

# Development of new syngas conversion routes beyond Fischer-Tropsch synthesis

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**Abstract:** Fischer-Tropsch synthesis is a classical process for the conversion of syngas to hydrocarbons. The products generally follow the Anderson-Schulz-Flory (ASF) distribution and the product selectivity is limited. By using reaction-coupling strategy, we have developed a novel bifunctional catalytic approach for direct conversions of syngas into lower olefins and aromatics with selectivities significantly breaking the ASF distribution. The selectivities of C<sub>2</sub>-C<sub>4</sub> olefins and aromatics both reached 75-80% at CO conversions of 20-30%. Here, we present the chemistry of this bifunctional catalytic approach, including the choice of catalyst components, role of each component, nanoscale proximity of the components and reaction mechanism.

**Keywords:** Bifunctional catalysis, C1 chemistry, Lower olefins and aromatics.

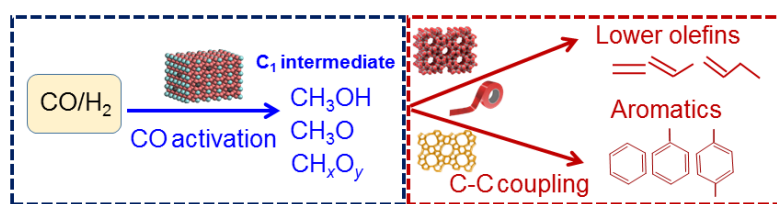
## 1. Introduction

Fischer-Tropsch (FT) synthesis, which transforms syngas (CO/H<sub>2</sub>) into hydrocarbons, is a key process for utilization of carbon feedstock such as natural gas (shale gas), coal, biomass or CO<sub>2</sub> to produce liquid fuels and chemicals. The selectivity control is one of the biggest challenges in syngas chemistry. Typically, FT synthesis proceeds via the dissociation of CO, formation of CH<sub>x</sub> ( $x = 1-3$ ), C-C coupling of CH<sub>x</sub> to C<sub>n</sub>H<sub>m</sub> and the hydrogenation or dehydrogenation of C<sub>n</sub>H<sub>m</sub> to paraffin or olefin products. The coupling of CH<sub>x</sub> is generally uncontrollable over metal catalysts (Ru, Co and Fe) capable of catalyzing CO dissociation, and thus the products follow a statistical distribution known as the Anderson-Schulz-Flory (ASF) distribution, which is non-selective for middle-distillate products. For example, the maximum selectivities to C<sub>2</sub>-C<sub>4</sub> (including both paraffins and olefins), C<sub>5</sub>-C<sub>11</sub> (gasoline range) and C<sub>10</sub>-C<sub>20</sub> (diesel range) hydrocarbons are 58%, 45% and 39%, respectively. Aromatics are difficult to obtain via FT synthesis.

Many studies have been devoted to developing new catalysts or new approaches for the conversion of syngas to specific hydrocarbon products with selectivity breaking the ASF limitation.<sup>1</sup> Our idea is that the conversion of syngas into hydrocarbons involves a series of tandem elementary steps including CO activation and C-C coupling, and thus cannot be precisely controlled by one catalyst as in the conventional FT synthesis. The coupling of tandem steps using well-designed multifunctional catalysts containing components suitable to the respective steps would be a promising methodology. In previous studies, we developed bifunctional catalysts, which were composed of an FT active metal (Ru or Co) nanoparticle for CO activation/C-C coupling and a mesoporous zeolite (H-ZSM-5 or NaY) for selective C-C cleavage, for the selective production of gasoline or diesel.<sup>2-5</sup>

Lower (C<sub>2</sub>-C<sub>4</sub>) olefins and aromatics are key building-blocks in the chemical industry. Many studies have contributed to the conversion of syngas into lower olefins via FT route over Fe- or Co<sub>2</sub>C-based catalysts, but the selectivity is limited to ~60%. Recently, we succeeded in developing new bifunctional catalytic approach for the direct conversion of syngas to lower olefins and aromatics by integrating the activation of CO and the selective C-C coupling (Figure 1).<sup>6,7</sup> Here, we will present the details of the chemistry of this bifunctional catalytic approach, including the choice of catalyst components, role of each component, nanoscale proximity of the components and reaction mechanism.

## 2. Results and discussion



**Figure 1.** Bifunctional catalytic approach for direct conversion of syngas to lower olefins and aromatics by integration of two active components.

The use of one catalyst to integrate CO to C<sub>1</sub> intermediate (e.g., methanol) and C<sub>1</sub> (methanol) to olefins or aromatics (MTO or MTA) in tandem is a challenging task. First, methanol synthesis is thermodynamically unfeasible at temperatures  $\geq 673$  K, whereas the MTO or MTA reaction must be performed at such high temperatures because of the kinetic requirement. Our thermodynamic analysis reveals that the MTO or MTA reaction can drive the conversion of syngas to methanol at 673 K. Second, the use of typical Cu-Zn-Al-O methanol-synthesis catalyst in combination with the MTO or MTA catalyst led to the formation of C<sub>2</sub>-C<sub>4</sub> paraffins but no olefins. We discovered that Zn-doped ZrO<sub>2</sub> (Zn-ZrO<sub>2</sub>) solid solution or composite oxide with spinel structure (e.g., ZnGa<sub>2</sub>O<sub>4</sub> and ZnAl<sub>2</sub>O<sub>4</sub>) could catalyze the conversion of CO to CH<sub>3</sub>OH/CH<sub>3</sub>OCH<sub>3</sub> and was unique in keeping lower olefins from further hydrogenation. The selectivity of C<sub>2</sub>-C<sub>4</sub> olefins reached about 75-80% at a CO conversion of  $\sim$ 30% over a bifunctional catalyst composed of Zn-ZrO<sub>2</sub> and zeolite SAPO-34 or SSZ-13. The Zn-ZrO<sub>2</sub>/ZSM-5 catalyzed the direct conversion of syngas into aromatics with a selectivity of 80% at CO conversion of 20%. The catalyst was very stable and no deactivation was observed in 1000 h.

We clarified that the Zn/Zr ratio in metal oxide, the density of Brønsted acid sites in zeolite, and the nanoscale proximity between metal oxide and zeolite are key controlling factors. Our work confirmed that CH<sub>3</sub>OH/CH<sub>3</sub>OCH<sub>3</sub> were formed as intermediates on metal oxide, which subsequently diffused into zeolite, and the Brønsted acid site in zeolite was responsible for the formation of lower olefins or aromatics. The in situ FT-IR studies indicated the generation of CH<sub>3</sub>O species on Zn-ZrO<sub>2</sub> surfaces under syngas atmosphere. We discovered a self-promotion effect of CO on the formation of aromatics over the Zn-ZrO<sub>2</sub>/ZSM-5 catalyst. The presence of CO accelerated the dehydrogenative aromatization of olefin intermediates on ZSM-5.

### 3. Conclusions

We have developed a new bifunctional catalytic approach for the direct conversion of syngas to lower olefins and aromatics. The combination of Zn-ZrO<sub>2</sub> solid solution with SAPO-34 or SSZ-13 results in a powerful bifunctional catalyst with C<sub>2</sub>-C<sub>4</sub> olefin selectivity of 75-80% at CO conversion of  $\sim$ 30%. The Zn-ZrO<sub>2</sub>/ZSM-5 catalyst shows 80% selectivity of aromatics at 20% CO conversion. These bifunctional catalysts are very stable. CH<sub>3</sub>OH and CH<sub>3</sub>OCH<sub>3</sub> are reaction intermediates. The control of hydrogenation ability of metal oxides and the density of Brønsted acidity in zeolites are crucial to selective formations of lower olefins and aromatics.

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