TOWARDS FUNDAMENTALS OF χ-Fe$_5$C$_2$-CATALYZED FISCHER-TROPSCH SYNTHESIS

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Abstract

Spin-polarized density functional theory calculations have been performed to investigate the mechanism of Fischer-Tropsch synthesis (FTS) on a χ-Fe$_5$C$_2$ catalyst, regarded as the dominant active phase of iron-based FTS catalysts. Facets exposed and their ratio of the catalyst can be obtained by Wulff construction on the basis of its orientation-dependent surface free energies. High miller index, thermodynamically stable terraced-like (510) surface is predicted as the dominant exposed facet. On this surface, systematic analyses of adsorption and activation properties of CO suggest direct CO dissociation as the preferred activation pathway. C-C coupling is shown to be much more favorable in comparison to CH$_4$ formation. Both C+CR and CH+CR (R≡H or alkyl) are discriminated as the favored pathways, which follow the carbide mechanism. Higher effective barrier of chain termination by C$_{2+}$ hydrogenation than C-C coupling indicates the favorable formation of long-chain hydrocarbons. Finally, a plausible catalytic cycle of FTS on this surface is proposed.

Keywords

χ-Fe$_5$C$_2$ catalyst, CO activation, Fischer-Tropsch synthesis mechanism

Introduction

Iron-based Fischer-Tropsch synthesis (FTS) is a sustainable and economically viable process in enabling direct conversion of biomass- and coal-derived syngas to clean fuels and value-added chemicals. Its fundamental understanding is, however, rather limited owing to the complex phase composition and transformation of working iron catalysts in comparison with other FTS catalysts (e.g., Ru and Co). Until recently it has been demonstrated by integrated theoretical and multiple advanced in-/ex-situ studies that among various iron species, Hägg iron carbide (χ-Fe$_5$C$_2$) is dominant active phase responsible for the high FTS activity. The objective of this study is to elucidate the mechanism of χ-Fe$_5$C$_2$-catalyzed Fischer-Tropsch synthesis by spin-polarized DFT calculations. All of the periodic spin-polarized calculations were performed at the density function theory (DFT) level within the Vienna Ab-initio Simulation Package (VASP).

Results and discussion

Surface energies of 11 facets of χ-Fe$_5$C$_2$ observed from the XRD patterns were first calculated, and then the corresponding equilibrium shape was obtained by Wulff construction. The thermodynamically stable (510) surface was predicted to have the largest percentage among the exposed crystal facets. Subsequently, two kinds of CO activation mechanisms (i.e., direct and H-assisted CO dissociation) and the corresponding six kinds of CO activation pathways on χ-Fe$_5$C$_2$ (510) were investigated. The systematic analysis of the activation properties of CO

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suggests the direct CO dissociation as the preferred activation pathway (Pham et al., 2014).

All possible reaction pathways including carbide and CO insertion mechanisms for CH_4 formation and C_1-C_1 coupling were further studied, aiming to discriminate the active sites and reaction mechanisms. The surface C-occupied site is inactive towards CH_4 formation, and other cases also exhibit high effective barriers, indicating unfavourable occurrence of CH_4 formation. The C+CH and CH+CH are the most likely coupling pathways in terms of the carbide mechanism. Furthermore, in order to quantify FTS selectivity between χ-Fe_5C_2(510) and other catalysts, the effective barrier difference between CH_4 formation and C_1-C_1 coupling (i.e., ΔE_{eff}) was used as a descriptor. As shown in Table 1, FTS selectivity is highly sensitive to the crystal phase and facet of catalyst, and the χ-Fe_5C_2 (510) surface exhibits the highest ΔE_{eff} and thus the lowest selectivity of CH_4 as well as the highest selectivity of C_{2+} (Pham et al., 2015).

Table 1. Effective barriers (eV) of CH_4 formation and C_1-C_1 coupling and their barrier differences on Rh, Ru, Co, Fe, and their carbide surfaces.

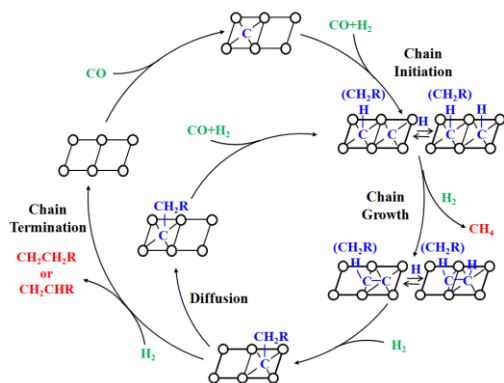| Surface	$E_{eff,CH4}$	$E_{eff,C1-C1}$	ΔE_{eff}	ref
Stepped Co_2C (001)	1.27	2.59	-1.32	Cheng et al., 2010
Stepped Co (0001)	1.31	1.55	-0.24	
χ-Fe_5C_2 (100)	1.89	1.94	-0.05	
Rh (211)	1.23	1.68	-0.45	Cheng et al., 2009
Fe (210)	2.13	2.19	-0.06	
Stepped Ru (0001)	1.44	1.34	0.1	
Fe(100)	2.13	1.92	0.21	Govender et al., 2012 and 2013
χ-Fe_5C_2 (510)	**2.39**	**1.66**	**0.73**	**This work**

Figure 1: Schematic diagram for FTS catalytic cycle of C species on χ-Fe_5C_2(510) surface.

In addition, the mechanism of chain growth and chain termination was also studied. It was found that the chain growth obeys carbide mechanism, and the most likely mechanism of C-C coupling involves the recombination of adsorbed C/CH and CR (R=H or CH_3) followed by the hydrogenation of C_β. The subsequent hydrogenation of C_α and elimination of β-hydride would result in the chain termination (i.e., the formation of alkane or alkene). Furthermore, the regeneration of active sites (i.e., the site regeneration), undergoing a synchronized pathway for CO dissociation and C-C coupling, was systematically investigated. The CO dissociation on the CR adsorbed surfaces show similar barrier compared to that on the clean surface. Finally, the plausible mechanism of hydrocarbon formation from syngas was proposed and shown in Figure1.

Conclusion

In summary, we have theoretically elucidated the mechanism of χ-Fe_5C_2-catalyzed Fischer-Tropsch synthesis. High miller index, thermodynamically stable terraced-like (510) surface is predicted as the dominant exposed facet. On this surface, direct CO dissociation mechanism is suggested as the preferred activation pathway, and C_1-C_1 coupling are significantly enhanced in comparison to CH_4 formation. The C+CR and CH+CR (R≡H or alkyl) are the mostly likely coupling pathways in terms of the carbide mechanism. Higher effective barrier of chain termination by C_{2+} hydrogenation than C-C coupling indicates the favorable formation of long-chain hydrocarbons. Moreover, a plausible FTS catalytic cycle of carbon species is also proposed. The insights revealed here might guide rational design and optimization of χ-Fe_5C_2 FTS catalysts.

Acknowledgments

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