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Challenges and Opportunities for Zeolites in the Conversion of Low-carbon Molecules

Zaiku Xie, Chuanming Wang, Jing Shi*

State Key Laboratory of Green Chemical Engineering and Industrial Catalysis, Sinopec Shanghai Research Institute of Petrochemical Technology Co., Ltd., Shanghai, China

*Corresponding author: xzk@sinopec.com

1.1 Introduction

Zeolites, i.e., molecular sieves, are inorganic solid porous crystallites with well-defined channel/pore structures, and contribute highly to the development of modern chemical industries in the fields of adsorption, separation, and catalysis. Last several decades have witnessed the wide applications of zeolites in a variety of important industrial catalytic processes, like fluid catalytic cracking, toluene disproportionation, aromatic alkylation, alkane isomerization, olefin catalytic cracking, and epoxidation [1]. With the increasing requirements for the development of a more sustainable and environmentally benign chemical industry, it is essential to utilize other resources like syngas, shale gas, CO_2, and biomass to produce diverse chemicals and fuels. Zeolites play a considerable role in these kinds of low-carbon hydrocarbon catalytic conversions [2, 3]. The unique catalytic properties are highly related to both confinement environments and acidity properties of zeolites. Despite the great progress of zeolite-catalyzed low-carbon hydrocarbon conversions, there still exist several challenges and opportunities attracting widespread interests from both academic and industrial communities.

1.2 Challenges in the Synthesis of Zeolites

Though it is theoretically possible to construct millions of hypothetical zeolite structures, only around 260 zeolites with distinct framework topologies until now have been successfully obtained, and only limited zeolites (e.g., FAU, MFI, MWW, BEA, MOR, CHA, AEI, etc.) have found widespread applications in the industrial practice

of chemical processes. Targeted synthesis of zeolites with the desired active sites and framework topologies is a great challenge [4]. Zeolites are usually synthesized via the hydrothermal method, which mainly consists of two stages, i.e., the homogenization and aging of the mixture at lower temperatures (usually <100 °C), and the heating of the mixture at elevated temperatures (usually >100 °C) to form crystals [5]. During the process of premixing raw materials into gel, reactive silicate and aluminate species quickly condense to form a gel structure, making the synthesis system highly viscous and causing it to easily delaminate. During the high-temperature heating process, aluminosilicate species are hydrolyzed, condensed, and rearranged, consequently leading to the onset of the nucleation and crystallization procedures. These transformations can occur in the liquid or solid phase, and more likely at the interface. The complex bonding and nonbonding interactions among multiple components complicate the understanding of the role of organic structure-directing agents (OSDAs), which could be space-filling, charge-balancing, structure-directing, or templating. The precise match between the rates of material transfer/mixing and intrinsic reaction in the complex synthetic system at the molecular scale plays a key role in controlling the crystallization time, zeolite morphology, and distribution of active sites. It is thus necessary to understand the crystallization mechanism and kinetics in order to prepare zeolites with specific topology, framework composition, and pore architecture (size, dimension, orientations, etc.).

1.3 Challenges in Zeolite-catalyzed Low-carbon Hydrocarbon Conversions

Zeolites also play indispensable roles in the low-carbon hydrocarbon conversions, e.g., methanol-to-olefins/aromatics (MTO/MTA) conversion, direct syngas/CO_2-to-olefins/aromatics (STO/STA, CTO/CTA) conversion within bifunctional catalysts, selective oxidation of methane to methanol (MTM), methane dehydroaromatization (MDA), propane dehydrogenation (PDH), etc. The confinement effect imposed by zeolite frameworks and the well-tuned active sites endow zeolites with high catalytic activity, selectivity, and stability toward low-carbon hydrocarbon conversions. However, systematic understanding of the underlying reaction mechanism and the relationships between zeolite structures and catalytic performances is the prerequisite toward the rational design and practical application of zeolite catalysts, which remains a great challenge.

Considering MTO conversion as an example, which has been successfully industrialized (DMTO, S-MTO, UOP-MTO, etc.) in this century using small-pore eight-membered ring SAPO-34 zeolite as the catalyst, the detailed reaction mechanism is still in great dispute [6, 7]. It is generally recognized that the active site for MTO conversion consists of inorganic Brønsted acid center and organic hydrocarbon pool species. While the characteristics of the intrinsic hydrocarbon pool species are under great debate, it is suggested that aromatics like polymethylbenzenes and/or olefins themselves are the dominating hydrocarbon pool species. As different hydrocarbon pool species follow different reaction cycles and dedicate

to distinct MTO catalytic performances, it is particularly important to address the distribution and relative contribution to MTO conversion of the hydrocarbon pool species as a function of zeolite structures and reaction conditions. It is also particularly necessary to identify and quantify the dynamic characteristics of the hydrocarbon pool species in zeolites under working conditions. However, the dynamic features of the hydrocarbon pool species formed in situ result in severe challenges in deciphering the structures and following the evolution of the dominating hydrocarbon pool species in detail during the reaction, let alone the complexities of the involved possible reaction pathways. Significant experimental and computational efforts have been dedicated to several challenging issues related to the MTO conversion, like the first C—C bond coupling in the induction period, the nature and evolution of organic hydrocarbon pool species, and the characteristics and effects of coking species formed in situ. It is highly desirable to decrease coking and methanol consumption and to tailor the selectivity of ethene and propene for the development of next-generation MTO zeolite catalysts.

The selective oxidation of methane to methanol is usually considered as one of the "holy grail" reactions in heterogeneous catalysis [8–10]. The traditional methane-to-methanol conversion usually involves two processes, i.e., the reforming of methane to syngas, and the syngas conversion to methanol; however, such an indirect process is quite energy-consuming. It is thus essential to develop a direct methane-selective oxidation process. Inspired by the natural methane monooxygenase (MMO) that can catalyze the selective oxidation of methane by oxygen molecule under ambient conditions, the Cu-based and Fe-based zeolites have shown potential prospect toward the selective oxidation of methane to methanol. Both stepwise and continuous catalytic processes have been suggested and exploited in a variety of zeolite matrixes. However, the conversion rate and the methanol yield are particularly low, far less than the catalytic performance as expected for possible industrialization. Several different Cu active centers confined with zeolites (e.g., $CuOH^+$, Cu_2O^{2+}, $Cu_2O_2^{2+}$, and $Cu_3O_3^{2+}$) were identified and proposed, while the intrinsic dominating active site for MTM reaction is still in dispute. It is likely that these motifs can be interconverted under working conditions. In addition, the critical role of water for reaction needs to be deciphered to enhance catalytic performance. It is also quite important and challenging to address the origin of oxygen atom in methanol and unveil the characteristics of oxidant (H_2O versus O_2). More attention thus should be paid to the dynamic evolution of active sites under working conditions.

Very recently, the bifunctional catalysts pioneered by Bao and other researchers received increasing interests for the direct conversion of syngas and CO_2 to light olefins and aromatics [11, 12]. Such bifunctional catalysts consist of oxide component for the conversion of syngas/CO_2 to bridging oxygenate, and the zeolite component for the conversion of bridging oxygenate to olefins and aromatics. Simpler assembling mode of two components and higher selectivity toward olefins and aromatics have evoked great interests on bifunctional catalysts for several conversion processes. A variety of oxides including binary spinel (e.g., $ZnCrO_x$, $ZnAlO_x$) and several zeolites with different ring openings (e.g., SAPO-34, SAPO-18, and ZSM-5) were taken into account to assemble fascinating bifunctional catalysts and establish

relay catalytic processes for the direct conversion of syngas or CO_2 to olefins, aromatics, or fuels. Despite the impressive catalytic selectivity for direct conversion, it is essential to improve the activity of oxides toward CO/CO_2, and balance the catalytic performance of oxides and zeolites under working conditions in order to achieve possible industrial practices. It is noteworthy that the characteristics of bridging oxygenate are still under debate; moreover, the similarities and differences for the conversion of methanol and ketene should be disclosed. It is also necessary to identify the intrinsic active sites of oxide surface (e.g., spinel $ZnCr_2O_4$ oxide) and understand the effects of surface structures and reducibility on syngas conversion. An impressive catalytic performance of more than 80% in both CO conversion and olefin selectivity was reported for the STO conversion using heteroatom-substituted Ge-AlPO-18 zeolite component [13], making it possible to industrialize.

1.4 Challenges in the Construction and Characterization of Active Sites in Zeolites

A typical zeolite-catalyzed reaction usually proceeds on Brønsted site, Lewis site, and/or confined metal cluster within the zeolite matrix. The catalytic performance highly depends on both the reaction and diffusion kinetics. It is thus essential to tailor the confinement effect and shape-selectivity performance of zeolites to balance both reaction and diffusion kinetics. For example, using eight-membered ring zeolites like SAPO-34 is the prerequisite to achieve high ethene and propene selectivity for MTO conversion as the eight-membered ring imposes strong confinement effect on the diffusion of propene and higher olefins. On the other hand, it is possible to construct mesopores in zeolites to decrease coking formation and prolong the lifetime of catalysts [14]. Modifying the hydrophilic or hydrophobic feature of zeolite channel provides another strategy to tailor the diffusion kinetics of zeolites. However, it is a great challenge to precisely construct well-defined structures of zeolites in terms of both isolated active sites and pore structures for achieving the balance in both reaction and diffusion kinetics. The challenge, on the one hand, lies in tracing the dynamic evolution of active sites of zeolite-catalyzed reactions; it also remains a great challenge, to establish both precise macroscopic and microscopic measurements and decipher the anisotropy of the diffusion characteristics in zeolites under working conditions (e.g., reaction–diffusion coupling, multiple components, and high temperature) [15].

1.5 Opportunities and Outlook

We are now stepping into a new era of green and carbon neutrality for sustainable development of chemical industry. The development of advanced in situ/operando characterizations, together with the first-principles-based computational approaches including density functional theory (DFT) calculations, microkinetic modeling (MKM), and ab-initio molecular dynamics (AIMD) simulations, is

playing an indispensable role in identifying the intrinsic active sites, uncovering the underlying reaction network, and establishing the relations between zeolite structures and catalytic performances [16–19]. The emergence of artificial intelligence (AI)-driven approach and high-throughput screening (HTS) techniques makes it possible to tackle complex systems involving complicated structures and reaction networks. It is anticipated that the next-generation catalytic processes can be progressed by taking advantage of the merits of zeolites.

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