Chemical and structural effects of strontium on iron-based Fischer-Tropsch synthesis catalysts

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ABSTRACT

A series of Fe/SiO$_2$ catalysts with different strontium/iron molar ratios were used to investigate the chemical and structural effects of strontium on the iron-based Fischer-Tropsch synthesis (FTS) catalysts. It was found that the chemical effect of strontium strengthened Fe−O bonds of Fe$_2$O$_3$ and hence suppressed the reduction of iron oxide. The chemical effect also suppressed the H$_2$ adsorption but improved the CO adsorption, which is responsible for the low surface H/C ratios and methane selectivity. At the same time, the promotion of strontium improved the dispersion of iron oxides. The dispersion effect facilitated the reduction and carburization of catalysts. It was also helpful for the H$_2$ adsorption and in turn led to high surface H/C ratios and methane selectivity. Under the combined action of the chemical and structural effects, the selectivity to methane of catalysts exhibited a parabola-like trend as a function of strontium loading and passed through a minimum at Sr/Fe molar ratio of 6/100. In contrast, the selectivity of heavy hydrocarbon demonstrated an opposite tendency.

1. Introduction

The growing concerns about depletion of crude oil have boosted global interest in finding alternative feedstocks for petrochemicals and liquid fuels [1,2]. Fischer-Tropsch synthesis (FTS) is an alternative route for converting syngas derived from coal, natural gas or biomass into liquid fuels and chemicals [3]. Iron, cobalt, ruthenium and nickel are active metals for the FTS, but only iron and cobalt are used industrially. Due to the low cost, high FTS and water-gas-shift (WGS) activity, feed flexibility (H$_2$/CO = 0.5–2.5), iron-based catalyst is the preferred catalyst for the FTS using low H$_2$/CO ratio syngas derived from coal [4].

To improve the FTS performance of iron-based catalyst, many studies have been performed to evaluate the effects of many promoters on FTS performances of iron-based catalysts, especially alkalis, copper, manganese and silicon [5–12]. Alkaline-earth metals are supposed to be significant promoters for iron-based FTS catalysts, owing to their alkaline properties similar to alkali metals. Luo et al. [13] investigated the influences of Be, Mg, Ca and Ba on iron-based catalysts for FTS. They concluded that Be, Mg, Ca and Ba improved the formation of liquid product but decreased the formation of gas fraction product. In our previous work [8], we systematically studied the effects of Mg, Ca, Sr

and Ba on the FTS performances of iron-based catalysts with a mole ratio of promoter/iron = 0.02. We found that the addition of Mg, Ca, Sr and Ba reduced the selectivity of CH$_4$ and facilitated the production of olefin and C$_5^+$ hydrocarbons obviously. More importantly, strontium was found to be the most effective promoter in tuning the product distribution among alkali-earth metals.

Generally, the promotional effect of promoter depends on its contents added. The variation of potassium loading content plays significant influences on its promotional effects [12,14–19]. The selectivity of olefins and higher molecular products increases, the activity of WGS increases, while the FTS activity either increases or passes through a maximum depending on the potassium loading. Gallegos et al. [20] studied the role of Mg on the FeSiO$_2$ FTS catalysts. The results indicated that the rate of total hydrocarbon formation inclined as a function of Mg content, and that the selectivity of olefins and heavy hydrocarbons was increased by the suitable level of Mg. Yang et al. [21] found that the carburization extent, the FTS activity, space time yields of C$_5^+$ increased with the increase of Mg content, and passed through a maximum at an Mg/Fe weight ratio of 0.07. Tao et al. [22] studied the effect of Ca on the Fe-Mn FTS catalysts. The results showed that the FTS and WGS activity, methane selectivity decreased with the increase of Ca contents. They also concluded that an appropriate amount of Ca

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promoted the reduction and carburization of Fe-Mn catalysts, but the excessive promotion would decrease the extent of the reduction and carburization. However, to the best of our knowledge, there is no report about the influences of different strontium loading on iron-based FTS catalysts. Besides, alkaline-earth metals simultaneously have some properties like structure promoters except for their chemical effects. The increase of strontium loading will boost its structural effects, which is helpful to get a deep insight into the structural effect, chemical effect and their synergistic effect of strontium on FTS iron-based catalysts.

This paper aims to investigate structural and chemical effects of strontium on precipitated Fe/SiO$_2$ catalysts. Many characterization techniques were employed to analyze the textural properties, structure, reduction and adsorption of catalysts. The characterization results were correlated with the FTS performance of catalysts in order to give a deep insight into the promotional effects of strontium.

2. Experimental

2.1. Catalyst preparation

The catalysts precursors used in this work were prepared by co-precipitation and spray-drying method as following steps: a solution of Fe(NO$_3$)$_3$ was mixed with silica sol with Si/Fe atomic ratio = 5:100. The mixed solution precipitated using NH$_4$OH solution at T = 70 °C and pH = 8.5–9.0. The obtained precipitate was washed with deionized water, and then filtered. The strontium was introduced by wetness impregnation with Sr(NO$_3$)$_2$, and followed by spray-dried and calcination at 500 °C for 5 h. The Sr/Fe was kept with mol ratio of xSr/100Fe, x = 0, 2, 4, 6, 10, and 15, these are denoted FeSi, 2Sr, 4Sr, 6Sr, 10Sr, and 15Sr.

2.2. Catalyst characterizations

The BET surface area was measured via N$_2$ physical adsorption in a Micromeritics ASAP 2420 equipment. XRD patterns were recorded using Bruker D8 Advance X-ray laboratory diffractometer with Cuκα radiation (γ = 1.5406 Å) at a rate of 0.02° (2θ)/second from 20° to 80°. Mössbauer characterizations were conducted in an MR-351 constant-acceleration Mössbauer spectrometer (FAST, Germany) drive with a triangular reference signal at room temperature. H$_2$/CO-TPR and H$_2$-TPD studies were performed on AutoChem II 2920 equipment (Micromeritics, USA) equipped with TCD detecter. CO-TPD studies were also carried out on AutoChem II 2920 equipment (Micromeritics, USA) equipped with a mass spectrum detector. (Details of the characterization are described in the supporting information)

The reduced catalyst samples used for Mössbauer characterization were prepared by reducing the fresh catalysts in a quartz tube with synthesis gas (H$_2$/CO = 2) at 553 K, 0.10 MPa and 1000 h-1 for 20 h. After reduction, the catalysts for Mössbauer measurements were coated with paraffin to prevent oxidation.

2.3. Catalyst evaluation

The catalytic tests were conducted in a tubular fixed-bed reactor (i.d. 12 mm). Prior to reaction, all catalysts were reduced in situ with syngas (H$_2$/CO = 2.0) at 280 °C, 0.10 MPa, and 1000 h^{-1} for 20 h. Following the pretreatment, the reactor was cooled to 200 °C, then the reaction system was set at 260 °C, 1.5 MPa, 2000 h^{-1}, and H$_2$/CO = 2.0. A detailed description of the reactor and the product analysis system has been provided elsewhere [12,23].

3. Results and discussion

3.1. Structural and chemical effects of strontium

Table 1 lists the BET surface area, pore volume, and average pore

Table 1
Textural properties of the as-prepared catalysts.

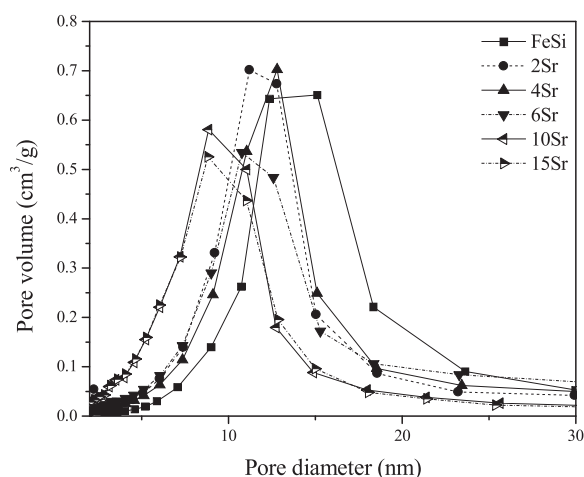| Catalyst	Surface area[a] (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
FeSi	50	0.20	12.6
2Sr	62	0.19	10.0
4Sr	57	0.19	11.0
6Sr	60	0.19	10.2
10Sr	86	0.21	7.4
15Sr	88	0.20	7.2

[a] Max error = ± 5%.

Fig. 1. The pore size distribution of the as-prepared catalysts.

diameter of the as-prepared catalysts. The surface area generally increases, while the average pore diameter decreases with the increase of the strontium contents. The pore size distribution (PSD) of the as-prepared catalysts is shown in Fig. 1. The PSD curve of strontium promoted catalysts moves to smaller pore diameter compared with that of the unprompted sample. With increasing strontium contents, the pore diameter shifts to small pore diameter continuously. This may be due to the fact that the incorporation of strontium into the porous precipitate precursor prevents the collapse of the pore structure during thermal treatments [11].

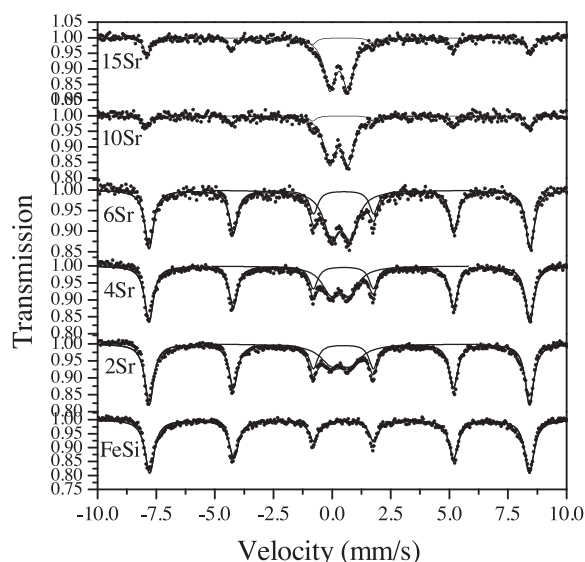Fig. 2 shows the Mössbauer spectra of the fresh catalysts, the spectra

Fig. 2. Mössbauer spectra of the as-prepared catalysts.