

# NOVEL IRON-BASED COMPOSITES AS CATALYSTS FOR THE FISCHER-TROPSCH SYNTHESIS OF LOWER OLEFINS

Di Wang<sup>1,2</sup>, Xuezhi Duan<sup>1,\*</sup>, Gang Qian<sup>1</sup>, De Chen<sup>2,\*</sup>, Xinggui Zhou<sup>1</sup> and Weikang Yuan<sup>1</sup>

<sup>1</sup> State Key Laboratory of Chemical Engineering, East China University of Science and Technology, 200237 Shanghai, China

<sup>2</sup> Norwegian University of Science and Technology, 7491 Trondheim, Norway

## *Abstract*

Two kinds of novel iron-based composite catalysts were prepared by redox reaction between carbon nanotubes and strong oxidants (e.g.,  $\text{KMnO}_4$  and  $\text{K}_2\text{FeO}_4$ ) followed by thermal treatments. Compared to traditional catalysts prepared by impregnation method, these novel catalysts show higher activity, selectivity and stability for direct conversion of syngas to lower olefins, which could be consequences of the highly dispersed iron nanoparticles, well-distributed promoters, weak metal-support interaction and high amount of defects on support. The catalyst structure-performance relationship was studied by multi-techniques, such as TEM, elemental mapping,  $\text{H}_2$ -TPR, Raman. Furthermore, catalyst microstructures, such as particle size, loading and distribution, were easily adjusted by changing the preparation and thermal treatment conditions.

## *Keywords*

Fischer-Tropsch synthesis, Lower olefins, Iron catalyst, Carbon nanotubes

## **Introduction**

Direct conversion of coal-, biomass- and natural gas-derived syngas to lower olefins ( $\text{C}_2$ - $\text{C}_4$ ) is an promising alternative non-petroleum based route for the production of key building blocks in the chemical industry, in view of high oil prices, environmental regulations and strategies to gain independence from oil imports. For this route, supported iron catalysts are more attractive than others not only for the low price, high mechanical stability and high water gas shift activity, but also for the high selectivity of lower olefins.

Promoters are employed to adjust the product distribution for the selective formation of lower olefins, the suppression of methane and the enhancement of catalyst stability. Manganese and potassium promoters are most commonly used ones. Generally, Mn and/or K promoted

iron catalysts are synthesized by co- or sequenced-impregnation method, which will usually leads to non-uniform distributions of iron species and promoters and consequently influence the selectivity of FTS products. Therefore, it is encouraged to develop a method to prepare highly dispersed Fe-based FTO catalysts with well-distributed promoters.

The objective of this study is to employ redox reactions between carbon nanotubes and strong oxidant (e.g., potassium permanganate and potassium ferrate) for the synthesis of K-doped transition metal oxides coated CNTs composite. The coating layers on the external surface of carbon nanotubes tend to transform into nanoparticles as the treatment temperature increases. The as-synthesized iron-based composite catalysts were tested

---

\* To whom all correspondence should be addressed. E-mail: xzduan@ecust.edu.cn; chen@nt.ntnu.no.

under FTO conditions. The catalyst structure-performance relationship was correlated by using multiple techniques.

## Experimental

Figure 1 schematically illustrates the synthesis procedures of novel iron-based composite catalysts. For case I, nitric acid-treated CNTs were modified by  $\text{KMnO}_4$  to prepare MnK-CNTs. Subsequently, MnK-CNTs were employed as supports to prepare iron-based catalysts by incipient wetness impregnation method. The as-prepared samples were denoted as Fe/MnK-CNTs. For case II, the pre-treated CNTs were soaked in a solution of  $\text{K}_2\text{FeO}_4$  in aq. KOH. The obtained material is denoted as FeK-OX.

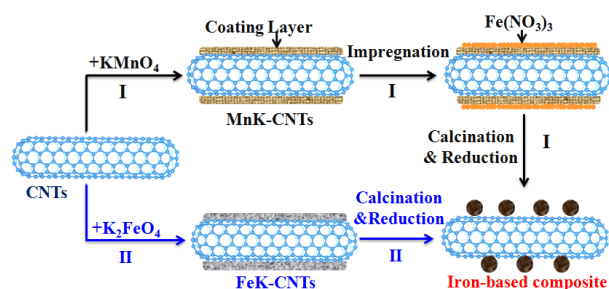


Figure 1. Two synthetic routes of iron-based composite catalysts

## Results and Discussion

### Case I

Employing MnK-CNTs composite as support is an efficient method to synthesize highly dispersed Fe-based catalyst with well-distributed Mn and K promoters (Figure 2). This novel Fe/MnK-CNTs catalyst not only is more active and stable than FeMnK/CNTs catalyst prepared by traditional co-impregnation method, but also exhibits higher selectivity of hydrocarbons especially lower olefins under similar CO conversions (Wang et al., 2015). The enhancement of catalytic performance could be ascribed to the highly dispersed small nanoparticles, well-distributed promoters, weak metal-support interaction and adequate defects on the surface of CNTs, which are consequences of the unique structural transformation of MnK-CNTs.

Moreover, the structure properties, such as microstructure, crystal phase, metal-support interaction and surface chemistry, of Fe/MnK-CNTs catalyst could be easily manipulated by taking advantage of the unique properties of MnK-CNTs as a function of temperature and atmosphere. The effect of varying the calcination temperature from 150 to 400 °C was examined on Fe/MnK-CNTs composite catalysts. The catalyst obtained from the calcination temperature of 220 °C is found to show the highest yield of lower olefins. The induction

period of the catalysts gradually decreases with the increasing calcination temperature.

### Case II

FeK-OX composite has been prepared by a redox reaction between CNTs and  $\text{K}_2\text{FeO}_4$  followed by thermal treatments. A comparison of catalytic behaviors between the FeK-OX and the other two catalysts prepared by impregnation method followed by thermal treatments has demonstrated that the novel composite catalyst shows shorter induction period, relatively higher activity, higher hydrocarbon selectivity, lower olefins selectivity, chain growth probability as well as better stability. This could be related to more uniform and smaller iron nanoparticles, weaker metal-support interaction and unique promotional effects of potassium. Furthermore, additional potassium promoters into the FeK-OX composite catalyst give rise to higher yield of lower olefins.

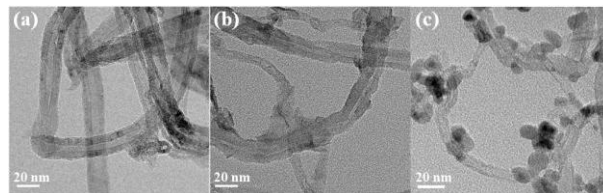


Figure 2. TEM images of (a) CNTs (b) MnK-CNTs and (c) reduced Fe/MnK-CNTs

## Conclusion

In summary, we have developed two novel synthetic routes of iron-based composite catalysts with highly dispersed iron nanoparticles, well-distributed promoters, weak metal-support interaction and high amount of defects on support. They are more active, selective and stable towards FTO reaction than traditionally synthetic iron-based catalysts. The insights revealed here might open a new avenue for the design and fabrication of iron-based FTO catalyst by changing the introduction method of promoters and iron species.

## Acknowledgments

This work was supported by the Natural Science Foundation of China (21306046) and the 111 Project of Ministry of Education of China (B08021).

## References

- Wang, D., Zhou, X. P., Ji, J., Duan, X. Z., Qian, G., Zhou, X. G., Yuan, W. K. (2015) Modified Carbon Nanotubes by  $\text{KMnO}_4$  Supported Iron Fischer-Tropsch Catalyst for the Direct Conversion of Syngas to Lower Olefins. *J. Mater. Chem. A*, 3, 4560.