First principle study of chain termination reactions during Fischer-Tropsch Synthesis on χ-Fe$_5$C$_2$(010)

José G. Rivera de la Cruz, Maarten K. Sabbe*, Marie-Françoise Reyniers

Laboratory for Chemical Technology, Ghent University, Technologiepark 914, B-9052 Ghent, Belgium

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ABSTRACT

Elementary steps for the chain termination reactions in the carbide mechanism of Fischer-Tropsch Synthesis (FTS) were studied on χ-Fe$_5$C$_2$(010), which is commonly accepted as an active phase for Fischer-Tropsch Synthesis (FTS). Rate coefficients for the *n*-alkyl hydrogenation and *n*-alkyl dehydrogenation were calculated as function of the chain length using spin-polarized density functional theory calculations with the vdW-DF2 functional. The kinetic parameters are independent of the hydrocarbon chain length from a chain length of three carbon atoms onwards for *n*-alkyl hydrogenation and for *n*-alkyl β-dehydrogenation. For small *n*-alkyl species the chain length dependence is the result of structural differences of the transition states and differences in bond strength of reactants and products. The dehydrogenation of *n*-alkyls leads to 1-alkenes that are strongly adsorbed to the catalyst surface.

1. Introduction

In Fischer-Tropsch Synthesis, the CO/H$_2$ mixture (syngas) is catalytically converted into a wide range of products such as hydrocarbons and oxygenated compounds. These products can subsequently be processed into clean fuels and high quality lubricants. Syngas can be generated from different sources, such as natural gas reforming or coal and biomass gasification, making FTS an alternative for crude oil [1–3].

Industrially, Co and Fe are used as catalyst for FTS, but the low cost of Fe as well as the high availability of the metal have increased the interest in Fe-based catalysts [4]. Moreover, compared with Co, Fe-based catalysts possess a higher resistance to contaminants, a high selectivity towards alkenes, a high activity for the water-gas-shift reaction and a low methanation activity when the process is operated at low temperatures (approximately 500 K). Furthermore, Fe based catalysts can be employed for the conversion of syngas with a lower H$_2$/CO ratio than the stoichiometric ratio. These low H$_2$/CO ratios are typically obtained when biomass or coal are used as feedstock in syngas production [1,5].

Fe-based catalysts consist of a mixture of different iron oxide phases that require an activation process in order to be active for FTS. During the activation process, in which Fe-based catalysts are typically treated with CO and H$_2$, the catalyst undergoes several transformations, leading to a mixture of metal, oxide and carbide phases, which composition is determined by the activation treatment conditions [1,5–12].

Among the different phases present in the activated catalyst,

Transmission Electronic Microscopy (TEM), X-ray diffraction (XRD), and Mössbauer spectroscopy suggest that iron carbides are the principal active phases for FTS [8–10,12–17]. Under FTS conditions, theoretical and experimental research has identified the χ-Fe$_5$C$_2$, Fe$_7$C$_3$, θ-Fe$_3$C, ϵ-Fe$_2$C and η-Fe$_2$C phases [1,6,9,10,13,15,18–24]. Among all the iron carbide phases present under FTS conditions, the χ-Fe$_5$C$_2$ phase (Hägg carbide) is generally accepted to be the main active phase [9,15,25,26].

Since the first FTS reaction mechanism was proposed by Fischer and Tropsch [27,28] the actual FTS mechanism has been a matter of debate. As a result, several mechanisms have been proposed, such as the carbide mechanism, the enol mechanism or the CO insertion mechanisms. In general, FTS reaction mechanisms can be described as successive elementary steps, as summarized by de Smit et al. [1] who reports three main families: chain initiation, chain propagation and chain termination reactions.

Particularly for iron carbides, most studies are devoted to the initiation step (CO and H$_2$ activation), resulting in different initiation mechanisms depending on the composition and morphology of the studied surface [18,19,21,22,26,29–37]. For instance, Li-Juan et al. [34] reported in a DFT study on θ-Fe$_3$C(100) the formation of C$_s$CO species to be the most favourable path for CO activation, with C$_s$ representing a surface carbon atom, whereas Ozbek et al. [33] proposed the formation of HCO species during the activation of CO on χ-Fe$_5$C$_2$(001).

Despite the importance of chain termination reactions in FTS there is a lack of fundamental studies about these elementary steps,

Nomenclature

Acronyms

DFT	Density Functional Theory
FTS	Fischer-Tropsch Synthesis
HO	Harmonic Oscillator
MEP	Minimum Energy Path
NEB	Nudged Elastic Band
PAW	Projector Augmented Wave
Syngas	synthesis gas
TEM	Transmission Electronic Microscopy
TS	Transition State
VASP	Vienna Ab initio Simulation Package
vdW	van der Waals
vdW-DF2	Langreth and Lundqvist exchange and correlation functional
XRD	X-ray diffraction

Greek symbols

π	type of bond
σ	type of bond
θ_*	fractional coverage of surface free sites
θ_{H}	fractional coverage of surface H
$\theta_{C_nH_{2n+1}}$	fractional coverage of surface C_nH_{2n+1}
$\theta_{C_nH_{2n+2}}$	fractional coverage of surface C_nH_{2n+2}
$\theta_{C_nH_{2n}}$	fractional coverage of surface C_nH_{2n}

Symbols

$\Delta H^{\ddagger}$	activation enthalpy, kJ mol^{-1}

$\Delta S^{\ddagger}$	activation entropy, J mol^{-1} K^{-1}
$\Delta_r H$	reaction enthalpy, kJ mol^{-1}
$\Delta_r S$	reaction entropy, J mol^{-1} K^{-1}
$\angle_{ABC}$	angle between atoms A, B and C, °
A_{for}	pre-exponential factor for forward reaction, s^{-1}
A_{rev}	pre-exponential factor for reverse reaction, s^{-1}
d_{A-B}	Distance between atoms A and B, Å
$E_{a_{for}}$	activation energy for forward reaction, kJ mol^{-1}
$E_{a_{rev}}$	activation energy for reverse reaction, kJ mol^{-1}
E_a	activation energy, kJ mol^{-1}
F	Hertz-Knudsen molecular flux, s^{-1}
h	Planck constant, J s
k	rate coefficient, s^{-1}
k_B	Boltzmann constant, J/K
k_{ads}	adsorption rate coefficient, bar^{-1} s^{-1}
k_{des}	desorption rate coefficient, bar^{-1} s^{-1}
K_{eq}	equilibrium coefficient
k_{for}	rate coefficient for forward reaction, s^{-1}
k_{rev}	rate coefficient for reverse reaction, s^{-1}
m	mass of adsorbate, kg
N	surface density of active sites, m^{-2}
p	pressure, bar
R	gas constant, J/K mol
r	rate of reaction, s^{-1}
s_0	initial sticking probability
T	temperature, K
n	n-alkyl chain length

particularly for long hydrocarbon chains [6,26,35], which are the most desired FTS products.

According to the most generally accepted FTS mechanism *i.e.*, the carbide mechanism, the chain termination reactions consist of hydrogenation and β-dehydrogenation of *n*-alkyls adsorbed on the catalyst surface, resulting in *n*-alkane and 1-alkene formation, respectively. Hence, understanding these elementary steps as well as the adsorption/readsorption of products can provide more insight in the formation of the final products of FTS.

Therefore, this work studies the hydrogenation and β-dehydrogenation of *n*-alkyls coupled with the desorption of 1-alkenes and *n*-alkanes as a function of the chain length, following the carbide mechanism.

2. Methods and models

2.1. Electronic structure calculations

Periodic Density Functional Theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP 5.3.3) [38–41], to calculate geometries and electronic energies at 0 K. Exchange and correlation energies were calculated using the vdW-DF2 functional of Langreth and Lundqvist et al. implemented in VASP by Klimeš et al. [42–45]. This functional is capable to describe long-range interactions such as van der Waals (vdW) interactions. In the context of FTS, the vdW-DF2 functional has shown to reliably predict physisorption energies of *n*-alkanes on different iron carbides phases (χ-Fe$_5$C$_2$, Fe$_7$C$_3$, θ-Fe$_3$C and η-Fe$_2$C) which is commonly underestimated or not accounted for PBE functionals [46]. Moreover, the vdW-DF2 has been reported to describe of CO adsorption on hcp-Co(0001) well [47].

Plane-wave basis sets via the Projector Augmented Wave method

(PAW) [48,49] describe the wave function close to the nuclei. The wave function is expanded in terms of plane-wave basis sets with an energy cutoff of 400 eV. Due to the magnetic properties of the system related to the presence of Fe atoms, spin polarization was included. Brillouin-zone integration for slab calculations was done on a 5 × 5 ×1 Monkhorst-pack grid [50]. Gas phase calculations were carried out in a 20 Å × 20 Å × 20 Å unit cell considering only the Γ point. To describe the partial occupancies close to the Fermi level, the first-order Methfessel Paxton method was applied with a smearing width of 0.01 eV. The electronic energy convergence was set to 1×10^{-6} eV. The geometry optimization was carried out until the maximum forces on the atoms were lower than 1.5×10^{-2} eV Å^{-1}. Those criteria are required in order to have strictly optimized geometries, which allow to perform reliable frequency analyses. Unit cells were repeated in three directions to create a periodic surface model in order to simulate the catalyst surface.

A vacuum layer of 20 Å was included in the axial direction, coupled with an artificial dipole layer, to avoid interactions between periodic images [51]. For geometry relaxations, only the atoms of the upper half of the slab were allowed to relax, together with the adsorbed species; the lower half of the slab remained fixed at its corresponding bulk position (the fixed atoms are indicated in Fig. S1 of the Supplementary Data).

The bulk geometry, imposed on the bottom layers, is obtained by minimizing the electronic energy of the bulk unit cell as function of the cell volume, using the same computational settings but using a 5 × 5 ×5 Monkhorst-pack grid [50].

Once that the optimized geometries of reactants and products are obtained, a preliminary Minimum Energy Path (MEP) between them is calculated (using very coarse convergence criteria) with the Nudged Elastic Band (NEB) method [52,53], which creates a series of images