of zeolite frameworks are usually compensated by extra-framework mono- or di-valent cations, which can be exchanged by other cations. The additional

## The Bigger Picture

Zeolites, also called molecular sieves, are traditionally referred to as a family of aluminosilicate materials consisting of orderly distributed micropores in molecular dimensions. They have been widely used as highly efficient catalysts, adsorbents, and ion exchangers in petrochemical industries and in our daily life. Beyond these traditional applications, zeolites are playing an increasingly important role in many sustainable processes. In particular, zeolites have found promising applications in the fields of renewable energy and environmental improvement, such as biomass conversion, fuel cells, thermal energy storage, CO<sub>2</sub> capture and conversion, air-pollution remediation, and water purification, etc. These applications make zeolites potential candidates as solutions to the sustainability issues in our society.

species (e.g., H<sub>2</sub>O) in the pores of zeolites can be removed, leaving void space for the selective entrance of guest species of suitable size, shape, and polarity. This is known as the molecular-sieving effect of zeolites. Moreover, the spatial confinement of zeolite pores coupled with catalytically active sites in their frameworks endows zeolites with unique shape-selective catalysis toward the formation of specific products. Finally, zeolites can act as host matrices to encapsulate and stabilize metal clusters or nanoparticles, forming multifunctional composite materials with superior properties. Because of these unique characteristics as well as their high hydrothermal stability and low production costs, zeolites have been widely used as highly efficient catalysts, detergents, adsorbents, and ion exchangers in many chemical processes.<sup>4,5</sup> In particular, zeolites are currently the most important heterogeneous catalysts in the oil-refining and petrochemical industries, producing the majority of the world's gasoline from crude oil via fluid catalytic cracking.<sup>6</sup>

Besides their traditional applications in the chemical industry, zeolites are playing an increasingly important role in many sustainable processes, particularly in the fields of renewable energy and environmental improvement, such as biomass conversion, fuel cell, thermal energy storage, CO<sub>2</sub> capture and conversion, air-pollution remediation, and water purification. In this review, we present the recent progress in zeolite applications in sustainable chemistry, and the key challenges in related fields are also briefly discussed.

## BIOMASS CONVERSION

In recent decades, biomass has become a promising sustainable feedstock to substitute non-renewable fossil resources. Zeolites have been widely used as the catalysts to convert biomass feedstock into high-value biofuels and platform chemicals. There are already a number of comprehensive reviews on biomass conversion over zeolites.<sup>7,8</sup> In this context, we present only a few examples to demonstrate the recent applications of zeolites in biomass conversions over their unique active sites, including Brønsted acid sites, Lewis acid sites, and multifunctional active sites (Figure 2).

### Brønsted Acid Catalysis

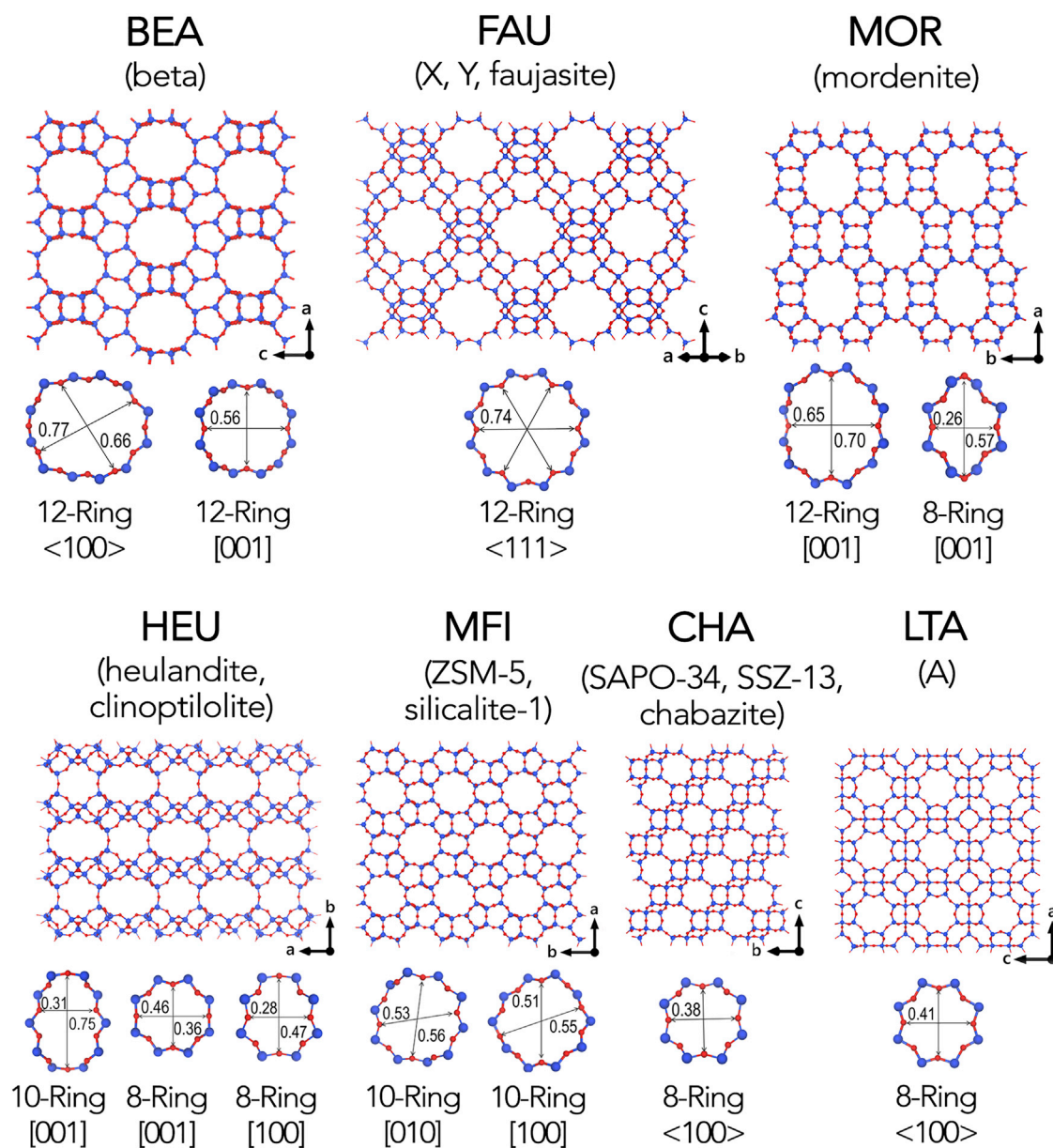
Brønsted acid sites are highly polarized hydroxyl groups in zeolite frameworks, which are very active to many catalytic reactions as proton donors. As applications in the oil-refining and petrochemical industries, Brønsted acidic zeolites are playing an important role in many processes of biomass conversion (Figure 2A).<sup>8,9</sup> For instance, Brønsted acidic zeolites can be used to catalyze the conversion of microbially produced lactic acid (LA) into lactide, which is the key building block for biodegradable and renewable polylactic acid. The traditional method for lactide synthesis from LA requires a time- and energy-intensive two-stage process involving polycondensation and transesterification at high temperatures *in vacuo*. Moreover, different lengths of LA oligomers form as the side products (Figure 3A). Taking advantage of their capability to facilitate condensation reactions and their suitable confinement effect toward cyclic lactide over growing oligomers, Dusselier et al.<sup>10</sup> utilized Brønsted acidic large-pore zeolites as the catalysts for a fast and selective lactide synthesis directly from LA. Record lactide space-time yields of >250 g L<sup>-1</sup> hr<sup>-1</sup> were attained with this one-step direct process. In particular, zeolite H-beta (BEA type) achieved 79% selectivity toward the formation of lactide at full LA conversion. In comparison, other acidic catalysts without suitable confinement effect mainly produced oligomers (Figure 3B). This Brønsted acid zeolite catalysis was also applicable to other  $\alpha$ -hydroxy acids of interest in polyester chemistry, facilitating

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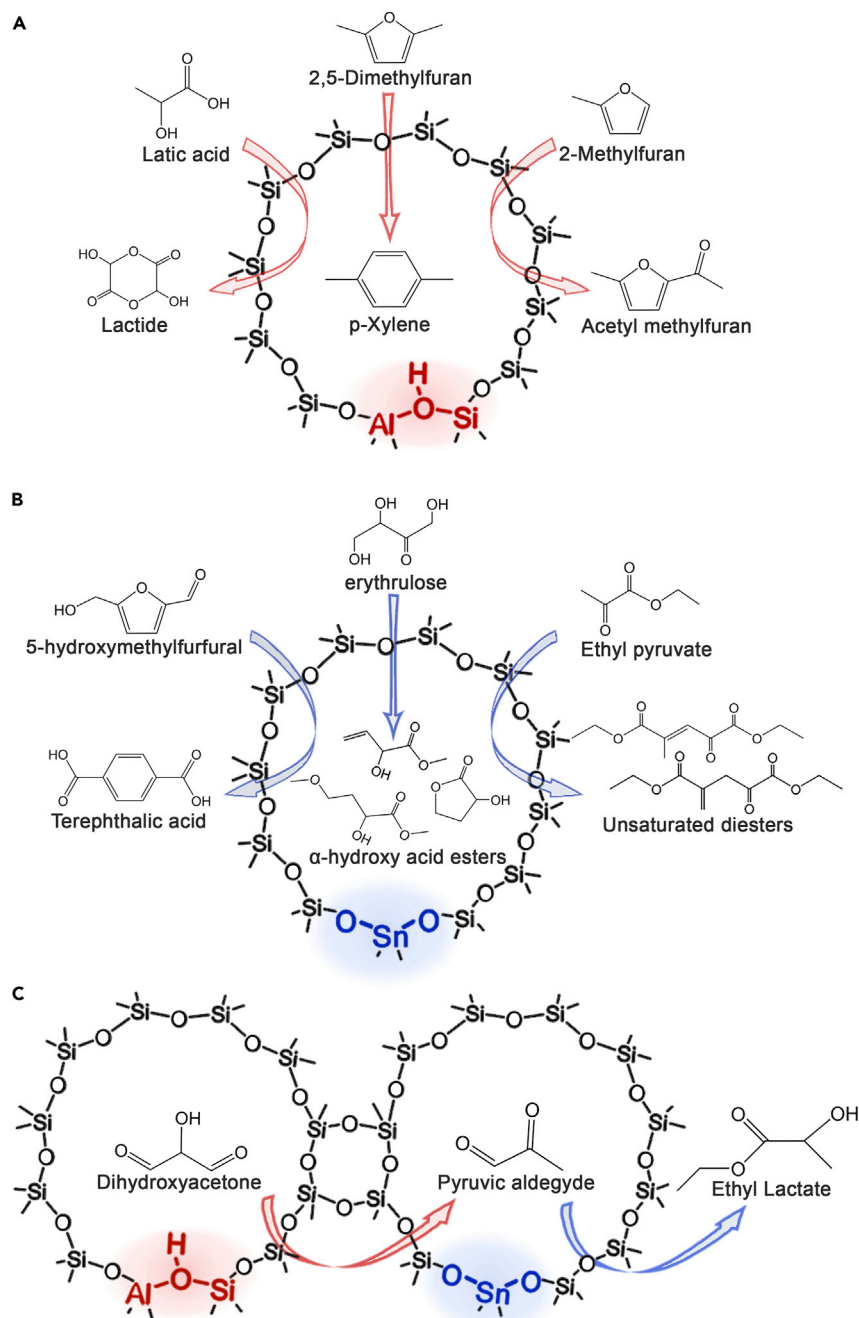
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**Figure 1. Selected Widely Used Zeolite Framework Types**

For each framework type, the three-letter code assigned by the International Zeolite Association (in bold), the names of zeolites belonging to the corresponding framework type, the ball-stick atomic model, and the pore windows are given. Blue spheres denote T atoms, and red spheres represent oxygen atoms. The size of the ring (in nm) and the pore directions are also given.

the synthesis of a wide range of renewable and degradable bio-based plastics. Brønsted acid zeolites can also be used in the conversion of sugar-derived 2,5-dimethylfuran into aromatics. Traditionally, furanic molecules are converted into aromatics by a Diels-Alder cycloaddition with high-pressure ethylene. Recently, the catalytic conversion of 2,5-dimethylfuran to aromatics with ethanol over Brønsted acidic zeolites H-ZSM-5 (MFI type) and H-USY (USY type) was reported.<sup>11</sup> The usage of liquid ethanol instead of gaseous ethylene made the production of aromatics much simpler and renewable. More importantly, much improved reaction rates (turnover frequency up to  $15 \times 10^2 \text{ hr}^{-1}$ ) and selectivity (up to 90%) to



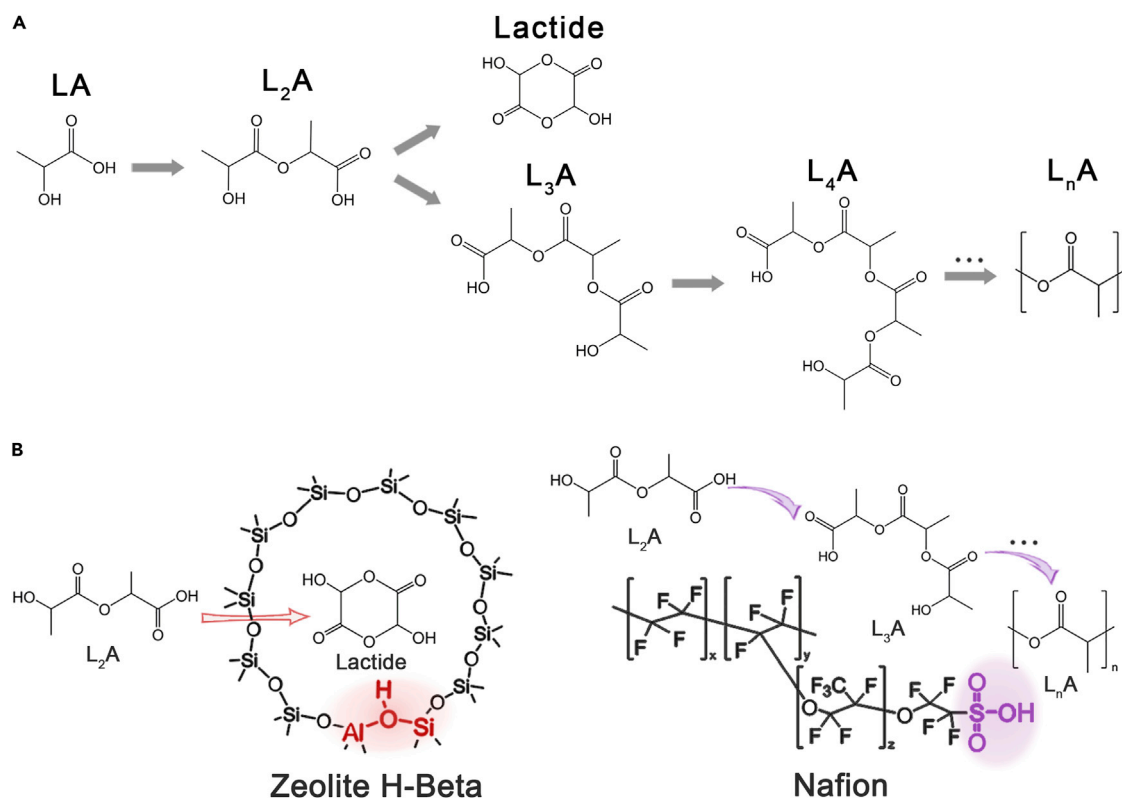
**Figure 2. Selected Examples of Biomass Conversion over Various Active Sites in Zeolite Catalysts**

(A) Reactions over a Brønsted acid site.

(B) Reactions over a Lewis acid site.

(C) Reactions over multifunctional active sites.

aromatics were attained as a result of the lowered activation barriers over the Brønsted acid sites in zeolites, especially in H-USY. Gumidyala et al.<sup>12</sup> studied the direct acylation of 2-methylfuran with acetic acid in the presence of water over Brønsted acid zeolites, demonstrating a promising route to direct C–C coupling for the production of high-value products from biomass while minimizing CO<sub>2</sub> emissions. Direct coupling of furanic species with acetic acid is very appealing,



**Figure 3. Conversion of Lactic Acid into Lactide over Acidic Catalysts**

(A) Reaction pathways.

(B) Different product selectivity over zeolite H-beta with a spatial confinement effect and over Nafion without a confinement effect.

but furanic species could undergo a wide range of side reactions over Brønsted acid sites, leading to uncontrolled polymerization and coke formation. The authors used medium-pore zeolite H-ZSM-5 as the catalyst, achieving a >95% selectivity toward acetyl methylfuran isomers without CO<sub>2</sub> loss. Such high performance was attributed to the effective stabilization of the transition state by methylfuran over the Brønsted acid site in H-ZSM-5, which significantly reduced the barrier for C–C coupling. In comparison, large-pore zeolite H-beta exhibited much lower reaction activity than H-ZSM-5, suggesting the importance of medium-pore confinement during this reaction.

## LEWIS ACID CATALYSIS

Besides Brønsted acid sites, substituting Si atoms in zeolite frameworks with tetrahedrally coordinated Ti, Sn, or Zr atoms can produce Lewis acid sites, which can accept electron pairs from guest molecules, facilitating many biomass conversion processes that cannot take place over Brønsted acid sites (Figure 2B).<sup>13</sup> For instance, Lewis acidic zeolites can be used to synthesize terephthalic acid, a key monomer in the synthesis of polyethylene terephthalate, from biomass-derived molecules. Traditionally, terephthalic acid is produced by oxidation of petroleum-derived *p*-xylene. Pacheco and Davis<sup>14</sup> proposed a strategy to synthesize terephthalic acid from 5-hydroxymethylfurfural by using large-pore Lewis acidic zeolites as the catalysts. In particular, 5-(hydroxymethyl)furoic acid derived from partial oxidation of 5-hydroxymethylfurfural was reacted with high-pressure ethylene over zeolite Sn-beta via Diels-Alder dehydration to produce 4-(hydroxymethyl)benzoic acid

with 31% selectivity at 61% 5-(hydroxymethyl)furoic acid conversion. 4-(Hydroxymethyl)benzoic acid could then be oxidized to produce terephthalic acid. Note that using Brønsted acidic H-beta as the catalyst significantly decreased the yield of Diels-Alder dehydration products, indicating the crucial role of Lewis acid sites in these reactions. In another study, the conversion of tetrose sugars to  $\alpha$ -hydroxy acid esters (such as methyl vinyl glycolate, methyl-4-methoxy-2-hydroxybutanoate, and  $\alpha$ -hydroxy- $\gamma$ -butyrolactone), which were useful building blocks for degradable functional polyesters, was realized over Lewis acidic zeolites.<sup>15</sup> With Sn-beta as the catalyst, 80% selectivity of  $\alpha$ -hydroxy acid esters at 95% conversion of tetrose sugar was achieved. In particular, a very high turnover frequency of  $330 \text{ mol mol}_{\text{Sn}}^{-1} \text{ hr}^{-1}$  was attained, which was a more than 6-fold increase in comparison with homogeneous  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ . In addition, the pore confinement of Lewis acidic catalysts strongly controlled the product selectivity. Microporous Sn-beta and Sn-MFI favored the formation of methyl vinyl glycolate, whereas mesoporous catalysts, such as Sn-MCM-41 and Sn-SBA-15, preferred the formation of more bulky methyl-4-methoxy-2-hydroxybutanoate. Another recent example of Lewis acidic zeolite catalysis was the synthesis of unsaturated diacid esters via aldol condensation of keto esters.<sup>16</sup> Traditional strategies for production of diacids and diesters from biomass-derived molecules suffered from poor selectivity and inefficient carbon utilization. With zeolites Sn-, Zr-, and Hf-beta as the catalysts, ethyl pyruvate was condensed into diethyl 2-methyl-4-oxopent-2-enedioate and diethyl 2-methylene-4-oxopentanedioate. In particular, Zr- and Hf-beta exhibited the best catalytic performance, giving the highest ethyl pyruvate conversions (>80%) with comparable selectivities (>64%) toward diesters. The heteroatoms at the Lewis acid sites in zeolite frameworks were crucial to this reaction. When Sn-beta, H-beta, and pure-silica beta were used as the catalysts, much lower conversions were observed.

### Multifunctional Catalysis

The transformation of biomass into chemicals and fuels often undergoes multistep reactions, each of which might require a distinct catalyst. Zeolite catalysts can be fine-tuned with combined active sites to allow multistep reactions occurring in a "one-pot" way. For instance, zeolite Sn-Al-beta contains both Brønsted and Lewis acid sites because of the presence of both tetrahedral  $\text{Al}^{\text{III}}$  and  $\text{Sn}^{\text{IV}}$ , respectively, which can be used for the cooperative catalysis of multistep conversion of 1,3-dihydroxyacetone into ethyl lactate (Figure 2C).<sup>17</sup> During this multistep reaction, the Brønsted  $\text{Al}^{\text{III}}$  acid sites accelerated the dehydration of dihydroxyacetone to form pyruvic aldehyde, and the Lewis  $\text{Sn}^{\text{IV}}$  acid sites catalyzed the hydride shift of pyruvic aldehyde into ethyl lactate with ethanol. In comparison with Sn-beta containing only Lewis acid sites, the Brønsted acid sites in bifunctional Sn-Al-beta facilitated the rate-determining step of dihydroxyacetone dehydration, giving a record high ethyl lactate production rate ( $2,113 \text{ g kg}_{\text{Sn-Al-beta}}^{-1} \text{ hr}^{-1}$ ). Moreover, the use of a physical mixture of Sn-beta and Al-beta showed modest lactate yield, implying a cooperative effect between Brønsted and Lewis acid sites in Sn-Al-beta.

Besides combining different acid sites, zeolites can form composite catalysts with noble-metal nanoparticles, exhibiting both the high activity of noble metals and the shape selectivity of zeolites. For instance, oxidizing bioethanol produced by fermentation, which contains up to 90% water, into high-value chemicals is very appealing. Metal/zeolite composite catalysts can be used for the catalytic oxidation of bioethanol to acetaldehyde with high activity and selectivity. In particular, a Au/silicalite-1 (MFI type) composite could be prepared by encapsulating hundreds of dispersed Au nanoparticles with a diameter of 2–3 nm in zeolite



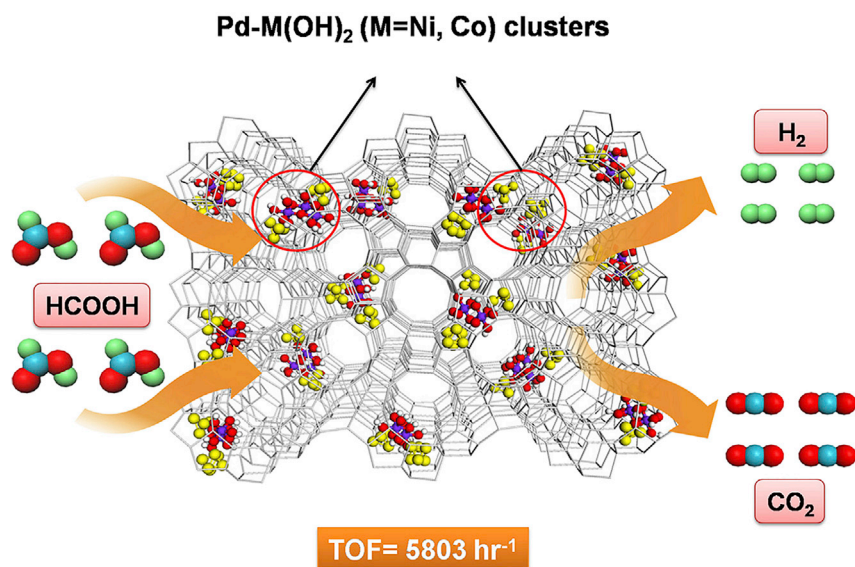
silicalite-1 crystals.<sup>18</sup> A broad range of mesopores were incorporated into the crystals of silicalite-1 via a recrystallization approach to enhance the mass transfer in the composite catalyst and the accessibility of Au. Because of the confinement effect and shape selectivity of silicalite-1, the encapsulated Au nanoparticles exhibited excellent stability and resulted in 50% conversion of bioethanol with 98% selectivity toward acetaldehyde formation. In a different study, a core-shell structured Pd@silicalite-1 composite catalyst with Pd nanoparticles (the core) encapsulated by a crystal of zeolite silicalite-1 (the shell) was prepared from a solvent-free crystallization.<sup>19</sup> Combining the highly activity of Pd nanoparticles and the selectivity of silicalite-1, this composite catalyst exhibited a high furan selectivity (98.7%) and furfural conversion (91.3%) for the hydrogenation of furfural at 250°C. In contrast, the furan selectivity over conventional silicalite-1-supported Pd nanoparticles (Pd/silicalite-1) was only 5.6%. Such extraordinary furan selectivity was attributed to the distinguishable mass transfer of the hydrogenated products in zeolite micropores.

In summary, zeolites have exhibited outstanding potential for future industrial biomass utilization by taking advantage of their unique Brønsted/Lewis acidic and multifunctional active sites. However, their stability, re-generatability, and product selectivity need to be further improved for these emerging applications. In particular, the catalytic capability of zeolites should be evaluated not only in batch reaction systems but also in scale-up reactors. Different from petroleum-derived chemicals, biomass-derived molecules usually contain a large amount of oxygen, making their catalytic conversions even more challenging. In addition, the reaction mechanisms of many biomass conversions over zeolite catalysts are still unclear. Therefore, comprehensive experimental and theoretical studies toward the biomass conversion mechanisms are needed in the future with the aid of operando characterization and high-level computer modeling. Meanwhile, the product distribution of biomass conversion is rather complex, which requires judicious utilization of the shape selectivity of different zeolites. Once their complex structure-activity relationship is revealed, new zeolite catalysts with particular structural features will be rationally designed toward specific catalytic reactions of interest in the future.

## FUEL CELLS

A fuel cell is an electrochemical device that converts chemical energy released by fuel oxidation into electrical energy, being an excellent power source for automobile applications. The working of fuel cells involves many electrochemical processes and component materials. Because of their superior catalytic, adsorption, and separation capabilities, zeolites can be used not only as catalysts for efficient production of fuels (such as hydrogen and methanol) but also as cell component materials (such as electrodes and membranes).

Hydrogen is one of the most important fuels for fuel cells. Traditional hydrogen generation methods, such as steam reforming of natural gas, produce a notable amount of impurities along with H<sub>2</sub>, such as CO, which can poison the electrodes in fuel cells. Developing green methods to efficiently generate pure H<sub>2</sub> has attracted much attention. Wang et al.<sup>20</sup> developed a facile strategy to synthesize ultrasmall Pd clusters encapsulated within the intersectional channels of nanosized silicalite-1 for highly efficient H<sub>2</sub> generation from the complete decomposition of formic acid under mild conditions without generating CO. Notably, the Pd/silicalite-1 catalyst prepared with the introduction of KOH afforded the highest turnover frequency values, reaching up to 856 hr<sup>-1</sup> at 25°C and 3,027 hr<sup>-1</sup> at 50°C, as a result of the



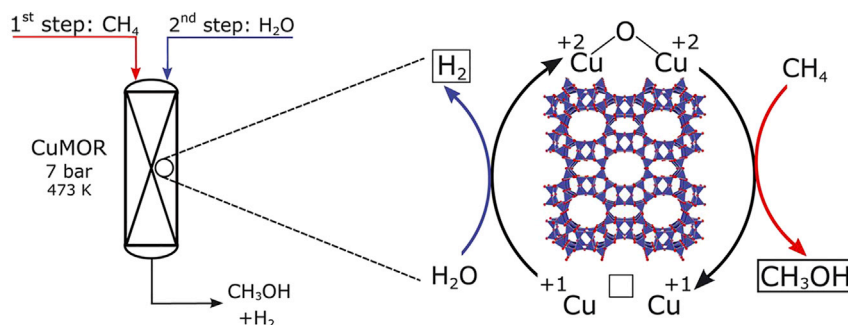
**Figure 4. Subnanometric Hybrid Pd-M(OH)<sub>2</sub> (M = Ni, Co) Clusters in Zeolite Silicalite-1 as Highly Efficient Nanocatalysts for Hydrogen Generation from Formic Acid**

Subnanometric hybrid Pd-M(OH)<sub>2</sub> clusters were encapsulated within silicalite-1 under direct hydrothermal conditions. The hybrid bimetallic nanocatalysts exhibited shape-selective catalytic performance, superior thermal stability, and exceedingly high dehydrogenation efficiency toward complete formic acid decomposition. Reprinted from Sun et al.<sup>21</sup>

further reduced Pd cluster size and basic sites introduced in silicalite-1. In addition, the as-synthesized catalysts possessed superior thermal stabilities as well as excellent recycling stabilities as a result of the suitable confinement of Pd clusters within the silicalite-1 matrix. Furthermore, Sun et al.<sup>21</sup> prepared a series of subnanometric hybrid bimetallic clusters Pd-M(OH)<sub>2</sub> (M = Ni, Co) within silicalite-1 (Figure 4). The hybrid bimetallic nanocatalysts exhibited excellent shape-selective catalytic performance and thermal stability at 600°C–700°C because of the stabilization effect from the confinement of zeolite and the bimetallic synergistic effect. In particular, the 0.8Pd0.2Ni(OH)<sub>2</sub>@silicalite-1 catalyst afforded the highest initial turnover frequency up to 5,803 hr<sup>-1</sup> toward the decomposition of formic acid without any additives at 60°C. Assuming an operation efficiency of 60%, 1.0 g of the 0.8Pd0.2Ni(OH)<sub>2</sub>@silicalite-1 catalyst was capable of producing H<sub>2</sub> for 4–14 small (0.5–2.0 Wh) proton exchange membrane fuel cell devices. These metal/zeolite composite catalysts are opening new prospects for practical hydrogen storage for fuel cells.

Methanol is another important fuel for fuel cells. Traditional methanol production from methane, an abundant greenhouse gas, is an indirect, expensive, and energy-intensive process that needs to overoxidize methane to syngas at extremely high temperature.<sup>22</sup> The direct conversion of methane to methanol is a promising alternative for methanol production, but quite challenging because methanol is easier to oxidize than methane. Transition-metal-exchanged zeolites have shown great potential in this process because of their unique metal active sites confined in zeolite pores. For instance, the trinuclear [Cu<sub>3</sub>(μ-O)<sub>3</sub>]<sup>2+</sup> clusters well confined in Cu-exchanged zeolite mordenite (MOR type) could serve as the single-site active centers for the efficient activation of C–H bonds in methane and its subsequent transformation into methanol;<sup>23</sup> the exceptional catalytic activity for low-temperature methane-to-methanol conversion over Fe-exchanged beta came from the two





**Figure 5. Two-Step Methane-to-Methanol Conversion Using Water as Oxidant over Cu-Mordenite**

Schematic representation of the reaction conditions of the partial oxidation of methane by water, involving the reduction of the mono( $\mu$ -oxo)di-copper site of mordenite and providing two electrons to stoichiometrically oxidize methane into methanol. Subsequent reduction of water into hydrogen returns two electrons for the rejuvenation of the mono( $\mu$ -oxo)di-copper active site. Reprinted with permission from Sushkevich et al.<sup>26</sup> Copyright 2017 AAAS.

consecutively formed mononuclear high-spin active sites,  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{IV}}=\text{O}$ , which were well confined in the distorted 6-rings in beta;<sup>24</sup> the Pd-exchanged ZSM-5 with singly dispersed  $\text{Pd}_1\text{O}_4$  active sites anchored in the micropores of ZSM-5 exhibited high selectivity and activity in methane-to-methanol conversion through partial oxidation with  $\text{H}_2\text{O}_2$ .<sup>25</sup> Very recently, Sushkevich et al.<sup>26</sup> developed an anaerobic direct stepwise method that uses water as the source of oxygen for methane-to-methanol conversion with high selectivity ( $\sim 97\%$ ) over Cu-exchanged mordenite. The whole process consisted of two consecutive steps over the mono( $\mu$ -oxo)di-copper active sites, i.e., methane oxidation and water reduction, consistently producing 0.2 mol of  $\text{CH}_3\text{OH}$  per mol of Cu in Cu-mordenite (Figure 5). Here, water molecules not only acted as a cheap and abundant source of oxygen to partially oxidize methane and regenerate the active sites in Cu-mordenite but also facilitated the desorption of methanol and stabilized the reaction intermediates. With water acting as the oxidant, no molecular oxygen was needed. In comparison with direct oxidation with oxygen leading to high operation temperatures and low yields, such stepped methane-to-methanol conversion routes are expected to receive increasing attention in the near future.

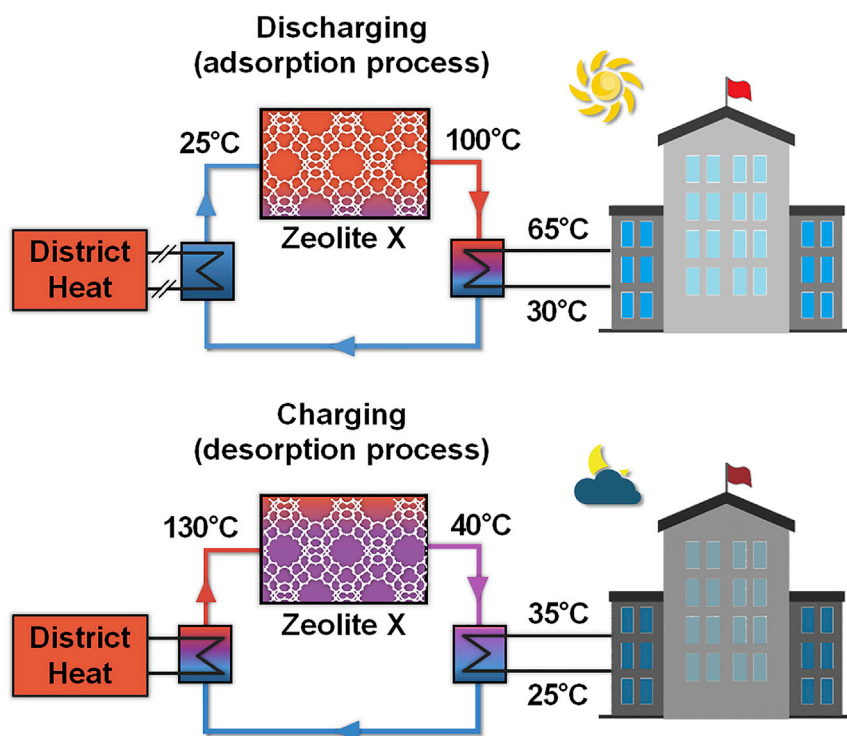
Besides being the catalysts for fuel production, zeolites can also be used for building fuel cells. For instance,  $\text{CeO}_2$ -decorated ZSM-5 nanocatalysts could be used to make  $\text{CeO}_2/\text{ZSM-5}$ -modified glassy-carbon electrodes for electrochemical oxidation of methanol.<sup>27</sup>  $\text{CeO}_2/\text{ZSM-5}$  exhibited approximately three times higher electrocatalytic activity than commercial  $\text{Pt}(20\%)/\text{C}$  catalyst as a result of the good dispersion of  $\text{CeO}_2$  nanocrystals on the large surface areas of ZSM-5. Moreover, the current density of  $\text{CeO}_2(30\%)/\text{ZSM-5}$  remained above 96% even after cycling 1,000 times, whereas commercial  $\text{Pt}(20\%)/\text{C}$  could retain only 9% of its original activity. Such a good cycling life was attributed to the catalytic capability of  $\text{CeO}_2(30\%)/\text{ZSM-5}$  to convert CO, a reaction intermediate that was poisonous to the Pt electrodes, into  $\text{CO}_2$ . Zeolites can also be used for preparing composite electrolyte membranes to improve the performance of fuel cells because of their high thermal and mechanical stability and tunable hydrophilicity. For instance, perfluorosulfonic acid/zeolite composite membranes could be fabricated for self-humidifying fuel cells that were operable at high temperature in the absence of external humidification.<sup>28</sup> In particular, Nafion-117/silicalite-1, Nafion-117/H-ZSM-5, and Nafion-117/H-ZSM-5/silicalite-1 composite membranes exhibited a much improved glass transition

temperature, open circuit voltage, maximum power density, and high-temperature durability over the standard Nafion 117 membrane because of the confinement and moisture zeolites provided toward perfluorosulfonic acid. Despite all these advantages, for the practical utilization of zeolites as electrodes and electrolyte membranes, more effort is still needed toward improving the electrical and proton conductivities of zeolites.

## THERMAL ENERGY STORAGE

Thermal energy storage techniques store and release the energy in the form of heat, and are promising candidates for the storage of intermittent energy, such as solar power and industrial waste heat. Hot water heating facilities are currently the most widely used thermal energy storage systems, but their energy densities are very low ( $10\text{--}50\text{ kWh m}^{-3}$ ).<sup>29</sup> Zeolite-water-adsorption energy storage is an emerging technology utilizing the energy stored and released during water desorption and adsorption over zeolites, respectively. Several types of zeolites have been investigated for adsorption energy storage, including zeolites X (FAU type), Y (FAU type), A (LTA type), SAPO-34 (CHA type), AIPO-34 (CHA type), and AIPO-18 (AEI type), etc.<sup>30</sup> For instance, silicoaluminophosphate SAPO-34, aluminophosphates AIPO-34, and AIPO-18 with high hydrophilicity exhibited similarly high water uptake capacity.<sup>31</sup> In particular, AIPO-34 possessed a high energy density of  $240\text{ kWh m}^{-3}$  in the  $40^\circ\text{C}\text{--}140^\circ\text{C}$  temperature range. Note that the desorption temperature of  $140^\circ\text{C}$  was in the range reachable by solar thermal collectors. In addition, AIPO-34 allowed unique sudden water uptake in a narrow pressure range because of the formation of  $\text{Al}\text{--}\text{H}_2\text{O}$  coordination. All these features make AIPO-34 a very promising adsorbent for practical water-adsorption energy storage. Very recently, an aluminophosphate zeolite AIPO-LTA (LTA type) was reported for adsorption energy storage, outperforming all other porous materials.<sup>32</sup> AIPO-LTA exhibited unprecedented high water uptake ( $0.42\text{ g g}^{-1}$ ) and energy density ( $527\text{ kWh m}^{-3}$ ). Such high energy storage was attributed to the hydrophilic nature of aluminophosphate and the formation of an H-bonded network of water molecules within the pores of AIPO-LTA. Its energy capacity dropped less than 2% after 40 adsorption-desorption cycles. More importantly, AIPO-LTA required a desorption temperature  $10^\circ\text{C}\text{--}15^\circ\text{C}$  lower than other materials, and it attained 90% of its capacity at only  $60^\circ\text{C}$ , making it more suitable for long-term solar-heat storage even in regions without intense solar irradiation.

Out of the laboratory, ZAE Bayern developed a water-adsorption system by using zeolite X to provide heating to a school building in winter (Figure 6).<sup>33</sup> When the thermal demand was high during the day, the stored heat was released through the adsorption process. The air from the school building was heated at the adsorption column and went back to the heating system of the school. The regeneration of zeolite X was done by district heating during the night when the thermal demand was low. The energy density of this system could reach  $124\text{ kWh m}^{-3}$ , much higher than those of the hot water storage systems. Besides on-site utilization, zeolite adsorbents can also be used as mobile thermal energy storage materials for off-site energy utilization. For instance, ZAE Bayern developed a  $2.3\text{ MWh}$  mobile thermal energy storage system, with a  $14\text{ t}$  packed bed of zeolite adsorbents.<sup>34</sup> It was used to recover the industrial waste heat from an incineration plant located  $7\text{ km}$  away from the heat demand. This real-scale system was able to save  $616\text{ kg}$  of  $\text{CO}_2$  per transport cycle, and the zeolite adsorbents showed no degradation during different tests.



**Figure 6. Zeolite/Water-Adsorption Energy Storage System for School Heating**

During the day, heat was released when water was adsorbed in zeolite X. Water was desorbed at night by district heat, thereby regenerating the adsorption energy storage system.

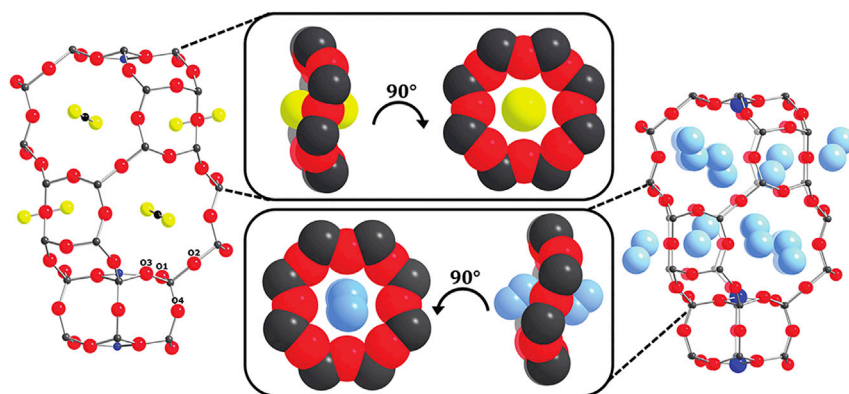
It can be anticipated that with the development of hydrophilic aluminophosphate adsorbents, adsorption energy storage techniques will receive more attention in the near future. Future work includes increasing the stability and recycling life of aluminophosphate zeolites, tuning the performance of zeolites by impregnation with other materials such as hygroscopic salts, and optimizing the technical factors, such as the adsorbent particle size, the design of the adsorption columns, and the operational temperatures, etc., to obtain cost-effective heating.

## CO<sub>2</sub> CAPTURE AND CONVERSION

The increase in CO<sub>2</sub> concentration in the atmosphere has caused serious environmental problems, such as global warming and extreme weather. CO<sub>2</sub> emissions mainly come from fossil fuel combustion, which unfortunately is and will continue to be our primary energy source for the next several decades. Many materials have been developed to reduce CO<sub>2</sub> emissions, such as activated carbon, metal-organic frameworks, mesoporous silica, metal, and metal oxides, etc., among which zeolites have attracted much attention because of their unique adsorption and catalytic properties.

### CO<sub>2</sub> Capture

CO<sub>2</sub> capture is a promising strategy to reduce CO<sub>2</sub> emissions. Zeolites, along with other porous materials, such as metal-organic frameworks, are among the best inorganic adsorbents for CO<sub>2</sub> adsorption. In particular, zeolite frameworks possess strong electric fields, preferentially adsorbing molecules with large dipole and quadruple moments such as CO<sub>2</sub>. Moreover, various active sites in zeolites as well as their particular porous structures provide a unique shape-selective effect toward



**Figure 7. CO<sub>2</sub> (Left) and N<sub>2</sub> (Right) Adsorption Sites in Cu-SSZ-13 at 4 K**

The positions of CO<sub>2</sub> and N<sub>2</sub> in relation to the 8-ring pore windows are shown as a space-filling representation in the middle (yellow spheres, O atoms; black spheres, C atoms; pale blue spheres, N atoms). Note that the figure represents only the adsorption sites and does not quantify the amounts of gas at each location; the actual occupancy is much greater for CO<sub>2</sub>. Reprinted with permission from Hudson et al.<sup>36</sup> Copyright 2012 American Chemical Society.

the adsorption of CO<sub>2</sub>. Therefore, zeolites have been studied extensively for capturing CO<sub>2</sub> from N<sub>2</sub>, CH<sub>4</sub>, or H<sub>2</sub> in various industrial processes.<sup>35</sup> For instance, the low-pressure adsorption of CO<sub>2</sub> and N<sub>2</sub> over H- and Cu-exchanged zeolites SSZ-13 (CHA type) was investigated.<sup>36</sup> The maximum CO<sub>2</sub> uptake for H- and Cu-SSZ-13 at 1 bar was 3.98 and 3.75 mmol g<sup>-1</sup>, respectively. More importantly, under ideal conditions for CO<sub>2</sub>/N<sub>2</sub> separation for industrial flue gas (a mixture of 0.15 bar CO<sub>2</sub> and 0.75 bar N<sub>2</sub>), H- and Cu-SSZ-13 exhibited the ideal adsorbed solution theory selectivity of 73.6 and 72.0, respectively. Such high CO<sub>2</sub> uptake and selectivity were attributed to the small-pore nature of SSZ-13, in which the 8-ring pore window matched the kinetic diameter of CO<sub>2</sub> well, producing a special binding effect toward CO<sub>2</sub> (Figure 7). Another family of small-pore aluminosilicate zeolites with extending complexity and embedded isorecticular frameworks were reported to exhibit high CO<sub>2</sub> uptake and selectivity.<sup>37</sup> In particular, at room temperature, Na-ZSM-25 (MTF type) in this family exhibited a CO<sub>2</sub>/CH<sub>4</sub> selectivity of 331 at 0.1 bar and 22 at 1.0 bar. Moreover, Na-ZSM-25 could achieve CO<sub>2</sub> adsorption equilibrium in 2 min and its CO<sub>2</sub> uptake remained the same over 100 adsorption-desorption cycles. Such high performance for CO<sub>2</sub> capture was attributed to the “molecular trapdoor” effect, by which the extra-framework cations blocked the 8-ring pore windows and only allowed the entrance of molecules strongly interacting with them, such as CO<sub>2</sub>.<sup>38</sup> The fast diffusion of CO<sub>2</sub> was also observed in other zeolites. Using interference microscopy, Lauerer et al.<sup>39</sup> studied the diffusion of CO<sub>2</sub>-C<sub>2</sub>H<sub>6</sub> mixtures in small-pore zeolite ZSM-58 (DDR type). The diffusion of CO<sub>2</sub> was so fast in comparison with C<sub>2</sub>H<sub>6</sub> that the CO<sub>2</sub> uptake instantly exceeded its final equilibrium value, which was known as the “overshooting” behavior of the fast-diffusive component as a result of the “uphill diffusion” effect. In comparison, the local C<sub>2</sub>H<sub>6</sub> concentration increased gradually to reach the final equilibrium value. Taking advantage of the diffusion speed difference, small-pore zeolites such as ZSM-58 could be utilized to kinetically separate CO<sub>2</sub> from other species.

Zeolites can be made into CO<sub>2</sub>-selective permeance membranes for CO<sub>2</sub> separation. For instance, a 0.5-μm-thick silica zeolite MFI membrane was reported with the straight channels along the *b* axis uniformly aligned.<sup>40</sup> This membrane exhibited a separation selectivity of 109 for a 50:50 CO<sub>2</sub>/H<sub>2</sub> mixture and a CO<sub>2</sub> permeance of

**Table 1. Selected Examples of CO<sub>2</sub> Conversion over Zeolite Catalysts**

Catalyst	Reactants	Main Products	Reference
Ti/H-ZSM-5	CO <sub>2</sub> , H <sub>2</sub> O	CO	Tong et al. <sup>44</sup>
Ni/H-USY	CO <sub>2</sub> , H <sub>2</sub> O	CH <sub>4</sub>	Westermann et al. <sup>45</sup>
Cu-ZnO/H-ZSM-5	CO <sub>2</sub> , H <sub>2</sub>	CH <sub>3</sub> OH	Ayodele <sup>46</sup>
Zn/H-ZSM-5	CO <sub>2</sub> , CH <sub>4</sub>	CH <sub>3</sub> COOH	Wu et al. <sup>47</sup>
CuO-ZnO-ZrO <sub>2</sub> /H-ZSM-5	CO <sub>2</sub> , H <sub>2</sub>	CH <sub>3</sub> OCH <sub>3</sub>	Frusteri et al. <sup>48</sup>
Ion-liquid- or amine-functionalized ZSM-5	epoxide (epichlorohydrin)	cyclic carbonate (chloropropyl carbonate)	Sarmah and Srivastava <sup>49</sup>
CuO-ZnO-Al <sub>2</sub> O <sub>3</sub> /H-beta	CO <sub>2</sub> , H <sub>2</sub>	CO, C <sub>2</sub> -C <sub>4</sub> hydrocarbons	Fujiwara et al. <sup>50</sup>
Na-Fe <sub>3</sub> O <sub>4</sub> /H-ZSM-5; In <sub>2</sub> O <sub>3</sub> /H-ZSM-5	CO <sub>2</sub> , H <sub>2</sub>	C <sub>5</sub> + hydrocarbons	Wei et al., <sup>51</sup> Gao et al. <sup>52</sup>

$51 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  at  $-35^\circ\text{C}$ , higher than those of all previously reported random-orientation zeolite membranes.

Despite these advantages, like all other porous materials, CO<sub>2</sub> capture over zeolites under humid conditions is still challenging because of the large dipole moments of H<sub>2</sub>O. One way to improve the CO<sub>2</sub> uptake under humid conditions is to graft functional groups on the surfaces of zeolite pores. For instance, an ethylenediamine-grafted zeolite Y was reported to possess excellent CO<sub>2</sub> adsorption capability, in which the amine groups could effectively capture CO<sub>2</sub> in a wet flue gas, whereas H<sub>2</sub>O adsorbed by zeolite Y protected the amine groups by suppressing their transformation to urea under desorption conditions.<sup>41</sup> Alternatively, molecular simulations indicated that some zeolite framework types, such as AEL and MFI, might have high CO<sub>2</sub>/H<sub>2</sub>O selectivity and low H<sub>2</sub>O uptake because of their predicted peculiar high-temperature adsorption and low-temperature desorption behaviors.<sup>42</sup> However, these predictions still need experimental validation. Meanwhile, for future practical CO<sub>2</sub> capture from industrial flue gas, the high-temperature CO<sub>2</sub> adsorption of zeolites should be further improved.

### CO<sub>2</sub> Conversion

Compared with CO<sub>2</sub> capture, catalytically converting CO<sub>2</sub> into fuels or high-value chemicals is much more eco-friendly and cost effective.<sup>43</sup> However, most studies have focused on converting CO<sub>2</sub> into short-chain products, such as CO, CH<sub>4</sub>, CH<sub>3</sub>OH, CH<sub>3</sub>COOH, CH<sub>3</sub>OCH<sub>3</sub>, and C<sub>2</sub>-C<sub>4</sub> hydrocarbons (Table 1).<sup>44–52</sup> Selectively converting CO<sub>2</sub> into gasoline-ranged hydrocarbons is still challenging because of the fast hydrogenation of reaction intermediates on the surfaces of conventional catalysts. Combining the high activity of iron-based catalysts for CO<sub>2</sub> hydrogenation and the shape selectivity of MFI-type zeolites, Wei et al.<sup>51</sup> recently prepared a highly efficient multifunctional Na-Fe<sub>3</sub>O<sub>4</sub>/H-ZSM-5 nanocomposite catalyst for the direct conversion of CO<sub>2</sub> to gasoline-range hydrocarbons. The multiple active sites in this catalyst enabled a tandem of reactions, including the initial reduction of CO<sub>2</sub> to CO over the Fe<sub>3</sub>O<sub>4</sub> sites, the subsequent hydrogenation of CO to olefins over the Fe<sub>5</sub>C<sub>2</sub> sites, and hydrocarbon oligomerization/aromatization/isomerization over the Brønsted acid sites in H-ZSM-5. This catalyst displayed an extremely high selectivity toward C<sub>5</sub>-C<sub>11</sub> hydrocarbons up to 78% and only 4% toward CH<sub>4</sub> at a CO<sub>2</sub> conversion of 22% under industrially relevant conditions. More importantly, it exhibited a remarkable stability for 1,000 hr on stream, showing its potential to be an industrial catalyst for CO<sub>2</sub> conversion to liquid fuels. Meanwhile, Gao et al.<sup>52</sup>

reported the direction conversion of  $\text{CO}_2$  into  $\text{C}_{5+}$  hydrocarbons with a selectivity of 78.6% and a very low  $\text{CH}_4$  production (1%) over  $\text{In}_2\text{O}_3/\text{H-ZSM-5}$  composite catalyst under industrially relevant conditions. The oxygen vacancies on the  $\text{In}_2\text{O}_3$  surfaces activated  $\text{CO}_2$  and  $\text{H}_2$  to form methanol, and the pores of H-ZSM-5 facilitated the formation of gasoline-range hydrocarbons with a high octane number via C–C coupling. The proximity of the two components was believed to be crucial to suppress the undesired reverse water-gas shift reaction.

Besides direct hydrogenation,  $\text{CO}_2$  can transform with  $\text{CH}_4$  over metal-modified zeolite catalysts into high-value chemicals, representing a promising direction toward the utilization of greenhouse gases. For instance, the direct formation of acetic acid from  $\text{CO}_2$  and  $\text{CH}_4$  over Zn/H-ZSM-5 bifunctional catalyst at temperatures ranging from 250 to 500°C was reported.<sup>47</sup> During this reaction, the extra-framework Zn efficiently activated  $\text{CH}_4$  to form  $-\text{Zn}-\text{CH}_3$  species, which further formed  $-\text{Zn}-\text{OOCCH}_3$  species via  $\text{CO}_2$  insertion, and the Brønsted acid sites in H-ZSM-5 facilitated the final formation of acetic acid by transferring protons to the surface acetate species. Despite all the success, developing composite catalysts with cheap metals that are active for  $\text{CO}_2$  conversion under mild conditions is still a big challenge. Meanwhile, the exact reaction mechanisms for many  $\text{CO}_2$  conversion processes are still under debate, and require more efforts in the future with the aid of operando characterization and computer modeling techniques.

## AIR-POLLUTION REMEDIATION

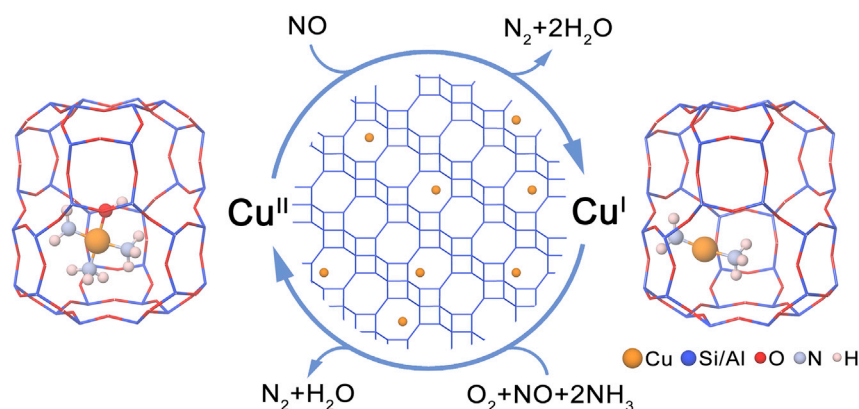
With global industrialization, air pollution has become a severe issue that harms human health and the environment. Currently, the main air pollutants include  $\text{NO}_x$ ,  $\text{NH}_3$ , and nonmethane volatile organic compounds (VOCs), etc. With their superior adsorption and catalytic capabilities, zeolites are playing an important role in air-pollution remediation.

### $\text{NO}_x$ and $\text{NH}_3$

$\text{NO}_x$  (mainly  $\text{NO}$  and  $\text{NO}_2$ ) are produced from combustion of fossil fuels in automobiles or coal-fired power plants, which can induce acid rain, photochemical smog, and direct damage to the respiratory systems of humans. Among various “de $\text{NO}_x$ ” technologies, the selective catalytic reduction of  $\text{NO}_x$  with  $\text{NH}_3$  ( $\text{NH}_3\text{-SCR}$ :  $\text{NO} + \text{NH}_3 + \text{O}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$ ) is currently the most widely applied. Metal-exchanged zeolite catalysts have played a key role in the development of  $\text{NH}_3\text{-SCR}$  technology, such as ZSM-5, Y, mordenite, and beta.<sup>53</sup> In comparison with previous  $\text{NH}_3\text{-SCR}$  catalysts, zeolites have the advantages of high activity, easy availability, and high stability at different operational temperatures.<sup>54</sup>

In 2010, Kwak et al.<sup>55</sup> synthesized Cu-exchanged zeolite SSZ-13 by using *N,N,N*-trimethyl-1-adamantanamine iodide as the template and studied its catalytic performance on  $\text{NH}_3\text{-SCR}$  reactions. In comparison with Cu-ZSM-5 and Cu-beta, Cu-SSZ-13 was not only more active over a wide temperature range (160°C–550°C) but also more selective toward nitrogen formation, significantly lowering the formation of undesired  $\text{NO}_2$  and  $\text{N}_2\text{O}$  byproducts. Since then, Cu-exchanged **CHA**-type zeolites have been extensively studied for  $\text{NH}_3\text{-SCR}$  reactions. Note that Cu-SSZ-13 has already been commercialized for  $\text{NO}_x$  emission control, and is today’s most common choice in automobile  $\text{NH}_3\text{-SCR}$  systems.<sup>54</sup> Although the exact mechanisms for  $\text{NH}_3\text{-SCR}$  reactions over Cu-exchanged **CHA**-type zeolites are still not clear, it is generally accepted that this process should involve a reduction half-cycle ( $\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{I}}$ ) and an oxidation half-cycle ( $\text{Cu}^{\text{I}} \rightarrow \text{Cu}^{\text{II}}$ ) (Figure 8).<sup>56</sup> Recent





**Figure 8. NH<sub>3</sub>-SCR over Cu-Exchanged CHA-Type Zeolite**

NH<sub>3</sub>-SCR over Cu-exchanged CHA-type zeolite involves a reduction half-cycle and an oxidation half-cycle.

studies utilized the state-of-the-art operando characterization and computational techniques to investigate the NH<sub>3</sub>-SCR process. For instance, the temperature-dependence of NH<sub>3</sub>-SCR reactions and the atomic-scale behavior of Cu active sites in the 150°C–400°C temperature range were studied via operando XAS/XES measurement;<sup>57</sup> [Cu<sup>I</sup>(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>–O<sub>2</sub>–[Cu<sup>I</sup>(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> intermediate was identified to play an important role in the reaction kinetics of low-temperature NH<sub>3</sub>-SCR;<sup>58</sup> mobilized Cu ions were found to travel through CHA windows and form dynamic ion pairs that participated in a Cu<sup>I</sup> → Cu<sup>II</sup> redox step.<sup>56</sup> These theoretical and experimental studies have provided important clues for the discovery of new NH<sub>3</sub>-SCR catalysts with improved performance. Recently, Cu-exchanged high-silica LTA zeolites were reported to be a promising alternative to commercialized Cu-SSZ-13.<sup>59,60</sup> Cu-LTA exhibited excellent NH<sub>3</sub>-SCR activity under simulated vehicle conditions even after hydrothermal aging at 900°C, a critical temperature that current commercial Cu-SSZ-13 catalyst could not overcome. Such superior performance was attributed to the Cu<sup>2+</sup> ions bound at the center of 6-rings in Cu-LTA, which acted not only as a catalytically active center but also as a dealumination suppressor. Another example is the MSE-type large-pore zeolite Cu-UZM-35, which was reported to possess a considerably wider operating temperature window after aging at 750°C than Cu-SSZ-13.<sup>61</sup> Its high-temperature stability was attributed to the formation of CuO<sub>x</sub> and CuAl<sub>2</sub>O<sub>4</sub> phases during NH<sub>3</sub>-SCR.

NH<sub>3</sub> is another N-containing air pollutant mainly present in coking wastewater streams. Metal-exchanged zeolite catalysts can be used for NH<sub>3</sub> elimination via selective catalytic oxidation of NH<sub>3</sub> into N<sub>2</sub> (NH<sub>3</sub>-SCO: NH<sub>3</sub> + O<sub>2</sub> → N<sub>2</sub> + H<sub>2</sub>O).<sup>53</sup> For instance, many transition-metal (Cr, Mn, Fe, Co, Ni, Cu) exchanged zeolites ZSM-5 were found to be active for NH<sub>3</sub>-SCO.<sup>62</sup> Among them, Fe-ZSM-5 exhibited the best performance, achieving 99% NH<sub>3</sub> conversion and 100% N<sub>2</sub> selectivity at 450°C. More importantly, Fe-ZSM-5 maintained a high NH<sub>3</sub> conversion of 94% at 500°C in the presence of water vapor and a small amount of SO<sub>2</sub>, which were often found in waste streams. The high activity of Fe-ZSM-5 was attributed to the variable valences of iron (Fe<sup>III</sup> and Fe<sup>II</sup>), favoring oxygen adsorption and activation during NH<sub>3</sub>-SCO. These results indicated that Fe-ZSM-5 might be a practical catalyst for NH<sub>3</sub>-SCO in a wet stream. Noble-metal-modified zeolites are another important group of NH<sub>3</sub>-SCO catalysts. For instance, zeolites H-Y loaded with 0.05–2.5 wt % Pd were reported to exhibit high N<sub>2</sub> selectivity (>90%) at 100% NH<sub>3</sub> conversion in the temperature range of 250°C–450°C.<sup>63</sup> In particular, H-Y loaded with 2.5 wt %

Pd attained 100%  $\text{NH}_3$  conversion at 250°C, in which  $\text{PdO}_x$  was believed to be the active sites for  $\text{NH}_3$ -SCO.

### Nonmethane VOCs

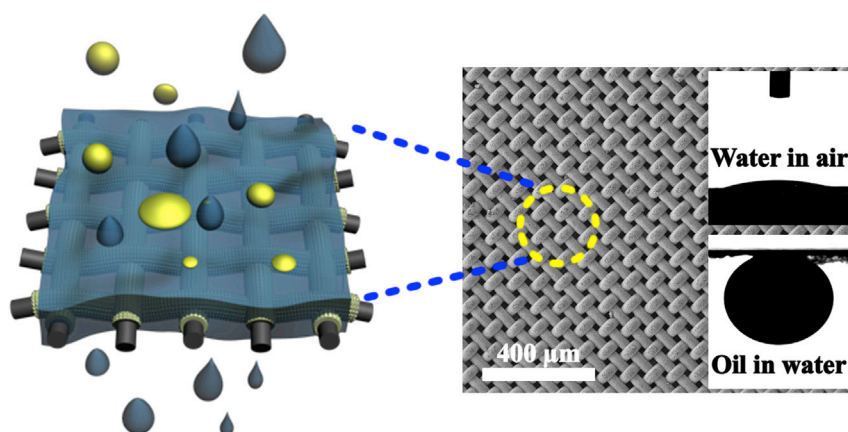
VOCs, such as benzene, toluene, formaldehyde, and chloromethane, etc., have high biological toxicity, which are mainly produced from combustion engines, industrial emissions, and domestic products. The total oxidation of VOCs into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  is a promising strategy for VOC abatement. Noble-metal/porous-material composites are excellent catalysts for VOC oxidation, and zeolites with large surface areas, tunable framework compositions, and high hydrothermal stability are ideal supports for noble metals.<sup>64</sup> For instance, a Pt/K-beta composite catalyst was reported to be highly active for toluene oxidation.<sup>65</sup> The temperature at 98% conversion of toluene was 150°C, which was much lower than conventional noble-metal and transition-metal-oxide catalysts. Here, K-beta was prepared through a template-free and seed-directed synthesis strategy, leading to relatively higher Al and K contents and fewer terminal silanol defects than conventional zeolite beta, favoring the adsorption of hydrophobic VOCs. In another study, Mn-containing zeolites ZSM-5 were synthesized via a one-step hydrothermal approach and exhibited high catalytic performance for toluene oxidation.<sup>66</sup> Among them, Mn(2%)/ZSM-5 exhibited 100% selectivity to  $\text{CO}_2$  at 65% conversion of toluene.

A major drawback of zeolites in the total oxidation of VOCs is the production of coke, which blocks the micropores of zeolites and deactivates the catalysts. Incorporating mesopores that are much larger than micropores into zeolites would increase the mass transfer during catalytic oxidation and is a promising strategy for overcoming the coking problem. For instance, a mesoporous Pt/beta composite catalyst was reported for the catalytic oxidation of toluene, exhibiting improved catalytic activity in comparison with its counterpart without mesopore incorporation.<sup>67</sup> More importantly, the mesoporous Pt/beta catalyst exhibited a longer catalyst life. After a reaction for 10 hr, the mesoporous Pt/beta maintained nearly 100% conversion of toluene and selectivity to  $\text{CO}_2$ , whereas its microporous counterpart gave 27% toluene conversion and about 60% selectivity to  $\text{CO}_2$ .

In summary, zeolites have found many applications in catalytic elimination of air pollutant molecules. Future work on  $\text{NH}_3$ -SCR should focus on lowering the production cost of Cu-SSZ-13 by finding a cheap template to realize its large-scale production. Meanwhile, SAPO-34 with the same CHA-type framework as SSZ-13, as well as zeolites with similar framework topology (such as OFF, LEV, and ERI etc.), should be explored for  $\text{NH}_3$ -SCR. Cu- and Fe-exchanged zeolites have exhibited high performance on  $\text{NH}_3$ -SCO. More efforts should be made to elucidate the detailed reaction mechanisms over these zeolites. Toward this end, operando characterization and high-level computer modeling should be relied on to locate the reaction intermediates and possible pathways.

### WATER PURIFICATION

Most of the surface water on the earth is seawater, which contains a large amount of salts, not suitable for direct consumption by humans. Meanwhile, various types of pollutants are threatening our water supply, such as spilled oil, heavy metals, and radioactive wastes. Developing materials and technologies to efficiently remove salts and unwanted contaminants from water is a promising direction to solve the global water crisis. Zeolites with superior adsorption and ion-exchange capability have found wide applications in these fields.



**Figure 9. Zeolite-Coated Mesh Films for Gravity-Driven Oil-Water Separation**

The crystals of silicalite-1 were grown on stainless-steel meshes under hydrothermal conditions. High separation efficiency of various oils was achieved on the basis of the excellent superhydrophilicity and underwater superoleophobicity of silicalite-1 surface. Reproduced from Wen et al.<sup>72</sup> with permission from the Royal Society of Chemistry.

Removing salt or spilled oil from water can be realized by membranes with high salt/oil rejection and water permeation. Zeolites with excellent molecular-sieving and mechanical properties could be made into membranes, a potential alternative to widely studied reverse osmosis membranes that are energetically inefficient and inapplicable to water containing organic compounds.<sup>68</sup> For instance, natural zeolite heulandite/clinoptilolite (HEU type) membranes were fabricated and tested for the removal of metal cations and toluene from synthetic seawater at 85°C and 1 atm feed-side pressure under a pervaporative operation.<sup>69</sup> These membranes exhibited rejection rates of 87.4%, 99.9%, 99.4%, and >96% for Na<sup>+</sup>, Mg<sup>+</sup>, K<sup>+</sup>, and toluene, respectively. Water flux was insensitive to toluene over a wide concentration range (10–220 mg L<sup>-1</sup>), but decreased rapidly when cation concentrations in the feed increased. Although computer simulations have predicted many zeolites with high salt rejection and water permeation,<sup>70</sup> their true performances need to be carefully investigated, because water transport inside zeolite membranes is a complex process highly influenced by many factors such as hydrophilicity and surface barriers.<sup>71</sup> In another study, zeolite-coated mesh films for oil-water separation were fabricated by growing the crystals of silicalite-1 on stainless-steel meshes through a seeding and secondary growth process under hydrothermal conditions (Figure 9).<sup>72</sup> As a result of the excellent superhydrophilicity and underwater superoleophobicity of silicalite-1, highly efficient gravity-driven oil-water separation was achieved. The underwater superoleophobic interface prevented the film from fouling by oils. More importantly, such films were highly stable under various harsh conditions, such as acid and concentrated salt, showing their potential for practical applications of oil-water separation. However, for practical applications of zeolite membranes, how to increase the relatively low water flux is still challenging. Developing thin supported zeolite membranes might be promising in the future. Meanwhile, most fabrication methods for zeolite membranes are facing scaling up issues. Moreover, long-term stability and production and regeneration costs of zeolite membranes should be further improved to allow practical applications in industry.

Heavy metals, such as Cr, Cd, Cu, Pb, Zn, Ni, and Co, are dangerous to human health because of their nonbiodegradability and toxicity. In comparison with other

heavy-metal removal methods, adsorption techniques are energy efficient and eco-friendly for the selective removal of heavy metals. In particular, zeolites have been attractive candidate adsorbents for heavy metals since the first attempt using zeolites to purify water in the 19<sup>th</sup> century. Many types of zeolites have been tested for heavy-metal removal, such as zeolites X, Y, A, and P (GIS type) and clinoptilolite, etc. Among these, zeolites X and A are generally the best adsorbents for heavy-metal removal.<sup>73</sup> Recent studies have focused on modifying zeolites with metals or metal oxides to improve their heavy-metal removal capability. For instance, iron-coated clinoptilolite displayed much improved adsorption capability for heavy metals, especially for Pt, in comparison with uncoated clinoptilolite.<sup>74</sup> This was probably because the iron could reduce Pb<sup>II</sup> ions on the surface of clinoptilolite to Pb<sup>0</sup>. Taking advantage of the reductivity of iron, nanoscale-zero-valent-iron/zeolite composites could be made. With large surface areas of iron nanoparticles and the stabilization effect of zeolites toward iron nanoparticles, the uptake for Pb<sup>II</sup> could be much improved.<sup>75</sup> On the other hand, metal-oxide/zeolite composites could be made for heavy-metal removal. For instance, core-shell ZnO/Y particles with zeolite Y as the core and ZnO nanoflakes as the porous shell could be fabricated as a multifunctional water purifier;<sup>76</sup> 200 mg of ZnO/Y core-shell composites exhibited equilibrium Pb<sup>II</sup> adsorption of 74.7 mg g<sup>-1</sup>, which was much higher than that of pristine zeolite Y (47.93 mg g<sup>-1</sup>). The enhanced Pb<sup>II</sup> adsorption could be attributed to the formation of a ZnO nanoflake layer on the surface of zeolite Y, which attained negative charges, attracting the positively charged Pb<sup>II</sup> ions. Meanwhile, with surface modification of ZnO nanoflakes, the ZnO/Y composite also exhibited high adsorption and photocatalytic activity toward organic pollutants (for instance, methylene blue dye) and antibacterial activity toward microorganisms (such as *Escherichia coli*, *Staphylococcus aureus*, and *Pseudomonas*). To realize practical large-scale heavy-metal removal by using zeolites, future efforts should be focused on metal recovery, zeolite regeneration, and competitive multi-component adsorption.

Methods dealing with nuclear wastewater have attracted much attention, especially since the Chernobyl and Fukushima Daiichi disasters. Zeolites are radiologically stable to gamma, alpha, and beta irradiation. Furthermore, small-pore zeolites exhibit high affinity for radionuclides such as <sup>90</sup>Sr and <sup>137</sup>Cs at very low concentrations. A recent study attributed such high affinity to the preferential binding between radioactive cations and 8-ring windows in small-pore zeolites.<sup>77</sup> These unique characteristics, as well as their easy availability, make zeolites currently the most widely used adsorbents for radioactive pollutants. For instance, natural zeolites, such as mordenite and clinoptilolite, were used to decontaminate wastewater discharged from the damaged nuclear power plants at Chernobyl.<sup>78</sup> During the cleanup after the Fukushima disaster, zeolites were used to concentrate <sup>137</sup>Cs in the radioactive waste.<sup>79</sup> In addition, an 80-m-wide underground zeolite wall was installed at Fukushima Daiichi, aiming to block leaked <sup>90</sup>Sr in the soil from migrating to the sea.<sup>80</sup> Besides metal cations, zeolites are also capable of adsorbing other radioactive molecules, such as iodine released during the dissolution of nuclear fuel rods. Recently, Pham et al.<sup>81</sup> investigated the capture of iodine by using various types of porous materials, including all-silica zeolites, aluminosilicate zeolites, active carbons, and metal-organic frameworks. All-silica zeolites exhibited superior capability over other porous materials for I<sub>2</sub> removal from highly acidic dissolver solution. In particular, hydrophobicity-intensified silicalite-1 (which was prepared with fewer defects than conventional silicalite-1) and all-silica beta captured 0.26 and 0.21 g g<sup>-1</sup> of I<sub>2</sub>, respectively, from a 5 M HNO<sub>3</sub> solution saturated with I<sub>2</sub> within 1 hr. Both hydrophobic zeolites remained intact after immersion in 5 M HNO<sub>3</sub>.

solution for 3 days. In contrast, active carbons only captured  $0.04 \text{ g g}^{-1}$  of  $\text{I}_2$  under the same conditions, and other electron-rich materials, such as aluminosilicate zeolites Na-X, Na-A, Na-Y, Ca-A, and metal-organic frameworks ZIF-8 and HKUST-1, readily dissolved in a diluted  $0.1 \text{ M HNO}_3$  solution. This study demonstrated the potential application of all-silica zeolites in the safe processing of nuclear fuel rods.

## CONCLUSIONS AND PERSPECTIVES

Besides renewable energy and environmental improvement, zeolites are playing an increasingly important role in many other sustainable fields, such as agriculture<sup>82,83</sup> and biomedicine.<sup>84,85</sup> In this review, we focus only on the applications of zeolites in biomass conversion, fuel cells, thermal energy storage,  $\text{CO}_2$  capture and conversion, air-pollution remediation, and water purification. Some of these applications, such as thermal energy storage and water purification, have already been commercialized or widely used in practice. In particular,  $\text{NH}_3$ -SCR over CHA-type zeolites for  $\text{NO}_x$  emission control has become the most common choice for on-board applications. However, the utilization of zeolites in other sustainable fields is facing challenges. For instance, the stability, re-generatability, and product selectivity of zeolite catalysts need to be improved for biomass conversion,  $\text{H}_2$  and  $\text{CH}_3\text{OH}$  production, and  $\text{CO}_2$  conversion; the adsorption capability of zeolites should be improved for the capture of  $\text{CO}_2$  from hot wet flue gas; water permeability should be improved for desalination and oil-water separation zeolite membranes; the production cost for zeolites should be further reduced, and so on. Therefore, developing new zeolites with superior catalytic and adsorption capability, high stability, long recycling life, and low production and regeneration cost is highly desired.

Considerable theoretical and experimental efforts have been made toward synthesizing high-performance zeolite materials with brand-new framework types.<sup>86</sup> For instance, Yu et al. proposed a roadmap to realize function-led synthesis of new zeolite framework types via high-throughput computations, machine learning over a synthesis database, and combinatorial hydrothermal synthesis.<sup>87</sup> Other approaches, such as the "ADOR" strategy<sup>88</sup> and the "ab initio" template selection method,<sup>89</sup> have also exhibited potential in the discovery of new zeolite framework types. Another efficient way for zeolite development is to modify the composition, structure, and morphology of existing zeolites to obtain improved properties. For instance, the introduction of mesopores with diameter of 2–50 nm or macropores with diameter >50 nm into microporous zeolites leads to hierarchical structures, which usually have improved catalytic performance because of the increase in mass diffusion;<sup>90,91</sup> making zeolites into nanoparticles or nanosheets could enhance the catalytic activity as a result of the increased accessibility of the active sites.<sup>5,92,93</sup> Introducing hetero-metal atoms, metal clusters, or metal nanoparticles into zeolite matrices to form multifunctional composites is also a promising approach to material innovation with combined or improved properties. Recently, Grand et al.<sup>94</sup> reported the one-pot synthesis of silanol-free nanosized MFI zeolite with tungsten atoms dispersed atomically. Because of the formation of highly stable W–O–Si bonds that suppressed the occurrence of Si–OH groups, the prepared W-MFI exhibited considerably higher stability, hydrophobicity, and Lewis acidity than conventional pure-silica MFI. These features are highly appealing for many biomass conversion processes. Despite all the success, function-led design and synthesis of new zeolite materials remains challenging, because the structure-property relationship for zeolites is still not quite clear. To this end, more efforts should be made to reveal the detailed mechanisms for the adsorption, diffusion, catalysis, and ion-exchange processes within zeolites via high-resolution and/or operando characterization techniques.<sup>95,96</sup>

Although zeolites have found many sustainable applications, their large-scale production is not a very energy-efficient process. Today, most industrially produced zeolites come from hydrothermal synthesis, which requires high pressure and reaction times of days. The usage of inorganic and organic templates requires additional procedures to remove them, which leads to additional production costs and secondary pollution. Methods of producing zeolites greenly and efficiently, such as organic-template-free synthesis, ionothermal synthesis, solvent-free synthesis, and microwave synthesis, etc., have attracted much attention recently.<sup>97</sup> In particular, the production of zeolites from fly ash, a main by-product generated from coal combustion, has been commercialized in several countries.<sup>98</sup> On the other hand, the discovery that zeolite synthesis can be accelerated by chemically or physically generated free radicals has shed light on green and efficient production of zeolites.<sup>99</sup> With all the experimental and theoretical advances, a growing number of zeolites with superior properties will be developed and applied in the fields of sustainable chemistry.

## AUTHOR CONTRIBUTIONS

Conceptualization, J.Y.; Writing – Original Draft, Y.L.; Writing – Review & Editing, Y.L. and J.Y.; Visualization, L.L. and Y.L.; Supervision, J.Y.; Funding Acquisition, J.Y. and Y.L.

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