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Design of efficient bifunctional catalysts for direct conversion of syngas into lower olefins via methanol/dimethyl ether intermediates†

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The direct conversion of syngas into lower olefins is a highly attractive route for the synthesis of lower olefins. The selectivity of lower olefins *via* the conventional Fischer–Tropsch (FT) synthesis is restricted to ~60% with high CH₄ selectivity due to the limitation by the Anderson–Schulz–Flory (ASF) distribution. Here, we report the design of bifunctional catalysts for the direct conversion of syngas into lower olefins with selectivity significantly breaking the ASF distribution. The selectivity of C₂–C₄ olefins reached 87% at a CO conversion of 10% and was sustained at 77% by increasing CO conversion to 29% over a bifunctional catalyst composed of Zn-doped ZrO₂ nanoparticles and zeolite SSZ-13 nanocrystals. The selectivity of CH₄ was lower than 3% at the same time. It is demonstrated that the molar ratio of Zn/Zr, the density of Brønsted acid sites of SSZ-13 and the proximity of the two components play crucial roles in determining CO conversion and lower-olefin selectivity. Our kinetic studies indicate that methanol and dimethyl ether (DME) are key reaction intermediates, and the conversion of syngas to methanol/DME is the rate-determining step over the bifunctional catalyst. Formate and methoxide species have been observed on Zn-doped ZrO₂ surfaces during the activation of CO in H₂, and the formed methanol/DME are transformed into lower olefins in SSZ-13.

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Introduction

Lower olefins (C₂–C₄ olefins), which are key building blocks for the manufacture of plastics, cosmetics and pharmaceuticals, are produced by cracking of petroleum-based naphtha in the current chemical industry.¹ The growing demand for lower olefins has motivated a lot of recent research activities for synthesis of lower olefins from alternative carbon resources such as natural gas or shale gas, coal and renewable biomass *via* synthesis gas (syngas, CO/H₂).^{2–4} Carbon dioxide can also be used as a renewable source of syngas.⁵

Fischer–Tropsch (FT) synthesis is a classic route for the conversion of syngas to hydrocarbons.^{6,7} Many studies have been devoted to synthesizing lower olefins from syngas *via* the FT route on Fe-based or Co₂C-based catalyst.^{2,4,7–14} However, the

selectivity of C₂–C₄ olefins can hardly exceed 60% due to the limitation by the FT reaction mechanism. Generally, FT synthesis proceeds *via* the dissociation of CO, formation of surface CH_x species (x = 1–3), coupling of CH_x species to C_nH_m intermediates and the hydrogenation or dehydrogenation of C_nH_m intermediates to paraffin or olefin products (Fig. 1a).^{15–17} The coupling of CH_x species is uncontrollable on surfaces of Fe- or Co-based catalysts, and the hydrocarbon products usually

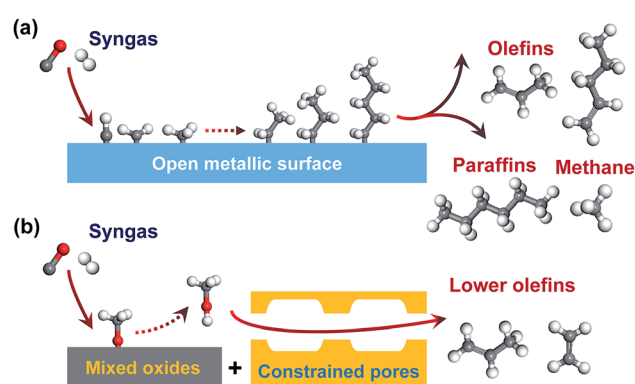


Fig. 1 Illustration of two types of direct conversion of syngas into lower olefins. (a) FT-synthesis route on a Fe-based catalyst. (b) SMO (syngas *via* methanol intermediate to olefin) route on one bifunctional catalyst.

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follow a statistical distribution known as the Anderson–Schulz–Flory (ASF) distribution.¹⁸ The maximum selectivity of C₂–C₄ hydrocarbons (including paraffins and olefins) is 58% according to the ideal ASF distribution.¹⁹

The conversion of syngas into lower olefins involves a series of elementary steps (at least including CO activation and C–C coupling), and thus cannot be precisely controlled by using one kind of active sites as in FT synthesis. Thus, we have recently proposed a new reaction-coupling strategy for selectivity control in syngas conversion.²⁰ The idea is to separate CO activation and C–C coupling on different active sites, which are integrated into one bifunctional catalyst. The reaction coupling may enable a better control of each step, in particular the C–C coupling by choosing an active component capable of performing selective C–C coupling. C₂–C₄ olefins can be produced from syngas *via* two consecutive processes, *i.e.*, syngas to methanol (methanol synthesis) and methanol to olefins (MTO). As compared to the two-process route, a single-process using reaction coupling, which we define as the SMO process (Fig. 1b), *i.e.*, the conversion of syngas *via* methanol intermediate into olefins, would be more energy- and cost-efficient. The product selectivity can be tuned by the shape selectivity of molecular sieves. Zeolites with chabasite (CHA) topology are known to be suitable for the selective formation of C₂–C₄ olefins.^{21,22}

Actually, some early papers reported the conversion of syngas to hydrocarbons using mixed catalysts composed of a methanol-synthesis component (*e.g.*, Pd/SiO₂ or Cu–Zn oxide) and a zeolite, but the major products were C₂–C₄ paraffins.^{23–25} The formation of aromatics was also observed in a few early studies,²⁶ and the selectivity of aromatics could be significantly enhanced recently through further improving the bifunctional catalyst.^{27,28} However, almost no C₂–C₄ olefins were formed in the early work.^{23–26} It is likely that C₂–C₄ olefins can easily undergo hydrogenation over the mixed catalysts, and thus the selective formation of C₂–C₄ olefins is a big challenge.

Recently, Jiao *et al.* reported an OX-ZEO process, *i.e.*, the use of a composite catalyst containing a mixed metal oxide (ZnCrO_x) and zeolite (MSAPO), for the direct conversion of syngas into lower olefins.³ The selectivity of C₂–C₄ olefins reached ~80% at a CO conversion of 17% at 673 K under 2.5 MPa of syngas with a H₂/CO ratio of 1.5. They excluded the possibility of methanol as a reaction intermediate and proposed that C₂–C₄ olefins were formed from syngas *via* a ketene (CH₂CO) intermediate.³ At the same time, we communicated that a bifunctional catalyst composed of ZrO₂–ZnO binary oxide and SAPO-34 could catalyse the conversion of syngas to lower olefins with a selectivity of 74% at 11% CO conversion at 673 K under 1.0 MPa of syngas with a H₂/CO ratio of 2.²⁹ The selectivity of C₂–C₄ olefins significantly breaks the upper limit of 60% for the conventional FT catalyst. These two pieces of work open a new avenue for the highly selective conversion of syngas beyond the classic FT process. However, the chemistry of this new process, in particular the reaction mechanism, is still unclear.

Here, we report our recent attempt to clarify the key factors that influence the catalytic behaviours of the bifunctional system. We adopt SSZ-13, an aluminosilicate zeolite with the same CHA-topology as SAPO-34, as the active component for the

selective coupling of the intermediate to form C₂–C₄ olefins. Similar to SAPO-34, SSZ-13 is an efficient catalyst for the MTO reaction.^{30,31} Furthermore, SSZ-13 has attracted much attention as a commercial catalyst for the selective catalytic reduction of NO_x with NH₃ because of its high structural stability.³² In this work, we first utilize H–SSZ-13 in combination with metal oxides for the direct conversion of syngas into C₂–C₄ olefins. The present work also aims to provide insights into reaction mechanism. The reaction kinetics, reaction intermediates and possible routes for the formation of products (including lower olefins and major by-products) will also be discussed.

Results and discussion

Active components matching with each other for direct conversion of syngas to lower olefins

The use of one bifunctional catalyst to integrate the two reactions in tandem, *i.e.*, syngas to methanol and subsequent MTO is quite challenging. The two reactions typically occur under different reaction conditions; methanol synthesis is operated at temperatures <573 K due to the thermodynamic requirement (Fig. S1a, ESI[†]), whereas the MTO reaction needs higher temperatures (typically 673–723 K) because of the high activation energy for C–C coupling and the removal of coke deposition.³³ The continuous removal of methanol from methanol-synthesis catalyst by the tandem MTO reaction can overcome the thermodynamic limitation based on Le Chatelier's principle (Fig. S1b, ESI[†]).^{29,34} The equilibrium conversion of CO into lower olefins (C₂H₄ as an example) is ~80% at 673 K and a syngas pressure of 3 MPa (Fig. S1b, ESI[†]). Thus, the catalyst being capable of selectively producing methanol at ~673 K should be developed. We clarified that methane became a dominant product at 673 K over Cu–Zn–Al oxide, a typical methanol-synthesis catalyst (Fig. S2a, ESI[†]). Moreover, due to the strong hydrogenation ability of Cu–Zn–Al catalyst, the formed C₂–C₄ olefins were easy to be transformed to C₂–C₄ paraffins by hydrogenation. Almost no C₂–C₄ olefins were obtained on the bifunctional Cu–Zn–Al/SSZ-13–45H catalyst, which composed of Cu–Zn–Al oxide and H–Na–SSZ-13 with a 45% H⁺-exchanging degree (denoted as SSZ-13–45H) (Fig. S2b, ESI[†]). Here, SSZ-13–45H was used as the typical component for C–C coupling in the present work. As already mentioned, many studies by integrating a Cu- or Pd-based methanol-synthesis catalyst with a zeolite only led to the formation of saturated C₂–C₄ paraffins or gasoline-range hydrocarbons from syngas.^{23–26,35–37} Therefore, the development of a high-temperature methanol-synthesis catalyst with proper hydrogenation ability is the key to matching the MTO reaction for the synthesis of C₂–C₄ olefins.

We discovered a Zn-doped ZrO₂ (denoted as Zn–ZrO₂) catalyst, which showed high selectivity of methanol and dimethyl ether (DME), a dehydrative product from methanol, from syngas in a wide-temperature range (Fig. 2a). The bifunctional catalyst composed of Zn–ZrO₂ and SSZ-13–45H provided CH₃OH/DME as the major products at <600 K (Fig. 2b), confirming that the zeolite-catalysed C–C coupling of CH₃OH/DME can only take place at higher temperatures. The selectivity of C₂–C₄ olefins increased at the expense of that of CH₃OH/DME





Fig. 2 Catalytic behaviours of Zn-ZrO₂ and Zn-ZrO₂/SSZ-13-45H catalysts for the conversion of syngas at different temperatures. (a) Zn-ZrO₂ (Zn/Zr = 1 : 16). (b) Zn-ZrO₂/SSZ-13-45H. (c) CO₂ selectivity. Reaction conditions: $W(\text{Zn-ZrO}_2) = 0.20$ g; $W(\text{Zn-ZrO}_2/\text{SSZ-13-45H}) = 0.60$ g; $\text{H}_2/\text{CO} = 2$; $P = 3$ MPa; $F = 30$ mL min⁻¹; time on stream, 10 h.

upon increasing the reaction temperature. At the same time, the conversion of CO also increased significantly, becoming much higher than that on the Zn-ZrO₂ catalyst at the corresponding temperature. These observations indicate the transformation of CH₃OH/DME into C₂-C₄ olefins over the SSZ-13 component, which thermodynamically drives the conversion of syngas. The C₂-C₄ olefin selectivity and the CO conversion increased to 75% and 23%, respectively, by increasing the reaction temperature to 673 K (Fig. 2b). A further increase in temperature decreased the selectivity of C₂-C₄ olefins and increased that of C₂-C₄ paraffins due to the hydrogenation of lower olefins.

CO₂ was also formed over both Zn-ZrO₂ and Zn-ZrO₂/SSZ-13-45H catalysts. The selectivity of CO₂ was calculated separately from the hydrogenation of CO and the values depended

on reaction temperature (Fig. 2c). The selectivity of CO₂ was slightly higher over the Zn-ZrO₂/SSZ-13-45H catalyst than over the Zn-ZrO₂, but the degree of difference of CO₂ selectivity between the two catalysts was much lower than that of CO conversion.

Key factors controlling the catalytic behaviour of bifunctional catalysts

Effect of composition of Zn-doped ZrO₂. We found that the ZrO₂/SSZ-13-45H catalyst without Zn showed a high selectivity of C₂-C₄ olefins (~80%), but the conversion of CO was very low (Fig. 3). The incorporation of a small amount of Zn (Zn/Zr = 1 : 64) could increase the conversion of CO from 3.9% to 17% without a significant change in the selectivity of C₂-C₄ olefins. The selectivity of C₂-C₄ olefins could keep at 75% with an increase in CO conversion to 23% by raising the Zn/Zr ratio to 1 : 16. A further increase in the ratio of Zn/Zr to $\geq 1 : 4$ considerably decreased the selectivity of C₂-C₄ olefins and increased that of C₂-C₄ paraffins, indicating that the hydrogenation of lower olefins became significant on catalysts with Zn/Zr ratios $\geq 1 : 4$. When the Zn/Zr ratio exceeded 1 : 1, CO conversion also decreased. Thus, the control of Zn/Zr ratio is crucial to both CO conversion activity and product selectivity.

We have performed characterizations to gain insights into the effect of Zn/Zr ratio on structures of Zn-ZrO₂ particles. The X-ray diffraction (XRD) measurements showed that ZrO₂ particles were mainly in the tetragonal crystalline phase with an average size of 6.0 nm (Fig. S3 and Table S1, ESI†). The addition of Zn did not change the crystal structure of ZrO₂ and no diffraction peaks belonging to ZnO were observed from XRD at Zn/Zr ratio of $\leq 1 : 16$. Thus, such a small amount of ZnO may be incorporated into ZrO₂ matrices, forming a solid solution, or may exist as small ZnO clusters on ZrO₂. The formation of ZnO-ZrO₂ solid solution was recently reported.³⁸ At a higher Zn/Zr

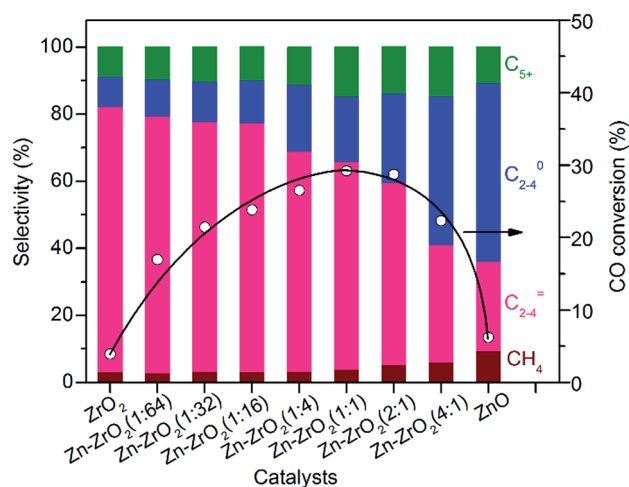


Fig. 3 Effect of Zn/Zr molar ratio on catalytic behaviours of the bifunctional Zn-ZrO₂/H-SSZ-13-45H catalyst. The selectivity of CO₂ did not change with the ratio of Zn/Zr and was in the range of 41–45% for each catalyst. Reaction conditions: catalyst, 0.60 g; $\text{H}_2/\text{CO} = 2$; $P = 3$ MPa; $T = 673$ K; $F = 30$ mL min⁻¹; time on stream, 10 h.



ratio ($\geq 1:4$), diffraction peaks ascribed to hexagonal ZnO became observable (Fig. S3, ESI†). The size of ZrO₂ crystallites estimated by the Scherrer equation from XRD patterns did not change significantly with Zn addition (Table S1, ESI†). The transmission electron microscopy (TEM) measurements showed that the addition of Zn increased the mean size of Zn-ZrO₂ particles (Fig. S4, ESI†). In particular, as the Zn/Zr $\geq 4:1$, the mean size of Zn-ZrO₂ particles increased steeply and the size distribution became significantly wide (Fig. S4 and Table S1, ESI†), possibly because of the segregation of large ZnO particles.

Effect of acidity of the zeolite component. To understand the effect of acidity of zeolite SSZ-13 on the catalytic behaviours of the bifunctional catalysts for syngas conversion, we have systematically tuned the density of Brønsted acid sites simply by changing the H⁺-exchanging degree. The acidity can be characterized by the NH₃ temperature-programmed desorption (NH₃-TPD) technique. Fig. 4a shows that the intensity of the high-temperature NH₃ desorption peak changes systematically with the H⁺-exchanging degree. The high-temperature peak arises from strong acid sites, which may be considered as the

Brønsted acid sites in zeolites.³⁹ The density of strong acid sites evaluated from the intensity of the high-temperature peak increased almost linearly with the H⁺-exchanging degree (Table S2, ESI†). We also measured the acidity by the Fourier-transform infrared (FT-IR) spectroscopy of adsorbed NH₃, a small alkaline molecule suitable for probing the acid site in CHA zeolite with small pore windows. Three IR bands at 1633, 1455 and 1405 cm⁻¹ were observed (Fig. 4b). The former IR band can be ascribed to the coordination of NH₃ with Na⁺, while the latter two splitting bands are assignable to the Brønsted acid sites (protonated NH₄⁺).^{40,41} The density of Brønsted acid sites evaluated by quantifying the NH₃-adsorbed FT-IR peaks at 1455 and 1405 cm⁻¹ was similar to that from the NH₃-TPD measurements (Table S2, ESI†). This confirms that the high-temperature peak in NH₃-TPD profiles corresponds to the Brønsted acid sites.

The bifunctional catalysts containing Zn-ZrO₂ with a Zn/Zr ratio of 1:16 and SSZ-13 with different densities of Brønsted acid sites were investigated for the conversion of syngas. The CO conversion increased significantly from 5% to ~25% with the density of Brønsted acid sites (Fig. 5a). The Brønsted acid site is known to catalyse the MTO reaction but is not responsible for CO activation. Thus, the significant increase in CO conversion should stem from the thermodynamic driving force because of the rapid removal of methanol/DME to form lower olefins by the Brønsted acid sites. This was confirmed by the change in product selectivity. CH₃OH and DME were formed as the major



Fig. 4 Characterization of acidity of SSZ-13 with different H⁺-exchanging degrees. (a) NH₃-TPD profiles. (b) NH₃-adsorbed FT-IR spectra. The number in the parentheses after each sample denotes the H⁺-exchanging degree.

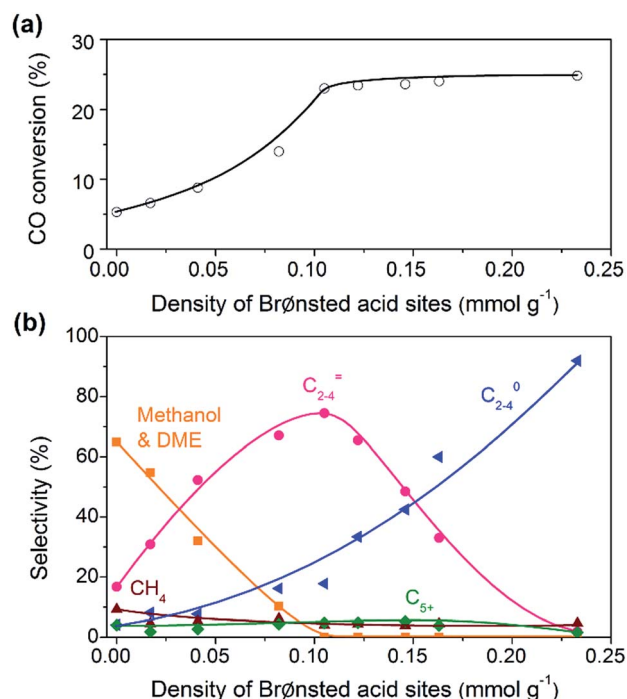


Fig. 5 Effect of density of Brønsted acid sites on catalytic behaviours of the bifunctional Zn-ZrO₂/SSZ-13 catalyst. (a) CO conversion. (b) Product selectivity. The selectivity of CO₂ did not change with the density of Brønsted acid sites and was in the range of 41–45%. Reaction conditions: catalyst, 0.60 g; H₂/CO = 2; P = 3 MPa; T = 673 K; F = 30 mL min⁻¹; time on stream, 10 h.



products over the bifunctional catalyst with a lower density of Brønsted acid sites (Fig. 5b). The increase in the density of Brønsted acid sites decreased the selectivity of CH₃OH/DME and increased that of lower olefins. The selectivity of C₂–C₄ olefins reached 75% when the density of Brønsted acid sites rose to 0.10 mmol g⁻¹. However, a further increase in the density of Brønsted acid sites rather decreased the selectivity of C₂–C₄ olefins and increased that of C₂–C₄ paraffins. Thus, there is an optimum density of Brønsted acid sites for the selective formation of lower olefins. These results clearly demonstrate that the Brønsted acidity is a key factor in determining not only the conversion of CO but also the selectivity of lower olefins.

Effect of proximity of the two components. We investigated the effect of the proximity of Zn–ZrO₂ (Zn/Zr = 1 : 16) and SSZ-13 in the bifunctional catalyst on catalytic behaviours. The separation of Zn–ZrO₂ and SSZ-13 by quartz wool in one reactor, *i.e.*, the dual-bed model, led to not only low activity but also decreased selectivity of C₂–C₄ olefins (Fig. 6a). We believe that the low CO conversion is due to the lack of the thermodynamic driving force when the zeolite SSZ-13 is far from the Zn–ZrO₂ or the two components are separated in such a millimetre distance. The high selectivity of CH₄ and C₂–C₄ paraffins probably results from the repeated contact of products with Zn–ZrO₂ in the first bed and SSZ-13 in the second bed, leading to deep hydrogenation and the formation of saturated products instead of lower olefins. The saturated lower paraffins could not be converted on the subsequent zeolite catalyst. The use of

mixture of Zn–ZrO₂ granules and SSZ-13 granules with sizes 250–600 μm increases the proximity of the two components to micrometre scale, resulting in significant increases in both CO conversion and C₂–C₄ olefin selectivity (Fig. 6b). The grinding of micrometre-sized SSZ-13 crystallites (Fig. S5, ESI†) with Zn–ZrO₂ powders with a mean particle size of 8.9 nm together, which was typically used in our work, caused the formation of Zn–ZrO₂ nanoparticles dispersed on micrometre-sized SSZ-13 crystallites, and this further increased the conversion of CO and the selectivity of C₂–C₄ olefins (Fig. 6c). To further increase the proximity of the two components, we have synthesized SSZ-13 with a mean size of 230 nm (Fig. S6, ESI†) and Zn–ZrO₂ nanoparticles with a smaller mean size of 4.8 nm by an alcogel method (Fig. S7, ESI†). The grinding of nano-sized SSZ-13 crystallites with powders of Zn–ZrO₂ nanoparticles with mean sizes of 8.9 nm and 4.8 nm further increased the proximity between the two components into nano-scale (Fig. S8, ESI,† 6d and e). The results in Fig. 6 display that the closer proximity between the two components results in higher CO conversion and higher C₂–C₄ olefin selectivity.

We obtained a CO conversion of 29% and a lower-olefin selectivity of 77% over the bifunctional catalyst containing Zn–ZrO₂ nanoparticles with a mean size of 4.8 nm finely dispersed on nano-sized SSZ-13, denoted as Zn–ZrO₂ (4.8 nm)/nano-SSZ-13. This combination of CO conversion and C₂–C₄ olefin selectivity is much better than that reported for our previous catalyst.²⁹ The selectivity of C₂–C₄ olefins was 71% at 22% CO conversion over the ZnCrO_x/MSAPO catalyst at H₂/CO ratio of 2 and 673 K reported by Jiao *et al.*³ A recently reported MnO/MSAPO catalyst showed a C₂–C₄ olefin selectivity of 79% at CO conversion of 10.1% at 673 K and the increase in CO conversion to 15.4% decreased the C₂–C₄ olefin selectivity to 68.9%.⁴² Thus, our present catalyst is outstanding for the direct conversion of syngas into lower olefins. The major by-products in hydrocarbons were C₂–C₄ paraffins and the selectivity of C₂–C₄ paraffins was 18% over our catalyst. We further displayed the detailed selectivities of C₂, C₃ and C₄ olefins and paraffins in Fig. 7a. It becomes clear that propylene with a selectivity of 49% is the most abundant olefin in the product, followed by ethylene (19%) and butenes (8.3%). Among C₂–C₄ paraffins, the selectivity of propane is the highest. The ratios of olefin to paraffin for C₂, C₃ and C₄ hydrocarbons are 3.9, 4.4 and 3.3, respectively. This catalyst was also quite stable during a long-term reaction (Fig. 7b). The CO conversion and C₂–C₄ olefin selectivity were sustained at 25% and 75% after 160 h of reaction. The selectivity of undesired CH₄ was around 3%. The changes in the selectivities of C₂, C₃ and C₄ olefins were also insignificant after 160 h of reaction.

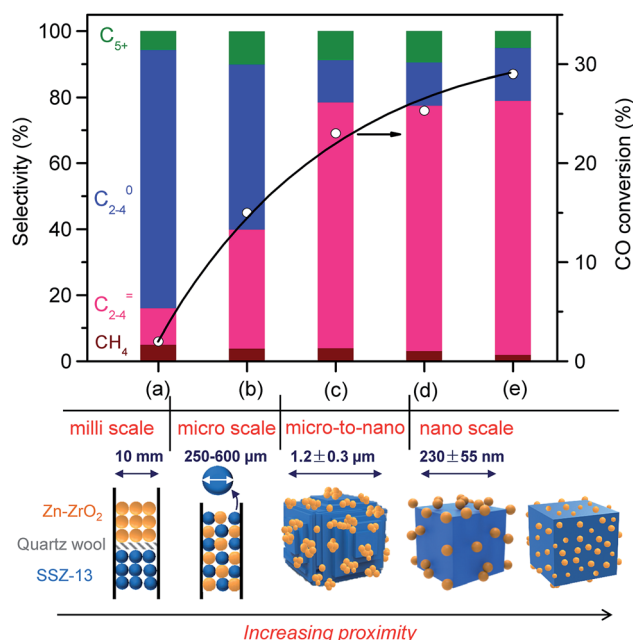


Fig. 6 Effect of proximity of Zn-doped ZrO₂ and SSZ-13 on catalytic behaviours of the bifunctional catalyst. (a) Dual bed (0.20 g Zn–ZrO₂ + 0.40 g SSZ-13–45H); (b) mixing of granules of two components with sizes of 250–600 μm; (c) Zn–ZrO₂ (8.9 nm)/micro-SSZ-13–45H; (d) Zn–ZrO₂ (8.9 nm)/nano-SSZ-13; (e) Zn–ZrO₂ (4.8 nm)/nano-SSZ-13. The selectivity of CO₂ was in the range of 41–45% for each type of proximity. Reaction conditions: catalyst, 0.60 g; H₂/CO = 2; P = 3 MPa; T = 673 K; F = 30 mL min⁻¹; time on stream, 10 h.

Structure–property relationship

The understanding of the roles of ZrO₂ and ZnO in the bifunctional catalyst is crucial to future catalyst design for the conversion of syngas into lower olefins. ZrO₂ is known to be capable of chemisorbing and activating CO.⁴³ However, the activity of the bifunctional catalyst containing ZrO₂ and SSZ-13 was very low (Fig. 3) probably due to its low capability of



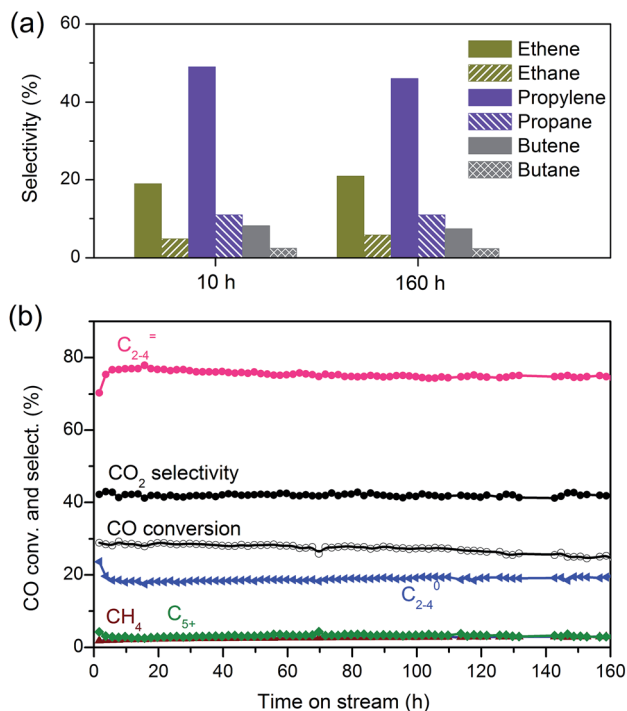


Fig. 7 (a) Selectivities of C₂, C₃ and C₄ olefins and paraffins over Zn-ZrO₂ (4.8 nm)/nano-SSZ-13. (b) Stability of Zn-ZrO₂ (4.8 nm)/nano-SSZ-13 catalyst. Reaction conditions: catalyst, 0.60 g; H₂/CO = 2; P = 3 MPa; T = 673 K; F = 30 mL min⁻¹.

activating H₂. An early report showed that the presence of Cu on ZrO₂ could help H₂ activation and enhance methanol synthesis.⁴⁴ Nevertheless, the presence of Cu would accelerate the hydrogenation of lower olefins more significantly, leading to lower paraffins as the predominant products as in the case of Cu-Zn-Al oxide catalyst (Fig. S2, ESI†). One of our most important discoveries is that ZnO is an efficient component for the activation of H₂, offering hydrogen species for the selective hydrogenation of CO with lower olefins surviving. The addition of small amount of Zn could significantly enhance CO conversion while keeping the high selectivity of lower olefins. It is well known that H₂ can be activated *via* heterolytic dissociation on ZnO.⁴⁵ The hydrogen species thus formed may be different from those formed *via* homolytic dissociation of H₂ on metallic surfaces. Our result further suggests that the catalyst with -Zn-O- domains incorporated into ZrO₂ lattice or with small ZnO clusters shows higher selectivity of lower olefins, whereas considerable paraffins are formed on catalysts containing larger ZnO particles. Therefore, the unique hydrogenation ability of heterolytically dissociated hydrogen species and their controlled surface concentration are the key to keeping lower olefins from hydrogenation.

The CHA topology of zeolite in the bifunctional catalyst is certainly an important factor for selective formation of lower olefins. Our result reveals that the present SSZ-13 is more selective toward the formation of propylene (Fig. 7a), possibly because the size of pore windows of SSZ-13 matches better with that of propylene molecule. In addition to the topology, the

Brønsted acidity is a key parameter. The Brønsted acid site catalyses the C-C coupling, transforming intermediates coming from Zn-ZrO₂ nanoparticles into lower olefins. Although the Brønsted acid site does not directly participate in CO activation, CO conversion can be significantly enhanced by increasing the density of Brønsted acid sites because of the thermodynamic driving force. The product selectivity also depends on the density of Brønsted acid sites; there is an optimum density for the selective formation of lower olefins. Methanol and DME are the major products at a lower density of Brønsted acid sites, while the higher density of Brønsted acid sites results in considerable formation of paraffins. Although zeolites are not typical hydrogenation catalysts, the hydrogenation of olefins on transition-metal-free zeolites has been reported in a few early papers.⁴⁶ The catalytic functions of Brønsted acid sites in zeolites for the dissociation of H₂ and the hydrogenation of olefins have also been studied both experimentally and theoretically.^{47,48}

How the proximity of the two functional sites affects the catalytic behaviour is a key issue for bifunctional catalysis but has not been well explored so far. A recent study uncovered that the too closer intimacy of Pt nanoparticles and the Brønsted acid sites in HY zeolite was detrimental to the selectivity of hydrocracking products.⁴⁹ Our present study suggests that the closer proximity favours CO conversion and C₂-C₄ olefin selectivity. We propose that the closer proximity can enable a faster transfer of reaction intermediates formed on Zn-ZrO₂ nanoparticles to SSZ-13, and thus is beneficial to the selective formation of lower olefins.

Kinetic studies

Activation energy. As shown in Fig. 2, CO conversion activities depended on the reaction temperature over both Zn-ZrO₂ and Zn-ZrO₂/SSZ-13-45H catalysts. The saturation of CO conversion at >673 K on Zn-ZrO₂ is probably due to the thermodynamic limitation. We calculated the apparent activation energy for CO conversion on Zn-ZrO₂ at ≤673 K, where methanol and DME were the major products, using the plot of logarithm of CO conversion rate against the reciprocal of temperature (Fig. S9, ESI†). The value is 72 ± 5 kJ mol⁻¹. CO conversion increased significantly even at >673 K on the ZrO₂/SSZ-13-45H catalyst owing to the thermodynamic driving force. The activation energy for CO conversion on this bifunctional catalyst was calculated to be 71 ± 5 kJ mol⁻¹, almost identical to that on Zn-ZrO₂ catalyst. This suggests that the rate-determining step for the conversion of syngas to lower olefins over the Zn-ZrO₂/SSZ-13-45H catalyst is the same as that for methanol synthesis over the Zn-ZrO₂ catalyst.

Effect of contact time. To gain further information about the reaction pathways, we have investigated the dependence of catalytic performance on the contact time, which is expressed as the ratio of catalyst weight to total flow rate (*W/F*), at 673 K. CO conversions increased almost linearly with contact time over the Zn-ZrO₂ and Zn-ZrO₂/SSZ-13 (Zn/Zr = 1 : 16) catalysts (Fig. 8). This indicates that the reaction proceeds steadily over both catalysts. CH₃OH and DME were formed as main products over



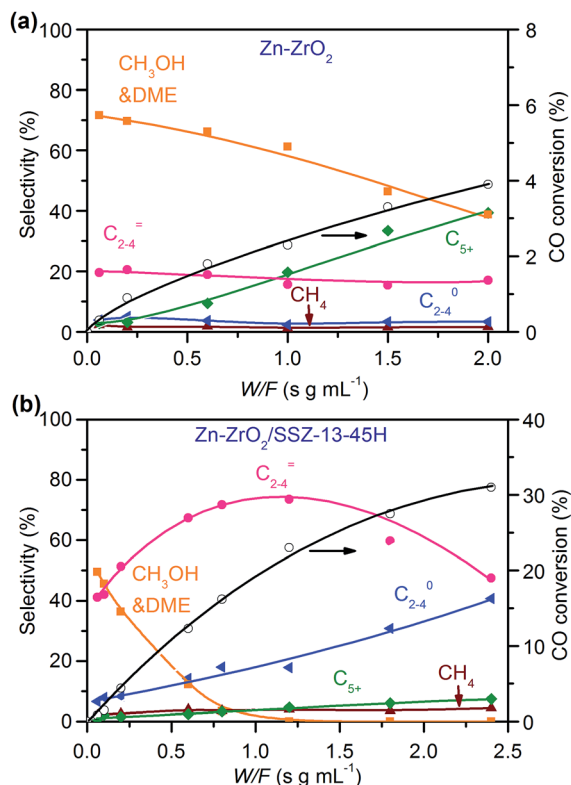


Fig. 8 Effect of contact time on catalytic behaviours of Zn-ZrO₂ and Zn-ZrO₂/SSZ-13-45H catalysts. Reaction conditions: $W(\text{Zn-ZrO}_2) = 0.030\text{--}1.0$ g; $W(\text{Zn-ZrO}_2/\text{SSZ-13-45H}) = 0.030\text{--}1.2$ g; $\text{H}_2/\text{CO} = 2/1$; $P = 3$ MPa; $T = 673$ K; $F = 30$ mL min⁻¹; time on stream, 10 h.

the Zn-ZrO₂ catalyst, and the total selectivity of methanol and DME exceeded 70% at shorter contact times. The prolonging of contact time decreased the selectivity of CH₃OH/DME and increased that of C₅₊ hydrocarbons (Fig. 8a). The formation of C₅₊ hydrocarbons at longer contact times may be catalysed by the acid sites on mixed oxides.⁵⁰ CH₃OH and DME were also formed as the major products over the Zn-ZrO₂/SSZ-13-45H catalyst at shorter contact time (Fig. 8b). The increase in contact time significantly increased the selectivity of C₂-C₄ olefins at expense of that of CH₃OH/DME. When the contact time exceeded 1.2 s g mL⁻¹, the selectivity of C₂-C₄ olefins decreased and that of C₂-C₄ paraffins increased more significantly due to the hydrogenation of olefins. These results are in agreement with those obtained by changing reaction temperature (Fig. 2b) and the density of Brønsted acid sites (Fig. 5b), providing further evidence that CH₃OH and DME are the reaction intermediates on our bifunctional catalyst. The major reaction pathways for the conversion of CO on the bifunctional catalyst can be expressed as:



Effect of syngas pressure. Fig. 9 shows the effect of total pressure of syngas on catalytic behaviours of the Zn-ZrO₂/SSZ-



Fig. 9 Effect of total pressure of syngas on catalytic behaviours of Zn-ZrO₂/SSZ-13-45H catalyst. Reaction conditions: catalyst, 0.60 g; $\text{H}_2/\text{CO} = 2/1$; $T = 673$ K; $F = 30$ mL min⁻¹; time on stream, 10 h.

13 catalyst at 673 K and a H₂/CO ratio of 2. At a syngas pressure of 1 MPa, the conversion of CO was 10% and the selectivity of C₂-C₄ olefins was 87% with a ratio of C₂-C₄ olefins/C₂-C₄ paraffins of 9.4. To the best of our knowledge, this is the highest C₂-C₄ olefin selectivity reported to date for the conversion of syngas. Upon increasing the pressure of syngas, the conversion of CO increased significantly but the selectivity of C₂-C₄ olefins decreased. The selectivity of C₂-C₄ paraffins increased at the same time, indicating the increase in the hydrogenation ability at a higher pressure of syngas. The selectivities of minor products, *i.e.*, CH₄ and C₅₊ hydrocarbons, also increased with an increase in the total pressure of syngas. Thus, there exists an optimum total pressure for the conversion of syngas into lower olefins over the bifunctional catalyst.

Effects of CO and H₂ pressures. We have further investigated the effects of partial pressures of CO and H₂, denoted as $P(\text{CO})$ and $P(\text{H}_2)$, on catalytic performances over the Zn-ZrO₂/SSZ-13 catalyst at 673 K. In the experiments, the total pressure of syngas was kept at 3 MPa and helium was used as a balance gas to regulate $P(\text{CO})$ while keeping $P(\text{H}_2)$ constant or to regulate $P(\text{H}_2)$ while keeping $P(\text{CO})$ constant. Fig. 10 shows the dependences of catalytic behaviours of the Zn-ZrO₂/SSZ-13 catalyst on $P(\text{CO})$ at a fixed $P(\text{H}_2)$ and on $P(\text{H}_2)$ at a fixed $P(\text{CO})$. The rate of CO conversion, denoted as $r(\text{CO})$, showed less than first-order dependence on $P(\text{CO})$ (Fig. S10a, ESI[†]). We found that the experimental data in Fig. 10a could be fitted to a Langmuir-adsorption model. The plot of $P(\text{CO})/r(\text{CO})$ versus $P(\text{CO})$ shows a good linear correlation with a correlation coefficient (R^2) of 0.992 (Fig. 10b). Thus, the rate of CO conversion at a fixed H₂ pressure can be expressed as:

$$r(\text{CO}) = k' \frac{K(\text{CO})P(\text{CO})}{[1 + K(\text{CO})P(\text{CO})]} \quad (2)$$

where k' and $K(\text{CO})$ are temperature-dependent constants.

The result on H₂-pressure dependence shows that the rate of CO conversion is less than 0.5-order dependent on $P(\text{H}_2)$ (Fig. S10b, ESI[†]). Our analysis suggests a Langmuir-adsorption



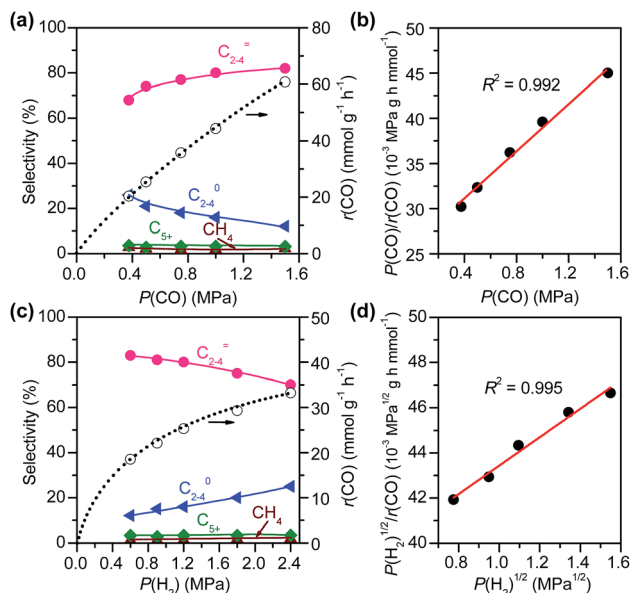


Fig. 10 Effects of pressures of CO and H₂ on catalytic behaviours of Zn-ZrO₂/SSZ-13-45H catalyst. (a) Effect of CO pressure at a fixed H₂ pressure. (b) Plot of $P(\text{CO})/r(\text{CO})$ vs. $P(\text{CO})$. Reaction conditions: $W = 0.40$ g; $P(\text{H}_2) = 1.5$ MPa; $T = 673$ K; $F(\text{total}) = 50$ mL min⁻¹; $P(\text{total}) = 3$ MPa; time on stream, 10 h. (c) Effect of H₂ partial pressure at a fixed CO pressure. (d) Plot of $P(\text{H}_2)^{1/2}/r(\text{CO})$ vs. $P(\text{H}_2)^{1/2}$. Reaction conditions: $W = 0.40$ g; $P(\text{CO}) = 0.6$ MPa; $T = 673$ K; $F(\text{total}) = 50$ mL min⁻¹; $P(\text{total}) = 3$ MPa; time on stream, 10 h.

model with H₂ dissociatively adsorbed on surface sites; the plot of $P(\text{H}_2)^{1/2}/r(\text{CO})$ versus $P(\text{H}_2)^{1/2}$ could be fitted to a good straight line with a R^2 of 0.995. Thus, the rate of CO conversion at a fixed CO pressure can be expressed as:

$$r(\text{CO}) = k'' \frac{K(\text{H}_2)^{1/2} P(\text{H}_2)^{1/2}}{[1 + K(\text{H}_2)^{1/2} P(\text{H}_2)^{1/2}]} \quad (3)$$

where k'' and $K(\text{H}_2)$ are temperature-dependent constants.

By combining the results described above, we can express the rate equation of CO conversion as:

$$r(\text{CO}) = k \frac{K(\text{CO})P(\text{CO})}{[1 + K(\text{CO})P(\text{CO})]} \frac{K(\text{H}_2)^{1/2} P(\text{H}_2)^{1/2}}{[1 + K(\text{H}_2)^{1/2} P(\text{H}_2)^{1/2}]} \quad (4)$$

where k is a temperature-dependent constant.

In addition to the CO conversion rate, the product selectivities are also dependent on the pressures of CO and H₂. A higher pressure of CO favours the selectivity of C₂-C₄ olefins, whereas the increase in H₂ pressure leads to higher selectivity of C₂-C₄ paraffins. This can be explained by the enhancement in hydrogenation of C₂-C₄ olefins at a higher H₂/CO ratio.

Reaction mechanism

To further confirm that CH₃OH is an intermediate, we have performed the conversion of CH₃OH at 673 K under high-pressure H₂ over zeolite SSZ-13 with different densities of Brønsted acid sites. Fig. 11 displays that the conversion of methanol increases with the density of Brønsted acid sites and

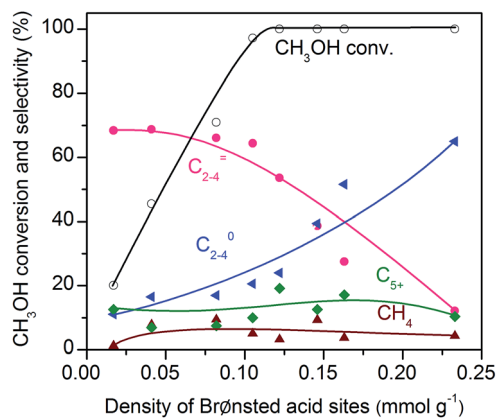


Fig. 11 Effect of density of Brønsted acid sites for the conversion of methanol over SSZ-13 zeolites. Reaction conditions: catalyst, 0.4 g; $F(\text{H}_2) = 30$ mL min⁻¹; $F(\text{liquid CH}_3\text{OH}) = 0.01$ mL min⁻¹; $P = 2$ MPa; $T = 673$ K; time on stream, 3 h.

reaches 97% at a density of Brønsted acid sites of 0.10 mmol g⁻¹. The selectivity of C₂-C₄ olefins was kept at 65–70% when the density of Brønsted acid sites was lower than 0.10 mmol g⁻¹. A further increase in the density of Brønsted acid sites caused the remarkable hydrogenation of C₂-C₄ olefins into C₂-C₄ paraffins. These trends agree well with those observed for the conversion of syngas; methanol/DME can be completely converted as the density of Brønsted acid sites increases to 0.10 mmol g⁻¹ and a higher density of Brønsted acid sites would cause the hydrogenation of C₂-C₄ olefins into C₂-C₄ paraffins (Fig. 5). These results provide further evidence that methanol and DME are key reaction intermediates for the formation of lower olefins from syngas over our bifunctional catalysts. Furthermore, the rapid conversion of CH₃OH over the catalyst with an adequate density of Brønsted acid sites agrees well with that the conversion of syngas into CH₃OH/DME is the rate-determining step for the formation of lower olefins over the bifunctional catalyst.

To gain further insights into the adsorbed species on the surfaces of Zn-ZrO₂ nanoparticles, we have performed *in situ* diffuse reflection infrared Fourier-transform spectroscopy (DRIFTS) studies. The adsorption of CO on the pre-reduced Zn-ZrO₂ surface resulted in IR bands at 2974, 2870, 2733, 1594 and 1366 cm⁻¹ at 553 K (Fig. 12). These IR bands can be ascribed to surface formate species.^{51,52} The intensity of formate species increased as the CO adsorption time increased from 1 to 30 min. The surface hydroxyl groups on metal oxide surfaces have been proposed to participate the formation of HCOO species.⁵³ Our DRIFTS studies confirmed the existence of multi-coordinated hydroxyl species on fresh Zn-ZrO₂ surfaces (Fig. S11, ESI†). The intensity of the hydroxyl group decreased after the adsorption of CO (Fig. S12, ESI†). This observation confirms the formation of HCOO species through the interaction of CO with surface hydroxyl groups. After switching from CO to CO/H₂, we observed the generation of methoxide species located at 2930, 2820, 1152 and 1052 cm⁻¹ together with formate species.^{51,52}





Fig. 12 *In situ* DRIFT spectra for the conversion of CO on Zn-ZrO₂ catalyst. (a) C-H region in 3050–2650 cm⁻¹. (b) C-O region in 1800–1000 cm⁻¹.

The results described above and from literature allow us to speculate a possible reaction mechanism for the hydrogenation of CO on Zn-ZrO₂ surfaces (Fig. 13). ZrO₂ surfaces may activate CO, while H₂ can be heterolytically dissociated on the -Zn-O- domains with H⁻ bonded to Zn²⁺ and H⁺ bonded to O²⁻.^{45,53,54} The surface reaction of adsorbed CO with hydroxyl groups to form formate species should be a facile step as indicated by our *in situ* DRIFT studies (Fig. 12).⁵⁵ The hydrogenation of formate species to form methoxide species needs the participation of H species from the heterolytic dissociation of H₂. Based on previous studies,^{56,57} we speculate that the H⁻ species might participate in the hydrogenation of formate, leading to the formation of methoxide species, whereas the H⁺ species might be involved in the formation of methanol and the recovery of surface hydroxyl groups (Fig. 13). Methanol can diffuse into the cages of SSZ-13, forming C₂-C₄ olefins catalysed by the Brønsted acid site. The rate equation (eqn (4)) could be interpreted by assuming that the surface reaction between adsorbed CO and dissociatively adsorbed H species on different active sites *via* a Langmuir-Hinshelwood mechanism is the rate-determining step (see details in ESI†). It is noteworthy that the hydrogen species formed by the heterolytic dissociation of H₂ should play



Fig. 13 A possible reaction mechanism for the conversion of syngas into lower olefins over Zn-ZrO₂/SSZ-13 catalyst.

a very important role in the selective hydrogenation of CO while keeping lower olefins from hydrogenation. Further experimental and computational studies on the nature of such hydrogen species and their working mechanism are definitely needed in the future work.

CO₂ was formed as a major by-product over our bifunctional catalyst. We found that the selectivity of CO₂ depended significantly on reaction temperature (Fig. 2c), but it did not change significantly with Zn/Zr ratio, the density of Brønsted acid sites and the proximity of the two components (Fig. 3, 5 and 6). The selectivity of CO₂ was in a narrow range of 41–45% for the bifunctional catalyst at 673 K. Jiao *et al.* also observed the formation of CO₂ with a selectivity of 45% at 673 K over the ZnCrO_x/MSAPO catalyst.³ They proposed that CO₂ was produced by the Boudouard reaction (2CO → CO₂ + C*), and the C* was responsible for the formation of CH₂ and CH₂CO (ketene) species in gas phase, which was believed to be the key intermediate for the formation of C₂-C₄ olefins in their system.³ However, we observed the formation of methoxide species on our catalyst surfaces. Thus, we consider that the breakage of C-O bond does not take place on our Zn-ZrO₂ surfaces but in the cage of zeolite SSZ-13. This is possibly because of the difference in metal oxide catalysts used for CO activation. It is quite interesting that the use of different metal oxides can lead to very different reaction mechanisms.

We speculate that the formation of CO₂ arises from the water-gas shift (WGS) reaction (CO + H₂O → CO₂ + H₂, ΔH₂₉₈⁰ = -41 kJ mol⁻¹), which is kinetically favourable at high temperatures. In fact, both ZnO and ZrO₂ have been reported to be the active catalysts for the WGS reaction.^{58,59} We confirmed that the WGS reaction could easily occur on our Zn-ZrO₂ catalyst. The H₂O conversion was >90% at a H₂O/CO molar ratio of ≤2.5/10 (Table S3, ESI†), which was the case on our catalyst by assuming a CO conversion <30%. This approaches the thermodynamic equilibrium for the WGS reaction. By assuming that the WGS reaction arrives at thermodynamic equilibrium over our catalyst, we have evaluated the selectivity of CO₂ contributed solely from the WGS reaction. The result reveals that the selectivity of CO₂ is around 45% at a CO conversion of 10–40% at 673 K (Table S4, ESI†). The selectivity of CO₂ observed experimentally on our Zn-ZrO₂/SSZ-13 catalyst was 43% at 673 K, which is very close to such an estimation. Thus, we believe that the generation of CO₂ over our Zn-ZrO₂-based catalysts is caused by the WGS reaction. The WGS reaction is helpful when the H₂/CO ratio in syngas is low, but this reaction should be inhibited if syngas is produced from natural gas or shale gas. We expect that the design of methanol-synthesis catalyst with suppressed WGS activity may lead to lower CO₂ selectivity.

Conclusions

We have demonstrated that the Zn-ZrO₂/SSZ-13 catalyst efficiently bridges syngas to methanol/DME and methanol/DME to lower olefins. The selectivity of C₂-C₄ olefins reaches 87% at a 10% CO conversion and 77% at a 29% CO conversion at 673 K. Propylene with a selectivity of 49% is the major component in



lower olefins. The bifunctional catalyst is stable during a 160 h of reaction. Our studies point out that the design of a high-temperature methanol-synthesis catalyst with controlled hydrogenation ability is one of the most important keys to realizing the selective formation of lower olefins. As compared to Cu-based catalysts, the Zn-doped ZrO₂ is outstanding in keeping methanol at a high temperature (673 K) and lower olefins from hydrogenation on the bifunctional catalyst under high-pressure H₂. There is an optimum molar ratio of Zn/Zr for the formation of lower olefins. Our work suggests that ZrO₂ works for CO activation, while the -Zn-O- domains or small ZnO clusters are responsible for the activation of H₂ possibly through heterolytic dissociation. The Brønsted acid site in the cages of zeolite SSZ-13 catalyses the C-C coupling to form lower olefins. The density of Brønsted acid sites affects both CO conversion and C₂-C₄ olefin selectivity. An appropriate density of Brønsted acid sites has been found for the selective formation of C₂-C₄ olefins because the hydrogenation of C₂-C₄ olefins also occurs on the Brønsted acid site. The proximity between Zn-doped ZrO₂ and SSZ-13 plays a pivotal role in determining the catalytic behaviours. The closer proximity can facilitate the transfer of reaction intermediates, thus favouring both the activity and lower olefin selectivity. Our kinetic studies strongly indicate that methanol and DME are the key reaction intermediates on our bifunctional catalyst and the formation of methanol/DME is the rate-determining step. We have observed the formation of formate and methoxide species on Zn-doped ZrO₂ surfaces, the precursors of methanol. Our studies also suggest that CO₂, a major by-product, is formed by the water-gas shift reaction. It should be pointed out that although this work provides a reaction-coupling approach for the direct conversion of syngas into lower olefins with high selectivity breaking the ASF distribution, there are still limitations in both the CO conversion and the product selectivity. The formation of CO₂ by the water-gas shift reaction decreases the final yield of C₂-C₄ olefins from CO. The control of hydrogenation ability of Zn-doped ZrO₂ to suppress the hydrogenation of lower olefin products limits the conversion of CO at the same time. The CO conversion obtained in this work is much lower than the equilibrium conversion (~80%). Future studies to improve the CO conversion and to inhibit the generation of CO₂ are needed.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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