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Fischer-Tropsch synthesis: XANES investigation of hydrogen chloride poisoned iron and cobalt-based catalysts at the K-edges of Cl, Fe, and Co

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Abstract:

The effect of co-fed hydrogen chloride (HCl) in syngas on the performance of iron and cobalt-based Fischer-Tropsch (FT) catalysts was investigated in our earlier studies [*ACS Catal.* 5 (2015) 3124-3136 and *DOE final report 2011; Catal. Lett.* 144 (2014) 1127-1133]. For an iron catalyst, lower HCl concentrations (< 2.0 ppmw of HCl) in syngas did not significantly affect the activity, whereas rapid deactivation occurred at higher concentrations (~20 ppmw). With cobalt catalysts, even low concentrations of HCl (100 ppbw) caused catalyst deactivation, and the deactivation rate increased with increasing HCl concentration in the syngas. The deactivation of the catalysts is explained by the chloride being adsorbed on the catalyst surface to (1) block the active sites and/or (2) electronically modify the sites. In this study, XANES spectroscopy was employed to investigate HCl poisoning mechanism on the iron and cobalt catalysts. Cl K-edge normalized XANES results indicate that Cl is indeed present on the catalyst following HCl poisoning and exhibits a structure similar to the family of compounds MCl; two main peaks are formed, with the second peak consisting of a main peak and a higher energy shoulder. At the Co K and Fe K edges, the white line was observed to be slightly increased relative to the same catalyst under clean conditions. There is then the additional possibility that Cl adsorption may act in part to intercept electron density from the FT metallic function (e.g.,

cobalt or iron carbide). If so, this would result in less back-donation and therefore hinder the scission of molecules such as CO.

Keywords: *Fischer-Tropsch synthesis; iron; cobalt; hydrogen chloride; activity; selectivity; XANES.*

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1. Introduction

Fischer–Tropsch synthesis (FTS) is a heterogeneously catalyzed polymerization reaction for the transformation of synthesis gas (a mixture of CO and H₂, also known as syngas) into valuable hydrocarbons (gasoline, diesel, jet fuel, lubricants, waxes, chemicals, etc.). It is suitable for the production of synthetic fuels from both fossil (e.g., coal, natural gas) and renewable (e.g., biomass) resources [1,2]. This reaction produces a wide variety of products, from gases to heavy waxes. The Fischer-Tropsch reaction is typically catalyzed by iron or cobalt catalysts. Utilization of iron catalysts also leads to the formation of (lower) olefins, the building blocks for a range of products such as polymers, solvents, and drugs [3]. Cobalt catalysts exhibit higher selectivity toward high-molecular weight, paraffinic waxes which can be hydrocracked to produce lubricants and diesel fuels [4–7].

The biomass-to-liquids (BTL) process involves syngas production through the gasification of biomass materials. The H₂/CO ratio derived from biomass varies depending on the oxygen source used for gasification (1.0–1.5 for air-blown gasification, and 1.5–2.2 for gasification using pure oxygen) [8,9]. However, Biomass-derived synthesis gas can contain both organic and inorganic impurities such as tars, benzene, toluene, xylene, NH₃, HCN, H₂S, COS, HCl, volatile metals, dust, and soot. Coal, which originates from biomass, typically contains all of the same inorganic impurities as found in biomass. These contaminants could behave as

catalyst poisons when their concentrations in the syngas reach certain limits. So far, there are few data in the open literature to define the optimum levels of these potential catalyst poisons [9-11]. In one review, the estimated Cl content of biomass feedstock is 160 – 8600 ppm by mass, while that of coal is ~300 ppm by mass [12]. Thus, defining the effect of Cl has a broader impact on not only BTL, but also coal-to-liquids (CTL) technology as well. Although a much more significant issue with BTL and CTL, Cl may also be present in trace levels in natural gas. For example, although Hg exists primarily in its elemental form, mercury chloride compounds such as HgCl_2 or CH_3HgCl may also be present [13], especially considering that a large fraction of the total mercury in various natural gas condensates is present as a variety of mercury compounds.

Generally, two approaches have been used to define the sensitivity of FTS catalysts to impurities in syngas. First one is to incorporate trace amounts of impurities into the catalyst and then to explore the differences in catalyst performance (activity, selectivity and stability) relative to those of the reference catalyst [14-16]. Second one is online co-feeding of an impurity-containing solution or gas with syngas and then studying the changes in catalyst performance with time [17-19]. The role of incorporated impurity may be similar to the addition of common promoters that modify CO or H_2 adsorption or change Co reduction/dispersion. On the other hand, the poisons added online may take effect by chemically changing the catalyst by competitive adsorption of impurities on the catalyst surface with reactant gas. Therefore, all our poisoning studies to date have been carried out by online co-feeding of an impurity containing gas or solution along with the syngas [20-29].

The slurry phase reactor is an ideal choice for catalyst sensitivity studies because of its capability of providing a uniform temperature distribution as well as uniform catalyst and poison concentrations in the reactor. A sensitivity study of Fe and Co-based FTS catalysts to various

contaminations that may be present in biomass derived syngas was carried out by our group under the financial support from US Department of Energy (DOE) [19]. In our previous investigations [20-29], we reported the effect of sulfur [20-22], ammonia [23-26], halides [27,28], and alkali [29] over iron and cobalt-based catalysts during the FTS reaction. Ma et al. [27], reported the effect of HCl in syngas over an iron catalysts and small amounts of HCl (< 2.0 ppmw) did not exhibit any significant effect. Moderate amounts of HCl (3.0 to 5.0 ppmw) caused a slow deactivation and higher amounts of HCl (> 20 ppmw) had a significant effect on activity and selectivity. Gnanamani et al. [28] reported the effect of HCl in syngas over cobalt catalyst, and small amounts of HCl (e.g., 1.0 ppmv) had a significant impact on activity and selectivity. The deactivation of activity by HCl impurities in syngas over iron and cobalt-based catalysts was explained by an absorption mechanism through blocking of active sites (iron carbides and metallic cobalt) [27,28]. To further investigate the role of HCl impurities present in syngas on the catalytic activity and selectivity, the iron and cobalt based catalysts were withdrawn from the reactor prior to and following exposure to FTS reaction, and the samples were investigated using XANES with soft X-rays at the Cl K-edge and hard X-rays at the Fe and Co K-edges.

2. Experimental

2.1 Catalyst preparation

2.1.1 Preparation of Fe/Si/K/Cu catalyst

Precipitated iron catalysts were prepared using a ferric nitrate solution obtained by dissolving iron (III) nitrate nonahydrate (1.17 M) in deionized water, and then tetraethylorthosilicate was added to provide the desired Fe:Si ratio (100:5.1). Details of catalyst preparation can be found elsewhere [19,30]. For this study, the Fe:Si catalyst base powder was then impregnated with

appropriate amounts of aqueous solutions of potassium nitrate and copper nitrate to produce the desired composition of atomic ratios related to iron of 100Fe:5.1Si:3.0 K:2.0Cu. The catalyst precursor was first dried at 110 °C overnight followed by impregnation, drying, and calcination at 350 °C in an air flow 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 [19].

2.1.2 Preparation of Pt-Co/Al₂O₃ catalyst

Sasol-Catalox alumina (high purity γ -alumina, 140 m²/g) was used as the support for the cobalt catalyst. The catalyst was prepared by a slurry impregnation method, and cobalt nitrate was the precursor. Details of catalyst preparation can be found elsewhere [24]. The Pt promoter was added by incipient wetness impregnation (IWI), and the precursor utilized for noble metal addition was tetraammineplatinum (II) nitrate. After Pt addition, the sample was dried and calcined at 350 °C for 4 h in the flowing of air.

2.2 Catalyst Characterization

2.2.1 XANES spectroscopy

The electronic structure of chlorine, iron and cobalt following catalyst poisoning was investigated by XANES in fluorescence mode near the Cl K-edge at the Soft X-ray Microcharacterization Beamline (SXRMB) at the Canadian Light Source, Inc. and in transmission mode at the Fe K-edge and Co K-edge at Beamline X-18 at the National Synchrotron Light Source at Brookhaven National Laboratory. The used catalyst sample, after HCl poisoning in a continuously stirred tank reactor (CSTR) under realistic Fischer-Tropsch synthesis conditions, was sealed in the wax product for analysis by comparison with reference compounds of interest. The spectra (in energy space) were background subtracted and

normalized with a two-polynomial method with degree 1 for both the pre- and post-edge regions using the WinXAS software [31].

2.2.2 Hydrogen TPD with pulse reoxidation

H-TPD experiments were carried out after activation with or without HCl poisoning. The 0.5%Pt-25%Co/Al₂O₃ catalyst (~0.17 g) was activated in 10 ccm H₂ blended with 20 ccm Ar. Following cooling in the H₂/Ar mixture, ~15 µL of HCl was added at 220°C under flowing H₂/Ar. The catalyst was then cooled to 100°C in flowing 10 ccm Ar. 10 ccm H₂ was then flowed to saturate Co⁰ surface sites, prior to a 30 ccm purge in Ar to remove weakly bound species. Then, TPD in 30 ccm Ar was conducted to 350°C. To determine extent of Co reduction, pulse reoxidation was carried out using 50 µL injections of pure O₂ in helium carrier with a sample loop. A run using the same procedure except for HCl addition (i.e., clean conditions) was performed with a fresh catalyst sample for the purpose of comparison.

With 100Fe:5.1Si:3.0K:2.0Cu, the catalyst (~0.42 g) was carburized for 24 h ex-situ at 270°C in pure CO and passivated with 1%O₂/N₂ at room temperature. The catalyst was then re-carburized for 10 h in-situ at 270°C in 10 ccm of 10%CO/He and cooled to 260°C in 10%CO/He. Approximately 15 µL of HCl was added at 260°C under 10 ccm Ar and the catalyst was cooled to 100°C in 10 ccm Ar. 10 ccm H₂ with 20 ccm Ar were then flowed to saturate surface sites (e.g., iron carbide), prior to a purge in 30 ccm Ar to remove weakly bound species. Then, TPD in 30 ccm Ar was conducted to 350°C. A run using the same procedure except for HCl addition (i.e., clean conditions) was carried out with a fresh catalyst sample for the purpose of comparison.

2.3. Catalytic activity testing

The FTS experiments were conducted using a 1 L CSTR equipped with a magnetically driven stirrer with turbine impeller, a gas-inlet line, and a vapor outlet line with a stainless steel (SS) fritted filter (2 μm) placed external to the reactor. A tube fitted with a SS fritted filter (0.5 μm opening) extending below the liquid level of the reactor was used to withdraw reactor wax (i.e., re wax, which is solid at room temperature), thereby maintaining a relatively constant liquid level in the reactor. Separate mass flow controllers were used to control the flow rates of hydrogen and carbon monoxide. Carbon monoxide, prior to use, was passed through a vessel containing lead oxide on alumina to remove traces of iron carbonyls. The gases were premixed in an equalization vessel and fed to the CSTR below the stirrer, which was operated at 750 rpm. The reactor temperature was maintained constant ($\pm 1^\circ\text{C}$) using a temperature controller.

The Pt-Co/alumina catalyst (~ 10.0 g) was ground and sieved to 45–100 μm before loading into a fixed-bed reactor for 12 h of ex-situ reduction at 350°C and atmospheric pressure using a gas mixture of H_2/He (60 NL/h) with a molar ratio of 1:3. The reduced catalyst (~ 8.0 g) was transferred to a 1-L continuously stirred tank reactor (CSTR) containing 310 g of melted Polywax 3000, under the protection of inert nitrogen gas. The transferred catalyst was further reduced in-situ at 230°C at atmospheric pressure using pure hydrogen (20 NL/h) for another 24 h before starting the FT reaction. In this study, the FTS conditions used were 220°C , 1.99 MPa, $\text{H}_2/\text{CO} = 2$, and 2.0 NL/g-cat/h.

The 100Fe:5.1Si:3.0K:2.0Cu catalyst (10 g) was activated *in-situ* in a CSTR using 2 NL/g-cat/h CO at 270°C and 1 atm for 24 h. The FTS reaction was carried out under the following conditions: 260°C , 6.0 NL/g-cat/h, 1.3 MPa, and H_2/CO ratio of 0.67. After a steady state was

established, an appropriate concentration of aqueous HCl solution was co-fed into the CSTR at 1.0 ml/h using a high performance precision syringe pump (ISCO 500 D).

Gas, water, oil, light wax, and heavy wax samples were collected daily and analyzed. Heavy wax samples were collected in a 200 °C hot trap connected to the filter. The vapor phase in the region above the reactor slurry passed continuously to the warm (100°C) and then the cold (0°C) traps located external to the reactor. The light wax and water mixture were collected daily from the warm trap and an oil plus water sample from the cold trap. Tail-gas from the cold trap was analyzed with an online HP Quad Series Micro GC, providing molar compositions of C₁–C₅ olefins and paraffins, as well as H₂, CO and CO₂. Hydrogen and carbon monoxide conversions were calculated based on GC analysis of the gas products, the gas feed rate, and the gas flow that was measured at the outlet of the reactor.

3. Results and discussion

The effect of HCl during FT synthesis was studied by co-feeding different concentrations of HCl added to the syngas for iron (1.7 ppmw – 23.0 ppmw) [27] and cobalt-based (100 ppbw – 10 ppmw) [19] catalysts. The partial pressures of the inlet hydrogen and carbon monoxide were kept constant during all periods. After attaining a steady state CO conversion level, the water was first introduced (1 mL/h) for a period of 2-3 days before adding the HCl to the reactor. After reaching a stable CO conversion with water addition, HCl (1 mL/h water containing HCl) was co-fed with the syngas. The effect of HCl on CO conversion for iron and cobalt-based catalysts is shown in Figure 1A and 1B, respectively [27,19].

Figure 1A shows that CO conversion remained relatively stable when the low HCl level, 1.7 ppmw, was examined between 763-954 h. However, the activity declined linearly when the high HCl level, 23 ppmw, was used over the next 153 h, and then it leveled off at 16% CO conversion between 1075 and 1100 h. The iron catalyst was exposed to the 1.7 ppmw HCl for

191 h and 23 ppmw HCl for 153 h during FTS. This result is rather similar to the phenomenon observed in the testing of 40 ppmw HCl at 270 °C, and it is postulated that HCl poisoning of the iron catalyst was through an adsorption process [27]. A significant impact of HCl on the adsorption of CO, H₂ and intermediates on the catalyst surface appears to occur at a certain conversion level, i.e. above 20%, and thereafter reaches saturation on the iron active sites [27].

Figure 1B shows the effect of HCl on CO conversion for the Pt promoted alumina supported cobalt catalyst. Similar to the iron run, after attaining the steady state CO conversion with water addition, 100 ppbw (concentration of HCl with respect to the syngas feed) was introduced. The addition of even very small amounts (100 parts per billion with respect to syngas feed) led to a significant drop in CO conversion, and the conversion was decreased with further addition of HCl. A stable CO conversion was achieved after 200 h of continuous addition of HCl, which is probably indicative of saturation of Cl by adsorption on the catalyst surface. More importantly, catalyst activity did not recover to the expected value after hydrogen chloride addition was terminated under normal FTS conditions, indicating that the catalyst had deactivated (e.g., chloride ions are irreversibly adsorbed onto active metal (cobalt and iron) sites. After attaining a steady state conversion level, 10 ppmw of HCl was introduced along with syngas. The sensitivities of Fe and Co catalysts to added hydrogen chloride were compared for HCl levels in the range of 100 ppb to 10 ppm. The iron catalyst showed significantly higher resistance to hydrogen chloride than the cobalt catalyst under typical Fe and Co FTS conditions. The addition of 10 ppmw HCl behaved similarly to the case of 100 ppbw addition (decrease in CO conversion) and the catalyst further deactivated with continuous addition of HCl. The rate of deactivation increased with increasing hydrogen chloride concentration. The cobalt catalyst was finally exposed to 0.1 ppmw HCl for 376 h, 10 ppmw HCl for 237 h and 50 ppmw HCl for 48 h during

FTS. The activity and selectivity results of the 50 ppmw HCl addition to the cobalt catalyst are not shown for the sake of brevity.

The effects of HCl addition on selectivity of methane and C₅+ of iron and cobalt catalysts are shown in Figures 2A and 2B, respectively. With the iron catalyst, methane and C₅+ selectivity were found to be similar both before and after addition of 1.7 ppmw HCl, whereas the addition of a higher concentration of HCl (23 ppmw) resulted in increased methane selectivity and diminished C₅+ selectivity (Figure 2A) [27]. In the case of the cobalt catalyst, a very small amount of added HCl (100 ppbw) led to an increase in methane selectivity and a decrease in C₅+ selectivity (Figure 2B) [19]. Carbon dioxide selectivity follows a similar trend with C₅+ selectivity of an iron catalyst (i.e., no change at lower concentrations and a significant drop at higher concentrations, as shown in Figure 3). The selectivity trends in the presence of high levels of HCl were explained by assuming that Cl ions adsorbed on the iron catalyst surface thereby influencing CO and/or H₂ adsorption [27].

Inductively coupled argon plasma (ICP) analysis of the used catalysts (HCl exposed) was conducted at Galbraith Laboratories. HCl exposed catalysts were extracted with hot o-xylene to remove high molecular weight FT wax; however, it was not possible to completely remove the FT wax from the catalysts particles by this method. ICP results of the used catalysts show that the chloride to metal ratios (weight percent) were 1.77% and 2.66% for cobalt and iron catalysts, respectively. These values are lower than the expected values assuming complete uptake of Cl; however, a fraction of chloride may be lost during extraction and/or passivation procedures. In our previous studies [27,28], the effect of HCl was explained assuming that chloride ions adsorbed on the catalyst surface and thereby block the active sites (e.g., iron carbides and metallic cobalt). To further confirm the adsorption mechanism, the iron and cobalt based catalysts were withdrawn from the reactor prior to and following exposure to the FTS reaction,

and the samples were investigated using XANES. The XANES spectra of the catalyst after running under clean conditions or after HCl poisoning at the Fe K-edge are shown in Figure 4 (left). Comparing with the reference compounds, the catalyst after running under clean conditions displays spectra consistent with primarily a mixture of Fe carbide and some residual Fe_3O_4 . The used HCl poisoned catalyst has a slightly higher white line, while the feature at 7712 eV consistent with reduced iron slightly decreased in intensity; and, the energy threshold shifted to slightly higher energy.

Analysis at the Cl K-edge, as shown in Figure 4 (right), reveals that Cl is indeed present on the catalyst following HCl poisoning. Spectral features, including number of peaks and their locations, are determined by electronic transitions (in this case, from 1s to empty 4p states) and coordination environment [32] due to multiple scattering. Three pronounced features were detected in the XANES spectrum of the FeCl_2 reference compound, in agreement with the Cl K absorption spectra of previous studies of MCl_2 materials [33-35]. The position of the first peak (typically labeled A) has been found to be sensitive to the nature of the metal, such that chemical shifts are consistent with changes in ionization energies. For example, peak A was found to shift to higher energy in moving along the series CuCl_2 , NiCl_2 , CoCl_2 , FeCl_2 , and MnCl_2 . Likewise, a similar line shape was observed for FeCl_3 in previous K absorption edge spectra [36], with a sharp peak A (2820 eV) located 7 eV below peak B. Peak C was merged with Peak B at ~3 eV higher energy.

The Cl K-edge spectrum of the HCl poisoned iron catalyst was significantly different from that of either the FeCl_2 or FeCl_3 spectrum. Therefore, it is evident that a bulk iron chloride compound was not formed. Rather, in surveying the literature, the spectrum resembles more closely that of HCl or KCl, as two main peaks are formed, with the second peak consisting of a

main peak and a higher energy shoulder. For example, two peaks were observed in papers for HCl [32,37]; and, two main peaks, with a splitting of the second peak, were observed in several papers for KCl [32,38,39]; a spectrum of the latter is included. Thus, the comparison reinforces the view that the electronic and coordination environment for Cl on the HCl poisoned catalyst is not of the form MCl_2 or MCl_3 , but rather of the family of MCl compounds.

A recent article by Paredes-Nunez et al. [40] has suggested, from DRIFTS investigations, that the effect of chlorine is to poison sites by not only site blocking, but also through an electronic effect. That is, the back-donation of electron density to the CO π^* anti-bonding molecular orbital may be weakened if intercepted by chlorine. If Cl removes electron density from Co, resulting in an increase in the availability of states above the Fermi level of Co, then one would expect to observe an increase in the white line intensity of Co. In typical FTS runs, net reduction of Co has been observed during the initial decay period [41-43]. However, as in the case of HCl poisoning of a cobalt catalyst, to be discussed, the white line for the HCl poisoned iron catalyst was slightly higher after exposure to HCl. Thus, taken as a whole, the results of XANES are consistent with site blocking by adsorption of Cl, but one cannot rule out the possibility of electronic modification of iron carbide that hinders CO bond scission.

The XANES spectra of the catalyst after running under clean (two separate runs) or after HCl poisoning at the Co K-edge is shown in Figure 5 (left). Comparing with the reference compounds, the catalyst after running under clean conditions displays spectra consistent with primarily a mixture of Co metal and some residual unreduced CoO. The used HCl poisoned catalyst has a higher white line intensity, while the feature at 7709 eV consistent with metallic cobalt slightly decreased in intensity.

Analysis at the Cl K-edge, as shown in Figure 5 (right), reveals that Cl is indeed present on the catalyst following HCl poisoning. Spectral features, including number of peaks and their locations, are determined by coordination environment [32]. Three pronounced features were detected in the XANES spectrum of the CoCl_2 reference compound, in agreement with the Cl K absorption spectra of previous studies of MCl_2 materials [33-35]. The position of the first peak (typically labeled A) has been found to be sensitive to the nature of the metal, such that chemical shifts are consistent with changes in ionization energies. For example, peak A was found to shift to higher energy in moving along the series CuCl_2 , NiCl_2 , CoCl_2 , FeCl_2 , and MnCl_2 .

The Cl K-edge spectrum of the HCl poisoned 0.5%Pt-25%Co/ Al_2O_3 catalyst was significantly different from that of the CoCl_2 spectrum. Therefore, it is evident that bulk CoCl_2 was not formed. Rather, as in the case of HCl poisoning of the iron catalyst, the spectrum resembles more closely that of the family of compounds such as HCl [30,35] or KCl [32, 38,39]; a spectrum of the latter is included. Thus, the comparison reinforces the view that the electronic and coordination environment for Cl on the HCl poisoned catalyst is not of the form MCl_2 , but rather structurally similar to MCl .

One cannot rule out the possibility that Cl may intercept electron density from Co that is back-donated to the $\text{CO } \pi^*$ anti-bonding molecular orbital. If Cl removes electron density from Co, then there should be an increase in the availability of states above the Fermi level of Co, and an increase in the white line intensity of Co, as in the case of Fe, is consistent with this. In typical FTS runs, net reduction of Co has been observed during the initial decay period [41-43]. However, in the current case, the white line for the HCl poisoned catalyst was slightly higher after exposure to HCl. Thus, taken as a whole, the results of XANES are consistent with both site blocking by adsorption of Cl as well as a possible electronic modification of Co.

To explore the possibility of site blocking further, hydrogen TPD experiments were carried out either after activation or after activation / HCl poisoning. Results are summarized in Table 1. HCl was found to have a more significant effect on the Co catalyst (88% decrease in site density) versus that of Fe (18% decrease in site density). However, HCl was injected at a higher temperature in the case of Fe (260°C versus 220°C for Co) so the results are not directly comparable. Nevertheless, the more significant decrease with Co is consistent with the greater sensitivity shown in Figure 1. 100 ppb HCl had a pronounced negative effect on the Co catalyst at 220°C (i.e., its typical operating temperature) as compared to 1.7 ppm HCl at 260°C for the Fe catalyst (i.e., again, its typical operating temperature). Therefore, the TPD experiments are consistent with some site blocking by HCl.

4. Conclusions

The effect of HCl was investigated during Fischer-Tropsch synthesis over iron and cobalt-based catalysts. For the iron catalyst, low concentrations of HCl (< 2ppmw) did not have a significant effect on activity, whereas at higher concentrations (> 20 ppmw), rapid deactivation was observed. Very small amounts of HCl (100 ppbw) had a significant effect on the activity for the cobalt catalyst. The product selectivities of HCl poisoned catalysts followed similar trends with the activity; that is, with decreasing CO conversion, the selectivity to light products (C₁-C₄) increased and the corresponding C₅+ selectivity decreased. The sensitivities of Fe and Co catalysts to added hydrogen chloride were compared for HCl levels in the range of 100 ppb to 10 ppm. The iron catalyst showed significantly greater resistance to hydrogen chloride than the cobalt catalyst under typical Fe and Co FTS conditions. The deactivation of the catalysts during the addition of HCl was explained by the chloride ions being adsorbed on the catalyst surface and subsequently blocking the active sites (iron carbide and metallic cobalt) of the catalysts. Cl K-edge normalized XANES results were similar after poisoning of Fe and Co catalysts, further

confirming that Cl is indeed present on the catalyst following HCl poisoning. By comparison with reference compounds, the spectra exhibit a structure similar to the family of compounds MCl. At the Co K and Fe K edges, the white line was observed to be slightly increased relative to the corresponding catalyst under clean conditions, suggesting that adsorbed Cl may also act to intercept electron density from the FT metallic function (e.g., cobalt or iron carbide). This has been proposed to lead to less back-donation and, in turn, hindering the scission of molecules such as CO. Hydrogen TPD results confirmed that HCl was capable of blocking sites, with a more pronounced effect observed for Co at 220°C than Fe at 260°C, the typical operating conditions of the two catalysts.

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Catalyst	Act. gas	Activation T (°C) / time (h)	H ₂ desorbed per g cat (μL per g cat)	Uncorr. % Disp.	Uncorr. Diam. (nm)	O ₂ uptake (μL per g cat)	% Red.	Corr. % Disp.	Corr. Diam. (nm)
0.5%Pt-25%Co/Al ₂ O ₃ (clean)	H ₂	350 / 10	121	5.7	18.2	1804	64	8.9	11.6
0.5%Pt-25%Co/Al ₂ O ₃ (HCl poi.)	H ₂	350 / 10	14	0.6	-	1838	65	-	-
100Fe:5.1Si:3.0K:2.0Cu (clean)	CO	270 / 10*	45	0.8	142.5	-	-	-	-
100Fe:5.1Si:3.0K:2.0Cu (HCl poi.)	CO	270 / 10*	37	0.3	-	-	-	-	-

Table 1 Hydrogen chemisorption / pulse reoxidation measurements.

* 10 h in-situ after an ex-situ 24 h carburization at 270°C / passivation in 1%O₂/N₂ at room temperature.

Figure 1: Effect of HCl concentration on CO conversion for (A) iron [27] and (B) cobalt [19] catalysts during Fischer-Tropsch synthesis.

Reaction conditions:

For iron catalyst: $T = 260\text{ }^{\circ}\text{C}$, $P = 1.3\text{ MPa}$, $\text{H}_2/\text{CO} = 0.67$, $\text{S.V.} = 6\text{ NL/g-cat/h}$

For cobalt catalyst: $T = 220\text{ }^{\circ}\text{C}$, $P = 1.99\text{ MPa}$, $\text{H}_2/\text{CO} = 2$, $\text{S.V.} = 2\text{ NL/g-cat/h}$

Figure 2: Effect of HCl concentration on product selectivities for (A) iron [27] and (B) cobalt [19] catalysts during Fischer-Tropsch synthesis.

Reaction conditions:

For iron catalyst: T = 260 °C, P = 1.3 MPa, H₂/CO = 0.67, S.V. = 6 NL/g-cat/h

For cobalt catalyst: T = 220 °C, P = 1.99 MPa, H₂/CO = 2, S.V. = 2 NL/g-cat/h

Figure 3: Effect of HCl concentration on CO₂ selectivity for the iron catalyst during Fischer-Tropsch synthesis [27].

Reaction conditions: T = 260 °C, P = 1.3 MPa, H₂/CO = 0.67, S.V. = 6 NL/g-cat/h

Figure 4: XANES spectra of the HCl exposed Fe catalyst (up to 23 ppmw HCl) in comparison with the spectra of reference compounds at the K edges of (left) Fe and (right) Cl

Figure 5: XANES spectra of the HCl exposed Co catalyst (up to 50 ppmw) in comparison with the spectra of reference compounds at the K edges of (left) Co and (right) Cl.