



Effects of sodium and sulfur on catalytic performance of supported iron catalysts for the Fischer–Tropsch synthesis of lower olefins

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ABSTRACT

The Fischer–Tropsch synthesis of lower olefins (FTO) is an alternative process for the production of major chemical building blocks from natural gas, coal, or biomass-derived synthesis gas. The addition of low concentrations of sulfur plus sodium to Fe/ α -Al₂O₃ resulted in catalysts with high C₂–C₄ olefins selectivity (~50%), enhanced catalytic activity, and decreased methane production (<20%) when the reaction was carried out at 340 °C, 20 bar and H₂/CO = 1. Sodium reduced methane selectivity by increasing the chain growth probability while sulfur probably reduced the hydrogen coverage of the catalyst resulting in even lower methane selectivities and higher olefin content of the products. The addition of extra sodium resulted in a detrimental effect on catalytic activity while favoring the formation of carbon deposits. Our results show that the nature and concentration of the promoters play a key role in the design of FTO catalysts with optimum catalytic performance.

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1. Introduction

Lower olefins (C₂–C₄), which are key building blocks of the chemical industry, are traditionally produced from naphtha cracking or fluid catalytic cracking (FCC). High prices of oil and the interest of many countries on reducing their dependence on imported oil have urged research efforts to the development of new processes to produce oil-derived chemicals from alternative sources such as natural gas, coal, or biomass. The interest on these processes is not new and was already an important matter of study after the first oil crisis in the 1970s. During that period, many researchers investigated the use of Fe-based catalysts for the direct production of lower olefins from synthesis gas (syngas).

For this reaction, iron is the metal of choice not only for its low price and high availability but also for its catalytic properties since the Fischer–Tropsch-to-Olefins reaction (FTO) is carried out at high temperatures [1]. Compared to cobalt, iron has a low methanation activity even when the reaction is performed at temperatures higher than 300 °C, which is necessary to drive product selectivity toward shorter hydrocarbon chains. Additional advantages of iron

over cobalt-based catalysts include a higher resistance to contaminants present in syngas, a higher selectivity to olefins and a higher water–gas shift (WGS) activity allowing for the use of CO-rich syngas. Therefore, iron catalysts are especially suitable for the conversion of syngas derived from coal or biomass which contains more contaminants and is rich in CO. Additionally, the products obtained with iron catalysts have a higher olefinic content compared to Co.

Many different elements have been investigated as possible promoters to improve the C₂–C₄ olefins selectivity such as potassium [2,3], sodium [4,5], manganese [6], titanium [7], zinc [8], and vanadium [9]. Sodium has been proposed as an effective promoter to decrease methane selectivity [5,10,11], to favor chain growth propagation [5], and to increase the olefin-to-paraffin ratio of the products [4,11]. It has been reported that sodium, as well as potassium, increase iron carbidization [4,5] and WGS activity [12]. Ribeiro et al. [4] have suggested that the addition of alkali promoters decreases the C–O bond strength resulting in an increase in the coverage of dissociatively adsorbed CO, which could explain the higher levels of carbidization. Additionally, the high CO coverage could inhibit olefin re-adsorption, thus decreasing the olefin hydrogenation rates. The high coverage of the surface C species also might increase the chain growth probability and the conversion rates [10].

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Studies have shown that these beneficial effects are only obtained at low concentrations of sodium. After achieving an optimum loading, further addition of the promoter has a detrimental effect inhibiting reduction and carburization, decreasing the CO conversion, and shifting the product selectivity to shorter hydrocarbons [4,13]. Similar effects have been reported for potassium [14]. Ngantsoue-Hoc et al. [12] have shown that not only the promoter loading defines its effectiveness but also the reaction conditions and CO conversion levels.

Studies on sulfur as a promoter are limited as this element has been considered as a poison for Fischer–Tropsch catalysts. However, Bromfield and other researchers have shown that for iron, low concentrations of sulfur may act as a promoter that improves activity, decreases methane selectivity [15–17], increases the chain growth probability, and enhances olefin selectivity, reduction, and carburization [18,19]. These positive effects of the addition of low amounts of sulfur have been observed by co-feeding low amounts of H₂S during the reaction and by direct addition of sulfur during catalyst preparation. The promoter effect for sulfur is also highly dependent on promoter concentration, catalyst pretreatment, and reaction conditions [20].

Research on the development of selective catalysts for the production of lower olefins has been mainly focused on bulk or unsupported catalysts with low cost and simple synthesis. These precipitated or fused catalysts can be modified by addition of promoters to increase the selectivity to lower olefins and to decrease methane production. Although catalysts with high selectivity to C₂–C₄ olefins and to short-chain hydrocarbons ($\alpha \sim 0.4$ – 0.6) have been reported [21], their industrial use has not materialized because of their low mechanical stability [22,23] under high temperatures and low H₂/CO ratios.

Recently, Schulte et al. [24] have reported high selectivities to lower olefins in combination with high activity and low methane production when using iron supported on nitrogen and oxygen functionalized-carbon nanotubes (N–CNT, O–CNT) under the Fischer–Tropsch reaction at 340 °C, 25 bar and a H₂/CO ratio of 1.8. Their results underline the importance of the weakly interactive nature of the support to achieve a high catalytic activity.

Most recently, a breakthrough in the selective production of lower olefins from synthesis has been reported [23,25]. Sodium- and sulfur-promoted iron catalysts prepared using support materials with weak interaction toward iron have displayed high activities and light olefins selectivities with a low methane production and an excellent mechanical and chemical stability [23,25]. However, still limited information is available about the effect of sodium, sulfur, or a combination of both promoters on supported catalysts studied under the stringent reaction conditions used for the production of lower olefins from CO-rich synthesis gas. Most of the above-mentioned promoter studies have been performed on precipitated or fused catalysts at temperatures lower than 300 °C.

Here, we discuss the effects of sodium and sulfur on iron catalysts supported on α -alumina [23,26] when the Fischer–Tropsch reaction is carried out at high temperatures (340–350 °C). The catalysts have been prepared using an inert support to improve mechanical stability and to allow a better interaction between the promoters and the iron phase.

2. Experimental

2.1. Catalyst preparation and characterization

2.1.1. Preparation of an unpromoted supported catalyst

A supported catalyst with a nominal loading of 5 wt.% Fe was prepared using the incipient wetness impregnation technique.

Catalyst AFe was prepared with a solution of 1.726 g of ammonium iron citrate, C₆H₈O₇·xFe³⁺·yNH₃ (Fluka, purum p.a. 14.5–16 wt.% Fe (Table S1)), in 3.4 ml of demineralized water. For the preparation, 5 g of α -Al₂O₃ (10 m² g⁻¹; Pore volume 0.4 ml g⁻¹, AL4196E, BASF) was impregnated with the above-mentioned solution until the support pores were filled. The impregnation steps were successively repeated until all the solution was incorporated to the support. After each impregnation step, the material was dried at 120 °C under static air for 1 h. Finally, the catalyst precursors were dried overnight at 120 °C under static air and calcined at 500 °C (Heating ramp: 10 K min⁻¹) for 2 h under air flow.

2.1.2. Preparation of promoted supported catalysts

Catalysts AFe/Na and AFe/S were prepared with a solution of 1.726 g of ammonium iron citrate (Fluka) in 3.4 ml of demineralized water. The promoters were incorporated in the precursor solution adding 0.047 g of sodium citrate dihydrate, HOC(COONa)(CH₂COONa)₂·2H₂O (Sigma–Aldrich, ACS reagent $\geq 99\%$) in the case of sodium-promoted sample and 0.011 g of ferrous sulfate heptahydrate, FeSO₄·7H₂O (Merck, for analysis) for the synthesis of sulfur-promoted catalyst. It is important to note that sulfur has been added to the catalyst in the form of a sulfate. It has been reported that the presence of sulfur as a sulfate or as a sulfide has a different effect on catalytic performance [15].

AFe/S/Na and AFe/S/2Na were prepared using an aqueous solution of 1.726 g of ammonium iron citrate (J.T. Baker, 14.5–16 wt.%, Na, S: ~ 750 mg/kg (Table S2)). For the preparation of sample AFe/S/2Na, 0.047 g of sodium citrate dihydrate (Sigma–Aldrich) was added to the precursor solution. The impregnation, drying, and calcination steps were performed as described for the unpromoted supported catalysts.

2.1.3. Preparation of unsupported catalysts

A bulk unpromoted catalyst (BFe) was prepared by calcination of 2 g of FeO(OH) (Sigma–Aldrich, catalyst grade, 30–50 mesh) at 500 °C (Heating ramp: 10 K min⁻¹) for 2 h under air flow. The bulk promoted catalyst (BFe/S/Na) was prepared by incipient wetness impregnation of 2 g of FeO(OH) with an aqueous solution of 0.243 g of sodium citrate dehydrate (Sigma–Aldrich) and 0.056 g of FeSO₄·7H₂O (Merck) in 0.7 ml of demineralized water. After impregnation, the catalyst precursor was dried at 120 °C for 2 h under static air. The catalyst was finally calcined using the same procedure as described for the unpromoted bulk sample.

2.1.4. Fresh and spent catalysts characterization

Iron, sulfur, and sodium contents were analyzed with ICP-OES (Inductively coupled plasma–optical emission spectroscopy) using a Spectro Ciros CCD spectrometer. The average iron oxide crystallite size for the unpromoted supported catalysts was determined by line broadening analysis of XRD (X-ray diffraction) patterns obtained with a Bruker AXS D8 ADVANCE diffractometer equipped with a Co_{K α 1} source ($\lambda = 0.1789$ nm) using an angle range from 20° to 90° in 2θ .

Fresh and spent catalysts were analyzed with TEM (Transmission Electron Microscopy) to determine the size distribution of iron-containing particles. The images were obtained using a Philips Tecnai-20 FEG (200 kV) microscope equipped with an EDX and HAADF detector.

The extent of carbon deposition on the spent samples was determined with thermal gravimetric analysis (TGA) during carbon burn-off experiments performed in a Perkin Elmer Pyris 1 TGA under oxygen flow (10 ml min⁻¹). For these experiments, temperature was increased from 30 °C to 600 °C (Heating ramp: 5 K min⁻¹) and the sample remained under the final temperature for 1 h. During the experiments, a mass increase originated by

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