Outlook

Tandem Reactions over Zeolite-Based Catalysts in Syngas Conversion

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ABSTRACT: Syngas conversion can play a vital role in providing energy and chemical supplies while meeting environmental requirements as the world gradually shifts toward a net-zero. While prospects of this process cannot be doubted, there is a lingering challenge in distinct product selectivity over the bulk transitional metal catalysts. To advance research in this respect, composite catalysts comprising traditional metal catalysts and zeolites have been deployed to distinct product selectivity while suppressing side reactions. Zeolites are common but highly efficient materials used in the chemical industry for hydro-processing. Combining the advantages of zeolites and some transition metal catalysts has promoted the catalytic production of various hydrocarbons (e.g., light olefins, aromatics, and liquid fuels) and oxygenates (e.g., methanol, dimethyl ether, formic acid, and higher alcohols) from syngas. In this outlook, a thorough revelation on recent progress in syngas conversion to various products over metal-zeolite composite catalysts is validated. The strategies adopted to couple the metal species and zeolite material into a composite as well as the consequential morphologies for specific product selectivity are highlighted. The key zeolite descriptors that influence catalytic performance, such as framework topologies, proximity and confinement effects, acidities and cations, pore systems, and particle sizes are discussed to provide a deep understanding of the significance of zeolites in syngas conversion. Finally, an outlook regarding challenges and opportunities for syngas conversion using zeolite-based catalysts to meet emerging energy and environmental demands is also presented.
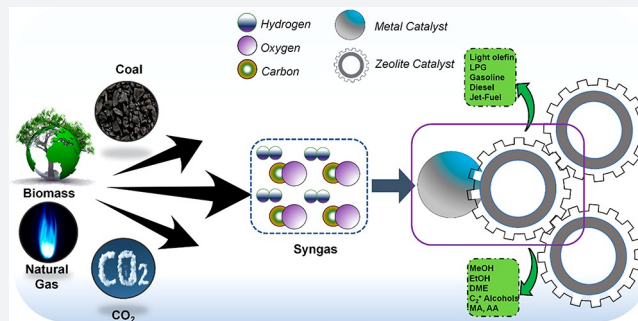
INTRODUCTION

It is immeasurable to estimate the astounding prosperity crude oil has offered to society with the provision of hydrocarbon fuels (gasoline, diesel fuel, and jet fuel), oxygenates (dimethyl ether, methanol, and higher alcohols), and other chemical building blocks (aromatics and light olefins).[1−5] However, growing concerns following crude oil depletion and environmental concerns about their exploitation have sparked the search for alternative carbon sources and processes that are sustainable and environmentally benign.[6−8] Accordingly, syngas (a mixture of CO and H_2), which can be produced from carbon(IV) oxide, biomass, coal, natural gas, and carbon-based waste has become a sustainable option to supply these chemical feedstocks, oxygenates, and fuels, traditionally produced from crude oil.[9−15] Syngas conversion is a catalytic process with extensive studies allocated to efficient catalyst development for the selective production of valued prod-ucts.[16−19] Catalysts required for the successful synthesis of the valued chemicals and fuels normally include a metallic species in the form of single atoms, clusters, carbides, oxides, or alloy particles (e.g., Co, Rh-, AuPd-, metallic Fe, Fe_5C_2-based catalysts).[18,20−25] However, these metallic species are challenged with poor catalytic stability with a hydrocarbon

product distribution that barely differs from the prediction of the Anderson-Schultz-Flory (ASF) probability model; thus, the production of desired products remains a difficult chal-lenge.[26−28] Overcoming product selectivity limitations with further improvements using composite materials for tandem catalysis via strategic designs have become important areas of research.

Zeolites are generally defined as porous crystalline aluminosilicates built up from SiO_4- and AlO_4-tetrahedrally linked. They can be obtained from nature as a result of volcanic activities or be synthesized from reagents in the laboratory.[29−31] The synthesized zeolites are mostly used because they have a high degree of purity in addition to the fact that most of the structures can easily be altered to execute specific functions.[32−35] Currently, there are over 252 known
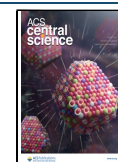
Scheme 1. Schematic Demonstration of Syngas Conversion to Valued Products and Some Popular Zeolite Framework Topologies Exploited in Syngas Conversion
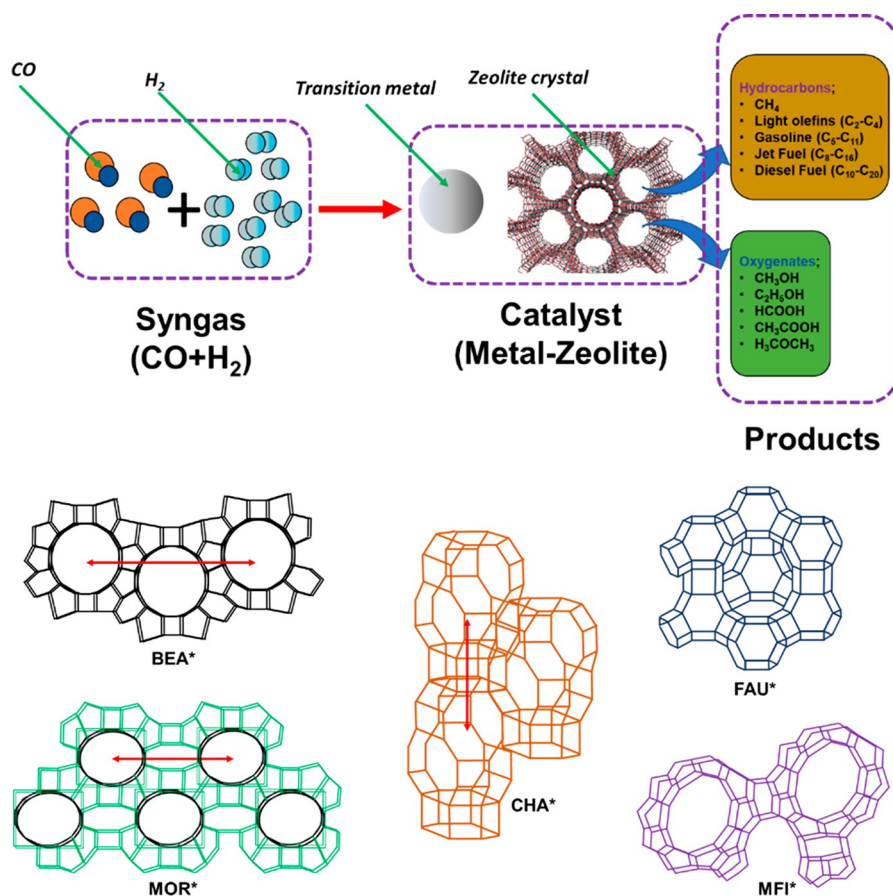

Table 1. Structural Parameters of Some Common Zeolites That Have Been Employed in Syngas Conversion[a]

Topology	Zeolite Identity	Channel Size	Channel Dimension
CHA	SAPO-34, SSZ-13	[001] 3.8*3.8 Å (8MR)	Topology:3D Sorption:3D
BEA	Beta	[100]6.6*6.7 Å (12MR) [001]5.6*5.6 Å (12MR)	Topology:3D Sorption:3D
MOR	Mordenite	[001]6.5*7.0 Å (12 MR) [001]2.6*5.7 Å (8 MR)	Topology:2D Sorption:1D
FAU	X, Y,	[111]7.4*7.4 Å (12 MR)	Topology:3D Sorption:3D
MFI	ZSM-5, Silicalite 1	[100] 5.1*5.5 Å (10 MR) [010] 5.3*5.6 Å (10 MR)	Topology:3D Sorption:3D
TON	ZSM-22, Theta-1	[001] 4.6*5.7 Å (10 MR)	Topology:1D Sorption:1D
AEI	SAPO-18, SSZ-39	[001] 3.8x3.8 Å (8-MR) [100] 3.8x3.8 Å (8-MR) [110] 3.8x3.8 Å (8-MR)	Topology:3D Sorption:3D

[a]*Data Obtained from the International Zeolite Association.

standardized zeolite structures not automatically composed of the "primary" SiO_4- and AlO_4-tetrahedra because many elements from the periodic table are now being used in the integral parts of the zeolite framework.[36] Zeolites as materials are widely used in the chemical industry for adsorption, ion exchange, and catalysis. Catalysis remains one of the largest applications of zeolites because of their shape-selective abilities, uniform pores, tunable acidities, and high thermal and

hydrothermal stabilities.[36−39] Specifically, the development of multifunctional catalysts that simultaneously exploit properties from both zeolites and the active metal catalyst has boosted the applications of zeolites in various catalytic processes. Syngas conversion is now one of the fastest-growing catalytic applications of zeolites.[40,41] Scheme 1 shows hydrocarbons and oxygenates that have been successfully enhanced via various routes over metal-zeolite composite catalysts in syngas

conversion.[42] It is observed that the properties of the zeolites tend to control reaction products from the metal catalysts, as intermediates, for secondary processing. They can further provide anchorage for some metallic species, thus simultaneously improving selectivity toward desired products and enhancing anti-sintering abilities during syngas conversion. The structural information for some popular zeolites preferred for selective syngas conversion to valued products is presented in Table 1.

To date, numerous state-of-the-art reviews concerning the catalytic conversion of syngas have been reported.[15,35,43] However, these reviews tend to be focused on a specific reaction route,[44] on one type of product,[45,46] or on a particular catalyst system.[45] Recently, comprehensive reviews that cover the application of zeolite-based catalysts to the transformation of C1 molecules into various value-added chemicals were reported.[47,48] However, because of the wide scope of the reviews, important and detailed properties of the zeolites that need emphasis and investigation in syngas conversion were omitted. In this outlook, we present advances, challenges, and prospects for the application of zeolite-based catalysts to syngas conversion. Various zeolite descriptors that influence the catalytic transformation of syngas into specific ranges of hydrocarbons and oxygenates are presented. These include framework topologies, nanoconfinement effects, Brønsted acidities, secondary-pore systems, particle sizes, extra-framework cations and atoms, and proximity between acid and metallic sites. Significantly, selecting a suitable zeolite with the desired characteristics may afford enormous opportunities to improve the conversion of syngas and maximize the production of a specific product. Chronologically, a brief Introduction contains a standardized introduction of zeolites as well as some common sources for producing syngas. The following two sections present some literature and progress in zeolite-catalyzed direct conversion of syngas to hydrocarbons and oxygenates, respectively. Within these sections, the major topics are the product ranges, while the breakdown highlights the effects of specific zeolite properties on the product distribution. In the Conclusion and Outlook, facile strategies for improving the catalytic syngas conversion based on accredited zeolite-based catalytic systems will be summarized. Some recent challenges will be highlighted, and essential future research directions will be proposed. These methods allow researchers to adjust the catalytic behaviors of reactants and products, as well as their reactivities.

■ SOURCES OF SYNGAS

Syngas is recognized as feedstock for the direct production of many major chemicals. Recognized routes developed for the production of syngas are highlighted below.

Dry Reforming of Methane (DRM). A green route for producing syngas is via CO_2 reforming of CH_4. Apparently, CO_2 and CH_4 are recognized as the two most abundant greenhouse gases to contain. Developments in CO_2 dry reforming will not only produce syngas as a feedstock for clean hydrocarbon production but also contribute to mitigating the effects of CO_2/CH_4 greenhouse gases. This procedure involves high-temperature reactions between CO_2/CH_4 as shown in eq 1 to obtain $H_2:CO = 1$. This process is often catalyzed by Ni-based catalysts.[49−51] Aside from the high energy requirements for this process, commercialization is further challenged by the in situ reactions between the produced H_2 and the reactant CO_2.[52−54]

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \tag{1}$$
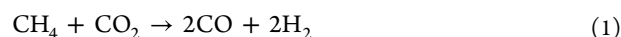
Gasification. A wide range of carbon-based materials can be used as feedstock in this process. Among them, coal, coke, and biomass are popularly used and already commercialized. This process normally results in the formation of syngas with an $H_2:CO$ ratio of 1.[55,56] The process involves a mixture of steam and carbon feed which results in the formation of syngas as shown in eq 2.

$$C + H_2O \rightarrow CO + H_2 \tag{2}$$

Partial Oxidation of Methane (POX). Partial oxidation of methane is also a plausible path for syngas production. Compared to SRM, it is defined as being much more cost-efficient, since it is less energy-intensive. If well developed, this process will be an industrially relevant path, since its operation is far cheaper.[57−60] The process involves the introduction of CH_4 and O_2 into a reactor to produce syngas with an $H_2:CO$ ratio of 2 as shown in eq 3.[61] Notably, the process is challenging with selectivity control to avoid total methane combustion.

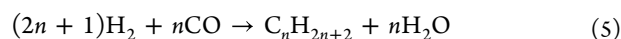$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \tag{3}$$
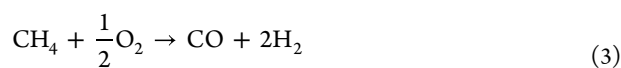
Steam Reforming of Methane (SRM). Steam reforming of methane is a traditional process for the production of hydrogen. The process involves the introduction of super-heated steam and natural gas (CH_4) into reactor tubes containing nickel-based catalysts.[62,63] The mixture flows through the tube, heated externally to produce hydrogen and CO. The H_2/CO ratio obtained is normally 3 as shown in eq 4.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{4}$$
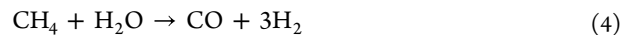
Syngas Conversion to Hydrocarbons. The catalytic conversion of syngas can be crucial for the production of valued hydrocarbons such as light olefins and liquid fuels via either the Fischer−Tropsch synthesis (FTS)[64−66] or the so-called intermediating alcohol/dimethyl ether molecule to hydrocarbon (MTH) route.[67−69] The FTS process was invented by two German scientists Han Fischer and Franz Tropsch in 1920.[70] They derived eqs 5 and 6 below to highlight chemical reactions following the production of paraffin and olefins in FTS. Both reactions are highly exothermic with $\Delta H = -165$ to -204 kJ/mol. FTS is currently being applied as the world takes steps toward net-zero.[71]

Selectivity for paraffins:

$$(2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \tag{5}$$

Selectivity for olefins:

$$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O \tag{6}$$
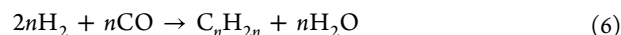
The MeOH or DME to hydrocarbon is also a pathway, equally feasible for sustainable syngas conversion to hydrocarbons. The traditional procedure engages the synthesis of methanol and subsequent conversion to hydrocarbons as two independent processes, thus the reference indirect route.[72] The MeOH can be produced over an industrially applicable Cu/Zn/Al catalyst which is then converted to hydrocarbons over solid acids such as zeolites. However, recent progress in the route converts syngas to hydrocarbons in single-step catalysis, using oxygenated compounds such as MeOH, EtOH, formic acid, etc., as intermediates.[73,74] The insights into the different
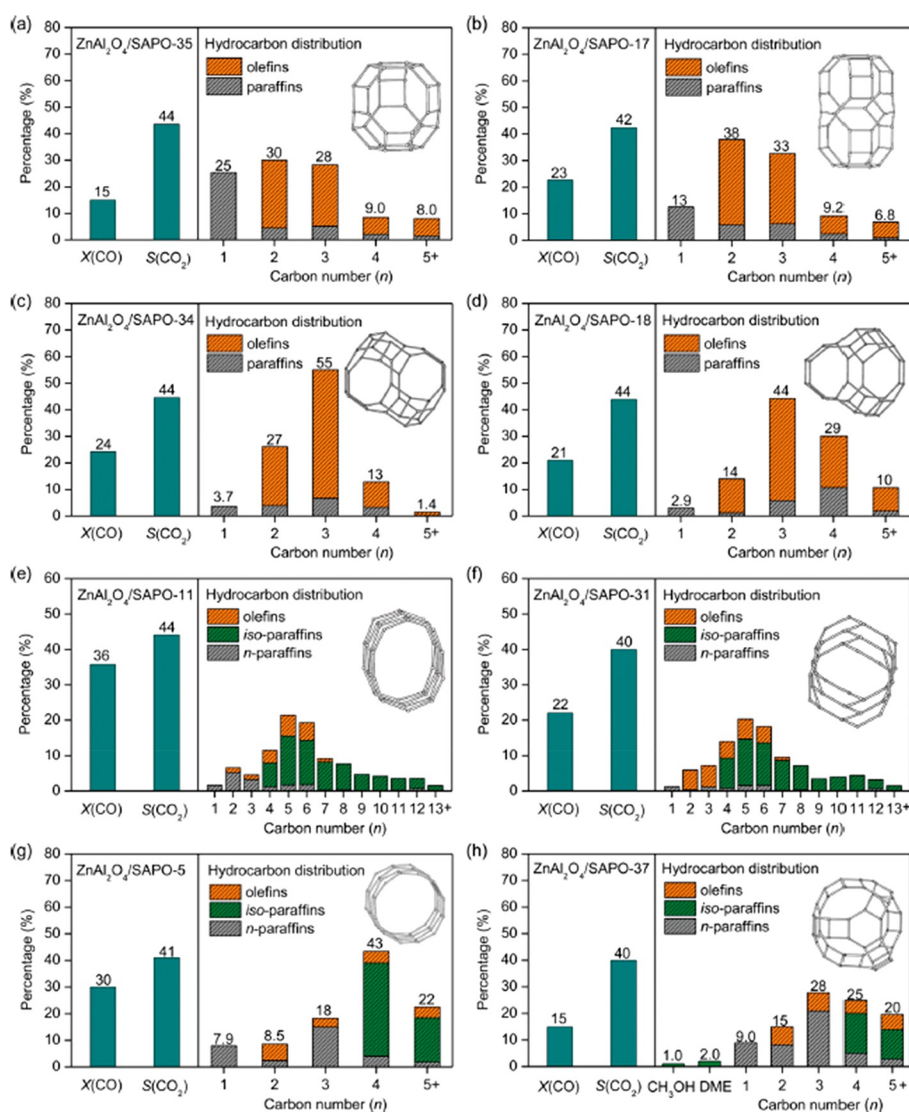
Figure 1. Effect of framework topology of SAPO zeolites on the catalytic performances of bifunctional ZnAlO/SAPO catalysts in syngas conversion. (a) ZnAlO/SAPO-35, (b) ZnAlO/SAPO-17, (c) ZnAlO/SAPO-34, (d) ZnAlO/SAPO-18, (e) ZnAlO/SAPO-11, (f) ZnAlO/SAPO-31, (g) ZnAlO/SAPO-5, and (h) ZnAlO/SAPO-37. Reaction conditions: W_{cat} = 0.5 g, H_2/CO = 2, P = 3 MPa, F_{syngas} = 25 mLmin^{-1}, T = 350 or 400 °C, time on stream = 0.5 or 10 h. $X(CO)$ and $S(CO_2)$ stand for CO conversion and the selectivity of CO_2, respectively. Reprinted with permission from ref 81. Copyright 2021 from Elsevier.

influences of the zeolite topology and acidity can correlate to identify the status quo for future references in catalyst fabrication. Here in this section, we highlight the major characteristics of zeolites that enhance the distinct production of valued products via syngas conversion.

Steric Effects of Zeolites in Syngas-to-Hydrocarbons. The distinct structure of a zeolite can afford a unique capability for shape-selective catalysis for enhancing activity toward desired products in syngas conversion. Zeolite comes with a unique structure such as dimensions (3D, 2D, 1D, etc.) and member rings (14 MR, 12 MR, 10 MR, 8 MR, etc.).[75,76] Recent modifications on zeolites for them to assume different shapes, sizes, and pores have also proven to be beneficial to improve the distinct selectivity of specific products in syngas conversion.[77] Additionally, strategies to couple the metal with zeolite in the quest to exploit certain morphological properties have also been studied.

Effects of Zeolite Framework Topology. Zeolite topology is the main characteristic exploited for the shape-

selective ability, attributed to zeolites. The framework in particular defines the threshold for various molecules to diffuse. The effects of the zeolite topology have been studied by many researchers in syngas conversion with a general conclusion that different frameworks provide different hydrocarbon products, deviating the overall distribution from the ASF model.[78]

Liu et al. investigated the one-pass synthesis of propane from syngas in a reaction system configured with the synthesis of syngas to DME over a CuZnAlO$_x$ + ZSM-5 catalyst in the upper bed, with subsequent transformation of DME to propane on SSZ-13 zeolite in the second bed.[79] A high propane selectivity was achieved as the oxy* intermediates are first converted to propylene, which is subsequently hydrogenated to propane. SSZ-13(CHA) demonstrated the best stability for propane production when compared with SAPO-18(AEI) and SAPO-34(CHA), possessing similar 8 MR microporous structures. Xing et al. investigated the direct syngas conversion to gasoline over Beta, ZSM-5, and SAPO-11
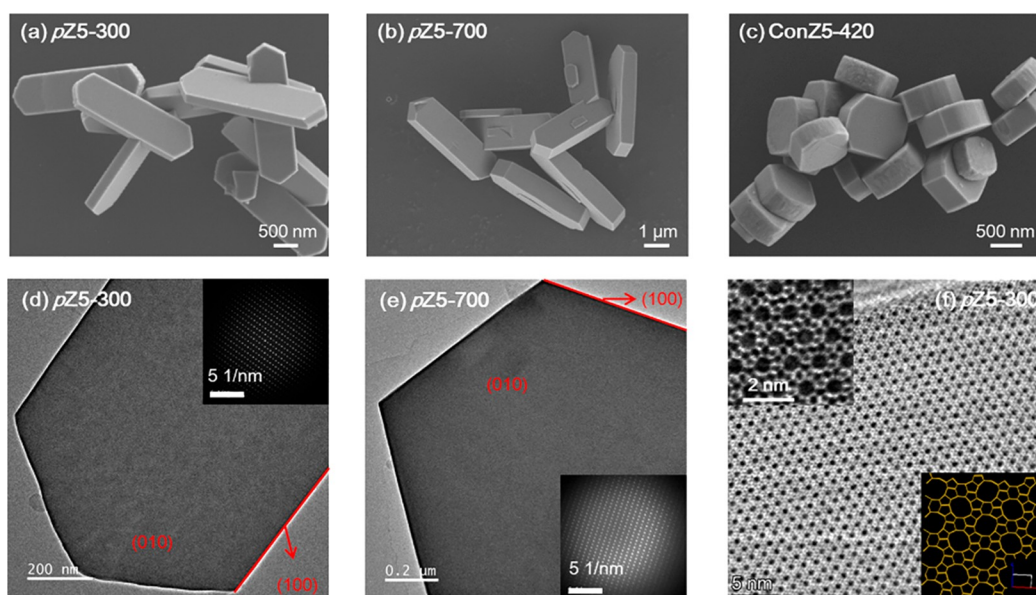
Figure 2. (a−c) SEM images of platelike and elliptic column-like ZSM-5. (d,e) TEM images, with the insets showing the corresponding SAED patterns. (f) STEM image of pZ5-300, with the inset on the top, the left showing the STEM image with high resolution and that on the bottom right showing the framework structure of ZSM-5 projected along [010]. Reprinted with permission from ref 84. Copyright 2020 from American Chemical Society.

zeolites employing Co/SiO_2 as the main FTS catalyst.[80] Their investigation revealed that the large 12 MR pores of Beta supported diffusion of olefin intermediates that enhanced oligomerization activity leading to the highest selectivity for gasoline. The 3D structures associated with Beta zeolite further enhanced the isomerization activity that led to the highest isoparaffin selectivity of 41.7%. The reaction of SAPO-11 demonstrated the lowest selectivity of 58.0% for gasoline but a high of 14.0% selectivity for $C_{12}+$ hydrocarbons. The authors concluded that, at the reaction condition, the 1D channels of SAPO-11 resist hydrocracking but were rather a platform for oligomerization of long-chained hydrocarbons.

Wang et al.[81] investigated 8 different SAPO-type zeolites, intending to reveal the effects of the framework topology on product distribution in syngas conversion (Figure 1). Their investigation revealed and confirmed earlier effects of different hydrocarbons on zeolites. They observed that the 8 MR zeolites favored the selectivity for $C_2−C_4$ olefins with selective distribution toward ethylene, propylene, and butene. SAPO-11(10 MR) and SAPO-31(12 MR) with 1D structures conversely favor the formation of gasoline-range hydrocarbons ($C_5−C_{11}$), which has also been reported by Li et al.[82]

The various results reveal the effects of the common zeolite structures in selective synthesis of desired products. A summarized conclusion can be reached that the 1D-type zeolite enhances chain growth for linear hydrocarbon formation, whereas the 3D-type favors branched hydrocarbon formation leading to high isomerization activities and cyclic hydrocarbon formation. A critical translation of member rings to product distribution suggests that the 8 MR zeolite such as SSZ-13 and SAPO-34 favor light hydrocarbon formation whereas zeolites with ≥10 MR such as ZSM-5, Silicate 1, and ZSM-22 offer structures for liquid hydrocarbon formation.

Effects of Zeolite Crystal Size and Pore Properties. The effects of zeolite crystal size and pore system have been investigated by many researchers to reveal how the different sizes influence the hydrocarbon product distribution. It has

been highlighted that modifying the intrinsic properties of the identical zeolite can directly influence their activity in hindering or promoting the diffusion of reactants and intermediates in syngas conversion.

Arslan et al. reported a high CO conversion and tetramethylbenzene selectivity of over 70% in hydrocarbon products over a bifunctional Zn−Cr oxide and nanosized ZSM-5 catalyst.[83] The high selectivity obtained can be attributed to the reduced diffusion limitations of H-ZSM-5 by shortening the length of straight channels [010] along the b-axis and reducing the crystal size. Enhanced diffusion of product and smooth surface alkylation of BTEX created an aromatic hydrocarbon pool deficiency which intensified the conversion of olefins to aromatics. Liu et. al reported that the selectivity for aromatics is strongly influenced by the crystal size of ZSM-5 (Figure 2).[84] Their study on the direct syngas conversion to aromatics over a Cr_2O_3/ZSM-5 composite revealed that altering the crystal size of the ZSM-5 along the b-axis of the crystal can drastically increase the selectivity for aromatics. The group reported a high of 49.1% selectivity for BTX in the total products. Xu et al. followed up with the design of a hollow mesoporous ZSM-5 zeolite with mixed ratios of TPAOH/NaOH treatment to boost gasoline production in FTS.[85] They reported that the mesopores created in the hollow materials enhanced selectivity to gasoline by accelerating mass transport to avoid repeated hydrocracking within the channels of the ZSM-5 zeolite. Compared with previous reports, the catalyst from this work demonstrated the best gasoline selectivity of 80.4% at a CO conversion of 69.3%. Wang's group had earlier demonstrated the influence of larger pores by introducing mesoporosity in zeolite Y to effectively control the hydrogenolysis in FTS.[86] Their reaction oriented the products toward $C_{10}+$ with a C_{10-20} selectivity of up to 60%, which is a very large deviation from the ASF model. Comparing the characterization from the various reports under study reveals that increasing pore sizes greatly enhances mass transfer of the reactants and intermediates, which enables

Scheme 2. Common Strategies Observed for Coupling Metal and Zeolites in Developing Efficient Catalysts for Syngas Conversion
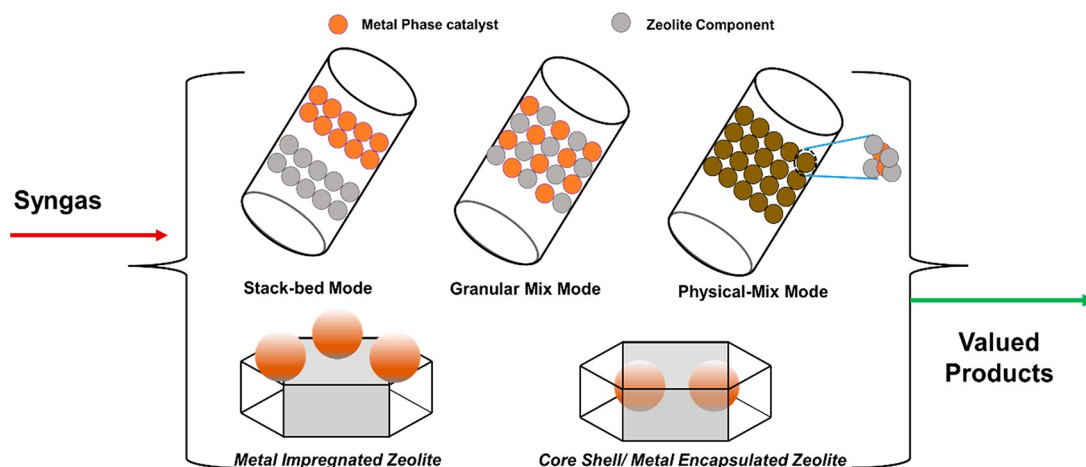
efficient hydroprocessing on the zeolites. Afterward, the products readily escape the catalyst, reducing any further contact with the intermediates and reactants. The properties of the zeolites are exploited well as they tend to enhance the selectivity toward desired long-chained hydrocarbons. The small crystal size of the ZSM-5 has also proven to be very efficient in converting oxygenates to aromatics. Syngas was converted to gasoline over a dual-bed catalyst $(CZA + Al_2O_3)$/N-ZSM-5(97).[42] The composite effectively transformed syngas to quality gasoline with an outstanding C_{5-11} iso/para ratio of 18. By comparison, the results indicated that the nanosized ZSM-5 highly restricted coking, thus prolonging the life span of the catalysts. More recently, as a series of MFI zeolite composites combined with CoMnAl reported to contain CO_2C was well utilized to transform syngas to aromatics.[87] The selectivity of aromatics reached 52.5% with less than 2.5% selectivity for CH_4. The summarized report indicated that nanosized ZSM-5 enhanced conversion and diffusion of olefin intermediates.

After a critical comparison, the literature accompanying the effects of crystal size and pore properties indicates that the size of the zeolites can effectively process intermediates for the enhanced formation of hydrocarbons. The reduced size increases the surface area which makes available more surfaces for adsorption of reactants and intermediates. Meanwhile, the large pore properties obtained over intrinsically large pore zeolites or modified meso- or hierarchical have proven to enhance the diffusion of reactant and intermediate for effective hydroprocessing. While this is the fact, an optimum status for the zeolite pore size is always required for effective selectivity to desired hydrocarbons.

Effects of Acidity and Cations. A key characteristic of highly desired zeolites is their amphoteric nature. Aside from the pure silica zeolites, a typical zeolite structure is compensated by cationic species to obtain "neutrality".[88] If the charge is provided by protons, the resulting zeolite often assumes a strong Brønsted acid site. The H^+ or protons could be replaced by other cations (Na, K, Li, Fe, Zn) to alter the Brønsted acidity and enhance Lewis acid sites as well as some basicity. This potential of zeolites has been employed widely in hydrogenolysis, oligomerization, and alkylation, especially in the hydrocarbon processing industry in which syngas conversion can be recognized.

The effects of acidity in direct syngas conversion to olefins were demonstrated by Liu et al. over a $Zn-ZrO_2-SSZ-13$ catalyst.[73] The Brønsted acidity was tuned by varying the degree of H^+ exchanging on 8 different SSZ-13 samples. The NH_3-TPD results indicated that the acidity increases accordingly. The results indicated that the SSZ-13 sample demonstrating average acidity favored the selective conversion of MeOH/DME intermediates to light olefins. The light olefin selectivity reached 87% at 10% and 77% at 29% CO conversion.

A recent study was reported by Su et al.,[89] who designed a bifunctional catalyst for the direct synthesis of olefins from syngas by coupling $ZnCrO_x$ with a low-Si AlPO-18 zeolite having an AEI framework. The 8 MR zeolite possessing 3.8 Å × 3.8 Å channels demonstrates outstanding performance, with a highlight olefins (C_{2-4}) selectivity and O/P ratio of 87% and 29.9%, respectively. In detail, the performance of the final composite catalyst can be attributed to the intrinsic acidity obtained over the final low-Si ALPO-18. Using SAPO-34 as a reference zeolite, the authors reported a much lower peak for the Si-OH-Al Brønsted acid sites for the low-Si ALPO-18. This reduced the acidity density and promoted isolation of the acid sites which reduced the secondary reaction, thus increasing the olefin selectivity.

Li et al.[90] demonstrated outstanding progress in the FTS with the development of rare-earth metal-exchanged mesoporous Y to directly produce gasoline, jet fuels, and diesel fuels. The Brønsted acidity was outstandingly high on the H-type Y zeolite, whereas the rare-earth metal options demonstrated mild Brønsted acidity. The pyridine FTIR spectra of the samples also indicated that while the H−Y was dominated by strong Brønsted acidity, the La^{3+} and Ce^{3+} options demonstrated mild acidity in both Lewis and Brønsted regions. A general conclusion from the results indicated that hydrocracking was more prevalent on the H-type zeolite, which demonstrated the highest selectivity for CH_4 and C_{2-4} hydrocarbons. Ce^{3+} and La^{3+} options demonstrated outstanding selectivity for gasoline and jet fuels, respectively.

Proximity Effects between Metal and Zeolite. Tuning product distribution in syngas conversion via a secondary reaction over zeolite-based catalysts is a technology bound to stay. The tandem catalysis can exploit zeolite properties; however, optimizing the potential is crucial. The two main
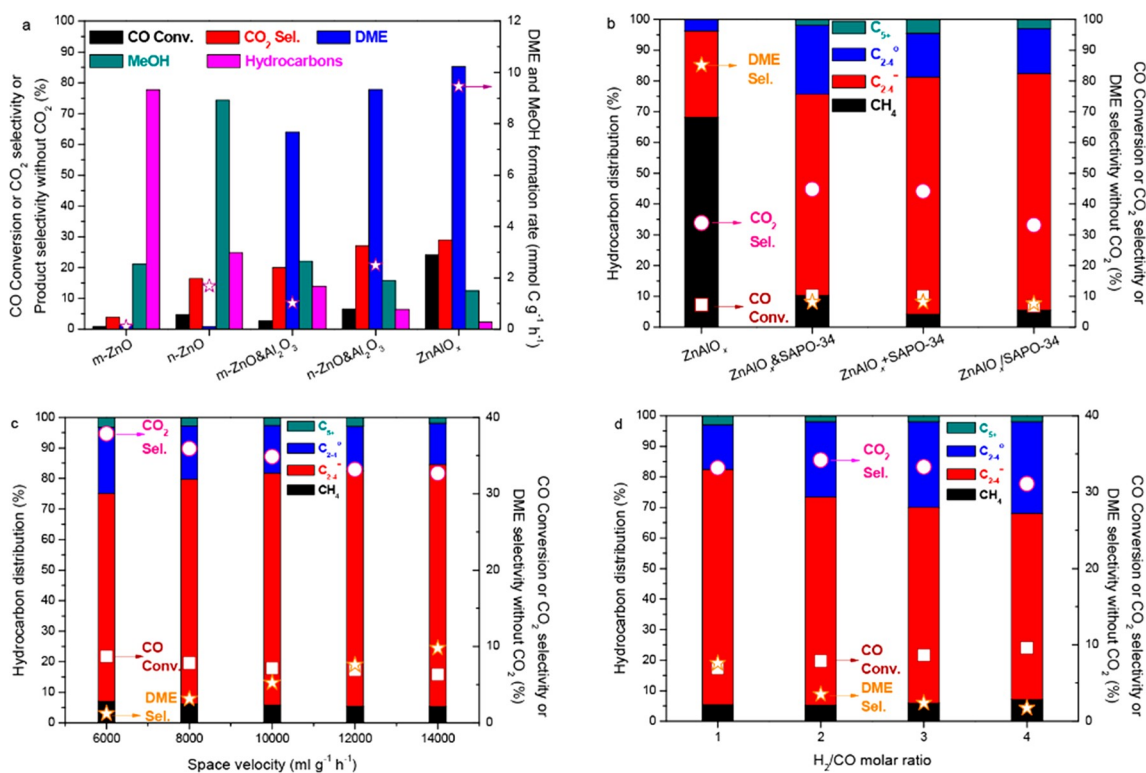
Figure 3. Catalytic results for syngas conversion over various catalysts. (a) STD performances. $H_2/CO/Ar = 2/1/0.1$. Space velocity (based on all reactants at STP in this paper) = 4000 mL g^{-1} h^{-1}, 633 K, 4.0 MPa. (b) STO performances over dual-bed and mixed catalysts. $H_2/CO/Ar = 1/1/$ 0.1, Space velocity = 12 000 mL g^{-1} h^{-1} (or 24 000 mL g^{-1} h^{-1} for ZnAlO$_x$), 663 K, 4.0 MPa. (c) Effect of space velocity over dual-bed ZnAlO$_x$/ SAPO-34. $H_2/CO/Ar = 1/1/0.1$, 663 K, 4.0 MPa. (d) Effect of H_2/CO ratio over dual-bed ZnAlO$_x$/SAPO-34. Space velocity = 12 000 mL g^{-1} h^{-1}, 663 K, 4.0 MPa. Note that C$_5$+ includes hydrocarbons with no less than 5 carbons. C$_{2-4=}$ and C$_{2-4}$° refer to C$_{2-4}$ olefins and paraffins, respectively; m-ZnO and Al$_2$O$_3$, n-ZnO and Al$_2$O$_3$, and ZnAlO$_x$ and SAPO-34 prepared by grinding; ZnAlO$_x$ + SAPO-34 prepared by granule mixing; ZnAlO$_x$/ SAPO-34 denoted as dual-bed catalyst. Reprinted with permission from ref 96. Copyright 2019 from American Chemical Society.

catalytic phases are strategically combined, which always results in a different distribution. To identify, correlate, and optimize the advantages of bifunctional metal-zeolite composite catalysts, the detailed effects of metal zeolite proximity are currently under study to answer the most challenging question, "how close?" In this part, as presented in Scheme 2, we highlight the common strategies employed to fabricate metal-zeolite composite catalysts in syngas conversion to valued hydrocarbons.

Syngas to Light Olefins (C$_{2-4}$). The proximity effects for fabricating bifunctional metal-zeolite catalysts in the syngas conversion to olefins have been investigated intensely.[91−93] Olefins remain promising for industrial applications; thus sustainable processes for production are intensely being researched. From syngas, two major routes have been popularly adopted to synthesize olefin, the FTs route[94] and process via oxy-* intermediates.[89] The proximity between Zn-ZrO$_2$ and SSZ-13 on olefin production was investigated by Liu et al. using the dual-bed mode, granular mix, and physical mix of both components.[73] Prior reactions on Zn-ZrO$_2$, in the absence of the zeolite, orient product distribution toward MeOH and DME. These chemicals served as intermediates on the zeolites for hydrocarbon formation. To conclude, the results of the different configurations suggest that the very close proximity between Zn-ZrO$_2$ and SSZ-13 components highly favors olefin formation via oxygenates as intermediates. The reduced selectivity for CH$_4$ and paraffins with increased metal-zeolite proximity was attributed to the reduced repeated contact of the intermediates with the catalyst phases. A similar

investigation involving the interaction of metal and zeolite phase catalysts was performed by Weber et al. for tunable synthesis of olefins and aromatics.[95] It was observed that the large spatial separation between the Fe-based and zeolite catalyst demonstrated the stable formation of CH$_4$ and aromatics; ample proximity favored olefins formation, while very close proximity hugely reduced olefin formation which was compensated by formation for more CH$_4$.

Ni et al. further investigated a multistage reaction to reveal the effects of proximity on syngas conversion to olefins via MeOH; intermediates (Figure 3).[96] The set of reactions involving ZnAlO$_x$/SAPO-34 composite realized a high 77.0% selectivity for olefins at a CO conversion and CO$_2$ selectivity of 6.9% and 33.1%, respectively. Comparison with a similar composition prepared by the physical mixing of ZnAlO$_x$ with SAPO-34 demonstrated much higher selectivity for olefins and CO conversion. However, the selectivity for CO$_2$ was increased to 44.1% decreasing for overall light olefins. These investigations suggest that proximity favors the conversion of oxygenated intermediates to olefins on zeolites. An interesting fact is that all investigations focused on the selective production of olefins have preferred the use of small pore 8 MR zeolites to enhance the shape-selective abilities for enhanced light hydrocarbons synthesis. However, several factors concerning the intrinsic property of the zeolite can either enhance or suppress the conversion rates of intermediates as well the overall catalyst stability.

Syngas to C$_5$+ Hydrocarbons. The production of C$_5$+ hydrocarbons from syngas has been studied extensively via

various routes. The enhanced synthesis of C_5+ hydrocarbons demonstrate the ability of novel catalysts to overcome the predictions of the ASF distribution.[26,97] The FTS route which is very common has incorporated different strategies to couple mainly Co and Fe-based catalysts with zeolites to orient products toward gasoline. Further research has been undertaken to significantly improve the gasoline quality, since its octane rating is crucial for standardization and engine performance.[98−100] Tsubaki's group can be identified as one popular in the direct syngas conversion to gasoline.[66,101−104] Zhang et al. rationalized the selectivity for gasoline-ranged isoparaffins via the induction of olefins.[105] Their work compared the influence of bifunctional phase proximity on isoparaffin selectivity. Their work concluded that oligomerization and isomerization are pronounced over ZSM-5 when there exists ample space between the FTS metal and zeolite phase. Cheng and his team also confined cobalt metal in ZSM-5 catalysts for direct gasoline (62.4%) and diesel (66.2%) production.[103] Their work concluded that confinement of small cobalt particles in the zeolites inhibits the escape of reaction intermediates leading to high selectivity toward heavy hydrocarbons. The references indicate that the selective synthesis of C_5+ hydrocarbons can be attributed not only to the zeolite topology but to acidity and porosity. These factors strongly facilitate C−C chain propagation, mass diffusion for intermediates, and easy escape of products.

Syngas to Aromatics. Aromatics are prominent chemicals that can improve the octane rating in liquid hydrocarbon fuels. Recently, Zhao et al. used Na-Zn-Fe_5C_2 coupled with hierarchical HZSM-5 to enhance the aromatic selectivity in syngas conversion.[105] The final catalyst structure that can be defined as metal@zeolite composite effectively enhanced aromatic selectivity by exploiting the proximity between the metal sites and Brønsted acid sites in the pores of the zeolites. Weber et al. investigated the effects of proximity on catalyst deactivation in syngas conversion to olefins and aromatics.[91] Their reactions indicated that in mixing Na promoted iron with zeolite; Na migration to the zeolite caused loss of activity due to Na migration. Reducing the proximity, however, inhibits the migration thus extending the activity longer. Cheng and his team designed a bifunctional Zn-ZrO_2-HZSM-5 composite catalyst system for the conversion of syngas to aromatics.[91] Their study revealed that very close proximity is essential for the transfer of intermediates to facilitate olefin production and the subsequent aromatization process.

The dynamics following the transformation of syngas investigated via the proximity reveals a lot about how structures are activated concerning distance to the intermediates. Zeolites in syngas conversion to hydrocarbons operate normally for secondary reactions or as auxiliary to the metal catalysts. Proximity as revealed by the literature favors the maximum exploitation of the characteristics of zeolites; however that does not define the distinct selectivity of products. Conversion of syngas to hydrocarbons via the oxy-* route is highly favored over very close proximity between the metal species and zeolite. Olefins and gasoline are the paramount products that are often obtained via this route. For the future, production of much longer-chain hydrocarbons such as jet fuel or diesel is being researched for the ultimate production of sustainable fuel.

■ SYNGAS TO OXYGENATES

Oxygenates such as MeOH, DME, C_2+ alcohols, esters, and aldehydes are the major essential products that can be derived from syngas using metal-zeolite composite catalysts.[106−108] Usually, deriving these oxygenates from syngas proceeds through the inset of an adsorbed CO into alkyl species formed by the prior dissociation of adsorption CO (Scheme 3).

Scheme 3. Simple Schematic Representing the Reaction Mechanism Following the Synthesis of CH_3OH, CH_3OCH_3, CH_3COOCH_3, and C_2H_5OH over a Metal-Zeolite Catalyzed Surface
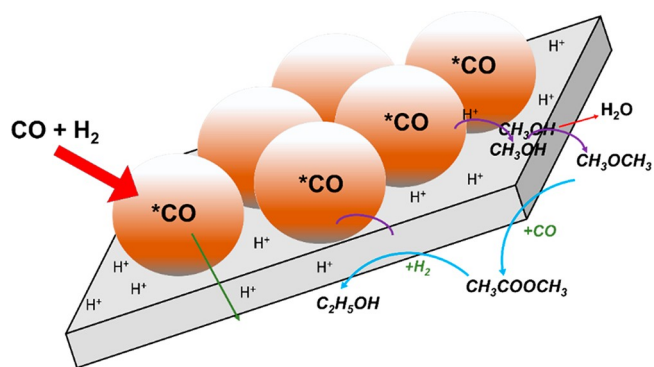
Accordingly, the selective synthesis of oxygenates involves the fabrication of bifunctionally active catalysts in which one active site stimulates the dissociate adsorption of CO for alkyl species formation, while the other facilitates the insertion of nondissociative adsorbed CO into alkyl species to form the oxygenate.[109,110] However, it is challenging to obtain high oxygenate selectivity because of the energy requirements of both processes. The energy barrier for hydrogenation of the alkyl species is usually lower than that required to couple the CO* intermediates with the alkyl species, resulting in lower selectivity toward oxygenates. Therefore, to improve selectivity, it is crucial to progress the CO insertion process by tuning the synergy between the two active sites, which could suppress side reactions to form undesirable hydrocarbons. In recent years, strategies have been developed to combine active metals and zeolites to tandemly catalyze syngas conversion to various oxygenated products. The metal and zeolite composite has been efficient in the catalysis of inserting the CO* in alkyl species in a single step to enhance the selective production of desired oxygenates. Therefore, this section will highlight the major characteristics of tandem metal zeolite composites, the synergy between them, and the zeolite properties that functionally convert syngas to selective oxygenates. This section will be divided by the catalyst structure and how key descriptors such as acidity, topology, porosity, and proximity factors affect the product selectivity.

Steric Effects of Zeolite. Different zeolite-based catalysts have been employed widely to enhance selectivity for oxygenates in syngas conversion. While it is easier to transform the selectivity for hydrocarbons by employing the shape-selective abilities accompanying different zeolite topologies, it has been conversely challenging if the products in focus are C_2+ oxygenates. However, a few recent studies have shown progress in this field using different routes.

Effects of Zeolite Framework Topology. Recently, Kang et al. exploited the frameworks from various zeolites and
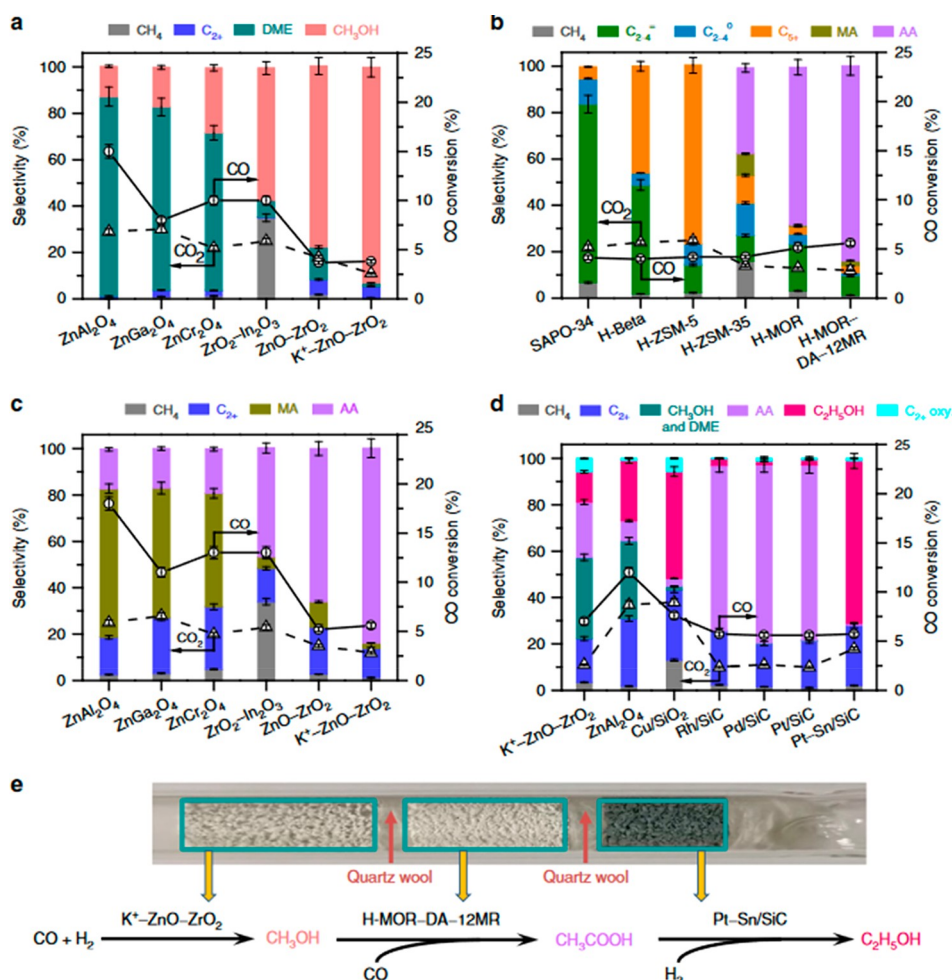
Figure 4. Catalytic behaviors and reaction pathways. (a) Metal oxide alone. (b) Combinations of K$^+$-ZnO-ZrO$_2$ and zeolites. (c) Combinations of metal oxides and H-MOR-DA-12MR. (d) Combinations of K$^+$-ZnO-ZrO$_2$, H-MOR-DA-12MR, and hydrogenation catalysts. (e) Reaction pathways for direct synthesis of ethanol from syngas. C$_2$+: C$_2$+ hydrocarbons; DME: dimethyl ether; C$_{2-4=}$: C$_2$−C$_4$ olefins; C$_{2-4}$°: C$_{2-4}$ paraffins; C$_5$+: C$_5$+ hydrocarbons; MA: methyl acetate; AA: acetic acid; C$_2$+ oxy.: ethyl acetate and methyl acetate. Reaction conditions: weights of metal oxide, zeolite, and hydrogenation catalyst = 0.66, 0.66, and 0.66 g; H$_2$/CO = 1:1; P = 5.0 MPa; T = 583 K; F = 25 mL min^{-1}; time on stream, 20 h. The selectivity was calculated on a molar carbon basis. Carbon balances were 95−99%. The experiments in each case were performed three times. The error bar represents the relative deviation, which is within 5%. Reprinted with permission from ref 18. Copyright 2020 Springer-Nature.

succeeded in obtaining an outstanding selectivity of 90% for ethanol via syngas conversion (Figure 4).[18] Their work involved the design of a tandem catalytic system that comprises K-modified ZnO-ZrO$_2$ (CO + H$_2$ → CH$_3$OH), modified H-MOR, DA-12MR (CH$_3$OH → CH$_3$COOH), and Pt-Sn/SiC(CH$_3$COOH → C$_2$H$_5$OH) in one reactor. The ethanol selectivity reaches 90% and 81% at CO conversions of 0.7% and 4.0% at 503 and 543 K, respectively. The modification by removing Al frameworks from the intrinsic 12 MR structures, MOR, resulted in reducing the Brønsted acid sites in the 12 MR region. This was reported to be the major influence in enhancing the acetic acid intermediates in the reaction. At a CO conversion of ~10%, the ethanol selectivity could be sustained at 64%. The system was very stable, and no deactivation was observed in 100 h.

Xie et al. investigated the synthesis of DME from syngas using a CuZnAl-zeolite composite catalyst.[111] The study focused on the influence of different 3D zeolites on the product distribution. After careful examination of the catalyst activity, it is revealed that all the zeolites were for a fact able to dehydrogenate the MeOH as intermediates for DME synthesis.

Among the different zeolites investigated, the highest DME selectivity of 70.4% was achieved on CZA/ZSM-5 with Si/Al ratio of 280. Different Si/Al ratios of ZSM-5 investigated demonstrated inferior DME selectivity with no linear correlation indicated that could vary the dehydrogenation mechanism on each ZSM-5. By comparison, the product distribution following different topologies in syngas conversion to oxygenates does not really exploit the shape-selective catalysis of zeolites as observed for hydrocarbon formation, but rather orientation of the molecular sieve avails other characteristics that may be exploited by the reaction intermediates.

Effects of Zeolite Crystal Size and Pore Properties. Crystal structure and pore properties can be essential for selective syngas conversion to valued carbon products. Different crystal sizes of zeolites were investigated for direct DME production from syngas by Cai et al. as presented in the Figure 5.[112] It was observed that the reaction rate for DME synthesis was highly favored over nanosized ZSM-5 which were more active than larger and intergrown agglomerated crystals. The core attribute of the nanosized materials was the
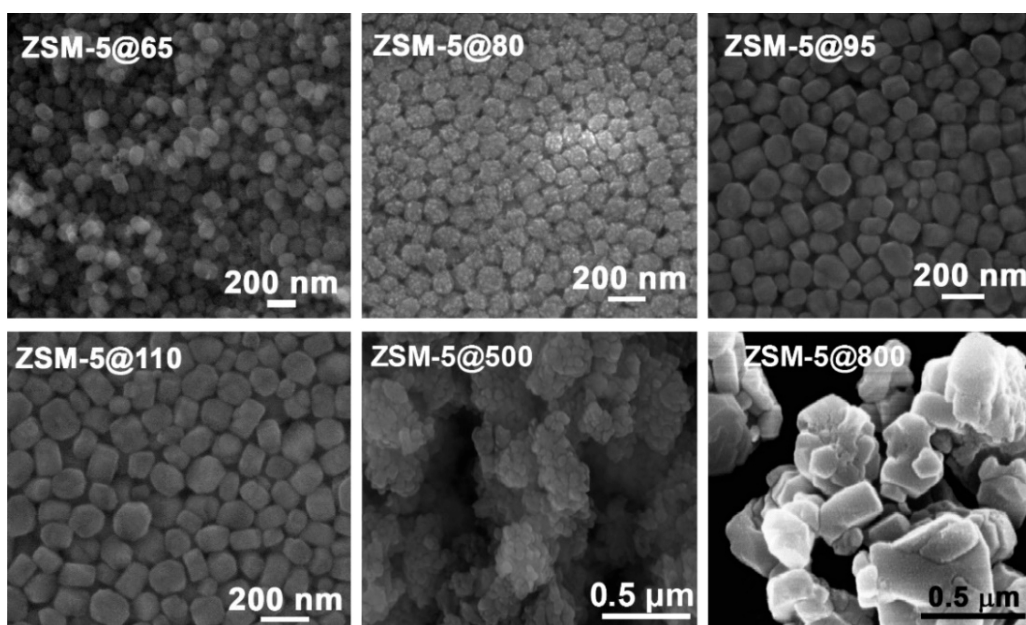
Figure 5. Representative SEM images of the series of ZSM-5 samples. Reprinted with permission from ref 112. Copyright 2016 Elsevier.
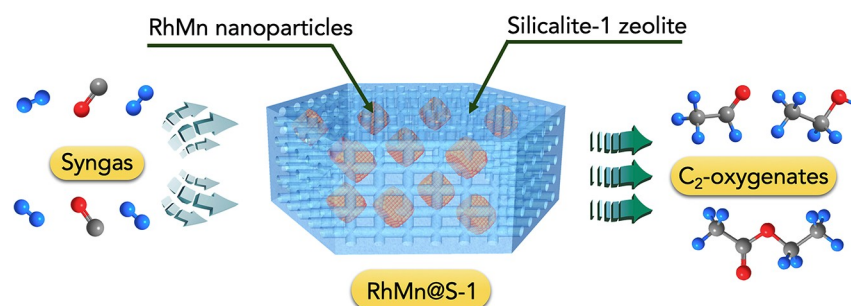

Figure 6. Schematic representing the direct conversion of syngas to ethanol. Reprinted with permission from ref 119. Copyright 2020 Elsevier.

ability to enhance mass transport over a larger surface area enabling easy access to acid sites. In another instance, varying crystal sizes of ZSM-5 were investigated to reveal the effects of combined syngas and DME conversion to ethanol.[113] The results demonstrated that the nanosized zeolites demonstrated a much higher surface, high density of pores, as well as highly accessible acid sites. The highlighted characteristics increased the DME carbonylation potential of the nanosized zeolites when compared with that of the conventionally sized ZSM-5. Large pores created in zeolites can also create a sufficient environment for the dehydration of MeOH to enhance the formation of DME.[114] In brief, large pores and high-surface-area zeolites reserve conditions for the suitable formation of oxygenates from syngas.

Effects of Zeolite Acidity and Cations. The direct impact of acidity in syngas conversion to higher alcohols was investigated by Luk et al.[115] Their investigation suggested that the difference in selectivity patterns can mainly be attributed to the carrier acidity following each zeolite. While using the density of the Brønsted acid sites as a linearized function, they identified that the selectivity for higher alcohols (HA), specifically the selectivity from 2-HA, was hugely improved via olefin hydration on acid carriers. In another study, a trifunctional catalyst system combining CuZnAl/HZSM-5 and HMOR improved the selectivity for ethanol to over 50% in products. The results indicated that the Brønsted acid sites

were the major key players in tuning the product distribution. In advanced experiments, the cations from MOR were exchanged with Zn which suppressed the overall acidity and improved the selectivity for ethanol to 69.6% at an increased CO conversion of 7.4%. In support, HZSM-5 with different Si/Al ratios was investigated to highlight the functions of acidity in the synthesis of DME from syngas.[116] Previous experiments have investigated rare earth metals modified zeolite Y for DME synthesis from syngas.[117] La, Ce, Pr, Nd, Sm, and Eu were introduced via ion exchange. Compared to the traditional H−Y zeolite, the rare earth metal modified ones demonstrate higher stability and activity in methanol dehydration for the formation of DME.

Generally, the zeolite functions as the dehydration catalyst to enhance DME synthesis from MeOH.[114] While more acidity will favor the dehydration of MeOH to DME, the opposite is required for MeOH production. Therefore, it is essential to strategically develop composite catalysts with optimum characteristics of the active sites for facile synthesis of each oxygenate disparate from each other.

Proximity Effects between Metal and Zeolite. The proximity between metal and zeolites has been investigated by many in research focused on transforming syngas into valued oxygenates. The reactions have been centered on exploiting the proximity between the metal and specific properties of zeolites

Table 2. Some Literature on Syngas Conversion to Various Valued Products

catalyst	T/(°C)	P/MPa	H_2/CO	CO Conv (%)	product selectivity (%)			ref
					$C_{2-4=}$[a]	C_5+	C_2+ oxy[b]	
FeMnK@HM-S-1	280	0.5	1.9	12	49	-	-	124
FeMn@HZSM-5	280	1	2	78.5	41.4	-	-	125
ZnAl$_2$O$_4$/MOR	370	3	1	10	77	6	-	123
ZnCrO$_x$/MOR	360	2	1	26	91	5	-	126
ZnO-ZrO$_2$/SAPO-34	400	1.0	2	7	69	5	-	127
Zn/Al$_2$O$_3$−SAPO-34	400	1.0	2	5	77	0	-	128
Zn-ZrO$_2$/SSZ-13	400	3	2	10	87	-	-	73
Ru/H-beta	260	1	2	78.8	-	71.7	-	66
Fe (0.1AC)@NaY	260	3	2	12.3	20.8	69.0	-	26
Ru/meso-ZSM-5	260	2	1	30	-	80	-	129
Co@S1	260	1	2	28.3	-	68.8	-	130
Co−Mn/Na-meso-Y	230	2	1	37	-	92	-	131
Cr$_2$O$_3$−ZnO-ZSM-5	400	4.0	0.5	63	-	44[c]	-	132
RhMn@S1	320	3	1	42.4	-	-	88.3[d]	119
CZA/ZSM-5(280)	260	5	2	44.6	-	-	70.4[e]	111
CZA-ZSM-5(25)	260	2	2	50.8	-	-	67.3[e]	133

[a]$C_{2-4=}$: lower olefins. [b]C_2+-oxy: C_2+ oxygenates. [c]aromatics. [d]ethanol. [e]DME.

in the quest to improve products and subsequently suppress side reactions.

Syngas to Ethanol Synthesis. Du et al. investigated a series of Cu, -MOR composite catalysts prepared as impregnated catalysts and core−shell catalysts to synthesize ethanol for syngas and DME. The results indicated that core−shell catalyst prepared with Cu/ZnO as core and Cu-MOR as shell demonstrated outstanding selectivity of 45.9% for ethanol.[118] Their increased proximity between the acid sites and the metal further reduced coking resulting in remarkable stability for the catalyst. Similar work was investigated for direct syngas conversion to ethanol over RhMn and S-1 catalysts. The impregnated option (RhMn/S-1) demonstrated a relatively lower CO conversion of 18.5% against the 42.4% over the RhMn@S-1 catalyst.[119] The metal encapsulated catalysts exhibit an outstanding ethanol selectivity of 88.3%. The authors attributed it to rigid zeolite cover that hindered the sintering of the Rh and Mn species stabilizing the Mn−O−Rh species responsible for facilitating C−C coupling elementary reaction for enhanced C_2+ oxygenate formation (Figure 6). Feng's group[113] investigated the proximity effects involving CZA and nanosized ZSM-5 for tuning syngas and DME to ethanol. It was observed that the closest proximity obtained via powder physical mixing favored MeOH formation with relatively little conversion for DME. Increasing the proximity using a granular mix mode demonstrated some increased conversion for DME; however, the selectivity for MeOH remains outstanding as the main product. When the catalysts are packed in a dual bed configuration, the results change dramatically. The DME conversion reaches a high of 43.6% with selectivity for EtOH reaching 44.5%. In discussion, it is revealed that the MA is a key intermediate for EtOH production, which is highly favored on the CZA catalysts. However, proximity with the zeolites reduces the CZA potential via competitive adsorption of the reactants on the zeolite thus lowering the MA production and ultimately ethanol production rate.

Syngas to DME. Paloma et al.[120] fabricated a series of ZSM-5 decorated CuO/ZnO/ZrO$_2$ for direct syngas conversion to DME. Their study suggested that the introduction of the zeolite on the optimized CZZ catalysts demonstrated improved CO conversion as well as enhanced selectivity for DME. By comparison, the results indicated that increasing the zeolite content increases the in situ methanol consumption via dehydration reaction to DME. This suggests that the selectivity trend over increased proximity between the metallic catalyst phase and the zeolite mass can be directly proportionated. In another instance, CuO-ZnO-Al$_2$O$_3$/HZSM-5 nanocatalysts were prepared by impregnation or coprecipitation/physically mixing, or combined coprecipitation/ultrasound methods, and their performance was investigated toward direct conversion of syngas to DME.[121] The authors concluded that the high dispersion of the active sites for CO hydrogenation was achieved on the catalyst prepared by the ultrasound method. The high dispersion demonstrated the highest proximity for enhanced selectivity for DME.

Syngas to MA. Jung et al. used the indirect production of MA using DME derived from syngas with subsequent carbonylation over a FER@FER catalyst.[122] The whole concept modeled the efficient production of MA via an integrated syngas production to DME production and subsequent MA production and separation. A total cost analysis was done by the authors to minimize the production cost. The proposed route was concluded to be economically feasible and hold potential as a renewable alternative for the commercialization of the process. To investigate the effects of catalyst phase proximity on MA production, Wang's group reported the enhanced MA production from syngas over a Cu/Zn/Al/HZSM-5|HMOR composite.[123] While the Cu/Zn/Al demonstrates outstanding selectivity for CH$_3$OH, the combined composite with Cu/Zn/Al/HZSM-5 demonstrates outstanding selectivity for DME indicating the function of the ZSM-5 zeolite.

CONCLUSIONS AND OUTLOOK

This paper reviews tandem catalysis involving mainly metal-zeolite composite catalysts for syngas conversion to value-added chemicals and fuels, with the focus on tuning product distribution. The recently increasing number of studies reveals that it offers an effective strategy to tackle the selectivity challenge of syngas chemistry. Here we have summarized some literature for the performance comparison (Table 2). Although

other reviews have been highlighted for zeolite-based catalysts, the scope has been very wide, limiting the focus on syngas chemistry over metal-zeolite composite. To date, there is no single review documenting the influence of zeolite as well as novel concepts for tuning product distribution over the metal-zeolite composite. This requires documents highlighting the catalytic disposition in syngas conversion reactions. The content of this outlook details some recent works focused on hydrocarbons and oxygenates synthesized from syngas. In summary, the shape-selective catalysis ability of zeolites can directly be attributed to the zeolite topology. In a direct proportion, small pore zeolites having 8 MR topology favor the formation of light hydrocarbons, while the larger $\geq$10 MR topology zeolites favor much longer-chain hydrocarbon production. 1D channels of the zeolites allow the diffusion and formation of linear hydrocarbons, thus favorable for oligomerization reactions. 3D channels conversely facilitate the isomerization and alkylation of molecules, thus favorable for the formation of branched and cyclic hydrocarbons. While comparing the sizes and porosities, the various literature indicated that the reduced sizes of the zeolites favor the mass transfer of reactants and intermediates over a high surface area. In addition, the large pores of the zeolites increase the capacity for larger molecule diffusion. The results from this review indicate the status quo and the vast opportunities available in this process. Nevertheless, some challenges need to be addressed. First and foremost, the conversion of syngas needs to improve drastically without lowering the selectivity and stability under really high space velocity, to make this technique more industrially demanding and competitive on the market. This demands a better understanding of reaction mechanisms and kinetics following the various routes. Therefore, operando studies on CO and H_2 activation are essential to clarify the structure and composition of the active sites for effective conversion of CO to essential products or intermediates for subsequent processing. While zeolite is essential for the selective synthesis of desired products, there is inadequate information to refer to in designing metal-zeolite composites for syngas conversion to valued products. Generally, specific characteristics of zeolites are exploited for the direct synthesis of products. With detailed operando studies at simulated reaction conditions, the various behaviors of the zeolite can be unveiled, which will be a major guide to the subsequent design of metal-zeolite composite catalysts in syngas conversion.

The topology of the zeolite is being exploited for the shape-selective synthesis of valued products. For instance, in olefin synthesis over Fe-based catalysts, alkali surfaces favor adsorption and subsequent transformation of CO to olefins. The Fe−C formation is favored over a high pH surface, which is an active phase for olefin synthesis. However, the acid density accompanying zeolites might alter the intrinsic pH of the Fe-zeolite composite catalyst focused on enhanced olefin formation from syngas.

Again, there is a lack of signifiers for the proximity between the two main active phases in tandem catalysis over metal-zeolite composite catalysts. Various effects of proximity have been studied rationally based on the physical investigation of proximity via catalytic reactions. While some information can be derived from these results, it is not enough to project future tandem catalyst developments at the kinetic level. It is essential for in situ reactions to be conducted in this respect to elucidate the effects of metal-zeolite proximity in syngas conversion to

various valued products. This will be an essential addition to future research in tandem catalyst design for syngas conversion.

Key step research keeps looking at the characteristic zeolite ability to function as a solid acid in hydroprocessing such as oligomerization, isomerization, alkylation, hydrocracking, etc. The mechanisms for the C−C formation, C−C cleavage, and subsequent processing are yet to be fully understood over zeolites, thus requiring more research. Particularly, the mechanisms of the first C−C bond are yet to be elucidated. It is also essential to elucidate which species are more favorable as intermediates in each hydroprocess. The stability of these intermediates, as well as the unstable and spectator molecules, needs to be revealed to clarify a route for future catalyst development. Currently, analytical techniques such as in situ IR, NMR, and synchrotron-based photoionization mass spectrometry have been used to study kinetics in syngas conversion; however, the actual intermediates remain in controversy. Additionally, the intricacy of the coexisting molecules and the effects of reaction conditions have rendered most of these techniques unable to reveal the state of intermediates. While metal-zeolite composite stands tall in various syngas conversion reactions, these basic revelations will be essential to boost research in this domain. More importantly, it will draw a large part of this process toward commercialization, ultimately taking a giant leap toward net-zero.

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Notes

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