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Hydrocarbon production rates in Fischer-Tropsch synthesis over a Fe/Cu/La/Si catalyst

Ali Nakhaei Pour[a*], Farshad Riyahi[c], Mohammad Reza Housaindokht[a]
Mohammad Irani[b], Seyed Mehdi Kamali Shahri[d], Behnam Hatami[b]

a. Department of Chemistry, Ferdowsi University of Mashhad, P. O. Box: 9177948974, Mashhad, Iran;
b. Research Institute of Petroleum Industry of National Iranian Oil Company, P. O. Box: 14665-137, Tehran, Iran;
c. Department of Chemical Engineering, Petroleum University of Technology (PUT), P. O. Box: 63431, Ahwaz, Iran;
d. Chemical Engineering Department, Penn State University, University Park, PA 16802-4400, USA

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Abstract

The detailed kinetics of Fischer-Tropsch synthesis over an industrial Fe/Cu/La/Si catalyst was studied in a continuous spinning basket reactor under the conditions relevant to industrial operations. Reaction rate equations were derived on the basis of Langmuir-Hinshelwood-Hougen-Watson type models for Fischer-Tropsch synthesis based on possible reactions sets originated from the carbide, enolic and combined enol/carbide mechanisms. Kinetic model candidates were evaluated by the global optimization of kinetic parameters, which were realized by first minimization of multi-response objective functions with conventional Levenberg-Marquardt method. It was found that an enolic mechanism based model could produce a good fit of the experimental data. The activation energy for paraffin formation is 95 kJ·mol^{-1} which is smaller than that for olefin formation (121 kJ·mol^{-1}).

Key words

Fischer-Tropsch synthesis; kinetics; iron catalysts; catalysts selectivity

1. Introduction

Fischer-Tropsch synthesis (FTS) that was discovered in Germany nearly three-quarters of a century ago has recently become a subject of natural gas, biomass and other carbon compounds to liquid transportation fuels [1,2]. The kinetic description of FT reaction is a very important task for the industrial FT process design, optimization and simulation [2−6]. The complexity of the reaction products, however, makes the kinetics of the process quite hard to be accurately described [7−10].

Two different approaches for the development of FTS kinetic models have been reported in the literature. For the first one, a rate law for reactants conversion (often based on empiric laws) and a product distribution model (like Anderson-Schulz-Flory, ASF) is separately developed. This is theoretically justified only if it can be assumed that the reaction products do not affect or participate in the monomer formation mechanism [2−13]. For the second more sound approach, all the mechanistic steps in which CO and H_2 are consumed and lead to the final products are considered jointly [2−13]. The mechanistic kinetic rate expressions for iron catalysts are based on the formation of monomer species as rate-determining step in the consumption of synthesis gas. Most popular theories proposed for the formation of monomer species postulated in literatures are: carbide, enolic and combined enol/carbide mechanisms [8−14]. In carbide mechanism, CO dissociates on the surface and the adsorbed carbon hydrogenates to a methylene species. In enolic mechanism, adsorbed CO is hydrogenated to a hydroxylated species and chain growth occurs by condensation with water elimination. Finally in combined enol/carbide mechanism, methylene species is formed by hydrogenation of the hydroxylated enolic CO-H_2 complex [8−14].

FTS has been characterized as a non-trivial surface polymerization since the monomer units are produced from the reagents hydrogen and carbon monoxide in situ on the surface of the catalyst instead of being fed to the reactor. Lox and Froment [13] developed a reaction network for the formation of linear hydrocarbons on a commercial precipitated iron

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* Corresponding author. Tel/Fax: +98-21-44739716; E-mail: nakhaeipoura@ripi.ir, nakhaeipoura@yahoo.com

catalyst. On the basis of carbide mechanism, they developed several kinetic models at a high level of conversion fitted well with Anderson-Schulz-Flory distribution. Unfortunately, their experiments were performed in an integral packed-bed reactor at high synthesis-gas conversions, which is unsuitable for fundamental kinetic studies. Their product formation rates and models do not predict the well-known deviations observed in nearly all FT product distributions. In ASF model, the formation of hydrocarbon chains was assumed as a stepwise polymerization procedure and the chain growth probability was assumed to be independent of the carbon number. However, significant deviations from ideal ASF distribution have been observed in many studies. Zimmerman et al. developed a model for both the formation of linear hydrocarbons and the water-gas-shift (WGS) reaction over iron catalysts [15]. In their model, the readsorption and secondary reaction of olefins were taken into account and the increase of paraffin/olefin ratio with the carbon number can be predicted. However, the results displayed significant deviations between model predicted and experimental mole fractions, especially for methane and ethene. Wang et al. [11] obtained FTS kinetics model including the olefin readsorption and secondary reactions over an industrial Fe-Cu-K catalyst, and more FTS reaction mechanisms and kinetics models were taken into account by Yang et al. [4] and Teng et al. [12] over an industrial Fe-Mn catalyst. However, all of these developed kinetic reaction rates are very complex and very difficult in modeling application so, the hydrocarbon production rates developed by Lox and Froment [13] are under consideration yet.

Iron-based catalysts often contain small amounts of potassium and other metals such as manganese, calcium, zinc, copper and magnesium as promoter to improve catalyst activity and selectivity [2,16,17]. Potassium has a stronger basicity and thus improves the adsorption of the reactants (CO and H_2) on catalytic active sites, leading to effects on the improvements in FTS activity [16,17]. Also it has been reported that manganese, as a promoter for iron catalysts, enhances the activity of iron-based FT catalysts, particularly in producing short-chain olefins [11,12]. Van der Laan and Beenackers evaluated FTS kinetics on potassium promoted iron catalyst with stronger basicity and high WGS activity [5]. Also Yang et al. and Wang et al. evaluated FTS kinetics on magnesium promoted iron catalyst with lower basicity [4,11].

The goal of this paper is to establish and test detailed mechanistic kinetic models for Fischer-Tropsch system over an industrial Fe/Cu/La/Si catalyst while considering many more possibilities in mechanism. The mechanisms are based on carbide, enolic and combined enol/carbide theories. The iron catalyst which used in this study was promoted by lanthanum as a low basicity promoter [17]. In our previous works, we studied LHHW kinetics of WGS and FTS reaction rates on this catalyst [14,18]. By the experimental data, a set of FTS kinetics models are estimated and discriminated separately.

2. Experimental

2.1. Catalyst preparation

Fe-Cu catalyst was prepared by co-precipitation procedure, described elsewhere [17]. La promoter was added by incipient wetness impregnation and calcined in 723 K. Final catalyst compositions were designed in terms of the atomic ratio as: 100Fe/5.64Cu/2La/19Si. The fresh catalyst was crushed and sieved to particles with diameters of $250-300$ μm, which has been proved to be a compromising particle size, safe for neglecting the intraparticle transfer limitations and promisingly easy operating for the reactor during the experiment [17]. The calcined catalyst was analyzed by ICP to determine accurate weight percentage of elements.

2.2. Experimental apparatus and procedure

Steady-state FTS reaction rates were measured in a continuous spinning basket reactor (stainless steel, $H = 0.122$ m, $D_0 = 0.052$ m, $D_{\rm i} = 0.046$ m) with temperature controllers (WEST series 3800). A detailed description of the experimental setup and procedures has been provided in our previous work [14].

Blank experiments showed that the spinning basket reactor charged with inert silica sand without catalyst has no conversion of syngas. The weight of the catalyst loaded was 2.5 g and diluted by 30 cm^3 inert silica sand with the same mesh size range. The catalyst samples were activated by a 5% (v/v) H_2/N_2 gas mixture with space velocity of 15.1 $\text{NL}\cdot\text{h}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$ at 1 bar and 1800 rpm. The reactor temperature increased to 673 K with a heating rate of 5 $\text{K}\cdot\text{min}^{-1}$, maintained for 1 h at this temperature, and then reduced to 543 K. The activation was followed by the synthesis gas stream with $H_2/CO = 1$ and space velocity of 3.07 $\text{nL}\cdot\text{h}^{-1}\cdot\text{g}_{\text{Fe}}^{-1}$ for 24 h at 1 bar and 543 K before setting the actual reaction temperature and pressure. After catalyst reduction, synthesis gas was fed to the reactor under conditions operated at 563 K, 17 bar, $(H_2/CO) = 1$ and a space velocity of 10.4 $\text{nL}\cdot\text{h}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$. A stabilization period of 12 h was conducted under the reaction conditions, and then the kinetic measurements were carried out. After the process conditions were changed, at least 12 h delay was used for the system stabilization before a new mass balance period. After reaching steady state activity and selectivity, the kinetic of FTS reaction rate was measured.

The external mass transfer limitation was investigated by comparing CO conversions under different stirring speeds of the reactor. Apparently, the stirring speed needed to eliminate the external mass transfer limitation, which increases correspondingly with the increase of the reaction temperature. This is due to the fact that the relative rate of external mass transfer versus the reaction rate decreases with the temperature increase. Therefore, the corresponding stirring speed should ensure that the measured experimental data are in the kinetically limited regime. The effect of stirring speed on CO conversion was investigated in the preliminary run to determine the