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Phase transformation and textural properties of an unpromoted iron Fischer–Tropsch catalyst

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Abstract

The phase transformations and textural properties were systematically investigated over an unpromoted iron Fischer–Tropsch synthesis (FTS) catalyst prepared from ferrous sulfate with different Fe^{3+}/Fe_{total} ratios at different preparation stages (precipitation, dryness and calcination). The catalyst samples were characterized by X-ray diffraction (XRD), Mössbauer spectroscopy and N_2 physisorption. The characterization studies show that after precipitation the samples are composed of α-FeOOH, Fe_3O_4 and α-Fe_2O_3. The content of Fe_3O_4 increases with the increase of Fe^{3+}/Fe_{total} ratio (R_m) and reaches the maximum content at the R_m of 0.72. There is not a significant phase transformation during the dryness of the catalyst samples. After being calcined at 500 °C for 5 h, α-FeOOH and Fe_3O_4 existed in the catalyst samples are transformed into α-Fe_2O_3. The characterization results from N_2 physisorption show that when the R_m of sample is 0.72, the BET surface area and pore volume have the maximum values (26 m^2/g, 0.21 cm^3/g) after the samples being calcined at 500 °C.

Keywords: Fischer–Tropsch synthesis; Fe catalyst; Phase transformation; Textural property; Fe^{3+}/Fe_{total} ratio

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1. Introduction

Fischer–Tropsch synthesis (FTS) converting syngas to liquid fuel and chemicals, has been recently attracted much attention [1,2]. Research and development (R&D) of a high performance catalyst is one of the key technologies for the syngas conversion. Fe-based catalyst is attractive due to its high FTS activity as well as high water–gas shift (WGS) reactivity, which helps to make up the deficit of H_2 in the syngas ($H_2 + CO$) derived from coal [3]. However, most precipitated Fe-based catalysts are made from ferric nitrate [4]. Compared with ferric nitrate, the price of ferrous sulfate is relatively low. If ferrous sulfate can be used as the precursor of precipitated Fe-based catalyst, the cost of Fe-based catalyst can be greatly decreased. To decrease the production cost and to improve the economics of the FTS process, ferrous sulfate can be used as precursor material of Fe-based FTS catalysts due to its low cost. But it is difficult to completely remove sulfate ion from the mixture slurry, which is generally considered as a poison for FTS reaction [5]. At the same time, the difference of precursor material can make the ultimate catalysts present different physicochemical properties such as crystallite structure, textural properties and thermal stability, which influence subsequently catalysts FTS performance (activity, selectivity and stability) [6–8]. Wu [8] studied the effect of the initial formed Fe_3O_4 on the catalyst FTS performance, and indicated that the catalyst with low Fe_3O_4 content in its as-prepared state had high content of iron carbides after reduction and the catalyst with certain amount of highly dispersed Fe_3O_4 exhibited high FTS activity.

Our group has attempted to use ferrous sulfate as the precursor of Fe-based FTS catalyst, and the catalyst show some application potentials. At the same time, when ferrous sulfate is used as feedstock of Fe-based FTS catalyst, the solution of ferrous sulfate must be partly or completely oxidized to ferric sulfate, and the unsaturated iron oxide is also oxidized to α-Fe_2O_3 during the drying and calcination processes. There is a complicated phase transformation of iron oxide during the process of catalyst preparation, which may subsequently affect the

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reduction and FTS performance of the catalyst. It is therefore critical to illustrate this complex phase transformation to well optimize Fe-based catalyst.

However, little efforts have been performed on the phase transformation and textural properties during the preparation of a Fe-based FTS catalyst with ferrous sulfate as precursor material. Previous studies [1,3,9–11] on the transformation of phase and structure for Fe-based FTS catalysts are mainly focused on that occurred during the reduction and reaction. While, phase transformation and structure change of Fe-based catalysts made from ferrous iron occur not only in reduction and reaction, but also precipitation, dryness and calcination [6,12]. The properties of the precipitate are dependent on many synthesis parameters such as precipitation agent, temperature, concentration of cations [13,14], nature and concentration of anions [13,15], and pH value [13,16], etc. At the same time, the temperature and the duration of dryness and calcination also play important roles in physicochemical properties of the final products [15,17]. Motjopel et al. [18] had studied the effect of precipitating agents on the catalyst structure and phase composition over a precipitated Fe-based FTS catalyst. They found that catalysts precipitated with carbonates as precipitating agents, had larger pores than those precipitated with hydroxides. However, precipitation with aqueous ammonia solution resulted in the formation of large crystallites of α-FeOOH.

The objective of the present study is to investigate the phase transformation and the textural properties of Fe-based catalyst made from ferrous sulfate during the different stages of the catalyst preparation. Characterization technologies of X-ray diffraction (XRD), Mössbauer spectroscopy and N_2 physisorption were used to characterize the catalysts after filtration, dryness and calcination. The results were used to elucidate the nature of phase transformation and structure change of the catalyst prepared with different Fe^{3+}/Fe_{total} ratios.

2. Experimental

2.1. Catalysts preparation

The catalyst samples used in the present study were prepared by coprecipitation of iron sulfate derived from the partial or complete oxidation of ferrous sulfate and aqueous ammonia solution (8.0 wt.%). Aqueous solution of ferrous sulfate (1.0 mol/l) was firstly oxidized with different amounts of hydrogen peroxide (1.0 mol/l) and sulfuric acid (1.0 mol/l) to produce mixed solution of iron sulfate with required Fe^{3+}/Fe_{total} ratio. After oxidation, the Fe^{3+}/Fe_{total} ratio of the mixed iron sulfate solution was analyzed by titration with a standard K_2CrO_7 solution using Na–diphenylamine–sulphonic acid as indicator. The mixed iron sulfate solution and ammonia solution were then heated to 80 (±1) and 50 (±1) °C, respectively. The two solutions were simultaneously introduced into a 20 l precipitated vessel. The flow rates of two solutions were controlled to maintain the pH value of the mixture at 9.0 (±0.1). The temperature of the precipitation system was maintained at 75 (±1) °C during the whole precipitation process. After precipitation, the precipitate was washed completely with deionized water (50 °C) until SO_4^{2-} could not be detected with $BaCl_2$ solution (0.1 mol/l). The precipitate was then filtered, and part of filter-cake was immediately transferred to a glove box flushing with nitrogen. In the glove box filter-cake was washed with acetone, dried at 50 °C and sealed in a glass vial with liquid wax for characterization. The other part of filter-cake was spry-dried at 105 °C and calcined at different temperatures in air. The Fe^{3+}/Fe_{total} molar ratio in the initial mixed solution of the sample was named as R_m at different preparation stages. The R_m and amount of reactants used during the initial solution preparation of each sample were shown in Table 1.

Table 1
Reactant quantity and Fe^{3+}/Fe_{total} ratio (R_m) of the samples

Sample	$FeSO_4$ (mol)	H_2SO_4 (mol)	H_2O_2 (mol)	R_m (Fe^{3+}/Fe_{total})
S1	5.0	2.5	0.8	0.27
S2	5.0	2.5	1.3	0.43
S3	5.0	2.5	2.3	0.72
S4	5.0	2.5	2.8	0.87
S5	5.0	2.5	3.5	0.95

2.2. Catalysts characterization

The crystalline structure of the catalyst samples were measured by powder X-ray diffraction (XRD) on a D/max-RA X-ray diffractometer (Rigaku, Japan), equipped with Cu Kα radiation ($\lambda = 1.5406$ Å) at 40 kV and 150 mA. The patterns were scanned at a rate of 4°/min from $2\theta = 15°$ to 75°. The phases were identified by comparing diffraction patterns with those on the standard powder XRD cards compiled by the Joint Committee on Powder Diffraction Standards (JCPDS). The average crystallite size of α-FeOOH (21.2°), Fe_3O_4 (35.5°) and α-Fe_2O_3 (33.2°) was calculated using Scherrer formula: $D = 0.9\lambda/\beta\cos\theta$, where D is the crystalline size, λ the wavelength of Cu Kα, β the full width at half maxima (FWHM) of the diffraction peaks and θ is the Bragg's angle [19].

The Mössbauer spectra of the catalyst samples were recorded with a MR 351 constant-acceleration Mössbauer spectrometer (FAST, German) at room temperature, using a 25 mCi ^{57}Co in Pd matrix. The spectrometer was operated in the symmetric constant acceleration mode. The spectra were collected over 512 channels in the mirror image format. Data analysis was performed using a nonlinear least square fitting routine that models the spectra as a combination of singlets, quadruple doublets and magnetic sextuplets based on a Lorentzian line shape profile. The spectral components were identified based on their isomer shift (IS), quadruple splitting (QS), and magnetic hyperfine field (Hhf). All isomer shift values were reported with respect to metallic iron (α-Fe) at the measurement temperature. Magnetic hyperfine fields were calibrated with the 330 kOe field of α-Fe at the ambient temperature.

The textural properties (BET surface area, average pore size and pore volume) of the catalyst samples were measured by N_2 physisorption at its normal boiling point (−196 °C) using a Micromeritics ASAP 2500 instrument, and the catalyst