catalysts

Review

Research and Application Development of Catalytic Redox Technology for Zeolite-Based Catalysts

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Abstract: Zeolites are porous materials with plentiful and adjustable pore structures, which are widely applied in various fields such as fossil fuel energy conversion, preparation of clean energy, chemical product conversion, CO_2 capture, VOC treatment, and so on. Zeolites exhibited advantageous adsorption compared with traditional adsorbents such as activated carbon; in addition, they can also provide abundant reaction sites for various molecules. The chemical composition, structural acidity, and distribution of pore size can distinctly affect the efficiency of the reaction. The modification of zeolite structure, the development of novel and efficient preparation methods, as well as the improvement of reaction efficiency, have always been the focus of research for zeolites.

Keywords: zeolite; catalyst; pore structure; redox; applications

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1. Introduction

Adsorption and catalytic oxidation technology have extensive uses in energy, chemical engineering, and environmental industries, such as the cracking of fossil fuels, conversion of biomass, synthesis of non-petroleum products, low-cost production of hydrogen, catalytic treatment of industrial exhaust gas, etc. [1,2]. The efficiency of catalytic reactions is strongly influenced by adsorbents and catalysts. Under normal conditions, adsorbents are porous materials with huge specific surface areas that can provide enough space for redox reactions. Activated carbons (ACs), porous alumina, metal-organic frameworks (MOFs), and molecular sieves are constantly used as adsorbents because of their pore structure. More specifically, considering the thermal stability and the modification of pore structure, molecular sieves exhibited better performance than activated carbons.

Zeolite has generally been utilized in various synthetic processes in industrial products since its development (as shown in Figure 1). For zeolites, the basic structural unit (TO_4) is connected by bridging oxygen atoms to form a secondary building structure (SBU), which can be further combined to form composite building structures (CBUs), and multiple rings (n) are simultaneously formed [3]. Zeolites can be classified as different types according to the pore size and the number of rings: (1) small pore zeolites with $n = 8$, (2) medium pore zeolites with $n = 10$, (3) large pore zeolites with $n = 12$, (4) extra-large pore zeolites with $n > 12$.

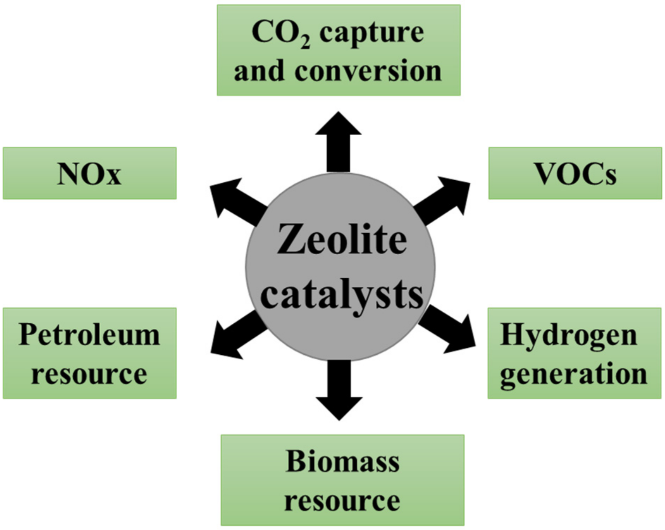

Figure 1. Various applications of zeolites in sustainable energy.

Due to the different combinations of basic units, there are significant differences in the pore structure and size of different types of zeolite molecular sieves. So far, A type, X type, Y type, β-zeolite, and ZSM-5 zeolite have been the most widely used zeolites.

A type (Linde type A, LTA) zeolites have a cubic crystal system. It has 3-dimensional channels ranging from 3 Å to 5 Å and an 8-membered topological structure. β zeolite is composed of 12-membered rings with an average channel size of 6 Å − 8 Å. X type and Y type zeolites are classified as FAU zeolites. Both of them belong to cubic crystals and are composed of hexagonal column cages and β cages formed from 6-membered rings. The Si/Al ratio of the X type varies from 2.2 to 3, and the Y type is higher than 3. Due to the special channels, X type and Y type zeolites have a large adsorption capacity for organic pollutant molecules. However, the adsorption capacity of organic molecules is reduced in moist gases. ZSM-5 is a typical MFI zeolite with a "zigzag" shaped 10-membered ring channel and vertically oriented 10-membered ring channels. The medium pore size (~5 Å) and excellent hydrothermal stability facilitated its application in the petrochemical industry.

Additionally, catalysts are pretty active components in the reaction process, including three types of catalysts: noble metals, non-noble metal oxides, and composite metal oxides. In order to increase the efficiency of the catalytic oxidation process, the selection of adsorbents and catalysts and the regulation of their modification should be prioritized.

This article illustrates the main applications of zeolite catalysts in summary and analyzes new advances in zeolite catalytic redox chemistry. The effects of porous structure, acidity, and other parameters, including zeolite type, catalyst, and reaction temperature, on the activity, selectivity, stability, and deactivation of zeolites are also summarized. Finally, the challenges and strategies of zeolite catalytic technology are discussed further.

2. The Application of Zeolite Catalysts

2.1. Catalytic Cracking of Petroleum Resources

Fluid catalytic cracking (FCC) technology is an effective alkyl removal technology that is increasingly widely utilized in the biomass oil and petrochemical industry. FCC catalysts consist of various zeolites with multi-component active ingredients that can greatly improve the efficiency of catalytic cracking [4,5].

For crude oil, it is extremely important to ameliorate the selectivity of catalysts towards products and increase the yield of specific products. In addition, Y-type zeolite has gained widespread use as a molecular sieve. Introducing and increasing mesoporous surface area can effectively reduce heavy oil production. Liu et al. prepared ordered silica aluminate on an industrial scale using a pre-crystallization unit of Y zeolite precursor. However, when a single layer of zeolite was dispersed on the catalyst surface, the composite catalyst exhibited the best activity for heavy oil cracking [6]. Pre-cracking is the first process to be carried out in the base pores, followed by further cracking and selective generation of its different products. Although Y zeolite is commonly used in heavy oil catalytic cracking and hydrocracking, the mass transfer efficiency between active sites is lower than expected. Cui et al. obtained mesoporous materials with octahedra by synthesizing ultra-stable mesoporous high-silicon molecular sieves directly. Compared to industrial FCC catalysts, the conversion rate was increased by 7.64%, and the gasoline yield was increased by 16.37%, even after these catalysts were aged at 800 °C [7].

Due to the requirements of the sixth national standard for the olefin content of automotive fuels, it is of great necessity to reduce the olefin content in gasoline. Through hydrothermal treatment, the acidity of ZSM-5 loaded metal catalysts (La-Ni-Zn) was reduced, and the B/L ratio (B = Brønsted acid, L = Lewis acid) was increased, which finally increased the aromatic production by 5% and the isoalkane production by 16%, making it an industrial catalyst for the catalytic cracking of gasoline [8]. To enhance the steam stability of Y zeolite, Yu et al. prepared rare earth (RE)-exchanged Y zeolite. The substitution of Y^{3+} ions for counter-ions Na^+ resulted in a noticeable shrinkage of the unit cell owing to the relatively small ionic radius and high charge density of Y^{3+} ions. Therefore, this kind of zeolite exhibited better performance in steam stability and was more favorable for the generation of liquefied petroleum gas and C_{5+} gasoline products in n-dodecane cracking [9]. Except for Y^{3+}, Al-exchanged Y zeolite was also proved to be able to promote liquefied petroleum gas production as a result of its strong acidity [10].

Except for routine chemical products, Li et al. have conducted extensive research on the production of high value-added products through dealkylation of light fraction light circulating oil and found that mesoporous BEA zeolite catalysts with appropriate acidity and mass transfer ability can greatly raise the yield of value-added products [11]. It can be seen that, although FCC was regarded as an efficient technology of dealkylation, the modifying of micropores and B acidic sites of zeolite need more research to elevate mass transfer ability. Thus, the optimization of catalysts in FCC, such as product selectivity, thermal stability, and cycle life, should receive focused attention so as to increase production.

2.2. Conversion of Biomass

Biomass is a promising green and renewable organic carbon source, but its calorific value is sharply lower than that of fossil fuels due to its abundant aerobic molecules, making it difficult to utilize directly [12,13]. It is necessary to transform biomass into valuable bioproducts. Two critical processes are involved in this strategy. One is the conversion of biomass into platform molecules, and the other is the upgrading of platform molecules into valuable fuels. Usually, the biomass comprised 40–50% cellulose, 25–35% hemicellulose, 15–20% lignin, and others [14]. Levulinic acid (LeA) and 5-hydroxymethylfurfural (HMF) are two common biomass platform molecules due to the highly reactive functional groups such as carboxyls, aldehydes, hydroxymethyls, and furan rings. LeA can be obtained from cellulose via the C_5 route or hemicellulose via the C_6 route, and HMF is usually produced from cellulose via the C_6 route.

(1) LeA via C_5 and C_6 route

In the C_6 route, cellulose was hydrolyzed to form C_6 sugar, which was dehydrated to form HMF. LA was obtained after the hydrolysis of HMF. Due to the high separation cost of LA and formic acid, synthesizing LA from C_6 sugar was mainly adopted in the laboratory. For the C_5 route, intermediates such as furfuryl and furfuryl alcohol (FAL) were successively converted to LeA, which made the carbon utilization more efficient than that of the C_6 route [15]. HY zeolite mixed with ionic liquid (ionic liquid: HY = 0.5) has more Lewis acid sites than Bronsted acid sites and exhibits a LeA yield of 62.2% [16]. ZSM-5 zeolite with mesopores was treated by tandem alkaline and acid washing, and ZSM-5-$OH_{0.2}$-H zeolite was therefore obtained; the modification of pore structure and Al distribution promoted the hydrolytic efficiency of FAL to LeA, the LeA yield reached 64.5% after three cycles [17].

(2) HMF via the C_6 route

HMF from biomass can be utilized to synthesize various biochemicals. The conversion of HMF from biomass can be divided into three processes: glucose hydrolyzed from cellulose, the isomerization of glucose to fructose, and the dehydration of fructose [15]. Therefore, fructose was usually used as a model molecule in HMF preparation, and many zeolites such as ZSM, HY, H-USY, and MAPO were adopted. Scholars prepared Cu-Cr/ZSM-5 zeolite using the ion-exchange method; when the zeolite was 20 wt.% of glucose, 50.4% HMF was achieved from glucose at 140 °C for 4 h [18]. To efficiently convert carbohydrates into HMF, β zeolite doping with 0.4 wt.% Cr was prepared and exhibited a superior 72% HMF yield and 83% selectivity due to the moderate L/B (Lewis acid sites/Brønsted acid sites) [19]. Low L/B hindered the isomerization of glucose to fructose; high L/B excessively accelerated the dehydration of fructose and led to the degradation of fructose to humin.

As the most abundant part of biomass, cellulose can be hydrolyzed and further converted into various chemical substances, one of which is lactic acid. Lactic acid (LA) from biomass was also among the top 30 candidates for synthetic fossil product substitutes [20]. Many important industrial chemicals can be derived from LA molecules, such as polylactic acid (PLA) [21], acrylic acid (AA), and propanoic acid (PA) (as shown in Figure 2). While cellulose was hydrolyzed to produce lactic acid (LA), various products such as levulinic acid and 5-hydroxymethylfurfural (HMF) were also produced, which resulted in a lower LA yield (around 30%). Therefore, it is necessary to improve the LA selectivity. In recent years, catalysts with acidic sites, especially solid Lewis acid catalysts, have received extensive research [22,23]. It was found that yttrium-modified siliceous material β zeolite catalysts can effectively regulate the surface acidity of zeolite and inhibit the yield of dehydration products such as HMF and other derivatives. The results indicated that when Lewis acidity was increased, the yield of LA from cellulose reached 49.2% within 30 min, more efficient than previous research studies [24].

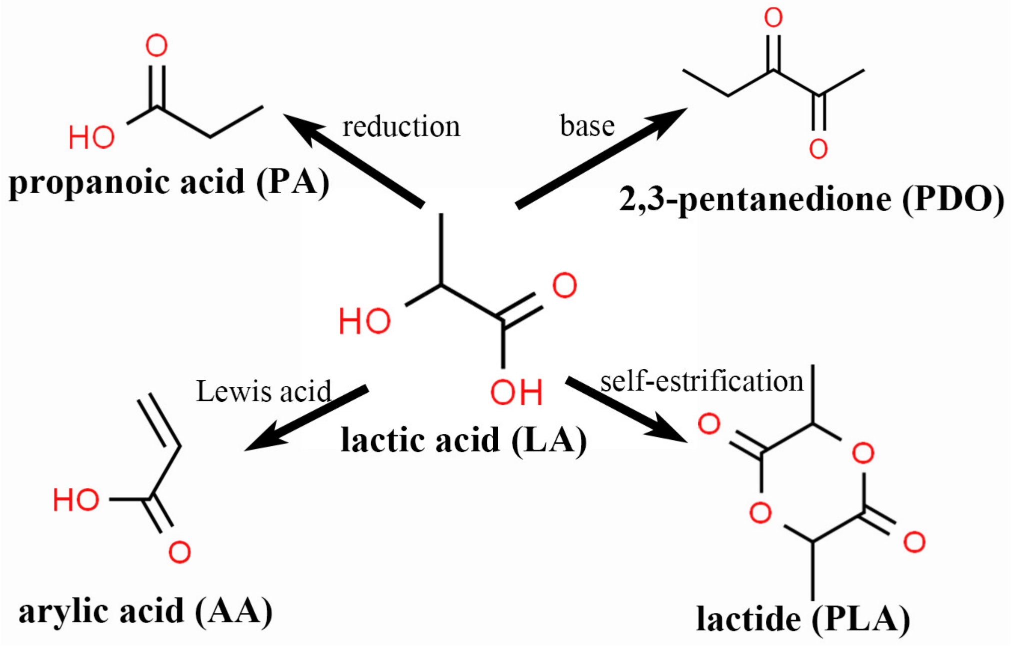

Figure 2. Reaction pathway of bio-renewable lactic acid (reproduced from reference [23]).

It was noteworthy that the composition of some organic compounds may have side effects on the catalytic performance of the catalyst. For example, phenolic substances derived from lignin not only contain O molecules but also have adverse impacts on catalysts. For this reason, the key to the catalytic cracking of bio-oil conversion is the optimization of efficient catalysts. Different catalysts have been adopted for different biomass and products.

In addition, NiMo/ASA Al_2O_3, Co Mo, HY zeolite, and ASA Al_2O_3 were simulated and found to be suitable for producing high distillate diesel [25]. The theoretical calculation results also indicated that larger mesoporous volume and surface area accelerated the diffusion rate of biomass inside the zeolite. However, this effect was continually weakened with increasing reaction time [26]. Because of the damage of by-products to catalysts and zeolites, the mass transfer efficiency was consequently decreased. To restrict the destruction of zeolites and catalysts and decrease the coke formation, an SFCC catalyst was employed in the cracking of high acid-value waste edible oil to produce biofuels. Moreover, the catalytic efficiency was attributed to doping with rare earth metals. Nguyen-Phuc et al. found that propylene and liquefied petroleum gas production were obviously improved by increasing the content of rare earth elements in ZSM-5 zeolite. Specifically, the yields of diesel, gasoline, and liquefied petroleum gas reached 29 wt.%, 42 wt.%, and 18 wt.%, respectively [27]. Additionally, to promote the conversion of biomass to valuable energy, a novel catalytic system similar to the Dylison Cycle Riser (DCR) should be designed and developed, which can produce hydrocarbon fuel intermediates from biomass-derived pyrolysis steam, such as pine and oak [28].

2.3. Preparation of Propylene

Propylene has been widely applied in diverse chemical products that are badly needed. Developing alternative methods to produce propylene using economical raw materials has attracted considerable interest, such as the hydrogenation of methanol to propylene and the dehydrogenation of propane to propylene [29–31].

2.3.1. Methanol to Propylene (MTP)

Methanol to propylene (MTP) was considered a substitutable approach to propylene production because of the extensive sources of methanol available. Due to its selectivity for propylene and the high resistance of the zeolite, ZSM-5 was preferred in the process (Table 1).

Si/Al makes a great difference to the morphology and aluminum distribution of molecular sieves. By increasing the Si/Al ratio in HZSM-5 zeolite, the selectivity of zeolite for propylene can be improved [32]. In the ZSM-5 catalyst, when the channel intersection is rich in Al pairs, the selectivity for ethylene and aromatics is higher. While the channel intersection has multiple single Al sites and lower Al pairs, it exhibits higher propylene selectivity and lower aromatic hydrocarbon selectivity [33].

Ion doping can also scale up the selectivity of zeolites towards specific products. When boron was introduced into the ZSM-5 structure through impregnation and hydrothermal synthesis, the orthogonal crystal structure of the zeolite was characterized, which retained the preferred growth orientation and high crystallinity hierarchical structure and changed the surface acidity. The selectivity of propylene was increased to 67%, and the propylene/ethylene ratio reached 8 [34]. When Mn enters the framework structure of ZSM-5, weak Brønsted acid sites increase the Al in the channel of the framework. Consequently, the carbon deposition rate was lowered, and the selectivity for propylene was improved [35].

Preventing catalyst deactivation and coke deposition from clogging pores and improving the lifespan of catalysts are still facing great challenges. Usually, modification of structural properties and catalyst acidity can efficiently solve these problems. To reduce acidity and consequently inhibit the aromatic hydrocarbon cycle, fluoride-assisted low-temperature crystallization can be applied to prepare plate-like MFI molecular sieves with similar crystal morphology and controllable acidity, which made propylene selectivity reach 52%, and catalyst lifespan 252 h [36]. In the initial process of MTP, long chain alkenes not being cracked diffused out from MFI zeolite and were found in the products (as shown in Figure 3, blue frame). Simultaneously, the long-chain alkenes propagated from olefins or alkenes were converted to polymethyl-benzenes and dienylic carbenium ions. Subsequently, lower olefins were produced in the aromatic cycle (as shown in Figure 3, red frame). Moreover, lower-density plate-like MFI can effectively inhibit the circulation of aromatic hydrocarbon groups, promote the hydrocarbon cycle, and exhibit excellent stability [37].

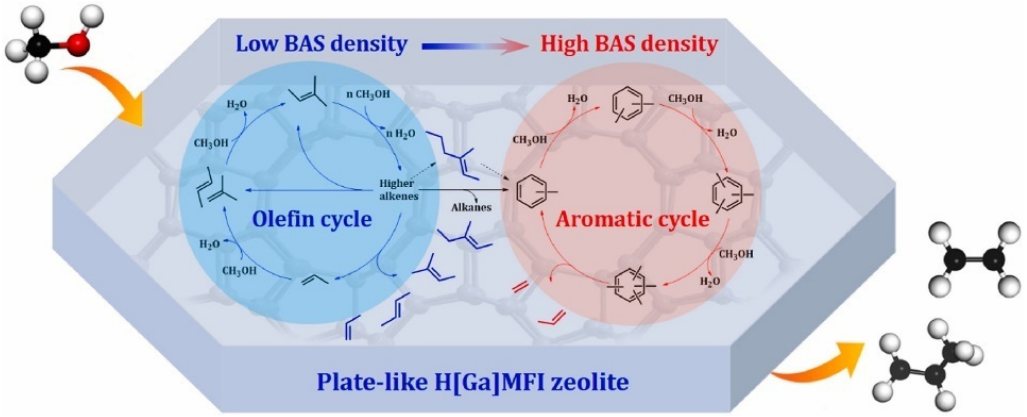

Figure 3. Dual-cycle mechanism in the MTP conversion over the plate-like H[Ga]MFI catalysts [36].

Table 1. Effects of Si/Al and specific surface area on the selectivity of propylene in MTP.

Catalysts	Method	Si/Al	S_{BET}	Selectivity of Propylene	P/E	
HZSM-5	two-stage crystallization	130	361	50.95	4.40	[32]
		130	356	48.13	4.44	
		124	352	49.68	5.89	
		139	340	50.10	7.48	
MFI	template	202	428	58	7.9	[34]
B-MFI		205	404	66.3	7.9	
Cr-MFI		201	408	59.8	2.7	
[Al/Ga]MFI	fluoride-assisted low-temperature crystallization	70–73	415–423	52%	-	[36]
		65–275 *	411–441			
ZSM-5	quasi-solid-phase	50	353	41.4%	-	[35]

* Si/Ga determined by ICP.

2.3.2. Propane to Propylene (PDH)

The dehydrogenation of propane (PDH) was a conventional way to produce propylene. Driven by the huge demand for propylene, Pt- or Cr- containing catalysts have drawn great attention and been applied to industrial manufacture. Although ZSM-5 is frequently used for PDH reactions due to its unique pore structure and good thermal stability, the high acidity of ZSM-5 can lead to a decrease in propylene selectivity. Through catalyst dealumination and additive regulation, the surface acidity of ZSM-5 can be reduced, and its propylene selectivity and catalytic stability in PDH can be improved. Some scholars have adopted the sequential impregnation method to introduce Ga and Mg to improve the Si/Al in HZSM-5, which can produce an effect on its stability and propylene selectivity (90.8%) [38].

Additionally, the separation of propylene and propane is another indispensable process in PDH, and it can be promoted by enhancing the propylene affinity of the adsorption site. What provided new ideas for the effective separation of propylene and propane is that scholars have prepared Ag exchanged Y zeolite (Ag-Y); this modified zeolite exhibited rapid adsorption kinetics and reversible propylene adsorption [39]. The results of molecular dynamics simulation research indicated that raising the temperature was beneficial for an increase in propane adsorption capacity, as the critical temperature of propane is higher than that of propylene. The smaller radius of non-skeletal cations in zeolite contributed to the higher efficiency of propylene adsorption [40]. After dealumination, vacant T-atom sites appeared in Si-BEA and silanol group forms. The introduced Co^{2+} can interact with silanol groups and form four coordinated structures in the zeolite (as shown in Figure 4), which consequently selectively activates the C–H bonds in propane, thereby improving the desorption efficiency after propylene generation and improving the long-term stability of the catalyst [41].

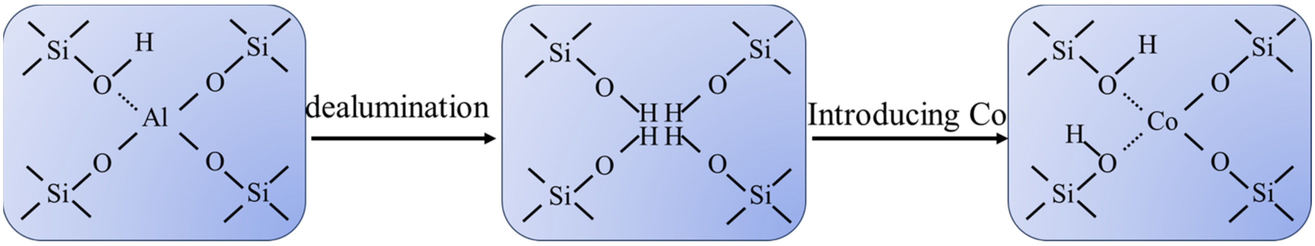

Figure 4. Local structure evolution of BEA zeolite during dealumination and Co^{2+} introduction (reproduced from reference [41]).

2.4. Selective Catalytic Reduction (SCR) of NO_x

Nitrogen oxides (NO_x) were one of the most destructive polluting gases that were mainly produced in the combustion of fossil fuels, such as car exhaust and coal combustion. In China, more than 90% of NO_x comes from vehicle exhaust emissions. Selective catalytic technology (SCR) is one efficient method to solve the problem of nitrogen oxide emissions. The catalytic reduction reactions between NO_x and NH_3 were conducted on the surface of the catalyst, and NO_x was therefore transformed into N_2. Currently, the adopted catalysts are mainly divided into metal matrix catalysts and zeolite-based catalysts. V_2O_5-WO_3/TiO_2 was once supposed to be the most effective catalyst for NO_x treatment. However, the biological toxicity, poor thermostability, and narrow working temperature range extremely restrained its application. In the 1980s, a ZSM-5 catalyst load with Cu^{2+} was discovered and exhibited excellent activity to NO_x and anti-toxicity.

Adsorption is the key process in catalytic oxidation and reduction. Zeolite catalysts exhibit good adsorption performance on NO_x owing to the large specific surface area, good thermal stability, adjustable acidity, excellent absorption, and ion exchange capabilities [42,43]. The overall efficiency of NO_x reduction can be greatly improved by metal doping and modification of zeolite catalysts. Cu-doped and Fe-doped zeolite catalysts have received more attention, such as Cu/ZSM-5, Cu/BEA, Cu/SAPO-34, and Cu/SSZ-13, which have been reported for the NH_3-SCR reaction of NO_x. The Cu-based catalyst exhibits excellent anti-propylene poisoning ability in the NH_3-SCR reaction. Researchers have found that moderately copper-doped zeolite, such as the $Cu_{7.55}$-ZK-5 catalyst, can isolate a large amount of Cu^{2+}, which is beneficial for the adsorption and activation of NO_x [44].

Based on Cu/MOR, the addition of promoting the separation of Cu^{2+} can create more Brønsted acid sites and inhibit the high-temperature ammonia oxygen reactions. This catalyst exhibited a NO_x conversion of about 88% and N_2 selectivity above 99% at 350–560 °C [45].

Hydrothermal stability is another factor influencing the application of zeolite catalysts. Yttrium-doped Cu-based zeolite catalysts can significantly reduce the fracture of Si-O-Al, improve the dispersion of Cu^{2+} active components and promote the adsorption and conversion efficiency of NO_x [46].

NO_x can be adsorbed with five reactions on Cu-ZSM-5 zeolites (as shown in Figure 5). The adsorption can be enhanced by the coordination interaction between Cu and N. Cu can be precisely dopped into H-ZSM-5 using an improved method called initial wetting impregnation microwave drying (IM). Compared with H-ZSM-5 and Na-ZSM-5, the desorption energy was reduced and the NO_x adsorption was significantly increased [47]. By designing novel pore structures, such as three dimensionally-ordered (3DOM) microporous zeolites, the contact area can be obviously extended. Some scholars have developed the steam seed-assisted colloid crystal template (SSAC) method to prepare 3DOM zeolites. After sonication, drying, and calcination, the $Pr_xMn_{1-x}O_\delta$/3DOM ZSM-5 catalyst with different Pr/Mn ratios was obtained (as shown in Figure 6) and showed an NO conversion rate of 90% [48].

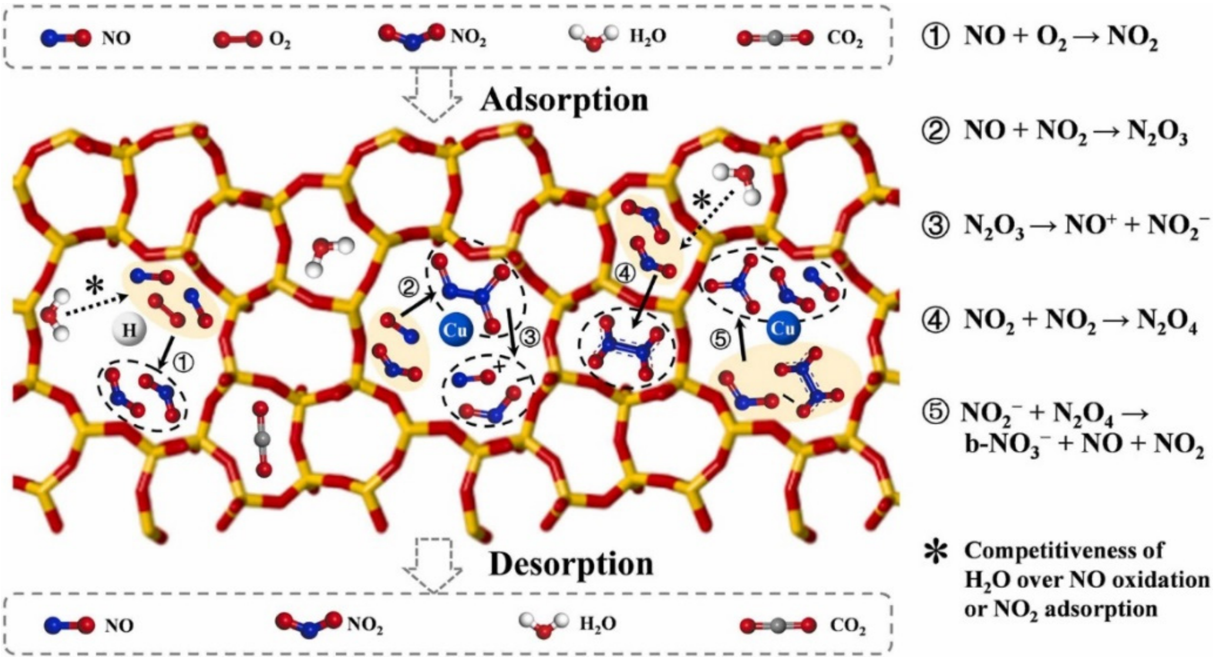

Figure 5. Proposed schematic diagram of NO_x adsorption process on Cu-HZSM5_IM [47].

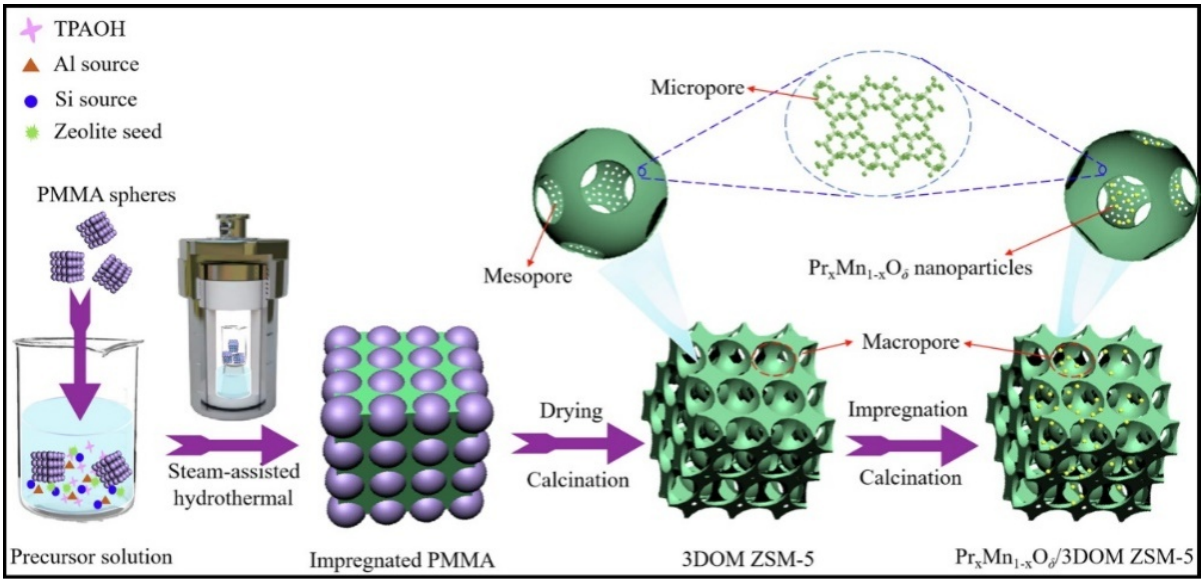

Figure 6. Schematic diagram for the preparation of $Pr_xMn_{1-x}O_d$/3DOM ZSM-5 catalysts [48].

Except for these zeolite catalysts, scholars tried to combine metal-based catalysts (V_2O_5-WO_3/TiO_2) with zeolite catalysts (H-ZSM-5) to prepare the composite catalyst PM. The PM catalyst exhibited higher catalytic activity than the V_2O_5 WO_3/TiO_2 catalyst because the PM catalyst adsorbed more NO_2 and N_2O_4 [49]. Given the complexity of the exhaust purification system in SCR, some researchers adopted an H_2 selective catalytic reduction method using Pt/KFI molecular sieve catalysts from 150 °C to 250 °C, and the conversion rate of NO_x reached 80% [50].

2.5. Hydrogen Preparation

Hydrogen energy has been viewed as a potential alternative energy in the future. However, producing hydrogen economically and environmentally is extremely challenging. Hydrogen can be prepared from natural gas (reforming of methane steam to produce hydrogen, SMR), coal gasification, electrolysis of water, and transformation of biomass. Various hydrogen production processes depend on catalysts. Due to the wide and renewable sources, the utilization of organic matter to produce hydrogen energy is gradually receiving attention. Relevant technical methods mainly include two methods. One is thermochemistry hydrogen production, which consists of high-temperature pyrolysis, liquefaction, and gasification, and the other is biomass hydrogen production which refers to the preparation of hydrogen from biomass after anaerobic fermentation, biological metabolism, and reforming. The catalysts used in hydrogen are mainly precious metals and transition metals, such as Rh, Ru, Pd, Pt, Cu, Co, Ni, etc. Molecular sieves are often used as carriers for these catalysts.

At present, ethanol steam reforming (ESR) is the most suitable industrial method for ethanol to produce hydrogen, but there are some vital problems with this technology: (1) high energy consumption; (2) expensive separation of CO_2 and H_2. Choosing appropriate catalyst carriers and catalysts can help improve catalytic activity and reduce costs. Furthermore, the Ni catalyst was relatively inexpensive and had good hydrogen generation activity. Zeolites have a large content of micropores, and the structure can be modified. However, carbon deposition during the catalytic process of Ni-loaded zeolite can easily lead to decreasing catalytic activity. A new type of quaternary ammonium cation cationic surfactant was introduced to synthesize the supported calcium-modified nickel-step classification β zeolite catalysts. The BET and pore volume of this modified zeolite were larger than that without modification. The introduction of Ca^{2+} changed the internal structure of the catalyst to some extent, which promoted the interaction between the carrier and Ni. Consequently, the yield of H_2 was increased [51,52]. When Mg was introduced into Rh/β zeolite, Rh clusters from the atomic level to the sub-nanometer scale were formed in microporous channels. It was found that the C=O formed in the reaction was the key to increasing selectivity, which can be promoted by Mg addition [53]. The DFT calculation results indicated that the stability was obviously affected by the zeolite structure. Specifically, after dealumination, the binding energy of Rh to the vacancy defect was reduced by 0.2 eV. If the Mg was added to the zeolite structure, the binding energy was additionally reduced to -1.927 eV (as shown in Figure 7a). Due to the proximity of Rh and Mg in zeolite with Mg, the energy barrier of O-H was significantly reduced, which was beneficial to the dissociation of phenol to phenoxy (as shown in Figure 7b). ITQ-6 zeolite loaded with Ni and Co can also be used in ESR. Among them, the ITQ–6 zeolite loaded with Co exhibited higher hydrogen production on account of the smaller size of Co particles. Moreover, the carbon deposition effect of Co/ITQ-6 was weaker, and the deactivation was lower [54].

In order to reduce catalyst deactivation, some scholars have tried to design catalysts with small metal nanoparticles. An encapsulated ultra-small Ni catalyst with mesoporous and hollow structure was prepared using separated metal dispersions Si-1 zeolite with high Ni dispersion (Ni@Si-1), which facilitated local mass transfer and reduced carbon deposition [55]. The research on supercritical water dynamics indicated that the gasification of catalysts such as Ni can be promoted by improving hydrogen selectivity. The pore distribution of Ni particles can be divided into micropores (1–10 nm) and mesopores (20–60 nm). When the size of the mesopores was distributed reasonably in zeolite, the active sites increased, and the catalytic activity was higher [56].

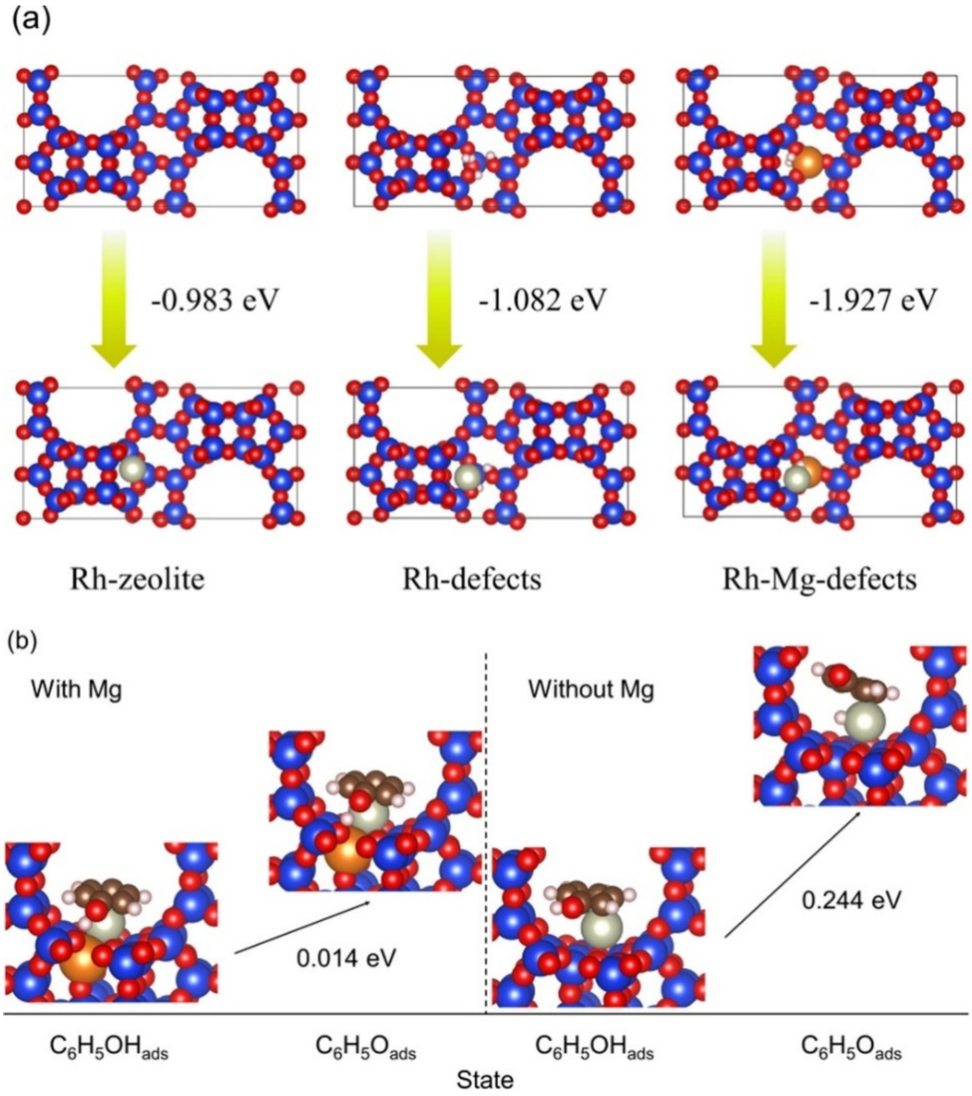

Figure 7. (**a**) Structural configurations of Rh located on three different supports and corresponding binding energies and (**b**) relative energy levels for O–H bond dissociation of phenol in zeolite Beta with and without Mg [53].

In addition to ethanol, methanol can also be used as the raw material for hydrogen production, that is, methanol steam reforming (MSR). A catalyst suitable for the catalytic reaction of MSR was prepared using an attapulgite molecular sieve as a carrier and Cu-Zr active components. The addition of Zr significantly increased the distribution of active metal particles and reaction sites, as well as the H_2 yield. At the same time, the sintering of active metals and coke were inhibited [57].

Photocatalysis is another important method for producing hydrogen gas, and zeolite loaded with TiO_2 photocatalyst was supposed to be one of the potentially efficient catalysts [58,59]. To improve the transmission efficiency of photoelectrons, some scholars have designed $Cu_2O@TiO_2@ZIF$-8, where an internal electric field was formed due to the p-n junction, which promoted the transfer of electrons to the conduction band. The photoelectrons generated from TiO_2 were transferred to the conduction band and further transferred through ZIF-8. The water can be therefore reduced by these photoelectrons (as shown in Figure 8) [52]. To provide more proton sources and active sites, $Na^+/K^+/Ca^{2+}$ can be added into zeolite, which consequently promotes the hydrogen evolution rate [60].

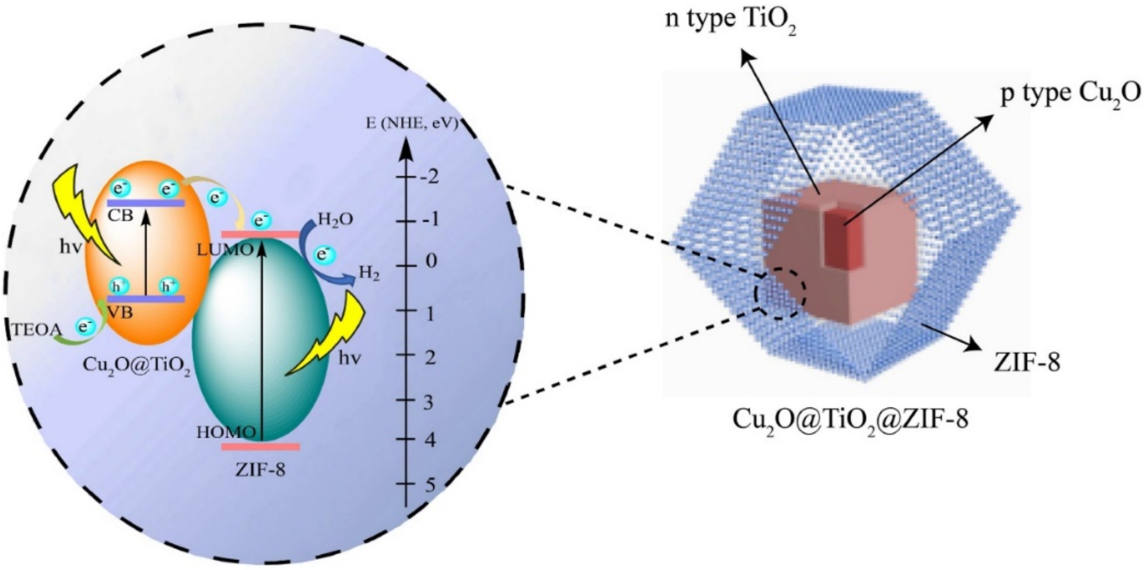

Figure 8. Proposed mechanism in the $Cu_2O@TiO_2@ZIF$-8 photocatalyst [58].

2.6. VOCs Abatement

Volatile organic compounds (VOCs) refer to organic compounds with a boiling temperature in the range of 50–260 °C. They were usually emitted in the petrochemical industry and the rubber industry and had serious effects on human health and the natural environment. With the rapid development of industry and increasing consumption of fossil fuel energy in vehicles, the emission of VOCs has dramatically increased in recent years. According to their boiling points, molecular structures, and molecular polarities, VOCs can be classified into different types [61]. They were hard to eliminate using direct combustion due to the low concentration of VOCs. To reduce the pollution and damage of VOCs, multiple technologies have been developed and applied, such as adsorption, a photocatalytic degradation method, plasma degradation, catalytic combustion, etc. Whether adopting an adsorption method or catalytic oxidation method, it is no wonder that developing efficient adsorbent and porous materials are principal considerations. An excellent adsorbent should have massive adsorption sites, good hydrothermal stability, and weak resistance to molecular diffusion. Worldwide, research studies show that activated carbons [62], metal-organic frameworks, and zeolites are all potential adsorption materials that have exhibited excellent adsorption performance in many experiments. However, the combustion of activated carbons and the high cost of metal-organic frameworks restrained their application in VOC treatment.

The zeolite of the 255 framework type, approved by the International Zeolite Association (IZA), was considered a promising absorbent due to its abundant micropores, adjustive chemical stability, etc. The adsorption efficiency of different zeolite structures on different VOCs molecules and the competitive adsorption mechanism of various VOCs have been a puzzle to reveal. The absorption of VOCs can be influenced by the specific surface area, pore structure, and surface functional groups. Additionally, the kinetic diameter and polarity of the VOC molecule may also affect the absorption process.

The absorption efficiency was also proved to be related to humidity. Therefore, developing novel zeolites and improving the hydrophobicity of zeolites contributed to the adsorption efficiency of zeolites under humid conditions. The hydrophobicity of zeolites can be improved through ion doping and coating. A Mo-doped MEL zeolite was developed using a self-developed recrystallization method for the adsorption and reduction of non-methane hydrocarbons (NMHC) in cooking oil fumes. The affinity for VOC molecules is significantly enhanced due to its high atomic coordination level and lack of silanol, especially under humid conditions. This Mo MEL zeolite exhibited longer adsorption saturation time, larger adsorption capacity, and better hydrophobicity, which led to the more excellent adsorption efficiency of Mo MEL than that of Si MEL and Al MEL [63]. In addition to Mo, introducing Mn (Cu or Fe) to replace Al can also improve the hydrophobicity of zeolites [64]. The addition of Mn affected the crystallization behavior of zeolites, which in turn, changed the distribution of Mn in zeolites and the properties of zeolites. Y-type zeolite, with a high specific surface area and unique microporous structure, can have its hydrophobicity and diffusion efficiency improved by being coated with mesoporous SiO_2 [65]. In general, after being coated with mesoporous hydrophobic materials, the diffusion activation energy of VOCs was decreased, and the diffusion coefficient was increased. The π-n electron pair interaction was weakened, while the dipole interaction was enhanced. The dispersion interaction plays a positive role in the adsorption of VOCs and gradually enhances with increasing relative humidity. However, the repeatability of core-shell composite materials needs to be verified. The evaporation-induced self-assembly (EISA) method was adopted to prepare NaY zeolite loaded with metal oxide nanoparticles. It strongly improved the adsorption capacity of VOCs. Li SHI et al. successfully prepared uniformly dispersed $Y@M_xO_y$ nanoparticles, which significantly improved the adsorption effect of Y-zeolite on isopropanol and acetone in humid environments under RH = 50%. The metal oxides enhanced the adsorption capacity of VOCs, and greatly reduced the competitive adsorption between water molecules and VOCs molecules [66]. Multilevel mesoporous USY molecular sieves can be prepared using etching and surfactant template processes, during which the non-skeletal aluminum was effectively removed inside the zeolite, leading to a mesoporous size of approximately 4 nm [67]. Some scholars have also proposed a new strategy called citric acid sacrifice that can synthesize non adhesive monolithic zeolites. The mechanical strength and the water resistance were obviously improved. After the in situ dealuminization, the specific surface area and mesoporous volume were greatly improved, the adsorption capacities of toluene and acetone were also increased. When the relative humidity was 90%, the adsorption efficiency of acetone and toluene reached 90% of that attained in dry conditions [68].

Adjusting the pore structure of molecular sieves is also vital for improving the adsorption and reaction rates of VOCs. The hierarchical design and synthesis of zeolite structures are gradually receiving attention [69,70]. For example, the microporous size of ZSM-5 zeolite is generally less than 2 nm, and larger VOC molecules have a slower diffusion rate during the adsorption process, making it difficult to quickly enter the reaction active center and the generation rate of specific products is pretty low. When ZSM-5 is modified with organic functionalized silica and organic additives, the size and surface morphology of ZSM-5 nanocrystals can be greatly improved, forming a hierarchical mesoporous structure, and the adsorption capacity for toluene is greatly increased [71]. According to the hierarchical crystallization mechanism revealed in the corresponding research (as shown in Figure 9), organic silica fragments modified by organosilane PHAPTMS were combined and then gathered around MFI. After hydrolysis of $-SiO_3$, PHAPTMS participated in the formation of nanocrystalline frameworks in a hydrothermal process. The inter-crystalline and intra-crystalline mesopores were finally formed after calcination.

The adsorption and catalytic efficiency of zeolite can be effectively improved by regulating the active sites. Effective regulation of active sites can reduce carbon deposition in pore structures and improve the durability of catalysts. Nano Pt is usually adopted as an active ingredient, and its high dispersibility facilitates the catalytic oxidation of aromatic hydrocarbons and alkanes. Synergistically, it can interact with surface acid sites that contribute to the removal of VOCs at low temperatures [72]. Generally, adjusting the Si/Al ratio in zeolites can help regulate the acidic sites. A controllable framework modulation strategy can be adopted to prepare high-silica zeolites. In this strategy, it was very important to control the matching degree of dealumination and Si-insertion. For Pt/β zeolite, Pt^0 has a stronger activation ability for O_2 and shows higher efficiency than $Pt^{\delta+}$. That makes it much easier to supply oxygen, which is more conducive to the ring opening reaction of the benzene ring, thus reducing the production of gaseous benzene on the high silicon catalyst. Furthermore, both high-silicon and low-silicon Pt/Beta catalysts show excellent durability and follow a similar toluene oxidation path to form intermediates, including alcohol oxide, carboxylate, and anhydride [73]. For Pt/ZSM-5, the main active oxidation site is Pt^0. For the deep catalytic oxidation of oxygen/nitrogen-containing VOCs, Pt/ZSM-5 had abundant acidic sites on its surface. Different SiO_2/Al_2O_3, Pt^0 ratio, and Pt dispersion equilibrium in the catalyst may be changed, and the synergistic effect of acidic sites and oxidation sites were promoted, which led to higher reaction activity of Pt/ZSM-5 (25), with a T90% value of only 207 °C for acetonitrile and 175 °C for ethyl acetate. It is beneficial for low-temperature catalytic degradation of specific VOCs [74].

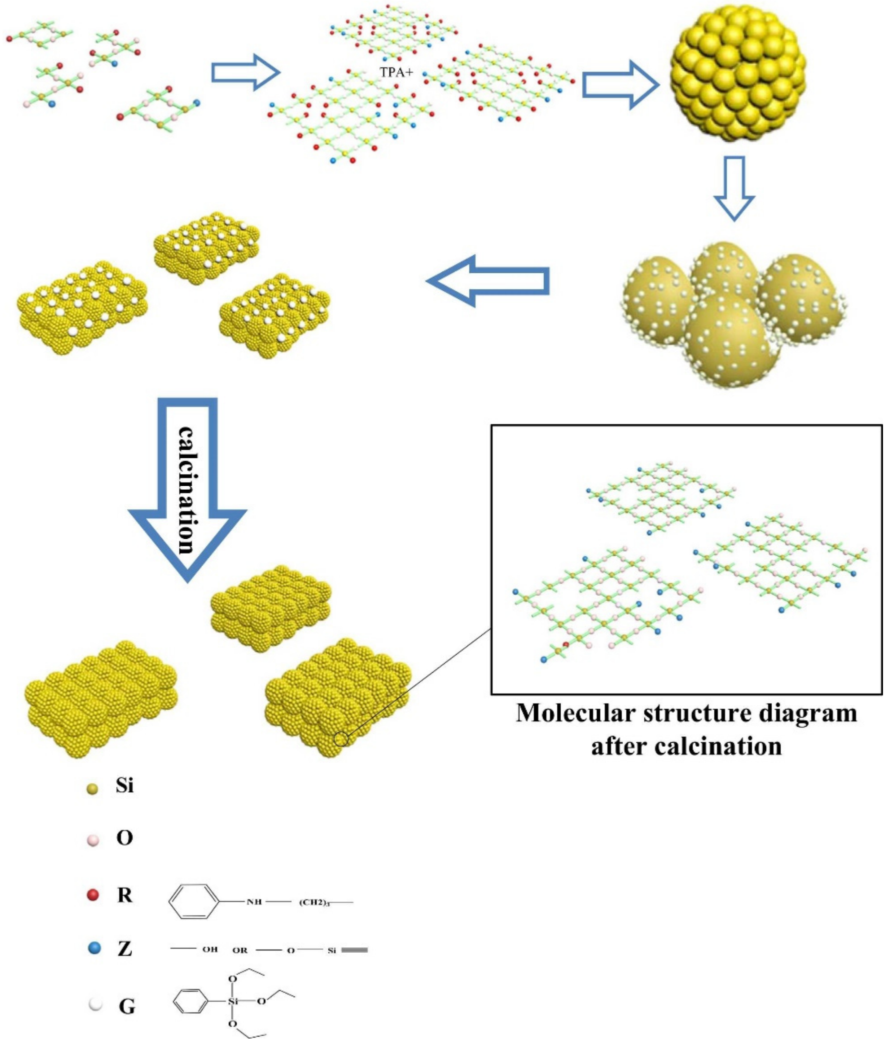

Figure 9. The crystallization mechanism diagram for the ZSM-5 zeolites [71].

In industrial activities, multiple types of VOCs are often generated simultaneously. Ideally, a single adsorbent and catalyst can simultaneously handle multiple VOCs. However, due to the various molecular structure of VOCs, the different pore structures, and the complexity of the catalyst's electronic structure, ensuring the treatment effect of VOCs is difficult. Therefore, it is particularly important to explore and understand the adsorption and oxidation mechanism of catalysts, which contributes to the development of novel catalysts and adsorbents aimed at VOC mixtures. The molecular polarity and volatility of VOCs play a crucial role in the adsorption process. For these VOC mixtures, the priority order of adsorption varies. For example, under static equilibrium conditions, the absorption order was determined as acetone > ethyl acetate > toluene. However, under dynamical conditions, molecular polarity and volatility played key roles. The absorption order was found to be ethyl acetate > toluene > acetone [75]. Complex interference effects were identified when this VOC mixture was adsorbed onto different zeolites. The adsorption effect of toluene on USY is significantly better than that on 13X. However, for acetone, the adsorption of 13X and ZSM-5 is better. ZSM-5 and β Zeolites can selectively adsorb ethyl acetate, as evidenced by DFT calculations. This competitive adsorption widely exists in the treatment of various VOCs, and the differential adsorption effect is one of the problems to be solved in the future [75]. To develop efficient catalysts, some scholars have attempted to explore the possibility of synergistic treatment of acetone and benzene by changing the amount of Mn added [76]. When Mn was introduced, the activity of the catalyst for acetone was significantly increased, while the activity for benzene was decreased. Because the introduction of Mn regulated the electronic structure of Pt, leading to the transfer of electrons to Pt, which enhanced the adsorption of acetone and gaseous oxygen and improved the performance of the acetone oxidation catalyst, and promoted the degradation of acetone. However, the high electron density of Pt inhibited the adsorption and degradation of benzene, reducing the production of formic acid products.

In addition, the treatment of VOCs in open spaces has gradually attracted the attention of researchers. For example, asphalt materials are often used in the process of road paving and continually release VOCs into the open air. Due to the limitations of open spaces, it is very difficult to collect and dispose of these VOCs. Steel slag and red mud were usually used as road materials, zeolites synthesized from these materials can reduce the volatility of asphalt and absorb VOCs in road structures [77]. Therefore, preparing efficient zeolites using in-road materials (such as steel slag) was the key approach to deal with VOC emissions in open spaces.

2.7. CO_2 Capture

CO_2 has been regarded as the main greenhouse gas resulting in global warming, which is one of the most challenging environmental issues. To prevent the damage caused by global warming, various technologies are being developed [78]. Among them, one technology called carbon capture, utilization, and storage (CCUS) has received great attention. In the CCUS system, CO_2 capture is the key stage that matures this technology. According to the manufacturing methods of CO_2, pre-combustion capture, post-combustion capture, and oxyfuel combustion were the main approaches. Regardless of different approaches, the CO_2 separation process was the critical part of CO_2 capture, such as absorption, membranes, adsorption, chemical looping combustion, and calcium looping, and adsorption has been considered one of the most promising ways to capture CO_2.

Compared with other CO_2 adsorbents, zeolite exhibited a stable cycle, huge surface area, and fast kinetics of CO_2 adsorption. X-type zeolite, Y-type zeolite, and A-type zeolite were usually studied as CO_2 capture adsorbents. Therefore, zeolite has received increasing attention in CO_2 capture over the past decades. It has been found that there are several factors influencing the capture efficiency of CO_2, such as Si/Al, distribution of pore sizes, exchangeable ions, and moisture effects.

As a kind of aluminosilicate, Al ions can replace Si ions in the TO_4 structure, which breaks the charge balance of the original structure and leads to increasing basicity. It was reported that higher basicity contributes to higher CO_2 adsorption [78]. Zeolites with a lower Si/Al ratio were more stable at high temperatures and less likely to exchange with other ions. To achieve higher CO_2 capacity, the chemical composition of zeolites can be optimized. Scholars found that the Si/Al of GIS-type zeolite strongly affected the mechanism of CO_2 adsorption. Specifically, for Na-GIS with Si/Al lower than 2.2, the CO_2 adsorption was hindered, and CO_2 uptake was negligible due to the large number of extra-framework cations near the 8-ring window [79].

The pore size of different zeolites was usually distributed in the range from 0.5 nm to 1.2 nm due to their crystalline nature. It means that only when the kinetic diameter of gas molecules is smaller than the pore size the gas can be adsorbed. To strengthen the adsorption efficiency of CO_2, it is very promising to synthesize zeolites with mesopores. Due to the hierarchical structure, the obstruction of molecular diffusion is obviously reduced, which can consequently promote CO_2 adsorption. Chen et al. prepared mesoporous LTA zeolite (Meso-LTA); it exhibited faster CO_2 adsorption kinetics (1 bar) and higher CO_2 adsorption capacities (>10 bar) at 298 K compared with microporous LTA zeolite [80].

CO_2 adsorption is essentially the interaction between CO_2 molecules and the electric field caused by ions in zeolites, which is similar to CO_2 desorption. Therefore, the CO_2 capture efficiency can be promoted by adjusting the chemical composition of zeolite, for instance, ion exchange. For instance, the simulation and experimental results of ion-exchanged 13X zeolite (FAU type) indicated that, compared with Na^+ and K^+, LiX-80 exhibited better separation of CO_2/N_2. Furthermore, the doping of Pd^{2+} and Ag^+ changed the gradient of potential and strengthened the electrostatic potential (ESP), which increased the CO_2 adsorption capacity (1.89%) and the CO_2/N_2 selectivity (85.97%) compared with LiX-80 [81].

Apart from the above factors, in flue gas, vapor is always accompanied by CO_2. The water molecules may compete with CO_2 molecules for the active sites in zeolites, which dramatically reduces the efficiency of CO_2 adsorption. Some scholars proposed a strategy that fabricating a shell around the zeolite using sol-gel coating and a poly-ethylenimine impregnation process, and the diffusion of water molecules was hindered [82].

As a kind of promising CO_2 solid adsorbent, zeolite has drawn great attention for the past decades and exhibited excellent performance. However, its application still faces a lot of challenges due to its structure characteristics and chemical composition. The modification of zeolite used for CO_2 capture will still be a research focus in the future.

3. Conclusions and Future Perspectives

Zeolite catalyst is featured in energy conversion, selective separation, pollution prevention, and treatment. Generally, it exhibited better adsorption when the pore size of zeolite was equivalent to that of the adsorbed molecule. Therefore, it was very important to select the appropriate zeolite for different catalytic reactions. Since a state of long-term hydrothermal treatment at high temperatures is a necessary condition for its synthesis, numerous problems such as long synthesis time, high energy consumption, high equipment cost, and safety issues caused by the use of high-pressure hot-pressing tanks continuously emerged. There is no doubt that shortening synthesis time and lowering synthesis temperature are desperately needed. Reducing synthesis costs (energy consumption, autoclave productivity, etc.) and environmental footprint and safety issues has always been the primary issue.

Despite the special structure and excellent properties, the promotion of the application of zeolite catalysts also faces great challenges, such as the selectivity of specific products, temperature adaptability, and the lifetime of catalysts. It was also noticed that the retention of the reaction medium leads to the generation of by-products, resulting in micropore blockage and reduced catalytic activity. However, it can be noticed that upgrading the preparation method, regulating the pore structure, and increasing acid sites are three awesome measures to improve the properties of zeolite catalysts. Zeolites are expected to show their great advantage in energy-saving catalytic processes, environmentally friendly adsorption and separation, and energy storage.

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