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Fischer–Tropsch synthesis and water gas shift kinetics for a precipitated iron catalyst

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ABSTRACT

A large number of kinetic data points (83 sets) was obtained over a wide range of CO conversion (7–90%), pressure (1.3–2.5 MPa) and H₂/CO ratio (0.67–1.5) with an iron catalyst (100 Fe/5.1 Si/1.25 K). The kinetics of the catalyst in the low (X_{CO} < 70%) and high conversion (X_{CO} > 70%) regions were studied separately. Twenty six Fischer–Tropsch synthesis (FTS) and water gas shift (WGS) kinetic models were tested and discriminated. Water and CO₂ inhibition was evaluated. While all thirteen FTS models gave a satisfactory fit, the new FTS models that included CO₂ inhibition surpassed the others. Water inhibition of the FTS rate was insignificant over both low and high conversion ranges. For the WGS kinetics of the iron catalyst, a newly constructed empirical model and one from the literature provided the best fits of the WGS rates, while nine mechanistic models and one power law WGS model were unable to satisfactorily fit the WGS kinetic data. Water did not significantly limit the WGS rate and CO₂ only inhibited the rate at high CO conversions. The equations obtained for the low and high CO conversion ranges varied greatly. The errors for the models for 85% of the FTS and WGS data points were less than 10%, and the errors of the remaining points fell in the range of 10–15%.

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1. Introduction

Because of the importance of defining the kinetics of Fischer–Tropsch synthesis (FTS) in the development of XTL (X = coal, natural gas and biomass) processes, numerous kinetic investigations of FTS over various catalysts have been conducted over the past several decades. In a large number of kinetic studies published [1–24], many mechanistic or semi-mechanistic kinetic models for Fe-based FTS have been developed on the basis of classic carbide and enol mechanisms (Table 1). However, little consensus in the kinetic equations was obtained in these earlier studies, which may be attributed to the complexity of the FTS reaction mechanism itself [23,24], and/or due to complexities associated with differences in catalyst preparation, catalyst composition, pretreatment, and process conditions [24]. The simple first-order kinetics in H₂ for the iron based FTS catalyst is an important model, and it was proven to be useful to predict FTS rates at low CO conversions, i.e., <70%, of fused or promoted Fe catalysts by Dry [1,15]. Meanwhile,

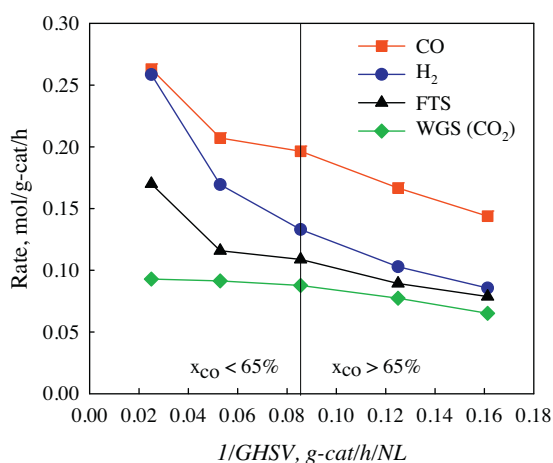
Dry [8], Anderson et al [1] and Huff and Satterfield [3] derived the same form of a mechanistic kinetic model for fused Fe or precipitated Fe catalysts according to enol and/or carbide mechanisms (Model 10 in Table 1). van Steen and Schulz [4] developed a model (Model 13 in Table 1) by assuming the formation of CH monomer being the rate determination step, and it successfully fit the kinetic behavior of several unpromoted and promoted iron and cobalt catalysts. All these models include a water effect term and suggest a negative role of water on the FTS reaction. Ledakowicz et al. [2,12] developed a mechanistic FTS model (Model 9) in terms of an enol mechanism that includes both the effect of water and CO₂ on the rate. More prevalent FTS mechanistic kinetic models developed by FTS researchers (e.g., Atwood and Bennett [9], Decker et al. [10], Zimmerman and Bukur [14], van der Lann and Beenackers [7], Bote and Breman [5] and Zhou et al. [6]) and a power law model without CO₂ and water inhibition ($P_{CO}^a P_{H_2}^b$) are also summarized in Table 1. In general, these mechanistic kinetic models can be lumped as functions of partial pressures of CO and/or H₂, $k P_{CO} P_{H_2}^a / (1 + \sum K_i P_i)^b$ (a = 0.5, or 1, b = 1 or 2; i = CO, H₂O, CO₂), and terms for contributions such as H₂O, CO₂, and/or vacant sites are reflected in the denominator.

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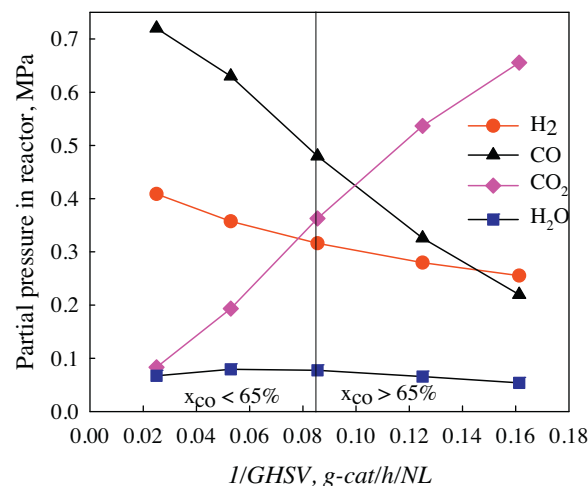
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Table 1
Summary of FTS kinetic models for Fe based catalysts.

Model #	Model	Mechanism involved	Reference
1	$r_{FT} = kP_{CO}^a P_{H_2}^b / (1 + cP_{H_2O} + dP_{CO_2})$	Generalized	This work
2	$r_{FT} = kP_{CO}^a P_{H_2}^b P_{H_2O}^c P_{CO_2}^d$	Power law	This work
3	$r_{FT} = kP_{CO}^a P_{H_2}^b$	Power law	18–21
4	$r_{FT} = kP_{CO}P_{H_2} / (1 + aP_{CO} + cP_{H_2O})$	Carbide/H ₂ assisted	7
5	$r_{FT} = kP_{CO}P_{H_2} / (1 + aP_{CO} + cP_{H_2O})^2$	Carbide, H assisted	7
6	$r_{FT} = kP_{CO}P_{H_2}^{0.5} / (1 + aP_{CO})^2$	Carbide, H assisted	5,6
7	$r_{FT} = kP_{CO}P_{H_2}^{0.5} / (1 + aP_{CO} + cP_{H_2O})^2$	Carbide, H assisted	7
8	$r_{FT} = kP_{CO}^{0.5}P_{H_2} / (1 + aP_{CO}^{0.5} + cP_{H_2O})$	Carbide, direct dissociation	7
9	$r_{FT} = kP_{CO}P_{H_2} / (P_{CO} + cP_{H_2O} + dP_{CO_2})$	Enol	2,12
10	$r_{FT} = kP_{CO}P_{H_2} / (P_{CO} + cP_{H_2O})$	Carbide/enol	1,8,9,22
11	$r_{FT} = kP_{CO}P_{H_2} / (P_{CO} + cP_{H_2O}/P_{H_2})$	Carbide/enol	3
12	$r_{FT} = kP_{CO}P_{H_2}^{0.5} / (P_{CO} + cP_{H_2O} + dP_{CO_2})$	Generalized	11
13	$r_{FT} = kP_{CO}P_{H_2}^{1.5} / P_{H_2O} / (1 + cP_{CO}P_{H_2} / P_{H_2O})^2$	Carbide, CO direct dissociation	4

**Fig. 1.** Change in CO conversion with 1/space velocity over 100Fe/5.1Si/3K/2Cu catalyst. 270 °C, 1.3 MPa, H₂/CO = 0.67, X_{CO} = 25–87%.

Another issue in the kinetic study of Fe catalysts may be linked to the conversion level; it has not been widely discussed to date. The reason for this is likely due to the difficulty of obtaining reliable kinetic data in the high conversion region i.e. (e.g., >70%), since deactivation of Fe catalysts occurs to a greater degree and at a more rapid rate in this region. This is exacerbated at certain process conditions (e.g., high P_{H_2O} in the reactor). It has been reported [25,26] that the FTS rate varies greatly with conversion over Fe based catalysts, and that this is likely due to changes in the extent of the water gas shift reaction (WGS) with CO conversion. The H₂ produced by the WGS reaction, in turn, influences the FTS rate and product selectivity. Fig. 1 shows changes in CO, H₂ and FTS rates with CO conversion/contact time over an iron based catalyst at 270 °C, indicating that productivity varies significantly in moving from low to high CO conversion levels. In the range of low CO conversion (below 65%, short contact time region), the productivity is high but decreases rapidly as contact time is increased in a nonlinear manner. On the other hand, the changes in the FTS rate, CO rate and H₂ rate become smooth and show nearly linear relationships with contact time at high CO conversion levels (greater than 65%), suggesting that the WGS reaction limits the FTS rate, since H₂ provided by WGS is needed to increase the extent of the FTS reaction. In Fig. 2, the partial pressures of CO, H₂, H₂O and CO₂ are plotted against contact time. Over the entire range of CO conversion, the partial pressures of CO and H₂ decreased almost linearly with

**Fig. 2.** Changes in partial pressures of CO, H₂, H₂O and CO₂ with 1/space velocity over 100Fe/5.1Si/3K/2Cu catalyst. 270 °C, 1.3 MPa, H₂/CO = 0.67, X_{CO} = 25–87%.

increases in contact time or CO conversion; this is a different trend from those of the CO, H₂ and FT rates (Fig. 1). Thus, the rate and pressure curves suggest that FTS kinetic behavior at low and high conversion levels may be different. However, most earlier kinetic studies were conducted at low to medium conversion levels or with only a few high conversion data points. In short, the kinetics of Fe catalysts at high conversion has not been systematically studied.

The partial pressure of CO₂, as shown in Fig. 2, increases remarkably, i.e., 0.1 to 0.7 MPa, with increases in CO conversion from 25 to 87%. This is probably a reason why many previous FTS kinetic models contain a CO₂ inhibition term. Fig. 2 also shows that the partial pressure of water inside the reactor was low (<0.08 MPa), about ten times lower than those of CO, H₂, or CO₂, which implies that the majority of the water that formed during FTS was consumed by WGS on the Fe catalyst. Moreover, the water curve passes through a maximum at about 60% CO conversion. The slight increase in water partial pressure with increasing CO conversion in the low CO conversion range probably results from a greater increase in the FTS rate relative to WGS, while the decrease in the partial pressure of water with increases in CO conversion above 60% CO conversion likely result from a relatively higher WGS rate. A number of previous kinetic studies [2–4,7–12,14] have reported that water inhibits the FTS rate of Fe catalysts. Recently, Bote and Breman [5] and Zhou et al. [6] developed a kinetic model, $r_{FT} = kP_{CO}P_{H_2}^{0.5} / (1 + mP_{CO})^2$ (Model 6 in Table 1) based on the assumptions of H-assisted CO

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