Journal of Catalysis 326 (2015) 149–160

Contents lists available at ScienceDirect

Journal of Catalysis

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

Fischer–Tropsch synthesis: Effect of ammonia in syngas on the Fischer–Tropsch synthesis performance of a precipitated iron catalyst

Wenping Ma [a], Gary Jacobs [a], Dennis E. Sparks [a], Venkat Ramana Rao Pendyala [a], Shelley G. Hopps [a], Gerald A. Thomas [a], Hussein H. Hamdeh [b], Aimee MacLennan [c], Yongfeng Hu [c], Burtron H. Davis [a,*]

[a] *Center for Applied Energy Research, University of Kentucky, 2540 Research Park Dr., Lexington, KY 40511, USA*
[b] *Department of Physics, Wichita State University, 1845 Fairmount, Wichita, KS 67260, USA*
[c] *Canadian Light Source Inc., 44 Innovation Boulevard, Saskatoon, SK S7N 2V3, Canada*

ARTICLE INFO

Article history:
Received 12 December 2014
Revised 27 March 2015
Accepted 1 April 2015
Available online 24 April 2015

Keywords:
Fischer–Tropsch synthesis
Fe catalyst
Biomass-to-liquids (BTL)
Slurry phase reactor
Ammonia (NH_3)
Ammonium nitrate (NH_4NO_3)
Nitric acid (HNO_3)
XRD
Mössbauer spectroscopy
XANES/EXAFS

ABSTRACT

The effect of ammonia in syngas on the Fischer–Tropsch synthesis (FTS) reaction over 100Fe/5.1Si/2.0Cu/3.0K catalyst was studied at 220–270 °C and 1.3 MPa using a 1-L slurry phase reactor. The ammonia added in syngas originated from adding ammonia gas, ammonium hydroxide solution, or ammonium nitrate (AN) solution. A wide range of ammonia concentrations (i.e., 0.1–400 ppm) was examined for several hundred hours. The Fe catalysts withdrawn at different times (i.e., after activation by carburization in CO, before and after co-feeding contaminants, and at the end of run) were characterized by ICP-OES, XRD, Mössbauer spectroscopy, and synchrotron methods (e.g., XANES, EXAFS) in order to explore possible changes in the chemical structure and phases of the Fe catalyst with time; in this way, the deactivation mechanism of the Fe catalyst by poisoning could be assessed. Adding up to 200 ppmw (wt. NH_3/av. Wt. feed) ammonia in syngas did not significantly deactivate the Fe catalyst or alter selectivities toward CH_4, C_{5+}, CO_2, C_4-olefin, and 1-C_4 olefin, but increasing the ammonia level (in the AN form) to 400 ppm rapidly deactivated the Fe catalyst and simultaneously changed the product selectivities. The results of ICP-OES, XRD, and Mössbauer spectroscopy did not display any evidence for the retention of a nitrogen-containing compound on the used catalyst that could explain the deactivation (e.g., adsorption, site blocking). Instead, Mössbauer spectroscopy results revealed that a significant fraction of iron carbides transformed into iron magnetite during co-feeding high concentrations of AN, suggesting that oxidation of iron carbides occurred and served as a major deactivation path in that case. Oxidation of χ-Fe_5C_2 to magnetite during co-feeding high concentrations of AN was further confirmed by XRD analysis and by the application of synchrotron methods (e.g., XANES, EXAFS). It is postulated that AN oxidized χ-Fe_5C_2 during FTS via its thermal dissociation product, HNO_3. This conclusion is further supported by reaction tests with co-feeding of similar concentrations of HNO_3. Additional oxidation routes of iron carbide to magnetite by HNO_3 and/or by its thermal decomposition products are also considered: $Fe_5C_2 + NO_x$ (and/or HNO_3) → Fe_3O_4. In this study, ion chromatography detected that 50–80% HNO_3 directly added or dissociated from AN eventually converted to ammonia during or after its oxidation of iron carbide, resulting from the reduction of NO_x ($NO_x + H_2 + CO \rightarrow NH_3 + CO_2 + N_2 + H_2O$) by H_2 and/or CO.

1. Introduction

The production of ultra-clean transportation fuels from biomass (biomass-to-liquids or BTL) through the Fischer–Tropsch synthesis (FTS) reaction has attracted increased attention in recent years; this is in addition to conventional routes from coal-to-liquids (CTL) and natural gas-to-liquids (GTL) [1–4]. The BTL process involves syngas production through the gasification of biomass materials. Depending on the oxygen source for gasification, the H_2/CO ratio derived from biomass varies in the range of 1.0–1.5 for air-blown gasification, and 1.5–2.2 for gasification using pure O_2 [1,4]. However, the biomass-derived syngas generally contains a number of impurities such as sulfur compounds (e.g., H_2S and COS), halide compounds (e.g., NaCl and KCl), nitrogen-containing chemicals (e.g., NH_3, NO_x, and HCN), traces of metals (e.g., Hg and Pb), and other compounds (e.g., $NaHCO_3$, $KHCO_3$, HCl, HF, and HBr) in addition to ash and tars. These contaminants could behave as catalyst poisons when their concentrations in syngas reach specific limits, and can significantly affect FTS catalyst

---

[*] Corresponding author.
E-mail address: burtron.davis@uky.edu (B.H. Davis).

http://dx.doi.org/10.1016/j.jcat.2015.04.004
0021-9517/© 2015 Elsevier Inc. All rights reserved.

performance. For this reason, purification of syngas must be performed before it is introduced into the FTS reactor. From an economic perspective, simplifying gas purification can benefit the overall gasification process, which is the most costly process in BTL technology (65–70% of total cost [5]). Therefore, laboratory-scale poisoning studies are very important to reduce the overall cost of the BTL process, improve catalyst lifetime, and even aid in designing better catalysts. However, there are few studies that quantify the optimum levels of these potential catalyst poisons for the purification process, especially for the case of catalysts being operated at commercially relevant conditions for an extended period of time.

Recently, the sensitivity of a precipitated Fe–K catalyst to alkali halide and alkali bicarbonate compounds (NaCl, KCl, $NaHCO_3$, and $KHCO_3$) was studied [6]. At levels of up to 40 ppm, poisoning with these alkali compounds was not found to significantly change catalyst performance at 260 or 270 °C during 400–1200 h of testing using a continuously stirred tank reactor (CSTR). The effects of other impurities (e.g., Na, K, Ca, Mg, Mn, Fe, P, and Cl with Co/Al_2O_3 catalyst [2] and Cl^-, SO_4^{2-}, and NO^{3-} with Fe catalysts [7]) have also been reported. These contaminants were all reported to decrease catalyst activity.

Furthermore, a number of sulfur studies (online or offline feeding) have also been reported for Fe- and Co-based FTS catalysts [2,8–18]. The results are somewhat controversial due to the complexities involved. For example, S decreasing [9,11,13,15,18] or even increasing the catalyst activity [12,16,17] has been reported; the mechanism of sulfur poisoning of the Fe catalyst and the relationship between metals and sulfur have not, to date, reached a consensus (e.g., metal/S ratio varied over a wide range of 2–20) [11,13,14,18]. These differences in conclusions likely stem from differences in sulfur concentrations and/or process conditions used. Moreover, the sulfur limit in syngas for the FTS catalyst has not reached a consensus, and is further complicated by the fact that the type of support or promoters used may impact the effect of sulfur. Therefore, the effect of sulfur on Fe catalyst behavior requires further investigation.

The effect of ammonia on FTS catalysts has been reported in a few studies. The effect of ammonia in syngas on the performance of a Co/Al_2O_3 catalyst using a CSTR has been investigated recently at the following conditions: 220 °C, 2.0 MPa, and $H_2/CO = 2.0$ [19]. Co-feeding 1.0–1200 ppmw ammonia was found to result in significant irreversible deactivation of the catalyst in the first 40 h; prolonged exposure at similar concentrations after that did not result in further significant changes in activity. The results are consistent with NH_3 adsorbing on some Co metal sites resulting in some deactivation of the cobalt catalyst. However, Borg et al. [2] did not observe deactivation of a $Re–Co/Al_2O_3$ catalyst when adding 4.0 ppm ammonia in syngas at similar reaction conditions. Ammonia was also found in two separate investigations to decrease CH_4 selectivity and improve C_{5+} selectivity of cobalt-based catalysts [19,20]. There are even fewer reports on the effect of ammonia on the FTS performance of Fe-based catalysts. Robota et al. [20] studied the effect of 6 ppm ammonia in the syngas feed on a precipitated iron catalyst at 240 °C, 2.25 MPa, and $H_2/CO = 1.63$. It was reported that the iron catalyst remained unaffected after adding the ammonia for 220 h. Results above this ammonia level were not reported.

Because of the limited information on the effect of ammonia on Fe catalysts as well as the significance and urgency of poisoning studies from both academic and industrial points of view, the current study was undertaken to further investigate the effect of this potential contaminant on Fe catalyst performance. Accordingly, a slurry phase reactor, which is able to provide a uniform temperature and contaminant concentration, was used to explore the sensitivity of a 100Fe/5.1Si/2Cu/3K catalyst to NH_3 compounds. The FTS reaction was conducted under typical FTS conditions with continuous co-feeding of the potential poison for an extensive period of time (e.g., 140–330 h) in order to obtain representative catalyst deactivation information resulting from contaminant addition. Ammonia may be added to the reactor in a number of different ways, for example, either directly as a gas, or by injecting it in an aqueous solution using a salt precursor. In the current study, ammonia impurity added to the syngas was made from three precursors, including direct addition of ammonia gas (i.e., in N_2), and by aqueous solution injection of ammonium hydroxide (NH_4OH) or ammonium nitrate (NH_4NO_3). This allows not only a determination of the ammonia limit, but also the effects of different ammonia precursors on the Fe catalyst. In the case of ammonium nitrate, the formation of ammonia and oxygen-containing nitrogen compounds is expected; this is important, as NO_x is also a contaminant of biomass-derived syngas [4], its concentration depending on gasification conditions (e.g., O_2 content [21]) and biomass source (e.g., seed corn > pine wood > maple + oak wood [21]). Meanwhile, in order to further shed light on the deactivation mechanism resulting from either ammonia or other possible impurity, i.e., NO_x dissociated from AN under FTS conditions, characterization of the working Fe catalyst sampled at different times on-stream using ICP-OES, XRD, Mössbauer spectroscopy, and synchrotron methods (e.g., XANES, EXAFS) was carried out. For the ICP-OES and XRD experiments, an extraction procedure using hot o-xylene was used to remove FT hydrocarbon products from the catalyst; on the other hand, the Fe catalyst samples withdrawn at different times were sealed in the wax product as a protective layer for analysis by Mössbauer spectroscopy or synchrotron techniques (e.g., XANES, EXAFS). Finally, the effects of ammonia on iron and cobalt catalysts are compared based on the results of the iron catalyst used in this study and those of a cobalt catalyst reported previously [19].

2. Experimental

2.1. Catalyst preparation and characterization

2.1.1. Preparation of Fe/Si/Cu/K catalyst

Details of catalyst preparation can be found elsewhere [22,23]. In brief, a base Fe catalyst with a composition of 100Fe/5.1Si/1.25K was first prepared using a precipitation method. The 100Fe/5.1Si/3.0K/2.0Cu catalyst used in this study was prepared by sequential impregnation of solutions containing appropriate amounts of K^+ (KNO_3, 99.9% purity) and Cu^+ ($Cu(NO_3)_2 \cdot 2.5H_2O$, 99.9% purity). Between each step, the catalyst was dried under vacuum in a rotary evaporator at 80 °C and the temperature was slowly increased to 95 °C. After the second impregnation/drying step, the catalyst was calcined under air flow at 350 °C for 4 h. The BET surface area, BJH pore volume, and pore diameter are 107 m^2/g, 0.154 cm^3/g, and 6 nm, respectively [23].

2.1.2. Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis of impurities on the catalyst surface

In order to determine trace amounts of poisons possibly retained on the Fe catalyst surface during FTS, a small amount of used Fe catalyst following wax extraction in hot o-xylene was analyzed by ICP-OES. Moreover, the ammonia concentrations in both the feed solution and the FTS aqueous products were analyzed using ion chromatography (IC) in order to quantify if any N was held up in the reactor.

2.1.3. X-ray diffraction (XRD) measurements of the used Fe catalyst

X-ray diffraction (XRD) measurements of the used Fe catalyst powder X-ray (XRD) was carried out for the used Fe catalysts at