



Cobalt and iron species in alumina supported bimetallic catalysts for Fischer–Tropsch reaction

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ABSTRACT

This paper focuses on the identification of cobalt and iron species in bimetallic alumina supported catalysts and their role in Fischer–Tropsch synthesis. The catalysts are prepared *via* aqueous coimpregnation of alumina with solutions of cobalt and iron nitrates followed by calcination in air and reduction in hydrogen. Qualitative and quantitative analyses of cobalt and iron phases were performed using XANES/EXAFS, XRD, TPR, XPS and magnetic method. The results show that Co_3O_4 and Fe_2O_3 are the major phases in the calcined monometallic cobalt and iron catalysts, while the bimetallic catalysts also exhibited the presence of mixed Co–Fe oxides. Reduction of these Co–Fe oxides leads to cobalt–iron bimetallic particles. The Fischer–Tropsch reaction rate increases with cobalt content in bimetallic catalysts. Formation of mixed cobalt–iron species increases selectivity to lighter olefins compared to cobalt monometallic catalyst but leads to lower Fischer–Tropsch reaction rates.

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1. Introduction

Fischer–Tropsch synthesis (FT) produces clean fuels from syngas (mixture of CO , H_2) [1–5]. The syngas can be manufactured from fossil and renewable feedstocks (natural gas, coal and biomass). The synthetic fuels obtained using FT synthesis have a high cetane number and do not contain sulfur or aromatics. They could be considered therefore as a real alternative to traditional fuels from crude oil. The contribution of renewable resources such as biomass to the global energy supply has been growing in recent years [3].

Cobalt catalysts are the catalysts of choice for synthesis of long-chain hydrocarbons *via* low temperature FT synthesis from syngas. Long-chain hydrocarbons generally are produced on cobalt catalysts supported on oxide supports such as alumina, silica or carbon materials [5–8]. It is known that the catalytic conversion of carbon monoxide occurs on the cobalt metal sites and that FT reaction rate is a function of cobalt dispersion, reducibility and stability. Iron catalysts which are much cheaper are also used commercially for low temperature FT synthesis, however with somewhat lower activity than cobalt catalysts. In this context, cobalt–iron bimetallic

catalysts with optimized catalytic performance seem to be a viable option for converting syngas into hydrocarbons [9–13]. In addition, iron species in bimetallic catalysts which may have a significant activity in the water gas shift (WGS) reaction [1] could be used to adjust H_2/CO ratio in syngas and thus, make the FT technology more flexible to different types of feedstock.

Previously cobalt–iron mixed catalysts have been a subject of several investigations. The obtained results were however rather contradictory. De la Pena O'Shea et al. [14] observed lower activity of silica supported cobalt monometallic catalysts in fixed bed reactor compared to iron counterparts. The activity of cobalt and iron catalyst supported on HMS mesoporous materials was studied by Bragana et al. [15]. HMS supported Co–Fe catalyst showed the highest activity and C_{5+} hydrocarbon selectivity, while Co–Fe/SBA-15 catalyst revealed highest selectivity to alcohols. Mixed cobalt–iron particles supported on carbon nanotubes were studied by Tavasoli et al. [16]. The monometallic cobalt catalyst exhibited high selectivity (85.1%) toward C_{5+} liquid hydrocarbons, while addition of small amounts of iron did not significantly affect the product selectivity. Lögdberg et al. [9] found that alloys of cobalt with small amount of iron improved the FT activity compared to the monometallic iron catalyst.

The present work focuses on the identification of different cobalt and iron phases present on the alumina supported catalysts with different Co/Fe ratio during catalyst preparation and activation

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using a combination of techniques: nitrogen adsorption, *ex situ* and *in situ* X-ray diffraction (XRD), X-ray absorption (XANES/EXAFS), temperature programmed reduction (TPR), *in situ* magnetization measurements and X-ray photoelectron spectroscopy (XPS). Particular attention is paid to interaction between cobalt and iron species in bimetallic catalysts at different catalysts preparation stages. The catalytic performance in FT synthesis has been evaluated in a Flowrence high-throughput unit (Avantium).

2. Experimental

2.1. Catalysts preparation

The monometallic cobalt or iron catalysts were synthesized *via* incipient wetness impregnation of alumina (Puralox SCCA 5/170 Sasol, $S_{\text{BET}} = 183 \text{ m}^2/\text{g}$, pore diameter = 8 nm) using aqueous solutions of cobalt or iron nitrates obtained from the following precursors: $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Fluka) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Fluka). The cobalt or iron content in the monometallic catalysts prepared in a single impregnation step was 10 wt.%.

The bimetallic catalysts were synthesized *via* one step incipient wetness (co)impregnation of the alumina support. The total content of metals in the catalysts was 10 wt.%. The prepared solids have the following weight compositions: $x\text{Co}y\text{Fe}/\text{Al}_2\text{O}_3$, with x and $y = 0$, 2.5 wt.%, 5 wt.%, 7.5 wt.% and $x + y = 10$ wt.%. The impregnated catalysts were dried at 383 K for 12 h and calcined at 673 K for 5 h ($1^\circ\text{C}/\text{min}$) in a flow of air. After calcination, the samples were sieved to remove catalyst particles smaller than 50 μm and larger than 150 μm , then reduced *in situ* in fixed bed reactor in hydrogen at 673 K for 12 h.

2.2. Catalyst characterization

At different stages of the preparation, the catalysts have been characterized by a wide range of *ex situ* and *in situ* techniques. The metal content in the catalysts was measured by X-ray fluorescence at the “Service Central d’Analyse du CNRS” (Vernaison, France). The elementary analysis data are in good agreement with the theoretical values (Table 1). The BET surface area and pore size distribution were measured using nitrogen adsorption at 77 K. Prior to the experiments, the samples were outgassed at 423 K for 5 h. The isotherms were measured using a Micromeritics ASAP 2010 system. The total pore volume (TPV) was calculated from the amount of vapor adsorbed at a relative pressure close to unity assuming that the pores are filled with the condensate in the liquid state. The pore size distribution curves were calculated from the desorption branches of the isotherms using the Barrett–Joyner–Halenda (BJH) formula [17].

Ex situ X-ray powder diffraction experiments were conducted using a Bruker AXS D8 diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.1538 \text{ nm}$) for crystalline phase detection. The XRD patterns were collected in $20\text{--}70^\circ$ (2θ) range at $1.2^\circ/\text{min}$. The identification was carried out by comparison with JCPDF standard spectra software. The average crystallite size of Co_3O_4 (Table 1) was calculated using the 511 ($2\theta = 59.5^\circ$) diffraction lines according to the Scherrer equation [18].

The *in situ* time-resolved XRD data of $5\text{Co}5\text{Fe}/\text{Al}_2\text{O}_3$ catalyst were measured at the BM01B-SNBL beamline (ESRF, France) using a high resolution diffractometer, a gas manifold system and a capillary cell reactor. The setup was described previously [19,20]. The known amount of catalyst was loaded in the quartz capillary ($m = 12.3 \text{ mg}$, $\text{OD} = 2 \text{ mm}$) and pressed from both sides with quartz wool. The capillary was attached to the stainless steel holder using high temperature epoxy glue. A Cyberstar gas blower was used to control the capillary reactor temperature. The total pressure in the reactor (up to 20 bar) was regulated by a back pressure controller. The gas lines before and after the reactor were heated up to 493 K using Horst heating tape to prevent condensation of liquid products. Before the FT tests the catalysts were reduced in hydrogen flow at 658 K at atmospheric pressure (temperature ramp of 3 K/min) and cooled down to 333 K in H_2 flow. After the reduction, the catalyst was cooled down to 433 K and exposed to the syngas ($\text{H}_2/\text{CO} = 2$) at atmospheric pressure. Then the reactors were pressurized up to 20 bar and temperature of the catalyst was risen up to 506 K with ramping rate of 1 K/min. The time-resolved XRD patterns were recorded *in situ* under gas flows first at 20 bar, $\text{H}_2/\text{CO} = 2$, $\text{GHSV} = 25,000 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$ for 145 min, then at 20 bar $\text{H}_2/\text{CO} = 1$, $\text{GHSV} = 17,500 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$ for additional 278 min. The measuring time per a XRD pattern in the 2θ range between 5° and 35° was close to 20 min.

XAS spectra at Co K-edge (7.709 keV) or/and Fe K-edge (7.112 keV) were acquired at the BM01B-SNBL beamline (ESRF, France) using a Si (1 1 1) double crystal monochromator in transmission mode. Crystalline Co_3O_4 , CoO, Co foil, Fe_3O_4 , and Fe_2O_3 were used as reference compounds for XANES and EXAFS analysis. The data analysis was performed applying the IFFEFIT software. The EXAFS oscillations were extracted using the program Athena. The XANES spectra after background correction were normalized by the edge height. The Co K-edge EXAFS was analyzed using the standard data analysis procedure. The EXAFS signal was then transformed without phase correction from k space to r space (k^3 , Hanning window, $0\text{--}12 \text{ \AA}^{-1}$) to obtain the radial distribution function (RDF).

The reducibility of the catalysts was studied by temperature programmed reduction (TPR) using an AutoChem II 2920 apparatus (Micromeritics), 0.2 g of the sample was treated by a 5 vol% H_2/Ar stream with a gas flow velocity of $30 \text{ cm}^3/\text{min}$. The temperature was increased from room temperature to 1273 K at a rate of 2.5 K/min.

In situ magnetic measurements were performed using a Foner vibrating-sample magnetometer as described previously [21]. The design of the magnetometer allows recording curves of magnetization during temperature-programmed heating or under isothermal conditions at 290–873 K. Temperature-programmed reduction experiments were carried out in pure hydrogen. The sample amount was about 30 mg in all experiments. The gas flow velocity was 60 mL/min and the rate of temperature ramping was 12 K/min. The appearance of cobalt metallic species, Fe_3O_4 and iron metallic species in the catalysts was monitored *in situ* by a continuous increase in sample magnetization during the reduction.

Surface analyses were performed using a VG ESCALAB 220XL X-ray photoelectron spectrometer (XPS). The Al $\text{K}\alpha$ non-monochromatized line (1486.6 eV) was used for excitation with a 300 W-applied power. The analyzer was operated in a constant pass

Table 1
Characterization of calcined supported catalysts.

Catalyst	Metal content (wt.%Co/wt.%Fe)	S_{BET} (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)	Size of Co_3O_4 crystallites by XPS (nm)	Size of Fe_2O_3 crystallites by XPS (nm)
10Co/ Al_2O_3	9.0/–	154	0.35	8	11	–
7.5Co2.5Fe/ Al_2O_3	8.2/2.6	158	0.36	6	17	2
5Co5Fe/ Al_2O_3	4.2/4.1	166	0.38	6	7	2
2.5Co7.5Fe/ Al_2O_3	2.4/7.4	165	0.38	6	–	4
10Fe/ Al_2O_3	–/9.8	179	0.41	8	–	6

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