



Intrinsic kinetics of Fischer–Tropsch reactions over an industrial Co–Ru/ γ -Al₂O₃ catalyst in slurry phase reactor

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ABSTRACT

The rate of Fischer–Tropsch synthesis over an industrial well-characterized Co–Ru/ γ -Al₂O₃ catalyst was studied in a laboratory well mixed, continuous flow, slurry reactor under the conditions relevant to industrial operations as follows: temperature of 200–240 °C, pressure of 20–35 bar, H₂/CO feed ratio of 1.0–2.5, gas hourly space velocity of 500–1500 N cm³ g_{cat}⁻¹ h⁻¹ and conversions of 10–84% of carbon monoxide and 13–89% of hydrogen. The ranges of partial pressures of CO and H₂ have been chosen as 5–15 and 10–25 bar respectively. Five kinetic models are considered: one empirical power law model and four variations of the Langmuir–Hinshelwood–Hougen–Watson representation. All models considered incorporate a strong inhibition due to CO adsorption. The data of this study are fitted fairly well by a simple LHHW form $-R_{H_2+CO} = ap_{H_2}^{0.988} p_{CO}^{0.508} / (1 + bp_{CO}^{0.508})^2$ in comparison to fits of the same data by several other representative LHHW rate forms proposed in other works. The apparent activation energy was 94–103 kJ/mol. Kinetic parameters are determined using the genetic algorithm approach (GA), followed by the Levenberg–Marquardt (LM) method to make refined optimization, and are validated by means of statistical analysis. Also, the performance of the catalyst for Fischer–Tropsch synthesis and the hydrocarbon product distributions were investigated under different reaction conditions.

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1. Introduction

Fischer–Tropsch synthesis (FTS) is a promising technology for the production of ultra-clean fuels and chemical feedstocks from indirect conversion of biomass, coal, or natural gas. The reaction stoichiometry involved in this process can be generalized as



The FT synthesis from natural gas is typically carried out over cobalt-based catalysts on a suitable support, because of their high activity and selectivity, low water–gas shift (WGS) activity and relatively slow deactivation. However, a major drawback of cobalt is its high cost, making catalyst replacement undesirable. Therefore, further improvements and developments of the Fischer–Tropsch catalysts are important to make Fischer–Tropsch synthesis more viable. Cobalt alumina catalysts for FTS have received renewed interest with the development of slurry phase reactors. Recently, slurry phase reactor processes employing a high stable and active cobalt alumina catalyst are employed commercially, for instance Oryx plant in Qatar. Both fixed-bed and slurry reactors is commonly used to

perform FT reaction. Principal advantages of the slurry reactors are a better temperature control, absence of intraparticle mass transfer limitation and a possibility to recycle the catalyst.

Supported Ru catalysts are excellent FTS catalysts, with high activity and chain growth probability. Indeed, supported ruthenium catalysts for FTS produce C₅₊ hydrocarbons with a selectivity of over 90% at temperatures as low as 373 K. The application of Ru catalyst in the FTS is restricted due to its high price. Therefore, usually a small amount of ruthenium is used as a promoter for the supported cobalt catalysts. Iglesia reported that addition of Ru to a cobalt catalyst tripled the activity of the catalyst and increased the C₅₊ selectivity from 84% to 91% [1]. Tsubaki et al. [2] investigated the effect of promotion of Co/SiO₂ catalyst with small amounts of Ru, Pt and Pd. They found that the Ru promoted catalyst had the highest CO hydrogenation rates. Ru enhanced the reducibility of the cobalt catalyst and enriched on the surface of cobalt particles.

The kinetic description of the Fischer–Tropsch reaction is extremely important for the industrial practice, being a prerequisite for the industrial Fischer–Tropsch process design, scale-up, optimization, and simulation. The reaction mechanism for FTS is complex with a large number of species involved. This made it difficult to describe Fischer–Tropsch reaction kinetics. However, in the recent years, the kinetics of the Fischer–Tropsch synthesis has been the subject of several studies, of which some are focused on cobalt-based catalyst [3–6, 27–30] due to their interesting selectivity toward heavy hydrocarbons and their

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low oxygenates selectivity and water gas shift activity, which makes this catalyst suitable for the hydrogen-rich syngas obtained from natural gas.

In the present study, an industrial Co–Ru/ γ -Al₂O₃ catalyst developed by Research Institute of Petroleum Industry (RIPI, Iran) is examined by using a mechanically stirred slurry reactor operated continuously with respect to synthesis gas feed and volatile products over a wide range of reaction conditions. The reactor behaved as a CSTR, providing content of uniform temperature and concentration, which simplified data analysis. We develop here an intrinsic kinetic model that accounts for the rate of synthesis gas conversion on cobalt catalyst over a wide range of industrially relevant conditions. The unknown kinetic parameters are estimated from experimental data using genetic algorithm, followed by non-linear regression (Levenberg–Marquardt) method and a number of statistical indicators such as confidence level and correlation matrix.

2. Experimental

2.1. Catalyst preparation

The catalyst employed, in the present study, is a 15 wt.% Co/Al₂O₃ catalyst prepared by incipient wetness impregnation of a γ -alumina support (Condea Vista Catalox B γ -alumina, 200 m²/g, impurities: sodium oxide (Na₂O) < 50 ppm; silica (SiO₂) < 0.9 ppm; sulfate (SO₄) < 1.5 ppm) with cobalt nitrate (Co(NO₃)₂·6H₂O) solution (cobalt nitrate purity > 99.5%). The support was calcined at 773 K for 10 h prior to the impregnation. Catalyst with 1 wt.% loading of ruthenium promoter was prepared by impregnation using a ruthenium nitrosyl nitrate solution. After impregnation, the catalyst was dried in a rotary evaporator at 393 K for 3 h, and calcined at 723 K for 3.5 h afterwards. The calcined catalyst was analyzed by ICP to determine accurate weight percentage of cobalt.

2.2. Catalyst characterization

BET measurements for the catalysts, as shown in Table 1, were conducted to determine the loss of area with loading of the metal. These measurements were conducted using a Micromeritics ASAP 2010 system.

The fresh catalyst was characterized by hydrogen chemisorption and pulse reoxidation. The amount of chemisorbed hydrogen was measured using the Micromeritics TPD-TPR 290 system. 0.25 g of the calcined catalyst was activated at 673 K for 12 h and then cooled under flowing hydrogen to 373 K. The sample was held at 373 K under flowing argon (about 30 min) to prevent physisorption of weakly bound species prior to increasing the temperature slowly, with a ramp rate of 10 K/min, to 673 K. Afterwards, the temperature programmed desorption (TPD) of the sample was obtained. The TPD was used to determine the cobalt dispersion and its surface average crystallite size. After TPD of hydrogen, the sample was reoxidized at 673 K by injecting pulses of 10% O₂ in He to determine the extent of reduction. After oxidation of the cobalt metal clusters, the number of moles of oxygen consumed was determined, and the percentage reduction calculated assuming that the Co⁰ reoxidized to Co₃O₄. While the uncorrected dispersions are based on the assumption of complete reduction (total

Co), the corrected dispersions include the percentage of reduced cobalt (reduced Co) as follows:

$$\%D_{\text{total Co}} = \frac{\text{Number of Co}^0 \text{ atoms on surface}}{\text{Total number of Co atoms}} \times 100 \quad (1)$$

$$\%D_{\text{reduced Co}} = \frac{\text{Number of Co}^0 \text{ atoms on surface}}{(\text{Total number of Co atoms})(\text{Fraction reduced})} \times 100. \quad (2)$$

Table 2 shows the results of hydrogen chemisorption and pulse reoxidation tests for the fresh Ru-promoted and un-promoted cobalt catalyst.

As shown in Fig. 1, the temperature programmed reduction (TPR) profiles of the fresh catalysts were obtained using a Micromeritics TPD-TPR 290 system equipped with a thermal conductivity detector (TCD). The catalyst samples were first heated to 673 K and purged in flowing argon to remove traces of water and then cooled to 313 K. The TPR profile of 50 mg of each sample was performed using 5.1% hydrogen in argon gas mixture with a flow rate of 40 cm³/min. The samples were heated from 313 to 1273 K with a heating rate of 10 K/min. In Fig. 1, the first peak, which occurs in the low temperature range (300–450 °C), is assigned to reduction of Co₃O₄ to CoO. The second peak, with a broad shoulder (500–750 °C) is attributed to the reduction of CoO to Co⁰. The addition of Ru caused the peaks shift markedly to lower temperatures, presumably due to spillover of hydrogen from the reduced promoter to reduce the cobalt oxide species [7].

2.3. Experimental apparatus and procedure

In this study, the experiments were performed in a 1-liter commercial continuous stirred tank reactor (CSTR) from Autoclave Engineers. A schematic diagram of the experimental setup is shown in Fig. 2. The reactor was initially filled with 50 g of cobalt catalyst, which crushed to a particle size smaller than 44 μ m (325 ASTM mesh). Catalyst is reduced inside the reactor (in situ reduction) by hydrogen at 400 °C (ramp rate: 2 °C/min), atmospheric pressure, and space velocity of 1188 (N cm³ g_{cat}⁻¹ h⁻¹). The reduction vessel (reactor) was held at 400 °C for 24 h and then pressurized with hydrogen and cooled to a specified reaction temperature. Afterward, 350 g of Merck paraffin wax (Merck index 1.07358, sulphate < 0.015%) was degassed using hydrogen flow at 100 °C and then added to the reduced catalyst under hydrogen atmosphere, in which the finely crushed cobalt catalyst was slurried with the liquid wax to produce a 12.5 wt.% suspension, based on unreduced catalyst. Inside the reactor, the mixture of liquid wax and catalyst particles is well mixed by a magnetically driven turbine agitator at 2000 rpm. Therefore, the solid phase is completely suspended in the liquid phase.

The feed gas is composed of H₂ (>99.999% purity) and CO (>99.995% purity) where they are taken from the cylinder. Their flow rates are controlled by two mass flow controllers (Type 5850E, Brooks Instruments Div.). For decomposing carbonyls possibly present in the CO, the syngas is passed through a bed of carbonyl trap. Also, before entering the reactor, the feed is passed through a static mixer and then preheated up to near the reaction temperature. The slurry reactor is operated in a semibatch fashion in that syngas is continuously sparged to the slurry and volatile products remove overhead. The gas outlet of the reactor is connected to a hot receiver (353 K) and then a cold receiver (273 K) at the system pressure. High molecular weight products are collected in hot receiver and remaining condensables are collected in cold receiver for a typically period of 15–20 h during steady state of the reactor system. In each receiver, the collected liquid products separated into an oil phase, which contained hydrocarbons, and aqueous phase, which consisted of water plus

Table 1
BET measurement.

Catalyst description	BET surface area (m ² /g)	Pore volume (single point) (cm ³ /g)	Average pore radius (nm)
γ -Al ₂ O ₃	270	0.639	4.72
15% Co/ γ -Al ₂ O ₃	214	0.419	4.22
1.0% Ru–15% Co/ γ -Al ₂ O ₃	215	0.374	3.11

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