



Catalytic performance of an iron-based catalyst in Fischer–Tropsch synthesis

Majid Sarkari^a, Farhad Fazlollahi^b, Hossein Ajamein^a, Hossein Atashi^{a,*}, William C. Hecker^b, Larry L. Baxter^b

^a Department of Chemical Engineering, Faculty of Engineering, University of Sistan and Baluchestan, P.O. Box 98164-161, Zahedan, Iran

^b Chemical Engineering Department, Brigham Young University, Provo, UT 84602, USA

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ABSTRACT

This paper documents the performance and kinetics of an iron/manganese oxide catalyst in a fixed-bed reactor by Fischer–Tropsch synthesis (FTS) under conditions favoring the formation of gaseous and liquid hydrocarbons (P: 1–12 bar; T: 513–543 K; H₂/CO: 1, 1.5, 2 mol/mol; gas hourly space velocity: 4200–7000 cm³ (STP)/h/g_{cat}). Based on the hypothesis that water inhibits the intrinsic FTS reaction rate, eight kinetic models are considered: six variations of the Langmuir–Hinshelwood–Hougen–Watson representation and two empirical power-law models. The kinetic expression/mechanism that most precisely fits the data assumes the following: (1) CO dissociation is reversible and does not involve hydrogen; (2) all hydrogenation steps are irreversible, or the first hydrogenation step is slow and rate determining. Also, the performance of the catalyst for FTS and the hydrocarbon product distributions were investigated under different reaction conditions.

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1. Introduction

The world energy crisis in recent years led to renewed interest in the Fischer–Tropsch synthesis (FTS) reactions. Fischer–Tropsch synthesis is the heart of the most established efficient and cost-effective conversion of non-petroleum feedstock such as biomass, natural gas or coal to transportation fuels. An early and the most expensive step in the process converts the feedstock to syngas, the most useful components of which are H₂ and CO. Reformers or gasifiers of various designs affect this conversion. A subsequent water–gas shift reactor adjusts H₂ to CO stoichiometry by converting water to hydrogen. Finally, the FTS reactor converts the pressurized gases to a large variety of ultra-clean olefin, paraffin and oxygenates fuels, which in some cases can happen simultaneously with water–gas shift reaction [1–3]. Catalysts play essential roles in the reformers, water–gas shift reactors, and the FTS reactors. The focus here is on the FTS catalysts. A variety of catalysts show FTS reactivity, including preparations involving Fe, Co, Ru, and Ni. Iron-based catalysts are especially attractive for synthesizing gas with H₂/CO ratios less than 2 due to their high activity in water–gas shift (WGS) reactions. In essence, the Fe-based catalysts combine some of the functions of the water–gas shift reactor with the FTS reactor. Fe-based catalysts are also more resistant to poisons and produce a more flexible product slate than alternatives [4,5]. Typically, iron-based catalysts contain small amounts of potassium to improve the carburization and suppress methane formation [6–8] and/or other metal promoters such as manganese,

calcium, zinc, copper and magnesium to boost catalyst activity and selectivity [6,9].

Among the promoted iron-based catalysts, the Fe–Mn catalyst has some industrial record and reportedly has a higher olefin and middle distillation cut selectivity [7,8,10–12].

Even though the kinetic model of the Fe-based Fischer–Tropsch synthesis reaction has been studied by many researchers, there is no general agreement on the form of the kinetic rate expression [13,14]. The Langmuir–Hinshelwood–Hougen–Watson (LHHW) mechanism represents one of the more detailed and common descriptions for industrial applications [15]. Application of this mechanism suffers from its complexity and the large number of species involved [16,17]. On the other hand, a combination of density functional theory (DFT) calculations and kinetic analyses describe a credible, stepwise chain growth process [18,19].

Two reported mechanisms for FTS include:

- (1) A direct (hydrogen-unassisted) CO dissociative adsorption, including direct CO dissociation that forms monomers where the surface carbide species, C*, forms the intermediate for all the reaction products [20,21], and
- (2) A hydrogen-assisted CO dissociation, where CO forms intermediates HCO* and HCOH* and finally the chain initiator intermediate CH* [22,23].

In direct (hydrogen-unassisted) CO dissociation, C* routes contribute primarily to monomer formation on alkali promoted Fe-based catalysts at high temperatures. H-assisted CO dissociation removes O atoms as H₂O, while direct dissociation forms chemisorbed oxygen

* Corresponding author. Tel.: +98 9121193366.

E-mail address: h.ateshy@hamoon.usb.ac.ir (H. Atashi).

atoms that desorbs as CO₂. On Fe catalysts, alkali promoters affect the contributions from these two pathways. CO activation occurs exclusively by hydrogen-assisted dissociation routes in the latter mechanism at relevant FTS conditions [24,25]. Fig. 1 illustrates the proposed primary surface steps for FTS on iron-based catalysts.

This investigation of Fischer–Tropsch synthesis over an impregnated iron–manganese catalyst in a fixed-bed reactor includes experimental data over a wide range of reaction conditions. Several detailed kinetic models fit the observed data with varying accuracy. The best fit, and by inference perhaps the most accurate mechanism, uses LHHW intrinsic kinetics. The non-linear regression analysis used the Levenberg–Marquardt method.

2. Experimental

2.1. Catalyst preparation

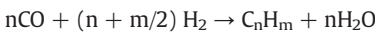
The catalysts were prepared by incipient wetness impregnation of Al₂O₃ with aqueous iron nitrate (Fe(NO₃)₂·6H₂O) (0.5 M) (99%, Merck) and manganese nitrate (Mn(NO₃)₂·6H₂O) (0.5 M) (99%, Merck) solutions. The Al₂O₃ support was first calcined at 600 °C in flowing air for 6 h before impregnation. For 50%Fe/50%Mn/5wt.%Al₂O₃ catalyst, the iron and manganese nitrate solution dispersed through a spray needle onto the support. The impregnated support dried at 120 °C for 16 h and calcined at 550 °C for 6 h. The BET surface area of the fresh catalyst was 120.2 m²/g. The phases identified in the fresh catalyst included monoclinic Fe₂O₃, cubic MnO₂ and Mn₂O₃, orthorhombic AlFeO₃ orthorhombic and tetragonal Al₂O₃. The sample after the FT reaction contained orthorhombic Fe₃C, monoclinic Fe₂C, orthorhombic Mn₂O₃, FeFe₂O₄, MnAl₂O₄/MnO, and cubic Al₂O₃. One gram of fresh, 0.15–0.25 mm (60–100 ASTM mesh) catalyst reacted with the simulated syngas, diluted 1 part to four with quartz of the same size.

2.2. Kinetic study

A differential fixed-bed micro-reactor (ID: 6 mm, H_b: 40 mm) provided steady-state kinetic data, the detailed description of which is found elsewhere [26,27]. The heat transfer analysis indicated an essentially isothermal catalyst under these operating conditions, with predicted conversion results based on an isothermal, one-dimensional, pseudo-homogeneous, plug-flow model [28,29]. The model equations consist of a mass balance for each component, which may be written as follows:

$$\frac{d(uC_i)}{dZ} + r_i \rho_b = 0,$$

where C_i refers to concentration of component *i* (mol/m³), *u* the superficial velocity (m/s), *r_i* the overall reaction rate of component *i* [mol/(kgcat·s)], and ρ_b the catalyst bed density (kgcat/m³). With the boundary conditions C_i = C_i⁰ at reactor entrance (Z = 0), the overall synthesis reaction can be written as follows:



where *n* is the average carbon chain length of the hydrocarbon product and *m* is the average number hydrogen atoms per hydrocarbon molecule.

The operating conditions were varied in the following ranges: T = 240–270 °C, P = 1–12 bar, GHSV = 4200–7000 cm³(STP)/h/g_{cat} and H₂/CO feed molar ratio = 1, 1.5 and 2. An equimolar, atmospheric-pressure, 60 ml/min flow of H₂ and N₂ reduced the fresh catalyst in situ for 16 h at 300 °C. The catalyst then cooled to 180 °C and was flushed with N₂. After catalyst treatment, they system shifted to process conditions of interest. Since the TCD–GC could not analyze water accurately, an oxygen balance determined the amount of water assuming that the

contribution from oxygenates in the products was negligible. These ideal tubular reactors have the following characteristics [30]:

$$\frac{ID}{D_p} > 25.$$

To minimize by-pass,

$$\frac{H_b}{D_p} > 100;$$

satisfying both relations minimizes back-mixing.

The carbon-containing products determine CO conversion (x_{CO}):

$$x_{\text{CO,out}}(\%) = \frac{\sum n_i M_i}{M_{\text{CO}}}$$

where *n_i* is the number of carbon atoms in product *i*, *M_i* is the percentage of product *i*, and *M_{CO}* is the percentage of carbon CO in feed stream.

The average reaction rate is

$$-r_A = \frac{F_{\text{CO}}^0 x_{\text{CO,out}}}{W}.$$

The total number of carbon atoms in the product determines the selectivity of product *i* (*S_i*) according to:

$$S_i(\%) = \frac{n_i M_i}{\sum n_i M_i}.$$

Eighteen sets of experimental data over a range of 1–12 bar, 513–543 K, 4200–7200 cm³ (STP)/h/g_{cat} space velocity, and 1–2 H₂/CO ratio produced overall conversions from 4–12.6% and form the primary kinetic data that determine the kinetic coefficients (Table 1).

2.3. Kinetic model evaluation

The rate of synthesis gas conversion depends on the partial pressure of the feed constituents, as well as temperature. CO absorbs more than H₂ on the iron-based catalyst surface at temperatures above 77 °C [31]. Iron catalysts are great reservoirs of surface inactive and active carbon and bulk carbon during FT reactions [32]. Some carbonic compounds cover the catalyst surface. Iron-based FT synthesis produces both water and carbon dioxide, representing two important routes for oxygen removal. Water substantially affects intrinsic FT reaction rates [33] while CO₂ has less effect on iron-based FT catalysts [34]. Therefore, CO₂ is not included in the rate expression of many kinetic models. Experimental evidence indicates CO and water competitively adsorb on active sites of iron-based catalysts [33].

This investigation compares statistical fits of six simplified forms of LHHW equations and two power law expressions to new experimental data. In represented kinetic models, it is assumed that all rate expressions were in inverse ratio to the number of vacant sites, CO and water content. This physically means that the FTS rate is inhibited by carbon monoxide and/or water.

The proposed rate expressions can be generalized as:

$$-R_{\text{CO}} = k_{\text{FT}} \frac{P_{\text{CO}}^\alpha P_{\text{H}_2}^\beta}{(1 + \text{or} + \sum k_{\text{CO}} P_{\text{CO}}^\gamma P_{\text{H}_2}^\lambda P_{\text{H}_2\text{O}}^\omega + k_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}})^\rho}$$

where *n* is the integer 0 or 1 and the remaining parameters have typical definitions (see nomenclature).

In all equations in Table 2, *k_{FT}* is a kinetic parameter group, that is considered as the reaction rate constant and *k_{CO}* and *k_{H₂O}* represent the adsorption parameter group of carbon species and water,

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