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Hierarchical zeolite-encapsulated metal nanoparticles for heterogeneous catalysis

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Abstract

Zeolites, characterized by their highly porous structure, have become integral to modern industry and environmental science due to their broad applications in adsorption, separation, and catalysis. Recent advancements in zeolite synthesis, particularly through hydrothermal methods and the incorporation of metal nanoparticles, have significantly expanded their utility. This review delves into the innovative strategies for encapsulating metal nanoparticles within zeolite matrices, enhancing catalytic reactions' efficiency, selectivity, and durability. Challenges such as nanoparticle agglomeration and catalyst deactivation are addressed through hierarchical zeolite encapsulation, which provides a novel route for the development of multifunctional materials. By examining methods ranging from *in situ* encapsulation to post-synthetic recrystallization, this review highlights the versatility and potential of metal@zeolite catalysts in various applications, including organic synthesis, pollutant treatment, and energy conversion. The review underscores the importance of optimizing the interaction between metal nanoparticles and the zeolite framework to achieve superior catalytic performance, offering new directions for research in catalytic science and industrial process optimization.

KEYWORDS. Hierarchical zeolite, Metal-encapsulated, Catalysts, Catalyst optimization

1. Introduction

In modern industry and environmental science, zeolite plays a pivotal role as a highly porous silicate mineral. Characterized by its orderly pore configuration, extensive specific surface area, and remarkable thermal stability, zeolite has found broad applications across various domains, including adsorption, separation, and catalysis.[1, 2] Its deployment significantly enhances chemical processes, boosts resource efficiency, and is vital in addressing global challenges like environmental conservation and energy transformation.

The synthesis of zeolites is mainly carried out by hydrothermal synthesis, which involves the crystallization of silicon- and aluminium-containing raw materials in an alkaline or neutral environment under specific temperature and pressure conditions.[3, 4] Figure 1 illustrates the development of zeolite research since as early as 1756 with first discovery of zeolite mineral publication by Cronstedt.[5] Recently, by altering synthesis conditions and using different templates or additives, researchers have successfully synthesized zeolites with different pore sizes, pore structures, and chemical compositions to meet the needs of specific applications.[3, 6] Advances in the synthesis of zeolites have not only expanded their application scope in traditional fields, but also opened up new application prospects, such as catalyst supports, molecular screening, and ion exchange.

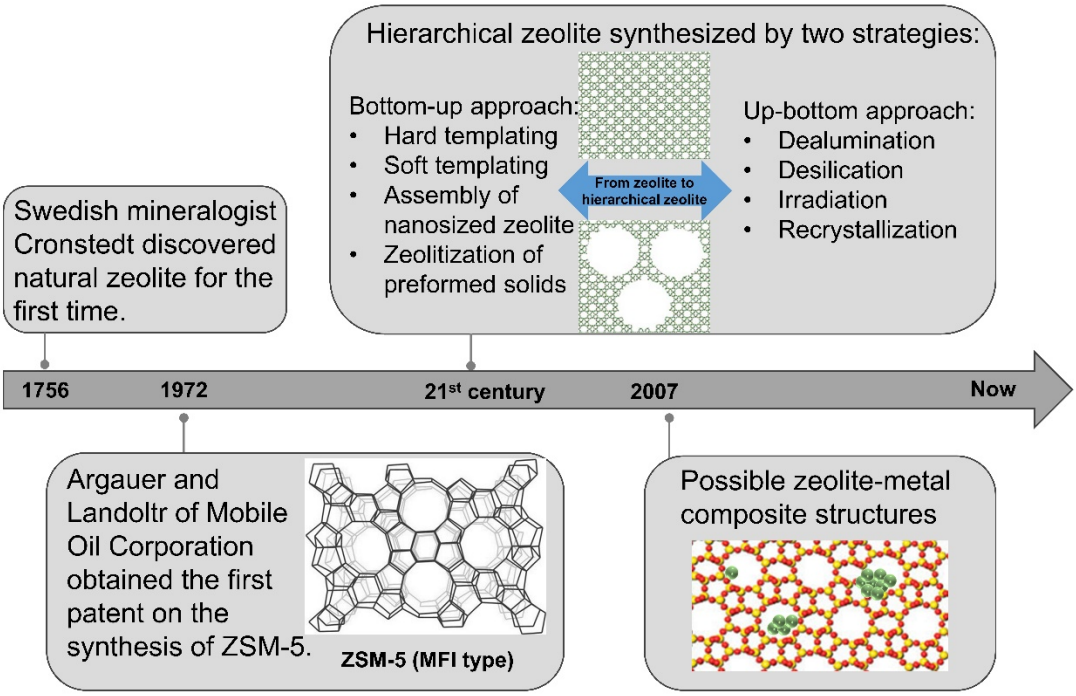


Figure 1. Summary of significant milestones in zeolite development.

To achieve more efficient catalytic reactions, researchers have been exploring methods of loading metal nanoparticles into zeolite pores.[7, 8] Notably, noble metals like platinum, palladium, and rhodium significantly boost catalytic reaction activity and selectivity due to their distinctive electronic properties and surface activities.[9-12] By precisely controlling the size, distribution, and chemical environment of metal nanoparticles, researchers have made significant progress in heterogeneous catalysis, including but not limited to organic synthesis reactions, pollutant treatment, and energy conversion.

Nevertheless, zeolite-based catalysts encounter challenges in practical applications, including the agglomeration of active metal species, catalyst deactivation, and carbon (coke) formation. Traditional microporous zeolites, used in critical catalytic process, such as biomass conversion,[13] the selective hydrogenation of alkenes,[14] isomerization,[15] and Fischer−Tropsch synthesis process,[16] often have metal nanoparticles immobilized on their outer surfaces or within micropores. Generally, metal nanoparticles cannot be

moved in micropore zeolites (pore size <2 nm), mainly on the outer surface of zeolites outer surface as shown in Figure 2.[17] During the reaction or some harsh thermal treatments, active species on the external surface can aggregate to form large nanoparticles (>5 nm), resulting in a decrease in catalytic activity[18]. Moreover, the metal nanoparticles trapped in micropores could block the pore access to reactants. Sometimes, the size of metal nanoparticles trapped in micropores is too small to contribute to catalytic activity. These problems not only reduce the stability and lifetime of the catalysts, but also limit their efficiency in industrial applications.

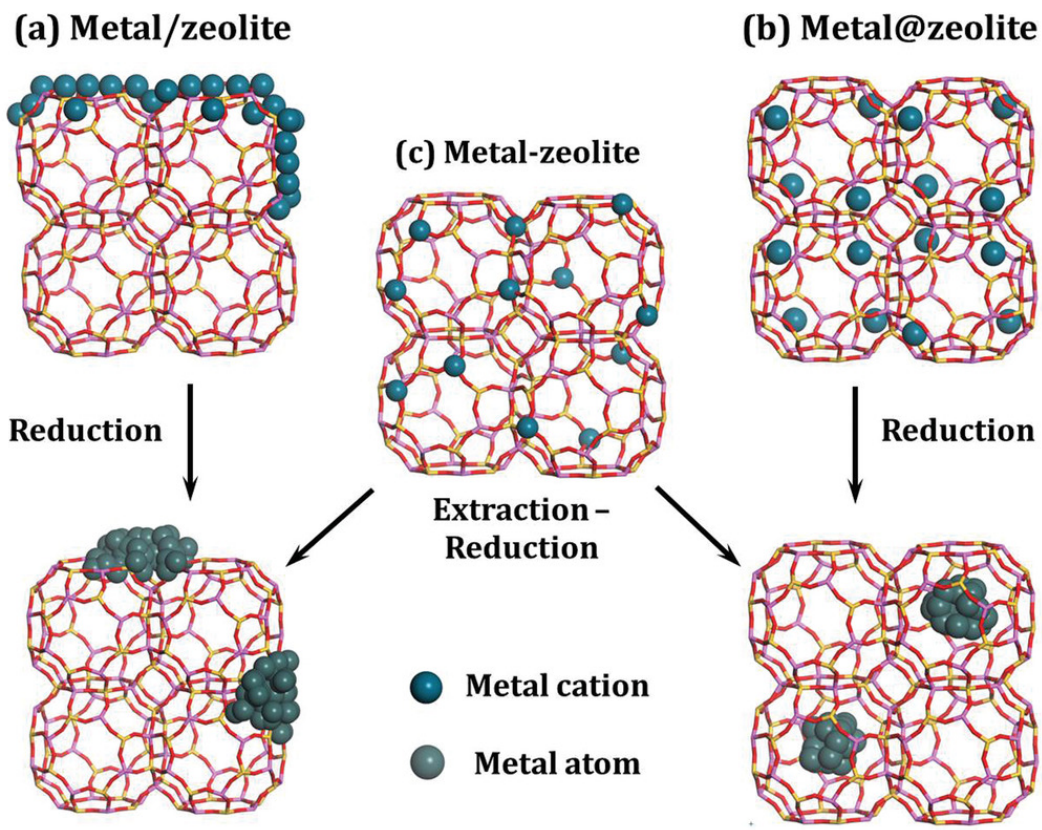


Figure 2. Different types of metal-containing zeolites. (a, metal/zeolites, metal on the zeolite surface; b and c, metal@zeolite, metal species in the zeolite and metal species incorporated into zeolite framework). Reprinted with permission from ref. [17]. Copyright 2019. Advanced science.

To address these challenges, researchers have used hierarchical zeolite encapsulation of metal nanoparticles. Through this method, hierarchical zeolites can serve as the

alternative host to disperse or entrap active metal nanoparticles.[16] The secondary porosity like mesopores (2-50 nm) or macroporous (>50 nm) present in hierarchical zeolites is an ideal space for the incorporation of metal nanoparticles, opening new routes for the preparation of multifunctional materials.[17] In this method, metal nanoparticles are evenly dispersed and encapsulated in the mesopores or macroporous of zeolite, effectively preventing the agglomeration of metal nanoparticles and the formation of coke deposits. The key to the encapsulation method is to utilize the pore structure of the zeolite, which not only protects the metal nanoparticles, but also keeps the pore channels of the zeolite unobstructed, thus ensuring efficient mass transfer and reactant contact. Especially, the encapsulation of noble and transition metal nanoparticles into hollow zeolites as core-shell or yolk-shell composites has been extensively studied for their great potential in catalytic applications.[19, 20] These hierarchical zeolite-encapsulated metal nanoparticles presented better dispersion of metal active sites, enhanced the catalyst stability via the pore confinement,[21] and improved the reactant accessibility by the hierarchical porous system. Using this method of encapsulating metal nanoparticles with multi-stage zeolites, the catalyst shows significant performance improvements in heterogeneous catalytic reactions, including higher catalytic activity, better selectivity and longer service life.[22, 23] This not only provides new research directions for catalytic science, but also opens up new possibilities for the optimization and development of industrial catalytic processes. In this review, we will first focus on the encapsulation types for hierarchical zeolite-encapsulated metal nanoparticles. Then the method of synthesizing encapsulated catalysts is summarized in detail. The final section demonstrates the optimization of chemical reactions using metal@zeolite catalysts. This Review provides a comprehensive overview of synthesis methods, structural features, and applications of hierarchically porous zeolites. In addition, this Review will help researchers in this field to understand the latest research progress on the hierarchically porous zeolites from synthesis to applications.

2. Encapsulation types for hierarchical zeolite-encapsulated metal nanocatalysts

Encapsulation of metal nanoparticles within hierarchical zeolites is a key strategy to enhance catalytic performance by protecting the active metal species and improving their stability and selectivity. This approach leverages the unique strucfitural properties of zeolites, including their high surface area, tunable pore size, and robust thermal stability. Different encapsulation methods have been developed to address the specific requirements of various catalytic processes. These methods vary in their complexity, effectiveness, and scalability, each offering distinct advantages and facing particular challenges. The following sections will explore some of the most prominent encapsulation types (Table 1), providing insights into their mechanisms and practical implications.

Table 1. Summary and comparison of encapsulation types in different structures

Encapsulation types	Advantages	Limitations
Encapsulating metal species inside hierarchical zeolite single crystals	- Enhanced stability and resistance - Improved catalytic activity - Increased selectivity	- Time-consuming preparation steps - Limited diffusion of reactants
Encapsulation of metal species in polycrystalline spheres	- Large specific surface area - Controllable metal species release and tuning reactivity	- Complex synthesis process - Diffusion limitations - Risk of metal leaching
Encapsulation of metal species in hollow zeolite crystals	- Enhanced catalytic stability - Improved selectivity - High metal dispersion	- Synthesis complexity - Limited accessibility of active sites - Potential for metal migration
Hierarchical core@shell zeolite-based materials	-Tailored catalytic properties -Improved mass transfer - Enhanced stability of	- Metastable structures - Potential leaching or migration of metal elements

	nanoparticles - Tunable shell thickness	- Scalability challenges
Yolk–shell metal-encapsulated zeolite-based materials	- Fine control of particle size and dispersion - Enhanced stability and durability	- Complex layer-by-layer assembly and etching methods - High cost - Limited industrial applications
Fish-in-hole metal-encapsulated zeolite-based materials	- Prevents sintering - Localized nanoparticles - Enhanced diffusion rate - Minimal coke formation	- Complex synthesis and optimization - Scalability challenges - Challenges in ensuring precise positioning of metal nanoparticles within the traps

2.1 Encapsulating metal species inside hierarchical zeolite single crystals

The encapsulation of nano-sized metal nanoparticles within zeolite single crystals helps prevent the common issue of nanoparticle aggregation at high reaction temperatures, significantly enhancing the stability of the catalyst. Gao et al. pioneered the *in situ* encapsulation of small-sized noble metal nanoparticles within titanium silicate zeolite (TS-1) utilizing a low-temperature hydrothermal synthesis method.[24] The synthesis procedure for Pd@MTS-1 is illustrated in Figure 3. Initially, to preclude the formation of isolated TiO_2 species, a silica-titanium mixture was prepared at 5°C. Then adding dichloro(ethylenediamine)palladium (DEAP), the resulting mixture was aged for 24 hours at a temperature of 90 °C to form protozeolitic MFI (Mobile Five) nanounits. These units merged with cetyltrimethylammonium bromide (CTAB), subsequently crystallizing into single crystals during the subsequent hydrothermal treatment at 100°C. After a calcination process in air and reduction in an H_2/Ar environment at 400 °C, Pd nanoparticles, with a diminutive size of 2.3 nm, were encapsulated within the

mesoporous TS-1 zeolite nanocrystals. This approach, featuring the aging of the mother liquid and the low-temperature hydrothermal treatment, effectively prevents the premature precipitation of the metal precursor, enabling the successful incorporation of Pd nanoparticles into the mesoporous TS-1 nanocrystals. The resulting catalyst demonstrated high catalytic activity, outstanding stability, and remarkable recyclability in the oxidation of CO and catalytic wet air oxidation (CWAO) of phenol.

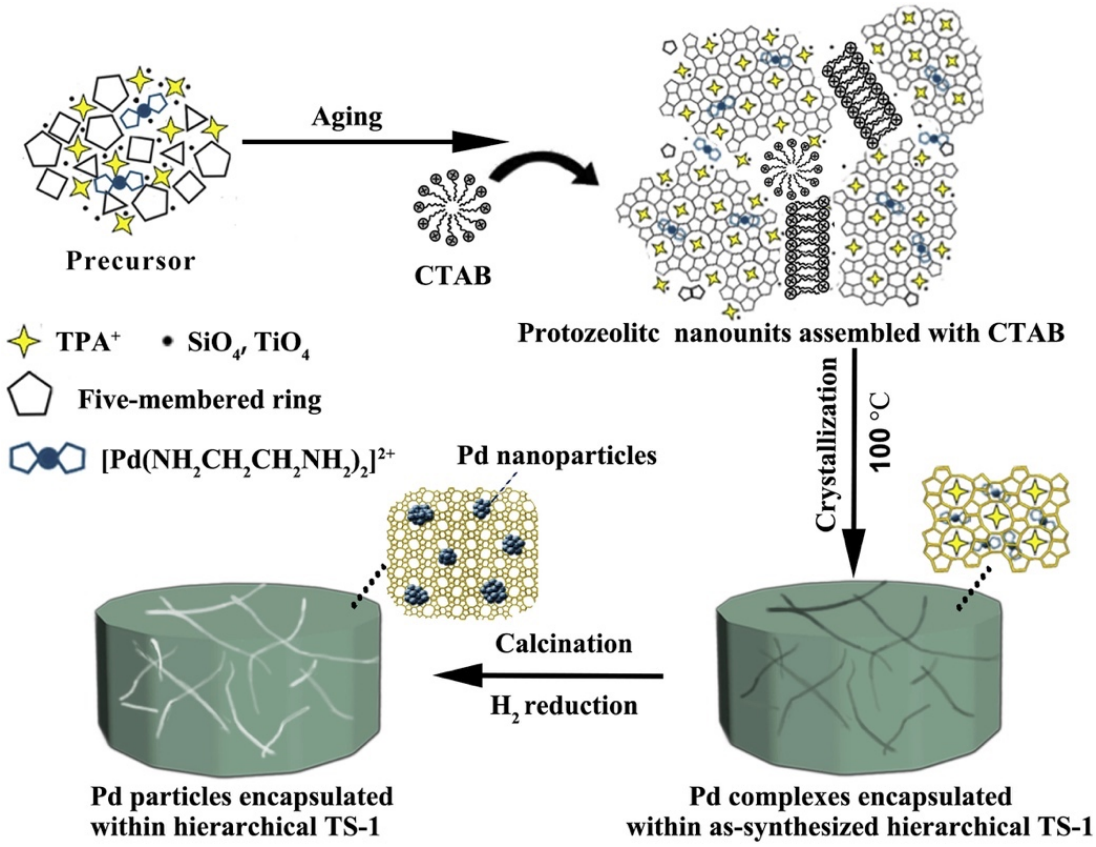


Figure 3. The synthesis of small-sized Pd nanoparticles (2.3 nm) encapsulated in hierarchical TS-1 by low-temperature hydrothermal synthesis method. Reprinted with permission from ref. [24]. Copyright 2023. Microporous and Mesoporous Materials.

To improve the efficient use of Pt metal resources in hydrogenation reactions, a variety of zeolites encapsulated Pt nanoparticles have been synthesized. For example, Wang et al. encapsulated Pt clusters (~2 nm) into the pure silica TON-type zeolite (ZSM-22) in

a dry gel conversion route, which make the Pt@ZSM-22 series have the advantages of possessed high crystallinity, large surface area, and ultrafine Pt clusters inside the zeolite crystals. This kind of catalyst exhibit remarkable activity in the semi-hydrogenation of phenylacetylene into styrene.[25] Pt@Silicalite-1 catalysts produced by crystal transformation of supported Pt/S-1 catalyst in Gao's group showed excellent catalytic performance in CH_4 conversion increased by 10% and CO selectivity 25% higher than the conventional supported Pt/S-1 catalyst.[26] Additionally, Pd nanoparticles encapsulated inside the mesoporous silicalite-1 nanocrystals[27] and TS-1zeolite[24] via one-pot method and low-temeperature hydrothermal treatment have been reported. The size of Pd nanoparticles in Pd@silicalite-1 remained nearly the same after 550 °C calcination in 6 h,[27] and showed aggregation and stability against sintering during 600 °C under air/N_2/H_2 atmosphere in TS-1 zeolite.[24] These effective catalysts can have the excellent catalytic activities recyclabilities in the CO oxidation (CO conversion: nearly 100% over 72 h) and the benzyl alcohol oxidation (benzaldehyde yield up to 94%).

Encapsulating metal species inside hierarchical zeolite single crystals offers several notable advantages. This method significantly enhances the stability of the catalyst by preventing nanoparticle aggregation at high reaction temperatures. But there are some disadvantages associated with this method. The synthesis process can be complex and requires precise control over conditions such as temperature and precursor concentrations to achieve the desired encapsulation and catalytic properties. Additionally, the initial preparation steps, such as the aging of the silica-titanium mixture and the controlled addition of metal precursors, can be time-consuming and may limit the scalability of the method for industrial applications. Finally, ensuring the uniform distribution of metal nanoparticles within the zeolite matrix is crucial, as any inconsistencies can lead to variations in catalytic performance.

2.2 Encapsulation of metal species in polycrystalline spheres

Hollow spheres (or capsules) with nano- and microscopic sizes are increasingly finding applications in chemistry, biotechnology, and material science due to the advantages of

low density, large specific surface area, and shell permeability. The effective preparation of hollow spheres often involves the use of various sacrificial cores, such as polymer and silica spheres. In general, inorganic silica materials exhibit stronger stability towards changes in the surrounding environment compared to polymers.[17, 19, 27] The shells, with microporous structure, work as a molecular filter, protecting metal nanoparticles from external poisoning agents, such as the sulfur-containing chemicals.[28-30] Encapsulation isolates nanoparticles from each other and inhibits sintering in metals under tough reaction conditions.[28, 31] The effective route for preparing hollow spheres always involves various sacrificial cores (e.g., polymer and silica spheres). The common method for preparing hollow spheres is the hard templating method, wherein zeolite is first crystallized on the outer surface of the template, forming a hollow structure by subsequently removing the template (Figure 4).

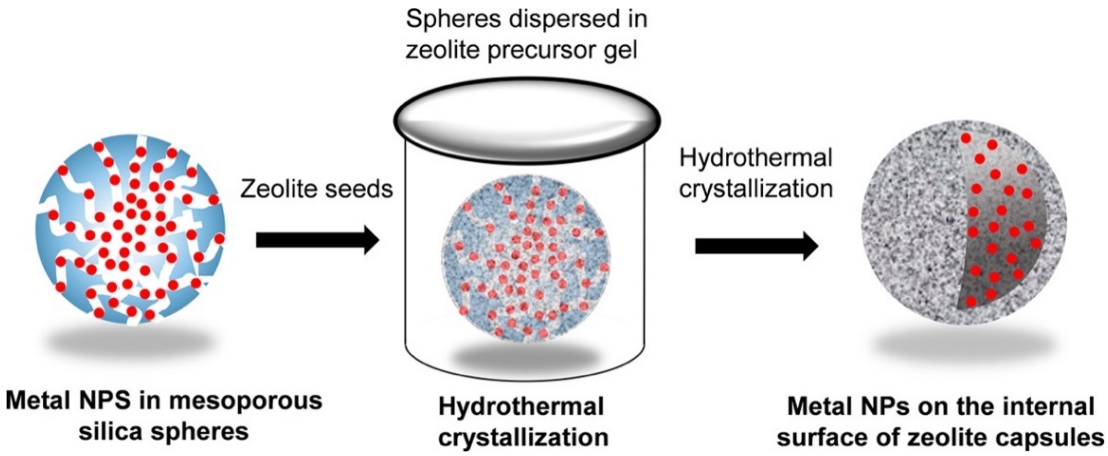


Figure 4. Formation of polycrystalline hollow zeolite spheres with encapsulated metal nanoparticles by hydrothermal crystallization. Reprinted with permission from ref. [28]. Copyright 2016, American Chemical Society.

The advantages of the above strategy can be illustrated by the example of Pt, Fe_2O_3 and Ag encapsulated in silicalite-1. Pt@silicalite-1 and Ag@silicalite-1 were synthesized

by this strategy and compared with commercial catalysts such as Pt/SiO_2 and Pt/Al_2O_3 for the catalytic oxidation of alcohols.[32] The reaction performance demonstrate that the microporous shells prevent large reactants and toxic molecules from entering the reaction environment inside the sphere and block these molecules to contact with the reaction active metal nanoparticles in the Pt@silicalite-1 and Ag@silicalite-1 catalysts. Thus, both catalysts contribute good reactant selectivity and resistance to toxicity. On the other hand, the shell prevents the leaching of the encapsulated metal nanoparticles from the zeolite shell, ensuring the high reusability of the catalyst. Therefore, While the encapsulation of metal species in polycrystalline spheres offers significant benefits in terms of catalytic efficiency, selectivity, and stability, it also presents challenges related to the complexity and scalability of the synthesis process.

2.3 Encapsulation of metal species in hollow zeolite crystals

The vesicular structure of the alveolus, featuring a porous nanovesicle framework, effectively facilitates oxygen and carbon dioxide transport. Inspired by the alveolar architecture, researchers invented hollow zeolites, now extensively utilized across the chemical industry. This hollow zeolite has the advantage of (i) their chemical and hydrothermal stability enhanced by crystalline structure, and (ii) a microporous network which functions as a shape-selective membrane.[19, 24] Dai et al. pioneered a novel approach by creating a hollow nanovesicle assembly incorporating metal-encapsulated hollow zeolite to improve the diffusion of reactants/products while preventing the sintering and leaching of active metals (Figure 5).[33] The metal-infused zeolitic nanovesicle (Fe_2O_3@ZSM-5) was initially synthesized through a one-pot hydrothermal synthesis, followed by a process of selective desilication-recrystallization and leaching-hydrolysis. This method transformed metal-containing solid crystals into metal-encapsulated hollow crystals. The resulting material (Fe_2O_3@ZSM-5) features a hollow crystal wall composed of silicon and aluminium, showing microporosity (0.4–0.6 nm) and a nanovesicle shell enriched with silicon, iron and aluminium, delineating mesoporosity (5–17 nm) with macropores iron oxide cores (approximately 350 nm).

This innovative zeolite structure aids in preventing metal sintering and leaching even at temperature as high as 800 °C during catalysis.

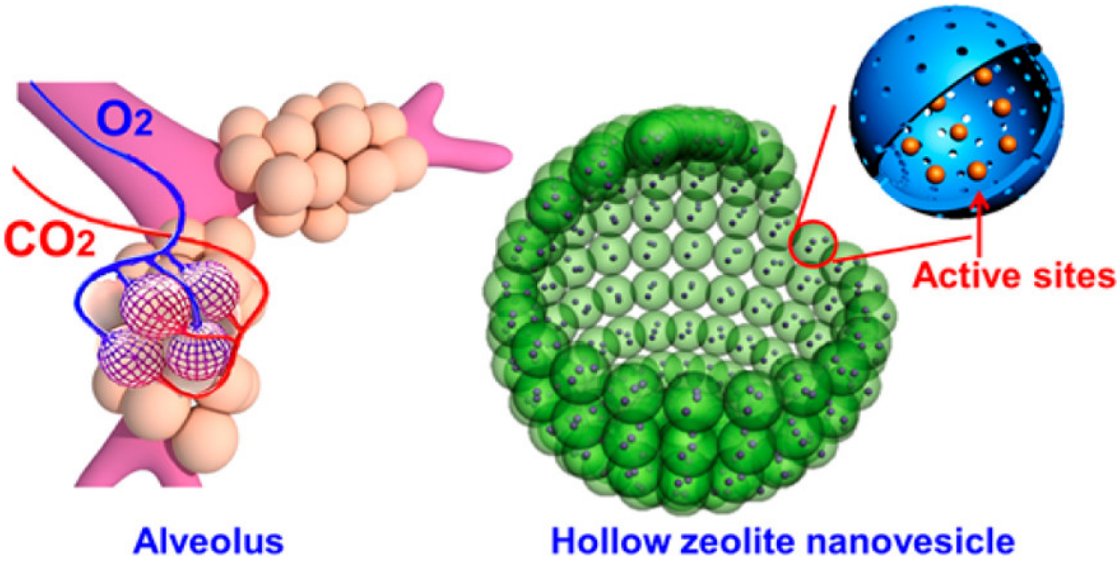


Figure 5. Hierarchical Structures in nature and chemical materials

(Left: vesicular structure of alveolus. Right: hollow hierarchical structure of nanovesicle assembly with metal-encapsulated hollow zeolite nanocrystals.) Reprinted with permission from Ref. [33] . Copyright 2016, American Chemical Society.

In addition, Pt@Hollow silicalite-1,[19] bimetallic nanoparticles (PtNi and Pd-CuO) encapsulated in hollow hierarchical zeolite catalyst,[19, 34, 35] and hollow spherical Co@hsZSM-5@metal dual-layer nanocatalysts,[36] by tetrapropylammonium hydroxide (TPAOH) hydrothermal treatment with an "impregnation-dissolution-recrystallization" strategy has been successfully prepared. The hollow hierarchical PtNi@HS-1 catalyst can show high catalytic activity and selectivity (up to 45) for converting methyl stearate into aviation fuel range alkanes at 360 °C under 3 MPa.[37] The interaction between copper and palladium in the bimetallic (Pd-CuO) catalyst addresses the challenge of Pd nanoparticle loss during TPAOH treatment, facilitating the preparation of multimetallic catalysts with well-dispersed nanoparticles.[19, 37] Moreover, the dual-layer Co@hsZSM-5@Pt catalyst exhibited desired acid catalysis with higher shape selectivity, as shown

by higher C_{2+} hydrocarbon selectivity (up to 46%) in tandem hydrogenation of CO_2 reaction, which have not been observed in catalyst made by conventional method.[36]

2.4 Hierarchical core@shell zeolite-based materials with metallic catalysts as cores and zeolites as shells

Materials based on zeolite with core@shell structure have been developed due to the advantages of stable nanoparticles and mitigating particle sintering. Prech et al. introduced a synthetic strategy for the preparation of hierarchical zeolite - metal nanocomposite catalysts (Figure 6).[38] Initially, the parent (core) zeolite is etched with an ammonium fluoride solution, creating mesopores within the zeolite crystals. Subsequently, Ru nanoparticles, formed via a water-in-oil microemulsion technique, are embedded within these mesopores. In the final stage, MFI-type zeolites (such as silicalite-1 or ZSM-5) are grown over the parent zeolite crystals, coating both the etched surface and the metal nanoparticles, thus encapsulating the Ru nanoparticles with the size of 3-20 nm completely within the zeolite matrix.

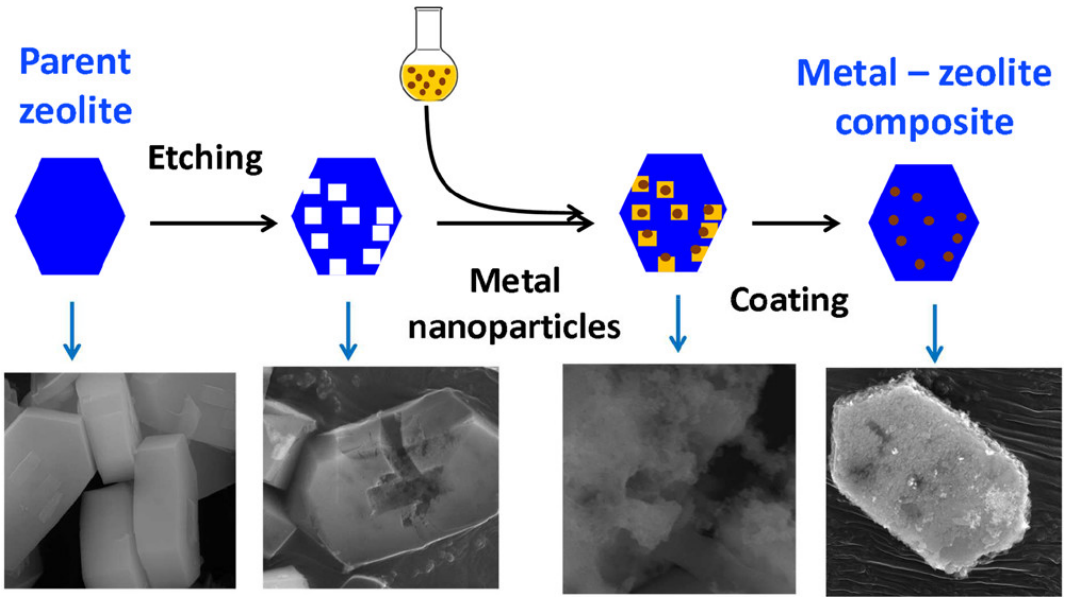


Figure 6. Synthesis process of Ru@ZSM-5 catalyst. Reprinted with permission from Ref. [38]. Copyright 2020, American Chemical Society.

Typically, core-shell structural materials comprise a porous shell and a catalytically active metal core. Iron, cobalt, and palladium-based cores are most prevalent.[39, 40] Enhancing the shell design can significantly improve the catalyst's efficiency. The Pd@S-1 catalyst, synthesized via a one-pot method can perform the methane combustion reactions in terms of both water vapor resistance and temperature tolerance below 700 °C. This improvement is largely attributed to the hydrophobic nature and strong confinement effect of the all-silica silicalite-1.[39] Furthermore, Xu et al discovered that the zeolite shell thickness of the Co@HZSM-5 core-shell catalyst can be easily controlled by adjusting the hydrothermal synthesis duration. Experimental findings revealed that the catalyst treated hydrothermally for four days optimized for gas-phase Fischer-Tropsch synthesis (FT_S) achieved a gasoline fraction selectivity of 79% at 250°C.[40] Similarly, Sun et al. managed to modify the HZSM-5 shell thickness from 1.3 μm to 9.7 μm by extending the hydrothermal period from 2 d to 8 d.[41] As hydrothermal time increases, the thickness of the zeolite shell also increases, leading to a larger specific surface area of the catalyst and a significant increase in the number of acidic sites on the catalyst. The Fe@HZSM-5 catalyst, treated hydrothermally for four days, exhibited the greatest CO conversion rate of 92% and gasoline fraction selectivity of 71% in the FT_S reaction using syngas with the H_2/CO molar ratio of 2 at 543 K. Thus, a zeolite shell of appropriate structure can significantly enhance the catalyst's lifespan and productivity.

The development of core-shell nanostructures with controllable size, shell thickness, surface morphology, and composition has significantly improved the catalytic performance of precious metal catalysts and expanded their potential for engineering applications. However, these core-shell structured materials are inherently metastable and may fail due to the leaching or migration of core-shell metal elements during the catalytic reaction cycle. This instability can cause the active surface area and catalytic performance to decrease rapidly over time, severely limiting the widespread use of core-shell structured catalysts in the industrial field. In industrial applications, the

stability of material performance is crucial. Continuous research and optimization are essential to overcome these challenges and fully realize the potential of this method in industrial applications.

2.5 Yolk–shell metal-encapsulated zeolite-based materials

Yolk-shell structured materials combine the features of hollow and core-shell materials to produce distinctive properties that are primarily the result of synergistic interactions between two or more materials. The yolk-shell structure means metal-zeolite composites obtained have the structure of a large zeolite shell enclosing a single metal particle inside.[42] One of the most common methods for preparing yolk-shell structured materials is the dissolution–recrystallization (DR) technique, as shown in Figure 7. Tuel et al. used this method to encapsulate Pt and Au nanoparticles within hollow zeolites with MFI structures, particularly in S-1.[43, 44] That is, metalates were impregnated into the parent zeolites, and the material and the material underwent secondary crystallization again in a TPAOH solution. During this process, the metal particles (Pt and Au nanoparticles) that remain aggregate into nuclei, thereby creating cavities within the zeolite interior. The DR strategy has been demonstrated to be one of the most effective and straightforward methods for encapsulating metal nanoparticles to date.[28] Using this method, Au@silicalite-1 demonstrates isolated Au nanoparticles with excellent size control below 10 nm and a narrow distribution. Moreover, the Pt@S-1 catalyst in the yolk-shell structure contributes to the high metal dispersion maintained during the reaction for selective oxidation of CO over C_3H_6, which results in turnover frequencies (TOFs) that are eight times higher for Pt@S-1 than for Pt/S-1 at 280°C.

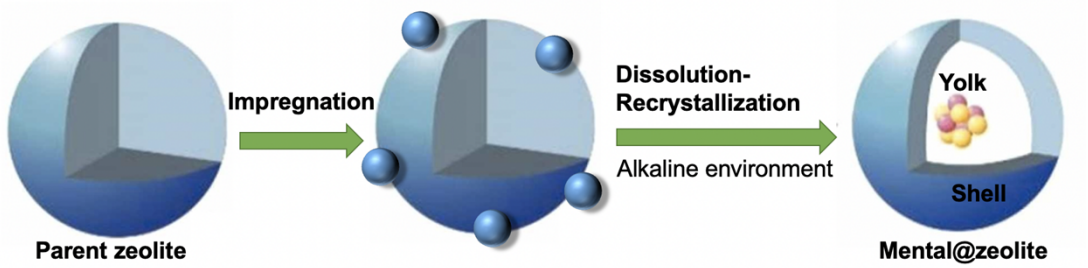


Figure 7. Schematic diagram of synthesizing yolk-shell structured mental@zeolite catalyst by dissolution-recrystallization method.

Beyond noble metals, transition-metal like Co, Ni, and Cu have been utilized to develop yolk-shell zeolite-based materials.[45, 46] Unlike noble metals, these common metals leave no particles within the interior cavities after treatment with TPAOH or Na_2CO_3 treatment. Transition metal cations react with silica species to generate phyllosilicates, which appear as elongated threads covering the interior surface of hollow crystals when dissolved at alkaline pH values. Nanoparticles are generated only following high-temperature reduction of these phyllosilicates, with a size and quantity that varies depending on the desilication process. It was possible to generate thin zeolite shells with more than 20 wt% Co in the form of regular particles of 10 - 15 nm when desilication was performed using Na_2CO_3. In the hydrogenation of substituted benzene, Ni particles in hollow silicalite-1 demonstrated excellent size selectivity, similar to Pt.

The yolk-shell structure offers several significant advantages. The distinct combination of a large zeolite shell and a metal core provides excellent protection against sintering and leaching of metal nanoparticles, thereby enhancing the stability and durability of the catalysts. This structural configuration also allows for fine control of metal particle size and dispersion within the zeolite, leading to improved catalytic performance and selectivity. However, challenges remain in this field. Firstly, the synthesis of core/yolk-shell nanoreactors generally involves layer-by-layer assembly and etching methods,

which significantly increase complexity and cost, limiting industrial applications. Additionally, yolk-shell nanoreactors have mostly been used in gas-phase heterogeneous tandem reactions in recent years, leaving more extensive fields awaiting exploration.

2.6 Fish-in-hole metal-encapsulated zeolite-based materials

Positioning metal nanoparticles in the traps of the solid support is known as the "fish-in-hole" technique. This method is instrumental in creating sinter-resistant materials through metal encapsulation. The technique success hinges on selecting a zeolite rich in cavities as the support. This setup ensures that metal precursors predominantly gather in these cavities, subsequently undergoing self-reduction to form metal nanoparticles within the zeolite crystal traps.[47, 48] These are identified as fish-in-hole structures because the metal nanoparticles are primarily localized within the various cavities (metal@zeolite, Figure 8), effectively preventing the nanoparticles from sintering by keeping them separate. Xiao and colleagues used this “fish-in-hole” method to situate Pd nanoparticles within the mesopores of zeolite crystals.[47] The concentration of Pd precursors was optimized in the traps, leading to the self-reduction of these precursors and the formation of Pd nanoparticles within the zeolite crystal traps. The naming of these structures as fish-in-hole (FIH-Pd@zeolite) reflects the fact that almost all Pd nanoparticles are confined within various traps, with the zeolite framework acting as a barrier to prevent the nanoparticles from sintering.

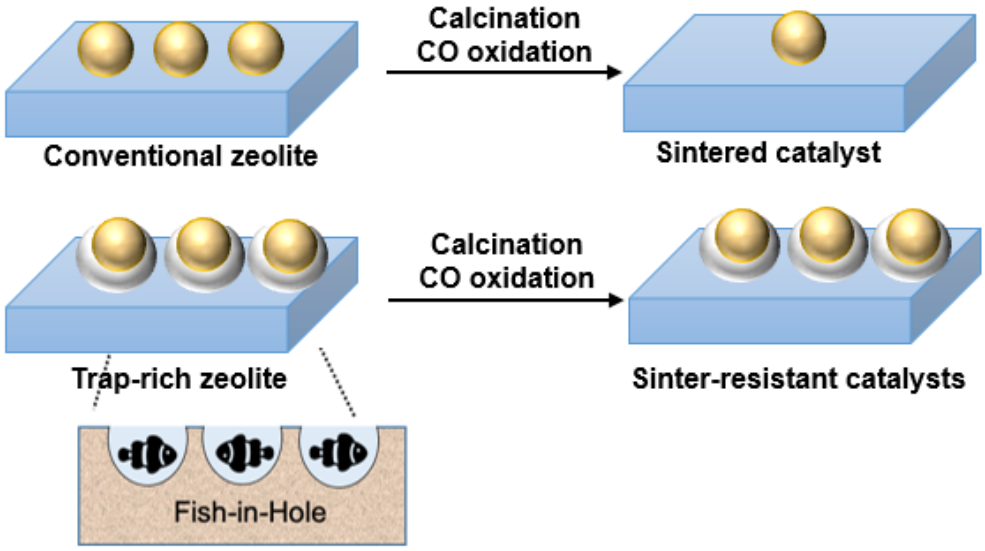


Figure 8. Design and synthesis of sinter-resistant catalysts by rationally positioning metal nanoparticles in the traps of zeolite crystals as a fish-in-hole distribution.

The development of zeolites abundant in traps is typically a result of nitric acid dealumination etching. Zou et al. delved into the effects of pore structures on the efficiency of catalytic oxidation of toluene.[49] They innovated by creating a ZSM-5 foam with polyurethane foam templates, as well as a version of this foam (ZF-D) that was further refined through acid etching to modify its pores. Platinum (Pt) nanoparticles were then applied to ZF-D using the wet impregnation method. Their research, employing IGA and toluene-TPD analysis, indicated that the distinct graded porous structure of Pt/ZF-D significantly improved the diffusion rate of toluene. With a Pt loading of 1%, the toluene conversion reaction reached a 90% conversion rate at only 148°C. Additionally, the TGA curve method was used to assess coke formation, revealing that Pt/ZF-D exhibited a minimal weight loss of only 2.3% between 300-900 °C. The study showed the importance of graded pore modification through acid etching, and this kind of strategy that features metal nanoparticles in fish-in-hole structured catalysts, promising for future industrial catalytic applications.[49]

3. Methods for demonstrating metal nanoparticles encapsulated in hierarchical zeolite

The encapsulation of metal nanoparticles within hierarchical zeolites has become a focal point of research due to its potential to significantly enhance catalytic performance. Various innovative synthetic strategies have been developed to achieve precise incorporation of metal species into zeolite frameworks, each offering unique advantages and facing specific challenges. These methods aim to optimize the distribution, stability, and activity of metal nanoparticles, while also addressing issues related to scalability and industrial applicability. The following sections will detail some of the most notable techniques used for the encapsulation of metal nanoparticles within hierarchical zeolites, highlighting their respective benefits and limitations (Table 2).

Table 2. Comparison of different synthetic methods for metal@zeolite catalyst

Synthetic strategy	Advantages	Limitations
One-pot method	- Convenient method	- Narrow synthesis conditions - Challenges in achieving high metal loading - Difficulties in scaling up for industrial applications
Ligand-protected method	- Prevents sintering of metal nanoclusters - Facilitates formation of subnano metal clusters	- High pH levels can cause precipitation of bulky hydroxides - Complex synthesis process requiring precise control
Inter-zeolite transformation	- Prevents premature precipitation of metal precursors	- Complex transformation process

	- Milder conditions and shorter synthesis time - Broad applicability for various metals and zeolites	- Precise control over synthesis conditions required - Scalability challenges - Limited flexibility with specific parent-daughter zeolite pairs
Dry-gel conversion method	- Reduces water usage - Simplifies operating process - Mild synthesis conditions	- Precise control over synthesis parameters required - Challenges in scaling up for industrial applications
Seed-directed growth technique	- Reduces cost and environmental impact - Rapid crystallization - High-quality zeolite synthesis without organic templates	- Complex and time-consuming seed preparation - Uniform distribution of seeds required - Challenges in scaling up for industrial applications
Post-synthetic recrystallization method	- Short crystallization time - Enhances diffusion of reactants/products - High metal loading - Broad applicability for various metals and zeolites	- Complex multi-step process - Precise control required - Challenges in scaling up for industrial applications - Ensuring complete encapsulation and uniform distribution of metal nanoparticles
Nanobox-encaged method	- Formation of bimetallic particles - High stability even under extreme	- Metal clusters may aggregate into larger particles

	conditions	- Poor dispersion at high metal loadings - Complex synthesis process- High production costs
Atomic layer deposition (ALD)	- Uniformly sized metal nanoparticles with excellent dispersion - Enhanced catalytic activity and selectivity - Modifies zeolite properties	- Time-consuming process - High cost and complexity of ALD equipment and precursor materials - Ensuring complete removal of by-products is crucial - Limited applicability for large-scale industrial production

3.1 *In situ* encapsulation of metal nanocatalysts in hierarchical zeolites

A one-pot encapsulation approach has been employed to incorporate metal nanoparticles within hierarchical (macro/microporous) Linde type A (LTA) zeolite.[50] This technique is accomplished through a direct transformation, eliminating the need for organic structure-directing agents or pre-formed seeds. The process involves an *in situ* dissolution-crystallization mechanism, illustrated in Figure 9, where mesoporous silica particles act simultaneously as a silica source and a template for space creation. This method successfully generated multi-hollow zeolite nanoreactor crystals with encapsulated metals, particularly when the initial mesoporous silica particles were pre-loaded with metal precursors. For instance, a simple one-pot method for encapsulating Pd nanoparticles within hierarchical MFI zeolite (Pd@mnc-S1), using silica nanoparticles and chloropalladic acid has been reported.[27] Chen et al. have reported encapsulating Pd nanoparticles in mesoporous silicalite-1 nanocrystals. The resultant

Pd@mnc-S1, with its distinctive nanostructure and porosity, demonstrates high stability and shape selectivity. This is evident in its consistent yield of 4-methoxybiphenyl, which remains around 93% across 15 reaction cycles in C–C coupling reactions. Additionally, Pd@mnc-S1 effectively reduces the formation of side products in the oxidation of benzyl alcohol by preventing the larger by-product benzyl benzoate from forming, due to its size exceeding the pore dimensions of silicalite-1. Furthermore, *in situ* encapsulation of small-sized noble metal nanoparticles within mesoporous TS-1 zeolite through direct hydrothermal treatment,[24, 25] along with solvent-free *in situ* synthesis of hierarchical Co-based zeolite,[15, 51-53] have been realized. These advancements aid in stabilizing reactions and enhancing the selectivity toward the desired product in high-temperature hydrogenation reactions.

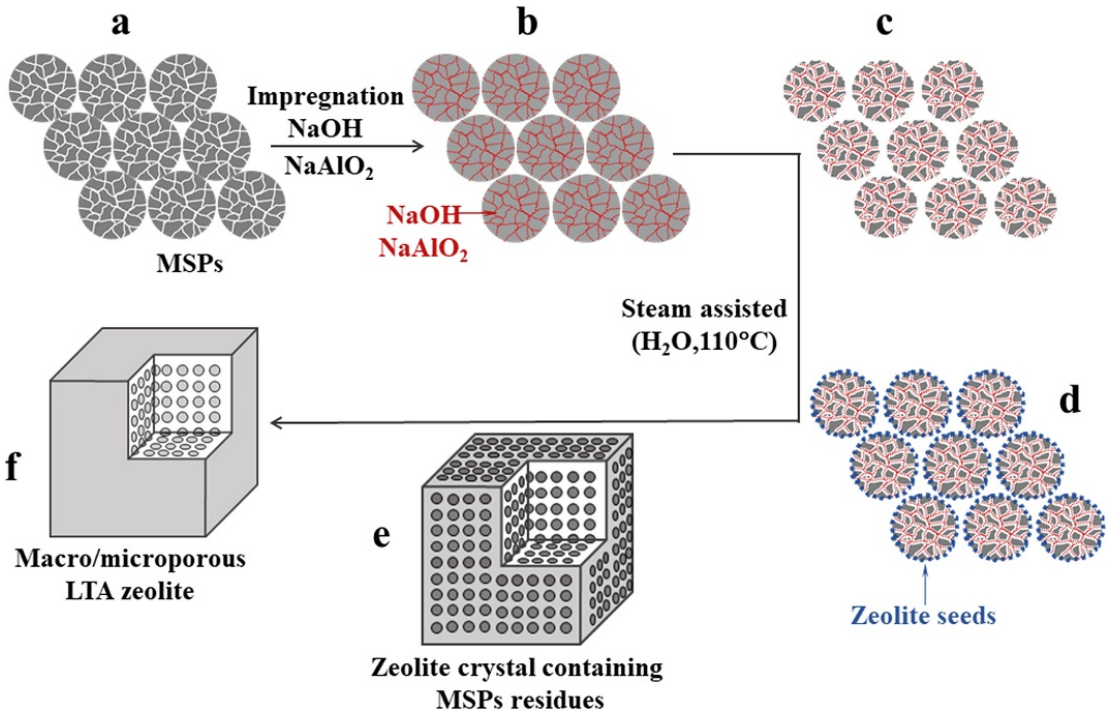


Figure 9. One-pot encapsulation approach for metal nanoparticles in hierarchical (macro/microporous) LTA zeolite. Reprinted with permission from Ref. [50]. Copyright 2020, Microporous and Mesoporous Materials.

The *in situ* encapsulation method offers several advantages, including the uniform distribution of metal nanoparticles within the zeolite framework, which is crucial for achieving high catalytic activity and selectivity. For example, the synthesis of Pt@ZSM-5 using a one-step hydrothermal method results in a homogeneous distribution of platinum nanoparticles within the ZSM-5 framework, enhancing its catalytic performance in benzene methylation reactions.[54] Additionally, the encapsulation of metal nanoparticles within the zeolite pores protects them from sintering, as seen with Au nanoparticles in hierarchical Y zeolite, which exhibit high stability against sintering during catalytic oxidation reactions. Hierarchical zeolites, with their dual-pore structure, offer improved mass transfer properties, facilitating the diffusion of reactants and products, leading to better catalytic efficiency, as demonstrated by Fe@MFI zeolites in the Fischer-Tropsch synthesis. Moreover, the synthesis process allows for the precise tailoring of the microenvironment around the metal nanoparticles, optimizing interactions between the metal sites and the reactants, as shown by Rh nanoparticles in MWW zeolite performing excellently in CO_2 hydrogenation.

However, the *in situ* encapsulation process can be complex and requires precise control over synthesis conditions such as temperature, pH, and precursor concentration to ensure the successful incorporation of metal nanoparticles. For example, synthesizing Fe@MFI zeolite requires careful control of the pH and temperature during the hydrothermal process to achieve uniform dispersion of Fe nanoparticles[55]. Achieving high metal loading without compromising the structural integrity of the zeolite can also be challenging, with high loading levels often leading to the formation of large metal particles outside the zeolite framework, as seen with Ru in hierarchical ZSM-5[56]. Additionally, during catalytic reactions, especially in liquid-phase conditions, there is a risk of metal leaching from the zeolite framework, which can lead to loss of catalytic activity and contamination of the products, such as Cu nanoparticles in ZSM-5 zeolite[57]. Scaling up the *in situ* encapsulation process for industrial applications can also be

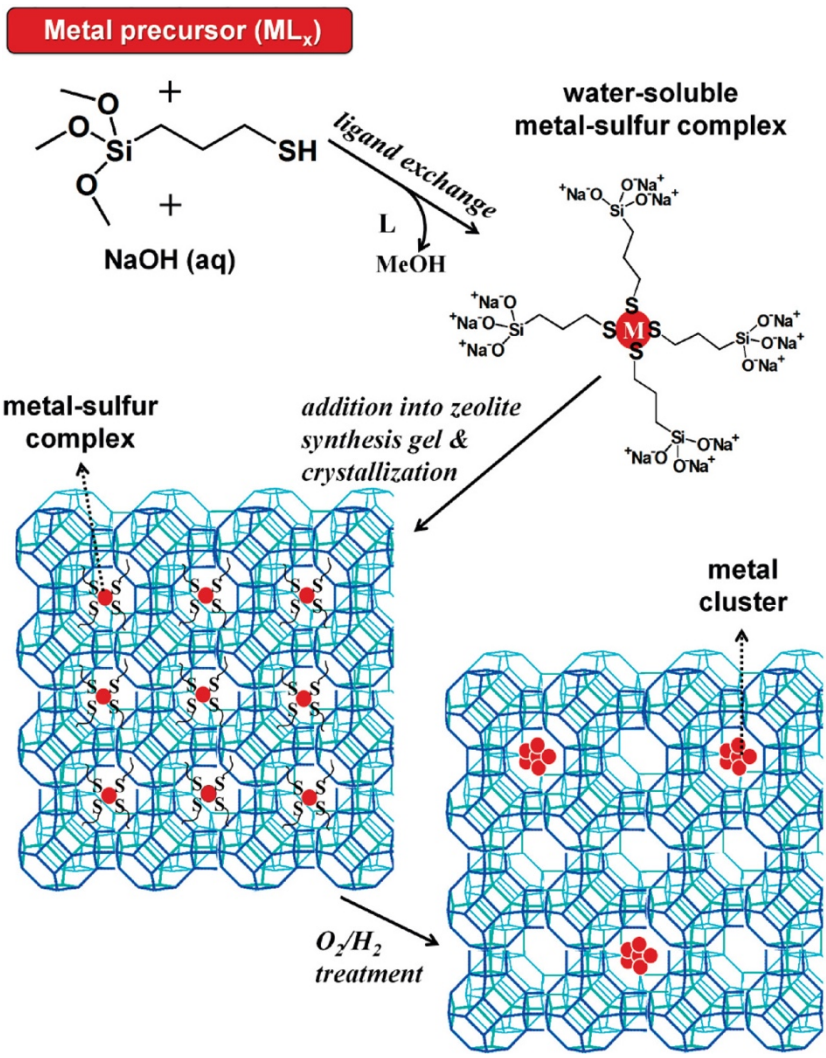
difficult, as maintaining the same level of control and uniformity in larger batches is a significant challenge.

3.2 Ligand-protected method

A series of small noble mono-/bimetal nanoclusters (1–2 nm) have been successfully introduced into the microporous cavities of various aluminosilicate zeolites using a ligand-protected method. This approach utilizes ligand-stabilized metal precursor such as $[Pd(NH_2CH_2CH_2NH_2)_2]Cl_2$ (DEAP), to effectively prevent the sintering of metal nanoclusters during the conventional calcination-reduction process, resulting in the formation of subnano metal clusters. Yan et al. demonstrated that zeolite-encased metallic catalysts could facilitate highly efficient CO_2-mediated hydrogen storage and release. Utilizing direct hydrothermal conditions, $[Pd(ethylenediamine)_2]Cl_2$ and (Mn-tetraethylenepentamine)Cl_2 complexes were used as precursors to embed sub-nanometer bimetallic Pd-Mn clusters into silicalite-1 zeolites. Through extended X-ray absorption fine structure (EXAFS) and scanning transmission electron microscopy (STEM) characterization, confirmed the full encapsulation of the sub-nanometer metal species within the zeolite matrix. The rate of formate formation during CO_2 hydrogenation over the PdMn@S-1 catalyst reached 526 and 2151 $mol_{formate}\ mol_{Pd}^{-1}\ h^{-1}$ at 298 and 353 K, due to the ultrasmall metal clusters and synergistic effect between Pd and Mn components that led to the formation of electron-enriched Pd surfaces.[58] In addition, the group of Yu also encaged bimetallic Pt-Zn within S-1 catalysts using a ligand-protected direct hydrogen reduction method. These Pt-Zn@S-1 catalysts exhibited a 99.3 % propylene selectivity at 550 °C.[59] Among them, the method of ligand-protected direct hydrogen reduction[59] obtained good results.

However, in ligand protection methods, direct hydrothermal synthesis without hydrogen reduction fails to encapsulate metal precursors successfully. This is since direct encapsulation of metal precursors during hydrothermal synthesis involves the introduction of solubilized cationic complexes into aluminosilicate gels and the assembly of zeolite structural units around such substances promoted by electrostatic or van der Waals interactions at the high pH values. At these pH levels, many cationic

precursors precipitate as bulky hydroxides in the alkaline medium necessary for zeolite crystallization, resulting in colloidal particles too large for encapsulation. For solving this problem, Lglesia et al. reported a novel method for directly encapsulating metal nanoparticles into zeolite with LTA structure without H_2 reduction (Scheme 1).[8] This method employs bifunctional ligands, specifically (3-mercaptopropyl)trimethoxysilane, which stabilize the metal precursors against precipitation and promote the condensation of silicate structures around the ligated precursors can be used. These ligands bind to late transition metals via the mercapto group (-SH) to form stable metal-sulfur adducts through ligand exchange, preventing the formation of bulk metal hydroxides even at high pH levels required for zeolite synthesis.[60] The alkoxysilane molecules of the mercaptosilane ligands undergo hydrolysis in alkaline environments, creating covalent Si-O-Si or Si-O-Al bonds with nucleating zeolite structures and ensuring encapsulation during zeolite crystal growth.[8, 61] This dual-function ligand approach leads to the selective and quantitative encapsulation of many catalytically relevant metals (such as Pt, Pd, Ir, Rh, and Ag) during hydrothermal zeolite crystallization, according to structural and functional characterization data.



Scheme 1. Process for mercaptosilane-assisted metal encapsulation during zeolite crystallization in a schematic. Reprinted with permission from Ref. [8]. Copyright 2010, American Chemical Society.

3.3 Encapsulation of metal nanocatalysts in hierarchical zeolites by inter-zeolite transformation

When the initial framework is heated under appropriate conditions, an inter-zeolite transformation can happen, allowing one type of zeolite to rearranged into another. This alternative method of zeolite production is favored because it prevents the premature precipitation of metal precursors as colloidal oxyhydroxides at the high pH and temperatures necessary for hydrothermal zeolite crystallization.[62, 63] Additionally, compared to the conventional procedure, this approach can be executed under milder

conditions and/or within a shorter synthesis time.[64] Iglesia, Zones, and collaborators pioneered the use of inter-zeolite transformation for encapsulating Pt, Ru, and Rh clusters within ZSM-5, starting with Beta or Y as the parent zeolite.[65, 66] They achieved encapsulation by embedding metal clusters into parent zeolites formed under milder circumstances (parent structure), then exposing the sample to conditions that transform the parent zeolite into the desired daughter structure, thereby preserving the encapsulation.[65] This process involved exchanging cationic metal precursors into a parent zeolite (BEA, FAU), reducing them with H_2 to form metal clusters, and then transforming these zeolites into daughter structures with higher framework density (MFI) under hydrothermal conditions (Figure 10). This encapsulation within MFI was confirmed through X-ray diffraction, electron microscopy, and H_2 chemisorption measurements.

Additionally, Goel et al. utilized this method to encapsulate noble metals (Pt, Pd, Ru, and Rh) within ANA zeolites.[7] They began by preparing small-pore zeolites (SOD and GIS) via direct hydrothermal synthesis, then synthesized ANA-encapsulated clusters from metal-containing GIS analogues through post-synthesis recrystallization. This approach not only prevented the decomposition or precipitation of metal clusters as colloidal hydroxides during hydrothermal synthesis at 380 K but also facilitated interactions between metal precursors and the forming aluminosilicate nuclei during the assembly of the microporous frameworks. The resulting metal cluster-encapsulated ANA zeolite catalysts proved to be effective for selective hydrogenation-dehydrogenation reactions, while protecting the active surface from large organosulfur toxins.

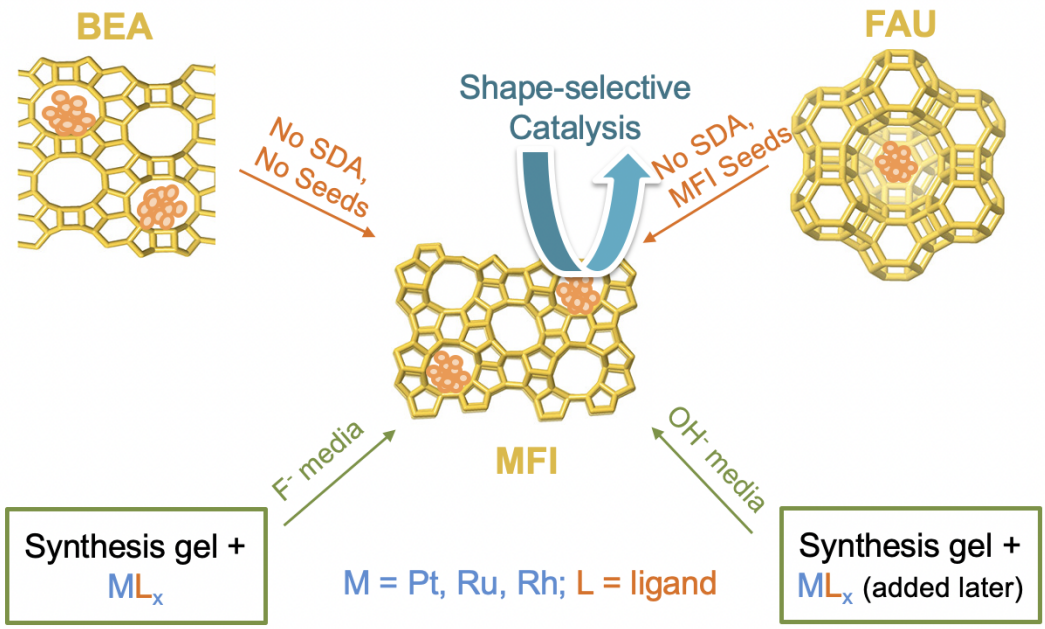


Figure 10. The process of metal encapsulation in zeolite via direct hydrothermal synthesis. Reprinted with permission from Ref. [65]. Copyright 2014, American Chemical Society.

The inter-zeolite transformation method offers several notable advantages. One major benefit is the ability to prevent the premature precipitation of metal precursors as colloidal oxyhydroxides, which is a common issue at the high pH and temperatures required for hydrothermal zeolite crystallization. This method also allows the encapsulation process to occur under milder conditions and within a shorter synthesis time than traditional methods. However, there are also some disadvantages associated with this method. The complexity of the transformation process requires precise control over synthesis conditions to ensure successful zeolite transformation and encapsulation of metal nanoparticles. Additionally, the scalability of this method for industrial applications can be challenging due to the need for controlled transformation conditions and the potential for variations in the final catalyst properties. The requirement for specific parent and daughter zeolite pairs also limits the flexibility of this method, potentially reducing its applicability to a broader range of zeolite types and metal

combinations. Finally, ensuring the complete transformation of the parent zeolite to the desired daughter structure while maintaining the encapsulation of metal nanoparticles can be difficult, requiring detailed characterization and optimization.

3.4 Dry-gel conversion method

The dry-del conversion (DGC) method has become an effective and popular method for the synthesis of zeolites due to its advantages of increasing yield, reducing water usage, simplifying the operating process, maintaining the consistency of the xerogel composition structure, and achieving mild synthesis conditions.[67, 68] Compared with traditional hydrothermal methods, the DGC method can be performed under milder conditions and can sometimes even shorten the synthesis cycle, which helps protect reactants and products while reducing energy consumption. Due to the reduced use of water and simplified synthesis process, the DGC method has less impact on the environment and is more in line with the principles of green chemistry.[69]

Ding's group used the DGC method to encapsulate Pt nanoparticles within ZSM-5 zeolites. The encapsulation process entails two steps. Initially, hierarchical micro-mesoporous ZSM-5 zeolite was produced via alkali treatment, with Pt primarily deposited within the pores (Figure 11).[20] Subsequently, this Pt-enriched alk-ZSM-5 (denoted as Pt/alk-ZSM-5) is dispersed in a Silicalite-1 synthesis gel. This not only fills the larger voids in the alk-ZSM-5 but also creates a silica coating that encases the Pt nanoparticles within the zeolite. This coating is preserved through the preparation of the dry gel, culminating in the production of various Pt-encapsulated MFI zeolites with differing Pt levels through steam-assisted crystallization. These products are characterized by their high thermal stability and have proven to be highly effective in size-selective hydrogenation reactions.

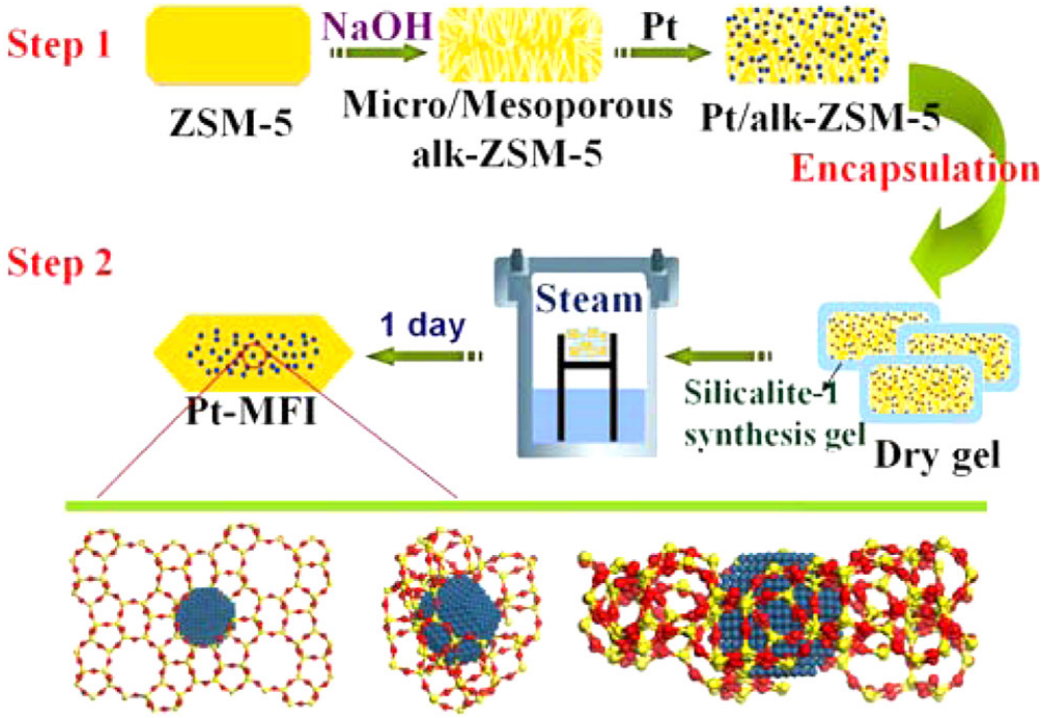


Figure 11. Dry-gel conversion method for encapsulating Pt nanoparticles in hierarchical micro-mesoporous ZSM-5 zeolite. Reprinted with permission from Ref. [20]. Copyright 2015, American Chemical Society.

Also, zeolites with BEA structure were prepared using the DGC method. This approach enables the synthesis of zeolite BEA with SiO_2/Al_2O_3 ratios ranging from 30 to infinity, utilizing tetraethylammonium hydroxide (TEAOH) as a structure-directing agent.[70] In addition, the group of Wei demonstrated that an active Sn-BEA catalyst can be directly synthesized in a non-fluoride medium using the DGC method with the aid of seed crystals. They found that seeding zeolite BEA crystals promotes crystal growth, leading to the development of BEA topology with framework-incorporated Sn.[71]

Although the DGC has many advantages mentioned above, it still has some disadvantages. The process can be limited by the need for precise control over the synthesis parameters to ensure uniform encapsulation and desired properties of the final product. The method may also face challenges in scaling up for industrial applications, as maintaining consistent quality and performance of the catalysts in larger batches can

be difficult. Additionally, the encapsulation efficiency and the stability of the nanoparticles within the zeolite framework can be influenced by the specific conditions used during the DGC process, requiring careful optimization and characterization. Future research and development efforts should focus on addressing these challenges to fully leverage the advantages of the DGC method for industrial applications.

3.5 Seed-directed growth technique

The utilization of organic templates in zeolite synthesis not only increases the cost of zeolite but also consumes energy and releases harmful gases during the template removal process, which involves burning at high temperatures.[72, 73] Consequently, the most effective solution to these issues is to circumvent the use of organic templates altogether.[74, 75] As a result, the technique of seed-induced crystal growth, which allows for the synthesis of zeolites without any organic templates, has emerged as a favoured approach for producing crystalline zeolite structures naturally.

Several studies have demonstrated the successful synthesis of zeolites rich in aluminium sites and high-silica zeolites using this method. The group of Xiao first showed an organ template-free and rapid method for synthesizing Beta zeolite by adding calcined Beta seeds to the starting aluminosilicate gel without the use of any organic templates.[74] The inclusion of Beta seeds, in the absence of organic templates, not only precisely controls the formation of Beta crystals within the aluminosilicate gel but also significantly reduces the crystallization period. Afterward, the groups of Mintova and Okubo demonstrated the synthesis of aluminium-rich Beta zeolite using the template-containing Beta seeds in the absence of any organic templates.[76, 77] In their research, the crystalline Beta product exhibited Si/Al ratios as low as 3.9 and 5.3. Their successful efforts in utilizing organically structure-directing agent-free zeolite seeds laid the groundwork for developing a completely organotemplate-free, environmentally friendly, and economically advantageous synthesis of high-quality Beta zeolite.

While the seed-directed growth technique provides significant benefits in terms of environmental impact, cost reduction, and product quality, it also presents challenges related to seed preparation and scalability. The initial preparation of high-quality seed crystals can be complex and time-consuming, which may offset some of the time savings gained during the crystallization process. Additionally, the uniform distribution of seeds within the starting gel must be carefully controlled to ensure consistent crystal growth and final product quality. Scaling up this method for industrial applications may pose challenges, as maintaining the uniformity and quality of the seeds and the final zeolite product on a larger scale requires precise control and optimization of the synthesis conditions. Addressing these challenges through further research and development can help fully realize the potential of this method for large-scale industrial applications.

3.6 Post-synthetic recrystallization method

Post-synthetic recrystallization is a viable method for creating metal-encapsulated hollow zeolite nanocrystals. Various strategies have been employed, including a top-down dissolution-recrystallization method,[19, 33, 35, 78] an "impregnation-dissolution recrystallization" process,[37] the addition of metal precursors during zeolite synthesis followed by crystallization, calcination, reduction, and a method combining reduction-deposition metal loading with zeolite dealumination.[79] For instance, the synthesis via dissolution-recrystallization involves two main steps (Figure 12). Initially, hollow aggregates of metal-containing zeolite nanocrystals are synthesized through hydrothermal treatment. Secondly, dealuminated Beta (D-Beta) is prepared using a nitric acid leaching technique.[80] Following this, a combined selective desilication-recrystallization and leaching–hydrolysis process is applied to convert the metal -containing zeolites into metal-encapsulated hollow zeolite crystals.[33] The resulting Pd@Beta catalyst exhibited excellent long-term stability, significantly enhanced water resistance, and achieves a high methane conversion over 99% at 375 °C with a space velocity of 30,000 ml $^{-1}$ g^{-1}. This synthesis approach is expected to provide a practical means of developing efficient noble metal catalysts supported by zeolite.

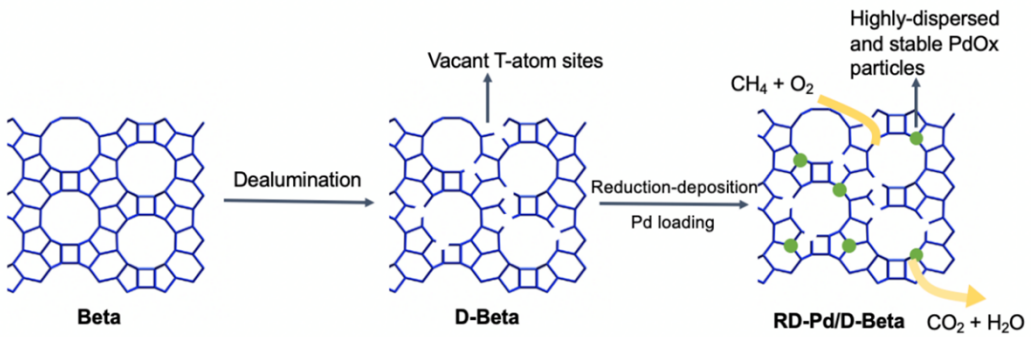


Figure 12. Post-synthetic recrystallization method for positioning Pd nanoparticles in Beta zeolite. Reprinted with permission from Ref. [80]. Copyright 2021, Catalysis Today.

The post-synthetic recrystallization method offers several advantages. One of the primary benefits is the ability to create hollow zeolite structures, which can enhance the diffusion of reactants and products, thereby improving catalytic performance. The method also allows for the precise incorporation of metal nanoparticles within the zeolite framework, leading to catalysts with high stability and resistance to leaching, as demonstrated by the Pd@Beta catalyst excellent long-term stability and water resistance. Additionally, the method is versatile and can be adapted to incorporate various metals into different types of zeolites, providing a broad applicability for the development of efficient catalysts for a range of reactions. However, the post-synthetic recrystallization method also has some drawbacks. The process can be complex and involves multiple steps, including hydrothermal treatment, acid leaching, and selective desilication-recrystallization, which require precise control to achieve the desired product characteristics. This complexity can increase the time and cost of synthesis. Additionally, the method may face challenges in scaling up for industrial applications, as maintaining consistent quality and performance of the catalysts in larger batches can be difficult. Ensuring the complete encapsulation and uniform distribution of metal nanoparticles within the zeolite framework can also be challenging, requiring detailed characterization and optimization. Future research should focus on simplifying the

process and optimizing conditions to make this method more practical for large-scale industrial applications.

3.7 Nanobox-encaged method

A new synthetic approach has recently been developed for producing hollow zeolite microcapsules through dissolution and recrystallization of single crystals. This method was first applied to create MFI (Mobile Five-membered)-structured hollow materials.[81] The technique involves recrystallizing metal-impregnated silicalite-1 to form noble metal clusters encased within MFI zeolite nanoboxes. For instance, individual rhodium (Rh) atoms were encapsulated in both MFI-type silicalite-1 (S-1) and aluminosilicate ZSM-5 zeolites.[82] Furthermore, non-noble-metal clusters and hybrid metal clusters were encapsulated within MFI zeolites using the nanobox-encaged technique. Using a ligand-protected method under hydrothermal conditions, materials such as Ni@silicalite-1 material[83] and sub-nanometer Pd–Mn,[84] Au-Ag, Pd-Ag, Pt-Ag, and Pd-Pt clusters[83] were successfully encapsulated within silicalite-1 (S-1) zeolites. The nanoboxes are unique in that they can act as nanoreactors that enable the formation of bimetallic particles and serve as ultra-microporous shells that provide resistance to sintering through coalescence even under extreme circumstances.[85]

Despite the advantages of this encapsulation technique within zeolite nanoboxes, it also presents several challenges. One significant issue is the tendency for the metal clusters to aggregate into larger particles during the Ostwald ripening process, which is closely associated with the metal loading quantity. High metal loadings often result in poor dispersion and reduced catalytic activity.[86] Therefore, the property amount of loading metal is another key factor when preparing the catalyst. In addition to the complexity of the synthesis process, which can lead to scalability issues and make it difficult to consistently produce large quantities of catalysts, material price and the need for precise control of synthesis conditions can increase production costs. Finally, the encapsulation efficiency may vary, leading to inconsistent catalytic performance across different batches. Addressing these challenges through careful optimization and control of

synthesis conditions can help fully realize the potential of this method for developing high-performance catalysts.

3.8 A general protocol to encapsulate metal nanoparticles into zeolites by atomic layer deposition (ALD)

Atomic layer deposition (ALD) has been employed to create a range of specialized catalysts that exhibit enhanced catalytic efficiency. ALD is a type of chemical vapor deposition in which a series of self-limiting reactions deposit metals, oxides, and other compounds on surfaces. The self-limiting nature of these reactions allows for homogeneous deposits on porous substances with large surface areas.[87, 88] As a result, ALD offers meticulous control over the substrate's structure and composition, the catalytically active sites, and the protective overlayer, facilitating the design and fabrication of advanced nanoscale catalysts.

Among the oxides frequently applied in ALD, alumina and titania are the most commonly observed oxides utilized via the ALD method deposited inside micropores in microporous materials with large aspect ratios and tiny pore diameters, such as zeolites. For instance, Vandegehuchte et al. have discovered that ALD using TMA and water can help to introduce additional alumina into the narrow pores of USY catalyst (Figure 13).[89] The catalysts after modifying can create new and stronger Brønsted acid sites in the zeolite micropores[89]. Similarly, Xu and their team have successfully used ALD to infuse platinum into the channels of KL zeolite.[90] This process, supported by various analytical techniques and DFT simulations, enabled the investigation of platinum's deposition sites and their interaction with the KL zeolite. Notably, this method achieved the deposition of platinum nanoparticles with a precisely controlled size of 0.8 nm and outstanding dispersion within the micropores of the KL zeolite.[91-93]

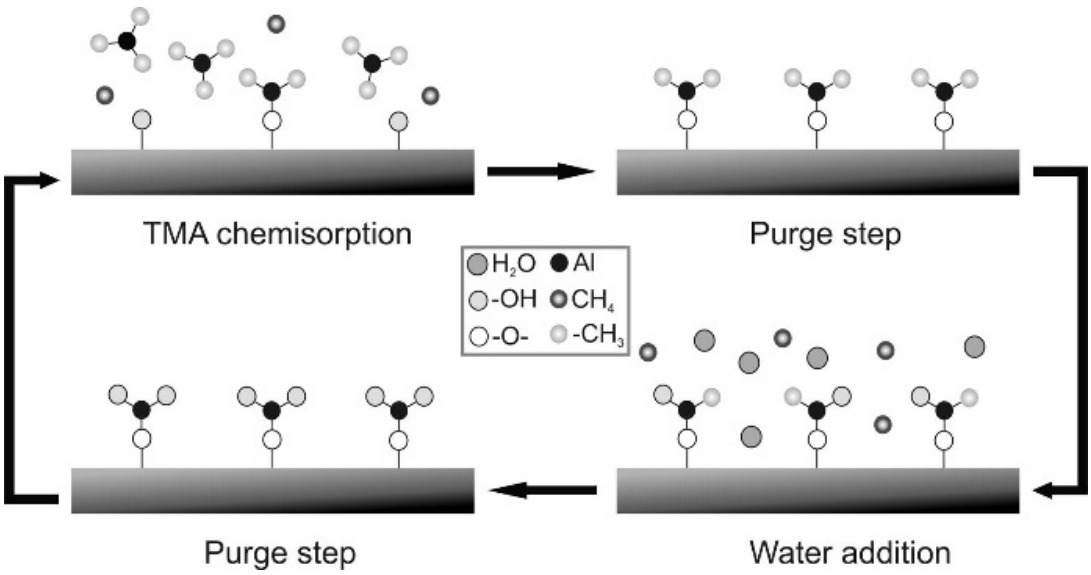


Figure 13. Schematic illustration of an ALD cycle involving consecutive TMA and water treatment. Reprinted with permission from Ref. [89]. Copyright 2014, Journal of Catalysis.

The atomic layer deposition (ALD) method offers several notable advantages. One significant benefit is the precise control over the deposition process, allowing for the creation of uniformly sized metal nanoparticles with excellent dispersion within the zeolite micropores. This precise control leads to enhanced catalytic activity and selectivity. Additionally, ALD enables the modification of zeolite properties, which can further enhance catalytic performance. The method ability to uniformly coat materials with high aspect ratios and tiny pore diameters, such as zeolites, ensures thorough utilization of the catalyst's surface area. However, the ALD method also has some disadvantages. The process can be time-consuming and requires multiple cycles to achieve the desired deposition thickness, increasing the overall synthesis time. Additionally, the complexity and cost of ALD equipment and precursor materials can be high, which may limit the method's applicability for large-scale industrial production. Finally, ensuring the complete removal of by-products from the ALD process is crucial, as any residual contaminants can negatively impact the catalyst's performance.

4. The importance of the metal nanoparticles and hierarchical zeolite structure optimization for enhanced catalytic performance

Improving the performance of traditional zeolite and broadening its application scope is an urgent issue. Combining materials with different pore structures or cavities and encapsulating the metal activate site in the zeolites will help optimize the transport of molecules within the material and provide a wider variety of catalytic sites. Jiesheng et al. encapsulated 2-5 nm Pd nanoparticles inside the hierarchical zeolite of silicalite-1.[27] Confined in the mesopores of the zeolite support, the metal site showed excellent thermal stability, and the dispersion and size were maintained after heat treatment at 550°C. In the catalytic reactions, the silicalite-1 with hierarchical structure effectively increased the mass transfer rate, which led to the high catalytic efficiency of Pd@ silicalite-1; and the unique pore structure of silicalite-1 and the Pd nanoparticle anti-sintering capability due to the confinement effect enabled the catalyst to exhibit excellent shape selectivity and stability in many types of reactions such as hydrogenation reduction, catalytic oxidation and coupling reactions. Due to the high surface energy of metallic single atom site, metal aggregation, and sintering are prone to occur during the catalytic process especially thermal relations with high input of heat energy, resulting in a significant decrease in catalytic performance. Zeolites are considered to be the ideal support for confining the metallic single-atom site, due to their regular micropore structure and excellent thermal stability. With a regular five-membered ring structure, Jihong Yu et al. confined Rh single atoms within the MFI zeolite, which showed excellent shape-selective catalytic performance in the cascade reaction of amine borane hydrolysis coupled with the reduction of nitro compounds, and its catalytic activity is thousand times higher than that of using hydrogen as a hydrogen source under the identical conditions.[82]

With an optimized metal site and hierarchical zeolite support structure, metal loaded hierarchical zeolite catalyst has shown great potential for Fischer-Tropsch (FT) synthesis, which yields hydrocarbons from syngas.[94-96] With Co nanoparticle encapsulated within the pores of hieratical HZSM-5 zeolite (Figure 14),[97] a selectivity

in the gasoline range of 71.6% with a molar ratio of iso-to-n-paraffins of 2.89 have been recorded. Zhang et al. discussed the significant effect of the relationship between the metal site and hierarchical zeolite support on the diffusion restrictions by comparing Co/HZSM-5 (Co on the outmost surface of support) and Co@HZSM-5 zeolites (Co encapsulated within the support).[98] Over-cracking and enhanced long-chain hydrocarbon diffusion time occur in the pores of support when small Co particles are buried deep within the zeolite crystals, resulting in significant undesirable hydrocarbon selectivity. In addition to over-cracking, diffusion constraints may also prevent primary hydrocarbons from reaching the active acid sites within the micropores of zeolite. Adding a second system of mesopores to the crystals can thus greatly enhance transport efficiency in the zeolite frameworks. Wang et al.[98] prepared hierarchical zeolites with tunable mesopore diameters, where Bronsted acid sites have been generated. The mesoporosity of the zeolite served to inhibit the formation of light hydrocarbons, while the Bronsted acidity was essential for the hydrocracking of heavy hydrocarbons. After further loading Co with optimized size (*ca.* 8.4 ± 1.8 nm) on the hierarchical zeolite, they found that the Co/H-meso-ZSM-5 catalyst showed a 70% selectivity to C5-11 hydrocarbons and the catalyst was very stable for over 100 hours continuous FT synthesis. Except for metal nanoparticles, the metal alloy can also be loaded within the hierarchical zeolite and work as a bifunctional catalyst. $ZnCrO_x$ metal alloy oxide loaded SAPO-34 zeolite with hierarchical structure showed up to 94% selectivity for C2-C4 on FT-synthesis.[99] On the outmost surface of the partially reduced $ZnCrO_x$ alloy oxide, the syngas CO and H_2 are absorbed and activated. It was followed by the C-C coupling that occurred on the active acid site within the pores of the zeolite.

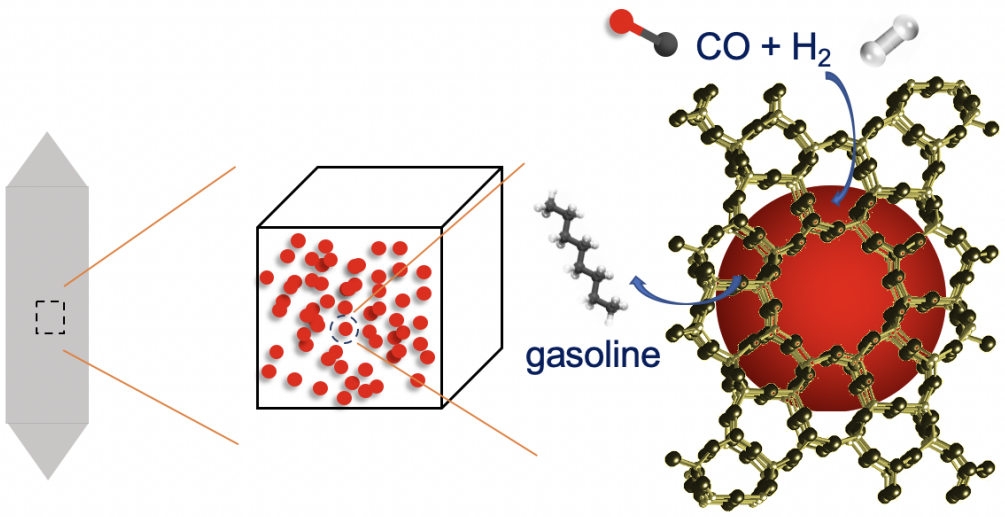
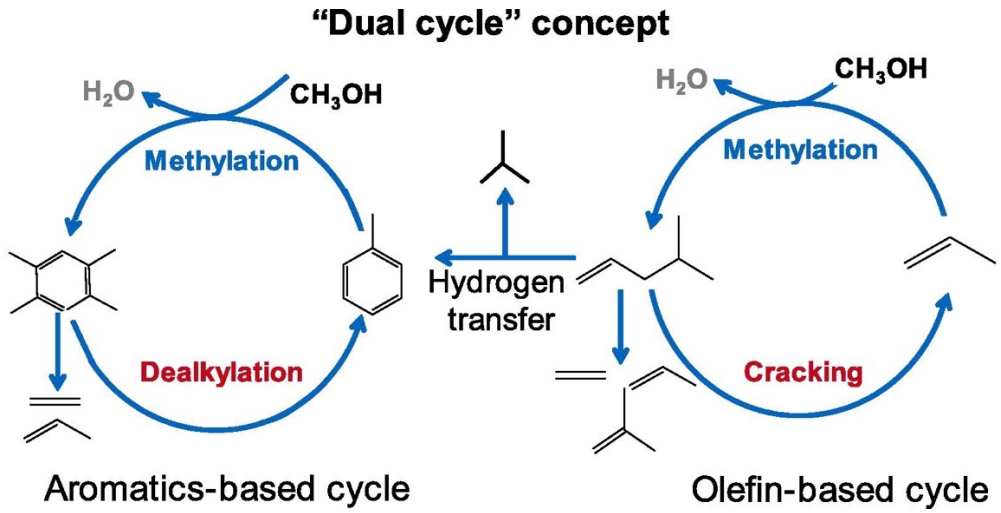


Figure 14. Schematic illustration of the CO and H_2 molecules reacting with the Co particle, which are embedded by the zeolite framework. Reprinted with permission from ref. [97]. Copyright 2013, Royal Society of Chemistry.

Besides, hierarchical zeolite is also commonly used for the methanol-to-olefins (MTO) conversion to produce light olefins based on the Dual-cycle mechanism (Scheme 2).[100-103] Cycle I (Olefin-based cycle) use the alkene cracking/methylation route to primarily produce propylene, butene, and higher alkenes, while Cycle II (Aromatics-based cycle) uses the cracking/methylation of polyalkyl aromatic intermediates to primarily produce ethylene and aromatic compounds. Through cyclization and hydride transfer processes with concurrent hydrogen production, the alkene intermediates of Cycle I were transformed into polyalkyl aromatic intermediates of Cycle II. Although the chemical structure of the MTO intermediate can be controlled by the pore structure and acidity of the zeolite, the product selectivity can hardly be controlled by merely tuning the physical and chemical properties of the zeolite support. Numerous studies showed that the loading of metal can further adjust the chemical properties of the support and provide an extra active site for tunning the selectivity of the MTO reaction. [104-106] For example, by encapsulating the Pt nanoparticle in a zeolite and forming a core-shell structure, dual active sites could be exposed with accessibility to reactants. The acid

sites on the outmost surface of zeolite work as the catalytic active site, while the alkenes hydrogenation occurs on the Pt nanoparticle and contributes to the formation of alkanes. With encapsulated Pt nanoparticle as the core, the catalyst showed enhanced catalytic performance on the MTO reaction. Compared to the Pt/ZSM-5 zeolite, it showed an increase in the alkylation of benzene with methanol activity.[54]



Scheme 2. Proposed "dual-cycle" mechanism in methanol-to-olefins conversion over HZSM-5[102]. Copyright 2014, Journal of Catalysis.

Recently, there has been a growing interest in mental@zeolite structural materials used for FTs and MTO conversion due to their attractive properties. The rational design and synthesis of these materials is crucial, not only as a fundamental challenge for materials science but also as a practical solution for organic transformations and other reactions in modern society. Table 3 below summarizes some typical cases of mental@zeolite structural catalysts mentioned in this chapter and in the past several years to support the above point. The optimization of materials for FT and MTO reactions will play a major role in the future not only in petrochemicals but also in eco-friendly catalytic processes.

Table 3. Summary table of the preparation methods of metal@zeolite structures catalysts using for FTs or MTO conversion in the last several years.

Catalyst name	Structure	Method	Applications	Years	Ref.
FeMn@hollow HZSM-5	Yolk-shell	Dissolution–recrystallization (DR) technique	FTs	2021	[107]
Co@HZSM-5	Hierarchical	Hydrothermal synthesis	FTs	2013	[97]
Fe/Silicalite-1@HZSM-5	Core-shell	*In situ* growth method	FTs	2023	[108]
Fe@HZSM-5	Hollow	Dissolution–recrystallization (DR) technique	FTs	2019	[109]
Zn-Cr@SAPO	Core-shell	Physical encapsulation method	MTO	2020	[110]
Fe@NaY	Hierarchical	*In situ* crystallization	FTs	2021	[111]
Co@silicalite-1	Core-shell	Hydrothermal synthesis	FTs	2018	[112]
Fe@NaY	Hollow spheres	*In situ* crystallization	FTs	2020	[113]
Fe@SAPO-34	Core-shell	Physically adhesive method	FTs	2019	[114]

Pt@ZSM-5	Hierarchical	Dry-gel conversion method	MTO	2017	[54]
Fe@silicalite-1	Hollow	Dissolution–recrystallization (DR) technique	FTs	2023	[115]
Fe@silicalite-1	Hierarchical	*In situ* crystallization	FTs	2018	[116]
Co@HZSM-5	Hierarchical	Hydrothermal synthesis	FTs	2013	[97]
Reney Fe@HZSM-5	Core-shell	One-pot strategy	FTs	2012	[117]
Al-ZSM-5@B-ZSM-5	Core-shell	Hydrothermal synthesis	Methanol-to-propylene	2019	[118]
Co@HZSM-5	Core-shell	Hydrothermal synthesis	FTs	2015	[119]

However, because the metal active site might be located on the pores of hierarchical zeolite and show spatial proximity to the surface acid site on zeolite which leads to a decrease in the acidity, it is still challenging to adjust the number of surface acid sites independently in metal-loaded zeolite.[120, 121] In a water-in-oil microemulsion solution, Tago et al successfully prepared hieratical ZSM-5 catalysts with encapsulated Ru nanoparticles. Most importantly, by the special method of encapsulating Ru nanoparticles in the amorphous silica and then transfer to zeolite, they managed to separately adjust the quantity of metal site and acid site.[12] They found that not only the

variation in Ru concentration give limited variation in the Ru nanoparticle size within the pores of zeolite, but also the metal site has little interaction with the acid site, demonstrating that the metal site and acid site were spatially separated. Compared to ZSM-5, the Rh@ZSM-5 catalyst showed higher propylene and butene yields. The methanol decomposition occurred over the Rh metal site producing hydrogen and the methanol to olefin reaction occurred over the surface acid site with strong acidity concurrently during the methanol conversion (Figure 15). The hydrogen produced on the surface of the Rh site further inhibited the production of aromatic intermediates to many ethylene and aromatic compounds.

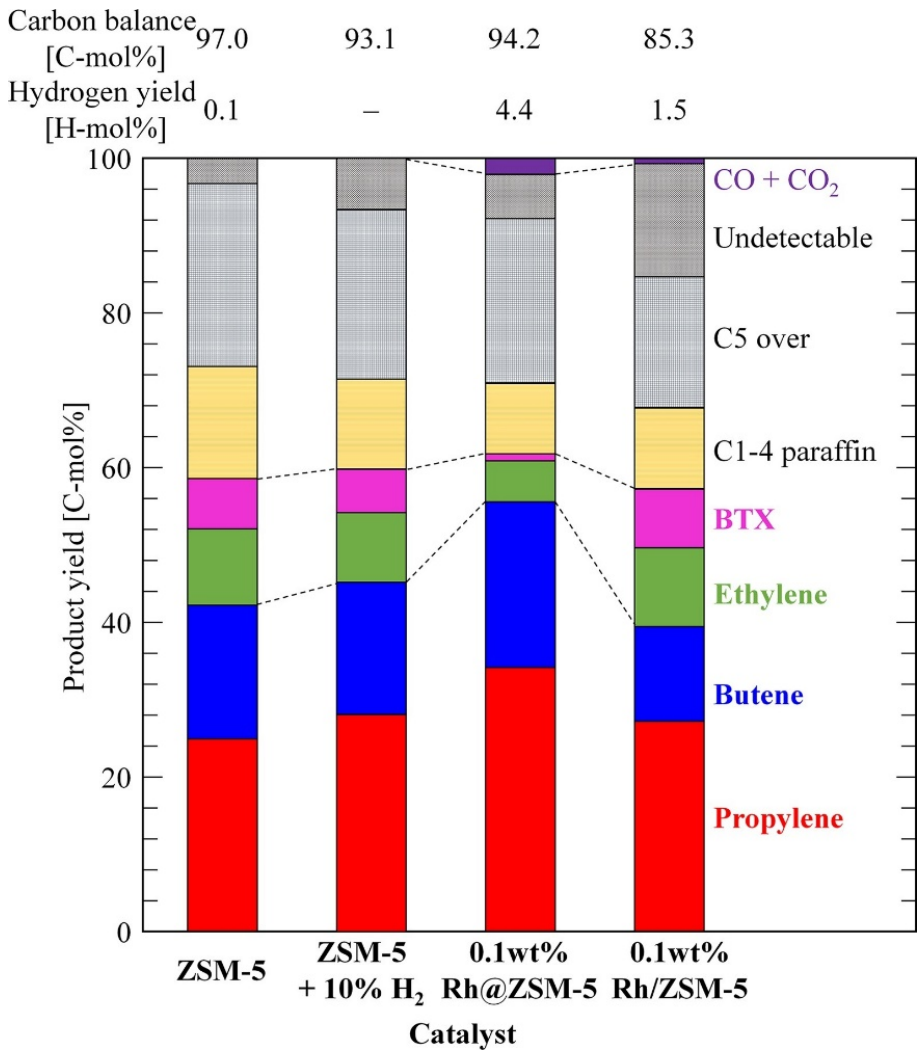


Figure 15. Product yield for the conversion of methanol over ZSM-5, Rh@ZSM-5, and Rh/ZSM5 (450 °C reaction temperature, 5.5 h on stream, and W/F of 0.25 (g-catalyst h)/g-methanol). Reprinted with permission from ref. [12]. Copyright 2021. Catalysis Today.

5. Conclusion and outlook

This paper reviews various types and preparation methods of zeolite-encapsulated metal nanoparticle (MNP) catalysts and their applications in redox reactions. Zeolite-encapsulated metal catalysts combine the high surface area, thermal stability, and tunable porosity of zeolites with the exceptional catalytic properties of metal nanoparticles, forming a versatile and powerful class of solid catalysts. The synergy between these components results in superior catalytic activity, selectivity, and stability, making them highly effective for a wide range of applications, including hydrogenation, dehydrogenation, and oxidation reactions.

Recent advancements in the synthesis and characterization of hierarchical zeolite encapsulated MNPs have significantly expanded their application scope. Innovative synthesis techniques, such as *in situ* encapsulation, ligand-protected methods, and inter-zeolite transformation, have enabled precise control over the size, distribution, and chemical environment of metal nanoparticles within zeolite frameworks. These developments have paved the way for the creation of catalysts with enhanced performance for Brønsted acid, Lewis acid, and metal-catalyzed reactions, as well as tandem reactions.

Developing new encapsulation methods and selecting suitable zeolite topologies to encapsulate specific MNPs can effectively open new directions for future nanocatalytic materials. However, there are still some problems and challenges with zeolite-encapsulated metal catalysts that need further research and resolution. In the following content, we share our perspectives on the challenges encountered with metal-encapsulated zeolites and how to improve and enhance their performance.

5.1 Addressing mass transfer limitations and enhancing sinter-resistance

One of the critical issues in the application of metal-encapsulated zeolite catalysts is the mass transfer limitation imposed by the microporous nature of zeolites. While microporous zeolites have unique channel structures, their small pore sizes restrict the types of reactant molecules that can access the active sites. Encapsulating MNPs in ultra-large pore zeolites or hierarchical zeolites can significantly alleviate mass transfer issues and broaden their application range. However, many ultra-large pore zeolites suffer from low hydrothermal stability and stringent preparation conditions. Improving the hydrothermal stability of these zeolites through methods such as increasing the silicon-germanium ratio via post-treatment (e.g., UV radiation) is a viable solution.[122]

Additionally, Improving the sinter-resistance of subnanometric metal species remains a significant challenge. When the diameter of the encapsulated MNPs is smaller than the zeolite's pore size, metal migration, aggregation, or sintering can occur under harsh conditions, leading to pore blockage and diffusion inhibition. This issue is mainly due to weak interactions between the zeolite framework and MNPs, as well as the high surface energy of MNPs. Potential solutions include enhancing spatial confinement interactions and constructing coordination interactions between metal species and zeolite frameworks are promising strategies. Locating metal species in positions with strong spatial confinement effects, such as 5-membered or 6-membered rings, can prevent sintering. Moreover, creating chemical, electrostatic, or van der Waals interactions between metal sites and zeolite frameworks enhances stability. Exploring the role of silanol defects, which can be controlled in layered and mesoporous zeolites, can lead to the development of robust catalysts. Engineering zeolite structures to enhance interaction with metal species and developing strategies based on silanol defect engineering are key research directions.

5.2 Reducing costs and enhancing efficiency

Considering the practical application of catalysts, not only catalytic activity, and stability but also the preparation cost is a crucial factor. Most current research is still

based on precious metals. So, it is important to reduce the loading of precious metal nanoparticles and improving their utilization efficiency. Future research needs to focus on using non-precious metals to replace precious metal nanoparticles while maintaining high catalytic activity. This approach can significantly reduce costs and make the catalysts more economically viable for industrial applications.

However, there are still many challenges associated with the leaching of precious metal precursors and the use of expensive ligands in the synthesis of mental@zeolite catalysts. The zeolite seed method, which offers controlled metal nanoparticle size, high metal utilization, and no need for organic ligands/stabilizers, is an ideal method for synthesizing metal@zeolite catalysts. Although this method is suitable for most zeolites, more examples are needed to further validate its effectiveness.

5.3 Enhancing structural characterization and understanding

There will be a need for advanced characterization techniques to gain deeper insights into the structure and catalytic mechanisms of the catalysts. Conventional characterization methods are not sufficient to fully understand the fine structure and reaction processes of the catalysts. Advanced techniques such as *in situ* XPS, XAS, and spherical aberration-corrected transmission electron microscopy (TEM) can provide more detailed information on the electronic structure evolution and precise location of metal nanoparticles. Density Functional Theory (DFT) simulations can further explore the activation and catalytic conversion processes of reactant molecules in metal@zeolite catalysts.

Moreover, most current studies focus on encapsulating precious metal nanoparticles, but the use of non-precious metals or high-content transition metals in zeolite crystals and metal species. Understanding this interface is crucial for elucidating the relationship between catalyst structure and catalytic performance. Encapsulating metal atoms, metal clusters, and nanoparticles within zeolite crystals can lead to random positioning, which may hinder the synergistic effects and catalytic activity. Achieving

uniform distribution of metal nanoparticles of specific sizes within the zeolite framework could enhance their performance.

5.4 Large-scale preparation and industrial application

Scaling up the production of hierarchical zeolite-encapsulated MNPs for industrial applications requires simple, green, and cost-effective synthesis methods. Ensuring reproducibility and maintaining catalyst performance at large scale are critical challenges. Future efforts should focus on developing scalable synthesis processes and conducting pilot-scale testing to facilitate the transition from laboratory research to industrial application. Researchers should prioritize economic, efficient, safe, and ecological synthetic conditions. Developing methods that output kilogram-scale catalysts using laboratory equipment without sacrificing properties and reproducibility is crucial for industrialization.

5.5 Expanding applications and addressing challenges

While most study of zeolite research focuses on liquid-phase catalytic reactions, the structural characteristics of zeolite pores make them more suitable for shape-selective reactions involving the conversion of small molecules to larger molecules. For example, converting C1 chemicals to high-value products using monolithic catalysts has been successful, but the large particle size of these catalysts can impede diffusion and negatively impact catalytic activity and stability. Future research should aim to encapsulate active species within monodisperse zeolite crystals to effectively catalyse the conversion of C1 chemicals to lower olefins or oxygenates, a challenging yet significant topic.

In summary, while metal-encapsulated zeolite catalysts have shown great potential, overcoming challenges related to mass transfer, sinter resistant ability, cost reduction, structural characterization, and optimizing catalyst structure are crucial for their future development and broader scale preparation and application. Advanced synthesis techniques, innovative characterization methods, and a focus on economically viable materials will pave the way for the next generation of high-performance catalysts.

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Notes.

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Reference

1. W. Hölderich, M. Hesse and F. Näumann, *Angew Chem Int Ed Engl*, 1988, **27**, 226-246.
2. R. M. Barrer, *J. Chem. Soc.*, 1948, 2158-2163.
3. X. Qinhua and Y. Aizhen, *Prog. Cryst. Growth Charact. Mater.*, 1991, **21**, 29-70.
4. B. Gates, *Chem. Rev.*, 1995, **95**, 511-522.
5. A. Cronstedt, *Svenska Vetenskaps Akademiens Handlingar Stockholm*, 1756, **17**, 120.
6. A. Corma, P. Concepción, M. Boronat, M. J. Sabater, J. Navas, M. J. Yacaman, E. Larios, A. Posadas, M. A. López-Quintela and D. Buceta, *Nat. Chem.*, 2013, **5**, 775-781.
7. S. Goel, Z. Wu, S. I. Zones and E. Iglesia, *J. Am. Chem. Soc.*, 2012, **134**, 17688-17695.
8. M. Choi, Z. Wu and E. Iglesia, *J. Am. Chem. Soc.*, 2010, **132**, 9129-9137.
9. X. Wang, C. Liu, L. He, B. Li, J. Lu, M. Luo and J. Chen, *Appl. Catal., A*, 2023, **655**, 119108.
10. J. Lei, R. Niu, S. Wan and J. Li, *Solid State Sci.*, 2020, **101**, 106097.
11. L. Meng, G. Vanbutsele, R. Pestman, A. Godin, D. E. Romero, A. J. van Hoof, L. Gao, T. F. Kimpel, J. Chai and J. A. Martens, *J. Catal.*, 2020, **389**, 544-555.
12. H. Fujitsuka, S. Oshima, Y. Matsumura and T. Tago, *Catal. Today*, 2021, **375**, 360-368.
13. T. Weissenberger, A. G. Machoke, B. Reiprich and W. Schwieger, *Adv. Mater. Interfaces*, 2021, 2001653.
14. D. Kerstens, B. Smeyers, J. Van Waeyenberg, Q. Zhang, J. Yu and B. F. Sels, *Adv. Mater.*, 2020, **32**, 2004690.
15. Y. Liu, Z. Li, Q. Yu, Y. Chen, Z. Chai, G. Zhao, S. Liu, W.-C. Cheong, Y. Pan and Q. Zhang, *J. Am. Chem. Soc.*, 2019, **141**, 9305-9311.
16. S. Li, A. Tuel, F. Meunier, M. Aouine and D. Farrusseng, *J. Catal.*, 2015, **332**, 25-30.
17. Y. Chai, W. Shang, W. Li, G. Wu, W. Dai, N. Guan and L. Li, *Adv. sci.*, 2019, **6**, 1900299.
18. L. Liu, U. Diaz, R. Arenal, G. Agostini, P. Concepcion and A. Corma, *Nat. Mater.*, 2017, **16**, 132-138.
19. C. Dai, A. Zhang, M. Liu, X. Guo and C. Song, *Adv. Funct. Mater.*, 2015, **25**, 7479-7487.
20. J. Gu, Z. Zhang, P. Hu, L. Ding, N. Xue, L. Peng, X. Guo, M. Lin and W. Ding, *ACS Catal.*, 2015, **5**, 6893-6901.
21. S. M. Wu, X. Y. Yang and C. Janiak, *Angew. Chem. Int. Ed.*, 2019, **58**, 12340-12354.
22. M. Choi, S. Yook and H. Kim, *ChemCatChem*, 2015, **7**, 1048-1057.
23. D. Farrusseng and A. Tuel, *New J. Chem.*, 2016, **40**, 3933-3949.

24. X. Gao, Y. Zhou, L. Feng, F. Tian, X. Liu, J. Xu and Y. Li, *Microporous Mesoporous Mater.*, 2019, **283**, 82-87.
25. J. Tang, P. Liu, X. Liu, L. Chen, H. Wen, Y. Zhou and J. Wang, *ACS Appl. Mater. Interfaces*, 2020, **12**, 11522-11532.
26. L. Ma, C. Ding, J. Wang, Y. Li, Y. Xue, J. Guo, K. Zhang, P. Liu and X. Gao, *Int. J. Hydrogen Energy*, 2019, **44**, 21847-21857.
27. T. L. Cui, W. Y. Ke, W. B. Zhang, H. H. Wang, X. H. Li and J. S. Chen, *Angew. Chem.*, 2016, **128**, 9324-9328.
28. C. Pagis, A. R. Morgado Prates, D. Farrusseng, N. Bats and A. Tuel, *Chem. Mater.*, 2016, **28**, 5205-5223.
29. A. Dong, Y. Wang, Y. Tang, Y. Zhang, N. Ren and Z. Gao, *Adv. Mater.*, 2002, **14**, 1506-1510.
30. A. Dong, Y. Wang, D. Wang, W. Yang, Y. Zhang, N. Ren, Z. Gao and Y. Tang, *Microporous Mesoporous Mater.*, 2003, **64**, 69-81.
31. A. Dong, N. Ren, W. Yang, Y. Wang, Y. Zhang, D. Wang, J. Hu, Z. Gao and Y. Tang, *Adv. Funct. Mater.*, 2003, **13**, 943-948.
32. N. Ren, Y. Yang, J. Shen, Y. Zhang, H. Xu, Z. Gao and Y. Tang, *J. Catal.*, 2007, **251**, 182-188.
33. C. Dai, A. Zhang, M. Liu, L. Gu, X. Guo and C. Song, *ACS nano*, 2016, **10**, 7401-7408.
34. X. Niu, X. Li, G. Yuan, F. Feng, M. Wang, X. Zhang and Q. Wang, *Ind. Eng. Chem. Res.*, 2020, **59**, 8601-8611.
35. C. Dai, S. Zhang, A. Zhang, C. Song, C. Shi and X. Guo, *Journal of Materials Chemistry A*, 2015, **3**, 16461-16468.
36. K. M. Kwok, L. Chen and H. C. Zeng, *J. Mater. Chem. A.*, 2020, **8**, 12757-12766.
37. C. Dai, X. Li, A. Zhang, C. Liu, C. Song and X. Guo, *RSC Adv.*, 2015, **5**, 40297-40302.
38. J. Prech, D. R. Strossi Pedrolo, N. R. Marcilio, B. Gu, A. S. Peregudova, M. Mazur, V. V. Ordomsky, V. Valtchev and A. Y. Khodakov, *ACS Catal.*, 2020, **10**, 2544-2555.
39. W. Wang, W. Zhou, W. Li, X. Xiong, Y. Wang, K. Cheng, J. Kang, Q. Zhang and Y. Wang, *Appl. Catal. B*, 2020, **276**, 119142.
40. K. Xu, Y. Cheng, B. Sun, Y. Pei, S. Yan, M. Qiao, X. Zhang and B. Zong, *Acta Physico-Chimica Sinica*, 2015, **31**, 1137-1144.
41. S. Dong, S. Bo, P. Yan, Y. Shirun, F. Kangnian, Q. Minghua, Z. Xiaoxin and Z. Baoning, *Acta Chim. Sin.*, 2021, **79**, 771.
42. J. Huang, Y. Fan, G. Zhang and Y. Ma, *RSC Adv.*, 2020, **10**, 13583-13590.
43. S. Li, C. Aquino, L. Gueudre, A. Tuel, Y. Schuurman and D. Farrusseng, *ACS Catal.*, 2014, **4**, 4299-4303.
44. S. Li, T. Boucheron, A. Tuel, D. Farrusseng and F. Meunier, *Chem. Commun. (Cambridge, U. K.)*, 2014, **50**, 1824-1826.
45. S. Li, A. Tuel, D. Laprune, F. Meunier and D. Farrusseng, *Chem. Mater.*, 2015, **27**, 276-282.

46. D. Fodor, T. Ishikawa, F. Krumeich and J. A. van Bokhoven, *Adv. Mater.*, 2015, **27**, 1919-1923.
47. G. Wang, S. Xu, L. Wang, Z. Liu, X. Dong, L. Wang, A. Zheng, X. Meng and F.-S. Xiao, *Chem. Commun. (Cambridge, U. K.)*, 2018, **54**, 3274-3277.
48. Y. Wang, Y. Liu, J. Li, Y. Liu, W. Zhang, M. Yang, Y. Jian, P. Zuo and Z. Gao, *Ind. Eng. Chem. Res.*, 2020, **59**, 11241-11249.
49. S. Zou, M. Zhang, S. Mo, H. Cheng, M. Fu, P. Chen, L. Chen, W. Shi and D. Ye, *Nanomaterials*, 2020, **10**, 30.
50. J. Zhang, Y. Wang, L. Dong, Z. Chen, Y. Wang and M. Hong, *Microporous Mesoporous Mater.*, 2020, **293**, 109813.
51. B. Mazonde, S. Cheng, G. Zhang, M. Javed, W. Gao, Y. Zhang, M. Tao, C. Lu and C. Xing, *Catal. Sci. Technol.*, 2018, **8**, 2802-2808.
52. Q. Chen, H. Kang, X. Liu, K. Jiang, Y. Bi, Y. Zhou, M. Wang, M. Zhang, L. Liu and E. Xing, *ChemCatChem*, 2020.
53. Q. Chen, T. Li, Y. Zhou, Y. Bi, S. Guo, X. Liu, H. Kang, M. Wang, L. Liu and E. Xing, *Ind. Eng. Chem. Res.*, 2020, **59**, 12004-12012.
54. Q. Wang, W. Han, J. Lyu, Q. Zhang, L. Guo and X. Li, *Catal. Sci. Technol*, 2017, **7**, 6140-6150.
55. A. Kurbanova, D. Zákutná, K. Gołąbek, M. Mazur and J. Přech, *Catal. Today*, 2022, **390**, 306-315.
56. Y. Chang, J. G. McCarty and E. D. Wachsman, *Appl. Catal. B*, 1995, **6**, 21-33.
57. S. A. Yashnik, O. P. Taran, T. A. Surovtsova, A. B. Ayusheev and V. N. Parmon, *J. Environ. Chem. Eng.*, 2022, **10**, 107950.
58. Q. Sun, B. W. Chen, N. Wang, H. Qian, A. Chang, C. Yang, H. Asakura, T. Tanaka, M. J. Hülsey and W. Chihwa, 2020.
59. Q. Sun, N. Wang, Q. Fan, L. Zeng, A. Mayoral, S. Miao, R. Yang, Z. Jiang, W. Zhou and J. Zhang, *Angew. Chem.*, 2020, **132**, 19618-19627.
60. R. Celis, M. C. Hermosín and J. Cornejo, *Environ. Sci. Technol.*, 2000, **34**, 4593-4599.
61. N. Zheng and G. D. Stucky, *J. Am. Chem. Soc.*, 2006, **128**, 14278-14280.
62. M. Limlamthong and A. C. Yip, *Bioresour. Technol.*, 2020, **297**, 122488.
63. S. Goel, S. I. Zones and E. Iglesia, *Chem. Mater.*, 2015, **27**, 2056-2066.
64. H. Geng, G. Li, D. Liu and C. Liu, *J. Solid State Chem.*, 2018, **265**, 193-199.
65. S. Goel, S. I. Zones and E. Iglesia, *J. Am. Chem. Soc.*, 2014, **136**, 15280-15290.
66. Y. Chen, X. Zhu, X. Wang and Y. Su, *Chem. Eng. J.*, 2021, **419**, 129641.
67. M. Matsukata, M. Ogura, T. Osaki, E. Kikuchi and A. Mitra, *Microporous Mesoporous Mater.*, 2001, **48**, 23-29.
68. H. Wen, Y. Zhou, J. Xie, Z. Long, W. Zhang and J. Wang, *RSC advances*, 2014, **4**, 49647-49654.
69. S. P. Naik, A. S. Chiang and R. Thompson, *J. Phys. Chem. B*, 2003, **107**, 7006-7014.
70. P. H. PrasadáRao, *Chem. Commun. (Cambridge, U. K.)*, 1996, 1441-1442.
71. C.-C. Chang, H. J. Cho, Z. Wang, X. Wang and W. Fan, *Green Chem.*, 2015, **17**, 2943-2951.

72. Y. Ji, Y. Wang, B. Xie and F.-S. Xiao, *Comments Inorg. Chem.*, 2016, **36**, 1-16.
73. K. Iyoki, K. Itabashi and T. Okubo, *Microporous Mesoporous Mater.*, 2014, **189**, 22-30.
74. B. Xie, J. Song, L. Ren, Y. Ji, J. Li and F.-S. Xiao, *Chem. Mater.*, 2008, **20**, 4533-4535.
75. B. Xie, H. Zhang, C. Yang, S. Liu, L. Ren, L. Zhang, X. Meng, B. Yilmaz, U. Müller and F.-S. Xiao, *Chem. Commun. (Cambridge, U. K.)*, 2011, **47**, 3945-3947.
76. Y. Kamimura, W. Chaikittisilp, K. Itabashi, A. Shimojima and T. Okubo, *Chem. Asian J.*, 2010, **5**, 2182-2191.
77. G. Majano, L. Delmotte, V. Valtchev and S. Mintova, *Chem. Mater.*, 2009, **21**, 4184-4191.
78. J. Huang, B. Liu, Z. Liao, H. Chen and K. Yan, *Ind. Eng. Chem. Res.*, 2019, **58**, 16636-16644.
79. L. Zhang, J. Chen, X. Guo, S. Yin, M. Zhang and Z. Rui, *Catal. Today*, 2020.
80. L. Zhang, J. Chen, X. Guo, S. Yin, M. Zhang and Z. Rui, *Catal. Today*, 2021, **376**, 119-125.
81. N. Wang, Q. Sun and J. Yu, *Adv. Mater.*, 2019, **31**, 1803966.
82. Q. Sun, N. Wang, T. Zhang, R. Bai, A. Mayoral, P. Zhang, Q. Zhang, O. Terasaki and J. Yu, *Angew. Chem. Int. Ed.*, 2019, **58**, 18570-18576.
83. S. Li, A. Tuel, J. L. Rousset, F. Morfin, M. Aouine, L. Burel, F. Meunier and D. Farrusseng, *ChemNanoMat*, 2016, **2**, 534-539.
84. Q. Sun, B. W. Chen, N. Wang, Q. He, A. Chang, C. M. Yang, H. Asakura, T. Tanaka, M. J. Hülsey and C. H. Wang, *Angew. Chem.*, 2020, **132**, 20358-20366.
85. D. Laprune, C. Theodoridi, A. Tuel, D. Farrusseng and F. Meunier, *Appl. Catal. B*, 2017, **204**, 515-524.
86. L. Wang, S. Xu, S. He and F.-S. Xiao, *Nano Today*, 2018, **20**, 74-83.
87. Z. Gao and Y. Qin, *Acc. Chem. Res.*, 2017, **50**, 2309-2316.
88. P. Zhai, L. Zhang, D. A. Cullen, D. R. Aireddy and K. Ding, *ACS Appl. Mater. Interfaces*, 2021, **13**, 51759-51766.
89. B. Vandegehuchte, J. Thybaut, C. Detavernier, D. Deduytsche, J. Dendooven, J. Martens, S. Sree, T. Koranyi and G. Marin, *J. Catal.*, 2014, **311**, 433-446.
90. D. Xu, B. Wu, P. Ren, S. Wang, C. Huo, B. Zhang, W. Guo, L. Huang, X. Wen and Y. Qin, *Catal. Sci. Technol*, 2017, **7**, 1342-1350.
91. D. Xu, S. Wang, B. Wu, B. Zhang, Y. Qin, C. Huo, L. Huang, X. Wen, Y. Yang and Y. Li, *ACS Appl. Mater. Interfaces*, 2019, **11**, 29858-29867.
92. D. Xu, J. Yin, Y. Gao, D. Zhu and S. Wang, *ChemPhysChem*, 2021, **22**, 1287-1301.
93. D. Xu, S. Wang, B. Wu, C. Huo, Y. Qin, B. Zhang, J. Yin, L. Huang, X. Wen and Y. Yang, *J. Catal.*, 2018, **365**, 163-173.
94. H. M. Torres Galvis, J. H. Bitter, C. B. Khare, M. Ruitenbeek, A. I. Dugulan and K. P. de Jong, *Science*, 2012, **335**, 835-838.

95. P. Thüne, C. Weststrate, P. Moodley, A. Saib, J. Van de Loosdrecht, J. Miller and J. Niemantsverdriet, *Catal. Sci. Technol*, 2011, **1**, 689-697.
96. A. Y. Khodakov, W. Chu and P. Fongarland, *Chem. Rev.*, 2007, **107**, 1692-1744.
97. J. Liu, J. Chen and Y. Zhang, *Catal. Sci. Technol*, 2013, **3**, 2559-2564.
98. K. Cheng, L. Zhang, J. Kang, X. Peng, Q. Zhang and Y. Wang, *Chem. Eur. J*, 2015, **21**, 1928-1937.
99. F. Jiao, J. Li, X. Pan, J. Xiao, H. Li, H. Ma, M. Wei, Y. Pan, Z. Zhou and M. Li, *Science*, 2016, **351**, 1065-1068.
100. D. Suttipat, K. Saenluang, W. Wannapakdee, P. Dugkhuntod, M. Ketkaew, P. Pornsetmetakul and C. Wattanakit, *Fuel*, 2021, **286**, 119306.
101. Y. Chen, S. Wang, Z. Wei, J. Li, M. Dong, Z. Qin, J. Wang and W. Fan, *J. Phys. Chem. C*, 2021, **125**, 26472-26483.
102. X. Sun, S. Mueller, H. Shi, G. L. Haller, M. Sanchez-Sanchez, A. C. van Veen and J. A. Lercher, *J. Catal.*, 2014, **314**, 21-31.
103. J. Li, Y. Wei, G. Liu, Y. Qi, P. Tian, B. Li, Y. He and Z. Liu, *Catal. Today*, 2011, **171**, 221-228.
104. S. Lopez-Orozco, A. Inayat, A. Schwab, T. Selvam and W. Schwieger, *Adv. Mater.*, 2011, **23**, 2602-2615.
105. W. Yingxu, D. Zhang, L. Zhongmin and S. Bao-Lian, *Chinese J. Catal*, 2012, **33**, 11-21.
106. Z. Hu, J. Han, Y. Wei and Z. Liu, *ACS Catal.*, 2022, **12**, 5060-5076.
107. Y. Xu, G. Ma, J. Bai, Y. Du, C. Qin and M. Ding, *ACS Catal.*, 2021, **11**, 4476-4485.
108. W. Wang, L. He, Q. Luo, L. Wang, J. Wang, H. Chen, Z. Miao, Q. Yao and M. Sun, *Microporous Mesoporous Mater.*, 2023, 112766.
109. K. M. Kwok, S. W. D. Ong, L. Chen and H. C. Zeng, *ACS Appl. Mater. Interfaces*, 2019, **11**, 14774-14785.
110. L. Tan, F. Wang, P. Zhang, Y. Suzuki, Y. Wu, J. Chen, G. Yang and N. Tsubaki, *Chemical Science*, 2020, **11**, 4097-4105.
111. H. Liu, Y. Fu, M. Li, J. Wang, A. Noreen, E. Maturura, X. Gao, R. Yang, C. C. Amoo and C. Xing, *J. Mater. Chem. A*, 2021, **9**, 8663-8673.
112. M. Javed, S. Cheng, G. Zhang, P. Dai, Y. Cao, C. Lu, R. Yang, C. Xing and S. Shan, *Fuel*, 2018, **215**, 226-231.
113. C. C. Amoo, M. Li, A. Noreen, Y. Fu, E. Maturura, C. Du, R. Yang, X. Gao, C. Xing and N. Tsubaki, *ACS Appl. Nano Mater*, 2020, **3**, 8096-8103.
114. Z. Di, T. Zhao, X. Feng and M. Luo, *Catal. Lett.*, 2019, **149**, 441-448.
115. R. Hu, T. Wang, Y. Wang, Y. Zhu, L. Xie, E. Xing, Y. Wu and Z. Da, *Catalysts*, 2023, **13**, 948.
116. S. Cheng, B. Mazonde, G. Zhang, M. Javed, C. Amoo, Y. Shi, K. Guo, M. Yao, C. Lu and G. Yang, *ChemistrySelect*, 2018, **3**, 13632-13637.
117. B. Sun, G. Yu, J. Lin, K. Xu, Y. Pei, S. Yan, M. Qiao, K. Fan, X. Zhang and B. Zong, *Catal. Sci. Technol*, 2012, **2**, 1625-1629.
118. Y. Zhai, S. Zhang, Y. Shang, Y. Song, W. Wang, T. Ma, L. Zhang, Y. Gong, J. Xu and F. Deng, *Catal. Sci. Technol*, 2019, **9**, 659-671.

119. K. Xu, Y. Cheng, B. Sun, Y. Pei, S. Yan, M. Qiao, X. Zhang and B. Zong, *Acta Physico-Chimica Sinica*, 2015, **31**, 1137-1144.
120. H. Kusama, K. K. Bando, K. Okabe and H. Arakawa, *Appl. Catal., A*, 2000, **197**, 255-268.
121. D. A. Bulushev, S. Beloshapkin and J. R. Ross, *Catal. Today*, 2010, **154**, 7-12.
122. Y. Li and J. Yu, *Chem. Rev.*, 2014, **114**, 7268-7316.