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# Study of phase transformation and catalytic performance on precipitated iron-based catalyst for Fischer–Tropsch synthesis

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ABSTRACT

Detailed phase transformation in syngas ($H_2/CO = 1.2$) on a precipitated iron-based catalyst was studied by $N_2$ physisorption, X-ray diffraction (XRD), Mössbauer effect spectroscopy (MES), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy (LRS). Fischer–Tropsch synthesis (FTS) performance of the catalyst was investigated in a slurry-phase continuously stirred tank reactor (STSR). The hematite in the fresh catalyst was reduced initially to magnetite, and then the magnetite in the bulk reached steady state slowly with increasing reduction time. Simultaneously, the $Fe_3O_4$ on the surface layers converted gradually to iron carbides, accompanied with the continual increase in the amounts of surface carbonaceous species. In the FTS reaction, the catalytic activity presented an increased trend with gradual carburization of the catalyst by keeping the stability in the bulk $Fe_3O_4$, suggesting that the conversion of magnetite to iron carbides in the near-surface regions provides probably the active sites for FTS. In addition, the chain growth reaction was restrained and the hydrogenation reaction was enhanced with increasing reduction duration.



## 1. Introduction

Fischer–Tropsch synthesis (FTS), as an important technology in production of clean transportation fuels and other chemicals from syngas derived from coal, natural gas or biomass [1], has been industrialized in SASOL over 50 years [2]. Due to the limited supplement and rapidly rising price of crude oil, an increasing attention has been renewedly paid on FTS in academic or industrial topic in recent years [3]. Although the Group VIII metals (including Ni, Ru, Co, and Fe) are the most common FTS catalysts, only Fe and Co catalysts have been industrially applied. Compared to Co-based catalyst, iron catalyst is more favorable for converting the syngas with low $H_2/CO$ ratio syngas derived from coal or biomass due to its high water-gas shift (WGS) activity, flexible product distribution and favorable engineering characteristics [4].

Complex phase transformation during pretreatment and reaction from the bulk to surface layers changes directly the Fischer–Tropsch synthesis performances (activity, selectivity and stability). It is well known that the iron oxide ($\alpha$-$Fe_2O_3$) is firstly transformed to magnetite ($Fe_3O_4$) irrespective of the activation gas used, which is then converted to different iron phases depending on the pretreatment parameters. When $H_2$ is used for activation, the metallic Fe phase is mainly formed, which is readily converted into a mixture of iron carbides ($Fe_xC$) and $Fe_3O_4$ under the reaction conditions [5]. Similarly, activation using CO continually transforms the magnetite to different types of iron carbides [6]. In contrast, pretreatment in syngas results in a more complex change in phase compositions, which is difficult to follow as it occurs. Rao et al. [7] investigated activation of a promoted iron-based catalyst and found that pretreatment in syngas for 12.5 h led to the formation of 48% magnetite and 35% carbide phases. The study of Li et al. [8] showed that $\alpha$-$Fe_2O_3$ in an un-promoted iron catalyst was firstly reduced to $Fe_3O_4$ in syngas, and the formed $Fe_3O_4$ was then gradually carburized with time on stream (TOS). However, the rate of reduction and carburization decreased after activation for 4 h. In addition, variation in pretreatment conditions (temperature, pressure and duration) as well as the reactor system would also cause further change in chemical structure of iron catalysts [9,10]. Due to the extensive phase transformation in syngas over different catalyst systems, understanding of the intrinsic relationship between the FTS performances and microcosmic structures of iron catalyst becomes very difficult [11].

Especially, numerous studies have been performed to investigate the active phases for Fischer–Tropsch synthesis in the working iron catalysts [5,9,11–13]. Some studies indicated that the formation of $Fe_3O_4$ promoted the FTS activity [12,13], while other

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reports claimed that iron carbides were the active phases for FTS [5,11]. Unfortunately, the nature of active sites is still a controversial issue [9]. Additionally, lots of studies reported the appearance of carbonaceous species on the catalyst accompanied with phase transformation during activation and FTS [3,14–18]. Niemantsverdriet et al. [15] claimed that the formation of inactive carbon (graphitic-like) blocked the active sites on the iron carbides, causing the deactivation of a precipitated iron catalyst. However, Ning et al. [3] found that the carbon deposition on mechanically mixed Fe catalysts was not responsible for the changes in catalytic activity. Hence, it needs to further investigate phase evolution from the bulk to surface layers as well as the formation of surface carbonaceous species for illustrating the connection between phase compositions and the FTS performances [10,16].

The objective of the present study was to investigate phase transformation in the bulk and surface layers of a precipitated iron-based catalyst in syngas ($H_2$/CO = 1.2), and its influence on the FTS performances. Due to the complexity of iron phase compositions, several techniques, including $N_2$ physisorption, X-ray diffraction (XRD), Mössbauer effect spectroscopy (MES), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy (LRS), were used together to characterize the textural properties and nature of bulk and surface phases, as well as the carbonaceous species formed on the surface layers.

## 2. Experimental

### 2.1. Catalyst preparation

A typical precipitated iron-based catalyst used in the present study was prepared by a combination of co-precipitation and spray drying method. The detailed preparation method has been described elsewhere [19] and protected by Chinese Patent ZL02121248.1 [20]. The freshly prepared catalyst was calcined at 773 K for 5 h.

### 2.2. Catalyst characterizations

BET surface area, pore volume and average pore diameter of the catalysts were measured by $N_2$ physisorption at 77 K using a Micromeritics ASAP 2010 instrument. The samples were degassed under vacuum at 393 K for 6 h prior to measurement.

Powder X-ray diffraction (XRD) patterns of the catalyst samples were measured on a D/max-RA X-ray diffractometer (Rigaku, Japan) with Cu Kα radiation (λ = 0.154 nm) operated at 40 kV and 100 mA.

The Mössbauer spectra of catalysts were recorded at room temperature with a MR 351 constant-acceleration Mössbauer spectrometer (FAST, German), using a 25 mCi $^{57}$Co (Pd) source. The spectrometer was operated in a symmetric constant acceleration mode. The spectra were collected over 512 channels in the mirror image format.

In situ XPS experiments were performed in an atmospheric quartz tube flow reactor, using He as the carrier gas. The feed gas with $H_2$/CO ratio of 1.2 passed through a series of columns for removing tiny amounts of oxygen, sulfur, carbonyls and water. The gas flow rate was 60 ml/min and the catalyst was pretreated at 538 K and 0.50 MPa for different durations. After pretreatment the sample was cooled in the carrier gas to room temperature, and then transferred into the ultra-high vacuum chamber (UHV) without exposure to air. XPS spectra were taken by a VG MiltiLab 2000 system with Al Kα (1486.6 eV) as the X-ray source. The C 1s as a reference signal was adjusted to 284.6 eV.

Raman spectra of the catalyst samples were collected using a single monochromator Renishaw system 1000 equipped with a thermoelectrically cooled CCD detector and holographic super-notch filter. The sample was excited with the 514.5 nm Ar line, and the spectrum acquisition time was 50 s. The spectra were recorded in the range between 100 and 1800 cm$^{-1}$.

**Table 1**
Textural properties of the catalysts reduced for different durations.

| Run no. | BET surface area ($m^2$/g) | Pore volume ($cm^3$/g) | Average pore size (nm) |
|---|---|---|---|
| T12 | 91 | 0.23 | 10.10 |
| T36 | 72 | 0.22 | 11.90 |
| T72 | 73 | 0.22 | 12.11 |

Reduction conditions: $H_2$/CO = 1.2, 538 K, 0.50 MPa and 1000 h$^{-1}$.

### 2.3. Reactor system and pretreatment procedures

The FTS tests were carried out in a 1 $dm^3$ slurry-phase continuously stirred tank reactor (STSR) loaded with 20.0 g of the catalyst sample and 380 g of liquid paraffin. The $H_2$ and CO were passed separately through a series of columns, an activated charcoal trap, an oxygen-removal trap, a sulfur-removal trap and a silica-gel/5 A molecular sieve trap, to remove tiny amounts of carbonyls, oxygen, sulfur and water before entering the reactor. The flow rates of $H_2$ and CO were controlled by two mass flow meters (Brooks 5850E). The outlet of the reactor was connected with a hot trap (393 K) and a cold trap (273 K) at the system pressure. A wet gas flow meter was used to monitor the flow rate of tail gas. All activations were conducted in situ in syngas ($H_2$/CO = 1.2), at 538 K, 1000 h$^{-1}$, 0.50 MPa and different durations (12, 36 and 72 h). These tests were labeled as T12, T36 and T72, respectively. After reduction, steady-state reaction conditions were set as 533 K, 1.50 MPa, 2000 h$^{-1}$ and $H_2$/CO = 1.2. Detailed description of the reactor and product analyst systems have been provided elsewhere [21].

## 3. Results and discussion

### 3.1. Textural properties of the catalysts

The textural properties of the catalysts during various reduction durations are listed in Table 1. The BET surface area, pore volume and average pore size of the fresh catalyst are 166 $m^2$/g, 0.36 $cm^3$/g and 8.55 nm, respectively. The BET surface area of the catalyst firstly decreased with TOS during pretreatment and then kept nearly unchanged (72–73 $m^2$/g) after reduction for 36 h. The phenomenon implies that the structure of the catalyst undergoes marked changes during the initial stage of reduction, possibly resulting from partial collapse of the porous of iron oxide network [2], and then the bulk structure of the catalyst might reach a stable state after 36 h of reduction. The combination of XRD and MES measurements (in the following section) showed that the amount of magnetite formed in the bulk increased gradually and then reached nearly steady-state values after 36 h of reduction, suggesting that the steady-state bulk $Fe_3O_4$ maybe the main contribution to the structure stability for the catalyst.

### 3.2. Phase transformation of the catalysts

#### 3.2.1. Phase transformation during reduction

The XRD and MES patterns of the fresh catalyst and reduced samples in syngas ($H_2$/CO = 1.2) at 538 K, 0.50 MPa and 1000 h$^{-1}$ for different durations are showed in Figs. 1 and 2, respectively. The corresponding iron-phase compositions of the catalysts are listed in Table 2. As described in the previous study [22], the fresh catalyst is mainly composed of α-$Fe_2O_3$. After reduction, the XRD patterns of the samples (Fig. 1) show several diffraction peaks at 2$\theta$ values of 30.0°, 35.4°, 57.0° and 62.6°, all of which correspond to $Fe_3O_4$. In