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Direct synthesis of lower olefins from syngas via Fischer–Tropsch synthesis catalyzed by a dual-bed catalyst



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<i>Keywords:</i> Lower olefins Fischer-Tropsch synthesis Zeolites Dual-bed catalysts	Direct synthesis of lower olefins ($C_{2.4}^{=}$) from syngas through Fischer–Tropsch synthesis (FTS) is a promising approach to satisfy increasing demand for such chemical feedstocks. However, control of selectivity remains a major challenge for the Fischer–Tropsch to olefins (FTO) process. Herein, we designed a dual-bed FTO catalyst FeZnNa/zeolites, which contained zeolites filled with a conventional FTS catalyst. We explored the catalytic performance of different zeolites in the dual-bed catalyst, namely HY, NaY, ZSM-5, SAPO-34, H β , Li β , Na β , K β , and Rb β . The integration behavior and mass ratios of the two active components, and reaction parameters of the FTO process were also optimized. The highest selectivity of $C_{2.4}^{=}$ up to 50.5 %, and a high CO conversion of 92.9 %, were achieved for the FeZnNa/Na β dual-bed catalyst. Importantly, the FeZnNa/Na β catalyst had outstanding long-term stability with no obvious deactivation over 100 h of testing, making it a potential catalyst for in- dustrial applications. The acidity and pore structure of the zeolite were found to be key factors for improving the yields of lower olefins from these dual-bed catalysts. The excellent catalytic performance of FeZnNa/Na β is

attributed to the suitable acidity and hierarchical pore structure of Naß.

1. Introduction

Lower olefins ($C_{2.4}^{=}$), as building blocks in the chemical industry, are traditionally produced from the cracking of naphtha or oil refining [1,2]. Owing to diminishing petroleum reserves, the production of lower olefins starting with syngas derived from non-petroleum resources has attracted considerable attention [3,4]. In comparison with the cracking performance of the Fischer–Tropsch synthesis (FTS) liquid products, and methanol or dimethyl ether to olefins (MTO or DMTO) synthesis, the strategy of Fischer–Tropsch to olefins (FTO) represents a more promising way to convert syngas directly into lower olefins quicker and more economically with low energy consumption [1–11]. However, with FTS, the highest selectivity towards $C_{2.4}$ hydrocarbons, including $C_{2.4}$ olefins and paraffins, is predicted to be less than 58 % owing to the restriction of Anderson–Schulz-Flory distribution [12].

In recent decades, a variety of modified FTS catalysts have been used in FTO reaction [6,7,10,11,13–16]. Co-based FTS catalysts are generally more selective for long-chain hydrocarbons and thus unfavorable for obtaining a high yield of lower olefins [7]. Nevertheless, recently, cobalt carbide nanoprisms have been reported to achieve an approximate 61 % selectivity for $C_{2.4}^{=}$ [17]. In contrast, Fe-based

catalysts have great potential for selective production of light olefins via FTS, because of their low-cost, high productivity of olefins, and low CH₄ selectivity at high temperatures [7]. de Jong et al. [6] reported Na and S modified iron particles supported on an inert support i.e. a-alumina and carbon nanofiber with weak interactions that achieved an outstanding selectivity of 61 C% towards lower olefins. They proposed that Na additives suppressed the formation of CH₄ by accelerating the chain growth reaction, whereas modification of S resulted in much lower selectivity for CH4 and promoted formation of olefins by decreasing the H coverage on the surface of catalysts [18]. More recently, Ma et al. [19] developed a Na- and Zn-modulated Fe₅C₂ catalyst, which achieved selectivity for olefins as high as 78 % and CO conversion of 63 %. For this Na- and Zn-modulated Fe₅C₂ catalyst, the selectivity towards CO2 was controlled to be less than 25 % and the utilization efficiency of carbon was as high as 64 %. However, the Na- and Znmodulated Fe₅C₂ catalyst mainly produced C₅⁺ alkenes rather than lower olefins.

In view of the rich production of long-chain olefins for Na- and Znmodulated Fe_5C_2 catalysts, a high selectivity for lower olefins might be achieved through combination with active components containing hydrocracking functions. Zeolites have space confining features, which

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restrict the final products, intermediates, and even transition states to be no larger than the size of the zeolite's cavities or channels [12,20]. These features limit chain growth, resulting in the production of more light hydrocarbons [20]. Furthermore, acid sites present in zeolites render it reactive towards cracking of long-chain hydrocarbons, which will also contribute to the formation of light hydrocarbons [21,22]. However, the confinement and cracking effects of zeolites should be precisely controlled, because if the zeolite pore channels are too small or strongly acidic, over-cracking might occur. This effect results in high selectivity for undesirable products (CH4 and C2-4 alkanes). In view of the confinement and acidic cracking features of zeolites, the combination of zeolites with conventional FTS catalysts, which are rich in longchain olefins, might achieve high selectivity for lower olefins and high utilization efficiency for carbon. Compared with other methods of combining FTS active metals supported on zeolites, or by physical mixing of FTS catalyst and zeolites, the dual-bed configuration is advantageous for withdrawing reaction heat and regenerating the catalyst [23]. However, the development of an efficient dual-bed catalyst for FTO would still be desirable.

Herein, we constructed a dual-bed configuration catalyst with zeolites downstream from the FTS catalyst FeZnNa, which is reported to be rich in heavier olefins [19] for the FTO process. By exploring different zeolites with hydrocracking function (HY [24], NaY, ZSM-5 [25], SAPO-34 [26], H β [27], Li β , Na β , K β , and Rb β) and optimizing the process parameters in detail (integration manners and mass ratios of the two active components, reaction temperature, pressure, space velocity, and ratio of H₂/CO), the dual-bed catalyst FeZnNa/Na β achieved selectivity as high as 50.5 % C_{2.4}⁼ and CO conversion up to 92.9 %. The catalyst also exhibited outstanding long-term stability and ran stably for 100 h without notable deactivation.

2. Experimental

2.1. Catalyst preparation

The FeZnNa catalyst was prepared by co-precipitation. Briefly, 1 M FeSO₄ and 1 M Zn(NO₃)₂ solutions were mixed in a volume ratio of 1:1. A 2M Na₂CO₃ solution was used as a precipitator to co-precipitate the former mixture solution. The temperature and pH value were controlled to be approximately 80 °C and 9.0, respectively. After the precipitation, the precipitant was aged at 80 °C for 5 h, followed by washing and filtration. The precursor was dried at 60 °C overnight and calcined at 400 °C for 4 h in a muffle furnace.

Hβ, HY, and SAPO-34 are commercial zeolites purchased from Nankai University Catalyst Co., Ltd. The NaY and Naβ were derived from a post-treatment of the HY and Hβ zeolite, respectively. In a typical treatment, 1.85 g of HY or Hβ zeolite was added to 50 mL of NaOH solution (0.25 M) and stirred vigorously. The mixtures were then transferred to an 80-mL Teflon-sealed autoclave and treated at 150 °C for 21 h. The treated zeolites were recovered by washing, filtering, and drying at 120 °C overnight and then calcined in a muffle at 550 °C for 5 h. The synthesis of ZSM-5 was performed according to the method reported by Zhou et al. [28]. Different alkalis-exchanged β zeolites (i.e., Liβ, Kβ and Rbβ) were prepared by ion exchange. Briefly, 1.0 g Naβ was exchanged with a 100 mL aqueous solution of alkali nitrate (0.2 M) at 80 °C for 12 h. The exchanged β zeolites were washed, filtered, dried at 120 °C overnight and calcined at 550 °C for 6 h. The obtained zeolites were denoted as Liβ, Kβ, and Rbβ.

2.2. Catalyst characterizations

The elemental components were detected using an inductively coupled plasma optical emission spectroscopy (ICP, Optima2100DV, PerkinElmer) or an XRF-1800 spectrometer with Rh radiation at working conditions of 60 KV and 95 mA. A micromeritics ASAP 2020 M system was applied to analyze the textural properties via N_2 adsorption-

desorption. The surface area was evaluated by the Brunauer-Emmett-Teller (BET) equation, whereas the microporous surface area was calculated by the t-plot method. The pore volume of micropores and mesopores were calculated by the t-plot method and Barrett-Joyner-Halenda (BJH) method, respectively. The pore size distribution was calculated by density functional theory (DFT) method. The X-ray diffraction (XRD) patterns were recorded by a Rigaku D/ MAX2550VB X-ray diffractometer. The Mössbauer spectroscopy (MES) were recorded in an MR-351 constant-acceleration Mössbauer spectrometer (FAST, Germany). A scanning electron microscope (SEM, Ouanta 200, FEI) was used to characterize the size and morphology of different zeolites. Raman spectroscopy with laser excitation at 532 nm were conducted on a DXR2xi (Thermo, America) apparatus at room temperature. Temperature-programmed desorption of ammonia (NH3-TPD) was conducted on an AutoChem II 2920 instrument (Micromeritics, USA) equipped with a mass spectrometry detector. The samples were pretreated in He at 400 °C for 1 h, then cooled to 100 °C and saturated with NH₃, followed by purging with He at 100 °C for 30 min and heating to 600 °C in He flow at a rate of 10 °C/min.

2.3. Catalyst performance

The catalytic performance was in a fixed-bed reactor with a stainless-steel reaction tube with an inner diameter of 12 mm. The FeZnNa and zeolites at a mass ratio of 1:1, unless otherwise stated, were filled into the isothermal region of the reaction tube and completely separated by silica wool. Before the FTO reaction, the samples were activated by $\rm H_2$ at a flow rate of 60 mL/min at 360 °C, at atmospheric pressure for 4 h. Then, the reaction systems were operated under the desired reaction conditions. The reaction products were analyzed by an on-line gas chromatograph (Agilent GC 6820) equipped with a 5A molecular sieve column connected to a TCD detector and an Al₂O₃ capillary column and two Propake Q columns connected to a FID detector. CH₄ was used as a reference bridge between TCD and FID. An ice trap was used to capture the oil phase and water phase. The oil phase products were analyzed by another gas chromatograph (Agilent GC 6820) equipped with an HP-5 column connected to the FID detector. Aromatics in the oil phase were determined from the gas chromatography-mass spectrum (GC-MS, GCMS-QP2010, SHIMADZU, Japan). The CO conversion, CO₂ selectivity, hydrocarbons (C_nH_m) selectivity excluding CO₂, and space time yield (STY) of $C_{2.4}^{=}$ were calculated with the following formulae:

$$CO \text{ conversion} = (CO_{in} - CO_{out})/CO_{in} \times 100 \%,$$
(1)

 $CO_2 \text{ selectivity} = CO_2 _{out} / (CO_{in} - CO_{out}) \times 100 \%,$ (2)

$$C_n H_m$$
 selectivity = $N_{CnHm}/(CO_{in} - CO_{out} - CO_{2 out}) \times 100 \%$, (3)

where CO_{in} and CO_{out} represent the moles of CO at the inlet and outlet, respectively; $CO_{2 out}$ represents moles of CO_{2} at the outlet; GHSV represents gas hourly space velocity; M_{Fe} represents mass of Fe in FeZnNa (g).

3. Results and discussion

3.1. Characterization

The textural properties of the different zeolites used in this work were determined from N₂ adsorption-desorption analysis. The surface area, pore volume and average pore diameter are summarized in Table 1. The ZSM-5 and HY zeolites had the largest surface area, up to $650 \text{ m}^2/\text{g}$. Relatively small surface areas were detected for SAPO-34 and H β . After post-treatment with NaOH, the surface area decreased from $655.2 \text{ m}^2/\text{g}$ of HY to $460.5 \text{ m}^2/\text{g}$ of NaY, and from $368.8 \text{ m}^2/\text{g}$ of

Table 1

Textural properties of the different zeolites^a.

Catalysts	S _{BET} ^b	S _{micro} ^c	V _P (cm ³ /	V _{micro} ^c	Average pore
	(m ² /g)	(m ² /g)	g)	(cm ³ /g)	diameter (nm)
Naβ Hβ NaY HY SAPO-34 ZSM-5	201.6 368.8 460.5 655.2 496.1 680.8	105.8 293.9 389.6 598.6 464.9 -	0.40 0.26 0.29 0.13 0.25 1.2	0.07 0.14 0.09 0.11 0.23	17.4 2.8 6.3 2.1 2.0 6.0

^a Determined by N₂ adsorption.

^b S_{BET}: from the BET method.

 $^{c}~S_{micro}$ and $V_{micro}{:}$ from the t-plot method.



Fig. 1. Pore size distribution of different zeolites.

H β to 201.6 m²/g of Na β . In particular, the surface area and pore volume of micropores sharply decreased upon treatment with NaOH. The pore size distribution shown in Fig. 1 indicates that mainly micropores were detected for HY, HB, and SAPO-34. For the NaB and NaY zeolites, in addition to micropores, mesopores in the size range of 15-20 nm were also observed, suggesting the formation of a mesopore structure upon NaOH treatment. The generation of a mesopore structure for Naß and NaY resulted from extraction of a small part of the framework silicon of H β or HY on post-treatment with NaOH [21,28]. Furthermore, the pore size distribution of ZSM-5 clearly showed a hierarchical pore structure, which agrees with previous reports [29]. The N₂ adsorptiondesorption isotherms of these different zeolites are presented in Fig. S1 in the Supporting information. The isotherms of HY, HB, and SAPO-34 exhibited the features of type I isotherm, further confirming the main presence of micropores in these three zeolites. In contrast, Naß, NaY, and ZSM-5 presented the combination of type I and IV isotherms with H4 type hysteresis loops, the hysteresis loop increased in the order of NaY, Naß, and ZSM-5. This result implied the coexistence of micropores and mesopores for NaY, Naß, and ZSM-5.

Fig. 2 shows the diffraction patterns of these different zeolites. As shown in Fig. 2a, H β presented intensive diffraction peaks at 7.8° and 22.5°, HY displayed mainly peaks at 6.2°, 10.2°, 12.0°, 15.8°, 19.2°, 20.5°, and 27°, while SAPO-34 exhibited typical peaks at 9.5°, 12.8°, 16.0°, 20.6°, 25.8°, and 30.5°. The diffraction patterns observed for H β , HY, and SAPO-34 matched well with the characteristic peaks of each other [30–33]. The XRD pattern of ZSM-5 also showed typical features of the ZSM-5 crystal structure as previously reported, mainly presented two regions of typical peaks at 1.0–9.0° and 23.0–25.0° [34,35]. Upon the NaOH treatment, the diffraction peaks of Na β and NaY broadened and decreased in intensity to different degrees compared with those of H β and HY, respectively. These results suggest that the structures of H β



Fig. 2. The XRD patterns of (a) different zeolites and (b) alkali-exchanged $\boldsymbol{\beta}$ zeolites.

and HY were partially destroyed by desilication through the NaOH treatment, which agrees with previous reports [21,29]. Similar results were obtained for H β treated with other alkalis, as indicated by XRD patterns shown in Fig. 2b. SEM experiments were performed to observe the morphology and measure the particle sizes of different zeolites (Fig. S3 in the Supporting information). The SEM results indicated that the particle size and morphology did not change obviously after alkali exchange for either the HY or H β zeolites.

The acidity of zeolites plays a critical role in the hydrocracking of long-chain FTS products. Thus, NH3-TPD was conducted to determine the acidity of these different zeolites. The results are shown in Fig. 3. As shown in Fig. 3a, two NH₃ desorption peaks were detected for ZSM-5, SAPO-34, H β and HY. The peak centered at around 200 °C was associated with weak acid sites, whereas the peak centered at 350-450 °C is assigned to strong acid sites. The amount of acid sites (Table S6 in the Supporting information) estimated roughly based on the peak area decreased in order of HY, ZSM-5, SAPO-34, and H_β. In the case of Na_β and NaY, only the NH₃ desorption peak belonging to weak acid sites was observed, this peak also decreased in intensity compared with their precursors $H\beta$ and HY, respectively. This result suggests that the NaOH treatment destroyed strong acid sites and reduced the number of weak acid sites. In addition, the amount of acid sites for the alkali metal exchanged β zeolites was also influenced by the basicity of the exchanged alkalis. The results in Fig. 3b clearly show that the amount of acid sites decreased as the atomic number of the exchanged alkalis



Fig. 3. $\text{NH}_3\text{-TPD}$ profiles of (a) different zeolites and (b) alkali-exchanged β zeolites.

increased. Upon treatment with alkali solution, a part of the framework silicon is thought to be extracted [21,29]. The SiO₂/Al₂O₃ ratio (Table S6 in the Supporting information) clearly decreased for both the HY and H β zeolites after being treated with NaOH. The SiO₂/Al₂O₃ ratio for the different alkali-exchanged β zeolites also declined as the atomic number of the exchanged alkali increased. Thus, the extraction of silicon might be also responsible for the decrease of acid sites for these zeolites treated by alkali solution.

The phase evolution of FeZnNa was detected with the use of XRD and MES characterization. As shown in Fig. 4a, the fresh FeZnNa mainly contained ZnFe₂O₄ and ZnO phases and no other phases of iron species were detected. Upon reduction with H₂, the sample was mainly composed of ZnO and metallic Fe phases, suggesting that iron oxide species in the form of ZnFe₂O₄ were reduced to metallic Fe. After the FTO reaction, only diffraction peaks for ZnO and a weak peak for Fe_xC were observed. The MES analysis was used to further validate iron carbide for the FeZnNa after FTO reaction. The MES spectra are depicted in Fig. 4b, and the Mössbauer parameters are summarized in Table 2. The results of MES analysis demonstrated that a mixture of iron carbide, including Fe_5C_2 , Fe_3C , and Fe_2C , formed after the FTO reaction. The FeZnNa after reaction for 24 and 100 h was composed of 80.2 % and 86.4 % of iron carbides, respectively. Surface FTS reaction and carbonization of Fe to form iron carbide occurred simultaneously during the FTO reaction process [36]. Therefore, as the reaction time was



Fig. 4. (a) The XRD patterns: (1) fresh, (2) after reduction, and (3) after reaction for 24 h, (b) Mössbauer spectra of FeZnNa catalyst.

Catalysts	IS (mm/s)	QS (mm/s)	Hhf (kOe)	Area (%)	Assignment
After reaction for	0.88	-1.78		9.0	Fe ²⁺
24 h	0	1.95		10.8	Fe ³⁺
	0.31	0.04	223	22.4	$Fe_5C_2(A)$
	0.22	0.04	182	22.4	$Fe_5C_2(B)$
	0.28	0.09	0.6	11.2	$Fe_5C_2(C)$
	0.35	0.18	210	12.0	Fe ₃ C(A)
	0.18	-0.20	204	6.0	Fe ₃ C(B)
	0.26	0.16	167	6.3	Fe ₂ C
After reaction for	0.7	-1.36		6.1	Fe ²⁺
100 h	0.02	1.56		7.5	Fe ³⁺
	0.31	0.03	220	27.2	Fe ₅ C ₂ (A)
	0.23	0.07	181	27.2	$Fe_5C_2(B)$
	0.23	0.17	106	13.6	$Fe_5C_2(C)$
	0.39	0.23	210	8.4	Fe ₃ C(A)
	0.13	-0.28	207	4.2	Fe ₃ C(B)
	0.29	0.09	167	5.9	Fe ₂ C

prolonged, an increase in the amount of iron carbides was observed.

3.2. FTO performance

Table 2

The FTO performances of these catalysts were tested at 330 °C, 2 MPa, 2400 h^{-1} , and a H₂/CO ratio of 1:1, the reaction results are

Table 3

The catalytic performance of the dual-bed FeZnNa/Zeolites catalysts^a.

Catalysts	CO conv. (%)	CO ₂ sel.(mol %)	CH distribution (mol %) ^b				C_{2-4} o/p ^c ratio	STY ^d of $C_{2-4}^{=}$
			CH ₄	C_{2-4}°	C ₂₋₄ =	C_5^+		
FeZnNa	87.6	38.6	12.4	5.4	26.4	55.8	4.9	8.0
FeZnNa/Naβ	92.9	53.5	12.8	7.7	50.5	29.0	6.5	12.3
FeZnNa/Hβ	95.4	49.8	13.3	7.5	39.7	39.5	5.3	10.7
FeZnNa/NaY	92.3	49.9	10.8	6.8	41.3	41.1	6.0	10.8
FeZnNa/HY	94.1	50.5	14.5	7.5	38.3	39.7	5.1	10.0
FeZnNa/ZSM-5	88.9	46.5	11.1	7.2	42.4	39.3	5.8	11.4
FeZnNa/SAPO-34	92.6	54.6	15.9	9.2	38.6	36.3	4.2	9.1
FeZnNa/Liβ	93.3	50.2	13.1	8.3	43.0	35.6	5.1	11.3
FeZnNa/Kβ	94.8	49.9	12.4	7.8	43.1	36.7	5.5	11.6
FeZnNa/Rbβ	93.7	53.5	11.8	7.2	43.8	37.2	6.0	10.8

^a Reaction conditions: FeZnNa/Zeolite mass ratio of 1:1, 2.0 MPa, H₂/CO = 1/1, 2400 h⁻¹, 330 °C. Pretreated with H₂ at 350 °C for 4 h. The data was collected at 24 h.

^b The selectivity of hydrocarbons in this work was calculated based on CO₂-free.

^c The ratio of olefin to paraffin for C_{2-4} . ^d Space time yield of $C_{2-4}^{-} = (\mu mol \cdot g_{Fe}^{-1} \cdot s^{-1})$.

listed in Table 3. We first tested the catalytic performance of the singlebed FeZnNa catalyst. As shown in Table 3, as high as 87.6 % CO conversion was obtained for FeZnNa, the selectivity for long-chain products C_5^+ reached as high as 55.8 %, together with 12.4 % CH₄ selectivity among the hydrocarbon products, whereas the selectivity of $C_{2.4}$ olefins was only 26.4 %. The ${\rm C_5}^+$ selectivity over FeZnNa was similar to that of previous results reported by Ma et al. [19].

To obtain a high yield of $C_{2-4}^{=}$ low olefins, we designed a dual-bed catalyst denoted FeZnNa/Zeolite, which had zeolite powders with hydrocracking functionality packed below the FeZnNa layer and completely separated by silica wool. We explored the performances of different zeolites filled in the lower bed, including ZSM-5, SAPO-34, HY, NaY, HB, and NaB. The reaction results summarized in Table 3 suggested that the filling of zeolites in the lower bed slightly increased the CO conversion and remarkably changed the distribution of hydrocarbon products. In the case of FeZnNa/SAPO-34, FeZnNa/HY, and FeZnNa/H β , the selectivity of C₂₋₄⁼ increased considerably as the selectivity of C₅⁺ decreased compared with that of the single-bed FeZnNa catalyst without zeolite packing below. However, the CH₄ selectivity also increased for these three dual-bed catalysts. For FeZnNa/ZSM-5 and FeZnNa/NaY, a relatively high selectivity for $C_{2-4}^{=}$ and low selectivity for CH4 were obtained. Compared with FeZnNa/ZSM-5, a much higher $C_{2-4}^{=}$ selectivity with lower C_5^{+} selectivity were achieved when Na β was packed in the lower bed. The highest C₂₋₄⁼ selectivity of 50.5 % was achieved with the use of the dual-bed catalysts FeZnNa/ Naβ. This sample also reached the highest space time yield (STY) of C2- $_{4}$ = of 12.3 µmol C₂₋₄ = g^{-1} Fe·s⁻¹, which was much higher than that of the single-bed FeZnNa catalyst. In the case of the dual-bed configuration, the primary hydrocarbon products produced on the upper bed FeZnNa FTS catalyst flowed down to the lower bed of the zeolite layer. Over the zeolite beds, a series of reactions, including hydrocracking, olefin readsorption, and isomerization occurred for the primary hydrocarbons, which mainly depended on the space confinement effect and acidity of zeolite [12,20]. The small pore size of the zeolite and strong confinement effects are disadvantageous for transport of primary hydrocarbons, usually resulting in over-cracking [21]. The strong acidity of the zeolite also caused over-cracking of the primary hydrocarbons. Thus, both the small pore size and strong acidity of the zeolite led to increasing formation of undesirable light hydrocarbons, such as CH₄ and C₂₋₄ alkanes, caused by over-cracking. Thus, the relatively low C2-4⁼ selectivity and high selectivity for CH₄ obtained for FeZnNa/ SAPO-34, FeZnNa/HY and FeZnNa/Hß are attributed to the strong acidity and micropore structure of SAPO-34, HY and HB zeolites, as evidenced by the NH3-TPD and N2 adsorption analysis. For FeZnNa/ ZSM-5, because ZSM-5 contained a hierarchical pore structure and had

efficient mass-transport, despite its strong acidity, it achieved relatively high selectivity towards $C_{2-4}^{=}$. The results of NH₃-TPD and N₂ adsorption analysis clearly demonstrated that Naß had a hierarchical structure and the weakest acidity among these different zeolites. Therefore the highest selectivity of 50.5 % towards $C_{2-4}^{=}$ was obtained for FeZnNa/Naβ.

In view of the excellent C_{2-4}^{-} selectivity obtained by filling Na β into the lower bed, we further explored the catalytic activity of the other alkali metals (Li, K, and Rb) exchanged β zeolites. The test results are also found in Table 3. The exchange of β zeolite by other alkali metals slightly influenced the conversion of CO, but changed the distribution of the hydrocarbon products. CH₄ selectivity decreased following the order of FeZnNa/Liß, FeZnNa/Naß, FeZnNa/Kß, and FeZnNa/Rbß, agreed with the decreasing trend of the acidity and the increase in alkali atomic number in the β zeolites as shown by the NH₃-TPD results. This phenomenon is attributed to the hydrocracking of long-chain hydrocarbon by acid sites on alkali-exchanged β zeolites. More acidic sites have stronger cracking effects, and therefore result in higher CH₄ selectivity. Accordingly, it is easy to understand that the relatively low C2- $_4$ ⁼ selectivity and high C₅⁺ selectivity obtained for FeZnNa/K β and FeZnNa/Rbb, is attributed to the relatively weak acidity of Kb and Rbb zeolites. Notably, Liß had the greatest amount of acid sites among these alkali-exchanged β zeolites; however, FeZnNa/Li β also achieved lower $C_{2-4}^{=}$ selectivity and higher C_5^{+} selectivity compared with FeZnNa/ Naß, suggesting that Liß has a weaker activity towards hydrocracking C_5^+ hydrocarbons. As indicated by N_2 adsorption analysis (see Table S1 and Fig. S2), Liß contained a higher proportion of micropores with smaller pore size than Naß. A part of the long-chain hydrocarbons, which were larger than the pore sizes of these micropores, would be inaccessible to these acidic sites located in the channels of micropores, resulting in a weak hydrocracking effect on C_5^+ . In contrast, these hydrocarbons entered into these micropores were over-cracked, owing to the small pore size and strong acidity of Liß. Thus, compared with FeZnNa/Na β , a relatively higher selectivity of CH₄ and C₅⁺ but a lower selectivity of $C_{2-4}^{=}$ was obtained for FeZnNa/Li β .

On account of the screening of different zeolites, FeZnNa/Naß was the best dual-bed catalyst for the direct synthesis of $C_{2-4}^{=}$ low olefins from syngas. Thus, we further optimized the process parameters based on FeZnNa/Naß as the dual-bed catalyst, including the mixed methods and mass ratios of these two active components, reaction temperatures, pressures, gas hourly space velocity (GHSV), and the ratio of H₂/CO.

The mixing method of the active components markedly influenced the hydrocarbon distribution for the direct conversion of syngas to lower olefins. As stated above, the use of a dual-bed configuration with Na β packed below FeZnNa gave a selectivity as high as 50.5 % towards



Fig. 5. Effect of integration manner of the active components (FeZnNa and Na β with a mass ratio of 1) on the catalytic performances at the identical reaction conditions.

 $C_{2,4}$ low olefins. We also investigated two other integration manners i.e., mortar-mixing and granule-stacking with a closer proximity for the two active components. The reaction results listed in Table S2 indicate that the integration method slightly affected the conversion of CO, whereas the product selectivities remarkably changed, as shown in Fig. 5. By mixing FeZnNa and Naβ powder in an agate mortar to ensure intimate contact of these two active components, the C₅⁺ selectivity clearly decreased because of the hydrocracking of long-chain hydrocarbon by the acidic Na β zeolite. However, the selectivity for C₂₋₄⁼ also decreased. In contrast, the formation of both $C_{2.4}^{\circ}$ and CH_4 increased. This result suggests that excessively close contact of these two active components promoted efficient cracking of long-chain hydrocarbons but simultaneously resulted in over-hydrocracking of hydrocarbon and secondary hydrogenation of olefins, therefore increasing the CH₄ and C2-4° selectivity. When the two active components were integrated in the manner of granule-stacking, the low olefins $C_{2\cdot4}{}^{=}$ selectivity increased to 40.9 %. For the three integration methods studied in our work, the distance of the two active components increased as the mixing method was changed from mortar-mixing to a dual-bed configuration. As shown in Fig. 4, the selectivity towards $C_{2-4}^{=}$ increased as the distance between these two active components was increased, and the STY of $C_{2\cdot4}^{=}$ also followed this same trend. Excessively close contact between FeZnNa and Naß appeared to be unfavorable for the formation of low olefins, which is well in line with previous findings [37,38]. It has been proposed that short distances between the two active components is detrimental for selective hydrocracking of hydrocarbons.

We investigated the dependence of the catalytic behavior on the mass ratios of FeZnNa/Na β under identical reaction conditions, the results are shown in Fig. 6. The highest selectivity and STY of C₂₋₄⁼ were obtained at a mass ratio of FeZnNa/Na β equal to 1. In the case of the dual-bed catalyst with a FeZnNa/Na β a mass ratio of 1:0.5 (i.e., a deficiency of Na β zeolite) the obtained relatively low C₂₋₄⁼ selectivity is attributed to weak hydrocracking of long-chain hydrocarbons. In contrast, when an excess of Na β was packed below FeZnNa, the long-chain alkanes and alkenes were over-cracked into CH₄, and thus a low selectivity for C₂₋₄⁼ was achieved.

Subsequently, we examined the influences of reaction temperature, pressure, GHSV, and ratio of H₂/CO on the catalytic behaviors over the dual-bed catalyst having a FeZnNa/Na β mass ratio of 1:1. As observed in Fig. 7, both the CO conversion and C_{2.4}⁼ selectivity initially increased and then slightly decreased with increasing reaction temperature. The optimal activity and C_{2.4}⁼ selectivity were achieved at 330 °C. The elevated reaction temperature enhanced CO dissociation and produced more surface carbon species on the catalyst surface of upflow FeZnNa [39]. and also promoted the cracking of Na β packed in the



Fig. 6. Influences of FeZnNa/Naß mass ratios on the catalytic performance.



Fig. 7. Influences of reaction temperature on catalytic performance of FeZnNa/Na β with a mass ratio of 1:1.

lower bed [12]. Furthermore, at high temperature, chain growth reactions and α -olefin readsorption were less favored [40]. Thus, as the temperature was increased from 300 to 330 °C, the conversion of CO and selectivity towards C₂₋₄⁼ increased notably. Conversely, as listed in Table S3 in the Supporting information, the carbon balance decreased with increasing reaction temperature, indicating that the carbon deposition was also accelerated by increasing reaction temperature. The acceleration of carbon deposition by increasing reaction temperature for iron-based FTS catalysts have also been proved by previous reports [41]. Especially, as reaction temperature is higher than 280 °C, graphitic carbon is mainly deposited [42]. The Raman spectroscopy of used FeZnNa catalyst (Fig. S5, Supporting information) also evidenced that the deposition of graphitic carbon occurred on the catalyst surface. Thus, the decrease in CO conversion when the temperature exceeded 330 °C was likely caused by partial coverage of active sites by carbon deposition. The carbon deposition might also take place at downflow of Naß zeolite layer and consequently weaken the cracking reaction. Thereby, further increasing the temperature to 340 °C, slightly increased the C_5^+ selectivity and decreased the C_{2-4}^- selectivity.

As shown in Fig. 8, at 330 °C, as the reaction pressure was increased, the conversion of CO advanced, whereas the selectivity of $C_{2.4}^{=}$ had a volcano-type variation tendency and reached the optimal value at 2 MPa. On increasing the reaction pressure, the collision probability and contact time of reactant species with the catalyst surface were enhanced [43], and the CO conversion was improved. The increased contact time of the hydrocarbons, which flowed from the upper bed of the FeZnNa layer, with the Na β packed lower bed improved the hydrocracking reaction. Therefore, the selectivity towards CH₄ and C_{2.4}⁼



Fig. 8. Influences of reaction pressure on catalytic performance of FeZnNa/Na β with a mass ratio of 1:1.

increased as the pressure was increased from 1 to 2 MPa; however, further increasing the pressure decreased the $C_{2.4}^{=}$ selectivity and caused a high selectivity for CH₄, owing to over-cracking.

The results in Fig. 9 clearly show that the CO conversion was slightly decreased by increasing the GHSV. The selectivity of $C_{2.4}^{=}$ also showed a volcano-type change in terms of the reaction GHSV. The highest value was obtained at 2400 h⁻¹. As the space velocity increased, the residence time of reactants in both the upper bed of FeZnNa and lower bed of Na β was reduced. These effects decreased CO conversion with increasing GHSV. When the GHSV was increased from 1200 to 2400 h⁻¹, the formation of light hydrocarbons by the FTS reaction in the upper bed was enhanced because of the shorter residence time for reactants [44]. The enhanced formation of light hydrocarbons in the upflow, combined with hydrocracking in the Na β downflow, increased C_{2.4}⁼. However, on further increasing GHSV, the cracking effect for the downflow of Na β weakened as the residence time was further decreased and the selectivity declined towards C_{2.4}⁼.

Furthermore, the ratio of H₂/CO for the feed gases also changed the catalytic behaviors of the FeZnNa/Na β dual-bed catalyst. As shown in Fig. 10, the CO conversion and CH₄ selectivity increased, and the selectivity of C₅⁺ decreased as the ratio of H₂/CO increased. In contrast, the selectivity towards C₂₋₄⁼ changed following a parabolic path and achieved the optimal value at the H₂/CO ratio of 1:1. The low H₂/CO ratio caused a scarcity of H species and excess of C species at the surface of the dual-bed catalyst, which resulted in low CO conversion and high C₅⁺ selectivity [39,40]. When the H₂/CO ratio increased, the amounts



Fig. 9. Influences of GHSV on catalytic performance of FeZnNa/Na β with a mass ratio of 1:1.



Fig. 10. Influences of H_2/CO ratio on catalytic performance of FeZnNa/Naß with a mass ratio of 1:1.

of surface H species also increased and more light hydrocarbons formed at the upflow of FeZnNa. Hydrocracking of the downflow of Na β was also strengthened. Thus, the CO conversion and selectivity of C₂₋₄⁼ and CH₄ increased, whereas the C₅⁺ selectivity declined. However, further increasing the H₂/CO ratio generated an excess of surface H species leading to over-hydrocracking for Na β bed, which decreased selectivity for C₂₋₄⁼ and further increased the CH₄ selectivity.

We also further investigated the long-term stability of the dual-bed catalyst with FeZnNa/Na β mass ratio of 1:1 under the optimized reaction conditions: 330 °C, 2.0 MPa, 2400 h^{-1} and a H_2/CO ratio of 1. As shown in Fig. 11, the CO conversion increased almost linearly during the initial 20 h, owing to the induction period required for FeZnNa to form enough FeC_x for the FTS reaction. After 20 h, the conversion of CO decreased and was maintained at approximately 80 % after 100 h reaction. For this dual-bed configuration of FeZnNa/Naß, the decrease of the CO conversion might have been caused by deactivation of the first FeZnNa bed or the second Naß zeolite bed. To determine the deactivation of the dual-bed FeZnNa/Naß catalyst, we further tested the longterm stability of the first FeZnNa bed (Fig. S7 in the Supporting information). As shown in Fig. S7, a similar decrease of CO conversion was observed for the single-bed FeZnNa catalyst; thus, deactivation of FeZnNa was mainly responsible for the decline of CO conversion for the dual-bed FeZnNa/Naß catalyst. Iron carbides are normally considered to be the active phase of FTS reaction for iron-based catalysts [45]. A decrease of iron carbide causes deactivation of iron-based FTS catalysts [46,47]. However, the amount of iron carbide increased as the reaction time was prolonged, as confirmed by Mössbauer spectroscopy



Fig. 11. Stability test for FTO over FeZnNa/Na β with a mass ratio of 1:1.

measurements. The FeZnNa catalyst also had good mechanical stability and the spent FeZnNa catalyst was undamaged (as indicated by the picture of spent catalyst, Fig. S6, Supporting information). The Raman spectroscopy results for the spent FeZnNa catalyst (Fig. S5, Supporting information) suggested that carbon deposition was detected for the spent catalyst. Therefore, the decrease of CO conversion after 100 h might be caused by carbon deposition over the FeZnNa catalyst surface. Nevertheless, the selectivity towards $C_{2.4}^{=}$ and CH₄ were sustained at 46.1 % and 9.0 %, respectively, which indicates a potential for industrial applications.

4. Conclusions

In summary, we have succeeded in constructing a dual-bed FTO catalyst denoted FeZnNa/Na β , which had high C₂₋₄⁼ selectivity and excellent long-term stability. Under the optimized reaction conditions: i.e., a FeZnNa/Na β mass ratio of 1:1, 2.0 MPa, H₂/CO = 1/1, 2400 h⁻¹, and 330 °C, the FeZnNa/Na β gave a selectivity as high as 50.5 % C₂₋₄⁼ and CO conversion up to 92.9 %. The system also exhibited outstanding long-term stability and ran stably for 100 h without significant deactivation. The suitable acidity and hierarchical pore structure of Na β were mainly responsible for the excellent FTO performance of FeZnNa/Na β .

CRediT authorship contribution statement

Yifeng Hou: Data curation, Investigation. Jifan Li: Data curation, Supervision, Writing - original draft, Writing - review & editing. Ming Qing: . Chun-Ling Liu: Writing - review & editing. Wen-Sheng Dong: Supervision, Writing - review & editing.

Declaration of Competing Interest

We declare that we have no conflicts of interest to this work. We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2020.110824.

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