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Fischer-Tropsch synthesis. Effect of KCl contaminant on the performance of iron and cobalt catalysts

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ABSTRACT

As a follow-up to a previous alkali chloride poisoning study, the effect of up to 100 ppm KCl on the Fischer-Tropsch synthesis (FTS) performance of representative iron (Fe-Si-Cu doped with Rb as the alkali) and cobalt (Pt-Co/Al₂O₃) catalysts was studied at 270 °C and 230 °C, respectively, by co-feeding KCl in a water/ethylene glycol (EG) solution. The used catalysts were characterized by XANES at the K and Cl K-edges; furthermore, ICP was used to analyze residual K and Cl ions possibly remaining in the FTS products. KCl was found to be a weak poison for the iron and cobalt catalysts. The addition of 20–100 ppm KCl deactivated the catalysts to only a low to moderate extent. For the cobalt catalyst, less than 25 ppm KCl was found to give negligible deactivation. The added KCl and EG-H₂O solvent was found to slightly modify the selectivity for both catalysts, such that KCl slightly promoted light hydrocarbon formation as well as olefins and slightly suppressed C₅₊ and 2-olefin formation, while the EG-H₂O solvent was found to have a different effect on the C₁–C₄ and C₅₊ selectivities. It appears that K and Cl played opposite roles in modifying hydrocarbon selectivities. The ICP results suggested 48–98% K and Cl ions were adsorbed by the iron catalyst. XANES results confirmed the presence of K and Cl ions on the used iron and cobalt catalysts and showed a structure with characteristics that were similar to bulk KCl. Two possible mechanisms, including site blocking by K and Cl ions and electronic modification impacting CO/H₂ adsorption, were proposed to explain the deactivating effect of KCl on the iron and cobalt catalysts.

1. Introduction

Minimizing the Fischer-Tropsch synthesis catalyst deactivation rate and extending catalyst life by understanding deactivation mechanisms have been important topics in recent decades. A large number of deactivation studies for Fischer-Tropsch synthesis (FTS) catalysts have been reported since the 1960s [1–32] and have been reviewed by several groups [3,19–21]. Prevailing deactivation mechanisms for cobalt and iron based FTS catalysts have included oxidation, sintering, carbon deposition, surface reconstruction, poisoning and mechanical disintegration/attrition. For Co catalysts, the structural requirements for oxidation and carbon deposition pathways are still being investigated [19–21]. Catalyst deactivation is further complicated by composition (e.g., presence of promoters, support type, structural modifiers, etc.), pretreatment conditions, and process conditions.

Among the deactivation mechanisms mentioned, poisoning of FTS catalysts by impurities can cause significant deactivation leading to increased operating costs. Furthermore, coal/biomass gasification is the

most costly process for XTL technology from an industrial point of view, taking up to 65% of total operating costs [33]. Therefore, it is important to determine the sensitivities of catalysts to these impurities to extend catalyst lifetime while at the same time minimizing syngas cleaning costs. Three types of impurities in the coal/biomass derived syngas have received the most attention.

Regarding alkali halides, a few groups studied 25–1000 ppm alkali, Cl, and Br ions, as well as KCl and NaCl on cobalt catalysts using a fixed bed reactor [6,14,15]. It was found that Li, Na, K, and Cl detrimentally affected catalyst activity but slightly increased olefin selectivity (e.g., C₂H₄) or had little effect on catalyst selectivity.

There have been only a few studies dealing with nitrogen-containing compounds (e.g., NH₃, HCN) [13,18,25,26]. These studies consistently reported that even 1 ppm ammonia led to severe irreversible deactivation on cobalt catalysts, while even 200 ppm ammonia had little effect on iron based catalyst performance.

Most poisoning studies in recent decades primarily focused on sulfur compounds (e.g., H₂S and COS). Numerous publications on this topic

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have been published, and have made use of advanced characterization techniques such as microscopy (e.g., SEM, TEM, STEM) and synchrotron techniques [12,19–21]. In addition to the characterization techniques used, computational quantum mechanical modeling methods (e.g., DFT) have also been applied [22]. Reports on deactivation of catalysts by sulfur have varied considerably in terms of concentration levels and sulfur precursor. It was reported that > 1 ppb COS and 10 ppb H₂S were sufficient for Ru catalyst deactivation [10], > 50 ppb H₂S was the onset for deactivation of Fe catalyst [7,29], and 1 ppm H₂S caused severe deactivation of a Co catalyst [28]. XANES results using soft x-rays at the sulfur K-edge revealed that sulfur compounds (e.g., metal sulfide) formed with both iron and cobalt catalysts [28,29]. Recent DFT results indicate that S affects the dissociation of carbon monoxide over iron surfaces. CO dissociation was proposed to change to being slightly endothermic from being exothermic when S was adsorbed on the Fe (100) surface [22].

The results of an extensive investigation of the sensitivity of various potential poisons to FTS catalysts [23], including the less studied alkali bicarbonate and chlorides (NaHCO₃, KHCO₃, NaCl, KCl), nitrogen-containing compounds (NH₃ and HCN), and hydrohalic acids (HCl, HF, and HBr), and the more extensively studied sulfur-containing compounds (H₂S and COS) have been reported. The focus was on determining tolerances, poisoning strength, and deactivation mechanisms of various impurities generated from gasification [23–32]. A summary of the concentrations of various poisons in the feed and the corresponding poisoning extent to Fe and Co catalysts is tabulated in Table 1. For the Co and Fe FTS catalysts, sulfur compounds presented the strongest poisoning ability followed by the hydrohalic acids, while alkali bicarbonates, alkali chlorides and ammonia were found to have significantly lower poisoning ability.

The effects of alkali bicarbonate and alkali chlorides (NaHCO₃, KHCO₃, NaCl, KCl) were previously studied; they were found to be weak poisons for iron and cobalt based catalysts [24]. The highest KCl level in the syngas examined was 20 ppm. XANES experiments were carried out at the Fe K-edge and no FeCl₂ compounds could be ascertained. Since only low KCl concentrations were investigated in our earlier study, it may be insufficient to serve as a guideline for purification of coal or biomass derived syngas in plants, as the K and Cl ions from coal/biomass can be significantly high (50–30,000 ppm) [34]. Thus, it is necessary to reevaluate the effect of KCl on Fe FTS performance.

In this paper the effects of 20, 40 and 100 ppm KCl on a 100Fe/5.1Si/2Cu/1.25Rb catalyst were studied at 543 K in a 1 l CSTR. Rb was utilized as a promoter instead of K to ensure that the detection of K by XANES pertained to the KCl contaminant. The effects were analyzed based on FTS reaction data collected over 720 h. The KCl solution was made using 25% H₂O and 75% ethylene glycol (H₂O-EG) as solvent.

Table 1
Summary of the sensitivity of Fe and Co catalysts to various contaminants.^a

Containment	Iron ^b		Cobalt ^c	
	ppm	impact	ppm	impact
NaCl	100	slight	500	slight
KCl	20	neglect	50	slight
NaHCO ₃	40	neglect	1000	none
KHCO ₃	40	neglect	1000	slight
HCl	20	Major	100	Moderate
HBr	20	Major	100	Moderate
HF	20	Major	100	Moderate
NH ₃	200	None	100	Moderate
H ₂ S	> 0.3	Major	≥ 1	Major
HCN	6	slight		

^a Refs. [23–32].

^b 260–270 °C.

^c 220–230 °C.

Thus, the effect of the H₂O-EG solvent was also studied to obtain a more accurate picture of the KCl effect. For the purpose of comparison, the effect of up to 100 ppm KCl on the 0.5%Pt–25%Co/Al₂O₃ catalyst was also investigated using a CSTR. The effect of KCl on the structure of both types of FTS catalysts was studied by characterizing the used catalysts by XANES.

2. Experimental

2.1. Catalyst preparation and characterization

A Rb promoted Fe-Si-Cu catalyst was employed in this study instead of a K promoted one, which was reported in our previous poisoning studies. This allowed us to investigate possible adsorption of the added K on the Fe catalyst by XANES. Details about catalyst preparation can be found elsewhere [23,35]. The BET surface area of the catalyst was measured to be 155.6 m²/g, and single point pore volume and pore diameter were determined to be 0.287 cm³/g and 7.4 nm, respectively.

2.2. XANES spectroscopy

The electronic structure of potassium and chlorine following catalyst poisoning was investigated by XANES in fluorescence mode near the K and Cl K-edges at the Soft X-ray Microcharacterization Beamline (SXRMB) at the Canadian Light Source, Inc. The used catalyst sample, after KCl 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 WinXAS software [36].

2.3. Fischer-Tropsch synthesis reaction in a CSTR

The 100Fe/5.1Si/1.25Rb/2.0Cu catalyst was activated in-situ by CO in a continuously stirred tank reactor (CSTR) at 270 °C and 1 atm for 24 h. The FTS reaction was carried out at 270 °C, 10.0 NL/g-cat/h, 1.31 MPa, and H₂/CO ratio of 0.77. The KCl, with appropriate concentration in the H₂O + EG solution, was fed to the CSTR at 0.5 ml/h using a precision syringe pump (ISCO 500 D). A steady state was required to be established before examining each level of KCl. In this paper, 20, 40, and 100 ppm of KCl were tested.

The 0.5%Pt–25%Co/Al₂O₃ catalyst (~15.0 g and 45–100 μm) was examined in a 1-l continuously stirred tank reactor (CSTR). Polywax 3000 was used as startup solvent. The catalyst was reduced using a standard procedure, i.e., first ex-situ reduction at 350 °C for 15 h by H₂/He (1/3) followed by an in-situ reduction at 230 °C for 24 h by H₂. The FTS conditions were 230 °C, 2.0 MPa, H₂/CO = 2, 4.0–6.5 NL/g-cat/h and a stirrer speed of 750 rpm. 5–50 ppm of KCl was added after a steady state was established.

The changes in CO conversion, selectivities to CH₄ and C₅₊ (carbon atom basis), C₄ olefin selectivity (100 × (rate of all C₄ alkenes)/(rate of all C₄ alkenes + rate of all C₄ alkanes)) and 1-C₄ olefin selectivity × (-rate of 1-C₄ alkenes)/(rate of all C₄ alkenes) as functions of time and contaminant concentration were examined.

2.4. ICP analysis of impurity ions in FTS products

In order to determine if K⁺ and Cl⁻ ions were present in aqueous, oil, or wax products, several selected samples collected during testing of different levels of KCl were sent for analysis by inductively coupled plasma (ICP).

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