MECHANISTIC INSIGHTS INTO FACET-DEPENDENT CH_4 FORMATION OF η-Fe_2C FISCHER-TROPSCH CATALYST

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Abstract

Spin-polarized density functional theory calculations have been performed to investigate the mechanism of CH_4 formation on a η-Fe_2C Fischer-Tropsch catalyst. Facets exposed and their ratio of the catalyst can be obtained by Wulff construction based on the surface energies of 13 facets observed by XRD patterns. The (011) and (110) surfaces are predicted as the dominant exposed facets. Their CH_4 formation pathways by surface C hydrogenation were comparatively studied. The results show that the surface C hydrogenation highly depends on the local environment of surface carbon and electronic property of iron atoms, and the (011) surface is more active towards CH_4 formation. A comparison of CH_4 formation between η-Fe_2C and other Fischer-Tropsch catalysts was carried out. Finally, the nature of iron Fischer-Tropsch catalyst active phases and sites was proposed.

Introduction

Conversion of coal-, biomass- or natural gas-derived syngas via Fischer-Tropsch synthesis (FTS) has recently gained a renewed interest as a non-petroleum, promising alternative route to produce clean fuels and value-added chemicals. Compared to commonly used Ru- and Co-based catalysts, Fe-based catalysts are more attractive not only for the lower cost and methanation activity, but also for the higher tolerance to the contaminants and water-gas shift activity enabling the direct use of CO-rich syngas without purification and H_2/CO ratio adjustment. The working iron catalysts exhibit the complex phase composition and transformation, and η-Fe_2C is suggested as the active phase of iron-based catalysts for low-temperature FTS. Taking into account that methane is the least desired product, mechanistic studies on how to reduce its selectivity or even suppress its formation are highly encouraged for designing and optimizing FTS catalysts. The purpose of this study is to unravel the mechanism of CH_4 formation on a η-Fe_2C Fischer-Tropsch catalyst. All calculations were performed by using the periodic spin-polarized DFT within the VASP.

Results and discussion

The surface energies of 13 facets observed from the XRD patterns were first calculated, and then the corresponding equilibrium shape was obtained by Wulff construction. As shown in Figure 1a, the (011) surface is predicted to have the largest percentage among the exposed facets, followed by the (110) surface. Top and side views of these two surfaces are shown in Figure 1b. On these two surfaces, CH_4 formation pathways by surface C hydrogenation were comparatively studies. The effective barrier of CH_4 formation ($E_{eff,CH4}$) was used as a descriptor to evaluate the reaction rate of CH_4 formation, which is defined as the energy difference between the highest transition state (TS)

and the most stable C1 species. The results show that the effective barrier of CH_4 formation on the (011) surface is 1.66 eV, while that on the (110) surface is 3.21 eV. This strongly indicates that the (011) surface is more active towards CH_4 formation. Moreover, systematic analyses of the geometric and electronic properties for the two cases present that the surface C hydrogenation highly depends on the local environment of surface carbon and electronic property of iron atoms.
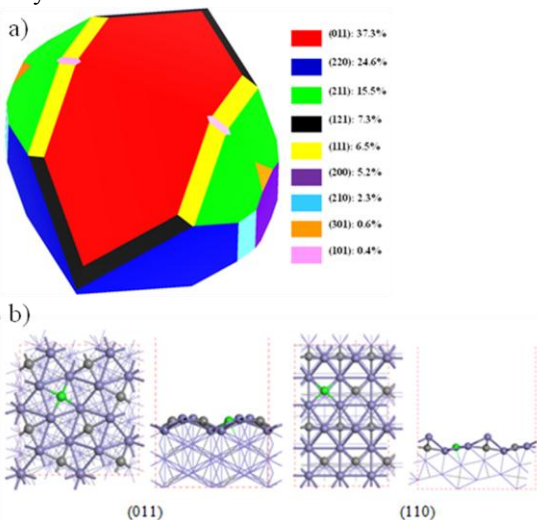

Figure 1. a): Equilibrium shape of η-Fe$_2$C obtained by Wulff construction. b): Top (left) and side (right) views of (011) and (110) surfaces (Blue: Fe atoms; gray: C atoms; green: C atoms involved in reactions).

Table 1. Effective barriers of CH_4 formation on Rh, Ru, Co, Fe and their carbide surfaces

Surface		$E_{eff,CH4}$	ref
η-Fe$_2$C	**011**	**1.66**	**This work**
	110	**3.21**	
χ-Fe$_5$C$_2$	100	1.89	Cheng et al., 2010
	510	2.43	Pham, 2015
	210	2.13	Cheng et al., 2009
Fe	100	2.13	Govender et al., 2012 and 2013
Stepped Co$_2$C	001	1.27	Cheng et al., 2010
Stepped Co	0001	1.31	
Rh	211	1.23	Cheng et al., 2009
Stepped Ru	0001	1.44	

Table 1 gives a comparison of $E_{eff,CH4}$ between η-Fe$_2$C and other reported Fischer-Tropsch catalysts (i.e., Rh, Ru, Co, Fe and their carbides). It can be clearly seen that in comparison to iron and χ-Fe$_5$C$_2$ catalysts, the η-Fe$_2$C(110) surface exhibits the lowest effective barrier of CH_4 formation and thus the highest CH_4 selectivity. This suggests that this surface is more active for CH_4 formation. Moreover, this surface shows higher effective barrier of CH_4 formation and thus lower CH_4 selectivity than Ru, Rh, Co and Co$_2$C surfaces. This is in good agreement with previous experimental results. All of these results reveal that manipulating the crystal phases and facets of iron catalyst could be an effective method to tune FTS selectivity, which would shed new light on preparing highly selective iron-based FTS catalyst by the well-defined preparation method.

Conclusion

In summary, we have employed spin-polarized density functional theory calculations to investigate the mechanism of CH_4 formation on a η-Fe$_2$C Fischer-Tropsch catalyst. On the basis of the surface energies of 13 facets observed by XRD patterns, the facets exposed and their ratio were determined by Wulff construction. The (011) and (110) surfaces are predicted as the dominant exposed facets. Comparative studies of CH_4 formation by surface C hydrogenation between the (011) and (110) suggest that the surface C hydrogenation highly depends on the local environment of surface carbon and electronic property of iron atoms, and the (011) surface is more active towards CH_4 formation. Systematic analyses of CH_4 formation between η-Fe$_2$C and other Fischer-Tropsch catalysts were carried out, and then the nature of iron Fischer-Tropsch catalyst active phases and sites was proposed.

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