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

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ABSTRACT

The effect of ammonia in syngas on the Fischer–Tropsch Synthesis (FTS) reaction over 100 Fe/5.1 Si/2.0 Cu/3.0 K 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 The Fe catalysts withdrawn at different times (i.e., after activation by carburization in CO, before and after co-feeding contaminants, and at the end of run) were characterized by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. NH₃/av. Wt. feed) ammonia in syngas did not significantly deactivate the Fe catalyst or alter selectivities toward CH₄, C₅+, CO₂, C₄-olefin and 1-C₄ 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

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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 -Fe₅C₂ 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 -Fe₅C₂ during FTS via its thermal dissociation product, HNO₃. This conclusion is further supported by reaction tests with co-feeding of similar concentrations of HNO₃. Additional oxidation routes of iron carbide to magnetite by HNO₃ and/or by its thermal decomposition products are proposed: $\text{Fe}_5\text{C}_2 + \text{NO}_x \text{ (and/or HNO}_3\text{)} \rightarrow \text{Fe}_3\text{O}_4$. In this study, ion chromatography detected that 50-80% HNO₃ 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 ($\text{NO}_x + \text{H}_2 + \text{CO} \rightarrow \text{NH}_3 + \text{CO}_2 + \text{N}_2 + \text{H}_2\text{O}$) by H₂ and/or CO.

Keywords: Fischer-Tropsch synthesis; Fe catalyst; biomass-to-liquids (BTL); slurry phase reactor, ammonia (NH₃), ammonium nitrate (NH₄NO₃), nitric acid (HNO₃), XRD, Mössbauer spectroscopy, XANES/EXAFS

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 to 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 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, lab-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/Al₂O₃ catalyst [2] and Cl⁻, SO₄²⁻ and NO₃³⁻ 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 S. 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/Al₂O₃ catalyst using a CSTR has been investigated recently at the following conditions: 220 °C, 2.0MPa and H₂/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 NH₃ 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/Al₂O₃ 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, 2.25MPa and $\text{H}_2/\text{CO} = 1.63$. It was reported that the iron catalyst remained unaffected after adding the ammonia for 220 hours. 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 100 Fe/ 5.1 Si/ 2 Cu/ 3 K 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 are expected; this is important, as NO_x is also a contaminant of biomass-derived syngas [4], its concentration depending on gasification

conditions (e.g., O₂ 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 100 Fe/5.1 Si/1.25 K was first prepared using a precipitation method. The 100 Fe/ 5.1 Si/ 3.0 K/ 2.0 Cu catalyst used in this study was prepared by sequential impregnation of solutions containing appropriate amounts of K⁺ (KNO₃, 99.9 % purity) and Cu⁺ (Cu(NO₃)₂·2.5 H₂O, 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 m²/g, 0.154 cm³/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

Powder X-ray diffraction (XRD) was carried out for the used Fe catalysts at room temperature using a Rigaku Diffractometer (DMAX-B) operating with Cu K α radiation (1.54 Å), in order to identify Fe carbides/oxides and potential Fe-poison compounds formed.

2.1.4. Mössbauer spectroscopy measurements of Fe catalyst

Mössbauer spectroscopy measurements were conducted in transmission mode, with a ⁵⁷Co source mounted in a standard constant acceleration velocity transducer. The Fe samples in slurry form, which were collected at different times during the run or at the end of the run, were placed in a cup holder, and were mounted near the finger of a vibration free closed-cycle refrigerator which provided for temperatures down to 20 K. Structural analysis of the samples was performed by least-squares fitting of the Mössbauer spectra to a summation of hyperfine sextets. The least squares fitting procedure employed user defined functions within the Peak Fit program. The parameters for each sextet in the fit consisted of the position, width and height of the first peak, the hyperfine magnetic field, and the quadrupole electric field. These parameters

were allowed to vary freely to obtain the best fit of the experimental data. Errors in the determined percent of Fe values are about ± 3 % for well resolved spectra; in those that contain several iron oxide and carbide phases, the uncertainty increases with the complexity of the spectrum (i.e., depending on the degree of overlap and the weakness of the signal).

2.1.5. X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) measurements of used Fe catalyst samples

To further identify the electronic structure and local atomic structure of the iron catalyst prior to and following exposure to HNO_3 in a makeup run, Fe catalysts in slurry form were characterized using XAS in transmission mode near the Fe K-edge at the Soft X-ray Micro-characterization Beamline (SXRMB) at the Canadian Light Source, Inc. The catalyst samples were extracted from the CSTR after exposure to realistic FTS conditions in the in-situ state and sealed in the wax product for analysis. The spectra (in energy space) were background subtracted and normalized with a Victoreen function and further normalized using a two-polynomial method with degree 1 for both the pre- and post-edge regions. Changes in the phase composition of the catalyst samples were analyzed by comparing the XANES region of the spectra using the WinXAS software [24]. EXAFS spectra were also treated using the WinXAS software. After background removal and normalization (previously described), the spectra were converted to k-space and background subtracted in k-space using a cubic spline fit. The spectra were then truncated within the range of $2.5\text{--}11 \text{ \AA}^{-1}$. To obtain the radial distribution function, the Fourier transform was carried out on the spectra in k-space making use of a Bessel window; a k-weighting of 1 was employed, to emphasize scattering by the light atoms (i.e., C and O). The first coordination shells were fitted in the k- and r-ranges of $3.0\text{--}10.5 \text{ \AA}^{-1}$ and $1.0\text{--}3.5 \text{ \AA}$, respectively. The experimental EXAFS data ($k^1 \cdot \chi(k)$) were fitted with theoretically generated

spectra derived from structural models, assuming the presence of χ -Fe_{2.5}C (Hägg carbide) and Fe₃O₄ (magnetite) (Fig.1). Hägg carbide has a monoclinic Bravais lattice with a C 2/c space group. The lattice parameters are $a = 11.504 \text{ \AA}$, $b = 4.524 \text{ \AA}$, $c = 5.012 \text{ \AA}$, and $\beta = 97.60^\circ$. Magnetite is isometric hexoctahedral with $a = 8.391 \text{ \AA}$ and a space group of F d3m. With the use of the ATOMS software [25], structural information of each of the phases (including information in Table 1) was transformed into spatial coordinates, which were then employed by the FEFF software [26] to calculate the scattering paths (Tables 2 and 3). The scattering paths specified in Tables 2 and 3 were thus used as inputs for the FEFFIT software [27] to generate theoretical $\chi(k)$, which were compared to their experimental counterparts. For the structural fitting, scattering paths up to $3.5 \text{ \AA}$ were considered. Structural fitting parameters used in the model included: two global lattice expansion coefficients, one for both Fe-C and Fe-Fe in the carbides and the other for both Fe-O and Fe-Fe in Fe₃O₄ phase; two global Δe_0 (one for iron carbide and one for Fe₃O₄) – the overall energy shift applied to each path; Debye-Waller factors for Fe-C and Fe-Fe in iron carbide and Fe-O and Fe-Fe in Fe₃O₄; and amplitude coefficients that account for the fraction of each phase (Hägg carbide and Fe₃O₄) and changes in the amplitude due to particle size (i.e., surface atoms have lower degree of coordination). In order to constrain the fits to achieve more physically meaningful results, the data sets were fitted simultaneously.

2.2. Fischer-Tropsch synthesis reaction tests

The 100Fe/ 5.1Si/ 3.0K/ 2.0 Cu catalyst was activated by CO using a CSTR under the following conditions: 270 °C, 0.1 MPa, and a 24 h time period. The catalyst poisoning study was carried out at three temperatures (i.e., 220, 260 or 270 °C) using a 1-L CSTR, while other process conditions were kept at 1.3 MPa (syngas), H₂/CO = 0.67-0.77, CO conversion = 40-75% Three ammonia precursors, i.e. ammonia/N₂ gas mixture (designated “AG”), ammonium hydroxide

solution (designated “AH”), and ammonium nitrate solution (designated “AN”) were employed to examine the effect of ammonia (with or without NO_x formation) on the Fe catalyst. At 220 °C, 150 ppm ammonia gas in N₂ was co-fed with the syngas for 240 h. Ammonia levels of 10, 30 and 80 ppm (maximum setting being reached) in the syngas feed were tested. This temperature was included in order to provide a useful comparison between the ammonia tolerance of the Fe catalyst (this work) and that of a cobalt catalyst (previously evaluated). At 260 °C, ammonium hydroxide solution (AH) was used as an ammonia precursor. The solution, having the desired NH₃ concentration, was delivered into the reactor at a rate of 0.5 ml/h using a high precision syringe pump (TELEDYNE ISCO 500 D). This yielded concentrations of 0.1-200 ppmw ammonia in syngas, with poisoning runs lasting 650 h. At 270 °C, AN solutions were co-fed with the syngas feed at a rate of 0.5 ml/ h using the same high pressure pump for about 400 h, such that ammonia impurity was produced through the dissociation of AN at above 210 °C [28-30]. This required the preparation of solutions having different levels of AN in order to provide up to 400 ppmw ammonia in the syngas. The AN precursor was chosen at this temperature for the purpose of not only further examining the ammonia effect, but also for studying the effect of ammonia precursor, with the AN precursor also emitting NO_x, another impurity in coal/biomass derived syngas, which forms above 210 °C [28-30]. Because of the rapid deactivation of the Fe catalyst occurring after co-feeding 400 ppm ammonia (AN), a separate run was performed whereby HNO₃ solution was co-fed in a concentration range of 50-1380 ppm in order to assess whether ammonia or HNO₃, produced from the thermal dissociation of AN, played a dominant role in deactivating the Fe catalyst. In all test runs, the ammonia precursor either in gas or solution form was co-fed after a steady state was established for at least 70 h. Moreover, for the purpose of characterization, a repeat run with co-feeding the higher level of AN (with 400 ppm

ammonia) was made for collecting slurry samples at different points in time. Changes in CO conversion, selectivities to CH₄ and C₅₊ (carbon atom basis), C₄ olefin selectivity ($100 \times (\text{rate of all C}_4 \text{ alkenes})/(\text{rate of all C}_4 \text{ alkenes} + \text{rate of all C}_4 \text{ alkanes}))$ and 1-C₄ olefin selectivity ($100 \times (\text{rate of 1-C}_4 \text{ alkenes})/(\text{rate of all C}_4 \text{ alkenes})$) as functions of time and contaminant concentration were used to evaluate the impacts of the poisons.

3 Results and Discussion

3.1 Effect of ammonia on iron Fischer-Tropsch synthesis catalyst performance

The effect of ammonia on the Fe catalyst performance was first examined at 260 °C and 270 °C, respectively. At 260 °C, three ammonia concentrations (i.e. 0.1, 20 and 200 ppmw) were tested for 173 (311-484 h), 140 (484-624 h), and 336 h (624-960 h), respectively. To obtain this level, ammonia solutions (AH) with concentrations of 9.5 ppmw to 1.9 wt. % NH₃ were prepared. At 270 °C, two low concentration levels (i.e., 0.1 and 0.4 ppm) ammonia and two high concentration levels (i.e., 40 and 400 ppm) were examined by using ammonium nitrate (AN) precursor solutions in two separate runs, in which up to 5.5% AN was prepared. Co-feeding 0.1-0.4 ppm ammonia (AN) for approximately 200 h changed very little the Fe catalyst activity and selectivities (results not shown for the sake of brevity). Testing of 40-400 ppm ammonia (AN) was carried out over longer periods of time (i.e., 144 and 240 h, respectively). Figs. 2a through 2d summarize the effects of ammonia on the FTS activity and selectivities (CH₄, C₅₊, and CO₂ selectivities, C₄/1-C₄ olefin selectivities) at the two temperatures.

Fig. 2a shows that the iron catalyst was stable (~56.3%) at 260 °C during co-feeding of 0.1-200 ppm ammonia (AH) for 650 h. The results suggest that the Fe catalyst is highly resistant to NH₃ such that it can tolerate at least 200 ppmw ammonia in syngas at the FTS conditions used.

The changes in the catalyst selectivities to CH_4 , C_{5+} , CO_2 , and C_4 olefin and internal C_4 olefin with time and ammonia (AH) concentration at 260 °C are shown in Figs. 2b, 2c and 2d, respectively. No measurable changes in the selectivities were observed during testing of 0.1-200 ppm ammonia (AH). This likely indicates that the catalyst physical structure remained unchanged when it is exposed to up to 200 ppm ammonia (AH).

From Fig. 2, the Fe catalyst activity and selectivities at 270 °C were essentially stable during 144 h (145-289 h) of continuously testing AN with 40 ppm ammonia (AN) in the syngas feed ($X_{\text{CO}} \sim 73\%$, $\text{CH}_4 \sim 3.8\%$, $\text{C}_{5+} \sim 80.6\%$, and C_4 and 1- $\text{C}_4 \sim 86.5\%$). CO_2 selectivity increased slightly from 48% to 49.5% due to enhanced WGS upon addition of the aqueous poisoning solution. This result further suggests that the Fe FTS catalyst is highly resistant to ammonia impurity under the FTS conditions used. Following these conditions, the ammonia concentration in the feed was dramatically increased to 400 ppmw at 289 h. The Fe catalyst deactivated rapidly from the second day of feeding the high concentration AN solution, and CO conversion decreased from 73% to 40% within 217 h (312-529 h in Fig 2a). The sharp drop in catalyst activity within this time period led to a slow increase in CH_4 selectivity (from 3.7 to 5.9%) and a decrease in C_{5+} selectivity (from 79 to 64%). Slight increases in C_4 olefin content in the latter stage of the testing period were also observed, which are likely attributed to deactivation as well. However, an unexpected stable CO_2 selectivity and a decrease in 1-olefin selectivity between 312 and 450 h were also observed. It is generally accepted that catalyst deactivation lowers CO_2 selectivity and increases 1-olefin (or decreases 2-olefin) content, the latter due to a lower activity for secondary reactions of alpha olefins, which are primary FTS products. Therefore, the opposite trends on the CO_2 and 1-olefin selectivities observed suggest

that AN altered the Fe catalyst surface structure, or that the Fe catalyst chemical structure changed when testing at high levels of AN solution.

The results of effect of ammonia gas (AG) at levels in the range of 10-80 ppm on Fe catalyst activity at 220 °C tended to be similar to using ammonium hydroxide (0.1-200 ppm) at 260 °C. Co-feeding up to 80 ppm ammonia (AG) in syngas for 240 h at 220 °C did not deactivate the Fe catalyst. This means that the Fe catalyst is also quite resistant to high levels of ammonia at lower temperatures. Therefore, the effect of ammonia on Fe catalyst performance at 220 °C is not presented in this section. Instead, the results of the Fe catalyst together with that of the cobalt catalyst obtained previously at the same temperature (220 °C) [19] are plotted in Figure 11 in Section 3.7, which compares the ammonia resistances of iron and cobalt catalysts.

In summary, NH_3 did not severely poison the Fe catalyst under the conditions used herein. The Fe catalyst was found to be able to resist up to as high as 200 ppm NH_3 in the syngas feed without significantly diminishing its activity or changing its selectivity. This is much higher than the value of 6 ppm NH_3 that was reported recently to be a safe concentration for a precipitated iron catalyst at 240 °C, 2.25 MPa, $\text{H}_2/\text{CO} = 1.63$ by Robota et al. [20]. The very high ammonia limit found in this work implies that syngas purification procedures could be simplified and operational costs of the BTL process may be lowered if the higher limit is applied. When the ammonia precursor was switched to the AN form, it was found that a moderate level of AN containing 40 ppm ammonia did not result in significant changes in the Fe catalyst activity and selectivity. However, increasing the level of ammonia in AN to 400 ppm led to rapid deactivation of the Fe catalyst. This was accompanied by an increase in CH_4 selectivity and decreases in both C_{5+} selectivity and 1-olefin selectivity; however, CO_2 selectivity and total C_4 olefin selectivity did not change significantly.

The fact that co-feeding a high level of AN deactivated the Fe catalyst could stem from the HNO_3 originating from thermal dissociation of AN, which may act to oxidize the Fe catalyst. Results of ICP-OES analyses did not reveal nitrogen uptake by the catalyst; this essentially rules out site blocking by NO_x , ammonia or the formation of iron nitrogen compounds as deactivation mechanisms. The same conclusion was also found regarding the used catalyst corresponding to low levels of ammonia (AH) run at 260 °C; in that case, if ammonia sorption had occurred, it is estimated that 50% N should be present in the used catalyst. Therefore, it is speculated that NH_3 under FTS conditions only weakly adsorbs onto the Fe catalyst surface; moreover, deactivation of the Fe catalyst observed at the high level of ammonium nitrate containing 400 ppm ammonia (AN) in the syngas must be caused by another mechanism. A likely candidate is the oxidation mechanism as mentioned above. This was confirmed by a HNO_3 co-feeding run as addressed below, as well as by results of XRD, Mössbauer and XANES/EXAFS as discussed in Sections 3.3 - 3.5.

3.2 FTS with co-feeding HNO_3

Since the possibility of HNO_3 oxidizing iron carbide was proposed, a separate run by co-feeding HNO_3 solution was conducted in order to confirm the hypothesis. The HNO_3 concentrations in the feed were between 50 and 1380 ppm under the same conditions (270 °C, $\text{H}_2/\text{CO} = 0.77$, 1.3 MPa and 10 NL/g-cat/h), and FTS results are shown in Fig. 3. Stable CO conversion of 78% was achieved at 96 h, at which 50 ppm HNO_3 was added to the feed. CO conversion remained unchanged during 72 h at this HNO_3 level. Subsequently, the HNO_3 level was increased to 100 ppm at 168 h, and CO conversion decreased from 77% to 71.5% the next day and then decreased further to 70% in the second day. However, the CO conversion leveled off when the HNO_3 solution was continuously fed for another two days (191-264 h). At this

condition, CH₄ selectivity increased and C₅₊ selectivity decreased slightly with time, while CO₂ and C₄ selectivities were changed to a lesser degree, similar to the observations in the AN test run. The HNO₃ level in the feed was finally increased to 1380 ppm, the highest level used, and the level which contained the same concentration of nitrate ion as that in the AN solution which provided 400 ppm ammonia (AN) in the feed. This resulted in a rapid decrease in the CO conversion from 70 to 20% within 169 h. Simultaneously, all selectivities were adversely impacted during the severe catalyst deactivation. Therefore, the HNO₃ co-feeding experiment confirmed that HNO₃ is a major cause of Fe catalyst deactivation by oxidizing iron carbide, and 100 ppm HNO₃ is sufficient to induce a moderate deactivation of the Fe catalyst.

However, during co-feeding AN solution, HNO₃ may be formed from AN hydrolysis to a lesser extent, and from its thermal dissociation under the FTS condition to a greater extent. In the case of AN hydrolysis at room temperature (i.e., $\text{NH}_4^+ + \text{H}_2\text{O} = \text{NH}_3 + \text{H}_3\text{O}^+$), H^+ concentration or activity was estimated to be 18.6 ppm in the AN solution that provided 400 ppm NH_4^+ when it is assumed to be an ideal infinite dilution, and the dissociation constant K_a ($\alpha_{\text{NH}_3} \alpha_{\text{H}^+} / \alpha_{\text{NH}_4^+}$) is $10^{-9.63}$ [31], which would correspond to a pH value of 4.7. Considering that this weakly acidic AN solution represents only 0.15% NH_4^+ being hydrolyzed and it provided only 0.6 ppm HNO₃ in the syngas feed – an amount which is significantly lower than the poison limit of 100 ppm HNO₃ determined in this study - the majority of HNO₃ if formed that participates in the oxidizing of iron carbides would occur through AN thermal dissociation at FTS conditions. Researchers have reported that AN in liquid thermally dissociated to ammonia and HNO₃ ($\text{NH}_4\text{NO}_3 = \text{NH}_3 (\text{g}) + \text{HNO}_3 (\text{g})$) between 210 and 270 °C, and HNO₃ can be further decomposed to NO_x [28-30], where x ranges between 0.5 and 2. Under the reducing environment of CO and H₂ and high temperature (i.e., 200-300 °C), oxygen transfer from NO_x to

carbon monoxide becomes possible to produce carbon dioxide and NO [32], which can be reduced further by H₂ to produce ammonia [33] and/or nitrogen [34,35]; simultaneously, CO₂ is evolved (i.e., NO_x + CO + H₂ → NH₃ + N₂ + H₂O + CO₂, equation not balanced). The above proposed dissociation mechanism suggests that a fraction of the nitrogen-containing species is converted to ammonia, whereas the other fraction converts to N₂. This is in line with the ammonia analysis results by IC as discussed in Section 3.6, where only 50-80% N from the NO₃ was converted to ammonia.

According to Figs. 2 and 3, CO₂ and C₄ olefin selectivities changed very little when adding low levels of HNO₃ (for example, 50-100 ppm HNO₃ or 400 ppm AN); high HNO₃ concentrations (i.e., 1380 ppm) led to significant decreases in CO₂ selectivity, which could be mainly ascribed to changes in catalyst chemical structure induced by the high concentration of poison. This deduction is in line with the results of Mössbauer spectroscopy described in Section 3.4.

3.3 XRD results of used Fe catalysts

To gain further insight into the nature of the deactivation caused by high levels of ammonia in AN form, XRD was conducted on the used Fe catalyst that did not exhibit measurable deactivation (i.e., from the run with 200 ppm NH₃ in the feed), and used iron catalysts following severe deactivation by the high level of AN (i.e., 400 ppm ammonia), for the purpose of comparison. The XRD spectra of the two used catalysts are depicted in Fig. 4. Both used iron catalysts show similar XRD patterns in the 2θ range of 20° - 80°. The most intense reflections are observed at 2θ of 30°, 35.5° and 40°, 42.6°, 45.0°, representing the characteristic peaks of Fe₃O₄ and Fe₅C₂, respectively. However, the peak intensities differ significantly

between the two samples. In the used Fe catalyst following testing of ammonia (AH) at the 200 ppm level, the diffraction peak for the iron carbides at $2\theta = 45^\circ$ is sharp and characterized by a high intensity; however, the intensity of the corresponding peak is much lower in the case of the used Fe catalyst exposed to the high level of ammonia (AN). Meanwhile, the iron carbide peaks detected at $2\theta = 40^\circ$ and 42.6° in the used Fe catalyst exposed to 200 ppm level ammonia (AH) were not apparent in the used Fe catalyst exposed to 400 ppm ammonia (AN). Meanwhile, four new and very pronounced peaks present at 35.5° , 43.2° , 57° , and 63° for the Fe catalyst in the case of the high levels of AN being used, indicate that a large amount of Fe_3O_4 was formed. Therefore, these changes in the characteristic peaks and intensities of the iron phases indicate that a significant fraction of iron carbide experienced a change in chemical structure to iron oxide, probably through oxidation when the Fe catalyst was exposed to a high concentration of AN. This is likely the primary cause of Fe catalyst deactivation in the case of high levels of AN being used. Two possibilities of AN oxidizing the surface of iron carbides could operate under the FTS conditions: (1) oxidation of the surface of iron carbides by NO_x ($x \sim 0.5-2$), a product produced in the thermal decomposition of AN or HNO_3 (i.e., $\text{Fe}_5\text{C}_2 + \text{NO}_x \rightarrow \text{Fe}_3\text{O}_4 + \text{N}_2 + \text{CO}_2$, unbalanced equation); or (2) reaction of Fe carbides with nitric acid that is produced by the dissociation of AN, with subsequent decomposition and reduction of Fe nitrate to magnetite by hydrogen. For example: $\text{Fe}_5\text{C}_2 + \text{HNO}_3 \rightarrow \text{Fe}(\text{NO}_3)_3 + \text{NO}_x + \text{CO}_2 + \text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 + \text{H}_2 \rightarrow \text{Fe}_3\text{O}_4 + \text{NO}_x + \text{H}_2\text{O}$ (unbalanced equations). In the latter case, the NO_x formed in the first case might be short-lived in the CO and H_2 environment, being subsequently reduced to ammonia and N_2 in line with the above discussion (Section 3.2).

Vogler et al. [36] used nitrous oxide (N_2O) to characterize the unpromoted and K promoted iron catalysts pretreated by CO/H_2 (1.0) at low (235°C) and high (275°C)

temperatures. After dosing N_2O gas at room temperature and atmospheric pressure, the infrared spectra indicated that N_2O reacted with ‘reduced iron species’ (iron carbides and magnetite) to produce N_2 , which was detected by mass spectrometry. A slow oxidation rate and a small amount of N_2 were observed on the Fe samples pretreated at the high temperature (i.e., where Mössbauer spectroscopy results showed that 100% iron carbides had been formed) compared to the low temperature case (where Mössbauer spectroscopy results revealed a composition of 90% Fe_3O_4 and 10% iron carbides). This was attributed to slower oxidation of FT sites which were blocked by carbon. K was shown to facilitate carburization, while K cations were not found to react with N_2O at room temperature. Therefore, the K promoter was suggested to either increase the reaction rate of N_2O with the Fe carbides or increase the availability of sites. Under FT synthesis conditions, any NO_x formed from the dissociation of AN or HNO_3 could oxidize the iron carbide catalyst to produce magnetite and N_2 . At the same time, the competitive reaction of NO_x with H_2 could produce NH_3 . This assumption is consistent with the IC results which showed that a certain amount of ammonia (i.e., ammonium hydroxide) was produced, as detected in the FTS aqueous products (see Section 3.6).

The proposed oxidation mechanism depletes iron carbides by its reacting with NO_x or HNO_3 to form magnetite and CO_2 . Therefore, the unexpected constant CO_2 selectivity occurring during severe catalyst deactivation observed when co-feeding the high level AN (Fig. 2c), could be explained reduction of NO_x by H_2 , and not CO, with AN dissociation as suggested in Section 3.2 and/or from enhanced WGS, since magnetite has also been proposed to be active for the WGS reaction [37-39]. Enhanced secondary reaction of butene (decreasing 1-olefin selectivity) during the deactivation is a more complicated issue, which might be not only related to the

changes in Fe phases but also to possible changes in the interaction of Fe and promoters after modification by nitrate ions.

As mentioned above, one point of view was that the K promoter increases the rate of iron carbide oxidation by N_2O [36]. However, K may weaken ammonia adsorption on Fe carbide sites, since it is proposed to enhance adsorption and dissociation of CO on Fe catalyst active sites [38]. Therefore, K in the Fe catalyst might enhance the resistance of the Fe catalyst to poisoning by ammonia. Additional study is necessary to confirm this assumption.

3.4 Mössbauer spectroscopy results

Mössbauer spectra of the four Fe samples collected at TOS of 0 h, 78 h, 145 h and 217 h, one sample at the end of the HNO_3 run (480 h), and one sample at the end of the ammonia (AH) test run (960 h) are shown in Figs. 5 a-f, respectively. The spectra vary significantly from sample to sample. Three phases of iron, i.e. χ - Fe_5C_2 , ϵ' -carbide, and magnetite (Fe_3O_4), are present in all samples, which are represented by three blue sextets, two green sextets and one red sextet, respectively, except that the catalyst exposed to HNO_3 contained small amounts of paramagnetic isolated Fe impurities. With increases in time, the intensities of the blue lines weakened while the red lines increased greatly; in contrast, the green lines remain relatively constant. Similar results were reported previously in the Mössbauer spectroscopy study of Fe FTS catalysts by Rao et al. [40], in which χ -carbide and ϵ -carbide were reported to produce a magnetic field. In this study, the measured magnetic field decreased in the following order: Green 1 > Blue 1 > Blue 2 > Green 2 > Blue 3. Note that Mössbauer spectra of all these samples do not display any Fe-N compounds, in line with the XRD results, which again tends to rule out

the formation of bulk Fe-N compounds as a deactivation mechanism in the current context. The results of data analysis by least-squares fitting are summarized in Table 4 and Fig. 6.

The data show that 81% iron carbides and 19% magnetite were formed after CO reduction (TOS = 0 h). However, the iron carbide content decreased to 56% and simultaneously, the magnetite content increased to 44% at 78 h, where a steady state with a CO conversion of 74% was established (Fig 6.). This result demonstrates that a fraction of the unstable iron carbides formed by CO activation was transformed into magnetite during the FTS startup period, probably through reaction with a main FTS byproduct, water (i.e., $3\text{Fe}_5\text{C}_2 + 32\text{H}_2\text{O} = 5\text{Fe}_3\text{O}_4 + 6\text{CO}_2 + 32\text{H}_2$). After that, the ammonium nitrate solution containing 400 ppm ammonia (AN) was co-fed and CO conversion started to decline rapidly with time. Corresponding to a sharp CO conversion drop (74% to 33%) induced by AN addition (Fig. 6), the amount of iron carbide decreased significantly to 49% at 145 h and further down to 37% by the end of run at 217 h, while the content of magnetite increased to 51% and 63% in the two time periods, respectively. Therefore, 34% of the iron carbides was oxidized by AN. Oxidation was also evident for the HNO_3 run, with even greater amounts of magnetite (i.e., 70%) being formed, and smaller amounts of iron carbide (i.e., 26%) remaining at the end of run, where CO conversion was only 20% (Fig.6). The Mössbauer spectroscopy data suggest that HNO_3 (i.e., either directly added or thermally dissociated from AN) oxidized iron carbides under FTS conditions, and that HNO_3 is a stronger poison to deactivate the Fe catalyst than AN. Turning to the Fe catalyst exposed to 200 ppm ammonia (AH) at 260 °C, iron carbides remained as high as 73% by the end of run (Table 4), consistent with stable activity being observed during co-feeding 20-200 ppm NH_3 for 650 h.

As shown in Table 4 and Fig. 6, $\epsilon\text{-Fe}_{2.2}\text{C}$ and $\chi\text{-Fe}_5\text{C}_2$ exhibited much different stability under oxidizing conditions. Before and during co-feeding a high level of AN between 78 and 193

h, the amount of ϵ -Fe_{2.2}C remained nearly unchanged, 7-11%, but the amount of χ -Fe₅C₂ significantly decreased from 48% to 19%. The results demonstrate that ϵ -Fe_{2.2}C is more stable relative to the χ -Fe₅C₂ phase under poisoning conditions. During co-feeding AN or HNO₃, χ -Fe₅C₂ was the primary phase that experienced oxidation, resulting in a direct correlation between the Fe catalyst rate and the content of χ -Fe₅C₂ (Fig. 6). de Smit et. al. [41] studied the stabilities and reactivities of various iron carbides, including ϵ -, χ - and θ -iron carbides under realistic FTS conditions. They found that the catalyst containing χ -Fe₅C₂ was highly susceptible to oxidation during FTS conditions, while θ -Fe₃C showed a lower activity and selectivity. At low temperatures and higher carbon chemical potential (μ_c), ϵ -carbides are stable with respect to the χ -Fe₅C₂ and θ -Fe₃C, but at high temperatures and lower carbon chemical potential (μ_c), χ -Fe₅C₂ and θ -Fe₃C are relatively stable and ϵ -carbides transform into χ -Fe₅C₂. Our current study also confirms this trend; for example, in Table 4, as much as 45% of ϵ '-Fe_{2.2}C was detected at 260°C, while only 7-11% of ϵ '-Fe_{2.2}C was observed at 270 °C. Thus, the stability and distribution of the carbides observed in this study are in line with the literature.

3.5 XANES/EXAFS results

The deactivation of Fe catalyst resulting from the addition of HNO₃ was further studied by XANES/EXAFS. Normalized XANES spectra of iron catalyst samples before and after HNO₃ addition, as well as reference spectra for iron carbide (i.e., a carburized - 10 h at 290 °C in CO - iron catalyst with composition 100Fe/4.6Si/1.5 K, from [42]) and Fe₃O₄ (i.e., an iron catalyst with composition 100Fe/4.6Si/1.5 K, taken from the point of maximum Fe₃O₄ content at 190.5 °C during carburization in CO from TPR/XANES from [42]) are displayed in Fig. 7. A comparison of line shapes between spectrum (a) and spectrum (b) reveals that the catalyst

sampled prior to HNO_3 addition consisted primarily of iron carbide, while a comparison between (c) and (d) demonstrates that the catalyst sampled after exposure to HNO_3 during FTS contained a significant fraction of Fe_3O_4 .

A similar conclusion is drawn from comparing the k^1 -weighted Fourier transform EXAFS magnitude spectra (Fig. 8). Like reference spectrum (a), spectrum (b) consists of two primary peaks, indicative of a range of Fe-C first shell interactions and a range of Fe-Fe first shell interactions in iron carbide. On the other hand, like the reference spectrum (c), spectrum (d) consists of two primary peaks, indicating a range of Fe-O and Fe-Fe first shell interactions in Fe_3O_4 (magnetite).

Table 5 and Fig. 9 display the results of the EXAFS fittings, and the r-factor of 0.011 indicates a relatively good fit of the theoretical model to the experimental data. The amplitude parameter A for Hägg carbide is significantly lower for the catalyst following HNO_3 addition, while the amplitude parameter for Fe_3O_4 is significantly higher. Thus, the results of both XANES and EXAFS analyses further confirm that the catalyst underwent oxidation by the HNO_3 contaminant, consistent with the results of XRD and Mössbauer spectroscopy as discussed in Sections 3.3 and 3.4.

3.6 IC analysis of FTS aqueous product

With the aim of verifying the presence of ammonia that might be produced by the oxidation and thermal dissociation of AN/ HNO_3 , as proposed in Section 3.2, IC analyses of the FTS aqueous products produced in the AN and HNO_3 poisoning runs were performed. The results are shown in Table 6. It is interesting to find that four representative FTS aqueous samples collected at different times contained 3575-4100 ppm NH_4^+ , which indicates that about

60% of the HNO_3 feed was converted to ammonia (Fig. 10). For the AN test runs, IC results show 1247 - 1319 ppm NH_4^+ present in the FTS aqueous product produced at different times during which 40 - 400 ppm ammonia (AN) was co-fed. This indicates that an additional 50-80% NH_3 eluted relative to the amount of NH_3 introduced (Fig. 10). Considering that NH_4^+ and NO_3^- are the only sources of N, the observed difference must be due to hydrogenation of the NO_3^- in the AN feed. Therefore, the ammonia analysis results for the HNO_3 and AN test runs are consistent, and unambiguously indicate that HNO_3 , either directly added or thermally dissociated from AN, was partly converted to ammonia through its reaction with the reducing agents of H_2 and CO under FTS conditions, in agreement with the AN dissociation mechanism proposed in Section 3.2.

3.7 Comparison of effect of ammonia on the FTS of Fe and Co catalysts

In a DOE-sponsored project (DE-FC26-08NT0006368), both Fe and Co catalysts were examined with different NH_3 levels. The effect of ammonia on a cobalt catalyst was studied at 220 °C and results are reported elsewhere [19]. To better compare the sensitivity of the Fe and Co catalysts to ammonia poisoning, the effects of 10, 30 and 80 ppm ammonia gas in the syngas feed on Fe catalyst performance were examined for over 240 h at the same temperature. Fig. 11 summarizes the effect of ammonia on the activities of the Fe and Co catalysts in the temperature range of 220 -260 °C. The Co catalyst displays a much higher sensitivity to ammonia than the Fe catalyst. The activity of the cobalt catalyst decreased by 20% in the first 24 h upon exposing to 10 - 1200 ppm NH_3 , however, the deactivation rate became slower after the first day, and it only decreased another 15% in the next 4-5 days of testing. More interesting is that the Co catalyst deactivation rate did not significantly change with NH_3 level, suggesting that NH_3 adsorbs on the

Co catalyst and quickly attains an equilibrium state [19]. Compared to the cobalt catalyst, the Fe catalyst is much more resistant to NH_3 poison. At the same temperature (i.e., 220 °C), the CO rate remained unchanged upon exposing the catalyst to 10-80 ppm NH_3 for 10 days (Fig. 11). At 260 °C, a higher ammonia level, 200 ppm, was tested over the Fe catalyst for a longer period of time (i.e., 16 days) without causing any significant loss in activity. The different sensitivities of Fe and Co catalysts to ammonia were also observed by Robota et al. [20], where only the low NH_3 level (6 ppm) was used. It should also be noted that co-feeding up to 1200 ppm ammonia resulted in slightly lower CH_4 selectivity, which was ascribed to NH_3 adsorption on Co sites inhibiting H_2 adsorption and creating a relatively H_2 poor surface [19], while co-feeding up to 200 ppm NH_3 in the syngas feed was not found to modify hydrocarbon selectivities of the Fe catalyst. The differences could originate from differences in the electronic or physical structure of the Fe and Co catalysts.

In the current context, the primary focus was on the effect of ammonia, and co-feeding of NH_3 or NH_4OH led to relatively minor effects on catalyst deactivation. However, using ammonium nitrate led to severe deactivation associated with the nitrate ion. Co-feeding of nitric acid led to a similar severe deactivation and the above results of XRD, Mössbauer spectroscopy, and X-ray absorption spectroscopy confirmed that deactivation was caused by oxidation of iron carbide. Because NO_x can be produced in significant levels with certain forms of biomass, the current results (albeit limited) indicate that more detailed co-feeding studies with different NO_x compounds would be important.

4 Conclusions

The Fe catalyst was quite resistant to high levels of ammonia, regardless of using ammonia gas or ammonium hydroxide was used. Up to 200 ppm NH_3 was not found to

significantly deactivate the Fe catalyst or measurably change the Fe catalyst selectivity. However, when 400 ppm ammonia in the AN form was used, it rapidly deactivated the Fe catalyst. The deactivation was proposed to occur via HNO_3 , thermally dissociated from AN, which oxidizes the iron carbides. This was confirmed by a test run with co-feeding 50-1380 ppm HNO_3 , where a similar deactivation pattern was observed at a high level of HNO_3 . Furthermore, adding a high level of AN or HNO_3 solution adversely changed the Fe catalyst selectivity toward light hydrocarbon products.

The deactivation mechanism in the case of high levels of ammonia (AN form) and HNO_3 was studied by characterizing the Fe catalysts collected at different times under FTS conditions using XRD, ICP-OES, Mössbauer spectroscopy and XANES/EXAFS. No N uptake was observed by ICP-OES and no Fe-N compounds were detected on the used Fe catalysts by XRD and Mössbauer spectroscopy. Analysis of Mössbauer spectra revealed that three main types of iron phases were present during FTS (i.e., $\epsilon\text{-Fe}_{2.2}\text{C}$, $\chi\text{-Fe}_5\text{C}_2$ and magnetite) and that the Fe catalyst deactivation correlated with losses in $\chi\text{-Fe}_5\text{C}_2$ by oxidation. It was found that 81% of iron was in the carbide phase after CO activation; however, about 31% of iron carbides (81→56%) was unstable and this fraction oxidized to magnetite before the catalyst reached a pseudo-steady state. During co-feeding the high level of AN solution, another 34% of iron carbides (56→37%) were transformed to magnetite. Adding HNO_3 solution with the same NO_3^- concentration led to more severe oxidation of iron carbides, and 54% of iron carbides converted to magnetite. However, a high content of iron carbides (73%) was maintained for the Fe catalyst exposed to 200 ppm ammonia (AH) at 260 °C, which resulted in little deactivation. Mössbauer spectroscopy results indicated that a higher fraction of $\epsilon\text{-Fe}_{2.2}\text{C}$ (45%) was formed at 260 °C relative to that (7-11%) at 270 °C, likely due to its transformation into $\chi\text{-Fe}_5\text{C}_2$ at the higher

temperature. However, ϵ' -Fe_{2.2}C displayed better stability under the ammonia poisoning conditions and during the startup period compared to χ -Fe₅C₂, which was the major iron phase to experience transformation to magnetite by AN or HNO₃. XRD results and XANES/EXAFS results further confirmed the oxidation of iron carbides by the addition of either a high level of AN or HNO₃.

A mechanism of χ -Fe₅C₂ oxidation by AN or HNO₃ was proposed. Fe carbides reacted with NO_x dissociated from AN or HNO₃, $\text{Fe}_5\text{C}_2 + \text{NO}_x \rightarrow \text{Fe}_3\text{O}_4 + \text{N}_2 + \text{CO}_2$, and/or directly reacted with nitric acid, with subsequent reduction of Fe nitrate to magnetite, $\text{Fe}_5\text{C}_2 + \text{HNO}_3 \rightarrow \text{Fe}(\text{NO}_3)_3 + \text{NO}_x + \text{CO}_2 + \text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 + \text{H}_2 \rightarrow \text{Fe}_3\text{O}_4 + \text{NO}_x + \text{H}_2\text{O}$ (unbalanced equations). Meanwhile, NH₄NO₃ thermal dissociation and a possible mechanism of its effect under FTS conditions was proposed. It was suggested that AN first dissociated to HNO₃ and NH₃, followed by CO and/or H₂ reduction of the NO_x product to produce both ammonia and N₂. The proposed dissociation mechanism is in line with the results of ammonia measured in the FTS aqueous products by IC, where 50-80% of the HNO₃ directly added or dissociated from the AN converted to ammonia under FTS conditions.

The sensitivities of Fe and Co catalysts to added NH₃ were compared for ammonia levels in the range of 10-1200 ppm. The Fe catalyst showed significantly higher resistance to ammonia than the cobalt catalyst under typical Fe and Co FTS conditions.

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Table 1 Atomic positions using Cartesian coordinates and corresponding Wyckoff positions.
Structures shown in **Fig. 1**.

Carbide compound	Atom	Color (see Figure 1)	Cartesian coordinates
Hägg carbide	Fe 8f	White	$(x_1, y_1, z_1) = (0.092, 0.091, 0.421)$
	Fe' 8f	Light Gray	$(x_2, y_2, z_2) = (0.207, 0.577, 0.302)$
	Fe'' 4e	Dark Gray	$(x_3, y_3, z_3) = (0.000, 0.566, 0.250)$
	C 8f	Black	$(x_4, y_4, z_4) = (0.109, 0.300, 0.082)$
Magnetite	Fe 8a	White	$(x_1, y_1, z_1) = (0.125, 0.125, 0.125)$
	Fe' 16d	Gray	$(x_2, y_2, z_2) = (0.500, 0.500, 0.500)$
	O 32e	Black	$(x_3, y_3, z_3) = (0.255, 0.255, 0.255)$

Table 2 Path parameters generated by FEFF (single scattering) for the carbides (structures shown in **Fig. 1**).

Hägg carbide	Atom	Interaction	#Degeneracies	Distance (Å)
	Fe2	Fe-C	1.0	1.9309
	Fe1	Fe-C	1.0	1.9433
	Fe1	Fe-C	1.0	1.9766
	Fe2	Fe-C	1.0	1.9921
	Fe3	Fe-C	2.0	2.0022
	Fe3	Fe-C	2.0	2.0388
	Fe2	Fe-C	1.0	2.3475
	Fe3	Fe-Fe	2.0	2.3616
	Fe2	Fe-Fe	1.0	2.3616
	Fe1	Fe-C	1.0	2.4964
	Fe1	Fe-Fe	1.0	2.4958
	Fe1	Fe-Fe	1.0	2.4965
	Fe3	Fe-Fe	2.0	2.4965
	Fe1	Fe-Fe	1.0	2.5415
	Fe2	Fe-Fe	2.0	2.5502
	Fe3	Fe-Fe	2.0	2.5762
	Fe1	Fe-Fe	1.0	2.5901
	Fe3	Fe-Fe	2.0	2.5901
	Fe2	Fe-Fe	2.0	2.6010
	Fe2	Fe-Fe	1.0	2.6170
	Fe1	Fe-Fe	2.0	2.6378
	Fe1	Fe-Fe	1.0	2.6428
	Fe2	Fe-Fe	1.0	2.6428
	Fe1	Fe-Fe	1.0	2.6463
	Fe2	Fe-Fe	1.0	2.6463
	Fe1	Fe-Fe	1.0	2.6737
	Fe2	Fe-Fe	1.0	2.6737
	Fe1	Fe-Fe	1.0	2.6937
	Fe3	Fe-Fe	2.0	2.6937
	Fe1	Fe-Fe	1.0	2.6988
	Fe2	Fe-Fe	1.0	2.6988
	Fe1	Fe-Fe	1.0	2.7788
	Fe2	Fe-Fe	1.0	2.7788
	Fe1	Fe-C	1.0	2.8702
	Fe1	Fe-C	1.0	3.4258
	Fe2	Fe-Fe	1.0	3.4642
	Fe3	Fe-Fe	2.0	3.4642
	Fe2	Fe-C	1.0	3.4887

Table 3 Path parameters generated by FEFF (single scattering) for magnetite (structure shown in **Fig. 1**).

magnetite	Atom	Interaction	#Degeneracies	Distance (Å)
	Fe1	Fe-O	1.0	1.8861
	Fe2	Fe-O	1.0	2.0602
	Fe2	Fe-Fe	1.0	2.9684
	Fe1	Fe-Fe	1.0	3.4807
	Fe2	Fe-Fe	2.0	3.4807
	Fe1	Fe-O	2.0	3.4933

Table 4 Results of Mössbauer spectroscopy least-squares fitting of Fe catalysts before and after co-feeding ammonia or HNO₃ poisons (G1 and G2 stand for the green sextets in the Figs 5a-f, B1, B2 and B3 stand for the blue signals in the **Figs 5a-f**).

Poison/TOS, h	Iron phases			Details of iron carbides					Summary of iron Carbides	
	Fe% in Magnetite	Fe% in Carbides	Fe%	Fe% in G1	Fe% in B1	Fe% in B2	Fe% in G2	Fe% in B3	G1+G2 (ε'-Fe _{2.2} C)	B1+B2+B3 (χ-Fe ₅ C ₂)
NH ₄ NO ₃ /0	19.0	81.0	0.0	5.0	28.0	28.0	2.0	18.0	7.0	74.0
NH ₄ NO ₃ /78	44.0	56.0	0.0	4.0	17.0	17.0	3.0	14.0	7.0	48.0
NH ₄ NO ₃ /145	51.0	49.0	0.0	5.0	16.0	13.0	3.0	12.0	8.0	41.0
NH ₄ NO ₃ /217	63.0	37.0	0.0	2.0	11.0	9.0	9.0	6.0	11.0	26.0
HNO ₃ /480	70.0	26.0	4.0	3.0	7.0	7.0	4.0	5.0	7.0	19.0
NH ₃ /960	27.0	73.0	0.0	16.0	11.0	7.0	29.0	10.0	45.0	28.0

Table 5 Results of EXAFS fittings for iron catalyst (100 Fe/5.1Si/2Cu/3.0K) before and after poisoning (50-1380 ppm HNO₃, 270 °C, 1.3 MPa, H₂/CO = 0.77 and 10 NL/g-cat/h). Model considers the presence of Hägg carbide and Fe₃O₄ (magnetite). Fitting intervals: 2.5 Å⁻¹ < k < 10.0 Å⁻¹; 1.0 Å < R < 3.5 Å. Note that S₀² was fixed at 0.9. Global parameters (i.e., over both samples) were used for the isotropic lattice expansion (α), energy shift (e₀), and Debye-Waller factor (σ²) parameters for Hägg carbide and Fe₃O₄ fractions. Local parameters (i.e., for each sample) were used for the amplitude function multipliers (A) of each component.

	phase	α	A	σ ² (Å ²)	e ₀ (eV)	r-factor
Catalyst before addition of HNO ₃	Hägg	0.012 ± 0.008	0.85 ± 0.20	0.00628 ± 0.00633 0.014 ± 0.004	-0.46 ± 2.49	0.011
	Fe ₃ O ₄	0.0055 ± 0.010	0.13 ± 0.08	0.00674 ± 0.00588 0.0115 ± 0.0032	0.98 ± 2.92	
Catalyst after addition of HNO ₃	Hägg	“	0.48 ± 0.16	“	“	
	Fe ₃ O ₄	“	0.64 ± 0.12	“	“	

Table 6 Results of IC analysis of ammonium cation in the FTS aqueous product.

Poison added	TOS (hrs)	CO conversion, %	NH ₄ (NH ₄ NO ₃ form) or HNO ₃ in the syngas feed, ppm	NH ₄ cation in FT water product by ICP, ppm
NH ₄ NO ₃	263.9	72.9	40	1319
	288.8	74.2	40	1658
	360.3	59.3	400	12473
	409.0	55.1	400	10301
HNO ₃	291.7	63.8	1380	4072
	338.4	46.8	1380	3669
	387.4	24.4	1380	3114
	433.3	20.1	1380	3575

Figure Captions

- Figure 1. Structural models for Hägg carbide and Fe_3O_4 (magnetite).
- Figure 2. Effect of up to 400 ppm ammonia from AH (260°C) or AN (270°C) on (a) CO conversion, (b) CH_4 , C_{5+} and CO_2 selectivities, and (c) C_4 olefin selectivity on 100Fe/5.1Si/3K/2Cu. FTS conditions: 270 °C, 1.3 MPa($\text{CO}+\text{H}_2$), $\text{H}_2/\text{CO} = 0.77$, $\text{SV}_{\text{CO}+\text{H}_2}=10$ NI/g-cat/h, and 260 °C, 1.3 MPa($\text{CO}+\text{H}_2$), $\text{H}_2/\text{CO} = 0.67$, $\text{SV}_{\text{CO}+\text{H}_2}=10$ NI/g-cat/h.
- Figure 3. Effect of up to 1380 ppm HNO_3 on (a) CO conversion, (b) CH_4 , C_{5+} and CO_2 selectivities, and (c) C_4 olefin selectivity on 100Fe/5.1Si/3K/2Cu. FTS conditions: 270 °C, 1.3 MPa($\text{CO}+\text{H}_2$), $\text{H}_2/\text{CO} = 0.77$, $\text{SV}_{\text{CO}+\text{H}_2}=10$ NI/g-cat/h.
- Figure 4. XRD spectra of used Fe-K catalyst after expose to (top) 200 ppm ammonia (AH); (bottom) 400 ppm ammonia (AN).
- Figure 5. Mössbauer spectra of the Fe catalysts (a) after reduction at 0 h, (b) before poisoning by AN at 78 h, (c) after AN poisoning at 145 h, (d) after AN poisoning at 217 h, (e) after HNO_3 poisoning at 480 h and (f) after ammonia (AH) poisoning at 960 h. Blue sextets alone correspond to Hägg carbide; green sextet G2 alone corresponds to $\epsilon\text{-Fe}_{2.2}\text{C}$; red sextets alone correspond to magnetite.
- Figure 6. Change in composition of iron phases with CO conversion. FTS conditions: 270 °C, 1.3 MPa, and $\text{H}_2/\text{CO} = 0.77$. The first three data points are from the AN run and the last data point is from the HNO_3 run.

Figure 7. Normalized XANES spectra of (a) reference of a carburized (10 h at 290°C in CO) iron catalyst, 100 Fe/4.6 Si/1.5 K, from [41]; (b) iron catalyst (100Fe/5.1Si/2Cu/3K) before addition of 50-1380 ppm HNO₃; (c) reference of an iron catalyst, 100 Fe/4.6 Si/1.5 K, at the point of maximum Fe₃O₄ content at 190.5°C during carburization in CO from TPR/XANES from [41]; and) iron catalyst (100Fe/5.1Si/2Cu/3K) after addition of 50-1380 ppm HNO₃.

Figure 8. k¹-weighted Fourier Transform magnitude spectra of (a) reference of a carburized (10 h at 290°C in CO) iron catalyst, 100 Fe/4.6 Si/1.5 K, from [40]; (b) iron catalyst (100Fe/5.1Si/2Cu/3K) before addition of 50-1380 ppm HNO₃; (c) reference of an iron catalyst, 100 Fe: 4.6 Si: 1.5 K, at the point of maximum Fe₃O₄ content at 190.5°C during carburization in CO from TPR/XANES from [41]; and) iron catalyst (100Fe/5.1Si/2Cu/3K) after addition of 50-1380 ppm HNO₃.

Figure 9. EXAFS results at the Fe K-edge, including (a) (left) the raw k¹-weighted $\chi(k)$ versus k (b) (middle) (solid line) the filtered k¹• $\chi(k)$ versus k and (filled circles) the result of the fitting; and (c) (right) (solid line) the Fourier transform spectra with (filled circles) the result of the fitting. Model considered contributions from Hägg carbide and Fe₃O₄. (I) iron catalyst (100Fe/5.1Si/2Cu/3K) before addition of 50-1380 ppm HNO₃; (II) iron catalyst (100Fe/5.1Si/2Cu/3K) after addition of 50-1380 ppm HNO₃.

Figure 10. Change of the ratio of mole of outlet NH₄⁺ to mole of inlet NO₃⁻ versus time in the AN and HNO₃ poison runs over 100Fe/5.1Si/1.25Cu/3.0K. FTS: 270 °C, H₂/CO = 0.77, 1.3 MPa, and 10 NL/g-cat/h.

Figure 11. Comparison of the resistance of Fe and Co catalysts to ammonia. Fe catalyst run conditions: 220-260 °C, 1.3MPa, $H_2/CO = 0.67$, $X_{CO} \sim 40\%$; cobalt catalyst data from ref. [19]: 220 °C, 2.0 MPa, $H_2/CO = 2.0$ and $X_{CO} = 38-25\%$.

Figure 1

Hägg Carbide

Magnetite

Figure 2a

Figure 2b

Figure 2c

Figure 2d

Figure 3a

Figure 3b

Figure 3c

Figure 3d

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11