Co₂C nanoprisms with strong facet effect for Fischer-Tropsch to olefins reaction

Yadong Li

Lower olefins refer to ethylene, propylene and butylene, which are vital building block in the chemical industry. They are fundamental chemicals of the greatest consumption among the organic chemicals all over the world. Large amount of chemical products, such as packing materials, cosmetics, synthetic rubber, coatings are the derivatives of lower olefins. In traditional petrochemical industry, lower olefins are mainly derived from oil-based feedstocks. With the rapid depletion of the limited petroleum, there is an urgent need for processes that can produce lower olefins from alternative feedstocks. The syngas, which is a promising alternative feedstock as it can be obtained from reforming of natural gas, gasification of coal or biomass, can be transformed into lower olefins through indirect or direct reaction. The indirect process mainly refers to the methanol to olefins (MTO) technology [1]. The direct conversion of syngas to lower olefins is one of the most challenging subjects in the field of C1 chemistry. It is considered as an attractive alternative non-petroleum-based production route due to its process simplicity and low energy consumption [2].

Bifunctional catalysis used composite catalysts, such as OX-ZEO and Fischer-Tropsch to olefins (FTO) reaction are two main routes for the direct conversion of syngas to lower olefins [3]. Recent work by Bao *et al.* [4] and Wang *et al.* [5] reported that oxides-molecular sieve coupling catalysts exhibited very high selectivity toward lower olefins at relative high temperature of ca. 400°C, but this method is not yet in commercial use. As the reaction process for FTO is very similar to that for typical FT synthesis, FT catalysts can be used for production of lower olefins after suitable catalyst modification. De Jong *et al.* [6] reported that Fe-based catalysts promoted by S and Na and using α -alumina or carbon nanofiber as weakly interactive supports exhibited ex-

cellent performance for selective formation of lower olefins (61 C%). They also found the particle size of iron carbide plays a crucial role for direct production of lower olefins via syngas, and they suggested lower olefins are produced at promoted terrace sites [7]. However, these reactions normally need temperatures from 300°C to 350°C, which would cause carbon deposition on the catalyst surface and catalyst sintering, deactivating the catalyst and shortening its lifetime [2].

The primary aims of FTO are to maximize lower olefins selectivity while reduce methane production with high stability. The maximum selectivity toward C₂–C₄ olefins is achieved with an alpha value of about 0.5 according to the ordinary Anderson–Schulz–Flory (ASF) model [8,9]. One of the most efficient ways of shifting product selectivity to low alpha values is by increasing reaction temperature. However, a decrease on the chain growth probability results in an increase of methane selectivity as indicated by the ASF product distribution. In addition, the produced olefins were prone to be further hydrogenated to paraffins especially at high temperature and resulted in decreased selectivity to lower olefins. Moreover, the particle sintering and coke formation at high temperature would lead to serious deactivation [10]. Due to the above limitation, there was no catalyst suitable for the industrial application of the direct conversion of syngas into lower olefins via the Fischer-Tropsch synthesis. Based on the general analysis, most of the reported FTO catalysts are still a kind of FT catalyst with low alpha value. The product distribution still obeys the ordinary ASF model. Obviously, with the goal of high selectivity to lower olefin, low methane selectivity and high stability simultaneously, it is necessary to develop new FTO catalyst which deviates from ASF distribution at mild reaction conditions.

Department of Chemistry and Collaborative Innovation Center for Nanomaterial Science and Engineering, Tsinghua University, Beijing 100084, China
Email: ydli@mail.tsinghua.edu.cn

Metallic cobalt is the active phase with high FT activity for production of long-chain paraffins. Cobalt carbide is always considered as one of the main deactivation reasons for Co-based FT reaction and produces a large amount of unwanted methane [11,12]. However, Zhong's and Sun's group [13] from Chinese Academy of Sciences' Key Laboratory of Low-Carbon Conversion Science and Engineering reported that, under mild reaction conditions (250°C, 1–5 bar), Co_2C nanoprisms catalyse the syngas conversion with high selectivity for the production of lower olefins (60.8 C%), while generating little methane (about 5.0 C%),

with the ratio of olefin/paraffin amongst the $\text{C}_2\text{--C}_4$ products being as high as 30. The product distribution deviates markedly from the classical ASF distribution with the highest selectivity to propylene. Based on the study of structure-performance relationship and density functional theory calculations, they stated that a strong facet effect was demonstrated for Co_2C nanoparticles during syngas conversion. Specifically, the {101} and {020} facets of Co_2C are beneficial for the production of olefins and inhibit the formation of methane (Fig. 1).

This result with amazing selectivity to olefins with rel-

Figure 1 TEM images of the CoMn catalysts after reaching steady state. (a, b) Low-resolution TEM images. (c–e) High-resolution images of Co_2C nanoprisms with exposed facets of {101}, $\{-101\}$ and {020}. d is distance (length) of the lattice fringes. (f) The Co_2C nanoprism has a parallelepiped shape, with four rectangular faces and two rhomboid faces. Reprinted with permission from Ref. [13], Copyright 2016, Macmillan Publishers Limited, part of Springer Nature.

ative low methane under mild condition is very astonishing. It can be considered as a good case for nanocatalysis with facet effect. The high activity, selectivity and stability at mild reaction conditions suggest promising potential industrial application. As Prof. Michael Claeys (one of the reviewers) has said in the NEWS & VIEWS [14], “their potential impact cannot be overestimated: they might open up pathways for the development of greatly improved systems for producing valuable chemicals from a variety of carbon sources” and “this is a groundbreaking contribution that further unlocks the immense potential of the Fischer–Tropsch process for producing chemicals. Zhong *et al.* have thrown open the reaction’s treasure chest, and added fresh momentum to research into methods for making olefins from synthesis gas”.

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