Direct And Highly Selective Conversion Of Synthesis Gas To Lower Olefins: Development Of A Bifunctional Catalyst Combining Methanol Synthesis And Carbon-Carbon Combination.

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ABSTRACT

Lower (C$_2$-C$_4$) olefins, the basic building blocks of chemicals, can be directly synthesized from synthesis gas (H$_2$/CO) from various non-petroleum carbon resources, but the selectivity for lower olefins is very high. We report that coupling the methanol synthesis and methanol-to-olefin conversion reactions with a bifunctional catalyst can realize the direct conversion of syngas to lower olefins with very high selectivity. We show that the choice of the two active components and the method of combining the components are crucial for the selectivity of olefins. The binary Zr-Zn oxide itself shows high selectivity for methanol and dimethyl ether even at 673 K, and the reduced acidity SAPO-34 compound provides approximately 70% selectivity for C$_2$-C$_4$ olefins in the conversion of 10% CO. The proximity of the components at the micro and nanoscale contributes to the low selectivity of olefins.

Keywords: Conversion, paraffins, olefins, catalyst, carbon, selectivity, strategy, hydrogenation, programmed desorption, methanol, methoxide.

The main building blocks of lower olefins safety. Currently, the production of modern naphtha based on lower olefins is carried out by thermal cracking. The increasing demand for lower olefins and the depletion of oil reserves have stimulated the development of processes for the synthesis of lower olefins from alternative feedstocks such as coal, natural gas (also shale gas), and biomass. [1] Synthesis gas (syngas, CO/H$_2$) serves as a major platform for the conversion of non-oil carbon resources. The synthesis of lower olefins from synthesis gas is a promising route. Most studies have focused on the hydrogenation of CO to reduce olefins via the Fischer-Tropsch (FT) synthesis over Fe catalysts. [1-5] However, the selectivity for C$_2$-C$_4$ olefins is limited. Typically, the FT synthesis proceeds by dissociation of CO, formation of CHx (x = 1-3), coupling of CHx to CnHm, and hydrogenation or dehydration of CnHm to paraffinic or olefinic products. [1] The binding of CHx is uncontrolled on metal catalysts capable of catalyzing the dissociation of CO (Fe, Co, and Ru), and therefore the hydrocarbon products generally follow a statistical distribution known as the Anderson-Schultz-Flory (ASF) distribution. [1] According to this distribution, the maximum selectivity for C$_2$-C$_4$ (including paraffins and olefins) is limited to 58%. Recently, C$_2$-C$_4$ olefin selectivities of about 60% have been achieved by carefully designing catalysts containing S- and Na-modified Fe nanoparticles. [2] Lower olefins can be produced from synthesis gas by two sequential processes, namely methanol synthesis and methanol to olefin (MTO) [6].

A direct route using bifunctional catalysts capable of catalyzing the hydrogenation of CO to heavier hydrocarbons and the selective C|C cleavage of heavier hydrocarbons has been reported to be effective for the production of gasoline or diesel fuel.[7] We expect that the development of a bifunctional catalyst containing active components for the conversion of CO to C1 intermediates (e.g., CH_3OH or CH_3O) and the selective coupling of C⁄C will be a promising strategy for realizing the selective conversion of syngas to C_2-C_4 olefins (Figure 1).

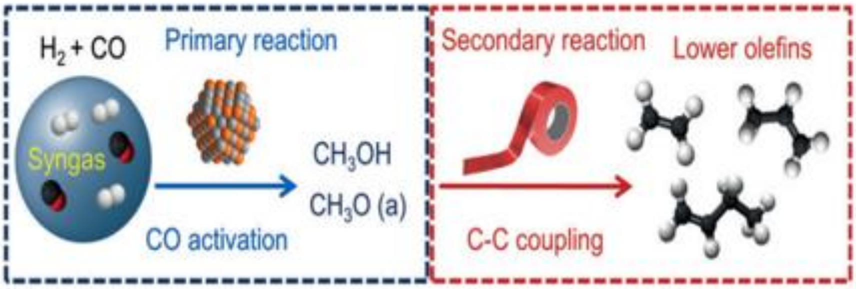
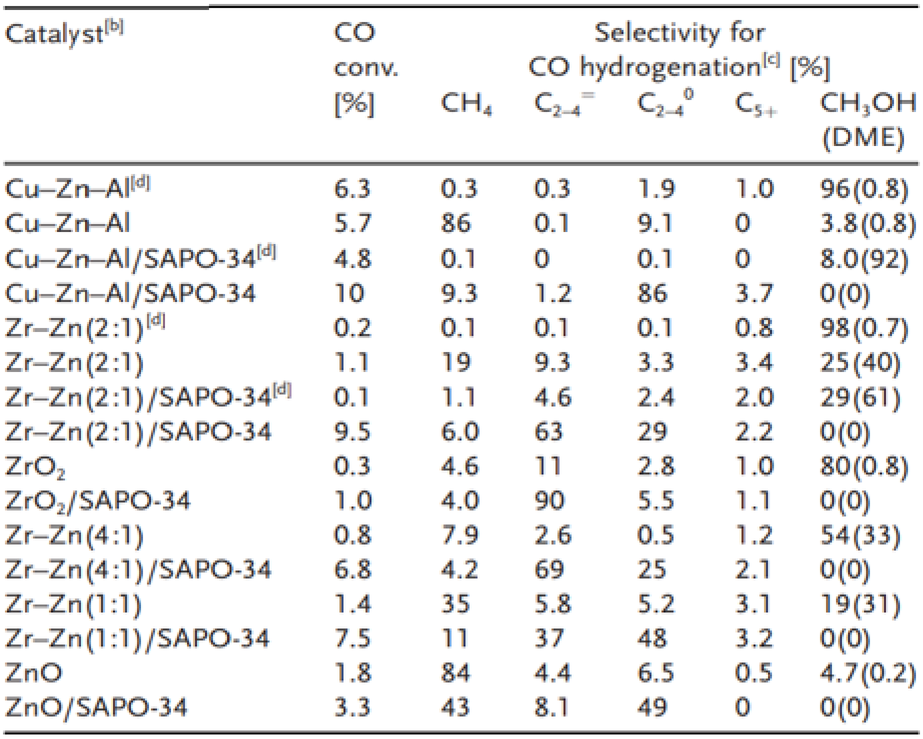


Figure 1. Reaction assembly for the direct synthesis of lower olefins from synthesis gas by integrating active components for CO activation and C C coupling. (a) = adsorbed.

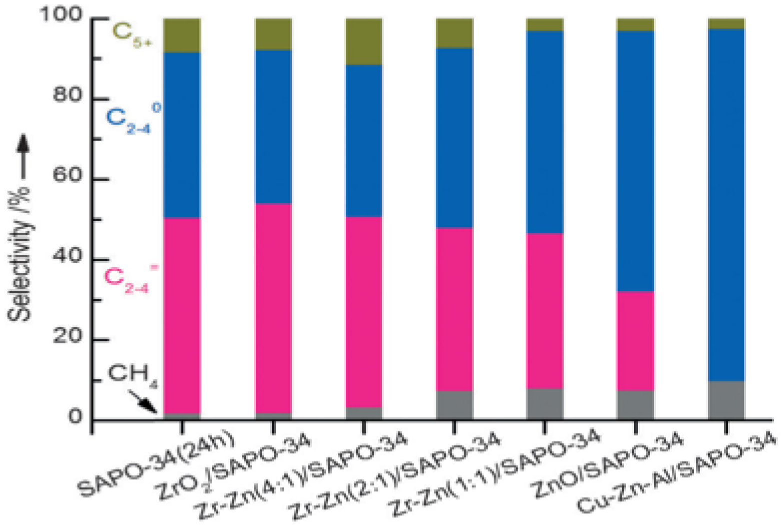
The C⁄C coupling and CO activation at different sites allow the coupling to occur in a controlled manner, thereby disrupting the ASF distribution. Some studies have combined catalysts for methanol synthesis and methanol to hydrocarbon conversion in a single reactor, but the main products are C_2-C_4 waxes. [8] Direct synthesis of C_2-C_4 olefins from synthesis gas with high selectivity (>60%) is a major challenge. Here, we report the successful development of bifunctional catalysts with very high selectivity for C_2-C_4 olefins by integrating catalyst components active in methanol synthesis and C⁄C coupling. We show that component selection and integration are critical for product selection. We chose SAPO-34 molecular sieve, an excellent MTO catalyst [6], as the C⁄C coupling component. The optimized temperature for SAPO-34-catalyzed synthesis of C_2-C_4 olefins is 673–723 K.[6] However, methanol synthesis at such high temperatures is thermodynamically limited. Our calculations show that the combination with the MTO reaction, which is thermodynamically more favorable at higher temperatures, can drive the conversion of syngas, and the formation of lower olefins is thermodynamically possible at 673 K. We first used a ball mill to combine the methanol synthesis catalyst, namely Cu-Zn-Al mixed oxide, with SAPO-34 to convert it into syngas. The Cu-Zn-Al catalyst itself showed high selectivity for methanol production at 523 K, but as the temperature increased to 673 K, the main product shifted to CH_4 (Table 1), indicating that the selectivity for C_4 olefin hydrogenolysis reached 63% with CO. The conversion was 9.5% at 673 K on the Zr-Zn/SAPO-34 catalyst with a Zr/Zn molar ratio of 2:1.

Table 1: CO hydrogenation over methanol synthesis catalysts and bifunctional catalysts consisting of methanol synthesis catalyst and SAPO-34.[a]



Catalyst[b]	CO conv. [%]	Selectivity for CO hydrogenation[c] [%]				
		CH_4	$C_{2-4}^{=}$	C_{2-4}^{0}	C_{5+}	CH_3OH (DME)
Cu–Zn–Al[d]	6.3	0.3	0.3	1.9	1.0	96(0.8)
Cu–Zn–Al	5.7	86	0.1	9.1	0	3.8(0.8)
Cu–Zn–Al/SAPO-34[d]	4.8	0.1	0	0.1	0	8.0(92)
Cu–Zn–Al/SAPO-34	10	9.3	1.2	86	3.7	0(0)
Zr–Zn(2:1)[d]	0.2	0.1	0.1	0.1	0.8	98(0.7)
Zr–Zn(2:1)	1.1	19	9.3	3.3	3.4	25(40)
Zr–Zn(2:1)/SAPO-34[d]	0.1	1.1	4.6	2.4	2.0	29(61)
Zr–Zn(2:1)/SAPO-34	9.5	6.0	63	29	2.2	0(0)
ZrO_2	0.3	4.6	11	2.8	1.0	80(0.8)
ZrO_2/SAPO-34	1.0	4.0	90	5.5	1.1	0(0)
Zr–Zn(4:1)	0.8	7.9	2.6	0.5	1.2	54(33)
Zr–Zn(4:1)/SAPO-34	6.8	4.2	69	25	2.1	0(0)
Zr–Zn(1:1)	1.4	35	5.8	5.2	3.1	19(31)
Zr–Zn(1:1)/SAPO-34	7.5	11	37	48	3.2	0(0)
ZnO	1.8	84	4.4	6.5	0.5	4.7(0.2)
ZnO/SAPO-34	3.3	43	8.1	49	0	0(0)

[a] Reaction conditions: catalyst 0.50 g; H_2/CO=2:1; 1 MPa; 30 ml/min1; operating time 30 h; 673 K. [b] Cu/Zn/Al=6:3:1 (molar ratio); Zr/Zn molar ratio is shown in parentheses; Composites were prepared by ball milling for 24 h [c] Selectivity is calculated on a molar carbon basis for CO hydrogenation; CO_2 production from the WGS reaction is shown in Table 1; C_2–4=, C_2–4 0 and C_5+ represent C_2-C_4 olefins, C_2-C_4 paraffins and hydrocarbons with more than 5 carbon atoms, respectively. [d] 523 K. In contrast to the Cu-Zn-Al catalyst, methanol and DME remained the main products over a wide temperature range on the Zr-Zn catalyst. The CO conversion was lower on the Zr-Zn catalyst, but the combination with SAPO-34 significantly accelerated the conversion at 673 K due to the thermodynamic driving force. We conducted further studies to understand the unique catalytic functions of the Zr-Zn catalysts. The use of ZrO2 alone provided high CH_3OH selectivity, but the CO conversion was low (Table 1). The ZrO2/SAPO-34 composite showed 90% C_2-C_4 olefin selectivity at 1.0% CO conversion. The high olefin selectivity is probably due to the poor hydrogenation ability of ZrO_2. Indeed, ZrO_2 is a unique catalyst for the activation of CO with surface oxygen vacancies, forming surface methoxide via formate in the presence of H_2 [9], but the low H_2 dissociation ability of ZrO_2 leads to its low activity even when combined with SAPO34. The presence of a second component that can accelerate the dissociative adsorption of H_2 favors the conversion of CO over ZrO_2. It is known that ZnO participates in the heterolytic dissociation of H_2, forming hydrogen bonds that can participate in hydrogenation reactions. [10] Table 1 shows that ZnO can activate H_2 in our system and thus enhance CO hydrogenation compared to the Zr-Zn/SAPO34 catalyst. The catalyst with a Zr/Zn molar ratio of 2:1 showed the highest activity for the formation of C_2-C_4 olefins. The high Zn/Zr ratio resulted in a high CH_4 selectivity and high hydrogenation capacity, resulting in a C_2-C_4 wax/olefin ratio. Characterization by XRD and TEM confirmed that the Zr-Zn binary oxide consists of nano-sized ZrO_2 and ZnO particles (Figures S3 and S4). Our results indicate that the active component of the hydrogenation significantly affects the product selectivity in the subsequent conversion of CO to methanol or methoxide intermediates. To gain further insight, we performed methanol conversion in the presence of H_2 at 673 K. The methanol conversion was more than 98% for the catalysts shown in Figure 2.



Compared with SAPO-34, C_2-C_4 olefins and paraffins were formed as the main products, which were ball milled for 24 h for better comparison and labeled as SAPO-34 (24 h). The presence of ZrO_2 did not significantly affect the product selectivity. Increasing the Zn/Zr ratio in Zr-Zn/SAPO-34 composites gradually increased the selectivity to CH4. The C_2-C_4 olefin/kerosene ratio decreased simultaneously. Only C_2-C_4 paraffins were formed on the Cu-Zn-Al/SAPO-34 catalyst. These trends are similar to those observed in the conversion of syngas (Table 1) and may explain why Zr-Zn/SAPO-34 is unique for the production of C_2-C_4 olefins. Thus, the selection of a CO hydrogenation active component with appropriate hydrogenation capacity is crucial for the selective production of C_2-C_4 olefins. It is noteworthy that for some catalysts, the C_2-C_4 olefin/paraffin ratio was lower in the methanol conversion in the presence of H_2 (Figure 2) than in the syngas conversion (Table 1) and the MTO reaction. [6] We determined that this behavior was due to the presence of H_2 or the effect of the difference in H_2 pressure. In the N_2 atmosphere, which is common for the MTO reaction, the selectivity for C_2-C_4 olefins reached approximately 80% compared to SAPO-34 (24 h) (Figure S5). Increasing the H_2 pressure led to a decrease in the selectivity for C_2-C_4 olefins and an increase in the selectivity for C_2-C_4 paraffins due to hydrogenation at the Brønsted acid sites of SAPO-34.[11] For the same reason, increasing the synthesis gas pressure from 1.0 to 2.0 MPa decreased the C_2-C_4 olefins/paraffins ratio in the conversion of synthesis gas over the Zr-Zn/SAPO-34 catalyst (Table S3). Since olefin hydrogenation can occur at Brønsted acid sites, the acidity of SAPO-34 may also affect the product selectivity. We found that ball milling reduced the crystal size (Figure S6), crystallinity (Figure S7a), and specific surface area (Table S4) of SAPO34. The coordination environments of Si, Al, and P in SAPO34 also changed simultaneously (Figure S8). The Brønsted acidity of SAPO-34 is known to arise from the substitution of Si with P or Al.[6] Thus, a change in the coordination environment may lead to a change in Brønsted acidity. Our NH_3 temperature-programmed desorption (NH3-TPD) studies showed that the density of Brønsted acid sites decreases with increasing ball milling time (Fig. S9a and Table S4). We also studied a series of SAPO-34 samples, designated SAPO-34 (Six) with different Si contents [x = Si/(Si + Al + P)] (Table S4) and good crystallinity (Fig. S7b), and therefore different densities of Brønsted acid sites (Fig. S9b and Table S4). The methanol conversion results with these two SAPO-34 samples in H_2 atmosphere indicate that the density of Brønsted acid sites is a key factor determining the C_2-C_4 olefin/paraffin ratio (Fig. 3a). A greater density of Bronsted acid sites resulted in decreased olefin/paraffin ratios or lower selectivity for C_2-C_4 olefins. Similar trends were observed in the conversion of synthesis gas over bifunctional catalysts prepared by simply mixing Zr-Zn oxide (Zn/Zr = 1:2) and SAPO-34 samples with different densities of Bronsted acid sites in agate mortar (Fig. 3b). . On the Zr-Zn/SAPO-34(Si0.048)-M catalyst (M = solution mixing), 74% C_2-C_4 olefin selectivity with 11% CO conversion was obtained at a Bronsted acid density of 0.21 mmolg¢1. The method of combining the active components for the conversion of synthesis gas to lower olefins is also important. The use of a two-layer configuration with SAPO-34 (24 h) downstream of Zr-Zn oxide provided very low CO conversion (Figure 4a). This result indicates that the thermodynamic driving force does not come from the separation of the two active components. The CH_4 selectivity remained high, but C_2-C_4 olefins and paraffins were formed due to the catalytic function of SAPO-34 in the downstream layer. Mixing the two components significantly increased the CO conversion and reduced the CH_4 selectivity (Figure 4b–d). As shown by the electron microscopy results (Figures S10–S13), the proximity of the two components increased when the integration method was changed from bead stacking to ball milling (Figures 4b–4d). For the typical Zr–Zn/SAPO-34 sample with two-component spheres milled for 24 h (Fig. 4d), smaller Zr–Zn particles (10–40 nm) were tightly attached to the 200–500 nm SAPO-34 particles (Figs. S12 and S13). On the other hand, in the sample prepared by simply mixing spherically ground SAPO-34 and Zr–Zn particles in an agate mortar (Fig. 4c), there was no contact between the 200–500 nm SAPO-34 particles and the disordered Zr–Zn particles (Fig. S11). The sample shown in Fig. 4b consisted of micrometer-sized particles attached to each other (Fig. S10). Approximately 10% CO conversion was obtained on the nano-sized catalysts (Fig. 4c,d). The selectivity for C_2-C_4 olefins decreased and for C_2-C_4 paraffins increased slightly as the two components approached each other (Figure 4, b–d).

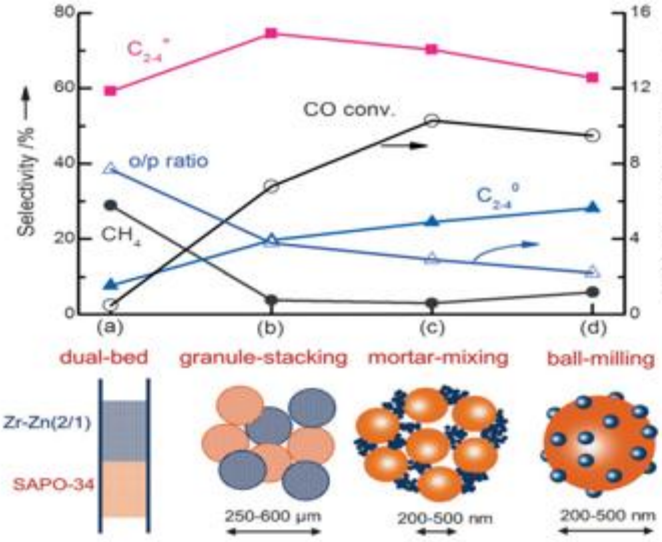


Figure 4. Effect of integration method on catalytic activity of composite catalysts containing Zr-Zn oxide (Zr/Zn=2:1) and SAPO34 (24 h). a) Double-layer configuration. b) Laying of granules with a size of 250-600 mm. c) Mixing the two components in an agate mortar is sufficient. d) Milling the two components for 24 h. The o/p ratio indicates the ratio of C_2-C_4 olefins/paraffins. See Table 1 for reaction conditions. Recently, de Jong and co-workers reported that very close proximity of bifunctional active sites is detrimental to the hydrocracking of hydrocarbons. [12] In our case, increased proximity may increase the likelihood of unfavorable hydrogenation of the target lower olefins formed in SAPO-34 by the nearby Zr-Zn oxides. We measured the stability of the composite in Figure 4. After 20 h of reaction, there was no significant change in CO conversion and product selectivity (Figure S14). The CO conversion and C_2-C_4 olefin selectivity remained at 9.2% and 68%, respectively, after 100 h of reaction. Thus, the present composite catalyst is stable enough to directly convert CO to lower olefins. In conclusion, we found that the integration of Zr–Zn binary oxide, which is responsible for the activation of CO to methanol or methoxide, and SAPO-34, which is responsible for the selective coupling of C¢C, can realize the direct synthesis. Of lower olefins from synthesis gas with excellent selectivity. The selectivity for C_2-C_4 olefins can reach 74% at 11% CO conversion at 673 K, thereby breaking the ASF distribution. We show that controlling the hydrogenation ability of the two components in a dual-functional catalyst is crucial for obtaining high selectivity for C_2-C_4 olefins. The proximity of both components also plays a key role in the direct conversion of synthesis gas to lower olefins.

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