

Article

A Dual-Bed Strategy for Direct Conversion of Syngas to Light Paraffins

Lina Wang , Fanhui Meng , Baozhen Li, Jinghao Zhang and Zhong Li *

State Key Laboratory of Clean and Efficient Coal Utilization, Taiyuan University of Technology, Taiyuan 030024, China

* Correspondence: mengfanhui@tyut.edu.cn (F.M.); lizhong@tyut.edu.cn (Z.L.)

Abstract: The authors studied the direct conversion of syngas to light paraffins in a dual-bed fixed-bed reactor. A dual-bed catalyst composed of three catalysts, a physically mixed methanol synthesis catalyst (CZA), and a methanol dehydration to dimethyl ether (DME) catalyst ($\text{Al}_2\text{O}_3(\text{C})$) were put in the upper bed for direct conversion of syngas to DME, while the SAPO-34 (SP34-C) zeolite was put in the lower bed for methanol and DME conversion. The effects of the mass ratio of CZA to $\text{Al}_2\text{O}_3(\text{C})$, the H_2/CO molar ratio, and the space velocity on catalytic performance of syngas to DME were studied in the upper bed. Moreover, a feed gas with a $\text{CO}/\text{CO}_2/\text{DME}/\text{N}_2/\text{H}_2$ molar ratio of 9/6/4/5 balanced with H_2 was simulated and studied in the lower bed over SP34-C; after optimizing the reaction conditions, the selectivity of light paraffins reached 90.8%, and the selectivity of propane was as high as 76.7%. For the direct conversion of syngas to light paraffins in a dual bed, 88.9% light paraffins selectivity in hydrocarbons was obtained at a CO conversion of 33.4%. This dual-bed strategy offers a potential route for the direct conversion of syngas to valuable chemicals.

Keywords: dual bed; syngas; methanol; dimethyl ether; light paraffins; propane



Citation: Wang, L.; Meng, F.; Li, B.; Zhang, J.; Li, Z. A Dual-Bed Strategy for Direct Conversion of Syngas to Light Paraffins. *Catalysts* **2022**, *12*, 967. <https://doi.org/10.3390/catal12090967>

Academic Editor: Javier Ereña Loizaga

Received: 10 August 2022

Accepted: 27 August 2022

Published: 29 August 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The overexploitation of petroleum resources makes it highly essential to develop a nonpetroleum way of producing chemicals. Syngas is an important platform for the utilization of carbon resources such as coal, natural gas, and biomass; moreover, it can be converted into a variety of chemicals and fuels [1]. Fischer–Tropsch synthesis (FTS) [2] and oxide–zeolite (OX–ZEO) bifunctional catalyst [3] routines are commonly applied for syngas conversion. For FTS, hydrocarbon selectivity remains a challenge due to the Anderson–Schulz–Flory limitation rule [4]. Recently, OX–ZEO catalysts have been intensively studied for the direct conversion of syngas to light olefins ($\text{C}_2\text{--C}_4$) [5–9], aromatics [10,11], and gasoline [12], which was due to the breakthrough of hydrocarbon selectivity.

The OX–ZEO catalyst is composed of a methanol synthesis catalyst and a methanol conversion catalyst. It is well-known the syngas to methanol conversion (STM, $\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$) has been realized in industrial production under high pressure since 1923; most of the new plants have adopted a low-pressure and low-temperature process since the middle of 1970s. Right now, the commonly used methanol synthesis catalysts for STM are Cu-based catalysts [13], and great efforts have been devoted to improve the catalytic performance of Cu-based catalysts [14], which is due to the fact that methanol is a platform that can be used as a fuel and also converted to valuable chemicals [15]. The conversion of methanol to DME (MTD, $2\text{CH}_3\text{OH} = \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$) has the same reaction temperature as that of STM, and the most widely used catalysts are the $\gamma\text{-Al}_2\text{O}_3$ [16] and ZSM-5 [17] zeolite. By combining the catalyst of STM and MTD, syngas can be directly converted to DME (STD, $2\text{CO} + 4\text{H}_2 = \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$) [18], and reports have shown that CO equilibrium conversion can be significantly enhanced by the STD process.

For the conversion of syngas to light olefins with an OX–ZEO catalyst, a high reaction temperature (400°C) to convert methanol to olefins (MTO , $\text{CH}_3\text{OH}(\text{g}) \rightarrow \text{C}_n\text{H}_{2n}(\text{g}) + \text{H}_2\text{O}(\text{g})$)

is needed, which needs the methanol synthesis catalyst to be operated at around 400 °C to match the MTO reaction for C_2 – C_4 synthesis. However, high temperature is not beneficial for the conversion of CO due to the thermodynamic limitation. Thus, a dual-bed fixed-bed reactor was designed for the conversion of syngas to DME to obtain high CO conversion at low temperatures, accompanied by the methanol/DME conversion performed at high temperatures [19]. In such a dual-bed fixed-bed reactor, the direct conversion of syngas to DME was performed in the upper catalyst bed, and the produced intermediate products were further passed through the lower catalyst bed. For the conversion of methanol or DME to olefins, the SAPO-34 zeolite is a commonly used catalyst [20], and the production of olefins has been commercialized in China since 2011. For the direct conversion of syngas, the presence of large amounts of unconverted H_2 could lead to the generation of olefins further hydrogenated to paraffins, which could result in the low ratio of light olefins to light paraffins (C_2 – C_4) [21–23]. The results indicate that product distribution can be regulated by changing the reaction conditions. To the best of our knowledge, the direct conversion of syngas to light paraffins in a dual-bed fixed-bed reactor has been seldomly studied.

In this work, a dual-bed strategy was adopted to directly convert syngas to light paraffins, which includes STD catalyst CZA + $Al_2O_3(C)$ in the upper bed and methanol/DME conversion catalyst SP34-C in the lower bed. For the STD process, the mass ratio of CZA to $Al_2O_3(C)$, the H_2/CO ratio, and the space velocity on catalytic performance were explored, while for the conversion of DME, a feed gas with a $CO/CO_2/DME/N_2/H_2$ molar ratio of 9/6/4/5 balanced with H_2 was simulated and studied in the lower bed over SP34-C. The adopted catalysts were characterized and the stability for syngas conversion to light paraffins was studied. This dual-bed strategy makes the different catalysts to be operated at different temperatures in the reaction process, which can save energy, and the synthesis of methanol at low temperature is beneficial to prolonging the catalyst life. Moreover, the dual-bed strategy provides a potential route for syngas conversion to valuable chemicals.

2. Results and Discussion

2.1. Catalyst Characterization Results

XRD patterns of the CZA and $Al_2O_3(C)$ catalysts are displayed in Figure 1a. The characteristic diffraction peaks at 2θ of 35.5°, 38.7°, and 61.5° are attributed to CuO (PDF#45-0937), while the diffraction peaks at 2θ of 31.8°, 34.4°, 36.2°, and 47.5° correspond to ZnO (PDF#36-1451). A diffraction peak appeared at 2θ of 26.6° accounting for graphite, which was generally used to enhance catalyst mechanical strength and heat transfer efficiency [24]. The $Al_2O_3(C)$ catalyst shows the characteristic diffraction peaks at 2θ of 19.6°, 31.3°, 37.6°, 39.5°, 45.8°, and 66.8°, confirming the existence of the γ - Al_2O_3 phase (PDF#29-0063). SP34-C in Figure 1b shows the characteristic diffraction peaks of SAPO-34 (PDF#47-0429) [25].

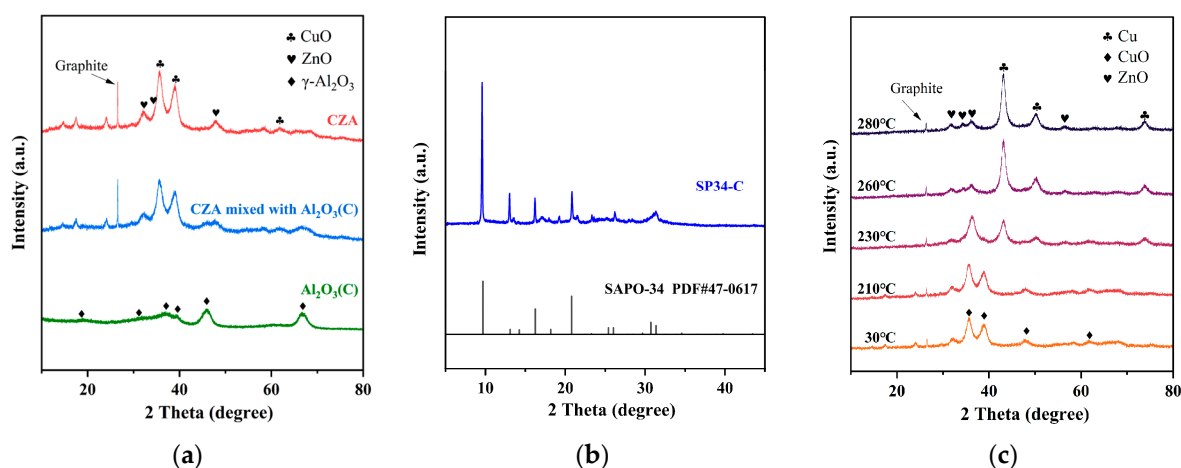


Figure 1. XRD patterns of the catalysts. (a) XRD patterns of CZA and $Al_2O_3(C)$; (b) XRD patterns of SP34-C; (c) in-situ XRD patterns of the CZA catalyst.

To evaluate the structural evolution of the CZA catalyst during the reduction process, in-situ XRD patterns of CZA were performed in an H_2 atmosphere under various temperatures. The results are shown in Figure 1c. It is obvious that when the temperature was 210 °C or below, the crystalline phase was not changed, indicating that the CZA catalyst cannot be reduced at this temperature. As the temperature increased to 230 °C, the peak intensity of CuO slightly weakened, and the diffraction peaks attributing to Cu metal at 2θ of 43.3°, 50.4°, and 74.1° (PDF#85-1326) appeared. With a further increase in temperature to 260 °C, the diffraction peaks of CuO disappeared. The diffraction peaks at 280 °C were almost the same as at 260 °C, indicating that CZA was completely reduced.

H_2 -TPR was performed to further study the reduction behavior of the CZA catalyst. The profile is displayed in Figure 2a. The ZnO species cannot be reduced at 400 °C or below [26]. Thus, the two peaks centered at 186 °C and 205 °C could be attributed to the reduction of CuO to Cu_2O and of Cu_2O to Cu, respectively [27], which was consistent with the in-situ XRD results. The profile of the CO adsorption ability is shown in Figure 2b. The amount of desorbed CO listed in Table 1 is 0.10 mmol/g. It is obvious that the CZA catalyst exhibited a large desorption peak for CO, which is beneficial to the conversion of CO.

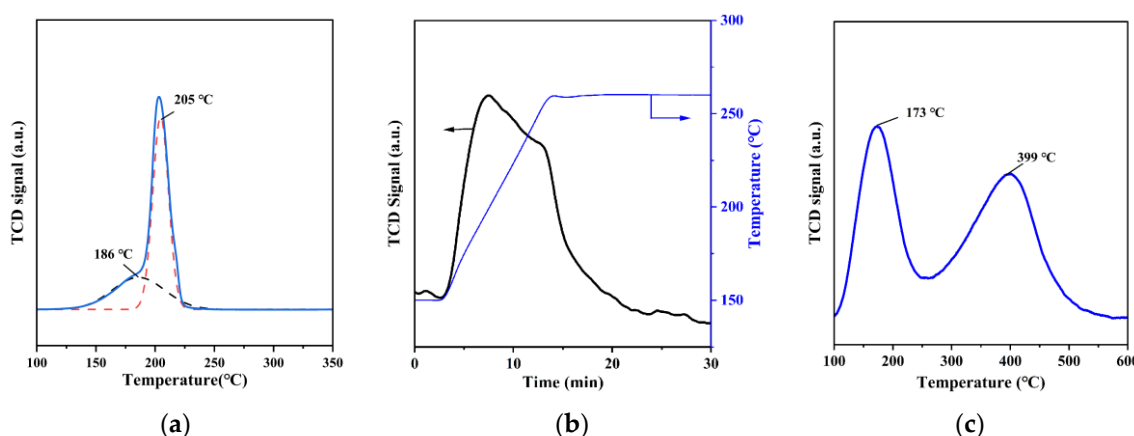


Figure 2. (a) H_2 -TPR profile of the CZA catalyst; (b) CO-TPD profile of the CZA catalyst; (c) NH_3 -TPD profile of the SP34-C catalyst.

Table 1. Textural properties of the catalysts and amounts of desorbed CO for CZA.

Samples	S_{total}^a ($m^2 \cdot g^{-1}$)	V_{total}^b ($cm^3 \cdot g^{-1}$)	D^c (nm)	Amounts of Desorbed CO ^d (mmol/g)
CZA	68	0.19	9.4	0.10
$Al_2O_3(C)$	238	0.41	4.9	—
SP34-C	488	0.49	68.7	—

^a S_{total} (total BET surface area) was calculated based on the multipoint BET equation. ^b Single-point desorption total pore volume of pores, $p/p_0 = 0.99$. ^c Barret-Joyner-Hallender (BJH) desorption average pore diameter. ^d Calculated from the CO-TPD profile.

The acidity of a SAPO-34 molecular sieve plays a vital role in determining the selectivity of light hydrocarbons [28]. NH_3 -TPD profiling for SP34-C was performed, and the result is shown in Figure 2c. It can be seen that SP34-C exhibits two desorption peaks at 173 °C and 399 °C. The desorption peak at low temperature belongs to the physically adsorbed ammonia, whereas the high-temperature desorption peak is attributed to Si—OH—Al groups of the molecular sieve (Brønsted acids) [29]. It has been reported that during the MTO reaction, weak acid sites do not have a strong influence on the formation of light olefins, only the Brønsted acid sites play an important role [30].

N_2 adsorption–desorption was used to determine the textural properties of the samples. Figure 3 shows that the CZA catalyst exhibits a typical IV-type isotherm curve and an H1-type hysteresis loop, indicating that CZA is a mesoporous material. The $Al_2O_3(C)$

catalyst also exhibits a IV-type isotherm with a type H3 hysteresis loop. The SP34-C catalyst exhibits a typical I-type isotherm characteristic, and when the relative pressure p/p_0 was lower than 0.01, the adsorption capacity increased sharply due to the filling of micropores, indicating the existence of large amounts of micropores [31]. The hysteresis loop appearing at p/p_0 of 0.98 was due to the stacking of SP34-C nanoparticles.

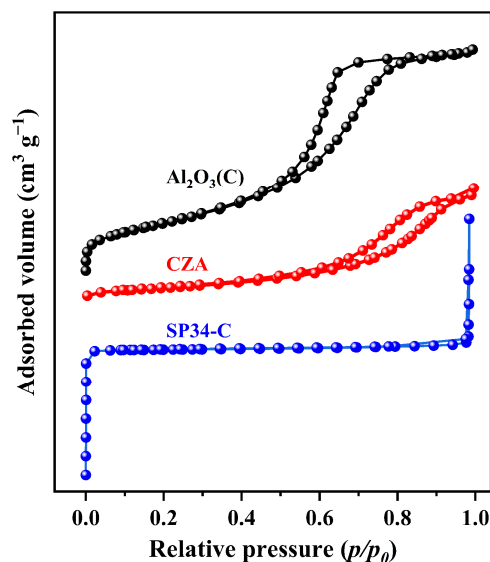


Figure 3. N_2 adsorption—desorption isotherms of the different catalysts.

The textural properties are summarized in Table 1. CZA possesses a BET surface area of $68 \text{ m}^2 \cdot \text{g}^{-1}$ with an average pore diameter of 9.4 nm. The $\text{Al}_2\text{O}_3(\text{C})$ sample shows a high surface area of $238 \text{ m}^2 \cdot \text{g}^{-1}$, while for SP34-C, the BET surface area increased to $488 \text{ m}^2 \cdot \text{g}^{-1}$. Both the $\text{Al}_2\text{O}_3(\text{C})$ and SP34-C samples exhibit a much larger total pore volume than CZA. The large average pore diameter of SP34-C was mainly attributed to the stacking of SP34-C nanoparticles.

2.2. Catalytic Performance of Syngas to DME

The direct conversion of syngas to light paraffins contains three reactions, i.e., the syngas conversion to methanol, the methanol dehydration to DME, and the DME conversion reaction. In this part, the catalytic performance for the direct conversion of syngas to DME over a bifunctional catalyst composed of CZA as the methanol synthesis catalyst and $\text{Al}_2\text{O}_3(\text{C})$ as the methanol dehydration catalyst was studied. The results are displayed in Figure 4. Figure 4a shows the effect of the mass ratio of CZA to $\text{Al}_2\text{O}_3(\text{C})$ on catalytic performance. As the mass ratio of CZA to $\text{Al}_2\text{O}_3(\text{C})$ increased from 1:10 to 2:1, the CO conversion increased from 30.4% to 72.2%, and the selectivity of byproduct CO_2 gradually decreased from 36.0% to 28.8%. It is because the content of the methanol synthesis CZA catalyst increased, which promoted the conversion of CO. Subsequently, the generated methanol converted to DME over the $\text{Al}_2\text{O}_3(\text{C})$ catalyst and thus produced water. The increase in the mass ratio of CZA to $\text{Al}_2\text{O}_3(\text{C})$ indicates that the relatively low content of $\text{Al}_2\text{O}_3(\text{C})$ in such a bifunctional catalyst generated less water, which was not beneficial for the water gas shift reaction ($\text{WGSR}, \text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2$) and thus decreased the selectivity of CO_2 . It is obvious that when the mass ratio of CZA to $\text{Al}_2\text{O}_3(\text{C})$ achieved 2:1, a high CO conversion and a low CO_2 selectivity were obtained; thus, the CZA-to- $\text{Al}_2\text{O}_3(\text{C})$ ratio was set at 2:1 in the following studies.

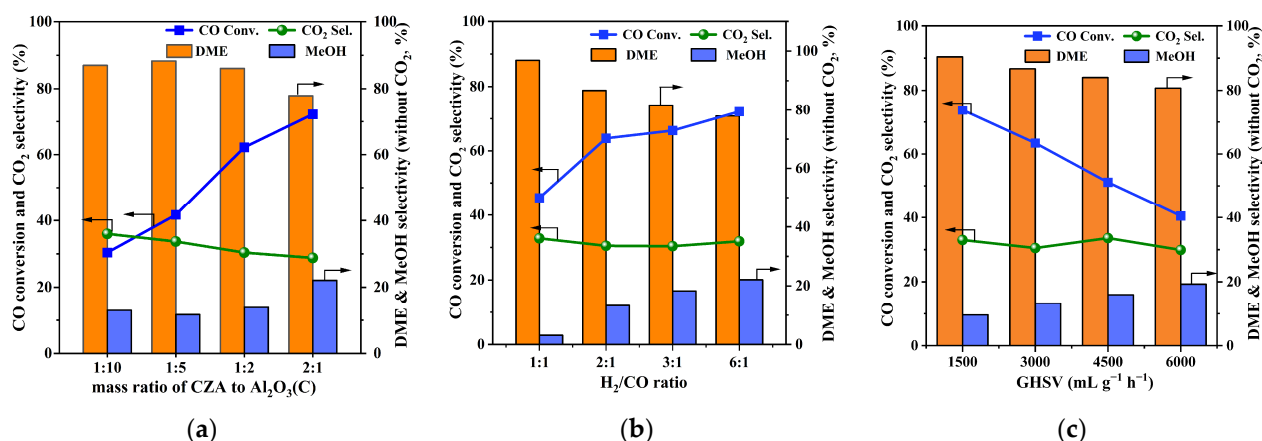


Figure 4. Effect of (a) the mass ratio of CZA to Al₂O₃(C), (b) the H₂/CO molar ratio, and (c) the GHSV on syngas conversion of DME. Reaction conditions: 260 °C and 2.0 MPa, (a) GHSV = 3000 mL·g⁻¹·h⁻¹, H₂/CO = 6:1; (b) GHSV = 3000 mL·g⁻¹·h⁻¹, m(CZA): m(Al₂O₃(C)) = 2:1; (c) H₂/CO = 2:1, m(CZA): m(Al₂O₃(C)) = 2:1.

The effect of the H₂/CO molar ratio on catalytic performance is shown in Figure 4b. It could be found that the CO conversion gradually increased from 45.4% to 66.3% as the H₂/CO ratio increased from 1:1 to 3:1 under the conditions of 260 °C, 2.0 MPa and 3000 mL g⁻¹ h⁻¹, while the selectivity of DME decreased from 96.9% to 81.7%. With a further increase in the H₂/CO ratio to 6:1, the conversion of CO increased to 72.2%. The results indicate that a high H₂/CO ratio benefits the CO conversion and methanol selectivity, while it goes against the selectivity of DME.

Figure 4c shows the effect of gas hourly space velocity (GHSV) on catalytic performance. As the space velocity increased from 1500 mL g⁻¹ h⁻¹ to 6000 mL g⁻¹ h⁻¹, the conversion of CO linearly decreased from 73.8% to 40.5%. The selectivity of MeOH gradually increased while the selectivity of DME gradually decreased. The reason was that a high GHSV reduced the residence time of methanol in the catalyst bed, which resulted in the methanol not being converted in time.

The CO equilibrium conversions of the STM and STD reactions were calculated using the HSC 6.0 software. The results are shown in Figure 5a. It is obvious that the CO equilibrium conversions of the STM and STD reactions both decreased as the temperature increased. The reason is that the STM and STD reactions are both thermodynamically exothermic: the increase in temperature is not conducive to the conversion of CO. For the STM reaction, the increase in the H₂/CO ratio gradually enhanced the CO equilibrium conversion, while for the STD reaction, the feed gas with the H₂/CO ratios of 3:1 and 6:1 exhibited almost the same CO conversions. It is because the presence of a large amount of H₂ inhibited the WGS in the STD reaction, which thus showed a similar CO conversion.

Figure 5b shows the effects of the H₂/CO ratio on CO equilibrium conversions for the STD and STM reactions at 260 °C and 2.0 MPa. Moreover, the CO experimental conversion for the STD reaction at 2.0 MPa and 260 °C was selected for comparison. It could be found that the increase in the H₂/CO ratio enhanced the CO conversion, and the CO equilibrium conversion of STD was much higher than that of STM. The CO experimental conversion was lower than the CO equilibrium conversion for STD; however, it was much higher than the CO equilibrium conversion for STM, which is due to the thermodynamic driving force that promotes CO conversion.

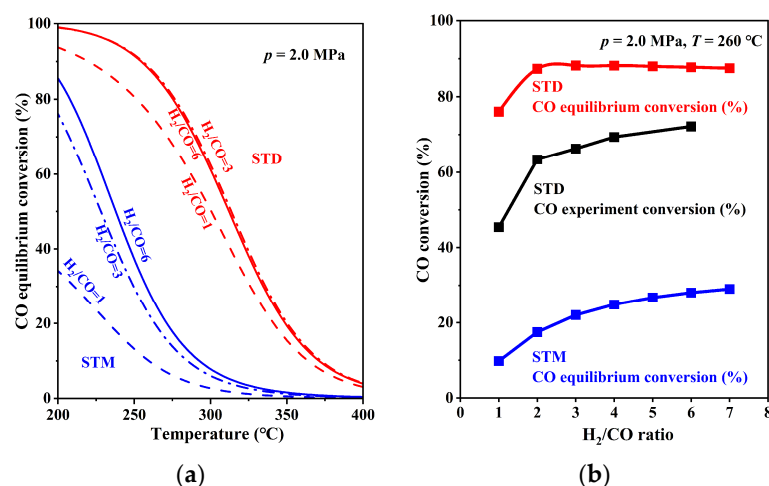


Figure 5. (a) Equilibrium conversion of the STD (red) and STM (blue) reactions with the H_2/CO ratios of 1/1, 3/1, and 6/1 at various temperatures, $p = 2.0$ MPa. (b) Comparison of the CO equilibrium conversion and the CO experimental conversion for STD and STM under the conditions of 260 °C and 2.0 MPa.

2.3. Catalytic Conversion of Reaction Intermediates

Under the reaction conditions of H_2/CO ratio = 3/1, GHSV = 3000 $mL \cdot g^{-1} \cdot h^{-1}$, and $m(CZA)/m(Al_2O_3(C)) = 2:1$, the component of the obtained products was close to the reaction intermediate with a molar ratio of $CO/CO_2/DME/N_2/H_2 = 9/6/4/5$ balanced with H_2 . Thus, the reaction intermediate was used as a feed gas to study the catalytic conversion of reaction intermediates over SP34-C. The results are shown in Figure 6. Under the reaction conditions, no DME was detected in the product, indicating that DME was completely converted. Figure 6a shows the effect of space velocity on product selectivity under the conditions of 410 °C and 2.0 MPa. As the space velocity decreased from 16,000 $mL \cdot g^{-1} \cdot h^{-1}$ to 6000 $mL \cdot g^{-1} \cdot h^{-1}$, the selectivity of light olefins decreased, while the selectivity of paraffins increased. The reason was due to the low space velocity possessing a long residence time in the catalyst bed for the generated products, which resulted in the excessive hydrogenation of the generated light olefins to paraffins. Specially, the ratio of light paraffins to light olefins increased from 0.9 to 24.5. Interestingly, it can be found that the selectivity of C_3H_8 increased from 36.9% to 76.7%. Thus, to enhance the selectivity of light paraffins, it is better to operate the reaction at a low space velocity.

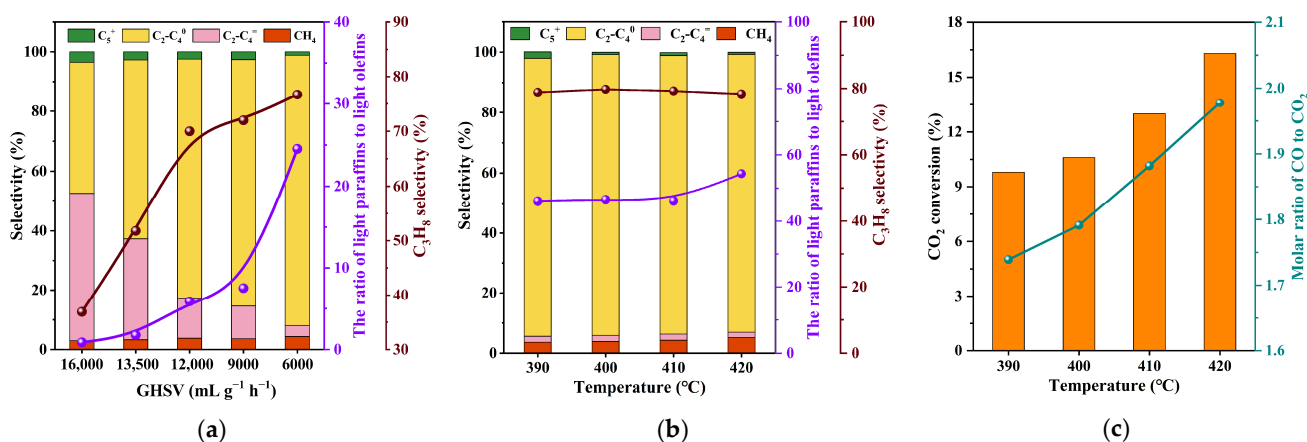


Figure 6. (a) Effect of space velocity on product selectivity. (b) Effect of reaction temperature on product selectivity. (c) Effect of reaction temperature on CO_2 conversion. Reaction conditions: $m(SP34-C) = 0.2$ g, $CO/CO_2/DME/N_2/H_2 = 9/6/4/5$ balanced with H_2 , (a) $T = 410$ °C, $p = 2.0$ MPa; (b,c) $p = 3.0$ MPa, GHSV = 7600 $mL \cdot g^{-1} \cdot h^{-1}$.

The effect of reaction temperature on product selectivity is shown in Figure 6b. It could be found that the increase in reaction temperature only slightly changed the selectivity of hydrocarbons. The ratio of light paraffins to light olefins at 420 °C reached 54.4, which is higher than those at low temperatures. It is because the selectivity of light olefins (1.7%) at 420 °C was slightly lower than at other temperatures (2.0%). The results also indicate that the reaction temperature has little effect on the hydrocarbons selectivity.

The performance for the conversion of CO₂ at different temperatures is shown in Figure 6c. As the reaction temperature increased from 390 °C to 420 °C, the conversion of CO₂ increased from 9.8% to 16.3%. Moreover, it could be found that the molar ratio of CO to CO₂ increased from 1.74 to 1.98, which was due to the increase in CO₂ conversion at high temperatures. The results also indicate that high temperature intensified the reverse water gas shift reaction (reverse WGSR, $\text{H}_2 + \text{CO}_2 = \text{CO} + \text{H}_2\text{O}$).

To study the performance of a reverse WGSR over SP34-C, the reaction was carried out by using H₂ and CO₂ as feed gases. The results in Figure 7a show that the conversion of CO₂ is approximately 13% under the reaction conditions of 410 °C and 3.0 MPa, the main product is CO (99.2%), with a tiny selectivity of byproduct CH₄ (0.8%). The results suggest that a reverse WGSR could occur over the SP34-C catalyst, and the catalytic performance is relatively stable during the reaction.

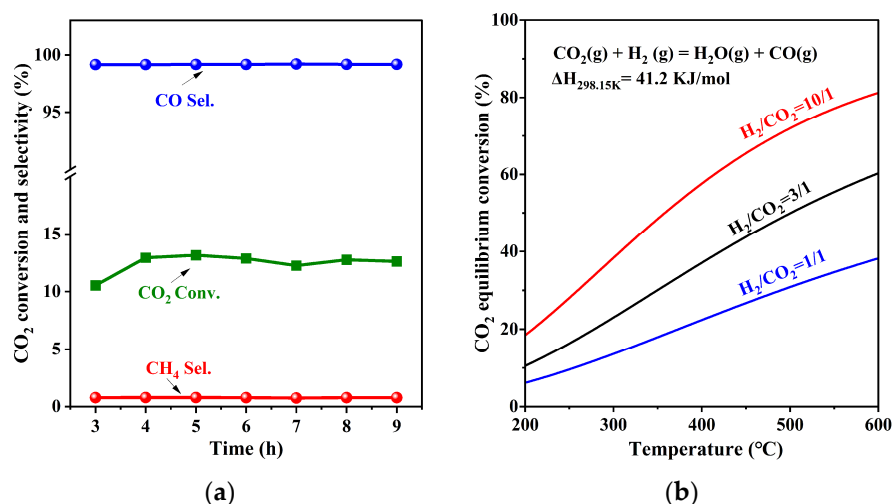


Figure 7. (a) Catalytic results of the reverse WGSR over SP34-C. Reaction conditions: $m(\text{SP34-C}) = 0.4 \text{ g}$, $\text{H}_2/\text{CO}_2 = 10/1$, $\text{GHSV} = 6000 \text{ mL g}^{-1} \text{ h}^{-1}$, $p = 2.0 \text{ MPa}$, $T = 410 \text{ °C}$. (b) Effect of the H_2/CO_2 molar ratio and temperature on the CO₂ equilibrium conversion for the reverse WGSR.

Figure 7b shows the equilibrium conversion of CO₂ for the reverse WGSR calculated by the HSC 6.0 software. It could be found that increasing the temperature enhanced the CO₂ equilibrium conversion, which is attributed to the endothermic characteristics of the reverse WGSR (41.2 kJ/mol). Moreover, as the H_2/CO_2 ratio in the feed gas increased from 1:1 to 10:1, the CO₂ equilibrium conversion increased from 22.4% to 57.6% at 410 °C, attributing to the presence of large amounts of H₂ in the reaction.

2.4. Catalytic Performance of Syngas to Light Hydrocarbons

The direct conversion of syngas to light paraffins was carried out over a dual-bed catalyst. The schematic diagram of the dual-bed reactor is shown in Figure 8. For the upper catalyst bed, the catalyst was CZA + Al₂O₃(C), with the $m(\text{CZA}):m(\text{Al}_2\text{O}_3(\text{C}))$ ratio of 2:1, used at 3.0 MPa, 260 °C, and $\text{GHSV} = 3000 \text{ mL g}^{-1} \text{ h}^{-1}$, while for the lower catalyst bed, the catalyst was SP34-C and the reaction temperature was 410 °C. The catalytic performance results are shown in Figure 8 and Table 2. During the reaction process, almost no methanol and DME were detected (both less than 0.2%), indicating that the generated methanol and DME both converted under the reaction conditions. Table 2 shows that the conversion

of CO was 33.4% and the selectivity of CO₂ was 32.6%, the selectivity of light paraffins reached 88.9%, which is much higher than the selectivity of light olefins (2.9%). Moreover, the selectivity of propane in hydrocarbons reached 75.4%. Figure 8 displays that the catalyst exhibited good stability after a reaction time for 1350 min.

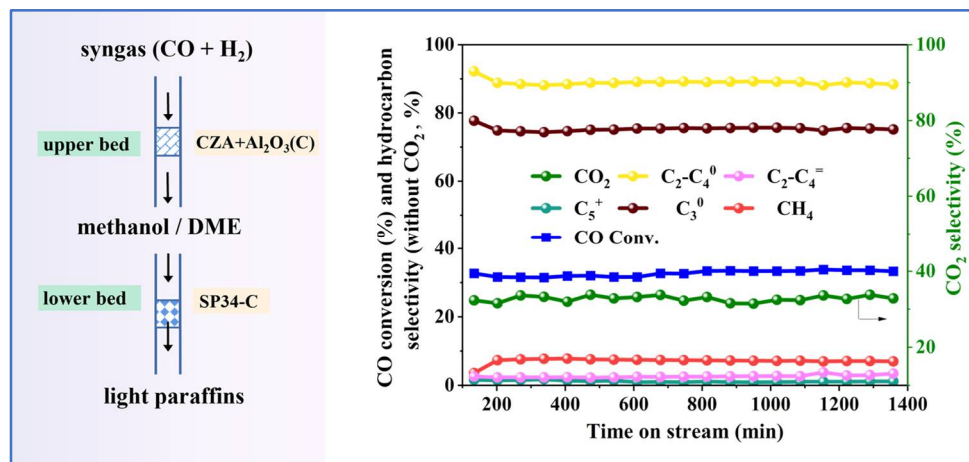


Figure 8. Schematic diagram of a dual-bed reactor and catalytic stability of syngas to light paraffins in a dual-bed reactor over the (CZA + Al₂O₃(C))/SP34-C catalysts. Reaction conditions: $p = 3.0$ MPa, T (upper bed) = 260 °C, $m(\text{CZA}):m(\text{Al}_2\text{O}_3(\text{C})) = 2:1$, $m(\text{CZA} + \text{Al}_2\text{O}_3(\text{C})) = 0.6$ g, GHSV = 3000 mL g^{−1} h^{−1}; T (lower bed) = 410 °C, $m(\text{SP34-C}) = 0.3$ g.

Table 2. Products selectivity in the direct conversion of syngas to light paraffins.

Product	CH ₄	C ₂ –C ₄ ⁰			C ₂ –C ₄ ⁼			C ₅ ⁺	CO ₂
		C ₂ ⁰	C ₃ ⁰	C ₄ ⁰	C ₄ ⁼	C ₄ ⁼	C ₄ ⁼		
Selectivity (%) ^a	7.2	7.3	75.4	6.2	1.1	1.0	0.8	1.0	32.6

^a Average value from Figure 8.

3. Materials and Methods

3.1. Catalyst Preparation

CuZnAlO_x (C302, denoted as CZA) was purchased from Southwest Chemical Industry Design and Research Institute (Chengdu, China); the alumina catalyst (Al₂O₃(C)) was purchased from TOAGOSEI Co., Ltd. (Tokyo, Japan); SAPO-34 (denoted as SP34-C) with a SiO₂/Al₂O₃ ratio of 0.5 was supplied by Tianjin Nanhua Catalyst Co., Ltd. (Tianjin, China).

CZA and the Al₂O₃(C) bifunctional catalyst: CZA powder and Al₂O₃(C) powder were mixed in an agate mortar and physically grinded for 10 min, then pressed into tablets and sieved to obtain 30–60 mesh particles. The SP34-C was also pressed and sieved to obtain 30–60 mesh particles.

3.2. Catalyst Characterization

Powder XRD of the catalysts was performed on a SmartLab SE (Rigaku, Tokyo, Japan), Cu Kα radiation was used as the radiation source ($\lambda = 0.154056$ nm) operated at 40 kV and 40 mA, with a scanning speed of 10° min^{−1}. In-situ XRD of the CZA measurement was carried out under a flow of 10% H₂ in Ar on a Max 2500 diffractometer equipped with an XRK-900 reaction chamber, the heating rate was 5 °C min^{−1}, and the gas flow was 20 mL/min.

H₂-temperature-programmed reduction (H₂-TPR) and temperature-programmed desorption of CO or NH₃ (CO-TPD, NH₃-TPD) were performed on an Autochem II 2920 (Micromeritics, Norcross, GA, USA) instrument.

For the H₂-TPR, 40 mg of the CZA catalyst were placed into a U-shaped tube and purged with N₂ at 300 °C for 30 min. After cooling to 50 °C, the N₂ was switched to a 10%

H₂/90% Ar gas mixture and heated to 600 °C at 10 °C/min. In this process, the signal of H₂ was detected by a thermal conductivity cell detector (TCD).

For the CO-TPD, 40 mg of the CZA catalyst were placed in a U-shaped tube and pretreated at 300 °C in a He atmosphere for 30 min. After the sample was cooled to 280 °C, the He was switched to 10% H₂/90% Ar and reduced for 30 min. Then, the sample was cooled to 50 °C in flowing He and allowed to fully adsorb 10% CO/90% He for 30 min; after that, the sample was purged with He for 1 h, the temperature increased to 150 °C and held for 10 min. Once the signal was stable, the temperature was further increased to 260 °C at 10 °C/min and maintained for 30 min. The amounts of desorbed CO were detected by the TCD.

For the NH₃-TPD, 100 mg of SP34-C were put in a U-shaped tube and pretreated in a He atmosphere at 300 °C for 1 h; after cooling down to 100 °C, the He was switched to 5% NH₃/95% He and held for 1 h; the TCD was purged with He until the baseline was stable, then the temperature was increased to 700 °C at 10 °C·min^{−1}, and the desorbed NH₃ was recorded by the TCD.

N₂ adsorption–desorption was carried out on a 3H-2000PS2 instrument (Beishide, Beijing, China). Before the test, 100 mg of the sample were weighed and degassed under vacuum and 250 °C for 4 h; the Brunauer–Emmett–Teller (BET) equation was used to calculate the specific surface area of the sample; the Barrett–Joyner–Halenda (BJH) method was used to calculate the pore size and pore volume.

3.3. Catalyst Performance Evaluation

The performance test of syngas to DME was carried out in a fixed-bed reactor furnished with a quartz tube. Typically, the physical mixed CZA and Al₂O₃© bifunctional catalyst was reduced at 280 °C for 4 h by using a mixture of 25% H₂/75% N₂. Then, the reduction gas was switched to feed gas with different CO/H₂ molar ratios, Ar was used as an internal standard gas, and the reaction was performed at 260 °C. During the reaction process, the products were analyzed by an on-line gas chromatography Haixin GC-950, the equipped Agilent DB-624UI column (30 m × 0.32 mm × 1.80 μm) was used to analyze methanol and DME, and the packed column TDX-01 was used to analyze Ar, CO₂, and CO.

The performance of simulated reaction intermediates (obtained from the component of syngas to DME) and the performance of reverse WGS were carried out in a fixed-bed reactor equipped with quartz reactor. Specifically, the direct conversion of syngas to light hydrocarbons was carried out in a dual bed, the upper layer is the physical mixed CZA and A©₃(C) catalyst, after reduction at 280 °C, the reaction was performed at 260 °C. The lower layer is SAPO-34 zeolite, and the reaction was performed at 400 °C unless otherwise stated. The gas products were analyzed by an on-line gas chromatography Agilent 7890A, the C1–C5 hydrocarbon components were analyzed by using a capillary column HP-AL/S (30 m × 530 μm × 15 μm) and a hydrogen flame ionization detector (FID). The packed column Porapak-Q, capillary column HP-PLOT/Q, and HP-MOLESIEVE series and thermal conductivity detector (TCD) were used to analyze CO₂, CO, H₂ and N₂. The gas chromatograms are calibrated before being used to analyze samples. Chromatographic standard gases containing all hydrocarbon products were formulated and the chromatogram was calibrated using an external standard method.

For the STD reactions, the CO conversion and the selectivity of products were calculated as follows:

$$\text{CO conversion (\%)} = \frac{F_{\text{O},\text{in}} - F_{\text{CO},\text{out}}}{F_{\text{CO},\text{in}}} \times 100\%$$

$$\text{Sel}_{\text{MeOH}} (\%) = \frac{F_{\text{MeOH},\text{out}}}{F_{\text{C},\text{in}} - F_{\text{CO},\text{out}}} \times 100\%$$

$$\text{Sel}_{\text{DME}} (\%) = \frac{2 \times F_{\text{DME},\text{out}}}{F_{\text{CO},\text{in}} - F_{\text{CO},\text{out}}} \times 100\%$$

$$\text{Sel}_{\text{CO}_2}(\%) = \frac{F_{\text{CO}_2, \text{out}}}{F_{\text{CO}_2, \text{in}} - F_{\text{CO}_2, \text{out}}} \times 100\%$$

Furthermore, for the syngas conversion to light hydrocarbons, the selectivity of hydrocarbons (C_nH_m) was calculated on a molar carbon basis in total hydrocarbons:

$$\text{C}_n\text{H}_m \text{ selectivity}(\%) = \frac{n F_{\text{C}_n\text{H}_m, \text{out}}}{\sum_1^n n F_{\text{C}_n\text{H}_m, \text{out}}} \times 100\%$$

where $F_{\text{CO}_2, \text{in}}$ and $F_{\text{CO}_2, \text{out}}$ are the molar flow rates of CO_2 at the inlet and outlet, $F_{\text{product}, \text{out}}$ is the molar flow rate of product at the outlet.

For the reverse WGSR, the CO_2 conversion and the selectivity of products were calculated as follows:

$$\text{CO}_2 \text{ conversion}(\%) = \frac{F_{\text{CO}_2, \text{in}} - F_{\text{CO}_2, \text{out}}}{F_{\text{CO}_2, \text{in}}} \times 100\%$$

$$\text{Sel}_{\text{CO}}(\%) = \frac{F_{\text{CO}, \text{out}}}{F_{\text{CO}_2, \text{in}} - F_{\text{CO}_2, \text{out}}} \times 100\%$$

$$\text{Sel}_{\text{CH}_4}(\%) = \frac{F_{\text{CH}_4, \text{out}}}{F_{\text{CO}_2, \text{in}} - F_{\text{CO}_2, \text{out}}} \times 100\%$$

where $F_{\text{CO}_2, \text{in}}$ and $F_{\text{CO}_2, \text{out}}$ are the molar flow rate of CO_2 at the inlet and outlet, $F_{\text{CO}, \text{out}}$ and $F_{\text{CH}_4, \text{out}}$ are the molar flow rates of CO and CH_4 at the outlet.

3.4. Thermodynamic Simulation

The thermodynamic calculations data for STM and STD were obtained by using the Equilibrium Compositions module in HSC Chemistry 6.0 software. The Gibbs free energy minimization method possesses the advantage that it is not needed to specify the reaction equation. The principle is to calculate the reaction equilibrium according to the minimum Gibbs free energy of the system when the reaction reaches equilibrium. It is only necessary to specify the state, temperature, pressure, and quantity of the initial reactants. The equilibrium conversion of CO or CO_2 is calculated as follows:

$$\text{CO equilibrium conversion}(\%) = \frac{n_{\text{CO}, \text{in}} - n_{\text{CO equilibrium}}}{n_{\text{CO}, \text{in}}} \times 100\%$$

$$\text{CO}_2 \text{ equilibrium conversion}(\%) = \frac{n_{\text{CO}_2, \text{in}} - n_{\text{CO}_2 \text{equilibrium}}}{n_{\text{CO}_2, \text{in}}} \times 100\%$$

where n_{in} in the formula refers to the molar amount of material of the raw material given initially, and $n_{\text{equilibrium}}$ refers to the molar amount of material of the material at equilibrium of the reaction.

4. Conclusions

In summary, a dual-bed strategy was adopted for the direct conversion of syngas to light paraffins by using CZA as methanol synthesis catalyst $\text{Al}_2\text{O}_3(\text{C})$ as methanol dehydration catalyst to DME, and SP34-C zeolite as DME conversion catalyst. The CZA and $\text{Al}_2\text{O}_3(\text{C})$ catalysts were physically mixed and put in the upper bed for syngas conversion to DME, while SP34-C zeolite was put in the lower bed. A high mass ratio of CZA to $\text{Al}_2\text{O}_3(\text{C})$, high H_2/CO ratio, and low space velocity are conducive to the conversion of syngas to DME. For the simulated feed gas $\text{CO}/\text{CO}_2/\text{DME}/\text{N}_2/\text{H}_2$ with a molar ratio of 9/6/4/5 balanced with H_2 over SP34-C, a low space velocity is conducive to the formation of light paraffins, a high reaction temperature intensified the reverse WGSR, while slightly affect the selectivity of light paraffins. After optimizing the reaction condition, the selectivity of light paraffins reached 90.8%, and the selectivity of propane was as high as 76.7%. For

the direct conversion of syngas to light paraffins in a dual-bed reactor, 88.9% of the light paraffins selectivity in hydrocarbons was obtained at a CO conversion of 33.4%.

Author Contributions: Conceptualization, F.M. and L.W.; methodology, F.M. and L.W.; software, L.W.; validation, L.W.; formal analysis, L.W.; investigation, L.W., B.L., and J.Z.; data curation, L.W. and B.L.; writing—original draft preparation, L.W.; writing—review and editing, F.M.; supervision, F.M. and Z.L.; funding acquisition, F.M. and Z.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Natural Science Foundation of Shanxi Province (202103021224073), the Key Research and Development Project of Shanxi Province (201803D421011), and the National Natural Science Foundation of China (U1510203).

Conflicts of Interest: The authors declare no conflict of interest.

References

- Yerga, R.M.N. Catalysts for production and conversion of syngas. *Catalysts* **2021**, *11*, 752. [\[CrossRef\]](#)
- Zhai, P.; Li, Y.; Wang, M.; Liu, J.; Cao, Z.; Zhang, J.; Xu, Y.; Liu, X.; Li, Y.-W.; Zhu, Q.; et al. Development of direct conversion of syngas to unsaturated hydrocarbons based on Fischer-Tropsch route. *Chem* **2021**, *7*, 3027–3051. [\[CrossRef\]](#)
- Pan, X.; Jiao, F.; Miao, D.; Bao, X. Oxide–zeolite-based composite catalyst concept that enables syngas chemistry beyond Fischer–Tropsch synthesis. *Chem. Rev.* **2021**, *121*, 6588–6609. [\[CrossRef\]](#) [\[PubMed\]](#)
- Torres Galvis, H.M.; de Jong, K.P. Catalysts for production of lower olefins from synthesis gas: A review. *ACS Catal.* **2013**, *3*, 2130–2149. [\[CrossRef\]](#)
- Lu, S.; Yang, H.; Zhou, Z.; Zhong, L.; Li, S.; Gao, P.; Sun, Y. Effect of In₂O₃ particle size on CO₂ hydrogenation to lower olefins over bifunctional catalysts. *Chin. J. Catal.* **2021**, *42*, 2038–2048. [\[CrossRef\]](#)
- Meng, F.; Li, X.; Zhang, P.; Yang, L.; Liu, S.; Li, Z. A facile approach for fabricating highly active ZrCeZnOx in combination with SAPO-34 for the conversion of syngas into light olefins. *Appl. Surf. Sci.* **2021**, *542*, 148713. [\[CrossRef\]](#)
- Meng, F.; Li, X.; Zhang, P.; Yang, L.; Yang, G.; Ma, P.; Li, Z. Highly active ternary oxide ZrCeZnOx combined with SAPO-34 zeolite for direct conversion of syngas into light olefins. *Catal. Today* **2020**, *368*, 118–125. [\[CrossRef\]](#)
- Zhang, P.; Meng, F.; Yang, L.; Yang, G.; Liang, X.; Li, Z. Syngas to olefins over a CrMnGa/SAPO-34 bifunctional catalyst: Effect of Cr and Cr/Mn ratio. *Ind. Eng. Chem. Res.* **2021**, *60*, 13214–13222. [\[CrossRef\]](#)
- Wang, Y. A new horizontal in C1 chemistry: Highly selective conversion of syngas to light olefins by a novel OX-ZEO process. *J. Energy Chem.* **2016**, *25*, 169–170. [\[CrossRef\]](#)
- Cheng, K.; Zhou, W.; Kang, J.; He, S.; Shi, S.; Zhang, Q.; Pan, Y.; Wen, W.; Wang, Y. Bifunctional catalysts for one-Step conversion of syngas into aromatics with excellent selectivity and stability. *Chem* **2017**, *3*, 334–347. [\[CrossRef\]](#)
- Zhou, W.; Shi, S.; Wang, Y.; Zhang, L.; Wang, Y.; Zhang, G.; Min, X.; Cheng, K.; Zhang, Q.; Kang, J.; et al. Selective conversion of syngas to aromatics over a Mo–ZrO₂/H-ZSM-5 bifunctional catalyst. *ChemCatChem* **2019**, *11*, 1681–1688. [\[CrossRef\]](#)
- Feng, J.; Miao, D.; Ding, Y.; Jiao, F.; Pan, X.; Bao, X. Direct synthesis of isoparaffin-rich gasoline from syngas. *ACS Energy Lett.* **2022**, *7*, 1462–1468. [\[CrossRef\]](#)
- Lin, Y.-G.; Hsu, Y.-K.; Chen, S.-Y.; Chen, L.-C.; Chen, K.-H. O₂ plasma-activated CuO-ZnO inverse opals as high-performance methanol microreformer. *J. Mater. Chem.* **2010**, *20*, 10611–10614. [\[CrossRef\]](#)
- van den Berg, R.; Prieto, G.; Korpershoek, G.; van der Wal, L.I.; van Bunningen, A.J.; Lægsgaard-Jørgensen, S.; de Jongh, P.E.; de Jong, K.P. Structure sensitivity of Cu and CuZn catalysts relevant to industrial methanol synthesis. *Nat. Commun.* **2016**, *7*, 13057. [\[CrossRef\]](#)
- Park, J.; Cho, J.; Lee, Y.; Park, M.-J.; Lee, W.B. Practical microkinetic modeling approach for methanol synthesis from syngas over a Cu-based catalyst. *Ind. Eng. Chem. Res.* **2019**, *58*, 8663–8673. [\[CrossRef\]](#)
- Bhan, A.; Iglesia, E. A link between reactivity and local structure in acid catalysis on zeolites. *Acc. Chem. Res.* **2008**, *41*, 559–567. [\[CrossRef\]](#)
- Aloise, A.; Marino, A.; Dalena, F.; Giorgianni, G.; Migliori, M.; Frusteri, L.; Cannilla, C.; Bonura, G.; Frusteri, F.; Giordano, G. Desilicated ZSM-5 zeolite: Catalytic performances assessment in methanol to DME dehydration. *Microporous Mesoporous Mater.* **2020**, *302*, 110198. [\[CrossRef\]](#)
- Bae, J.W.; Kang, S.-H.; Lee, Y.-J.; Jun, K.-W. Synthesis of DME from syngas on the bifunctional Cu–ZnO–Al₂O₃/Zr-modified ferrierite: Effect of Zr content. *Appl. Catal. B* **2009**, *90*, 426–435. [\[CrossRef\]](#)
- Liu, Z.; Ni, Y.; Fang, X.; Zhu, W.; Liu, Z. Highly converting syngas to lower olefins over a dual-bed catalyst. *J. Energy Chem.* **2021**, *58*, 573–576. [\[CrossRef\]](#)
- Yang, M.; Fan, D.; Wei, Y.; Tian, P.; Liu, Z. Recent progress in methanol-to-olefins (MTO) catalysts. *Adv. Mater.* **2019**, *31*, 1902181. [\[CrossRef\]](#)
- Ni, Y.; Liu, Z.; Tian, P.; Chen, Z.; Fu, Y.; Zhu, W.; Liu, Z. A dual-bed catalyst for producing ethylene and propylene from syngas. *J. Energy Chem.* **2022**, *66*, 190–194. [\[CrossRef\]](#)

22. Arora, S.S.; Nieskens, D.L.S.; Malek, A.; Bhan, A. Lifetime improvement in methanol-to-olefins catalysis over chabazite materials by high-pressure H₂ co-feeds. *Nat. Catal.* **2018**, *1*, 666–672. [[CrossRef](#)]
23. Zhao, X.; Li, J.; Tian, P.; Wang, L.; Li, X.; Lin, S.; Guo, X.; Liu, Z. Achieving a superlong lifetime in the zeolite-catalyzed MTO reaction under high pressure: Synergistic effect of hydrogen and water. *ACS Catal.* **2019**, *9*, 3017–3025. [[CrossRef](#)]
24. Zhang, X.; Hao, X.; Hao, J.; Wang, Q. Heat transfer and mechanical properties of wood-plastic composites filled with flake graphite. *Thermochim. Acta* **2018**, *664*, 26–31. [[CrossRef](#)]
25. Zhang, Y.; Ren, Z.; Wang, Y.; Deng, Y.; Li, J. Synthesis of small-sized SAPO-34 crystals with varying template combinations for the conversion of methanol to olefins. *Catalysts* **2018**, *8*, 570. [[CrossRef](#)]
26. Liu, H.; Chen, T.; Wang, G. Effect of preparation method on the structure and catalytic performance of CuZnO catalyst for low temperature syngas hydrogenation in liquid phase. *Catal. Lett.* **2018**, *148*, 1462–1471. [[CrossRef](#)]
27. Unutulmazsoy, Y.; Cancellieri, C.; Lin, L.; Jeurgens, L.P.H. Reduction of thermally grown single-phase CuO and Cu₂O thin films by in-situ time-resolved XRD. *Appl. Surf. Sci.* **2022**, *588*, 152896. [[CrossRef](#)]
28. Park, S.; Inagaki, S.; Kubota, Y. Selective formation of light olefins from dimethyl ether over MCM-68 modified with phosphate species. *Catal. Today* **2016**, *265*, 218–224. [[CrossRef](#)]
29. Cheng, K.; Gu, B.; Liu, X.; Kang, J.; Zhang, Q.; Wang, Y. 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.* **2016**, *55*, 4725–4728. [[CrossRef](#)]
30. Meng, F.; Liang, X.; Wang, L.; Yang, G.; Huang, X.; Li, Z. Rational design of SAPO-34 zeolite in bifunctional catalysts for syngas conversion into light olefins. *Ind. Eng. Chem. Res.* **2022**, *61*, 11397–11406. [[CrossRef](#)]
31. Thommes, M.; Kaneko, K.; Neimark, A.V.; Olivier, J.P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K.S.W. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87*, 1051–1069. [[CrossRef](#)]