

Reaction Mechanism and Kinetics of Iron-based Fischer-Tropsch Synthesis of Lower Olefins

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Highlights

- χ -Fe₅C₂ catalyst shows unique structural and electronic properties.
- The nature of the active sites mainly originates from the charge of the involved surface Fe atoms for the CO activation.
- A new catalytic cycle is proposed for the χ -Fe₅C₂-based FTO process.
- Addition of appropriate promoters is necessary to obtain the highly active and stable Fe-based FTO catalysts.

1. Introduction

Iron-catalyzed Fischer-Tropsch synthesis to lower olefins (FTO) is of prime scientific and industrial importance in enabling the direct conversion of CO-rich syngas derived from coal and biomass. A central prerequisite for the knowledge-based design of the iron-based Fischer-Tropsch catalyst is to understand the reaction mechanism and kinetics of FTO on the χ -Fe₅C₂ catalyst, which is suggested as the dominant active phase. However, it remains a substantial challenge to realize the catalyst rational design owing to the complex/dynamic catalyst structural nature and reaction pathways. In this work, the nature and active sites of the χ -Fe₅C₂ Fischer-Tropsch catalyst as well as why and how to introduce promoters for the FTO process were revealed from theoretical and experimental viewpoints.

2. Methods

All periodic spin-polarized DFT calculations were performed with the GGA-PBE exchange-correlation functional on χ -Fe₅C₂ surfaces using the Vienna Ab-initio Simulation Package (VASP). The atomic charge was obtained by the Bader analysis.

The unpromoted and promoted catalysts were prepared according to our previous studies.¹⁻³ The catalytic testing was carried out in a stainless steel fixed-bed reactor at 270°C, 1-2MPa with H₂/CO of 1. The outlet products were analyzed on-line using a gas chromatograph. Steady-state isotopic transient kinetic analysis (SSITKA) experiments were carried out at 543.15 K and a total pressure of 1.85 bar by switching between H₂/¹²CO/Ar and H₂/¹³CO/Kr. The isotopic reactants and products were monitored with mass spectrometry and the isotopic distribution of C₂-C₅ hydrocarbons was calculated as a linear combination of the fragmentation patterns of the corresponding isotopic products.

3. Results and discussion

Compared to the traditional monometallic Fischer-Tropsch catalyst, the χ -Fe₅C₂ catalyst exhibits remarkably different structural and electronic properties. On this catalyst, the thermodynamically stable and terrace-like (510) and (021) surfaces were predicted to have large percentage among the exposed crystal facets.⁴ These terrace-like surfaces show not only preferential CO adsorption, but also lower overall CO activation barrier compared to the step-like χ -Fe₅C₂ (001) and (100) surfaces, suggesting unique CO activation behaviors. In order to understand such unique behaviors, the nature of the active sites was further explored. The charge of the involved surface Fe atoms for the CO activation, mainly determined by the (sub)-surface carbon of the χ -Fe₅C₂ catalyst, is discriminated as a good descriptor for the facet-dependent CO activation. This simple and efficient descriptor can be extended to quantitatively describe the CO activation on the χ -Fe₅C₂ catalyst with more complex surface properties involving K promoter, non-stoichiometric termination and/or carbon vacancy as shown in Figure 1a.

Considering the existence of the surface carbon atoms of the χ -Fe₅C₂ catalyst, we employed SSITKA to further understand the role of the surface carbon for the FTO. The isotopic distribution of C₃H₆ intermediates over time on stream during the switching between H₂/¹²CO/Ar and H₂/¹³CO/Kr suggests that the surface C atoms are involved in the FTO reaction and always locate at the end of the carbon chain of the lower olefins. The further DFT calculations on the mechanism of chain growth, chain termination and the site regeneration validated the new catalytic cycle for the χ -Fe₅C₂-based FTO process as shown in Figure 1b.

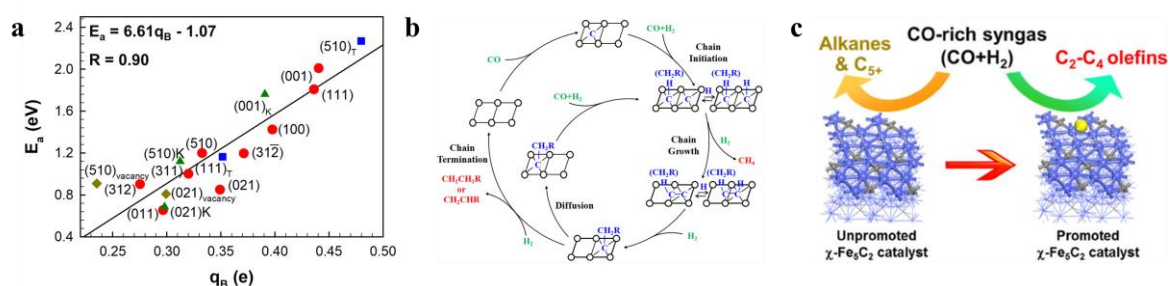


Figure 1. (a) Trends in the direct CO dissociation barrier (E_a) as a function of the average Bader charge (q_B) of the involved surface Fe atoms for the CO activation. (b) Schematic diagram of catalytic cycle for the χ -Fe₅C₂-based FTO process. (c) Schematic diagram for the effects of promoter on the product distribution from direct conversion of CO-rich syngas on χ -Fe₅C₂ catalyst.

For the selectivity, it is not expected that χ -Fe₅C₂ catalyst shows both the unfavorable formation of methane and lower olefins. Based on the kinetic analysis, the effective barrier difference between CH₄ formation and C₁-C₁ coupling (ΔE_{eff}) of the χ -Fe₅C₂(510) surface are found to be the highest among several Fischer-Tropsch catalysts and thus the lowest selectivity of CH₄.⁵ The further exploration of the mechanism of chain growth and chain termination showed that the χ -Fe₅C₂ catalyst is favorable for the formation of long-chain hydrocarbons instead of the lower olefins. To address these issues, effects of promoters and how to be introduced are systematically probed. The redox reaction between strong oxidants and carbon support followed by thermal treatments was demonstrated an effective method to promote the micro-mixing of Fe and promoters and their distributions on the support surfaces and the resultant catalysts exhibit higher activity, lower olefins selectivity and stability.¹⁻³ Therefore, it is necessary to introduce appropriate promoters for the rational design of highly active and stable Fe-based FTO catalysts (Figure 1c).

4. Conclusions

In summary, we have theoretically and experimentally elucidated reaction mechanism and kinetic characteristics of iron-based Fischer-Tropsch synthesis of lower olefins. On the χ -Fe₅C₂ catalyst, the nature of the active sites mainly originates from the difference in the charge of the involved surface Fe atoms for the CO activation, and the surface C atoms are found to be involved in the FTO reaction, which always locate at the end of the carbon chain of the lower olefins. The χ -Fe₅C₂ catalyst is unfavorable for the formation of lower olefins, and introduction of appropriate promoters is necessary to obtain highly active and stable Fe-based FTO catalysts.

References

- [1] D. Wang, X.P. Zhou, J. Ji, X.Z. Duan, G. Qian, X.G. Zhou, D. Chen, W.K. Yuan, J. Mater. Chem. A 3 (2015) 4560-4567.
- [2] D. Wang, J. Ji, B.X. Chen, W.Y. Chen, G. Qian, X.Z. Duan, X.G. Zhou, A. Holmen, D. Chen, J. C. Walmsley, AIChE J. 63 (2017) 154-161.
- [3] X.Z. Duan, D. Wang, G. Qian, J. C. Walmsley, A. Holmen, D. Chen, X.G. Zhou, J. Energy Chem. 25 (2016) 311-317.
- [4] T.H. Pham, X.Z. Duan, G. Qian, X.G. Zhou, D. Chen, J. Phys. Chem. C 118 (2014) 10170-10176.
- [5] T.H. Pham, Y.Y. Qi, J. Yang, X.Z. Duan, G. Qian, X.G. Zhou, D. Chen, W.K. Yuan, ACS Catal. 5 (2015) 2203-2208.

Keywords

Fischer-Tropsch synthesis; χ -Fe₅C₂ catalyst; lower olefins; reaction mechanism.