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Water gas shift reaction kinetics in Fischer–Tropsch synthesis over an industrial Fe–Mn catalyst

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Abstract

The kinetics of water gas shift (WGS) reaction over an Fe–Mn catalyst under Fischer–Tropsch synthesis (FTS) reaction conditions is studied in a spinning basket reactor. Experimental conditions are varied as follows: temperature of 533–573 K, reactor pressure of 10.0–26.5 bar, H_2/CO feed ratio of 0.66–2.0 and space velocity of 0.66–2.65$\times 10^{-3}$ Nm^3 kg$_{cat}^{-1}$ s^{-1}. By separately fitting WGS kinetics parameters with experimental data, which is possible in the spinning basket reactor with neglecting concentration and temperature gradients, different kinetics models of WGS are derived and discriminated on the basis of four sets of WGS elementary reactions. Kinetics experimental results show that the WGS reaction under FTS reaction conditions is far from equilibrium. Two types of WGS mechanisms are investigated. One is the formate mechanism, and the other is the direct oxidation mechanism. It is found that the formate mechanism is better in fitting experimental data than the direct oxidation mechanism over the Fe–Mn catalyst under the FTS reaction conditions. The optimized kinetics model with formate intermediate dissociation as the rate-determining step (RDS) can fit the WGS experimental results well. The simplified WGS kinetics model can easily be used for industrial modeling applications.

Keywords: Kinetics; Water gas shift reaction; Fischer–Tropsch synthesis

1. Introduction

With the depleting resource of crude oil all over the world, the Fischer–Tropsch synthesis (FTS) process, which converts syngas to mainly straight chain hydrocarbons with wide carbon number distribution, becomes a promising route to meet the continuously increasing demand for liquid fuels and chemical feedstocks conventionally obtained from crude oil [1–3]. The syngas feedstock for FTS processes can be produced from all kinds of carbon containing resources, namely coal, biomass and carbon-containing wastes through gasification, and natural gas through partial oxidation. For the coal-derived syngas, the iron-based catalysts have normally been used for FTS due to the low cost and high activity for both FTS and water gas shift (WGS) reactions [4]. The sufficient WGS activity enables to use the coal derived syngas with a low H_2/CO ratio.

The mechanism and kinetics of the individual WGS reaction has systemically and extensively been studied using many methods [5–10]. An excellent review for the WGS mechanism and kinetics over iron-based, copper-based and cobalt molybdenum-based catalysts was published by Newsome [11] in 1980. However, the kinetics study of WGS under FTS reaction conditions receives relatively little attention [12–20]. This is partially due to the fact that the WGS kinetics in a FTS process becomes difficult to address because of the accompanying FTS reactions, which remarkably increases the complexity in the discrimination of WGS kinetics models as well as in the WGS kinetics parameter estimation.

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Nomenclature

E_v	activation energy for WGS reaction, kJ mol^{-1}
$F_{obj,W}$	objective function of WGS reaction
k_{W4}	WGS rate constant of the forward reaction in WGSI RDS4, mol^{-1} kg^{-1} s^{-1} bar^{-1}
$k_{W4,0}$	preexponential factor of rate constant of CO_2 formation, mol^{-1} kg^{-1} s^{-1} bar^{-1}
k_{W-4}	WGS rate constant of the reversible reaction in WGSI RDS4, mol^{-1} kg^{-1} s^{-1} bar^{-1}
K_{W1}	equilibrium constant of CO adsorption elementary step in WGSI RDS4, bar^{-1}
K_{W2}	equilibrium constant of H_2O dissociation elementary step in WGSI RDS4, bar^{-1}
K_{W3}	equilibrium constant of surface reaction of [COS] with [OHS] in WGSI RDS4
K_{W5}	equilibrium constant of H_2 desorption elementary step in WGSI RDS4, bar
K_P	equilibrium constant of WGS reaction
$m_{i,exp}$	experimental molar flow rate, mol s^{-1}
$m_{i,cal}$	calculated molar flow rate, mol s^{-1}
MARR	mean absolute relative residual
N_{exp}	the number of experimental points
NRS	the number of responses for FTS
P_i	partial pressure of component i, bar

Models describing the complex FTS reaction have recently been developed by simultaneously fitting both WGS and FTS kinetics with experimental data [17–20]. This conventional treatment is systematic. However, our experiences in the kinetics development of FTS have indicated that the complex FTS kinetics can also bring about uncertainties to the 'simple' WGS kinetics as long as the two coupled reaction routes (WGS and hydrocarbon formation) are simultaneously treated typically over iron FTS catalysts. The coupling nature cannot be separated in the kinetics study using a fixed-bed reactor because the reaction environment is different along its axis. However, in a continuous spinning basket reactor, the reaction environment is uniform all over the reactor. Thus in a continuous spinning basket reactor, the WGS kinetics model discrimination and parameter estimation can be separated from the FTS kinetics models in a FTS process.

The objective of this work is to systematically establish and discriminate Langmuir–Hinshelwood–Hougen–Watson (LHHW) kinetics models for the WGS reaction on the basis of possible detailed mechanisms over an industrial Fe–Mn catalyst under FTS reaction conditions. By using the experimental data from a continuous spinning basket reactor, a set of WGS kinetics models are estimated and discriminated separately.

2. Kinetics models

The formate intermediate and direct oxidation mechanisms for the WGS reaction are proposed in literature [21], and are shown in Fig. 1. For the formate intermediate mechanism, the formate species is formed through the reaction between carbon monoxide and a hydroxyl species or water. The hydroxyl intermediate is formed via the decomposition of water. Another mechanism is the direct oxidation mechanism via a regenerate or redox mechanism to form adsorbed or desorbed CO_2. On the basis of the mechanisms shown in Fig. 1, four sets of elementary reactions for the WGS reaction are derived in this work, and are listed in Table 1.

For the derivation of the rate expressions, the WGS reaction and the FTS reaction (hydrocarbon formation) are assumed to proceed on different active sites [22–24], and one rate-determining step (RDS) is assumed in the sequence of WGS elementary reactions. Corresponding to the mechanisms listed in Table 1, WGSI RDS4 means that the reaction mechanism is WGSI, and the RDS is the 4th elementary reaction step. The remaining steps can be considered to be at quasi-equilibrium. The rate of formation of CO_2 can be written as:

$$R_{CO_2} = k_{W4}[\mathrm{COOHS}] - k_{W-4}P_{CO_2}[\mathrm{HS}] \quad (1)$$

From the elementary reaction step listed in Table 1, the intermediates can be expressed as follows:

$$[\mathrm{COS}] = K_{W1}P_{CO}[\mathrm{S}] \quad (2)$$

$$[\mathrm{HS}] = \sqrt{P_{H_2}/K_{W5}}[\mathrm{S}] \quad (3)$$

$$\begin{aligned}[\mathrm{OHS}] &= K_{w2}P_{H_2O}[\mathrm{S}]^2/[\mathrm{HS}] \\ &= K_{w2}P_{H_2O}[\mathrm{S}]/\sqrt{P_{H_2}/K_{w5}} \quad (4)\end{aligned}$$

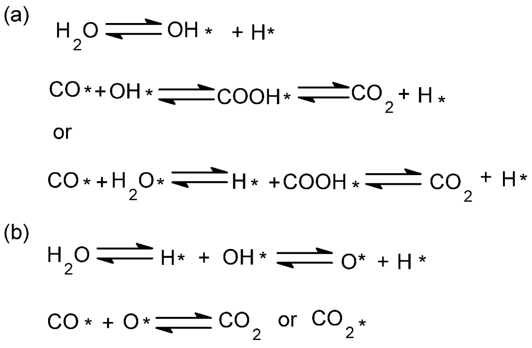

Fig. 1. Water gas shift reaction via the formate species (a) and the direct oxidation mechanism (b).