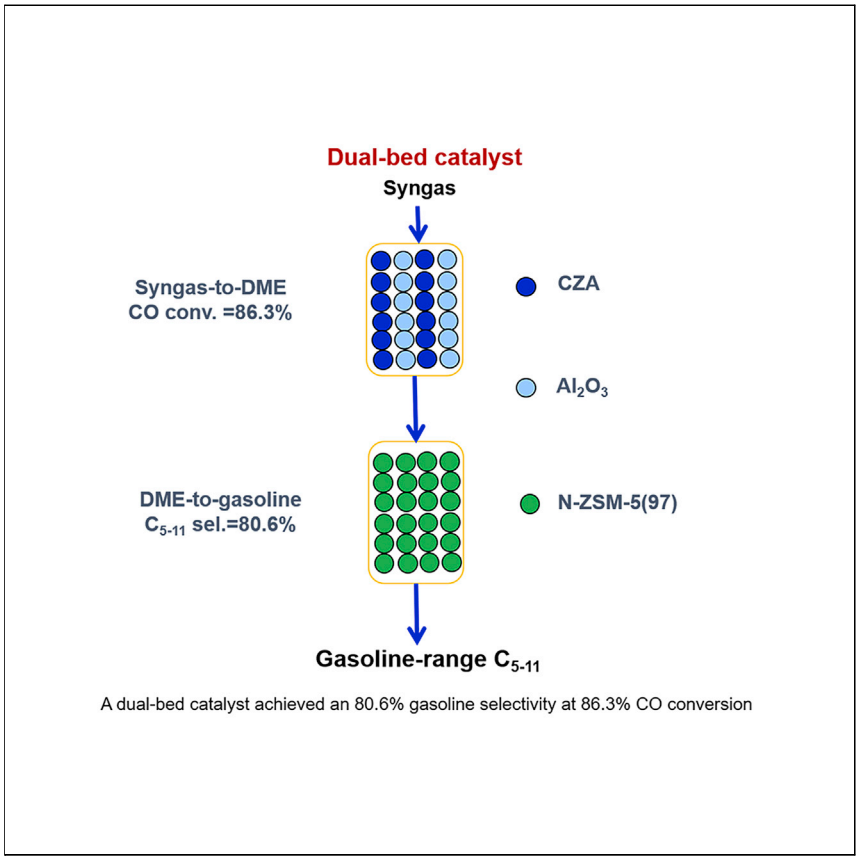
Chem Catalysis

CellPress

Article

Realizing high conversion of syngas to gasoline-range liquid hydrocarbons on a dual-bed-mode catalyst



Youming Ni, Kunyuan Wang, Wenliang Zhu, Zhongmin Liu

wlzhu@dicp.ac.cn (W.Z.)
liuzm@dicp.ac.cn (Z.L.)

Highlights

High and selective conversion of syngas to gasoline is achieved by a dual-bed catalyst

The dual-bed catalyst contains upper CZA + Al_2O_3 and lower N-ZSM-5(97) catalysts

Nano-sized structure of N-ZSM-5(97) is beneficial to reduce coke and prolong lifetime

The low acid content of N-ZSM-5(97) helps to increase gasoline selectivity

An 80.6% selectivity of gasoline-range hydrocarbons at 86.3% CO conversion can be achieved over a dual-bed catalyst that consists of a syngas-to-DME catalyst CZA + Al_2O_3 (a mixture of CuZnAl methanol synthesis catalyst and acidic γ-Al_2O_3 catalyst) in the upper bed and a DME-to-gasoline catalyst N-ZSM-5(97) (nano-sized H-ZSM-5 zeolite with Si/Al ratio = 97) in the lower bed. The dual-bed catalyst suggests a promising application in producing gasoline from syngas.

Ni et al., Chem Catalysis 1, 383–392
July 15, 2021
https://doi.org/10.1016/j.checat.2021.02.003

Chem Catalysis

CellPress

Article

Realizing high conversion of syngas to gasoline-range liquid hydrocarbons on a dual-bed-mode catalyst

Youming Ni,[1,2] Kunyuan Wang,[1,2] Wenliang Zhu,[1,2,*] and Zhongmin Liu[1,2,3,4,*]

SUMMARY

Achieving high conversion of syngas to fuels and basic chemicals with excellent selectivity and stability remains a challenge. Here, we report an 80.6% selectivity of gasoline-range C_{5-11} hydrocarbons at 86.3% CO conversion over a dual-bed catalyst (CZA + Al_2O_3)/N-ZSM-5(97) that consists of an upper-bed syngas-to-dimethyl ether (DME) catalyst (CZA + Al_2O_3) and a lower-bed DME-to-gasoline catalyst (nano-sized N-ZSM-5(97) zeolite). This dual-bed catalyst exhibits an excellent stability in a 110-h reaction test. The *iso*/*n*-paraffin ratio in the C_{5-11} is up to 18. For the lower-bed zeolite catalyst, the nano-sized structure is beneficial to reduce coke and prolong lifetime; meanwhile, the low acid content is advantageous to increase C_{5-11} selectivity. The 2,3-dihydro-1H-inden-1-one species can be definitely detected and identified in the spent lower-bed micro-sized M-ZSM-5(18) catalyst. They are regarded as intermediates to generate polycyclic aromatics, which generally lead to catalyst deactivation. The dual-bed catalyst (CZA + Al_2O_3)/N-ZSM-5(97) suggests a promising application in producing gasoline from syngas.

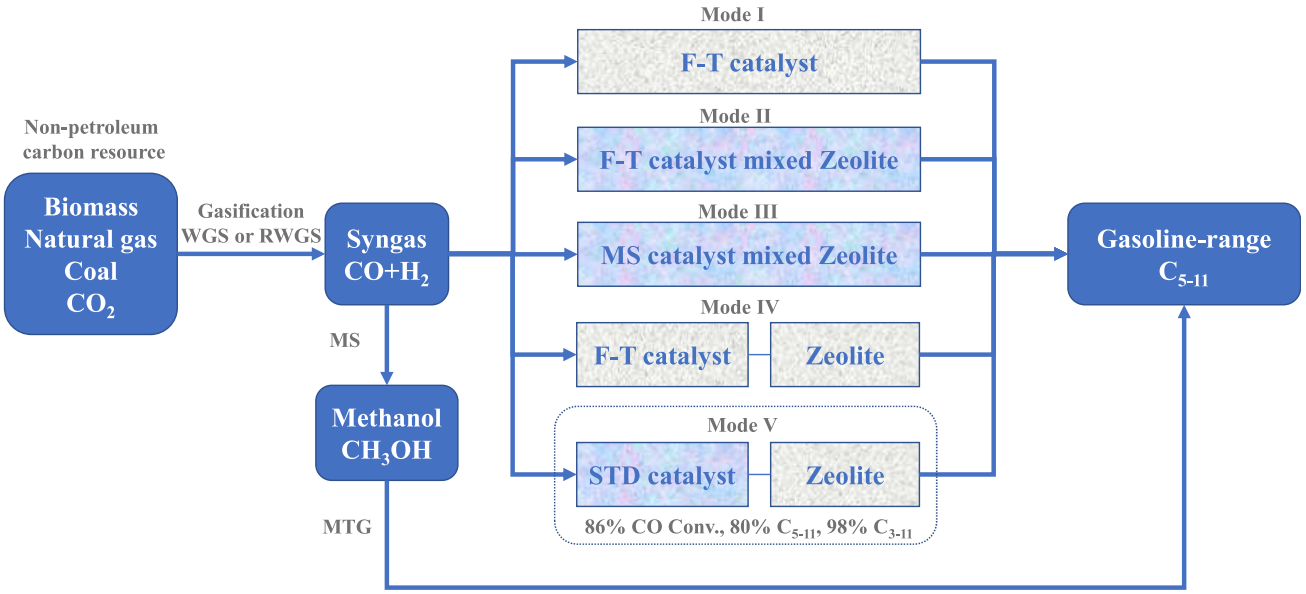
INTRODUCTION

In the past century, petroleum has made important contributions to the rapid development of economy and society. As a result of the gradual depletion and non-renewability of petroleum, the use of non-petroleum resources instead of petroleum is of great significance. This alternative route can be generally achieved through syngas (the mixture of H_2 and CO) chemistry because syngas cannot only be derived from non-petroleum carbon resources such as natural gas, coal, biomass, and CO_2 by gasification, water-gas-shift reactions, or reverse-water-gas-shift reactions (Scheme 1) but also directly or indirectly synthesize a wide variety of fuels and basic chemicals.[1–3] At present, the industrial technology for syngas production is relatively mature, but there are still many challenges in highly selectively and stably converting syngas into target products.[4–6]

The primary transportation fuel gasoline, which contains hydrocarbons with 5–11 carbons (C_{5-11}) and is almost entirely derived from petroleum now, can also be produced from non-petroleum syngas.[7] As illustrated in Scheme 1, syngas can be initially converted into methanol via methanol synthesis (MS) reaction and then transformed into gasoline via a methanol-to-gasoline (MTG) reaction. Over 30 years ago, Mobil MTG technology was industrialized in New Zealand.[8] To reduce investment and save energy consumption, directly synthesizing gasoline from syngas (STG) without separating intermediate products has been receiving extensive attention.[4] It is well known that gasoline can be obtained from Fischer-Tropsch (F-T) synthesis (mode I). However, because of the limitation of the Anderson-Schulz-Flory

The bigger picture

Because of the gradual depletion and non-renewability of petroleum, the use of non-petroleum resources instead of petroleum is of great significance. This alternative route can be generally achieved through syngas chemistry. The primary transportation fuel gasoline, which contains hydrocarbons with 5–11 carbons and is now almost derived from petroleum, can also be produced from non-petroleum syngas by some methods. However, stably obtaining high gasoline selectivity at high syngas conversion is still challenging. We have achieved this goal by designing a dual-bed catalyst (CZA + Al_2O_3)/N-ZSM-5(97) that includes a syngas-to-dimethyl ether (DME) catalyst CZA + Al_2O_3 in the upper bed and a DME-to-gasoline catalyst N-ZSM-5(97) in the lower bed. This dual-bed catalyst suggests a promising application in producing gasoline from syngas.



Scheme 1. The routes of converting non-petroleum carbon resources to gasoline

distribution, the selectivity of C_{5-11} is less than 50%.[9] Moreover, the carbon chain-growth mechanism determines that *n*-paraffins with low-octane value are predominant.[10] Zeolites (or molecular sieves) have uniform pore structures and acidity, which can not only limit the distribution of hydrocarbons according to the size of the micropores but also catalyze the isomerization of *n*-paraffins.[1,2] Therefore, they are often used to mix with F-T catalysts (mode II) to upgrade F-T hydrocarbons. However, it is not easy for zeolite to effectively convert the inert short-chain hydrocarbons, such as methane and ethane, or the heavy hydrocarbons larger than its pores, resulting in a low C_{5-11} selectivity.[6] Enhancing diffusion of heavy hydrocarbons by increasing the mesoporosity of zeolites or improving the proximity of acid sites and metal by well designing core-shell structures can help alleviate this problem. For example, Tsubaki and colleagues obtained approximately 74% C_{5-11} at 34% CO conversion on mesoporous Y zeolite combined with Co,[11] while Khodakov and colleagues acquired approximately 61% C_{5-12} at 37% CO conversion over core-shell ZSM-5/Ru/ZSM-5.[10] Unlike the mode II catalyst, where hydrocarbons are initially produced on the F-T catalyst, the mode III catalyst, which is made by a mixture of MS and zeolite catalysts, yields hydrocarbons at acid sites of zeolite micropores. As a result, heavy hydrocarbons are difficult to generate due to the limitation of micropores. Conventional CuZnAl (CZA) MS catalyst is not suitable for preparing the mode III catalyst because its optimal reaction temperature (473–543 K) cannot effectively start the reaction catalyzed by zeolite.[12,13] Therefore, high-temperature MS catalysts have usually been selected. For example, Bao and colleagues recently reported a 76.7% gasoline selectivity with 20.3% CO conversion at 633 K over $ZnMnO_x$-SAPO-11 composite catalyst.[14] Compared with the mode II catalyst, the mode III catalyst tends to achieve high C_{5-11} selectivity, but because of the low activity of the MS catalyst at high temperature, the conversion efficiency of the latter is significantly lower than that of the former. Taking into account the inconsistency of the reaction temperature and lifetime of the metal (oxides) and zeolite catalysts, placing them in two independent reactors in tandem (dual-bed) is expected to achieve better performance.[15–18] Just like the mode II catalyst, the mode IV catalyst, which contains an F-T catalyst and zeolite separately in a dual-bed reactor, can also adjust the distribution of F-T products. Ding and colleagues recently reported that CO conversion and

[1]National Engineering Laboratory for Methanol to Olefins, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

[2]Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

[3]University of Chinese Academy of Sciences, Beijing 100049, China

[4]Lead contact

*Correspondence: wlzhu@dicp.ac.cn (W.Z.), liuzm@dicp.ac.cn (Z.L.)

https://doi.org/10.1016/j.checat.2021.02.003

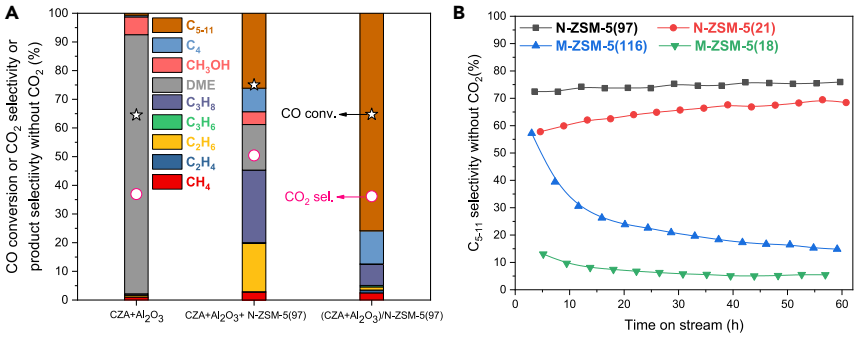


Figure 1. The catalytic performances of syngas conversion

(A) Comparison of results over various catalysts. CZA + Al_2O_3 was prepared by granule mixing with catalyst mass = 0.6 g, CZA + Al_2O_3 + N-ZSM-5(97) was prepared by granule mixing with catalyst mass = 1.0 g, and the dual-bed catalyst (CZA + Al_2O_3)/N-ZSM-5(97) was configured by 0.6 g CZA + Al_2O_3 on the upper bed and 0.4 g N-ZSM-5(97) on the lower bed. T = 573 K, P = 3.0 MPa, H_2 = 16.6 mL min^{-1}, CO = 8.3 mL min^{-1}, Ar = 2.3 mL min^{-1}. Data were collected at approximately 41 h on stream.

(B) C_{5-11} selectivity for the dual-bed catalysts with various lower-bed catalysts: 0.6 g CZA + Al_2O_3 on the upper bed, 0.4 g ZSM-5 zeolite on the lower bed, T = 573 K, P = 3.0 MPa, H_2 = 16.6 mL min^{-1}, CO = 8.3 mL min^{-1}, Ar = 2.3 mL min^{-1}.

C_{5-11} selectivity could both achieve 67% over the dual-bed catalyst Fe_3O_4@MnO_2/H-ZSM-5.[19] Besides the four types of catalysts mentioned above, the dual-bed mode V catalyst, which consists of a syngas-to-DME (STD) catalyst and DME-to-gasoline (DTG) zeolite catalysts in separate beds, can also transform syngas to gasoline. The STD process is very good at converting syngas, which helps to improve the efficiency.[20] In 1987, the Haldor Topsøe TIGAS process, based on the mode V catalyst, was successfully demonstrated in Houston, Texas.[21,22] In addition, the Karlsruhe Institute of Technology has developed a similar technology called the bioliq process.[23] Although some technologies for this dual-bed mode V process have existed, still few studies obtain high C_{5-11} selectivity at high syngas conversion or the mechanism of the zeolite characteristics on selectivity and stability.

Here, we report an 80.6% C_{5-11} selectivity without CO_2 at 86.3% CO conversion over a dual-bed catalyst (CZA + Al_2O_3)/N-ZSM-5(97) that includes a STD catalyst CZA + Al_2O_3 in the upper bed and a DTG catalyst N-ZSM-5(97) in the lower bed (Figure S1). A low amount of acid and the nano-sized structure of the ZSM-5 zeolite are beneficial to C_{5-11} selectivity and stability, respectively. The deactivation mechanism is also explored and discussed.

RESULTS

The performance of syngas conversion on various catalysts was compared at 573 K and 3.0 MPa with identical syngas feed. As shown in Figure 1A, CZA + Al_2O_3 is a typical STD catalyst that gives a 90.4% DME selectivity at 64.5% CO conversion. When this STD catalyst is mixed with N-ZSM-5(97) (nano-sized ZSM-5 with Si/Al = 97), the CO conversion and CO_2 selectivity are significantly improved, and a considerable amount of the DME is converted to hydrocarbons. The selectivity of C_{1-2} light hydrocarbons is as high as 20.0%, whereas the selectivity of C_{5-11} liquid hydrocarbons without CO_2 is only 26.1%. Increasing the proximity by three-component grinding and pressing leads to further decrease the selectivity of C_{5-11} hydrocarbons (Figure S2). It is interesting to find that the reaction result of the dual-bed catalyst (CZA + Al_2O_3)/N-ZSM-5(97), which is configured by CZA + Al_2O_3 on the upper bed and N-ZSM-5(97) on the lower bed, is quite different from the mixed catalyst

(CZA + Al_2O_3+N-ZSM-5(97)). The DME and MeOH are completely converted, the C_{5-11} selectivity reaches up to 75.9%, and the C_{1-2} selectivity is as low as 4.6% over (CZA + Al_2O_3)/N-ZSM-5(97). The effect of the structure and Si/Al ratio of ZSM-5 catalysts in the lower bed on the performance of the STG reaction was explored. The conversion of CO over the four dual-bed catalysts in Figure 1B is close because the upper-bed STD catalysts and the reaction conditions are the same. However, their C_{5-11} selectivity and stability are quite different. As shown in Figures 1B and S3A–S3D, the dual-bed catalyst with the nano-sized N-ZSM-5(97) or N-ZSM-5(21) has much better stability than the micro-sized M-ZSM-5(116) or M-ZSM-5(18), respectively. Furthermore, the dual-bed catalyst with N-ZSM-5(97) or M-ZSM-5(116) with a high Si/Al ratio exhibits considerably higher C_{5-11} selectivity than that with N-ZSM-5(21) or M-ZSM-5(18) with a lower Si/Al ratio, respectively. This suggests that the nano-sized structure, which generally means good diffusion ability,[24] is beneficial to extend the lifetime; meanwhile, the high Si/Al ratio, which usually represents a low amount of acid, is conducive to inhibit the formation of light hydrocarbons. It should be mentioned that the above results were obtained by a high-throughput reactor, and the reaction temperatures (573 K) of the upper and lower beds were the same. In fact, such a high temperature is not suitable for the STD reaction (Figure S4). To gain better results, we studied in detail the STG reaction over the dual-bed (CZA + Al_2O_3)/N-ZSM-5(97) catalyst at different reaction temperatures for the two beds.

The STG reaction on (CZA + Al_2O_3)/N-ZSM-5(97) was investigated at T (upper bed) = 533 K, T (lower bed) = 593 K, P = 3.0 MPa, H_2/CO = 2, and gas hourly space velocity (GHSV) = 1,500 mL g^{-1} h^{-1}. As shown in Figure 2A, the selectivity of C_{5-11}, C_{3-11}, aromatics, or CO_2 was kept at approximately 79%, 34%, 98%, or 32%, respectively, with 87% CO conversion. The light C_{1-2} selectivity was less than 1.7%. The activity of this dual-bed catalyst did not decrease at all within 110 h on stream. The detailed distribution of gasoline-range C_{5-11} can be observed in Figure 2A. The selectivity of *iso*-paraffins reached approximately 40%, whereas the selectivity of olefins was less than 2%. Moreover, the *iso*/*n*-paraffin ratio reached 18, which is much higher than that in F–T products.[6,25–28] Figures S5 and S6 indicate that increasing GHSV or H_2/CO ratio had little effect on C_{5-11} selectivity. Figure 2C shows that increasing the pressure significantly increased the CO conversion without affecting the C_{5-11} selectivity, which is extremely valuable for improving the efficiency of the STG process. Notably, at P = 4.0 MPa, H_2/CO = 2, and GHSV = 3,000 mL g^{-1} h^{-1}, the CO conversion was as high as 86.3%, while the selectivity of C_{5-11}, C_{3-11}, and CO_2 reached 80.6%, 98.2%, and 30.6%, respectively. By calculation, the space time yield was up to 0.28 g C_{5-11} per hour per gram of dual-bed catalyst. The main research progress concerning the conversion of syngas to C_{5-11} liquid hydrocarbons (including aromatics) in the past 3 years is listed in Table S1.[10,11,14,19,29–36] It is apparent that, compared with F-T-based catalysts (modes I, II, or IV), this dual-bed catalyst (mode V) has significant advantages in suppressing the low-value light C_{1-2} and achieving a high C_{5-11} and *iso*/*n*-paraffin ratio. Besides, compared with MS-catalyst-based physically mixed catalysts (mode III), this mode V catalyst has remarkable advantages in achieving high CO conversion and regenerating the deactivated catalyst after long-term operation. The effect of the reaction temperature on the lower bed was studied. It can be seen from Figure 2D that increasing the temperature is harmful to the generation of C_{5-11}.

Note that the dual-bed catalyst (CZA + Al_2O_3)/N-ZSM-5(97) for all of them was configured by 1.5 g CZA + Al_2O_3 (upper bed) and 1.0 g N-ZSM-5(97) (lower bed).

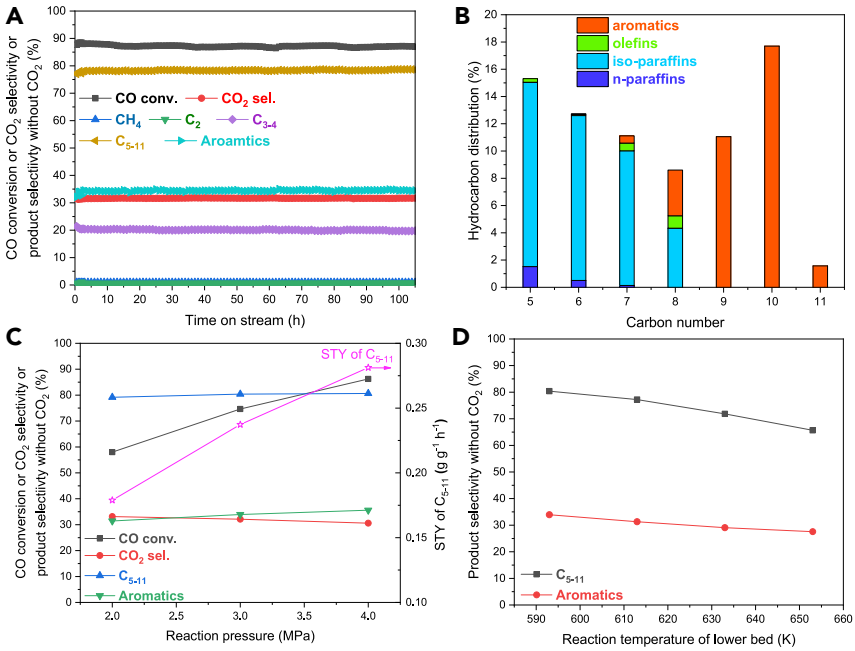


Figure 2. The catalytic performances of syngas conversion over a dual-bed catalyst (CZA + Al_2O_3)/N-ZSM-5(97)

(A) Stability test: T (upper bed) = 533 K, T (lower bed) = 593 K, P = 3.0 MPa, CO = 20.1 mL min^{-1}, H_2 = 40.2 mL min^{-1}, Ar = 2.1 mL min^{-1}.

(B) Detailed distribution of the gasoline-range C_{5-11} hydrocarbons: T (upper bed) = 533 K, T (lower bed) = 593 K, P = 3.0 MPa, CO = 20.1 mL min^{-1}, H_2 = 40.2 mL min^{-1}, Ar = 2.1 mL min^{-1}.

(C) Effect of reaction pressure: T (upper bed) = 533 K, T (lower bed) = 593 K, CO = 40.3 mL min^{-1}, H_2 = 80.6 mL min^{-1}, Ar = 4.2 mL min^{-1}.

(D) Effect of the reaction temperature for lower bed: T (upper bed) = 533 K, P = 3.0 MPa, CO = 40.3 mL min^{-1}, H_2 = 80.6 mL min^{-1}, Ar = 4.2 mL min^{-1}. CO conversion and CO_2 selectivity are approximately 76% and 32%, respectively.

The X-ray diffraction (XRD) patterns in Figure 3A indicate that the four ZSM-5 zeolites in this study possess a typical pure MFI structure. The XRD patterns in Figure S7 suggest that CZA and Al_2O_3 exhibit the structures of a conventional industrial CuZnAl MS catalyst and a γ-Al_2O_3 catalyst, respectively.[37] The NH_3-TPD results in Figure 3B show that the acid amount follows the order M-ZSM-5(116) < N-ZSM-5(97) < N-ZSM-5(21) < M-ZSM-5(18), which is exactly the reverse order of the Si/Al ratio (Figures 3C–3F). The NH_3-TPD result in Figure S8 proves that Al_2O_3 has an acid property, which should be derived from Lewis acid sites.[20] The XRF results listed in Table S2 show that the Cu/Zn/Al molar ratio is 4.8:1.8:1 for CZA. It can be observed from Figures 3C–3F that N-ZSM-5(97) and N-ZSM-5(21) are composed of approximately 200 and 50 nm particles, respectively, while M-ZSM-5(116) and M-ZSM-5(18) are both made up of 2–5 μm hexagonal crystals. Table S3 shows that N-ZSM-5(97) has the highest Brunauer-Emmett-Teller (BET) area and external area. Combined with the results in Figures 1B, S3, and 3C–3F, there is no doubt that reducing the crystal size of the lower-bed ZSM-5 zeolite will considerably prolong the lifetime of the overall dual-bed catalyst. In addition, it can be inferred from Figures 2B and 3B that, whether using nano- or micro-structured ZSM-5 zeolite, low acid content can facilitate the formation of C_{5-11} and depress the generation of light hydrocarbons. Generally, the growth of the carbon chains largely depends on the oligomerization of the initial light olefins.[38] However, the hydrogenation of light olefins, which can be catalyzed by the acid sites (especially Brønsted acids) of H-form ZSM-5 zeolite,[39,40] is

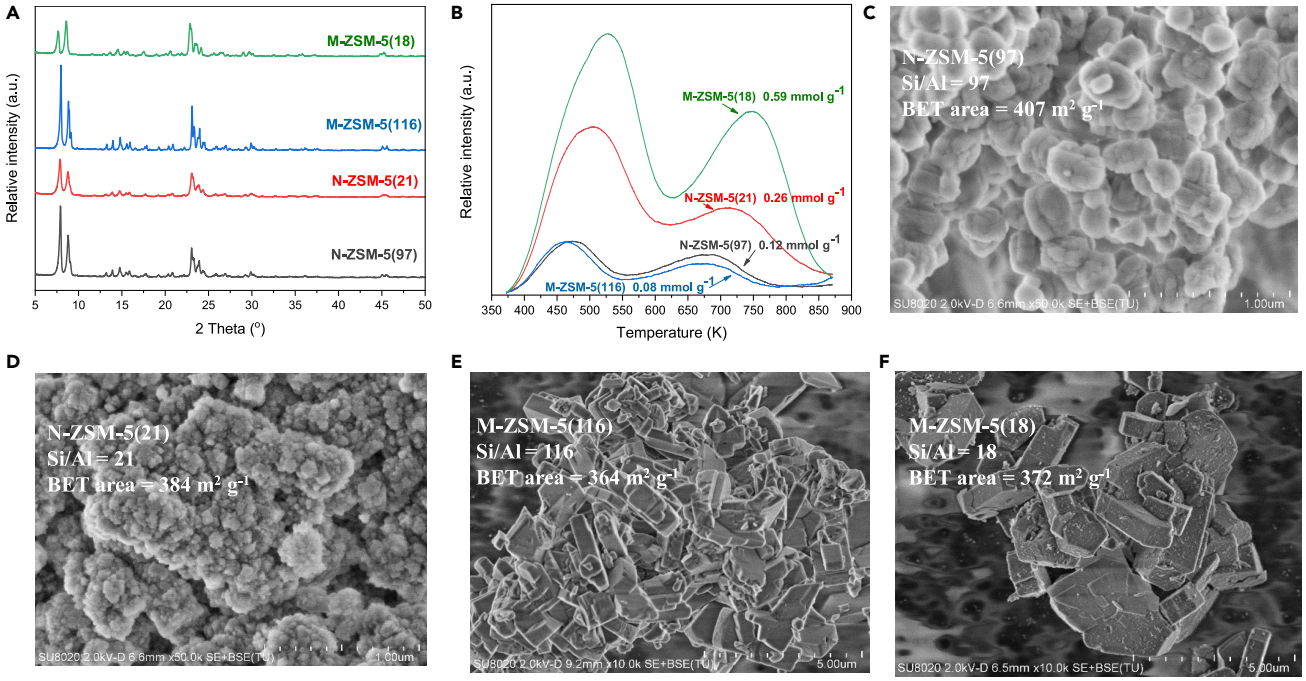


Figure 3. Results of characterization for lower-bed ZSM-5 zeolite catalysts

(A) XRD patterns.

(B) NH_3-TPD profiles.

(C–F) Scanning electron microscopy images, Si/Al, and BET areas.

disadvantageous. Compared with oligomerization, a higher acid content for ZSM-5 zeolite can be more beneficial to the hydrogenation, which results in a lower C_{5-11}.

The four ZSM-5 zeolite catalysts in the lower bed after reaction shown in Figure 1B were analyzed by the thermogravimetric method. As presented in Figure 4A, their weight losses follow the order N-ZSM-5(97) < N-ZSM-5(21) < M-ZSM-5(116) < M-ZSM-5(18). This demonstrates that for ZSM-5 zeolites with approximate Si/Al ratios, nano-sized structures are more resistant to coke, while for ZSM-5 zeolites with similar structures, a low Si/Al ratio (or high acid content) is ready to cause carbon deposits. Also, the catalytic results of a lower-bed ZSM-5 catalyst with a particle size of approximately 500 nm also prove that decreasing the zeolite particle size is beneficial to reduce coke and prolong lifetime (Figures S9A–S9D). During syngas conversion reactions, after the zeolite catalyst is mixed with the metal catalyst, the coke formation rate will be generally significantly reduced, and the catalyst stability will be greatly improved.[41,42] As shown in Figure 4A, the weight loss of the spent N-ZSM-5(97) in the dual-bed catalyst is close to that in the mixed catalyst, which implies that the dual-bed catalyst (CZA + Al_2O_3)/N-ZSM-5(97) has the potential for long-term use. After reaction, the four ZSM-5 zeolite catalysts in the lower bed were dissolved by hydrofluoric acid, and then the retained organic species were extracted by dichloromethane and analyzed by gas chromatography-mass spectrometry. As presented in Figure 4C, the content of aromatics (species 1, 2, 5, 6, and 8) with no more than ten carbons (or no larger than tetramethyl-benzene) in the spent N-ZSM-5(97) is much less than that in the others. However, the selectivity of aromatics for (CZA + Al_2O_3)/N-ZSM-5(97) is substantially higher than that for the other three dual-bed catalysts in Figures S3A–S3D. This indicates that the products no larger than the size of micropores (0.53 × 0.56 nm) for MFI topology are easily diffused out of N-ZSM-5(97).

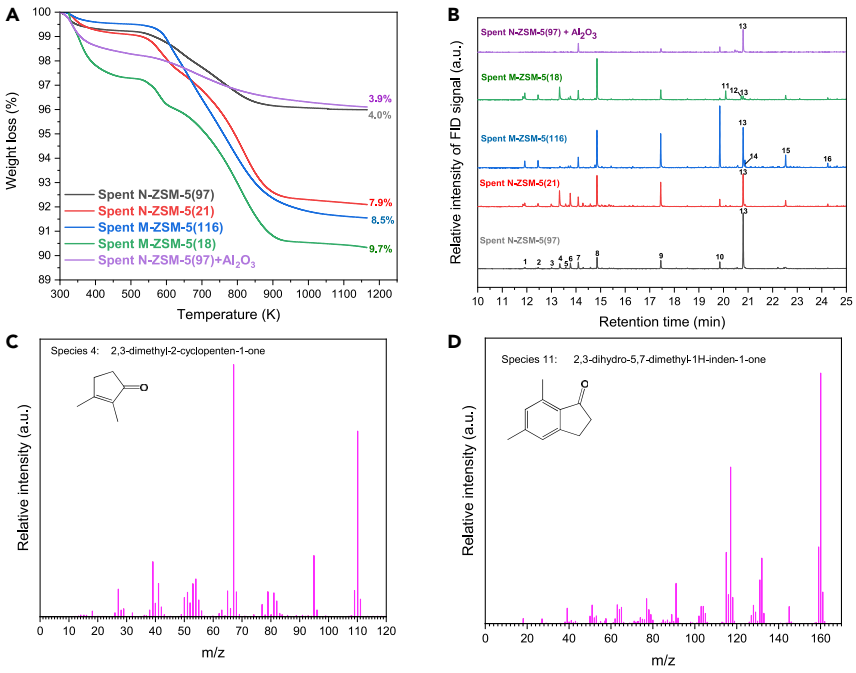


Figure 4. Results of analysis for spent ZSM-5 zeolite catalysts

(A) Thermogravimetric analysis.

(B) Gas chromatography-mass spectrometry chromatograms of the retained organic species: (1 or 2) trimethyl-benzene, (3 or 4) dimethyl-2-cyclopenten-1-one, (5 or 6) trimethyl-2-cyclopenten-1-one, (7) C2Cl6, (8) tetramethyl-benzene, (9) pentamethyl-benzene, (10) hexamethyl-benzene, (11 or 12) 2,3-dihydro-dimethyl-1H-inden-1-one, (13) phenol derivatives, (14) trimethyl-naphthalene, (15 or 16) dimethyl-methylethyl-naphthalene.

(C) Mass spectrum of species 4.

(D) Mass spectrum of species 11.

It also can be seen that the naphthalene derivatives (species 14–16) are hardly generated for N-ZSM-5(97). These polycyclic aromatics are too large to block micropores and cause catalyst deactivation.[43] Besides methylbenzenes and polycyclic aromatics, a considerable amount of oxygenates, which include the derivatives of 2-cyclopenten-1-one (species 3–6) and phenol (species 13), can be observed in Figure 4B. The mass spectra of the typical oxygenates are shown in Figures 4C and S10. Our previous researches have proved that the 2-cyclopenten-1-one species, which can be produced via a series of C–C bond formation reactions, such as carbonylation, aldol, prins, and hydroacylation, are important intermediates for the formation of single-ring aromatics.[44–46] Compared with the spent N-ZSM-5(97), the spent N-ZSM-5(21) obviously contains more 2-cyclopenten-1-one species. However, the selectivity of aromatics over (CZA + Al_2O_3)/N-ZSM-5(97) is apparently higher than that over (CZA + Al_2O_3)/N-ZSM-5(21) (Figures S3A and S3B). This means that there are other ways to generate aromatics. Recently, Wei and colleagues found that phenol species formed by the aldol cycle in the syngas atmosphere can be transformed to aromatics.[47] The amount of phenol species in spent N-ZSM-5(97) is more than that in spent N-ZSM-5(21), which is positively related to the selectivity of the aforementioned aromatics. This suggests that phenol species are likely to act as intermediates for aromatics. In the spent N-ZSM-5(97) of the mixed catalyst (CZA + Al_2O3 + N-ZSM-5(97)), 2-cyclopenten-1-one species can be hardly found, whereas phenol species can be detected. This mixed catalyst can actually produce few aromatics (6%), which also suggests that the speculation above is reasonable.

Although the mechanism of synthesizing single-ring aromatics from these oxygenates, such as 2-cyclopenten-1-one and phenol species, has been well explored by the previous works of ourselves and others,[15,44,45,47] the pathway of generating polycyclic aromatics, which are the main factors leading to catalyst deactivation, has still not been revealed. The weight loss for the spent M-ZSM-5(18) is more than twice that for the spent N-ZSM-5(97) (Figure 4A); however, the amount of their soluble organics is relatively close (Figure 4B). This demonstrates that there is a large amount of insoluble heavy carbon deposits, which are generally polycyclic aromatics,[43] in the spent M-ZSM-5(18). Interestingly, some 2,3-dihydro-1H-inden-1-one oxygenates (species 11 and 12) can be definitely detected and identified in the spent M-ZSM-5(18) (Figures 4B, 4D, and S3D). We consider that they can be generated through carbonylation and condensation of phenol species and transformed to polycyclic aromatics by reactions such as isomerization and dehydration because this is similar to the mechanism for the formation and conversion of 2-cyclopenten-1-one species.[44–46]

Conclusion

In summary, high and selective conversion of syngas to gasoline-range C_{5-11} liquid hydrocarbons can be simultaneously achieved over a dual-bed catalyst (CZA + Al_2O_3)/N-ZSM-5(97) that consists of a STD catalyst CZA + Al_2O_3 (a mixture of CuZnAl MS catalyst and acidic γ-Al_2O_3 catalyst) in the upper bed and a DTG catalyst N-ZSM-5(97) (nano-sized H-ZSM-5 zeolite with Si/Al ratio = 97) in the lower bed. The selectivity of C_{5-11} and C_{3-11} can reach 80.6% and 98.2%, respectively, along with 86.3% CO conversion at T (upper bed) = 533 K, T (lower bed) = 593 K, P = 4.0 MPa, H_2/CO = 2, and GHSV = 3,000 mL g^{-1} h^{-1}. This dual-bed catalyst exhibits an excellent stability during a 110-h test. The *iso*/*n*-paraffin ratio in the C_{5-11} is up to 18. By comparing four lower-bed ZSM-5 zeolite catalysts with various particle sizes and acid content, we found that the nano-sized structure is beneficial to reduce coke and prolong lifetime; meanwhile, the low acid content is advantageous to increase C_{5-11} selectivity. The 2,3-dihydro-1H-inden-1-one species can be definitely detected and identified in the spent lower-bed micro-sized M-ZSM-5(18). They are regarded as intermediates to generate polycyclic aromatics, which generally lead to catalyst deactivation. The dual-bed catalyst (CZA + Al_2O_3)/N-ZSM-5(97) suggests a promising application in producing gasoline from syngas.

EXPERIMENTAL PROCEDURES

Full experimental procedures are provided in the supplemental information.

Resource availability

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Professor Zhongmin Liu (liuzm@dicp.ac.cn).

Materials availability

This study did not generate new unique reagents.

Data and code availability

The published article includes all datasets generated or analyzed during this study.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.checat.2021.02.003.

ACKNOWLEDGMENTS

We acknowledge financial support from the National Natural Science Foundation of China (grant nos. 21978285, 21991093, and 21991090) and the "Transformational Technologies for Clean Energy and Demonstration" Strategic Priority Research Program of the Chinese Academy of Sciences (grant no. XDA21030100). We thank Weichen Zhang for assistance in the experiments.

AUTHOR CONTRIBUTIONS

Y.N. designed and performed the experiments, analyzed the data, and wrote the manuscript. K.W. discussed the results. W.Z. and Z.L. supervised the study, discussed the results, designed the experiments, and revised the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

Received: October 29, 2020
Revised: December 26, 2020
Accepted: February 9, 2021
Published: April 2, 2021

REFERENCES

1. Zhang, Q., Yu, J., and Corma, A. (2020). Applications of zeolites to C1 chemistry: recent advances, challenges, and opportunities. Adv. Mater. *32*, e2002927.

2. Kasipandi, S., and Bae, J.W. (2019). Recent advances in direct synthesis of value-added aromatic chemicals from syngas by cascade reactions over bifunctional catalysts. Adv. Mater. *31*, e1803390.

3. Yang, M., Fan, D., Wei, Y., Tian, P., and Liu, Z. (2019). Recent progress in methanol-to-olefins (MTO) catalysts. Adv. Mater. *31*, e1902181.

4. Zhou, W., Cheng, K., Kang, J., Zhou, C., Subramanian, V., Zhang, Q., and Wang, Y. (2019). New horizon in C1 chemistry: breaking the selectivity limitation in transformation of syngas and hydrogenation of CO_2 into hydrocarbon chemicals and fuels. Chem. Soc. Rev. *48*, 3193–3228.

5. Su, J., Zhou, H., Liu, S., Wang, C., Jiao, W., Wang, Y., Liu, C., Ye, Y., Zhang, L., Zhao, Y., et al. (2019). Syngas to light olefins conversion with high olefin/paraffin ratio using $ZnCrO_x$/AlPO-18 bifunctional catalysts. Nat. Commun. *10*, 1297.

6. Martínez-Vargas, D.X., Sandoval-Rangel, L., Campuzano-Calderon, O., Romero-Flores, M., Lozano, F.J., Nigam, K.D.P., Mendoza, A., and Montesinos-Castellanos, A. (2019). Recent advances in bifunctional catalysts for the Fischer–Tropsch process: one-stage production of liquid hydrocarbons from syngas. Ind. Eng. Chem. Res. *58*, 15872–15901.

7. Stöcker, M. (1999). Methanol-to-hydrocarbons: catalytic materials and their behavior. Microporous Mesoporous Mater. *29*, 3–48.

8. Keil, F.J. (1999). Methanol-to-hydrocarbons: process technology. Microporous Mesoporous Mater. *29*, 49–66.

9. Gao, P., Li, S., Bu, X., Dang, S., Liu, Z., Wang, H., Zhong, L., Qiu, M., Yang, C., Cai, J., et al. (2019). Direct conversion of CO_2 into liquid fuels with high selectivity over a bifunctional catalyst. Nat. Chem. *9*, 1019–1024.

10. Přech, J., Strossi Pedrolo, D.R., Marcilio, N.R., Gu, B., Peregudova, A.S., Mazur, M., Ordomsky, V.V., Valtchev, V., and Khodakov, A.Y. (2020). Core-shell metal zeolite composite catalysts for *in situ* processing of Fischer–Tropsch hydrocarbons to gasoline type fuels. ACS Catal. *10*, 2544–2555.

11. Li, J., He, Y., Tan, L., Zhang, P., Peng, X., Oruganti, A., Yang, G., Abe, H., Wang, Y., and Tsubaki, N. (2018). Integrated tuneable synthesis of liquid fuels via Fischer–Tropsch technology. Nat. Catal. *1*, 787–793.

12. Cheng, K., Zhou, W., Kang, J., He, S., Shi, S., Zhang, Q., Pan, Y., Wen, W., and Wang, Y. (2017). Bifunctional catalysts for one-step conversion of syngas into aromatics with excellent selectivity and stability. Chem *3*, 334–347.

13. Xiao, W., Li, M., Nawaz, M.A., Xu, L., Song, G., Yang, S., Wang, Z., and Liu, D. (2020). Integrated catalyst of CuZnAl-Zr and Nb-HZSM-5 for one-step synthesis of aromatics from syngas and Nb-HZSM-5 for one-step synthesis of aromatics from syngas. Chin. J. Chem. *38*, 1311–1316.

14. Li, N., Jiao, F., Pan, X., Chen, Y., Feng, J., Li, G., and Bao, X. (2019). High-quality gasoline directly from syngas by dual metal oxide-zeolite (OX-ZEO) catalysis. Angew. Chem. Int. Ed. *58*, 7400–7404.

15. Ni, Y., Liu, Y., Chen, Z., Yang, M., Liu, H., He, Y., Fu, Y., Zhu, W., and Liu, Z. (2019). Realizing and recognizing syngas-to-olefins reaction via a dual-bed catalyst. ACS Catal. *9*, 1026–1032.

16. Hou, Y., Li, J., Qing, M., Liu, C., and Dong, W. (2020). Direct synthesis of lower olefins from syngas via Fischer–Tropsch synthesis catalyzed by a dual-bed catalyst. Mol. Catal. *485*, 110824.

17. Fujimoto, K., Asami, K., Saima, H., Shikada, T., and Tominaga, H. (1986). Two-stage reaction system for synthesis gas conversion to gasoline. Ind. Eng. Chem. Prod. Res. Dev. *25*, 262–267.

18. Varma, R.L., Bakhshi, N.N., Mathews, J.F., and Ng, S.H. (1987). Performance of dual-reactor system for conversion of syngas to aromatic-containing hydrocarbons. Ind. Eng. Chem. Res. *26*, 183–188.

19. Xu, Y., Wang, J., Ma, G., Zhang, J., and Ding, M. (2020). Hollow zeolite nanoparticles combined with Fe_3O_4@MnO_2 tandem catalyst for converting syngas to aromatics-rich gasoline. ACS Appl. Nano Mater. *3*, 2857–2866.

20. Saravanan, K., Ham, H., Tsubaki, N., and Bae, J.W. (2017). Recent progress for direct synthesis of dimethyl ether from syngas on the heterogeneous bifunctional hybrid catalysts. Appl. Catal. B *217*, 494–522.

21. Topp-Jorgensen, J. (1988). Topsøe integrated gasoline synthesis—the TIGAS process. Stud. Surf. Sci. Catal. *36*, 293–305.

22. Bellussi, G., Millini, R., and Pollesel, P. (2015). An industrial perspective on the impact of Haldor Topsøe on research and development in catalysis by zeolites. J. Catal. *328*, 11–18.

23. Dimitriou, I., Goldingay, H., and Bridgwater, A.V. (2018). Techno-economic and uncertainty analysis of biomass to liquid (BTL) systems for transport fuel production *88*, 160–175.

24. Ni, Y., Sun, A., Wu, X., Hai, G., Hu, J., Li, T., and Li, G. (2011). The preparation of nano-sized H[Zn,Al]ZSM-5 zeolite and its application in the

aromatization of methanol. Microporous Mesoporous Mater. *143*, 435–442.

25. Kang, J., Cheng, K., Zhang, L., Zhang, Q., Ding, J., Hua, W., Lou, Y., Zhai, Q., and Wang, Y. (2011). Mesoporous zeolite-supported ruthenium nanoparticles as highly selective Fischer-Tropsch catalysts for the production of C_5-C_{11} isoparaffins. Angew. Chem. Int. Ed. *50*, 5200–5203.

26. Kim, J.-C., Lee, S., Cho, K., Na, K., Lee, C., and Ryoo, R. (2014). Mesoporous MFI zeolite nanosponge supporting cobalt nanoparticles as a Fischer–Tropsch catalyst with high yield of branched hydrocarbons in the gasoline range. ACS Catal. *4*, 3919–3927.

27. Zhang, Q., Cheng, K., Kang, J., Deng, W., and Wang, Y. (2014). Fischer-Tropsch catalysts for the production of hydrocarbon fuels with high selectivity. ChemSusChem *7*, 1251–1264.

28. Bao, J., He, J., Zhang, Y., Yoneyama, Y., and Tsubaki, N. (2008). A core/shell catalyst produces a spatially confined effect and shape selectivity in a consecutive reaction. Angew. Chem. Int. Ed. *47*, 353–356.

29. Wang, Y., Zhan, W., Chen, Z., Chen, J., Li, X., and Li, Y. (2020). Advanced 3D hollow-out ZnZrO@C combined with hierarchical zeolite for highly active and selective CO hydrogenation to aromatics. ACS Catal. *10*, 7177–7187.

30. Sun, T., Lin, T., An, Y., Gong, K., Zhong, L., and Sun, Y. (2020). Syngas conversion to aromatics over the Co_2C-based catalyst and HZSM-5 via a tandem system. Ind. Eng. Chem. Res. *59*, 4419–4427.

31. Javed, M., Cheng, S., Zhang, G., Amoo, C.C., Wang, J., Lu, P., Lu, C., Xing, C., Sun, J., and Tsubaki, N. (2020). A facile solvent-free synthesis strategy for Co-imbedded zeolite-based Fischer-Tropsch catalysts for direct gasoline production. Chin. J. Catal. *41*, 604–612.

32. Fu, Y., Ni, Y., Zhu, W., and Liu, Z. (2020). Enhancing syngas-to-aromatics performance of ZnO&H-ZSM-5 composite catalyst via Mn modulation. J. Catal. *383*, 97–102.

33. Javed, M., Zhang, G., Gao, W., Cao, Y., Dai, P., Ji, X., Lu, C., Yang, R., Xing, C., and Sun, J. (2019). From hydrophilic to hydrophobic: a promising approach to tackle high CO_2 selectivity of Fe-based Fischer-Tropsch microcapsule catalysts. Catal. Today *330*, 39–45.

34. Arslan, M.T., Qureshi, B.A., Gilani, S.Z.A., Cai, D., Ma, Y., Usman, M., Chen, X., Wang, Y., and Wei, F. (2019). Single-step conversion of H_2-deficient syngas into high yield of tetramethylbenzene. ACS Catal. *9*, 2203–2212.

35. Zhu, C., and Bollas, G.M. (2018). Gasoline selective Fischer-Tropsch synthesis in structured bifunctional catalysts. Appl. Catal. B *235*, 92–102.

36. Ma, G., Wang, X., Xu, Y., Wang, Q., Wang, J., Lin, J., Wang, H., Dong, C., Zhang, C., and Ding, M. (2018). Enhanced conversion of syngas to gasoline-range hydrocarbons over carbon encapsulated bimetallic FeMn nanoparticles. ACS Appl. Energy Mater. *1*, 4304–4312.

37. Ereña, J., Sierra, I., Olazar, M., Gayubo, A.G., and Aguayo, A.T. (2008). Deactivation of a $CuO-ZnO-Al_2O_3/\gamma$-Al_2O_3 catalyst in the synthesis of dimethyl ether. Ind. Eng. Chem. Res. *47*, 2238–2247.

38. Yarulina, I., Chowdhury, A.D., Meirer, F., Weckhuysen, B.M., and Gascon, J. (2018). Recent trends and fundamental insights in the methanol-to-hydrocarbons process. Nat. Catal. *1*, 398–411.

39. Kanai, J., Martens, J.A., and Jacobs, P.A. (1992). On the nature of the active sites for ethylene hydrogenation in metal-free zeolites. J. Catal. *133*, 527–543.

40. Senger, S., and Radom, L. (2000). Zeolites as transition-metal-free hydrogenation catalysts: a theoretical mechanistic study. J. Am. Chem. Soc. *122*, 2613–2620.

41. Jiao, F., Li, J., Pan, X., Xiao, J., Li, H., Ma, H., Wei, M., Pan, Y., Zhou, Z., Li, M., et al. (2016). Selective conversion of syngas to light olefins. Science *351*, 1065–1068.

42. Cheng, K., Gu, B., Liu, X., Kang, J., Zhang, Q., and Wang, Y. (2016). Direct and highly selective conversion of synthesis gas into lower olefins: design of a bifunctional catalyst combining methanol synthesis and carbon-carbon coupling. Angew. Chem. Int. Ed. *55*, 1–5.

43. Wang, N., Zhi, Y., Wei, Y., Zhang, W., Liu, Z., Huang, J., Sun, T., Xu, S., Lin, S., He, Y., et al. (2020). Molecular elucidating of an unusual growth mechanism for polycyclic aromatic hydrocarbons in confined space. Nat. Commun. *11*, 1079.

44. Chen, Z., Ni, Y., Zhi, Y., Wen, F., Zhou, Z., Wei, Y., Zhu, W., and Liu, Z. (2018). Coupling of methanol and carbon monoxide over H-ZSM-5 to form aromatics. Angew. Chem. Int. Ed. *57*, 12549–12553.

45. Ni, Y., Zhu, W., and Liu, Z. (2021). Formaldehyde intermediate participating in the conversion of methanol to aromatics over zinc modified H-ZSM-5. J. Energy Chem. *54*, 174–178.

46. Ni, Y., Zhu, W., and Liu, Z. (2019). H-ZSM-5-catalyzed hydroacylation involved in the coupling of methanol and formaldehyde to aromatics. ACS Catal. *9*, 11398–11403.

47. Arslan, M.T., Ali, B., Gilani, S.Z.A., Hou, Y., Wang, Q., Cai, D., Wang, Y., and Wei, F. (2020). Selective conversion of syngas into tetramethylbenzene via an aldol-aromatic mechanism. ACS Catal. *10*, 2477–2488.