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Role of water-gas-shift reaction in Fischer–Tropsch synthesis on iron catalysts: A review

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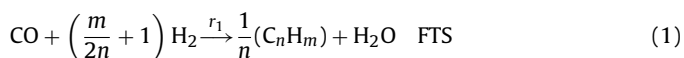
ABSTRACT

Water-gas-shift (WGS) reaction plays a significant role in industrial application of Fischer–Tropsch synthesis (FTS) for coal-to-liquid (CTL) processes with iron-based catalysts. This reaction provides necessary hydrogen for synthesis gas with low H₂/CO molar ratio, and has influence on concentrations of reactants, water and carbon dioxide, which in turn has effect on product distribution, rate of FTS and catalyst deactivation. We provide information on the effect of process conditions (H₂/CO feed ratio, reaction temperature and pressure), syngas conversion, and catalyst composition and activation procedure on the WGS activity. H₂/CO consumption (or usage) ratio and the exit H₂/CO ratio vary with conversion and the extent of WGS reaction. The extent of variation is much greater for H₂/CO feed ratios greater than 1.7, than it is for the CO rich syngas (H₂/CO=0.5–1). This in turn places limits on maximum practical single pass conversion which can be achieved with different feed compositions and results in different types of operation (low single pass conversion with tail gas recycle, and high once through single pass conversion).

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1. Introduction

Fischer–Tropsch Synthesis (FTS) reaction is a key part of technology to convert natural resources, such as coal, natural gas and biomass, into liquid hydrocarbon fuels. FTS is a heterogeneous reaction discovered in the early twentieth century [1]. Reactants, carbon-monoxide and hydrogen (syngas), are converted to an array of hydrocarbons (mainly n-paraffins and olefins), and FTS reaction can be described by the following stoichiometry:



The catalysts of choice for industrial FTS are cobalt and iron. If the raw material is coal, then the preferred catalyst is iron [2,3]. One of the main features of iron FTS catalysts is their water-gas-shift (WGS) activity. WGS reaction can be presented as:



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The WGS reaction provides additional hydrogen for FTS, which is needed in the case of coal-derived syngas. Coal-derived syngas normally has a H₂/CO ratio below 2, the latter being an approximate stoichiometric H₂/CO ratio (i.e. $m/n=2$) needed to produce hydrocarbons according to equations (1).

The main objectives for industrial FTS plants are to achieve efficient utilization, high productivity, long term operation and high selectivity to C₅₊ hydrocarbons and low methane selectivity. Kinetics of various parallel reactions (FTS, WGS and olefin secondary reactions) determines the overall selectivity of FTS products. Proper selection of process and syngas feed conditions is essential in achieving activity, stability and selectivity targets in commercial FTS reactors. With Fe-based catalysts the effect of WGS is very significant. This reaction affects concentrations (partial pressures) of CO, H₂, CO₂ and H₂O in the system, which in turn has an impact on kinetics of both primary FTS and 1-olefin secondary reactions and thus the product distribution.

In this work we focus on the role of WGS in FTS and review available information on the effect of process conditions on the WGS activity, and the impact of WGS reaction on selection of process conditions used in industrial practice and reactor design considerations.

This paper is dedicated to Professors Mark Dry and Hans Schulz, two giants in the field of FTS catalysis, who have made pioneering

contributions to our knowledge about various aspects of industrial applications of FTS and its fundamentals.

2. Measures of WGS activity, stoichiometric constraints and equilibrium calculations

2.1. Measures of WGS activity and stoichiometric constraints

The extent of WGS reaction, or WGS activity, has been expressed in terms of: (1) magnitude of H₂/CO usage ratio, U ; (2) CO₂ selectivity; (3) partial pressure quotient $P_{Q_{WGS}} = P_{CO_2}P_{H_2}/P_{CO}P_{H_2O}$ or $P_{WGS} = P_{CO_2}/(P_{CO_2} + P_{H_2O})$; or (4) as ratio of WGS rate to FTS rate, r_{WGS}/r_{FTS} . First we introduce definitions and provide some useful relations between different variables and conversions of reactants.

Fractional conversion of a reactant (X_i), is defined as:

$$X_i = \left(\frac{n_i^0 - n_i}{n_i^0} \right) \quad (3)$$

where: n_i^0 = molar flow rate of i entering the reactor; n_i = molar flow rate of i leaving the reactor, $i = H_2$ or CO.

Usage ratio is defined as a ratio of moles of H₂ consumed and moles of CO consumed, and can be expressed in terms of reactant conversions, and H₂ to CO molar ratio in the feed, $F = n_{H_2}^0/n_{CO}^0$:

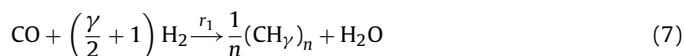
$$U = F \frac{X_{H_2}}{X_{CO}} \quad (4)$$

In FTS it is common to express conversion in terms of consumption of H₂ + CO, since the rate of syngas consumption is independent of the extent of WGS reaction. From definitions of reactant conversions and usage ratio (Equations (3) and (4)) one can obtain the following relations between the syngas conversion, X_{CO+H_2} , and the conversions for H₂ and CO:

$$X_{H_2+CO} = X_{H_2} \frac{F(1+U)}{U(1+F)} \quad (5)$$

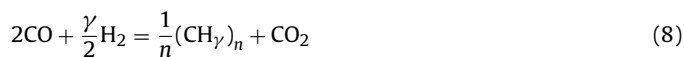
$$X_{H_2+CO} = X_{CO} \frac{(1+U)}{(1+F)} \quad (6)$$

If the usage ratio is not reported directly, one can use Eqs. (4)–(6) to calculate it from reported values of any two values of conversions (X_{H_2} , X_{CO} or X_{H_2+CO}) and F . Next we describe stoichiometric limitations on the usage ratio arising from the stoichiometry of reactions (1) and (2). First we rewrite Eq. (1) in a more convenient form as:



where: $\gamma = m/n$ (average H/C ratio in hydrocarbon products). Typically, $\gamma = 2.1$ –2.4.

If there is no WGS activity then the usage ratio from Eq. (7) is: $U = 1 + \gamma/2$. In the other extreme if all water formed in FTS reaction is consumed by WGS (high WGS activity), the overall reaction can be written is:



and the corresponding usage ratio is: $U = \gamma/4$. Thus, the usage ratio values are constrained by stoichiometry and the extent of WGS reaction to:

$$\frac{\gamma}{4} \leq U \leq 1 + \frac{\gamma}{2} \quad (9)$$

The magnitude of the usage ratio, subject to the above constraint, provides indication of the extent of WGS reaction (or WGS activity), low values of U are indicative of high WGS activity, whereas high values correspond to low WGS activity.

The complete utilization of feed gas is possible only when the usage ratio equals the H₂/CO feed ratio, i.e. when $U = F$. If $U < F$ then

the CO is the limiting reactant and the maximum possible syngas conversion is obtained from Eq. (6) with $X_{CO} = 1$, yielding:

$$(X_{H_2+CO})_{\max} = \frac{(1+U)}{(1+F)} \quad (U < F) \quad (10)$$

On the other hand if $U > F$ then H₂ is the limiting reactant and the maximum possible syngas conversion is obtained from Eq. (5) with $X_{H_2} = 1$, yielding

$$(X_{H_2+CO})_{\max} = \frac{F(1+U)}{U(1+F)} \quad (U > F) \quad (11)$$

If the partial pressures of inorganic species at the reactor exit are reported they can be used to estimate the extent of WGS activity. Partial pressure quotient value $P_{Q_{WGS}} = P_{CO_2}P_{H_2}/P_{CO}P_{H_2O}$ can be compared to the equilibrium constant value for the WGS reaction, $K_{WGS}(T)$, to determine the extent of the WGS activity. If $P_{Q_{WGS}}$ value is close to that of K_{WGS} , this would be indicative of high WGS activity, whereas if $P_{Q_{WGS}} \ll K_{WGS}$ this would imply low WGS activity. Likewise the magnitude of $P_{WGS} = P_{CO_2}/(P_{CO_2} + P_{H_2O})$ provides the same qualitative information; if $P_{WGS} \ll 1$ the WGS activity is low, whereas if $P_{WGS} \approx 1$ the WGS activity is high. However, values of partial pressures are often not reported, whereas a value of so called CO₂ selectivity is usually reported. CO₂ selectivity represents a fraction of CO converted to CO₂ by WGS reaction, i.e.

$$S_{CO_2} = \frac{r_{CO_2}}{(-r_{CO})} = \frac{r_2}{r_1 + r_2} \quad (12)$$

where: $r_1 = r_{FTS}$ and $r_2 = r_{WGS}$ are intrinsic rates of reactions (1) and (2) (as per Eqs. (1) and (2)); $r_{CO_2} = r_2$ is the rate of CO₂ formation (i.e. rate of WGS reaction); $(-r_{CO})$ = rate of CO disappearance.

If there is no CO₂ and water in the feed it can be shown that P_{WGS} and CO₂ selectivity, S_{CO_2} , are related as follows:

$$P_{WGS} = \frac{S_{CO_2}}{1 - S_{CO_2}} \quad (13)$$

From the definition of P_{WGS} and Eq. (13) it can be concluded that the maximum possible value of CO₂ selectivity is 0.5. Thus, small values of CO₂ selectivity indicate low WGS activity, whereas $S_{CO_2} \approx 0.5$ would be indicative of high WGS activity.

2.2. Comparison between equilibrium calculations and experimental data

WGS reaction is a reversible reaction and when the reaction is very fast it will reach equilibrium. The usage ratio can be predicted from equilibrium calculations and reaction stoichiometry as described in [4,5]. The relevant equations are:

$$U = \frac{[(1 + \gamma/2)x - y]}{(x + y)} \quad (14)$$

$$X_{H_2+CO} = \frac{(2 + \gamma/2)x}{(1 + F)} \quad (15)$$

$$K_{WGS} = \left(\frac{P_{CO_2}P_{H_2}}{P_{CO}P_{H_2O}} \right)_{\text{eq}} = \frac{y[F + y - (1 + \gamma/2)x]}{(x - y)(1 - x - y)} \quad (16)$$

where: x = moles of H₂O formed in FTS reaction, y = moles of CO₂ formed by WGS.

The equilibrium constant for the WGS reaction as a function of temperature is given by [6].

$$K_{WGS} = 0.0132 \exp \left(\frac{4578}{T} \right) \quad (17)$$

For a given temperature (T in K), F , γ and syngas conversion one can calculate the corresponding usage ratio as follows: calculate x from Eq. (15) and K_{WGS} from Eq. (17), then y from Eq. (16) and finally U from Eq. (14).

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