



## Study on an iron–nickel bimetallic Fischer–Tropsch synthesis catalyst



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### ABSTRACT

A systematic study was undertaken to investigate the effects of the addition of nickel on the bulk phase composition and reduction/carburization behaviors of a Fe–Ni bimetallic catalyst. The catalyst samples were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), Mössbauer spectroscopy, X-ray photoelectron spectroscopy (XPS) and H<sub>2</sub> (or CO) temperature-programmed reduction (TPR). The Fischer–Tropsch synthesis (FTS) performance of the catalysts was measured at 1.5 MPa, 250 °C and syngas with H<sub>2</sub>/CO ratio of 2.0. The characterization results indicated that the fresh nickel-promoted catalysts are mainly composed of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and NiFe<sub>2</sub>O<sub>4</sub>. The addition of nickel improves the dispersion of iron oxides and decreases the crystallite size of metal oxides. The presence of nickel increases the rates of reduction and carburization in H<sub>2</sub> and CO, respectively, while suppresses the formation of the iron carbides in the syngas reduction. The incorporation of nickel improves the selectivity to methane and suppresses the formation of heavy hydrocarbons (C<sub>5+</sub>). The catalyst with high nickel content has a high selectivity to methane and low selectivity to heavy hydrocarbons (C<sub>5+</sub>).

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### 1. Introduction

As an environmental-friendly and economically promising solution for the production of middle distillate fuels, petroleum blending-stock, and a wide variety of hydrocarbons and oxygenates from either coal or natural gas or biomass-derived syngas, Fischer–Tropsch synthesis (FTS) has been paid great attention by numerous governments and academic institutions in recent years due to high oil prices, decreasing oil reserves and environmental pollution [1–3]. The performance of FTS catalyst plays a critical role in its industrial applications [4]. Although all group VIII metals display some activity in the C–C coupling reaction during CO hydrogenation, the most active metals for FTS are Fe, Co, Ni and Ru [5–8]. However, only Fe and Co based catalysts are applicable for industrial processes due to their high activity, selectivity and low cost [9,10]. Other active metals, namely Ni and Ru, have been utilized only as promoters for iron and cobalt based catalysts [11,12]. Compared with Co-based catalysts, iron-based catalysts are more suitable for the conversion of syngas with low H<sub>2</sub>/CO ratio derived from coal, due to their high FTS activity as well as high water–gas shift (WGS) reactivity, which helps to make up the deficit of H<sub>2</sub> in the syngas [11,13,14]. Modification of the traditional iron-based FTS catalysts by Ni promoter has provided one way of manipulating the FTS product spectrum [15], science mixtures of iron and nickel oxides are effective catalysts for the conversion of syngas to desired products [16–18]. Ishihara et al. [19] investigated the hydrogenation of CO over pure Fe, Ni and

bimetallic Fe–Ni catalysts supported on silica at 523 K and 1.0 MPa. They indicated that, compared to the pure metal catalyst, the bimetallic Fe–Ni catalyst exhibited higher activities for CO conversion. Similar results were also reported by other research groups [16,20–22] over supported or unsupported bimetallic Fe–Ni catalysts. However, Amelse et al. [23] reported that the activity of silica supported Fe–Ni catalysts was found lower than that of pure Fe or pure Ni. At the same time, the effects of nickel incorporation on the product distributions of the iron FTS catalysts were also investigated by earlier research works [16,19–22]. Jothimurugesan and Gangwal [20], Cooper and Frost [21], and Arai et al. [22] reported that the incorporation of nickel resulted in high selectivity to heavy hydrocarbons and low methane selectivity. However, Loosdrecht et al. [16] pointed out that the selectivity towards higher hydrocarbons remained the same or decreased slightly for the iron catalyst incorporated with nickel. In addition, Ishihara et al. [19] indicated that for the iron–nickel system, the selectivity to hydrocarbons higher than methane did not depend on the Fe:Ni ratio. Besides that, the promotion effects of nickel on the iron reduction for the iron–nickel system were also reported by earlier works [19,24–28]. Unmuth et al. [24,25] studied the alloying effect of the iron–nickel system on activities and characteristic product distributions, and pointed out that the addition of Ni to Fe catalysts accelerated the reduction rate of Fe during the reduction–oxidation cycle, whereas the possibility that the formation of carbide was restricted by the addition of Ni due to the fact that nickel hardly formed carbide under the reaction conditions. However, in the study of Zhang et al. [28], the presence of Ni facilitated the oxygen removal and increased the carbon introduction content for the FeMnK/SiO<sub>2</sub> catalyst. The presence of these controversial results may

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be due to the different catalyst preparations, pretreatments and FTS conditions. Although the effects of nickel on the performance of iron catalysts have been investigated intensively, most investigations are focused on the activity and selectivity, and little efforts have been performed to illustrate the effect of Ni on the reduction–carburization behavior, bulk phase structure and their correlation over coprecipitated Fe–Ni bimetallic catalyst.

The main objective of the present work is to investigate the effects of nickel on the coprecipitated Fe–Ni bimetallic catalyst under industrially relevant operation conditions. Particular attention is focused on the effect of nickel on the textural properties, reduction, and bulk phase and surface compositions of the catalyst at different stages. FTS activity and hydrocarbon product distribution of the catalyst are well correlated with the characterization results.

## 2. Experimental

### 2.1. Catalyst preparation

The catalysts used in the present study were prepared using the combination of coprecipitation and spray drying. In brief, a solution containing  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with a desired Fe/Ni atomic ratio of 100/x ( $x = 0, 1, 3, 5$  and 15) was preheated to 85 °C and introduced into a precipitation vessel at a flow rate of 60 ml/min. A  $\text{NH}_3 \cdot \text{H}_2\text{O}$  solution (preheated to 40 °C) was added simultaneously into the vessel to maintain the pH value in the range of 8.2 to 8.5. The temperature of the precipitation vessel was kept at 80 °C during the whole precipitation process. After the precipitation, the precipitate was washed thoroughly with deionized water and filtered subsequently. The final cake was reslurried in deionized water and spray dried in air at 250 °C. The obtained catalyst precursors were calcined at 550 °C for 5 h in air. The calcined catalysts were crushed and sieved to obtain 20–40 mesh for reaction. The compositions of the final obtained catalysts are 100Fe/xNi ( $x = 0, 1, 3, 5$  and 15) in an atomic ratio, which are labeled as Ni-00, Ni-01, Ni-03, Ni-05 and Ni-15, respectively.

### 2.2. Catalyst characterization

The BET surface area, pore volume and average pore diameter of the fresh catalysts were measured with the nitrogen physisorption at –196 °C in ASAP 2420 (Micromeritics, USA). Each sample was degassed under vacuum at 90 °C for 1 h and 350 °C for 8 h prior to the measurement.

The crystalline structures 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 K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 40 kV and 100 mA. The patterns were scanned at a rate of 4°/min from  $2\theta = 15^\circ$  to  $75^\circ$ . 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).

Transmission electron microscopy (TEM) analysis was performed on a Hitachi H-600 electron microscope operated at an accelerating voltage of 100 kV. The TEM specimen was prepared by ultrasonically suspending the powder sample in ethanol, and drops of the suspension were deposited on a carbon-coated copper grid dried at room temperature before analysis.

The Mössbauer spectra of the catalysts were recorded with an MR 351 constant-acceleration Mössbauer spectrometer (FAST, German) at room temperature, using a 25 mCi  $^{57}\text{Co}$  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 ( $\alpha\text{-Fe}$ ) at the measurement temperature.

XPS spectra were taken by a VG MultiLab 2000 system with Al K $\alpha$  (1486.6 eV) as the X-ray source. The C 1 s as a reference signal was adjusted to 284.6 eV. High-resolution spectral envelopes were obtained by curve fitting synthetic peak components using the XPS peak software. Symmetric Gaussian–Lorentzian product functions were used to approximate the line shapes of the fitting components.

Temperature-programmed reduction (TPR) studies of the fresh catalysts were carried out using a chemisorption analyzer (Micromeritics, Model 2920) over 30 mg sample with 50 ml/min reducing gas composed of 5%  $\text{H}_2$ /95% Ar ( $\text{H}_2\text{-TPR}$ ) or 5%  $\text{CO}$ /95% He ( $\text{CO-TPR}$ ). The reactor was heated from room temperature to 800 °C ( $\text{H}_2\text{-TPR}$ ) or 750 °C ( $\text{CO-TPR}$ ) at a heating rate of 10 °C/min.

### 2.3. Fischer–Tropsch synthesis reaction procedures

The FTS performance of the catalysts was tested in a stainless steel fixed bed reactor (12 mm i.d.) loaded with 4.0 g of catalyst sample. Detailed description of the reactor and product analysis systems was provided elsewhere [29]. In brief, the  $\text{H}_2$  and  $\text{CO}$  were passed separately through a series of purification traps to remove trace amounts of carbonyl compounds, water, oxygen, sulfur and other impurities. The flow rates of  $\text{H}_2$  and  $\text{CO}$  were controlled by two mass flow controllers (Brooks, model 5850E). The exit stream passed through a hot trap (120 °C) and a cold trap (0 °C) to collect liquid products, and a back-pressure regulator. A wet gas flow meter was used to monitor the flow rate of tail gas.

Prior to reaction, the catalyst was reduced in situ by syngas ( $\text{H}_2/\text{CO} = 2.0$ ) at 280 °C, 0.10 MPa and 1000  $\text{h}^{-1}$  for 24 h. Following reduction, the reactor was gradually cooled to 200 °C, and the system was pressurized to 1.50 MPa. After the activation period, steady-state reaction conditions were set as 250 °C, 1.5 MPa,  $\text{H}_2/\text{CO} = 2.0$  and 2000  $\text{h}^{-1}$ . The tail gas was analyzed online by gas chromatography (GC) 6890N and 4890D (Agilent, USA). The liquid sample was withdrawn every 24 h and analyzed on an off-line GC 6890N (Agilent, USA).

The reduced catalyst samples used for XRD and Mössbauer spectroscopy characterizations were obtained by reducing the fresh catalysts in a quartz reactor with syngas ( $\text{H}_2/\text{CO} = 2$ ) at 280 °C, 0.10 MPa and 1000  $\text{h}^{-1}$  for 24 h. After reduction, the quartz reactor was sealed and transferred to a glove box. Under the  $\text{N}_2$  atmosphere, the reduced catalysts were transferred to a glass vial and coated with liquid paraffin for further characterization test.

## 3. Results and discussion

### 3.1. Textural properties of the fresh catalysts

Textural properties and pore size distributions of the fresh catalysts with different nickel contents are shown in Table 1. As shown in Table 1, the BET surface areas of all catalysts are in the range of 18 to 44  $\text{m}^2/\text{g}$ , which are much lower than those of the supported catalysts reported in earlier works [12,28,30] due to the absence of supports. The surface area of the catalysts gradually increases with the increasing of the

**Table 1**  
Textural property of the catalysts as-prepared.

Catalysts	Ni/Fe atomic ratio( $\times 10^2$ )		BET Surface area ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )	Average pore size (nm)
	Theoretical	Analyzed <sup>a</sup>			
Ni-00	0	0	18	0.14	31.49
Ni-01	1.0	0.92	21	0.19	16.97
Ni-03	3.0	2.71	26	0.23	35.10
Ni-05	5.0	4.34	29	0.22	30.44
Ni-15	15.0	12.88	44	0.19	14.43

<sup>a</sup> Analyzed by the atomic emission spectrometer (AES).

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