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Study on reduction and carburization behaviors of iron phases for iron-based Fischer–Tropsch synthesis catalyst[☆]

Mingyue Ding^{a,b,*}, Yong Yang^{b,*}, Baoshan Wu^b, Yongwang Li^b, Tiejun Wang^a, Longlong Ma^a

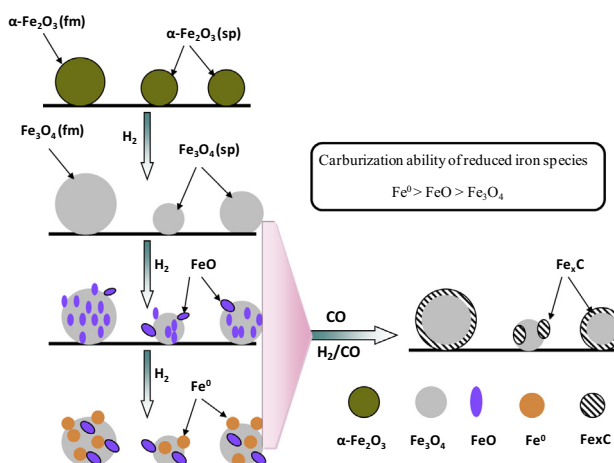
^a Key Laboratory of Renewable Energy, GIEC, CAS, Guangzhou 510640, PR China

^b State Key Laboratory of Coal Conversion, SXICC, CAS, Taiyuan 030001, PR China

HIGHLIGHTS

- Phase transformation during reduction is following as $\alpha\text{-Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \alpha\text{-Fe}$.
- Carburization ability of reduced iron phases is following as $\alpha\text{-Fe} > \text{FeO} > \text{Fe}_3\text{O}_4$.
- Iron carbides are formed on the Fe(II) oxide species.
- Hydrocarbons species are formed gradually on the surface of iron carbides.

GRAPHICAL ABSTRACT



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ABSTRACT

Reduction and carburization behaviors of iron phases over a precipitated iron-based Fischer–Tropsch synthesis (FTS) catalyst were investigated by some techniques of Mössbauer effect spectroscopy (MES), X-ray photoelectron spectroscopy (XPS) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) as well as H_2 & CO temperature-programmed desorption (H_2 & CO -TPD). It was found that in H_2 atmosphere phase transformation of iron phases involved $\alpha\text{-Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \alpha\text{-Fe}$, both occurring in the bulk and on the surface layers. All of reduced iron species took place the carburization reaction, whereas carburizing ability was following the order $\alpha\text{-Fe} > \text{FeO} > \text{Fe}_3\text{O}_4$. During FTS both iron carbides and Fe(II) oxide species reached a balance state without appearing the intermediate $\alpha\text{-Fe}$. The conversion of reduced iron phases to iron carbides (especially for $\chi\text{-Fe}_3\text{C}_2$) on the surface layers played a positive role in promoting the formation of hydrocarbons species.

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1. Introduction

Fischer–Tropsch synthesis (FTS) is a highly developed and technically proven route to transform coal, natural gas and lignocelluloses biomass into liquid alkanes, which are suitable for gasoline, diesel and jet fuel applications [1–3]. Due to higher water–gas shift activity, lower cost and favorable engineering characteristics, the

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* Corresponding authors at: Key Laboratory of Renewable Energy, GIEC, CAS, Guangzhou 510640, PR China (M. Ding). Tel.: +86 20 87057790; fax: +86 20 87057789.

E-mail addresses: dingmy@ms.giec.ac.cn (M. Ding), yyong@sxicc.ac.cn (Y. Yang).

Fe-based catalysts are used widely in the commercial FTS processes with lower H_2/CO ratio syngas derived from coal or biomass [4,5]. However, the Fe catalyst undergoes the most complicated phase changes during FTS compared to other Fischer–Tropsch synthesis catalysts (including Ru, Ni and Co) [6–8].

Generally, the fresh Fe catalyst is consisted mainly of $\alpha\text{-Fe}_2\text{O}_3$, which may be converted to different reduced iron species (such as Fe_3O_4 , FeO or metallic iron) under H_2 atmosphere [9,10]. Furthermore, the reduced Fe_3O_4 is transformed continually to metastable FeO phase, or reduced directly to metallic iron [11]. It is generally accepted that the strong interaction of metal-support in the supported iron catalysts may stabilize the metastable FeO. Under CO or syngas atmosphere these reduced iron species could be converted to different types of iron carbides (such as $\chi\text{-Fe}_5\text{C}_2$, $\varepsilon\text{-Fe}_{2.2}\text{C}$, and $\theta\text{-Fe}_3\text{C}$). The results of Chen et al. [12] indicated that Fe_3O_4 was reduced firstly to metallic Fe, and then carburized to iron carbides, whereas Li et al. [13] reported that the reduced Fe_3O_4 was transformed directly to iron carbides without the formation of intermediate metallic iron during FTS. In addition, several iron phases including reduced iron species and iron carbides have been found to coexist or transform each other during reduction and carburization processes [14,15]. Bukur et al. [16] suggested that magnetite, metallic iron and iron carbides could be coexisted in the Fe-based catalysts under syngas atmosphere. The results of Zhang et al. [17] showed that there was only the appearance of Fe_3O_4 and iron carbides during FTS, without observing metallic iron. Due to complex changes of iron phases during reduction and carburization processes, reduction and carburization behaviors of different iron phases are not still understood clearly.

On the other hand, a large number of studies are devoted to investigate the adsorption properties of surface iron species [18–20]. Some compounds such as formats, hydrocarbons and carboxylates have been reported to be appeared on the catalyst surface, whereas these species are influenced obviously by the complex nature of iron phases [21]. The surface adsorption properties of iron-based catalysts supported on SiO_2 , Al_2O_3 and MgO have been widely investigated by infrared spectroscopy [22,23]. The surface species may be adsorbed on the support and metal particles, respectively, exhibiting different vibration properties. In addition, adsorption of CO and NO on unsupported iron catalysts has been extensively studied [24,25]. The results of Jiang et al. [25] indicated that both the Fe(III) and Fe(II) species were located on the surface of oxidized Fe sample. However, the adsorbed species may be different on the surface of different iron phases, and take place further changes with phase transformation during reduction and carburization, affecting ultimately the FTS performances. The reports on adsorption properties of different iron phases are very rare.

Therefore, the aim of this work is to investigate reduction and carburization behaviors as well as adsorption properties of different iron phases over a precipitated Fe–Mn FTS catalyst. The bulk and surface phase compositions as well as surface adsorbed species were characterized by Mössbauer effect spectroscopy (MES), X-ray photoelectron spectroscopy (XPS), hydrogen & CO temperature-programmed desorption (H_2 &CO-TPD) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), respectively. This systematic approach provided a detailed observation of surface species and micro-compositions of the iron catalyst in different FTS stages.

2. Experimental

2.1. Catalyst preparation

A typical precipitated Fe–Mn–K– SiO_2 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 [26]. In brief, a solution containing $\text{Fe}(\text{NO}_3)_3$ and $\text{Mn}(\text{NO}_3)_2$ with the desired ratio was added into a continuously stirred tank containing de-ionized water at 80 °C. A NH_4OH solution was added simultaneously into the tank to maintain the pH value of 9.0. After precipitation, the precipitate was washed completely, and then filtered. Required amounts of silica sol solution, K_2CO_3 solution and de-ionized water were successively added into the filtrate, and the mixture was re-slurried, spray-dried and calcined at 450 °C for 3 h. The compositions of the catalyst were as follows Fe:Mn:K:Si = 100:15:3:30 (molar ratio).

2.2. Catalyst characterizations

MES was tested in a MBF-1100 micro-reactor with Mylar windows, which allows the experiments using different agents such as H_2 , CO or syngas. The catalyst was reduced or carburized in different temperatures (such as 260, 280, 300 and 350 °C) with 60 ml/min of gas flow rate and 1 °C/min of heating rate. After pretreatment the sample was cooled in nitrogen atmosphere to 50 °C and the Mössbauer spectra were recorded. Isomer shift (IS), quadruple splitting (QS) and magnetic hyperfine field (Hhf) were used as the spectral components.

XPS spectra were taken by a VG MultiLab 2000 system with Al K α (1486.6 eV) as the X-ray source. The C 1s as a reference signal was adjusted to 284.6 eV. All XPS results were obtained from samples treated in situ in the reaction cell and then transferred into the ultra-high vacuum chamber without exposure to air.

DRIFTS spectra were collected using an infrared spectrometer (Equinox 55, Bruker, Germany), equipped with KBr optics and a MCTD316 detector at the liquid nitrogen temperature (77 K). The infrared cell with ZnSe windows was connected to a feed system with a set of stainless steel gas lines, which allows in situ measurements for CO or CO + H_2 adsorption using argon as the flushing gas. In all cases, the gas flows were maintained at 60 ml/min by mass flow control meters. All spectra were recorded with a resolution of 4 cm^{-1} and accumulation of 64 scans.

TPD experiments were performed on an Autochem 2920 characterization system equipped with a thermal conductivity detector (TCD), using Ar (H_2 -TPD) or He (CO-TPD) as the carrier gas. The sample loading was 200 mg. The gas flow rate was 60 ml/min and the heating rate was 1 °C/min. The pretreatment conditions were the same as MES. After pretreatment the sample was cooled to 50 °C for the TPD tests. H_2 or CO adsorption on catalyst was performed at 50 °C for 30 min, and then the sample was purged with Ar or He for 30 min to remove weakly adsorbed species, respectively. After this step, H_2 - or CO-TPD was carried out while the temperature was increased to 800 °C.

3. Results and discussion

3.1. Reduction behavior of iron phases

3.1.1. Phase evolution in the bulk regions

The MES patterns of the catalyst reduced in H_2 atmosphere with different temperatures are shown in Fig. 1. Table 1 lists the corresponding iron-phase compositions in the bulk regions. The Mössbauer spectrum of the fresh catalyst shows one sextet (IS of 0.37 mm/s, QS of 0.19 mm/s and Hhf of 507 kOe) and one doublet (IS of 0.32 mm/s and QS of 0.82 mm/s), which correspond to $\alpha\text{-Fe}_2\text{O}_3$ and superparamagnetic (spm) Fe^{3+} ions, respectively. Reduction at 260 °C for 12 h results in the formation of Fe_3O_4 and (spm) Fe^{2+} . The values of the doublets with IS of 0.80–0.82 mm/s and QS of 1.10–1.23 mm/s for (spm) Fe^{2+} are attributed to the formation of metastable FeO [27]. The appearance of metastable FeO during

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