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Full Length Article

Kinetic modeling of the Fischer-Tropsch reaction over a zeolite supported Fe-Co-Ce catalyst prepared using impregnation procedure

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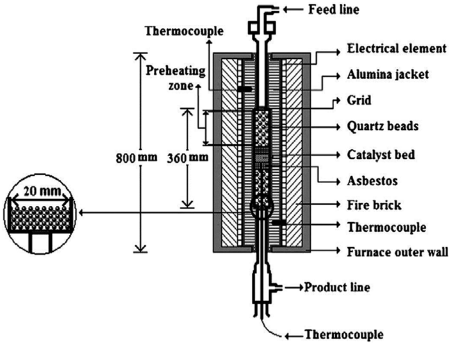
GRAPHICAL ABSTRACT

The structure and different parts of fixed-bed reactor.



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ABSTRACT

The kinetic of Fischer-Tropsch synthesis over a zeolite supported Fe-Co-Ce catalyst prepared using impregnation, was investigated in a fixed bed micro-reactor under the following conditions: reaction pressure 1–10 bar, H_2/CO feed ratio of 1:2, and gas space velocity (GHSV) of 3000 h^{-1} at temperature range of 185–295 °C. 35 rate equations for CO consumption, according to the Langmuir-Hinshelwood-Houngen-Watson (LHHW) type, were derived on the basis of a detailed set of possible reaction mechanisms. In order to perceive the effect of water on the FT rate equation, a water term was included in the FT rate equations. The kinetic parameters were estimated with the non-linear regression method, and the activation energies of CO consumption and the FT rate equation (including water term) were obtained as 50.22 and 95.74 kJ/mol, respectively. It was concluded that water has an inhibition effect and changes CO consumption.

1. Introduction

Fischer-Trosch Synthesis (FTS) is a heterogeneously catalytic process employed for the production of clean fuels and chemicals from biomass, pent, coal, and natural gas [1,2]. The main reaction of this polymerization process consists of the formation of CH_x monomers via the hydrogenation of the carbon adsorbed on a solid catalyst to produce hydrocarbons and oxygenate with a broad range of chain lengths as well as functional groups such as methane, alkanes, alkenes, alcohols, aldehydes, ketones, and fatty acids [3–6]. Group VIII metals are known to be employed as active catalysts for the FTS [7,8]. Iron and Cobalt are the most common commercial FTS catalysts. Cobalt catalysts have been

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Nomenclature

r_{FT}	rate of reaction (mol/g_{cat}.min)
k	reaction rate constant
P_{CO}	CO pressure (bar)
P_{H2}	hydrogen pressure (bar)
F_{co}^{0}	molar flow rate of CO at the inlet
R	universal gas constant (8.314 J/mol.K)
T	temperature (K)
W	catalyst mass (g)
X_{CO}	conversion of CO
θ_C	surface occupied with C
θ_{H2}	surface occupied with H_2
C_V	the concentration of free sites
b_{CO}	adsorption coefficient of CO
Ea	activation energy (kJ/mol)
ΔH	heat of adsorption (kJ/mol)
$k_{ads,CO}$	rate constant of adsorption of CO
$k_{des,CO}$	rate constant of desorption of CO
*	unoccupied active sites
$-r_{CO}$	the consumption rate of CO
ν°	the total volumetric flow rate (ml/min)
N	number experimental data points

applied in the FT process because of their high activity and selectivity for long-chain paraffins and waxes. In addition, cobalt seems to be a reasonable compromise in low-temperature FT synthesis [9,10]. Fe-based catalysts are the preferred catalysts for FTS because they yield high amounts of olefins in hydrocarbon distribution. Iron is used when the synthesis gas is produced from coal [11–17]. Nowadays, with decreasing oil reserves and the rise of petroleum prices, the development of new catalysts for the FTS has dramatically intensified [18]. A survey of the inclusion of other components within traditional catalysts shows that mixed metal catalysts improve the activity and selectivity of catalysts [19]. It has been reported that the inclusion of Ce within cobalt catalysts is accompanied by an increase in the formation of olefins with lower molecular weight [20,21]. Investigating the kinetic of the FTS is a very important task for commercial process design, optimizing, and simulation. Many research groups have investigated the kinetic of reaction and several kinetic models developed [22–24], which can be organized into two classes [25]. The first has been derived to describe the rate of syngas (carbon monoxide and hydrogen) consumption on the basis of the FT reaction mechanism through the use of lumped kinetic models. Other approach has been developed for the calculation of total hydrocarbon product distribution due to the probability of the addition of a carbon intermediate to the chain. Several investigators follow the first method to describe the kinetic of the FT reaction and many rate expressions have been proposed that are divided into three categories; these are: Power low, Langmuir-Hinshelwood-Hougen-Watson (LHHW), and Eley-Rideal. The power low type of expression has been applied for the gas phase reaction; its form is as follow:

$$-r_{Co} = k\,(P_{H2})^{x}(P_{CO})^{y}$$

It was found that the reaction order of carbon monoxide (y) was from +0.65 to −1.0, and the order of hydrogen was generally positive from 0.5 to 2 [26–28]. Some rate expressions are derived based on the LHHW or the Eley-Rideal mechanisms. The LHHW kinetic model describes bi-molecular and ter-molecular surface reactions while the Eley-Rideal model depicts the interactions of gas-phase reactions. The Eley-Rideal and the LHHW rate expressions can be lumped as a function of the reactants particle pressure as follows:

$$-r_{co} = \frac{kP_{co}P_{H2}^{a}}{(1+\sum k_iP_i)^{b}} \quad (\text{ i= CO,H}_2\text{,H}_2\text{O, and CO}_2)$$

k, which appeared in the rate expression, is the equilibrium constant. According to these facts that on the Fe-based catalyst in the H_2/CO ratio less than 2, during the reaction the excess amount of CO is converted to CO_2 by water-gas-shift (WGS) reaction. As there is competition between water and CO_2 for adsorption on the catalyst surface, in LHHW type kinetic rate expressions, it is essential to include a water term in the rate expression. In this research, the main aim is to investigate the kinetic and the mechanism of FTS on the zeolite supported Fe-Co-Ce catalyst, which was prepared through the impregnation procedure firstly based on the consumption rate of CO and then, with the consideration of the water effect on the reaction kinetic expression. Upon acquiring the appropriate kinetic model, the kinetic parameters was appointed by the use of the non-linear regression method.

2. Experimental

2.1 Catalyst preparation

The catalyst used in this research, 45%Fe/45%Co/10Ce/70 wt% zeolite, was prepared through the impregnation method as follows: an optimum amount of iron nitrate, $Fe(NO_3)_3{\cdot}9H_2O$(6.97 g), cobalt nitrate, Co $(NO_3)_3{\cdot}6H_2O$(4.811 g), and cerium nitrate, Ce (NO3)3.6H2O (0.661 g) were dissolved in an adequate amount of distilled water. Then, calcined zeolite was added to the mixture of salts.

After rotating the aged solution in a rotary evaporator, for 5 h at 70 °C, the solution was filtered. The precipitate was then dried in an oven for 5 h at 120 °C to produce a material denoted as the catalyst precursor. To obtain the final catalyst, the precursor was calcined at 400 °C in state air within an electric furnace for 6 h.

2.2 Catalyst testing

The kinetic experiments of FTS were carried out in a fixed-bed micro-reactor. The exact details, equipment, and system of the reactor have been reported in previous literature [29,30]. The reactor was constructed from stainless steel with an internal diameter of 20 mm, surrounded by an alumina jacket to maintain a uniform wall temperature. An electrical element wrapped around the alumina jacket; provided external heating, placed in through the fire-brick portion. Three separate thermocouples checked the temperature of the preheating zone, the catalyst bed, and the underneath zone of the reactor. The preheating zone ahead of the catalyst packing was filled with inert quartz glass beads. The inlet feed gas was imported from the top of the reactor. The flow rate of the inlet gases (CO, H_2 and N_2 with purities of 99.99%) were automatically adjusted by the means of three mass flow controllers (Brooks, model 5850B). Before entering the reactor, the gases (CO + H_2) were mixed in a container, and then introduced into the reactor tube. Before the measurement activity of the catalyst, the flow (30 ml/min) of hydrogen was used to reduce the catalyst at 250 °C for 16 h at atmospheric pressure. The reactor pressure was controlled by an electronic back-pressure regulator. Prior to the reaction, the catalyst was meshed (1 g) and was then held in the catalyst bed in the middle of reactor using quartz wool.

Experiments were carried out with a mixture of H_2, N_2, and CO within a temperature range of 185–295 °C, a H_2/CO feed rate of 1–2, and a pressure range of 1–10 bar. In each test, the GHSV (gas space velocity) was 3000 h^{-1}. The catalyst was loaded into the reactor and reduced at 250 °C for 16 h in H_2 (99.99%) at a flow rate of 30 ml/min. After the catalyst reduction, the flow of the H_2 gas was replaced with a mixture of H_2 and CO gases. The products of the FT synthesis were analysed using a gas chromatograph (Thermo ONIX UNICAM PROGC+) equipped with a sample loop, two Thermal Conductivity