

Functional Catalyst Molecular Sieves in Green Chemical Applications

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Abstract: *With the development of green chemical industry and the continuous improvement of environmental awareness, the application of various catalysts in environmental protection has been widely concerned. As a green catalyst, molecular sieve catalyst has superior environmental performance, which is mainly reflected in its ability to improve the selectivity of reaction products, can be reused, good thermal stability and strong adaptability. This paper mainly introduces the types, development history, synthesis technology and application of zeolite catalysts, due to the development of science and technology, a large number of new synthetic zeolite catalysts are used in the field of catalysis and meet the requirements of green chemistry, and its synthesis technology is gradually trending towards environmental protection with the development of green chemistry. Zeolite catalysts are widely used in chemical industry and other fields, and their green environmental protection performance promotes the development of chemical processes in the direction of green chemicals.*

Keywords: Molecular sieve; Green catalyst; Green chemical industry.

1. Introduction

In the context of sustainable development strategy in the new era, a series of environmental problems caused by economic growth urgently need to be solved. Therefore, green chemical technology has emerged in the chemical industry. The key to green chemical industry is to eliminate the pollution of a process from the source, while emphasizing green products, Committed to developing economically viable industrial processes that reduce risks to human health and the environment. In general, the goal of green chemicals is to achieve the best overall performance, including economic, technical and environmental impacts[1]. According to this goal, the development of new efficient, non-toxic and harmless catalysts has become one of the directions of green chemical processes. Green chemical industry requires that the catalyst itself should be non-toxic, especially to prevent the catalyst from decomposing at high temperature to produce toxic gases, and the subsequent separation process of the catalytic reaction should also be environmentally friendly operation. At the same time, to achieve the principle of economy, it is necessary to ensure that the catalyst has the characteristics of low cost, stable chemical properties, and good activity. With the promotion of green chemical industry, traditional acid-base homogeneous catalysts are being replaced by solid catalysts. Among these heterogeneous catalysts, zeolite and zeolite are benign from an environmental point of view and can be considered true "green" catalysts[2].

The presence of a natural aluminosilicate in nature, which is a catalytic zeolite, has stimulated an increasing interest in the use of zeolite and zeolite materials in the chemical industry, especially in catalysis and gas separation[3]. Synthetic zeolite is also known as molecular sieve. The most basic skeleton structure of molecular sieve is SiO_4 and AlO_4 tetrahedron, through the combination of common oxygen atoms to form a three-dimensional network crystal structure, zeolite molecular sieve this unique regular crystal structure, with a certain size,

shape of pore structure, and has a large specific surface area. Most zeolite molecular sieve surface has a strong acid center, and there is a very large coulomb field in the crystal pores to play a polarization role, it is these characteristics of zeolite molecular sieve that become an excellent catalyst. In general, the catalytic function of zeolite catalysts is not only related to the active components, but also to the structure and texture of the support. Molecular sieves with different pore structures have their own advantages and disadvantages[4]. Zeolite catalyst is a material that catalyzes the reaction by breaking down macromolecular substances into small molecules. It is also a composite material, Constructed of tiny solid particles, each with a specific structure, shape and surface properties. These particles can move around the solution and break down macromolecules into small molecules, facilitating catalytic reactions. In addition, it can also be used to improve solubility and flowability, improving reaction conditions and performance. The molecular sieve support of different crystal forms has the selectivity of different active components and co-catalysts, and can be further processed and produced into catalysts for different purposes according to the characteristics of different molecular sieves; molecular sieves of the same crystal form can also be modified differently and are suitable for different catalytic reaction processes. As a solid catalyst, molecular sieve catalyst is easy to recycle, non-toxic, tasteless and non-corrosive, and is a new environmentally friendly catalytic material.

Catalysts are important media affecting chemical reactions, and more than 90% of industrial processes involve the use of catalysts, including chemical, petrochemical, biochemical, environmental protection and other fields. There are many types of molecular sieve catalyst products, mainly used in environmental protection and chemical and other fields. According to the classification of pore size, molecular sieve catalysts can be divided into microporous molecular sieve, mesoporous molecular sieve and macroporous molecular sieve, among which microporous molecular sieve has strong acidity and high hydrothermal stability, but because the pore

size is very small, the diffusion resistance is large; Macromolecules formed in their cavities cannot escape quickly[5] and easy to coke[6]. Mesoporous molecular sieve has the characteristics of high specific surface area, large adsorption capacity and large pore size. But the acid strength of mesoporous molecular sieve is not enough, and poor hydrothermal stability, also limits its application range[7]. According to the classification of application fields, molecular sieve catalysts can be divided into environmentally friendly catalytic molecular sieve (automobile exhaust catalytic molecular sieve), petrochemical catalytic molecular sieve and coal chemical catalytic molecular sieve. Different kinds of molecular sieve have broad application space in chemical, environmental protection and other fields. For example, nanozeolite has a large external specific surface area and a high intragranular diffusion rate. It shows superior performance over macrograin zeolite in improving the utilization rate of catalyst, enhancing macromolecular conversion capacity, reducing depth reaction, improving selectivity and reducing coking[8][10]. CHA molecular sieve is widely used in the field of environmental protection and catalyzed in methanol to olefin[11], ammonia selective catalytic reduction of nitrogen oxides[12] and other fields show excellent properties. As a representative of green catalyst, molecular sieve catalyst has great application value and significance.

2. Development and Types of Zeolite Catalysts

2.1 Natural Molecular Sieve

Early people discovered natural molecular sieve, that is, zeolite, and naturally occurring and operational zeolite in nature are: clinoptilolite zeolite, mercerized zeolite, siderite and so on. The properties of natural zeolites depend strictly on their crystal structure, and the main disadvantage is that the channel diameter is too small (in the case of clinoptilolite most common in nature, its diameter is 0.3–0.4 nm[13]), which does not allow the adsorption of larger gas molecules and organic compounds.

2.2 Synthetic Zeolite

With the increase of its use and the limitation of industrial applications, people began to study the synthesis of various new zeolite catalysts, and with the deepening of research, the structure and properties of the synthesized zeolite have also undergone many changes. The early synthesis of molecular sieve has a simple structure, poor stability and hydrothermal stability of molecular sieve, low catalytic efficiency, and the application field is limited to the petroleum and chemical industries. With the advancement of synthesis technology and the diversification of synthesis methods in recent years, a large number of zeolite catalysts with complex structure, stable performance, wide application fields and high catalytic efficiency have been synthesized, and Si can be adjusted in the synthesis process. The high silica content obtained by the Al ratio of Si content has a greater active center capacity, which promotes their catalytic properties[14]. In addition, synthetic zeolite can adjust physical and chemical properties to serve many applications more closely, and their quality is more uniform than natural zeolite[15].

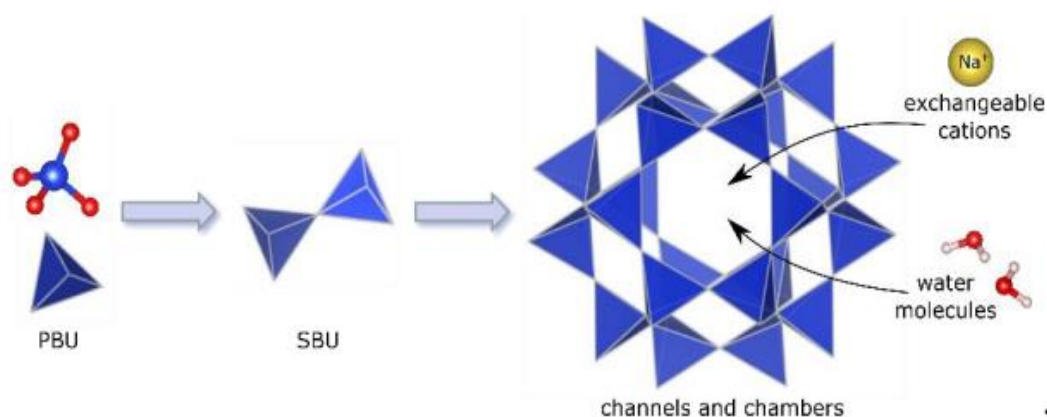


Figure 1: Scheme of zeolite structure. Reproduced with permission from ref[15].

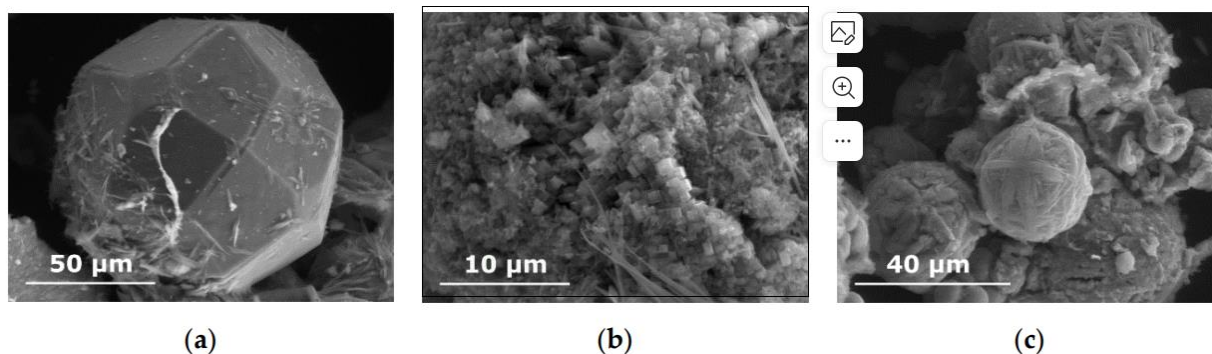


Figure 2: Microstructures of zeolites obtained in hydrothermal conditions at elevated pressure: (a) analcime; (b) zeolite Na-P1; (c) hydroxysodalite. Reproduced with permission from ref[15].

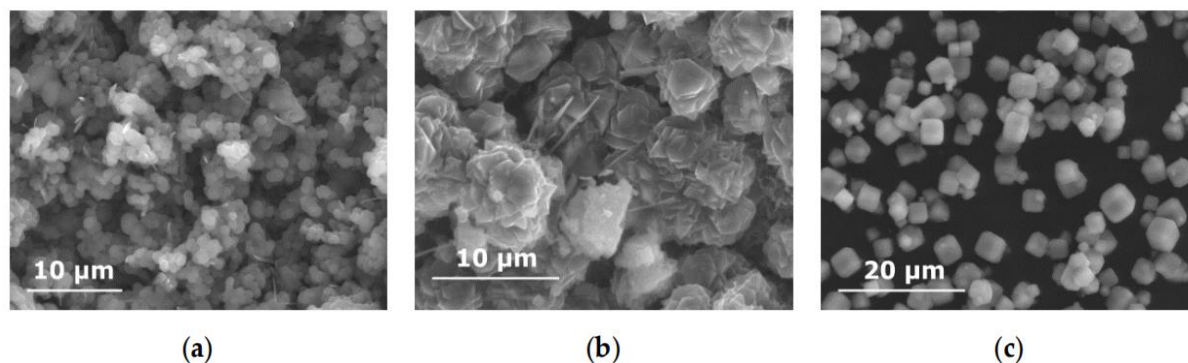


Figure 3: Microstructures of zeolites obtained in hydrothermal conditions at low temperatures ($<100^{\circ}\text{C}$): (a) zeolite X; (b) zeolite Na-P1; (c) zeolite. Reproduced with permission from ref[15].

2.3 Typical Zeolite Catalysts

According to the catalytic properties, zeolite catalysts can be divided into acid catalysts, bifunctional catalysts and selective catalysts. Acid catalyst, which uses the acidity of the surface of the molecular sieve for catalytic reactions. Bifunctional catalyst, molecular sieve can be loaded with platinum and palladium metals, and bifunctional zeolite catalyst with both metal catalytic function and acid catalytic function is obtained. Since the catalytic effect of molecular sieve generally occurs in the crystal space, the pore size and pore structure of molecular sieve have a great influence on the catalytic activity and selectivity. The molecular sieve has regular and uniform intracrystalline pores, and the pore size is close to the molecular size, so that the catalytic performance of the molecular sieve changes significantly with the change of the geometric size of reactant molecules, product molecules or reaction intermediates. The following describes several zeolite catalysts with wide applications and excellent catalytic performance and their applications.

2.3.1 ZSM-5 Zeolite Catalyst

Because it has many unique features in chemical composition (containing organic amine cations), microporous structure (longitudinal straight cylinder pores and transverse sinusoidal pores), it has shown excellent catalytic efficiency in many organic catalytic reactions, and has been more and more widely used in industry, becoming a promising new catalyst in petrochemical industry. ZSM-5 zeolite shows broad application prospects in the field of catalytic reaction of alkane aromatization due to its excellent selective catalytic effect and low carbon deposition content. The main specific applications are diesel hydrogen deoagulation catalyst, fixed-bed catalytic cracking catalyst, and flow-bed catalytic cracking reaction, FCC's catalyst adding ZSM-5 molecular sieve is of great benefit to increase the octane number of gasoline and increase the olefin content of gas. However, its unique microporous structure limits the diffusion and mass transfer of reactants, intermediates and products with large steric hindrance in the pores, so it is necessary to adjust the pores to optimize the pore structure of the zeolite sieve. In addition, the strong acidity and high acid density of ZSM-5

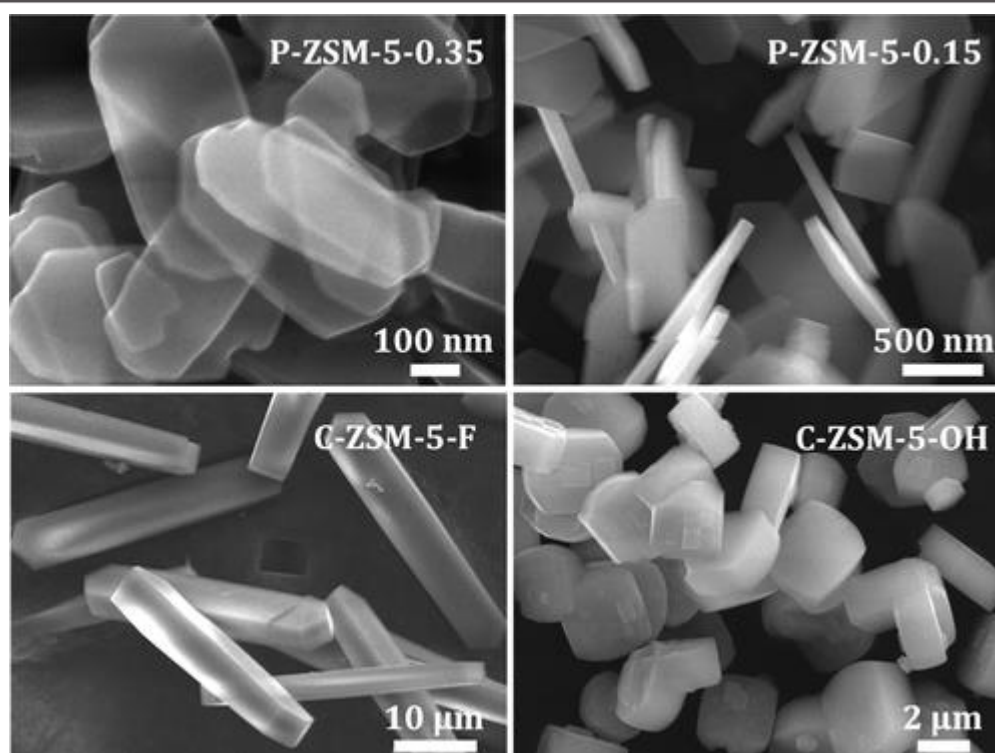
zeolite will make the corresponding catalyst have high initial activity and quickly inactivate due to the rapid formation of carbon deposits, which has an important impact on reactivity activity, product selectivity and catalyst life, so it is necessary to properly modify and adjust ZSM-5 zeolite to adapt to the specific reaction.

Long and others [16] used the initial impregnation method to modify H-ZSM-5 with different MgO contents using magnesium nitrate as a precursor. It is believed that after the introduction of magnesium ions into ZSM-5 zeolite zeolite can be used as cations to balance the negative charge of the skeleton, and improve the hydrothermal stability of the skeleton aluminum in the steam reforming reaction of dimethyl ether. Yarulina et al [17] prepared a Ca-modified ZSM-5 catalyst using ZSM5 (Zeolyst, CBV 8014) as a raw material, and Ca was incorporated into ZSM-5 after synthesis, resulting in the formation of $\text{CaO}^+\text{CaOH}^+$ species, which strongly weakened the acid strength of the parent zeolite. As a result, the rate of hydride transfer and oligomerization at these sites is greatly reduced, resulting in an inhibition of the aromatic cycle and an increase in total light olefin selectivity to around 90%. These results further demonstrate the importance of acid strength to product selectivity and zeolite lifetime in MTO chemistry, and improve the activity stability in MTP reactions. Blasco and others [18] prepared a P-modified ZSM-5 zeolite catalyst by impregnation, and studied the effects of P dosage and impregnating agent on the stability of the skeleton aluminum in ZSM-5, and the results showed that the hydrothermal stability of the phosphorus-modified ZSM-5 zeolite in the catalytic cracking reaction was significantly improved. Proper and accurate metal modification will improve the catalytic performance of the ZSM-5 catalyst. The results show that the hydrothermal stability of ZSM-5 zeolite modified by phosphorus is significantly improved in the catalytic cracking reaction, and it is believed that the introduced phosphorus species form a chemical bond with the skeleton aluminum, which reduces the density of B acid. At the same time, it improves the inertness of skeleton aluminum to water vapor and improves the hydrothermal stability of molecular sieve. Proper and accurate metal modification will improve ZCatalytic performance of SM-5 catalysts.

Table 1: Textural and catalytic properties of the ZSM-5 catalyst materials under study. Reproduced with permission from ref [17].

Entry	Catalyst	$V_{total}^{[a]}$ [cm ³ g ⁻¹]	$V_{micro}^{[a]}$ [cm ³ g ⁻¹]	$S_{BET}^{[a]}$ [m ² g ⁻¹]	$S_{micro}^{[a]}$ [m ² g ⁻¹]	$C_{AS}^{[b]}$ [μmol g ⁻¹]	$C_{BAS}^{[c]}$ [μmol g ⁻¹]	$C_{LAS}^{[c]}$ [μmol g ⁻¹]	Throughput ^[d] [g _{MeOH} g _{catalyst} ⁻¹]	$S(C_{3=})$ [C mol%]
1	ZSM-5	0.256	0.152	448	363	387	232	35	88	25
2	Ca-ZSM5-IE	0.273	0.145	429	344	402	138	108	264	39
3	6Ca-ZSM5-SSIE	0.212	0.111	323	267	171	128	0	136	39
4	6Ca-ZSM5-EW	0.199	0.110	336	276	374	38	208	304	43
5	6Ca-ZSM5-IWI	0.226	0.124	385	310	384	29	240	504	53
6	4Ca-ZSM5-IWI	0.223	0.126	387	313	381	27	240	480	45
7	2Ca-ZSM5-IWI	0.238	0.128	392	315	332	40	228	792	39
8	1Ca-ZSM5-IWI	0.246	0.138	418	334	347	66	198	272	46

[a] From N₂ adsorption. [b] Concentration of acid sites (AS) derived from NH₃ TPD. [c] Concentration of Brønsted (BAS) and Lewis (LAS) acid sites derived from pyridine IR spectroscopy. [d] Amount of methanol (g) converted per gram of zeolite before conversion decreases below 80%.


Figure 4: SEM images of the zeolite samples: P-ZSM-5-0.35, P-ZSM-5-0.15, C-ZSM-5-F, and C-ZSM-5-OH. Reproduced with permission from ref[18]错误!未找到引用源。

2.3.2 Beta-zeolite Catalysts

β zeolite catalyst is a catalyst widely used in the chemical industry, which has high catalytic activity and selectivity, and can play an important role in chemical reactions. β molecular sieve is the only high-silica aluminum molecular sieve with a medium-pore chiral pore network structure, and it is also the only one with a three-dimensional structure, Large-porous molecular sieve with 12-membered annular skeleton structure[19]-[22] The silicon-aluminum ratio of β zeolite can be modulated in the range of tens to hundreds of times, showing the advantages of good anti-coking performance, long service life and high catalytic activity in a series of catalytic reactions, and has rapidly developed into a new type of catalytic material in recent years[23][25] In order to make the β zeolite catalyst produce good catalytic performance for different catalytic reactions, it is necessary to study the modification of various methods, mainly including metal/non-metal modification, acid/alkali modification and high-temperature water vapor treatment modification.

Sheemol et al.[26] A series of rare earth metal modified β zeolite was prepared for catalyzing toluylation. The results show that the Si/Al ratio, crystallinity and acidity of the modified β zeolite are quite different, and then show different catalytic activities. Wang Ying and others [27] Zeolite β treated with water vapor catalyzes the reaction of methanol and isobutylene etheration to form methyl tert-butyl ether. The results showed that the high pretreatment temperature (550°C) was conducive to improving the catalytic activity of the zeolite catalyst. The catalytic activity of zeolite treated β alkaline atmosphere is higher than that of zeolite treated β neutral atmosphere. In addition, dynamic water vapor treatment was found to not change the skeleton structure of β zeolite, but it could change the acid properties of the catalyst [28]. Bai and others [29] During the study of the alkylation reaction of indole and benzaldehyde, it was found that citric acid modified H β has higher catalytic activity than unmodified H β . This is because the modified H β active center increases, the specific surface area increases, the weak acid content decreases, and the stability of the catalyst is enhanced.

2.3.3 SAPO-11 Zeolite Catalyst

Aluminum silica phosphate-11 (SAPO-11) is a microporous molecular sieve of aluminum silica phosphate composed of three tetrahedral units (SiO_2 , AlO_2 , and PO_2^{2+}), which is a weakly acidic carrier with AEL structure and one-dimensional pores. Due to its unique pore structure and mild acidity, it is considered to be an ideal carrier for alkane hydrogenation catalysts, and has been widely used in the process of petrochemical hydroisomerization and achieved good economic benefits [30]. SAPO-11 zeolite catalyst belongs to mesoporous zeolite. SAPO-11 zeolite exhibits different acid strength due to different synthesis conditions, so it presents unique catalytic performance.

The acidity, redox characteristics, cleanliness and pore structure of SAPO-11 zeolite catalyst can be changed by loading and doping to achieve the modification of zeolite catalyst. According to the current research results, the loading of precious metals has achieved a good catalytic effect. Murthy [31] Studies have shown that the introduction of transition elements such as Cr, V, and Ti into molecular sieve will lead to a decrease in the crystallinity of SAPO-11, and an increase in pore volume and average pore size, which may be due to the large ion radius of transition elements after replacing Al and Si. Li Xu [32] and other studies show that the Pd content in the Pd/SAOP-11 catalyst has a greater influence on the catalytic performance, and the conversion rate and isomerization selectivity increase with the increase of Pd content, and when the loading is 0.5%, the obtained catalyst has the best effect and good stability, and the conversion rate and selectivity reach the best state.

3. Synthesis of Zeolite Catalysts

The synthesis method of molecular sieve catalyst can be roughly divided into two types, classical synthesis and new green synthesis, with the development of green chemical industry and the advancement of technology, synthesis technology continues to move in the direction of green environmental protection, high efficiency and low consumption.

3.1 Classical Synthesis

3.1.1 Hydrothermal Synthesis Method

Hydrothermal synthesis method is used to prepare the most widely used method in the early zeolite method, the method uses water as the crystallization medium, the raw materials required for the synthesis of zeolite are prepared into a reaction mixture in a certain proportion, made into a gel, placed in the reactor, crystallization reaction at a certain temperature, and then through filtration, washing, ion

exchange, molding, activation and other processes to prepare molecular sieve catalyst. Zhang et al. [33] Crystallization behavior of hydrogels and dry gums when SAPO-37 zeolite is synthesized by hydrothermal synthesis. The product prepared by this method has high purity, but it is not environmentally friendly, the performance requirements of raw materials are high, the process is complex, the production cost is high, and the strength, adsorption performance and thermal stability of the zeolite prepared are poor.

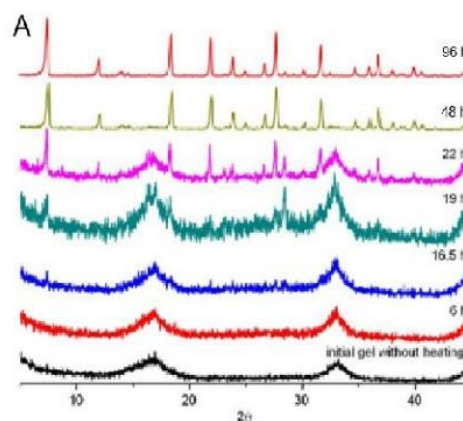


Figure 5: XRD plot of a SAPO-37 zeolite sample synthesized by hydrothermal synthesis. Reproduced with permission from ref[33].

3.1.2 Ion Exchange Method

Ion exchange method refers to the method of adding some salts in the preparation of molecular sieve, exchanging the anions and cations in these salts with the anions and cations in the molecular sieve through ion exchange, or the organic matter containing functional groups grafts the special ions or functional groups in the organic matter to the inside or surface of the molecular sieve through ion exchange, so as to provide various adsorption sites and catalytic centers. The ion exchange method can increase the pore wall thickness of the mesoporous molecular sieve, change the pore structure, hydrophobicity and thermal stability of the molecular sieve, make many metal catalysts easier to load into the molecular sieve structure, increase its surface area and change the catalytic center, and improve the catalytic activity and efficiency of the [34]-[36]. Kondru et al. [37] explored the loading of active metal Fe on a Y-zeolite and applied to wet-catalyzed Congo red dye wastewater, studying the effects of various operating parameters such as temperature, initial pH, hydrogen peroxide concentration, and catalyst loading on dye removal from aqueous solutions at atmospheric pressure. Using a 0.6 mL H_2O_2 /350 mL solution and a 1 g/L catalyst, the removal percentages for dye, color, and COD were 97% (within 4 hours), 100% (within 45 minutes), and 58% (within 4 hours) at an optimal $\text{pH}_0=7$, 90°C.

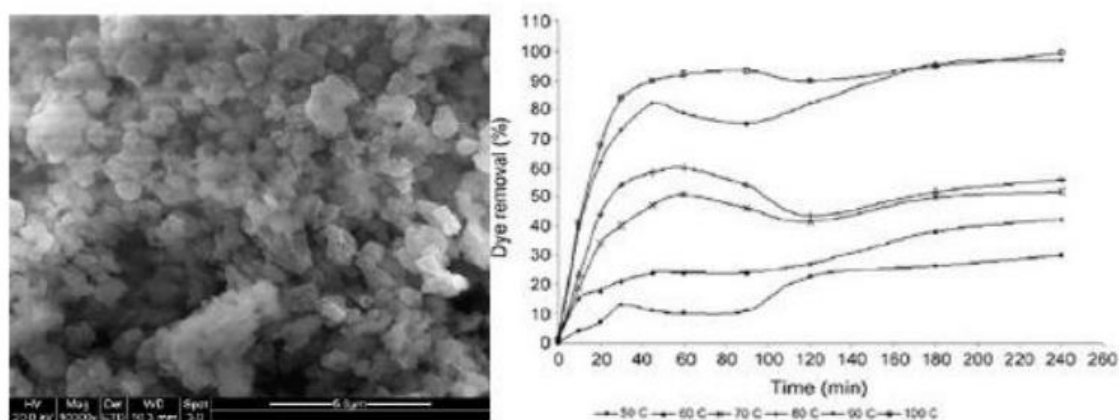


Figure 6: Ion-exchange Y-catalyst SEM diagram and results of CWPO dye at different temperatures. Reproduced with permission from ref [37].

3.1.3 Soft and Hard Template Methods

The "hard" template method means that the structure of the template agent used is relatively "hard", that is, structurally rigid substances, such as solid materials such as carbon materials or inorganic particles [38]. Method for synthesizing zeolite catalysts. Soft template agent refers to molecules or aggregates of molecules with "soft" structure, soft template agent and the formation of mesoporous inorganic skeleton species to have a strong effect, after removing the template agent to form mesopores, the method is convenient to operate and low cost. For example, EU-1 zeolite samples are synthesized under hydrothermal conditions using carbon black as a hard template. **Figure 7** shows the XRD spectra of an EU-1 zeolite sample synthesized with different carbon blacks. It can be found that the sample synthesized by adding carbon black is basically consistent with the characteristic diffraction peak of EU-N and is consistent with the literature [39], indicating that EU-1 zeolite is successfully synthesized after adding carbon black and no heterocrystalline phase is generated. **Table 2** shows the N₂ adsorption-desorption data of EU-1 zeolite samples, with the increase of carbon black addition, the microporous volume of the sample continues to decrease, while the specific surface area and mesoporous volume increase first and then decrease, and the increase of mesopores will significantly improve the mass transfer performance of molecular sieve.

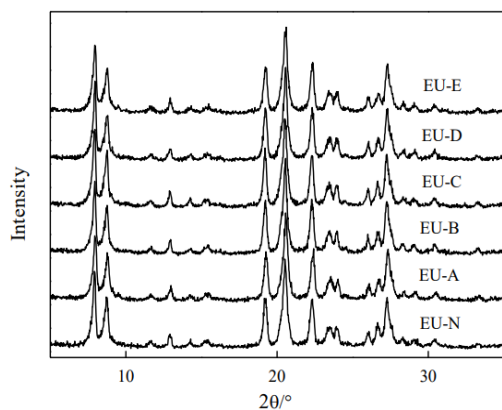


Figure 7: XRD spectra of EU-1 zeolite samples synthesized with different carbon blacks. Reproduced with permission from ref [39].

Table 2: N₂ adsorption-desorption data for EU-1 zeolite samples. Reproduced with permission from ref [39].

Sample	$S_{BET}(m^2/g)$	$S_{mic}(m^2/g)$	$S_{ext}(m^2/g)$	$V_{total}(cm^3/g)$	$V_{meso}(cm^3/g)$
EU-N	342.48	306.16	36.32	0.209	0.055
EU-A	353.59	304.68	48.91	0.217	0.071
EU-B	359.97	301.40	58.57	0.242	0.107
EU-C	372.23	303.31	68.92	0.258	0.127
EU-D	364.13	299.20	64.93	0.250	0.123
EU-E	363.45	300.31	63.14	0.242	0.120

3.2 Green Synthesis Method

3.2.1 Direct Synthesis

Direct synthesis is a method for preparing zeolite by synthesis without organic template and crystal seed. After mixing the deionized water and alkali source well, add aluminum sulfate, add silicon source under stirring conditions, and continue stirring until silicon-aluminum gel is formed; Crystallization is carried out in the reaction kettle, filtered and dried to obtain molecular sieve raw powder. The method is not only environmentally friendly and energy-saving, but also has high yield and raw material utilization, stable aluminum species and relatively strong acidity, and has high industrial application value [40].

3.2.2 Mother Liquor Induction Method

The mother liquor induction method is a method of synthesizing zeolite catalyst by filtering the mother liquor once in molecular sieve synthesis as an inducer. By modulating the amount of inducer, the stirring strength can be very low (30 r/min) or at rest, molecular sieve synthesized in a short time. The molecular sieve synthesized by the mother liquor induction method has a larger specific surface area and higher relative crystallinity, which not only ensures product quality, but also shortens the reaction time, reduces the treatment cost and reduces environmental pollution [41]. For example, during the preparation of SAPO-34 molecular sieve by mother liquor induction method, triethylamine (TEA) was used as a template agent to collect fresh mother liquor during

the preparation of SAPO-34 molecular sieve by traditional hydrothermal method. Take multiple parts of mother liquor to dry, roast and calculate the solid content and then take the average value as the solid content of small crystal fragments in the mother liquor, and add the mother liquor as a benchmark. SAPO-34 zeolite was prepared by mother liquor induction. As shown in **Figure 8**, M-TEA/Al₂O₃=0.5, 1.0, 1.5, 2.0, 3.0 were samples synthesized by mother liquor induction at different template dosages, respectively. **Figure 9** shows the crystallinity curve of the synthesized sample under different template dosages by mother liquor induction method [42].

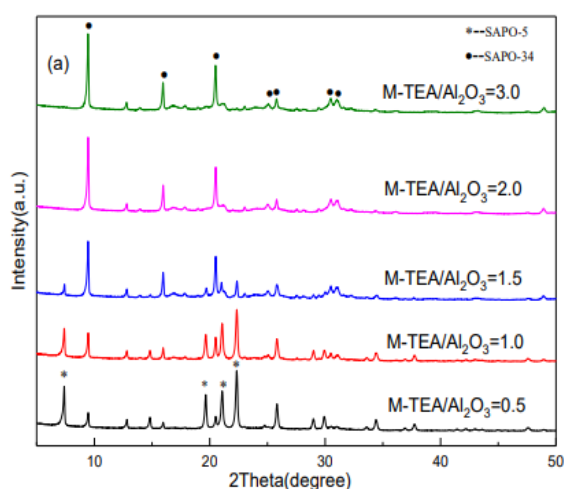


Figure 8: Sample of SAPO-34 zeolite synthesized by mother liquor induction at different template dosages. Reproduced with permission from ref[42].

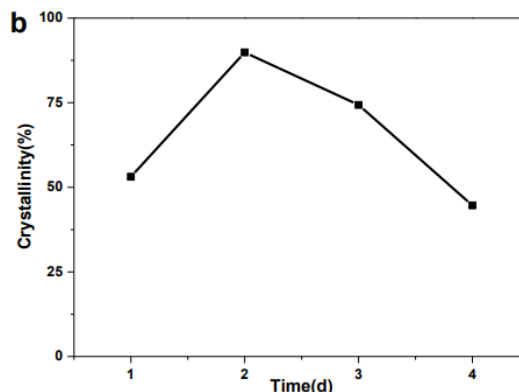
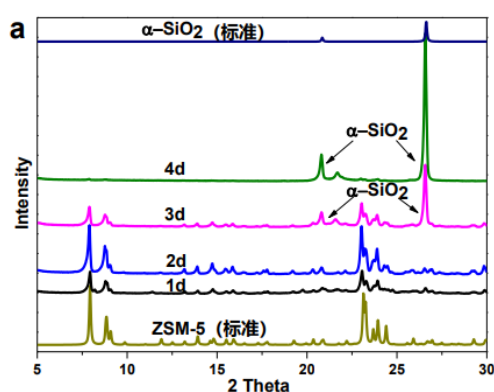


Figure 10: Effect of reaction time on ZSM-5 synthesis: (a) XRD spectra; (b) crystallinity trends. Reproduced with permission from ref[44].

4. Application of Zeolite Catalyst in Green Chemical Industry

Early zeolite catalysts were mainly used in petroleum and chemical fields, with the advancement of technology, now zeolite catalysts have been widely used in petrochemical, environmental protection, pharmaceutical and other fields.

4.1 Petrochemical Sector

4.1.1 Crude Oil Desulfurization and Denitrification Catalyst

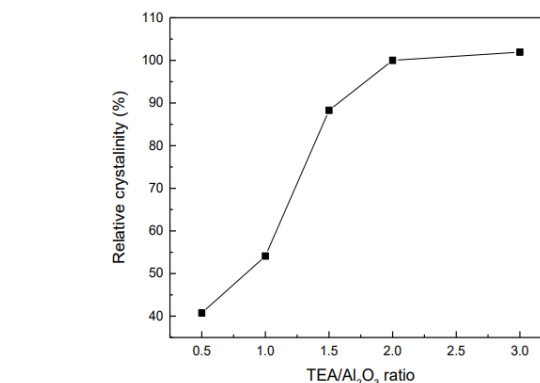


Figure 9: The crystallinity curves of samples were synthesized by mother liquor induction method at different template dosages. Reproduced with permission from ref[42].

3.2.3 Solid Phase Grinding Method

Solid phase grinding method, also known as solvent-free synthesis method, the method is based on solid silicon source, aluminum source, template agent, etc. as the starting material, in the synthesis process without adding water or solvent, after simple grinding and the use of the starting material crystal water or adsorption hydrolysis polysilicon source and aluminum source, and crystallized at an appropriate temperature, washed and dried and roasted in the air to prepare a molecular sieve with high crystallinity. The method has simple synthesis steps, low synthesis pressure, high production efficiency, less waste liquid discharge, and combined with the organic-free template method, which can minimize environmental pollution and cost[43]. For example, ZSM-5 zeolite is prepared by adding seed solid-phase synthesis, so that the synthesis method is environmentally friendly and economical to the greatest extent[44].

In terms of environmental protection, it can be used as crude oil desulfurization and denitrification catalyst, and molecular sieve catalyst plays an irreplaceable role in solving the problem of motor vehicle exhaust pollution. Some researchers have reported vanadium silicate zeolite sieves (containing highly dispersed substance V in a silica frame) catalyzes the oxidation of aromatics, alkanes, olefins and alkyl sulfides more effectively than titanosilicates, can be used as a catalyst for light oil desulfurization. Ti-HMS catalyst (Titanium-silicon molecular sieve) Accelerate nitrogen and sulfurization of light oils, and Ti-HMS can be reused without loss of catalytic activity, V-HMS catalyst (Vanadium silicon

molecular sieve) Reusability in further desulfurization and denitrification of light oils[45].

4.1.2 Oil Hydrogenation Process

In the process of petroleum hydrotreatment, molecular sieve catalytic reaction technology can reduce the emission of carbon dioxide, a greenhouse gas, promote sustainable development, and reduce the amount of molecular sieve catalyst, which makes great contributions in the field of environmental protection. Ibida et al. [46] prepared a multi-stage porous molecular sieve HY-A with a Si/Al molar ratio of 8.0 and a mesoporous pore size of about 2.0 nm using Y-type molecular sieve as raw material, hydrothermal treatment and moderate acid treatment at 670°C, and investigated the hydrocracking activity of Ni-HY-A catalyst by hydrocracking reaction of heavy distillate (distillation range 340~530°C). The catalyst with multi-stage porous HY-A zeolite as the carrier has obvious performance advantages in the heavy oil reaction, and the yield of unconverted oil is reduced to 21% and 11% at the reaction temperature of 340°C and 380 °C, respectively, and the yield of light fractions with boiling point < 253°C increases to 51% and 66%, respectively, and the gas yield decreases under the same reaction temperature.

4.2 Environmental Protection Field

4.2.1 Photocatalytic Degradation of Formaldehyde

Zeolite catalyst for photocatalytic degradation, Dong et al. [47] prepared a thin layer of TiO₂ on HZSM-5 zeolite by sol-gel method, and the specific surface area and pore volume of the prepared TiO₂/HZSM-5 composites increased, and the photocatalytic activity was greatly enhanced. Through photocatalysis, organic matter, dyes and other pollutants can be degraded; It can catalyze the degradation of formaldehyde at room temperature to improve indoor air quality. A novel Bi_{0.9}La_{0.6}SAPO-34 composite zeolite photocatalyst was prepared by in situ modification of SAPO-34 zeolite and the photochemical properties of the prepared catalyst were systematically studied by photodegradation of formaldehyde. Under light conditions, Bi_{0.9}La_{0.6}SAPO-34 catalyst has a degrading process for formaldehyde in 6hThe degradation rate has increased by more than 3 times[48].

4.2.2 Sewage treatment

The application of zeolite catalyst in sewage treatment mainly plays a role in the degradation of organic matter and the removal of heavy metal ions. Organic matter is an important part of sewage, most of which are toxic and harmful and refractory to degrade. Generally, organic matter is relatively stable and the effect of direct oxidation removal is general, so in the process of treating organic matter, the target organic matter is usually oxidized by adding catalyst. Xi Hong'an et al. [49] synthesized the catalyst by adding titanium dioxide in the pores of mesoporous silica SBA-15 by post-synthesis method during the titanium dioxide modification process of SBA-15. TS-L2 maintains the original regular pore structure of SBA-15, a mesoporous material, and forms a Ti-O-Ti network structure on the pore wall. In the reaction process, TS-L2 adsorbs phenol and quinone intermediates too much, which to

a certain extent hinders the combination of pores and water to form HO, resulting in reduced catalytic efficiency, but it can be seen that the intermediate products are prioritized during the reaction, and further degradation reactions occur to achieve good removal effect. Heavy metal ions are toxic substances that cannot decompose on their own, and water quality is generally improved by adsorption.

5. Future Development and Problems of Zeolite Catalysts

Compared with ordinary catalysts, green catalyst zeolite is environmentally friendly, high catalytic performance, low pollution, long life, and the waste zeolite will not cause pollution to the environment. Compared with ordinary silicon-aluminum catalysts, molecular sieve is highly selective and has higher catalytic efficiency. Therefore, the application field of molecular sieve catalyst will be more extensive, and its research and application have good development prospects.

It is precisely because of the high performance of molecular sieve that its preparation cost is high and difficult, so the future research direction is more inclined to new and modified molecular sieve, and the significant diversity in structure and chemistry of new and modified molecular sieve and other crystalline microporous materials provides almost unlimited parameters for customized catalytic performance. As a result, a unique combination of catalysts with acidity and shape selectivity can be developed, which is not possible with ordinary zeolite or other existing catalysts. The ability of these materials to perform selective and sometimes novel chemical reactions will play a major role in the catalytic specificity required in the future. These catalysts will be key to developing advanced processes to meet the environmental, feedstock, product and economic requirements of the 21st century[50].

6. Conclusion

In summary, according to the future development trend of catalysts, molecular sieve catalysts, as environmentally friendly and efficient green catalysts, have a wide range of application prospects in the field of chemical environmental protection. The special structure of molecular sieve catalyst makes its catalytic performance efficient and specific, and important catalytic materials such as molecular sieve catalyst will continue to play a key role in the greening process of the future chemical process.

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