CO-insertion mechanism based kinetic model of the Fischer–Tropsch synthesis reaction over Re-promoted Co catalyst

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ABSTRACT

A detailed kinetic model of the Fischer–Tropsch synthesis (FTS) product distribution based on the CO-insertion mechanism has been derived. The model was developed using the Langmuir–Hinshelwood–Hougen–Watson approach. The intrinsic kinetic parameters were estimated using a set of data obtained in a stirred tank slurry reactor with a rhenium promoted cobalt catalyst over a range of operating conditions (T = 478, 493, 503 K; P = 1.5, 2.5 MPa; H_2/CO = 1.4, 2.1; WHSV = 1.0–22.5 NL/g_{cat}/h). Physical meaningfulness of the model and its parameters was verified. Consistent with reported measurements, model predicts that adsorbed CO is the most abundant surface species. The observed increase in the chain growth probability factor and decrease in olefin-to-paraffin ratio with increase in carbon number is explained utilizing the chain length dependent desorption of 1-olefins concept.

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1. Introduction

The interest in clean synthetic fuel production through Fischer–Tropsch synthesis (FTS) technology has been rekindled during the first decade of the 21st century due to increased global energy demands and stricter environmental regulations. Commercial processes utilize supported cobalt catalysts due to their high activity and good selectivity toward desired C_{5+} products [1].

FTS is a complex reaction that involves a large number of product species and surface intermediates. Additional difficulties include three phase operation, possible mass and heat transport resistances, catalyst deactivation, etc. All these factors have made investigations of the FTS mechanism very difficult and even now there is no consensus about the exact mechanism for this reaction. However, careful experimental studies [2–6] and recent advances in computational chemistry [7–10] identified two distinct mechanisms, i.e. carbide and CO-insertion mechanism, as the most probable ones. The carbide mechanism was originally proposed by Fischer and Tropsch [11] and modified by Brady and Petit [4]; its basic premise is that hydrocarbons are formed by hydrogenation of

metal carbide forming C_1 monomer, which is subsequently polymerized. This theory was questioned by Kummer et al. [3] whose experimental results did not support CO dissociation and metal carbide formation. This led to a series of mechanistic proposals, out of which a CO-insertion mechanism [6] could explain the formation of all typical FTS products (paraffins, olefins, and oxygenates) [12]. Recent transient kinetics experiments by Schweicher et al. [13] performed at low pressure, have provided some new evidence for this mechanism of chain growth. Their conclusion is consistent with some of the computational chemistry studies over Co catalysts that also support chain growth by CO-insertion [8,14,15]. Several useful reviews relevant to the FTS mechanism are available [7,10,12,16,17].

The selectivities of FTS products over Co-based catalyst depend on process conditions [1]. However, despite the industrial importance of this process, only few detailed product distribution models have been proposed for this catalyst [18–23]. One of the main issues these models need to deal with is accounting for deviations from the ideal Anderson–Schulz–Flory (ASF) product distribution, which include high yield of methane, low yield of ethylene and increasing chain-growth probability (α) and decreasing olefin-to-paraffin ratio (OPR) with carbon number. Anfray et al. [18] proposed a Langmuir–Hinshelwood–Hougen–Watson (LHHW) model based on the carbide mechanism and solubility enhanced readsorption of 1-olefins [24,25]. They reported a good prediction of n-paraffin rates, but a poor fit for 1-olefins. The model predicted only a minor

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Nomenclature

A_i	preexponential factor of rate constant for elementary step i
c	constant determining chain length dependence
[CO–S]	surface coverage of adsorbed CO
E_i	activation energy of elementary step i, kJ/mol
ΔE	change in 1-olefin desorption activation energy caused by weak force interactions, kJ/mol/CH$_2$ group
$E_{d,o}^n$	overall activation energy for the 1-olefin desorption step, kJ/mol
F_{obj}	multi-response objective function
H$_2$/CO	reactant feed ratio, mol/mol
ΔH_i	enthalpy of elementary step i, kJ/mol
[H–S]	surface coverage of adsorbed atomic hydrogen
k_i	reaction rate constant for elementary step i
K_i	equilibrium constant for elementary step i
N_{resp}	number of responses
N_{exp}	number of experimental balances
P	pressure, MPa
P_i	partial pressure of species i, MPa
R	universal gas constant, kJ/kmol/K
R_i	reaction rate of species i, mol/g$_{cat}$/h
[R–S]	surface coverage of growing hydrocarbon chains
S	vacant active site
T	temperature, K
TOS	time on stream, h
W	catalyst mass, g$_{cat}$
WHSV	weight hourly space velocity, NL/g$_{cat}$/h
X_{CO}	CO conversion

Greek symbols

α_0	chain growth probability for the low hydrocarbon range (double-alpha theory)
α_{inf}	chain growth probability for the high hydrocarbon range (double-alpha theory)
α_n	chain growth probability for carbon number n ($n \geq 1$)

Subscripts and superscripts

cal	calculated value
exp	experimental value
M	methane
E	ethene
n	number of carbon atoms

model derivations and resulting models were subjected to statistical and physicochemical tests. An interesting result was that the best model was based on a form of the carbide mechanism that had several similarities with the CO-insertion pathway. The chain length dependent 1-olefin desorption concept of Botes [29] was extended and included in a detailed LHHW model of FTS kinetics [23]. All equations for product formation rates were explicit, and the estimated values of kinetic parameters were physically and statistically meaningful. Also, deviations from the ASF distribution and the exponentially decreasing OPR with carbon number were predicted by the kinetic model.

In this study we focus on the application of the CO-insertion mechanism in the development of a detailed LHHW model for FTS. Deviations from ASF distribution and OPR decrease with increase in molecular weight are explained utilizing the chain length dependent 1-olefin desorption concept.

2. Experimental

The experiments were performed over a Re-promoted Co catalyst supported on alumina (25%Co/0.48%Re/Al$_2$O$_3$) using a stirred tank slurry reactor (STSR). Details on catalyst preparation, as well as other experimental procedures, can be found elsewhere [23]. A fractional factorial experimental design with two-three levels of four factors (temperature, pressure, feed ratio and gas space velocity) was used. To provide a sufficiently wide range of experimental data needed for kinetic modeling, three temperatures (478, 493 and 503 K), two pressures (1.5 and 2.5 MPa), two H$_2$/CO ratios (1.4 and 2.1) and three levels of space velocities (from 1 to 22.5 NL/g$_{cat}$/h) were chosen. An appropriate range of catalyst particle sizes (i.e. diameters of 44–90 μm) and a high STSR impeller speed (750 rpm) were selected to minimize physical transport resistances, allowing for intrinsic kinetic measurements. In total, 24 usable mass balances were collected, with atomic closures typically better than $100 \pm 4\%$. Process conditions were maintained for about 24 h and steady state samples were usually collected during the last 8 h. Because of potential issues with the accumulation of heavy products (above C$_{17}$) [30], our kinetic analyses focused only on hydrocarbons in the C$_1$–C$_{15}$ range. Species considered were C$_1$–C$_{15}$ n-paraffins and C$_2$–C$_{15}$ 1-olefins, while minor FTS products, like 2-olefins and oxygenates, were neglected. The data from these experiments were used to estimate kinetic model parameters.

3. Detailed kinetic model of FTS

Two main issues that are addressed in the development of this FTS kinetic model are those of reaction mechanism and the reason for increasing chain growth probability and decreasing olefin-to-paraffin ratio (OPR) with carbon number.

3.1. CO-insertion mechanism

Elementary steps of FTS can be grouped into few basic sets, including: (1) reactant (CO and H$_2$) adsorption; (2) CO activation (or chain initiation); (3) chain propagation; and (4) chain termination (product formation). Fig. 1 shows possible CO activation steps in the carbide (also referred to as the alkyl or methylene) and the CO-insertion mechanisms. For the classical carbide mechanism, the CO activation step consists of a direct CO dissociation (i.e. the C—O bond is severed before C is hydrogenated), whereas in the CO-insertion pathway CO is first hydrogenated and only then is the C—O bond broken to give the chain starter (CH$_3$—S). Newer modification of the carbide mechanism assumes that hydrogen assists in the C—O bond scission [8]. The primary difference between the two mechanisms is the type of species being inserted into the growing chain: CH$_x$ for

effect of 1-olefin readsorption on the product distribution, and experimentally observed increase of chain growth probability and decrease in OPR with carbon number could not be adequately explained. Visconti et al. [19] utilized a micro-kinetic approach assuming that all elementary steps are irreversible. Steady-state balances for each species were solved simultaneously with the reactor model equations; which resulted in highly implicit and complex models. Visconti et al. [19,20] also included solubility enhanced 1-olefin readsorption concept and, unlike Anfray et al. [18], a good fit of the olefin formation data was reported; however, rates and probabilities of 1-olefin readsorption were not discussed. Kwack et al. [21] model, based on [19], did not predict increasing chain growth probability with increasing carbon number. In our recent study of kinetics of FTS over a Re promoted Co/Al$_2$O$_3$ catalyst in a STSR [23] we followed methodology developed by Lox and Froment [26], which was later extended by Li and coworkers [27,28]. Several forms of the carbide mechanism were used in the