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Studies on product distribution of nanostructured iron catalyst in Fischer–Tropsch synthesis: Effect of catalyst particle size

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ABSTRACT

The dependencies of hydrocarbon product distributions of Fischer–Tropsch synthesis by iron catalysts on catalysts particle size are studied. The concept of two superimposed Anderson–Schulz–Flory distributions applied for represent size dependency of product distributions. A series of catalysts with different particle size are prepared by microemulsion method. It is found that the carbon number of produced hydrocarbon decreased with decreasing the catalyst particle size. These results indicate the H_2 concentration on catalyst surface decreased by increasing the catalyst particle size. Thus the concentration of monomers that exhibited higher degree of hydrogenation (like CH_2 species) on the surface of catalyst increased with decreasing the catalyst particle size.

1. Introduction

Strong interest in the Fischer–Tropsch synthesis (FTS) that converts synthesis gas into hydrocarbons is reappearing because it is one of the major routes that convert natural gas into liquid energy carriers [1–3]. The Fischer–Tropsch synthesis (FTS) consisting of a complex multi component mixture of linear and branched hydrocarbons and oxygenated products. Main products are linear paraffins and α-olefins. Herington first treated the molar distribution of hydrocarbons from FTS in terms of a polymerization mechanism [4–6]. The same formulation was rediscovered by Anderson et al. in 1951 and named the Anderson–Schulz–Flory (ASF) distribution [4,5,7,8]. In the ASF model, the formation of hydrocarbon chains was assumed as a stepwise polymerization procedure and the chain growth probability was assumed to be independent of the carbon number. For all FTS catalysts deviations from the ideal Anderson–Schulz–Flory (ASF) distributions are observed in many studies [9–11]. The usual deviations of the distribution of the linear hydrocarbons are a relatively higher selectivity to methane, a relatively lower selectivity to ethene, and an increase in the chain growth probability with increasing molecular size. Some authors interpreted the deviations from the standard ASF distribution by the superposition of two ASF distributions [10,12–14]. They suspected the existence of two sorts of sites for the chain growth on the catalyst surface and each site might individually yield the ideal ASF distribution with different chain growth probabilities. Madon and Taylor [15] interpreted this bimodal distribution by differently sites causing different growth probabilities. König and Gaube [10] supposed that in the case of alkali promoted iron catalysts, all active sites are not influenced by alkali. Therefore the distribution of higher growth probably was attributed to products formed on promoted active sites while the other part of the product is formed on unpromoted sites with a similar growth probability as evaluated for the product formed on unprompted iron catalysts. Patzlaff et al. [11] studied the effects of 1-alkene readsorption and secondary chain growth on the product distribution of FTS on iron and cobalt catalyst by cofeeding 1-alkenes. They found that chain length distributions of products obtained on cobalt catalysts are slightly modified by secondary chain growth of readsorbed alkenes and hydrogenolysis of hydrocarbons.

The FTS reaction is a surface phenomenon, therefore for optimum catalyst performance, maximum metal usage must be achieved. A rule of thumb in heterogeneous catalysis is that smaller metal crystallites provide largest surface area on which the reaction may happen [16–20]. In our previous work the effect of presence of the zeolite on product distributions of iron catalyst studied [21]. In the other our previous work the effect of Ca, Mg and La promoters on physico-chemical properties and the catalytic activity and selectivity during FTS performance studied [22,23].

In this experiment the effect of catalyst particle size on the carbon number distribution of Fischer–Tropsch products on iron catalysts are studied, using a modified Anderson–Schulz–Flory (ASF) distribution with two chain growth probabilities.

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2. Experimental

2.1. Catalyst preparation and characterization

Fe–Cu nanoparticles were prepared by coprecipitation in a water-in-oil microemulsion [24–28]. The precipitation was performed in the single-phase microemulsion operating region. In order to achieve a series of catalysts displaying different hematite particle size the surfactant-to-oil (S/O) weight ratio was set to a value of 0.3 the water-to-surfactant molar ratio (W/S) was varied from 4 to 12.

2.2. Catalyst characterization

The surface area was calculated from the Brunauer–Emmett–Teller (BET) equation and pore volume, average pore diameter, and pore size distribution of the catalysts were determined by N_2 physisorption using a Micromeritics ASAP 2010 automated system. A 0.5 g catalyst sample was degassed at 373 K for1 h and 573 K for 2 h prior to analysis. The analysis was done using N_2 adsorption at 77 K. Both the pore volume and the average pore diameter were calculated by Barret–Joyner–Hallender (BJH) method from the adsorption isotherm.

XRD was used to determine the phase composition of catalysts before and after pretreatments. The XRD spectrum of the catalysts were collected by a X-ray diffractometer, Philips PW1840 X-ray diffractometer, using monochromatized Cu/K_α radiation (40 kV, 40 mA) and a step scan mode at a scan rate of 0.02° (2θ) per second from 10° to 80°. XRD peak identification was recognized by comparison to the JCPDS database software. The average crystallite size of samples, d_{XRD}, can be estimated from XRD patterns by applying full-width half-maximum (FWHM) of characteristic peak (1 0 4) Fe_2O_3 located at $2\theta = 33.3^\circ$ peak to Scherrer equation:

$$d_{XRD} = \frac{0.9\,\lambda}{\text{FWHM}\cos\theta} \tag{1}$$

where λ is the X-ray wavelength (1.5406 Å in this study) and θ is the diffraction angle for the (1 0 4) plane.

The H_2-TPD experiments were performed by means of the temperature-programmed desorption (TPD) of H_2 on the catalyst (0.5 g), which was packed in a shallow-bed quartz reactor with a low dead volume from 300 K to 1100 K at a linear heating rate of 5 K/min while Ar was used as a carrier gas. A thermal conductivity detector (TCD) was used to measure the H_2 desorbed in the TPD quantitatively. The catalyst was first reduced with H_2 at 673 K and 1 bar for 11 h. Then the sample was heated in Ar from 323 K to 673 K, held at 673 K until the baseline leveled off (ensuring complete removal of adsorbed species on the reduced catalyst surface has been achieved), and finally cooled to 323 K for TPD tests. In the subsequent steps, H_2 adsorption on the catalyst was performed at 323 K for 30 min, and then the sample was purged with Ar in order that weakly adsorbed species could be removed until the baseline leveled off. Following this, H_2-TPD was being carried out while the temperature increased to 1050 K. H_2 chemisorptions uptakes determined by integrating the area of H_2-TPD curves as compared to the certain amounts of gas passed through the TCD.

2.3. Experimental apparatus and procedure

Steady-state FTS reaction rates measured in a continuous spinning basket reactor. A detailed description of the experimental setup and procedures has been provided in our previous works [29]. The fresh catalyst is crushed and sieved to particles with the diameter of 0.25–0.36 mm (40–60 ASTM mesh). The weight of the catalyst loaded was 2.5 g and diluted by 30 cm^3 inert silica sand with the same mesh size range. The catalyst samples were activated by a 5% (v/v) H_2/N_2 gas mixture with space velocity equal to 15.1 nl/g_{cat}/h at 1 bar and 1800 rpm. The reactor temperature increased to 673 K with a heating rate of 5 K/min, maintained for 1 h at this temperature, and then reduced to 543 K. The activation is followed by the synthesis gas stream with H_2/CO ratio of 1 and space velocity equal to 3.07 nl/g_{cat}/h for 24 h at 1 bar and 543 K. After catalyst activation, synthesis gas was fed to the reactor at conditions operated at 563 K, 17 bar, H_2/CO ratio of 1 and a space velocity equal to 4.9 nl/g_{cat}/h. After reaching steady state, the FTS reaction rate was measured.

The out gas was analyzed by a gas chromatograph (Varian CP-3800) equipped with TCD and FID detectors. The CO, CO_2, N_2, and O_2 were analyzed through two packed column in series (Molecular sieve13× CP 81025 with 2 m length, and 3 mm OD, and Hayesep Q CP1069 with 4 m length, and 3 mm OD) connected to TCD detector. The C_1–C_5 hydrocarbons were analyzed via a capillary column (CP fused silica with 25 m × 0.25 mm × 0.2 μm film thickness) connected to FID detector. Hydrogen was analyzed through Shimatzu, GC PTF 4C, equipped with TCD detector and two column in series (Propack-Q with 2 m length, and 3 mm OD for CO_2, C_2H_4 and C_2H_6 separation and molecular sieve-5A with 2 m length, and 3 mmOD for CO, N_2, CH_4 and O_2 separation), which were connected to each other via a three way valve.

The collected liquid (including hydrocarbons and oxygenates) analyzed offline with Varian CP-3800 gas chromatograph equipped with capillary column (TM DH fused silica capillary column, PETRO COL 100 m × 0.25 mm × 0.5 μm film thickness) connected to FID detector.

Total mass balances were performed with the carbon material balance closed between 97 and 103%. This criterion was adopted since compounds containing carbon and hydrogen might accumulate in the reactor, in the form of high molecular weight hydrocarbons.

3. Data analysis

Hydrocarbon products of the Fischer–Tropsch synthesis are generally taken to follow the ASF distribution. For carbon number i, the mole fraction of product x_i as determined by a single chain growth probability α is given by:

$$x_i = (1-\alpha)\alpha^{i-1} \tag{2}$$

In this work the carbon number distribution of Fischer–Tropsch products on iron catalysts studied by modified Anderson–Schulz–Flory (ASF) distribution with two chain growth probabilities. This method proposed by Donnelly et al. [14] to characterize the carbon number distribution of FTS hydrocarbon products by ASF distributions with different chain growth probabilities.

$$x_i = A\,\alpha_1^{i-1} + B\,\alpha_2^{i-1} \tag{3}$$

Note that at the break point on ASF diagram, the contributions of each term in Eq. (3) are equal:

$$A\,\alpha_1^{i-1} = B\,\alpha_2^{i-1} \quad i = \zeta \tag{4}$$

In break point, i illustrate as ζ and necessarily is not an integral carbon number. In this model A and B were not correspond directly to the fractions of products produced from α_1 and α_2, respectively. Instead the sum of the mole fractions over all carbon numbers is unity:

$$\sum_{i=1}^{\infty} x_i = \sum_{i=1}^{\infty} [A\,\alpha_1{}^{(i-1)} + B\,\alpha_2{}^{(i-1)}] = 1 \tag{5}$$

Methane and ethene do not obey the ASF equation and after removing C_1 and C_2 products to fit theoretical distributions to data