Journal of Catalysis 307 (2013) 283–294

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Comparing silver and copper as promoters in Fe-based Fischer–Tropsch catalysts using delafossite as a model compound

Zandile H. Chonco [a,1], Alta Ferreira [b], Lonzeche Lodya [b], Michael Claeys [a], Eric van Steen [a,*]

[a] Centre for Catalysis Research, Department of Chemical Engineering, University of Cape Town, Private Bag X3, Rondebosch 7701, South Africa
[b] Sasol Technology R&D, Sasolburg 1947, South Africa

ARTICLE INFO

Article history:
Received 3 May 2013
Revised 5 August 2013
Accepted 7 August 2013
Available online 12 September 2013

Keywords:
Copper
Silver
Iron
Delafossite
Fischer–Tropsch
Reduction
Carburization

ABSTRACT

The role of the group 11 metals copper and silver is investigated using delafossite as a model compound (and maghemite and hematite for comparison). The presence of group 11 metals in the crystal structure facilitates the reduction of trivalent iron into magnetite during the catalyst pretreatment in either hydrogen or carbon monoxide as evidenced using an in situ XRD study. Furthermore, the consecutive conversion of magnetite to α-Fe under H_2-pretreatment is facilitated, implying the ability of these metals to spillover hydrogen to magnetite. The conversion of magnetite to predominantly χ-Fe_5C_2 under CO-treatment is not facilitated by the presence of the promoter element. The model catalysts were tested for their activity and selectivity in the Fischer–Tropsch synthesis at 250 °C, 20 bar, $H_2/CO = 2.1$. The samples *ex* $AgFeO_2$ were the most active with a good selectivity toward the formation of liquid products, but at the expense of the CO_2-selectivity in the Fischer–Tropsch synthesis. Mössbauer adsorption spectroscopy showed that the samples containing group 11 elements contained large amount of magnetite in small crystalline domains (superparamagnetic iron in the analysis at room temperature). The CO_2-selectivity obtained over the samples containing the group 11 elements can be correlated with the amount of superparamagnetic iron in the spent catalyst samples.

1. Introduction

Heterogeneous catalysts are typically multi-component systems containing the catalytically active phase and different types of promoters to enhance the activity, selectivity, and stability of the catalyst. These promoters have been classified according to their primary roles [1] as structural promoter, i.e., assisting or maintaining the dispersion of the catalytically active phase, reduction promoter, i.e., facilitating the transformation to the reduced catalytically active phase, or chemical promoter, i.e., affecting the intrinsic activity of the catalytically active site. However, the role of one promoter may affect the functioning of another promoter [2] or may even play a dual role [3,4]. Hence, the search for the best catalyst for a particular process often involves an empirical process optimizing the various components in a complex mixture. A more rational approach would utilize a priori knowledge on both the primary and secondary functioning of promoters in the catalyst system.

The iron-based Fischer–Tropsch catalyst is one of the many complex, heterogeneous catalyst systems. This catalyst, used for the low-temperature conversion of synthesis gas ($CO + H_2$) to liquid hydrocarbons, contains besides silica or alumina as a binder and potassium as a chemical promoter also copper [5] as a reduction promoter [1,6–12]. The functioning of copper as a reduction promoter requires the close proximity of copper to the iron phase [6]. Recently, we explored the role of copper using spinel copper ferrite as a model compound [13]. It was deduced that copper is capable of hydrogen spillover during H_2-activation.

Iron-based Fischer–Tropsch catalysts contain a mixture of iron oxide and iron carbide phases under reaction conditions [14–16]. A high catalytic activity is maintained by increasing the fraction of iron present as iron carbide in the catalyst [17–20]. Typically, the iron catalysts contain large magnetite crystallites in addition to small iron carbide crystallites [13,21]. Thermodynamically, the conversion of large magnetite crystallites to iron carbide under the reported conditions is favored [22]. The conversion of magnetite to iron carbide during the Fischer–Tropsch synthesis is assisted by the presence reduction promoter copper [13], which might be a consequence of hydrogen spillover from the copper to the magnetite phase. The partially reduced magnetite phase might be carburized more easily under Fischer–Tropsch conditions, thus enhancing the activity of promoted iron-based catalyst. The enhanced rate of carburization would be associated with an increased CO_2-selectivity [13,23].

The role of copper during the Fischer–Tropsch synthesis might also be fulfilled by other metals capable of dissociative hydrogen

---

[*] Corresponding author. Fax: +27 (0)21 650 5501.
E-mail address: eric.vansteen@uct.ac.za (E. van Steen).
[1] Present address: Sasol Technology R&D, Sasolburg 1947, South Africa.

0021-9517/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcat.2013.08.005

chemisorption in the presence of CO, but whose bonding to the metal is weaker. A less strong bonding to the activating metal may enhance the likelihood for hydrogen spillover [24]. Metals, such as gold [25] and silver [26,27], adsorb hydrogen less strongly than copper [28,29], but more importantly also adsorb CO less strongly than copper [30]. This may enable the dissociative adsorption of hydrogen under Fischer–Tropsch conditions. Only a few studies have looked at the incorporation of silver [6,31] in iron-based catalysts. It has been stated that an intimate contact between silver and the catalytically active phase is required to obtain the required promotional effect [6].

The required, intimate contact between the promoter element and the catalytically active phase may be obtained by starting with a catalyst precursor, in which the promoter element and the catalytically active element are present in a single phase, e.g., as a mixed metal oxide. In this study, copper delafossite and silver delafossite were used as the model starting compounds. Their behavior during the activation procedure and the Fischer–Tropsch synthesis was investigated. The utilized synthesis methods result in differences in the crystallite size of the starting material. It is well-known that the performance of catalysts in the Fischer–Tropsch synthesis is dependent on the crystallite size [32]. Hence, the behavior of the model compounds was compared to pure iron oxide samples with approximately the same average crystallite size of the starting material.

2. Experimental

The model compounds were synthesized using (co)-precipitation from the metal nitrate solution. The dried precipitate was subsequently calcined to obtain starting materials. *Hematite* and *maghemite* were prepared by dropwise addition of a 25 wt.% aqueous ammonia solution (20 ml) to 150 ml of a 0.3 M aqueous solution of $Fe(NO_3)_3{\cdot}9H_2O$ with constant stirring until pH of ~10 [33]. The solution was stirred for 4 h at room temperature. After stirring, the precipitate was recovered by filtration and washed five times with 250 ml of de-ionized water. Thereafter, the sample was dried in an oven at 120 °C for 16 h and subsequently calcined in a fluidized bed in air (30 ml(NTP)/(min g)) at 950 °C (heating rate of 10 °C/min) for 8 h for the synthesis of hematite and at 350 °C (heating rate of 10 °C/min) for 6 h for the synthesis of maghemite. *Delafossite copper ferrite*, $CuFeO_2$, was prepared by dropwise addition of a 16.6 M aqueous NaOH-solution (25 ml) to 150 ml of a 3 M metal nitrate solution (ratio of $Cu(NO_3)_2{\cdot}3H_2O$ to $Fe(NO_3)_3{\cdot}9H_2O$ of 1:2) at 70 °C until pH of ~12. The mixture was refluxed at 70 °C for 6 h. The precipitate was washed 6 times with 250 ml of de-ionized water and dried at 120 °C for 16 h. After washing and drying, the precipitate was calcined in argon (40 ml(NTP)/(min g)) at 950 °C (heating rate of 15 °C/min) for 48 h with intermediate grinding every 12 h in an agate mortar [34] (under these conditions, the formation of $CuFeO_2$ is favored if the partial pressure of oxygen is less than 0.035 atm [35]). *Delafossite silver ferrite*, $AgFeO_2$, was prepared by co-precipitation in an alkaline solution [36]. A16.6 M aqueous NaOH-solution (25 ml) was added dropwise to 150 ml of a 3 M metal nitrate solution (0.8 M $AgNO_3$ and 2.2 M $Fe(NO_3)_3{\cdot}9H_2O$) at 70 °C until pH of ~12. An excess of iron was used to ensure incorporation of all silver in the delafossite phase [37]. The mixture was refluxed at 70 °C for 6 h. The precipitate was washed 6 times with 250 ml of de-ionized water and dried at 120 °C for 16 h. After washing and drying, the precipitate was calcined in air (30 ml(NTP)/(min g)) at 400 °C (heating rate of 10 °C/min) for 8 h. A relatively low calcination temperature was chosen, since silver ferrite decomposes in air to metallic silver and hematite at temperatures above 700 °C [38].

The elemental composition of the digested materials was verified using AAS (Varian SpectraAA 110). For this, 0.12 g of the sample was digested in a mixture of HCl/HF (4:1), HNO_3 and $HClO_4$ and then diluted in distilled water for analysis. The composition of the calcined materials was further determined using energy dispersive X-ray spectroscopy (SEM–EDX, Nova NanoSEM 230) equipped with a four quadrant back scatter detector and an energy dispersive Fissons Kevex X-ray spectrometer.

The phase composition of the calcined and the wax-embedded activated and spent samples was determined using a Bruker AXS D8 Advance X-ray laboratory diffractometer utilizing a Co source ($\lambda_{Co\ K\alpha 1}$ = 0.178897 nm) and a VÅNTEC position-sensitive detector. The activated and spent samples were analyzed within a day from recovering the sample to minimize the likelihood of oxidation of the sample [21] (storage of the wax-embedded samples of up to 10 months showed only a minor extent of oxidation of in particular the minor phases FeO and Fe_3C as determined using XRD – see Supplementary material). The average sizes of the crystalline domains were determined using Rietveld refinement of the X-ray diffractograms using TOPAS 4.2 (Bruker AXS). In situ activation studies were carried out in a XRK-900 reaction chamber (Anton-Paar, Austria). The calcined samples were heated up to 270 °C (heating rate 0.5 °C/min) at 1 bar in either hydrogen (50 ml(NTP)/g/min) or CO (50 ml(NTP)/g/min) and kept at this temperature for 16 h.

Mössbauer spectroscopy measurements were performed using a conventional acceleration constant spectrometer operating in the absorption mode (MAS). Low temperatures and applied magnetic fields were attained using Spectromag SM4000-10 cryomagnet from Oxford Instruments operating in the temperature range 1.5–300 K and applied magnetic field up to 10 T generated by a split-pair superconducting magnet system. The velocity scale was calibrated using metallic iron foil (α-Fe). MAS data of the calcined, and the wax-embedded activated and spent samples were typically recorded at room temperature. Low temperature (4.2 K) and applied magnetic field (10 T) MAS measurements were performed on a few selected samples.

The activity and selectivity of the samples for the Fischer–Tropsch synthesis were determined in a slurry reactor. The model compound (5.00 g) was slowly added to 300 g of molten wax (H1-hardened Sasolwax) in a 1 dm^3 reactor vessel. The suspension was stirred at 350 rpm and heated in Ar (30 ml(NTP)/(min g)) to 270 °C (heating rate 1 °C/min). The samples were activated in either H_2 or CO (100 ml(NTP)/(min g)) at this temperature for 16 h. After the activation procedure, the suspension was cooled under Ar (30 ml(NTP)/(min g)) to the reaction temperature of 250 °C and pressurized to 20 bar. The Fischer–Tropsch synthesis was carried out using synthesis gas (H_2:CO:Ar = 2.1:1:0.6; $F_{CO,0}/W$ = 0.13 mol/(h g)) at 250 °C and 20 bar. The CO-conversion and CO_2-yield were monitored using an online GC–TCD. Ampoule samples were taken off the effluent to analyze the product composition [39]. After 48 h, the gas flow to the reactor was switched from synthesis gas to Ar (10 ml/(min g))) and the temperature was decreased to 150 °C. The spent catalyst was allowed to settle overnight, after which the mixture was cooled down to room temperature and the wax-embedded sample was removed from the reactor.

3. Results and discussion

Table 1 shows the characterization of the 4 model systems. In all samples, the Na-content was below 0.01 wt.%. The dominant phases in the starting materials have intentionally almost the same crystallite size (viz. ~100 nm for the comparison between *hematite* and *delafossite copper ferrite* and ~8 nm for *maghemite*