



Adsorption energy-driven carbon number-dependent olefin to paraffin ratio in cobalt-catalyzed Fischer-Tropsch synthesis



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ABSTRACT

The factor dominating olefin to paraffin ratio in cobalt-catalyzed Fischer-Tropsch synthesis has been identified via experimental kinetic studies and theoretical calculations including the van der Waals interaction between the adsorbates and Co surfaces. The olefin to paraffin ratio for each carbon number is expressed as a function of adsorption energies of olefin and activation energies of hydrogenation steps. Density functional theory calculations on Co (0001) surface were performed to provide a comprehensive fundamental insight for the chemistry governing the olefin to paraffin ratio. The calculated olefin to paraffin ratio decreases with chain length except for ethylene, which agrees well with the experimental results. The differences introduced to the adsorption energies of olefin by van der Waals functional are correlated with d-band center changes of the Co surface. The carbon number dependent adsorption energies of olefin, rather than the activation energies of their hydrogenation reactions, are the driven force for the carbon number dependent olefin to paraffin ratio. The insights may delineate a new blueprint for the rational design of catalysts with enhanced olefin to paraffin ratio.

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1. Introduction

Fischer-Tropsch synthesis (FTS) is an attractive route to convert syngas derived from coal, natural gas and biomass, which plays an important role in the industrial production of valuable chemicals and clean liquid fuels. Olefins, as important feedstocks in the chemical and petrochemical industry, are the primary product of FT reaction. Sustainable production of olefins through syngas conversion via FTS, could be a promising practical approach to meet the increasing demand for the feedstock [1]. Cobalt, featuring high carbon utilization, high selectivity to long-chain paraffins, better stability [2–7], is a promising catalyst for Fischer-Tropsch to light olefins [8]. It is of particular interest to gain a better fundamental understanding of olefin and paraffin formation in FTS. In addition, the light hydrocarbons are often deviated from Anderson-Schulz-Flory (ASF) product distribution, and a full understanding of the origin of its deviation is still missing [9,10].

Traditional kinetic studies e.g. macro-kinetics, treating the catalyst activity as a function of easily measured macroscopic quantities and aiming at providing a better understanding of reaction pathways, are useful for various applications e.g. reactor design.

They are inefficient to discriminate different reaction mechanisms since it treats the whole reaction as a black box and various kinetic expressions may fit data equally well. In situ techniques may assist to identify the intermediate and establish the nature of reaction mechanism, but it is not facile for discriminating the complex reaction mechanism of the FTS reaction involving a large number of species and elementary steps. First-principles modeling, a key contributor in modern heterogeneous catalysis research, can achieve the electronic, structural and energetic characterization of every surface species and each elementary step, and be employed to understand the reaction mechanism giving rise to catalytic activity and selectivity at a molecular level. In this study, kinetic analyses based on experimental results and first-principles modeling were developed to explore the underlying nature of carbon number-dependent olefin to paraffin ratio.

The adsorption/desorption of hydrocarbons on metallic surfaces is generally of fundamental and applied interest, in view of its importance in understanding catalytic reactions in the chemical industry [11–13]. For the FTS process, the desorption of α -olefins (to form primary olefin) as well as re-adsorption of primary formed α -olefins (to undergo further reactions) is crucial step. The accurate description of the bonding between olefins and metal surface is a prerequisite for the investigation of the origin for olefin selectivity to achieve the rational design of catalyst with better

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olefin yield [14]. The extensive exploration of the adsorption characteristics via characterization techniques including low energy electron diffraction (LEED) [15], ultraviolet photoemission spectroscopy (UPS) [16,17], and X-ray spectroscopy (XPS) [15,18], thermal desorption spectroscopy (TDS) [15], and microcalorimetric adsorption [19] has been performed, but the exact adsorption heat is difficult to measure owing to the occurrence of the reaction involving ethylene (e.g. decomposition) during the adsorption process. In addition, the investigation is hampered by the complexity of the cobalt crystallographic structures (i.e. the hexagonal close-packed (HCP) phase and the face-centered cubic (FCC) phase) and surface dynamic self-organization during the reaction [20]. Ab initio calculations serve as a versatile tool for the fundamental investigation of the adsorption characteristics at a molecular level. A DFT study of olefin selectivity has demonstrated that the Van de Waals (vdW) interaction between adsorbed olefin and metal is an important factor determining the olefin to paraffin ratio [14]. However, the functional used could not efficiently incorporate convoluted bonding between organic compounds and metals, so the vdW interaction was evaluated based on empirical values. Recent developments in accurate and efficient vdW-inclusive DFT approach [21,22] could provide new insights into the carbon number-dependent olefin to paraffin ratio and thus a vdW-inclusive functional was used to take into account the effect of Van de Waals interaction herein.

Metallic cobalt is normally dispersed on supports in order to maximize its exposure to gaseous reactants and enhance stability. Al₂O₃ is one of the most used supports for cobalt FT catalysts. The C₅₊ selectivity of α -Al₂O₃ based catalysts was higher than the selectivity of the γ -Al₂O₃ based catalysts at all particle sizes [23]. It was found that the effect of water on the olefin distribution can be minimized on large particles [24]. Thus, 20 wt% Co/ α -Al₂O₃ with large-sized cobalt were employed in the experimental studies. Terrace surfaces predominate over large particle size according to the model of Van Hardeveld and Hartog [25]. Moreover, it is suggested that terrace is the active site for chain growth as reported in recent review paper of Niemantsverdriet's group [26]. The chain growth intermediates are the starting point for olefin and paraffin formation. Besides, scanning tunneling microscope experiments observed that long chain products form on terraces [27]. Based on all above, Co (0001) is selected as a model to perform calculations and comparisons with our experiments.

Herein, we performed a combined experimental kinetic study and vdW corrected DFT calculations to gain a better understanding of the mechanism for chain termination in F-T synthesis leading to olefin and paraffin formation. Bayesian Error Estimation Functional with van der Waals Correlation (BEEF-vdW) functional [28], which was specifically designed to address vdW interaction reasonably well while maintaining an accurate description of adsorption energies of molecules on surfaces [29], was used in DFT investigation of olefin adsorption and hydrogenation of C₂-C₅ hydrocarbons. Changes in adsorption energies introduced by vdW interaction were further analyzed and correlated with the changes in electronic properties of the Co surface. Furthermore, DFT-based kinetic analysis was carried out, which predicts similar carbon number dependence of the olefin to paraffin ratios to experimental values. The factor dominating carbon number-dependent olefin/paraffin ratio is obtained by kinetic analysis and sensitivity analysis.

2. Methods

2.1. Experimental methods

The experiments were carried out using a fixed-bed quartz reactor (4 mm i.d.) over 20 wt% Co supported on α -Al₂O₃ catalysts at 483 K, 1.85 bar and H₂/CO = 2–4. The detailed preparation method and characterization methods of the catalyst have been reported previously [30]. A summary of the catalyst properties is given in Table 1. The catalyst was first reduced in 10 Nml/min H₂ at 623 K and then cooled down to 483 K. H₂/CO/Ar (6/3/41 Nml/min for H₂/CO = 2, 15/4.5/30.5 Nml/min for H₂/CO = 3.3, 15/3.7/31.3 Nml/min for H₂/CO = 4.1) mixture was introduced and the total pressure was adjusted to 1.85 bar. Once the steady state was achieved after 6 h on stream, the catalytic performance was evaluated. The concentrations of H₂, CO, Ar and C₁-C₆ hydrocarbons were analyzed with a GC-MS (Agilent GC7890B – MSD5977A) equipped with TCD, FID and MSD detectors, which have been reported previously [31].

2.2. Computational details

All periodical DFT calculations were carried out on Co (0001) using the Vienna ab initio simulation package (VASP) [33–35] with the BEEF-vdW functional [28]. BEEF-vdW works most satisfactorily among the selected functional since it has the smallest mean absolute error by comparing results from different functionals such as BEEF-vdW, RPBE, and PBE with a database of 30 adsorption reaction energies [36]. The electrons-ion interaction is described by the projector augmented wave (PAW) method [37]. The calculations were performed with a cutoff energy of 500 eV and a first-order Methfessel-Paxton scheme with a smearing width of 0.2 eV. Spin polarization is included in the calculations. Brillouin-zone integration for the slab calculations is done on 5 × 5 × 1 Monkhorst-Pack grid. A (3 × 3) super cell structure is modeled with five layers and the bottom two layers are fixed during the optimizations. To keep the distance between the top of adsorbate and the bottom layer in the above unit cell at around 10 Å, the vacuum changes with the carbon number. The size of surface and vacuum region is validated to be enough as shown in Table S1, Supporting Information (SI). The nudged elastic band method is employed to search initial transition states, which are subsequently optimized by the dimer method [38]. All the optimizations are converged with a force criterion of 0.01 eV/Å. The vibrational frequencies were calculated to confirm the transition states with one negative mode corresponds to the desired reaction coordinates.

Adsorption energies of surface species and activation energies of elementary steps were calculated as shown in Eqs. (1) and (2):

$$E_{ads} = E_{A+slab} - E_A - E_{slab} \quad (1)$$

$$E_a = E_{TS} - E_{IS} \quad (2)$$

where E_A is the total energy of molecule A in the gas phase, E_{slab} is the total energy of the slab, E_{A+slab} is the minimum total energy of the surface species on the slab, E_a is the activation energy of elementary step, E_{TS} is the total energy of the transition state, and E_{IS} is the total energy of the reactants. Units of energies are eV.

Table 1
Dispersion and BET surface area of the supported cobalt catalyst.

Catalyst	Co [%]	Dispersion [%]	BET surface area [m ² /g]	Co particle size [nm] ^a
Co/ α -Al ₂ O ₃	20	2.1	9	45.7

^a H₂ adsorption has been carried out at 313 K and cobalt metal particle size was calculated from H₂ chemisorption using the formula $d(\text{Co}) = 96/D$ [32], where D is dispersion in %.

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