



Research paper

A density functional theory based elementary reaction mechanism for early steps of Fischer-Tropsch synthesis over cobalt catalyst. 2. Microkinetic modeling of liquid-phase vs. gaseous-phase process

Alireza Asiaee, Kenneth M. Benjamin*

Department of Chemical and Biological Engineering, South Dakota School of Mines and Technology, 501 E. Saint Joseph St., Rapid City, SD 57701, USA

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ABSTRACT

The process of Fischer-Tropsch synthesis (FTS) is conducted commercially under both gaseous- and liquid-phase conditions. For decades, numerous studies have been performed to better understand this heterogeneous catalytic process, where some of them have tried to compare the reaction rates and product distributions of FTS under different phase conditions. In spite of several provided models, the actual reaction mechanisms and kinetics of important elementary steps at each phase condition are still under investigation, especially in the liquid-phase. In this work, we have utilized the generalized-gradient approximation method of density functional theory (DFT-GGA) to estimate the rate parameters of elementary reactions in liquid-phase FTS on a flat Co(0001) catalyst surface. In this regard, using the continuum-based conductor-like screening model (COSMO) for the liquid solvent environment, the activation energies and rate constants of individual reactions, suggested in an existing microkinetic model, have been calculated in the presence of n-hexane solvent at $T = 493$ K and $P = 25$ bar. The preferred reaction pathway has been discussed and the quantitative results have been compared to that of the gaseous-phase in order to find the impact of liquid solvent, as well as differences in the probable surface reactions under each phase condition. It has been found that while the carbide mechanism is the dominant mechanism of chain growth under both phase conditions, the presence of the liquid solvent enhanced the CO insertion sub-mechanism of chain growth, which can describe some of the experimental observations in FTS studies.

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1. Introduction

Fischer-Tropsch synthesis (FTS) is considered an economic way toward conversion of natural gas to more valuable hydrocarbon products [1]. Industrially, catalytic FTS processes are conducted under two different conditions of gaseous-phase in a fixed- or fluidized-bed reactor and liquid-phase in a slurry bubble column reactor. While the fixed-bed reactor is normally used to produce diesel fuel, the fluidized-bed reactor produces gasoline fraction along with high yield of methane. Both types of gaseous-phase reactors suffer from continual catalyst deactivation. On the other hand, liquid-phase FTS in a slurry bubble column reactor provides less methane production and catalyst deactivation. Unfavorably, due to low concentration of the reactants and larger diffusion barriers, the

overall reaction rates in the liquid-phase are significantly slower than those in the gaseous-phase [2].

Another classification divides FTS in two categories of high-temperature processes, operating within the range of 300–350 °C, and low-temperature processes with a temperature range of 200–240 °C. Generally, the high-temperature FTS processes operate under gaseous-phase conditions. However, the low-temperature process can be conducted under gaseous- or liquid-phase reaction conditions [3]. Among all suggested transition metal catalysts with enough activity for FTS, only the iron- and cobalt-based catalysts have the desired product distribution with affordable preparation cost for commercial production. While the iron-based catalysts can be used in both temperature ranges, the cobalt-based ones are only applicable in low-temperature FTS [4].

For decades, the product distribution of FTS has been the subject of numerous investigations [3,5–9], where some studies have tried to compare the product distribution of gaseous- and liquid-phase FTS processes under similar reaction conditions [1,2,10,11]. Based on a summary and comparison of experimental observations

* Corresponding author.

E-mail address: kenneth.benjamin@sdsmt.edu (K.M. Benjamin).

from the literature, CO conversion and selectivities of methane and other light alkanes (C₂–C₄) are higher in the gaseous-phase FTS than in liquid-phase operation. On the other hand, using the liquid solvent results in more production of mid-range hydrocarbons (C₅–C₁₁), while no particular comparison has been reported for production rates of heavy fractions (C₁₂+) and olefins [1,3,12]. Logically, because of low diffusivity in the liquid solvent, the overall reaction rates and consequently the CO conversion in the liquid-phase would be smaller than those of gaseous-phase FTS. On the other hand, in addition to preventing catalyst deactivation [1,2], the liquid-phase FTS provides several advantageous features, such as better thermal distribution and a selective condition for dissolving of products. The improved temperature control in the slurry bubble column reactor has been considered as the main reason for less production of methane [2]. Moreover, it has been discussed that the liquid-phase medium tends to dissolve the mid-range hydrocarbon products more than the light ones, resulting in less production of undesired products [3]. However, it appears that a fundamental investigation of the effect of liquid solvents on the elementary surface reaction kinetics and pathways has been neglected in the accomplished theoretical and experimental studies to date.

Generally, a better understanding of a reactive process can be achieved by studying the elementary reaction pathways. During the past two decades, several microkinetic models have been suggested for FTS [12–17]. However, the majority of the provided models were established in order to predict the gaseous-phase FTS reaction paths. In an individual study, Lozano-Blanco et al. have tried to extend their model for simulation of liquid-phase FTS in a slurry-bubble column reactor [18]. In light of the recent advances in quantum mechanics calculations and their accuracy to predict experimental catalytic results [19], several studies have used density functional theory (DFT) approaches to model the surface reactions as well as adsorption and desorption steps in the FTS reaction mechanism [16,20–23]. Despite all of the previous investigations and findings, due to the high computational cost of quantum calculations, few studies have tried to characterize and quantify the effect of liquid solvent on surface reactions in a heterogeneous catalytic process, particularly in FTS.

One of the suggested approaches for considering liquid solvent effects in quantum calculations is applying the continuum-based conductor-like screening model (COSMO), which evaluates the dielectric screening effect of the solvent. In this technique, provided by Klamt and Schüürmann [24], the liquid solvent is modeled as a homogeneous medium where the solute molecule is placed in a cavity within the dielectric continuum of permittivity, representing the solvent. Later, the COSMO theory was implemented into the DFT program DMol, where the modeling results for solvation energies showed a promising agreement with experimental values [25]. In 2009, Zuo et al. applied a COSMO-based model in order to compare the CO adsorption energies upon copper-based catalyst under two different conditions of gaseous- and liquid-phase solvent [26], where their results showed significant influence of solvent phase condition on the energy of adsorption. As a continuum-based model, COSMO calculations are much less computationally expensive than an explicit atomistic approach [such as quantum molecular dynamics or hybrid quantum and molecular mechanical (QM/MM) treatments] to modeling the solvent environment.

Assuming that the surface reactions and intermediate species would be identical under different phase conditions [18], the confirmed reaction mechanism in the preceding study is considered here [27]. This approach assumes the liquid solvent only contributes physically – i.e. through solvation – and not chemically to the FTS reaction network, meaning that the liquid solvent does not create otherwise new reaction pathways on the catalyst surface. In a FTS study by Marvast et al., the authors modeled the overall con-

version reactions by fitting the rate parameters to experimental data [28]. In their model, they combined all the hydrocarbon products beyond the light fractions (C₅⁺) into a pseudo component of C_{6.05}H_{12.36}. Hence, in the current study, all the elementary reactions are modeled using the DFT program DMol, where the liquid-phase solvent is considered by the pseudo component of n-hexane, via applying the COSMO model. (It is assumed that solvation with hexane represents solvation with any large hydrocarbon molecule environment produced by FTS.) Through comparison of reaction barriers and rate constant parameters with those of gaseous-phase, the effect of liquid solvent on FTS reaction pathways over cobalt catalyst is probed from both energetic and kinetic aspects.

2. Computational method

Similar to the preceding paper [27], the flat Co(0001) surface in the modeled unit cell contained 4 layers of $p(3 \times 3)$ cobalt atoms, representing a surface coverage of 1/9 monolayer (ML) for the adsorbed species occupying a single active site. The thickness of vacuum slab above the catalyst surface was set to 10 Å and the unit cell boundaries were periodic in all the Cartesian directions. During all calculations, the Co atoms in the bottom two layers of the catalyst slab were fixed at their initial positions (with the minimum level of energy), while the two top layers were allowed to relax. All DFT calculations were performed with the DMol3 program of BIOVIA Materials Studio [29] using the generalized-gradient approximation of Perdew and Wang (GGA-PW) [30]. Due to the ferromagnetic nature of cobalt, calculations included spin polarization. In order to reduce the computational expense, the core electrons were replaced by a single effective potential via DFT semi-core pseudopotentials (DSPP). The optimized structures of reactants and products with the minimum energy levels were found by considering the maximum energy tolerance of 1.0×10^{-5} Ha. While the tolerance for self-consistent field (SCF) convergence was set to be less than 1.0×10^{-6} Ha, the calculated maximum displacement of atoms and force deviation were less than 5.0×10^{-3} Å and 2.0×10^{-3} Ha/Å, respectively. The transition state (TS) for each reaction and its relative energy level were found using the LST/QST method [31] with the convergence criteria of 2.0×10^{-3} Ha/Å and 1.0×10^{-6} Ha for root mean square (RMS) deviations of force and SCF tolerance, respectively. However, due to the sensitivity of these calculations, not all the TS search calculations could meet the above convergence criteria. Therefore, for some of the reactions, a set of 1.0×10^{-2} Ha/Å and 1.0×10^{-5} Ha convergence values were considered for the root mean square (RMS) deviation and the SCF tolerance, respectively. To estimate the pre-exponential factor of rate constants using the calculated vibrational frequencies and moments of inertia, the geometry refining procedure and TS search calculations were followed by frequency calculations. By applying Monkhorst-Pack grids [32], the density of k-points was kept below 0.05 \AA^{-1} through all simulation runs.

As mentioned earlier, DMol calculations with the COSMO model were applied to probe the liquid-phase solvent effect. Considering n-hexane (as a pseudo-component) instead of all the hydrocarbons present in the industrial liquid-phase FTS, the dielectric value of hexane at the implemented operating condition was required for COSMO calculations. Mopsik had experimentally measured the dielectric values of hexane in the temperature range of –50 to 25 °C and pressures up to 2000 atm [33]. In another study by Straty and Goodwin, measurements at saturated liquid conditions showed that the methane dielectric values have a linear functionality with temperature up to near-critical conditions [34]. Therefore, by assuming linear variations with respect to both temperature and pressure, the dielectric value of n-hexane was estimated as 1.594 at the considered operating conditions of 220 °C (493 K) and

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