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On the kinetics and mechanism of Fischer–Tropsch synthesis on a highly active iron catalyst supported on silica-stabilized alumina

Trent J. Okeson[a], Kamyar Keyvanloo[a], John S. Lawson[b], Morris D. Argyle[a], William C. Hecker[a,*]

[a] Department of Chemical Engineering, Brigham Young University, Provo, UT 84602, United States
[b] Department of Statistics, Brigham Young University, Provo, UT 84602, United States

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ABSTRACT

The kinetics of a supported iron Fischer–Tropsch (FT) catalysts were investigated and a physically meaningful model that fits the data very well is proposed. Kinetic data (reported herein) were obtained at 250 °C and 20 atm in a fixed bed reactor at a variety of P_{H_2} and P_{CO}. Measured P_{H_2} and P_{CO} power law dependencies were found to be in the same range as those for unsupported Fe FT catalysts previously reported. The kinetic models in this study were tested using a statistical lack-of-fit test. Eight, two-parameter Langmuir–Hinshelwood rate expressions based on various mechanistic routes and assumptions were derived and tested, but all gave relatively poor fits to the data. An adjustment of the P_{H_2} dependency of the derived expressions to the 0.875 power resulted in three reasonable semi-empirical models, one of which fit the data extremely well. This approach also allowed us to determine the best function of P_{CO} dependency. The results suggest that supported Fe FT catalysts follow a direct CO dissociation pathway, that carbon is one of the most abundant species on the surface of the catalyst, and that the hydrogenation of either C* or CH* is the rate-determining step.

1. Introduction

Fischer–Tropsch (FT) Synthesis (FTS) is a commercially proven and environmentally sound method for production of fuels from natural gas, coal, or biomass. FTS catalysts are typically unsupported iron (Fe) or supported cobalt (Co), each with its own advantages and disadvantages [1]. Although unsupported Fe catalysts, typically promoted with Cu, K, and SiO_2 show promising activity and selectivity [2], they are generally too mechanically weak to be used in slurry bubble column reactors (SBCR's). There is specific interest in using SBCR's because they have excellent heat transfer properties and are very economical [3]. Unfortunately, the severe conditions in SBCR's tend to grind weaker unsupported Fe catalysts into fine powders, resulting in attrition loss with concomitant plugging of catalyst filter systems [4]. Although *supported* Fe catalysts are preferred for SBCR's, historically their activity has been 3–6 times lower than unsupported Fe catalysts and their selectivity has also been less favorable [2,5,6]. However, a highly active and stable silica-stabilized alumina-supported Fe catalyst was recently developed and reported [7,8]. This breakthrough opens new possibilities for supported Fe catalysts and leads to a renewed interest in characterization of supported Fe FTS catalysts, including their kinetic behavior and mechanism.

FTS involves two primary steps: the formation of CH_2 monomers and polymerization of those monomers to form hydrocarbon chains. The majority of kinetic studies are based on the assumption that the formation of the CH_2 monomers is significantly slower than and independent of the polymerization reaction [9]. This simplifies the kinetic analysis to obtain derivable rate equations that describe FTS, allowing for explicit models for monomer formation to be used instead of implicit models that rely on the distribution of products. A selection of proposed rate expressions (based on this assumption) from the literature is shown in Table 1. A more complete review of kinetic studies for Fe FTS catalysts can be found elsewhere [10].

Table 1 includes a power law model, one Eley-Rideal model and three Langmuir–Hinshelwood–Hougen–Watson (LHHW) rate models for unsupported Fe. The last two models are LHHW models for supported Fe. In early FTS research, FTS was assumed to follow an Eley-Rideal type mechanism; now, the LHHW type reaction is

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Abbreviations: FT, Fischer–Tropsch; FTS, Fisher-Tropsch Synthesis; SBCR, slurry bubble column reactor; LHHW, Langmuir–Hinshelwood–Hougen–Watson; MASI, most abundant surface intermediate; ΔH_{ads}, heat of adsorption; L.o.F., lack-of-fit; SE, semi-empirical; LCM, linear combination model; MAPM, multiple adsorption parameter model.

* Corresponding author.
E-mail address: hecker@byu.edu (W.C. Hecker).

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Table 1
Summary of kinetic models of FTS on iron catalysts found in literature.

Catalyst	Reactor	Operating conditions			Kinetic expression	Ref.
		T (°C)	P (MPa)	H_2/CO		
Prec. $FeKAl_2O_3$	Berty CSTR	200–240	1.0	1.0–2.0	$-r_{CO} = aP_{H_2}^{0.6}P_{CO}^{-0.05}$	[11]
Prec. $FeCuSiO_2$	Spinning Basket Reactor	270–330	1.3–2.5	0.5–2.0	$r_{FT} = \frac{aP_{CO}P_{H_2}}{bP_{CO}+cP_{H_2O}}$	[12]
Prec. $FeCuKSiO_2$	Slurry Reactor	250	1.2–4.0	0.5–2.0	$r_{FT} = \frac{aP_{CO}^{1/2}P_{H_2}^{1/2}}{(1+bP_{CO}^{1/2}+cP_{CO_2})^2}$	[13]
FeKZnCu	Packed Bed	235	0.8–2.4	1.0–4.8	$r_{FT} = \frac{aP_{CO}P_{H_2}+bP_{CO}}{(1+cP_{CO})^2}$	[14]
Prec. FeK	CSTR	240	0.5–4.0	1.6	$r_{FT} = \frac{aP_{H_2}^{0.5}P_{CO}}{(1+bP_{CO})^2}$	[15]
$FePt/LaAl_2O_3$	Berty CSTR	220–239	0.5–1.4	1.0–10	$r_{FT} = \frac{aP_{H_2}^{5/6}P_{CO}^{2/3}}{(1+bP_{H_2}^{1/3}P_{CO}^{2/3})^2}$	[16]
$FeKPt/Al_2O_3$	Berty CSTR	220–260	2.0	1.8–14	$-r_{CO} = \frac{aP_{H_2}^{3/4}P_{CO}^{1/2}}{(1+bP_{H_2}^{1/4}P_{CO}^{1/2})^2}$	[17]

generally accepted and is the primary type of mechanism explored in this study [18].

The first model in Table 1 is an example of a power law rate expression for a potassium promoted Fe catalyst. There have been many power law rate expressions proposed for Fe catalysts with varying orders of H_2 and CO. The reported reaction orders with respect to H_2 and CO differ greatly as the catalyst promoters are varied; however, when examining only K promoted iron catalysts, the dependence on H_2 is reported to be between 0.6 and 0.9, while CO dependence varies between −0.2 and 0.2 [11].

In more than a dozen previous studies of reaction kinetics of FTS, only two included the kinetics of supported Fe FT catalysts. In the first study, Critchfield and Bartholomew [16] examined the kinetics of a Pt-promoted (20% Fe, 1% Pt) catalyst supported on a lanthanum-stabilized alumina in a Berty reactor. In the second study, Paul and Bartholomew [17,19] examined the kinetics of FTS on an alumina-supported, K-promoted (20% Fe, 1% K, 1% Pt) catalyst. Rate equations were derived from a variety of mechanistic models and then fit to the data using the Levenberg–Marquardt algorithm for nonlinear least squares regression. Although these studies made good progress in kinetic modeling of supported Fe FT catalysts, they had challenges with deactivation. In addition, the activities of their catalysts were below commercial standards and one included Pt which is not commercially viable.

In summary, the kinetics of supported Fe catalysts have been explored only sparsely. The lack of interest is due to their poor performance relative to unsupported catalysts, which has made supported Fe appear to be commercially unattractive. With the recent development of a potentially competitive supported Fe FTS catalyst [7], kinetic modeling of supported Fe catalysts is now more relevant. In this paper, we explore kinetic rate models that best describe rate data obtained on a highly active, supported Fe catalyst prepared in our laboratory.

2. Experimental

2.1. Catalyst preparation

The catalyst used in this study was iron supported on silica-stabilized alumina (5% silica) promoted with copper and potassium (FeCuK/AlSi). It was prepared using a non-aqueous solution (50 vol% acetone and 50 vol% iso-propanol) containing ferric nitrate and copper nitrate in multiple impregnation steps using a rotary evaporator. In each step, 10 wt% Fe with the desired amount of Cu was dissolved in an appropriate volume of solution followed by drying and calcination at 300 °C. After the last step of Fe and Cu addition, potassium was added by incipient wetness impregnation as potassium bicarbonate. The final catalyst contained nominally 40 wt% Fe, 3 wt% Cu, and 1.6 wt% K and was sieved to a particle size of 125–177 μm (80–120 mesh) to eliminate pore diffusion effects. The detailed catalyst preparation procedure (as well as characterization data) can be found elsewhere [7,8].

2.2. Kinetic data

The kinetic data for FTS were obtained in a fixed-bed reactor (stainless steel, 3/8 in. OD). The catalyst sample (0.25 g) was diluted with 1 g of SiC to provide a nearly isothermal profile throughout the catalyst bed. The catalyst was reduced in situ at 320 °C in H_2 for 16 h. The reactor was then cooled to 180 °C and pressurized to 20 atm in flowing syngas (31.5% CO, 31.5% H_2, 3.5% Ar, balance He). The catalyst was activated at 280 °C for approximately 72 h with a target CO conversion level of 50% during this carburization period. The effluent product passed through a hot trap (~90 °C) and a cold trap (~0 °C) to collect solid and liquid products, respectively. The gaseous product was analyzed using an HP 5890 gas chromatograph. Details of the reactor system can be found elsewhere [20]. The H_2 and CO partial pressures were varied systematically to collect the kinetic rate data. The ranges over which the partial pressures were varied as well as the other operating conditions of this study are shown in Table 2.

Obtaining rate data without being effected by catalyst deactivation is a common challenge in the kinetic modeling of FTS. The Fe catalyst used in this study was very stable, as evidenced by essentially no activity change during the data collection period (200–700 h TOS). As shown in Fig. 1, the variation in rate is minimal, indicating that there is no need to correct data for deactivation.

All the rate data were obtained at low CO conversions (17–21%) and were calculated assuming differential reactor conditions. Average partial pressures of H_2 and CO between inlet and outlet

Table 2
Range of operating conditions for the FeCuK/AlSi catalyst.

Operating conditions	Value
H_2:CO	0.7–1.5
P_{H_2} (atm)	2.0–9.0
P_{CO} (atm)	3.0–8.9
P_{tot} (atm)	20
T (°C)	250
Time on stream (TOS) (h)	200–700
CO conversion	0.17–0.21