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Highly active and stable supported iron Fischer–Tropsch catalysts: Effects of support properties and SiO_2 stabilizer on catalyst performance

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ABSTRACT

The effects of support properties including pore size, hydroxyl group concentration, and support stabilizer were investigated for six alumina-supported FeCuK Fischer–Tropsch catalysts containing 20% or 40% iron. Catalysts were supported on one of four aluminas stabilized with La_2O_3 or SiO_2. A large pore support was found to accommodate 40% Fe without pore blockage. Catalyst activity was found to increase with increasing support pore size, lower OH group concentrations, and higher extents of reduction. SiO_2 was found to be a more effective hydrothermal stabilizer than La_2O_3 as it suppresses the high-temperature transformation of γ-Al_2O_3 to α-Al_2O_3 up to 1200 °C allowing SiO_2-stabilized catalysts to be dehydroxylated at higher temperatures. SiO_2 stabilization also inhibits deactivation by sintering and increases activity, possibly due to surface silicate groups. Indeed, the activity of Fe/Si–Al_2O_3 continues to increase after 700 h on stream, while the Fe/La–Al_2O_3 catalysts lose activity over the same time period.

1. Introduction

The Fischer–Tropsch (FT) Synthesis (FTS) is a commercially proven, economically viable, and environmentally sound process for the production of hydrocarbon fuels from natural gas, coal, and biomass. Nevertheless, improvements in catalyst technology are desirable to improve the efficiency and economy of this process. Iron catalysts are considered to be more favorable than cobalt catalysts for the production of long-chain hydrocarbons from coal or biomass because of their low cost, low methane selectivity, and high water–gas shift (WGS) activity; WGS activity is needed for internal production of H_2 during FTS because of the inherently low H_2/CO ratios in syngas from coal or biomass.

Typical commercial iron FT catalysts consist of unsupported iron promoted with copper, potassium, and silicon dioxide. Precipitated FeCuK catalysts have been used successfully at Sasol for more than 50 years to produce long-chain hydrocarbons from coal synthesis gas in their low-temperature Arge tubular fixed-bed reactors [1]. Several publications from Bukur et al. [2–4] describe development of active, selective and stable precipitated iron catalysts. Upon optimization of catalyst composition and pretreatment conditions, a weight-time yield of 450 mmol $(CO + H_2)/g_{Fe}/h/MPa$ and a C_{2+} hydrocarbon productivity of 0.86 $g_{HC}/g_{Fe}/h$ for 100Fe/3Cu/4K/16SiO_2 at 260 °C and 2.2 MPa were reported [5]. This activity is among the highest reported for iron catalysts. Unfortunately, despite favorable high activity and selectivity properties, precipitated iron catalysts are generally mechanically too weak for use in slurry bubble column reactors (SBCRs) due to high rates of attrition to fine particles leading to difficulty in solid/wax separation. For example, extensive catalyst attrition was observed in an SBCR reactor operated by DOE at LaPorte, Texas requiring shutdown after only one day of operation [6]. Spray drying the catalyst with silica binders followed by calcination has been used by Sasol and Synfuels China to alleviate this problem [7] but the attrition resistance of unsupported Fe catalyst may not be adequate for the long-term, given higher rates of attrition observed during high velocity operation in large diameter SBCRs [8].

It is well known that supported metal catalysts have high attrition resistance due to the inherently high mechanical strength of the support [9]. Supports also generally (1) facilitate preparation of catalysts with much higher dispersion of the active phase or phases and (2) stabilize the active phase(s) against sintering [1].

Previous attempts to develop supported iron catalysts have largely met with limited success, i.e. most of these catalysts were found to have low activity and high methane selectivity [9–11].

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Interestingly, the poor catalyst performance can be correlated in most cases with preparation methods which led to strong Fe oxide-support interactions and low reducibility or in the case of Fe/carbon catalysts contamination or decoration of the active phase by the support [10–12]. For example, Cagnoli et al. [13] studied the influence of Al_2O_3 and SiO_2 supports on the activity and selectivity of iron catalysts of very high dispersion and small crystallite diameter (average diameters of 1.2 and 1.4 nm for Al_2O_3 and SiO_2, respectively). The activity of the alumina supported catalyst was one order of magnitude lower than the silica supported. Since the crystallite diameter in both catalysts was the same, this difference in activity was attributed to higher metal-support interaction of the iron with alumina. This assumption was also verified by the formation of two compounds; namely, $FeAlO_3$ and $FeAl_2O_4$. The alumina supported catalyst also showed higher methane selectivity and lower olefin selectivity. Bukur et al. [2] found that FTS activity was decreased by the addition of silica or alumina to precipitated Fe (basis of 100 parts of Fe) as follows: unpromoted unsupported $>8\ Al_2O_3 \sim 8\ SiO_2 > 24\ Al_2O_3 > 24\ SiO_2 > 100\ SiO_2$. The order can be explained by a lower extent of reduction of Fe and lower effectiveness of potassium due to its interaction with the alumina or silica. In another study of supported Fe, Bukur et al. [10] found that a silica-supported iron catalyst was nearly 3-fold less active than their most active precipitated (unsupported) iron catalyst on a per-gram-catalyst basis (100 vs. 269 mmol$(CO + H_2)/g_{cat}$/MPa/h) while their alumina-supported catalyst was 5-fold less active.

In contrast to other studies [10,13,14], O'Brien et al. [9] found Fe/Al_2O_3 to be twice as active as Fe/silica but still 5-fold less productive than unsupported iron (0.09 vs. 0.45 g_{HC}/g_{cat}/h). Methane selectivity was also higher on silica-supported catalysts, which is opposite from the results observed in Cagnoli's study [13].

Barrault et al. [15] found that the activity of iron dispersed on high surface area alumina was lower and its methane selectivity higher than for iron dispersed on low-surface area alumina; activity was highest on an alumina of mid-range surface area (80 m^2/g). These results corroborate the hypothesis that well-dispersed iron generally interacts strongly with the support, leading to low activity and high methane selectivity.

Rameswaran and Bartholomew [12] demonstrated that iron interaction with the support declines with decreasing hydroxyl concentration of the support. Increasing the dehydroxylation temperature enhanced the TOF and decreased methane selectivity. Xu and Bartholomew [11] adapted the same principles in their preparation of 10% Fe/silica and FePt/silica catalysts via nonaqueous evaporative impregnation of a previously dehydroxylated silica support. Nevertheless, their reported activity was still 4-fold lower than Bukur's best unsupported catalyst (62 vs. 269 mmol$(CO + H_2)/g_{cat}$/MPa/h), probably due to the low Fe loading.

Weakly interactive α-alumina and carbon nanofiber supports were used by de Jong's group [16] to decrease the interaction between iron and the support for high-temperature FT to produce olefins. Iron oxide crystallite diameter was reported to be 14 ± 5 nm on a 6% $Fe/\alpha\text{-}Al_2O_3$ catalyst. Unfortunately, the low-surface area support limited Fe loading and metal dispersion to less than optimal. In another paper, de Jong et al. [17] showed that activity increases with decreasing iron carbide crystallite size on an inert support.

In summary, the catalytic performance of supported Fe catalysts and particularly the effects of support properties on their activity and stability have not been thoroughly investigated. Previous efforts to develop an active supported Fe catalyst have been largely unsuccessful, in our opinion, due to strong Fe oxide-support interactions and low reducibility caused by less than optimal choices of preparation method, support material and support pretreatment. Consequently, the purpose of the subject study was to investigate systematically the role of the support variables. To acquire a reliable data set, six different catalysts were prepared on alumina supports using the same preparation method and either 20% or 40% Fe loading. Selecting four different alumina supports with different physical and chemical properties and two different Fe loadings allowed us to investigate the effects on catalyst activity and stability of:

(1) Physical properties of the support, e.g. pore volume and pore diameter.
(2) Surface chemistry of the support, i.e. hydroxyl groups which can be controlled by thermal pretreatment of the support.
(3) Silica vs. lanthana as a stabilizer.

It will be demonstrated that by carefully tailoring these properties, it was possible to develop alumina-supported Fe catalysts having higher activity per gram than previously reported. The use of silica-stabilized alumina, which enables high-temperature dehydroxylation while still maintaining high surface area and large pore volume, was a key to producing very active and stable catalysts. This approach may have general application to improvements in catalyst performance resulting from higher dispersion and lower metal oxide-support interactions.

2. Experimental

2.1. Catalyst preparation

A series of six alumina supported iron catalysts with four different alumina supports (St. Gobein alumina (AlG), Alfa-Aesar (AlA), AlC, and AlSi; the last two made by Cosmas Inc.) were investigated in this study. To increase the thermal stability of the supports, 3 wt% La was added to AlG, AlA, and AlC, while AlSi consisted of alumina doped with 5% SiO_2 as described previously [18]. The supports were first sieved to 30–60 mesh and calcined at 700 °C in air for 4 h prior to impregnation, except AlSi, which was calcined at 1100 °C. All four catalysts were promoted with Cu and K and prepared by slurry impregnation using a non-aqueous solution (50% iso-propanol and 50% acetone) containing desired amounts of ferric nitrate and copper nitrate in multiple steps. In each step, 10 wt% Fe with the desired amount of Cu was dissolved in a volume of solution corresponding to 10% above incipient wetness and then was placed in a rotary evaporator and mixed for 12 h to give uniform Fe and Cu deposition. After each impregnation step, the catalysts were dried very slowly in vacuum at 50 °C followed by 80 °C in an oven overnight and calcined at 300 °C for 16 h. Following the final addition step of Fe and Cu, potassium was added by incipient wetness impregnation as potassium bicarbonate. Nominal compositions (on a relative mass basis) of reduced catalysts were $100Fe/7.5Cu/4K/400Al_2O_3$ for a nominal iron loading of 20% and $100Fe/7.5Cu/4K/150Al_2O_3$ for an iron loading of 40%.

2.2. Catalyst characterization

2.2.1. Nitrogen adsorption/desorption

Surface area, pore volume, and pore size distribution (PSD) were calculated by nitrogen adsorption/desorption isotherms measured using a Micromeritics TriStar 3000 instrument. The samples (0.3 g) were degassed at 120 °C for 12 h before measurement.

2.2.2. X-ray diffraction

To estimate crystallite diameters, X-ray diffraction patterns were collected for all the catalysts using a PANalytical X'Pert Pro diffractometer with a Cu source and a Ge monochromator tuned to the Cu Kα1 wavelength (λ = 1.54 Å). Samples (reduced or carbided and then passivated) were scanned from 10° to 90° using a step size of 0.016° and a step time of 350 s. Diffraction patterns were compared to standard patterns in the database. The average