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Effect of high-temperature pre-reduction in Fischer–Tropsch synthesis on Fe/ZrO_2 catalysts

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ABSTRACT

Fischer–Tropsch synthesis of low molecular weight (C_2—C_4) olefins is a valuable alternative process for the production of key chemicals from non-petroleum precursors such as a renewable C source like biomass. The influence of the H_2 treatment temperature of zirconia-supported iron catalysts on the conversion of synthesis gas has been investigated. The CO conversion rate, based on steady-state, increased with the pretreatment temperature up to a maximum and then decreased at higher temperatures. Moreover, methane selectivity was found to decrease slightly from the lowest H_2 treatment temperatures (46%) to the highest ones (34%), while C_2—C_4 and C_5^+ hydrocarbons followed an opposite trend. Presumably, methane formation takes place at highly active low coordination sites residing at corners and edges, which are more abundant on small iron carbide particles. Lower hydrocarbons are mainly produced at terrace sites that are available and active, quite independent of the iron crystallite size.

1. Introduction

The production of transportation fuels and chemicals by Fischer–Tropsch synthesis (FTS) is currently gaining greater importance fostered by environmental concerns and the necessity of many countries to reduce their reliance on oil imports. The catalytic production of hydrocarbons via FTS reaction from syngas mixtures involves a number of consecutive reactions resulting in a broad spectrum of linear and branched hydrocarbons, olefins and oxygenated products [1–3] with the simultaneous production of water according to the following simplified reactions:

$$\text{Paraffins}: \quad (2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \qquad (1)$$

$$\text{Olefins}: \quad nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O \qquad (2)$$

$$\text{Oxygenates}: \quad H_2 + CO \rightarrow CH_xO_y + H_2O \qquad (3)$$

Other parallel reactions such as: (i) water gas-shift (WGS): $CO + H_2O \rightarrow CO_2 + H_2$; (ii) methanation: $CO + 3H_2 \rightarrow CH_4 + H_2O$; and (iii) Boudouard reaction: $2CO \rightarrow C + CO_2$ occur simultaneously.

It is established that the nature and composition of catalysts control the selectivity of products from FT reactions; therefore, proper catalyst selection as well as optimization of the reaction parameters are of prime importance in FT process. The active and selective catalysts for the FT reaction are mainly based on cobalt or iron. Cobalt-based catalysts have been widely investigated since they favor the formation of long-chain hydrocarbons [4,5]. As opposed to cobalt-based catalysts, iron-based ones are highly attractive not only because of their relatively low cost but also due to their broad operation conditions and high product selectivity toward light olefins [6]. In addition, iron disfavors the competing formation of methane, and furthermore catalyzes the WGS reaction, enabling the direct processing of synthesis gas with a low H_2/CO ratio derived from modern energy-efficient coal gasifiers without an additional WGS reactor [2,7,8].

Despite these promising features, however, Fe-based catalysts for FTS are often used as unsupported catalysts. One of the major drawbacks related to the use of massive unsupported catalysts is physical degradation, producing catalyst fines as a consequence of the volume changes that occur during the FTS reaction. These fines will either plug the fixed-bed reactors, generating a large pressure drop, or will hinder catalyst separation in slurry reactors [9]. The development of appropriate supports and/or binders, which increase attrition resistance of the samples, improves the catalyst life-time. High surface area oxides like silica (SiO_2), alumina (Al_2O_3), titania (TiO_2), magnesia (MgO), manganese oxide (MnO) and zirconia (ZrO_2) are among the supports most frequently used. Several advantages of supported iron catalysts, such as an improved catalytic stability and lower deactivation rate, have been reported [10].

In addition, the FTS is a structure-sensitive reaction [11], which means that the crystallite size of the iron phase plays an important role in FTS activity and product selectivity. It is emphasized that

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whereas these size effects of cobalt metal catalysts and ruthenium-based catalysts in CO hydrogenation reactions [1,12–22], the number of researches focused on the effect of iron cluster size in FTS reaction is limited. To the best of our knowledge, the performance of the ZrO_2-supported iron catalysts and the crystallite size effects of the activity and selectivity in FTS reactions have been scarcely investigated. Therefore, this work was undertaken with the aim to investigate the relationship between cluster size of iron oxide and its FT performance. For this purpose, Fe/ZrO_2 catalysts were prepared with different crystallite sizes and their performance evaluated in FTS performed with a laboratory-scale fixed bed reactor.

2. Experimental

2.1. Catalysts preparation

The catalysts used in this study were prepared by the conventional incipient wetness impregnation methods. Zirconia-supported iron catalysts were impregnated on a high surface area of silica-stabilized zirconium hydroxide (zirconium hydroxide (stabilized with 4% silica) grade XZ0645/01, Magnesium Elektron Ltd.) with ($Fe(NO_3)_3{\cdot}9H_2O$) (Iron(III) nitrate nonahydrate (Aldrich, ≥98%)) aqueous solution. Zirconia-supported iron catalysts were prepared with appropriate amount of 10 wt.% metal loading. $Fe(NO_3)_3{\cdot}9H_2O$ (Aldrich) was dissolved in appropriate deionized water and were added into the support drop by drop. The slurry was then kept at room temperature for overnight in ambient air then dried at 110 °C for 3 h. In order to obtain different particles size of metallic iron, aliquots of Fe/ZrO_2 precursor were treated under flowing of pure hydrogen (50 $cm^3\ min^{-1}$). Based on the treatment temperature and period of the treatment under hydrogen environment the catalysts are referred to hereafter as Fe_x and $Fe_{x(yh)}$, where x in Fe_x denotes the pretreatment temperature for 1 h and both x and y in $Fe_{x(yh)}$ denote the pretreatment temperature and period of the pretreatment in hours, respectively.

2.2. Catalysts characterization

2.2.1. Nitrogen adsorption–desorption isotherms

Nitrogen adsorption–desorption isotherms were recorded at the temperature of liquid nitrogen (−196 °C), using a Micromeritics ASAP 2000 apparatus. The samples were degassed at 140 °C for 16 h prior to the determination of the adsorption isotherm [2]. Specific areas were calculated by the BET method applied to the region of relative pressure $0.05 < P/P^0 < 0.30$ and taking a value of 0.162 nm^2 for the cross-section of adsorbed N_2 at −196 °C.

2.2.2. Hydrogen temperature programmed reduction (H_2-TPR)

Hydrogen temperature programmed reduction (H_2-TPR) experiments were carried out in a Micrometrics 3000 equipment interfaced to a data station. About 30 mg of the catalyst were pretreated under dry helium at 180 °C for 0.5 h. The TPR profile was recorded by heating the sample from room temperature (around 30 °C) to 950 °C at a rate of 10 °C/min under a flowing of 10 vol% of H_2/Ar. The hydrogen consumption was monitored with a thermal conductivity detector (TCD). The effluent gas was passed through a cold trap placed before the TCD to avoid water condensation from the exit stream. More details of the procedure can be found elsewhere [2].

2.2.3. Powder X-ray diffraction (PXRD)

Powder X-ray diffraction (XRD) patterns of the precursor and calcined sample were recorded using a Seifert 3000 XRD diffractometer equipped with a PW goniometer with Bragg–Brentano $\theta/2\theta$ geometry, an automatic slit, and a bent graphite monochromator [2]. Using nickel-filtered Cu $K\alpha_1$ ($\lambda = 0.15406$ nm) radiation. A scanning step of 0.02° was taken between 5° and 90° Bragg· angles in the scan mode (0.05°, 2 s).

2.2.4. Laser Raman spectroscopy

Raman spectra were recorded with a Renishaw in Via Raman Microscope spectrometer equipped with a laser beam emitting at 532 nm, and a 100 mW output power. The photon scattered by the sample were dispersed by an 1800 lines/mm grating monochromator and simultaneously collected on a CCD camera. The collection optic was set at 50× objective. The samples selected to be studied by Raman microscope spectrometer were both the pretreated catalysts under hydrogen environment and used samples after FTS reaction. Both samples were directly mounted into the analysis chamber of the Raman Microscope spectrometer without further treatment.

2.2.5. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectra (XPS) were acquired with a VG Escalab 200R spectrometer in the pulse-count mode at a pass energy of 50 eV using an Mg Kα ($h\nu = 1253.6$) X-ray source. Kinetic energies of photoelectrons were measured using a hemispherical electron analyser working in the constant pass (20 eV) energy mode. The background pressure in the analysis chamber was kept below 3×10^{-8} mbar during data acquisition. The powder samples were pressed into copper holders and then mounted on a support rod placed in the pretreatment chamber. The XPS data were signal averaged for at least 200 scans and were taken in increments of 0.1 eV with dwell times of 50 ms.

Binding energies were calibrated relative to the C 1s peak from adventitious carbon of the samples at 284.6 eV to correct the potential contact differences between the sample and spectrometer. Both binding energy (BE) values and peak areas were computed by fitting the experimental spectra to Gaussian/Lorentzian lines after removing the S-shaped background. The samples were exposed to a synthesis gas stream (62.0% H_2, 31.0% CO, and balance N_2, air liquid) at room temperature and then the temperature was increased from room temperature until reach 150 °C under heating rate of 10 °C/min then decrease heating rate from 10 °C into 1 °C/min beyond 150 °C until reach the activation temperature (300 °C) and keep it for 1 h under following of the syngas at atmospheric pressure. Finally the sample was cooled to ambient temperature and degassed (residual pressure about 10^{-6} mbar) before passing it to the analysis chamber.

2.3. Catalytic performance

The catalysts were tested in the CO hydrogenation reaction using a fixed-bed microreactor (stainless steel 316, 165 mm long and 8.5 mm ID. The reaction temperature was measured with a K-type thermocouple buried in the catalytic bed. The reactor was held within a furnace equipped with a temperature controller. All pipes after reactor outlet were kept at 130 °C. The reaction system was provided with a stainless steel hot trap set at 110 °C to collect the heavier products (waxes). Flow rates were controlled using Bronkhorst High-Tech Series mass flow controllers. The calcined catalyst precursors (200 mg, 0.212–0.315 mm particle size) were diluted with 1.5 g of silicon dioxide (sand SiO_2, Sigma Aldrich) to avoid hot spots owing to the exothermal character of the reaction, and also to facilitate the heat transfer. First, the catalysts were activated in situ at 300 °C (the temperature was increased from room temperature until reach 150 °C under heating rate of 10 °C/min, then heating rate was decreased to 1 °C/min beyond 150 °C until reach the activation temperature (300 °C) and keep it for 1 h in syngas ($31CO/62H_2/7\,N_2$, GHSV = 0.0042 $L/g_{cat}\ s$) at