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Fischer-Tropsch synthesis: Effect of carbonyl sulfide poison over a Pt promoted Co/alumina catalyst

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ABSTRACT

The effect of carbonyl sulfide (COS) impurity present in syngas on the performance of a traditional cobalt catalyst (0.5%Pt-25%Co/Al_2O_3) was investigated for Fischer-Tropsch synthesis (FTS) using a continuously stirred tank reactor (CSTR). Reports about the use of COS as sulfur carrier for the poisoning of cobalt catalysts for FTS are scarce. The S-poisoned and un-poisoned catalysts were tested at industrially relevant FTS conditions and also compared at the same CO conversion level in order to evaluate the effect of sulfur on catalyst activity and product selectivity. The COS (1.8 ppmv) addition caused a significant irreversible effect on the activity. At similar CO conversion level, the COS poisoned catalyst exhibited higher methane and C_2–C_4 selectivities and lower C_5+ selectivity compared to the clean or un-poisoned catalyst. The COS poisoned catalysts were characterized by X-ray adsorption near edge structure (XANES) analysis to find out the reason for the deactivation and altering of the product selectivities. The sulfur K-edge XANES results clearly indicate the formation of cobalt sulfide, which is known to enhance the hydrogenation ability. The olefin/paraffin ratio of the COS poisoned catalyst was found to be lower than that of the clean catalyst, providing further indication of the higher hydrogenation activity of the COS poisoned catalyst.

1. Introduction

Fischer–Tropsch synthesis (FTS) has been a promising technology for producing clean alternative fuels and chemicals from synthesis gas (CO and H_2), which is derived by gasification of coal, biomass and reforming of natural gas [1–5]. High molecular weight hydrocarbons (waxes) can be effectively produced using a cobalt-based catalyst, which has a higher FTS activity, selectivity to linear paraffins, and a lower water-gas-shift (WGS) activity compared to an iron-based catalyst [6,7]. Gasification is the process in which a carbon source is converted to synthesis gas in the presence of oxygen and/or steam. The composition of the synthesis gas is highly dependent on the type of gasification technology and conditions employed. This synthesis gas (or syngas) can then be converted to transportation fuels via FT synthesis. Biomass-derived synthesis gas can contain both organic and inorganic impurities such as tars, benzene, toluene, xylene, NH_3, HCN, H_2S, COS, HCl, volatile metals, dust, and soot [8]. Coal, which originates from biomass, typically contains all of the same inorganic impurities as found in biomass [9]. In some cases, the presence of parts per billion and/or million amounts of impurities in the synthesis gas can have a significant impact on downstream of the cobalt FT catalysts.

Sulfur-based impurities, mainly H_2S, COS and organic sulfur, are formed by the conversion of sulfur present in coal, biomass and natural gas [10]. The sulfur content in coal is often comparatively higher than the biomass and natural gas, although sour gas can contain greater than 20% H_2S, along with other S compounds (*e.g.*, COS, CS_2, mercaptans, *etc.*). The amount of sulfur present in syngas mainly depends on the source and type of coal. It is well known that the poisoning of cobalt-based catalysts by sulfur compounds is a critical problem in FTS to hydrocarbons from coal-derived syngas. The effects of poisoning by sulfur compounds (H_2S, COS, CS_2, C_2H_6S and $C_4H_{10}S$) have been investigated in various studies over iron [10–14] and cobalt-based FT catalysts [15–25]. Only few studies have been reported in the literature on the effect of sulfur by using COS as a sulfur carrier over Fe-based catalysts [11,12], whereas, to the best of our knowledge, for the first time we are reporting the effect of sulfur by using COS as a sulfur carrier over cobalt-based catalysts.

In the literature, generally two types of approaches have been used to define the sensitivity of FTS catalysts to impurities in syngas. The first is to incorporate trace amounts of sulfur impurities into the catalyst

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(*ex-situ* addition) and then to explore the differences in catalyst performance (activity, selectivity and stability) relative to those of the reference catalyst [15–19]. The second is online co-feeding of a sulfur impurity-containing solution or gas with syngas (*in-situ*) and then studying the changes in catalyst performance with time [11,12,20–25]. 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. However, 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 [13,24–32].

It has been reported that small amounts (≤ 100 ppbv) of sulfur had a positive effect on activity and moderate amounts (100–500 ppbv) of sulfur had no effect, while higher amounts (≥ 500 ppbv) had a significant irreversible deactivation effect on activity over supported cobalt catalysts [16,19,21,22,24]. The effect of sulfur on product selectivity is quite controversial. In FT synthesis, it is well known that the conversion level influences the selectivity and stability, in part due to increasing partial pressure of water and by decreasing the partial pressure of reactants [33,34]. In the open literature, most studies have not reported product selectivities at similar CO conversion level. Recently Borg et al. [20] studied the effect of sulfur by co-feeding various concentrations of H_2S gas over a $CoRe/NiAl_2O_4$ catalyst. They reported that low S levels had no positive effect, but rather a consistent negative effect at all higher concentration levels. In that work, the CO conversion and product selectivity were varied with sulfur concentrations. These authors concluded that S does not affect the selectivity of C_5+ hydrocarbons, and that the change in selectivity is in line with changes in CO conversion. Pansare and Allison [21] studied the effect of sulfur by co-feeding $(CH_3)_2S$ as a sulfur carrier over a Co/alumina catalyst using a CSTR. They reported that sulfur decreases the long chain hydrocarbon (C_5+) selectivity and increases the light gas product (C_1–C_4) selectivity.

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. In this investigation an attempt was made to evaluate the effect of COS as a sulfur carrier on the activity and product selectivity of a Pt-promoted Co/alumina catalyst. The product selectivity results of the S-poisoned catalyst were compared with an un-poisoned catalyst at similar CO conversions. The effects of COS impurities on the activity and selectivity was investigated by using XANES with soft X-rays at the S K-edge by withdrawing the COS exposed cobalt catalyst slurry samples from the reactor, and sealing them in their in-situ like state in the waxy product.

2. Experimental

2.1. Catalyst preparation

Sasol-Catalox alumina (high purity γ-alumina, 140 m^2/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. In this method, which follows a Sasol patent [35], the ratio of the volume of solution used to the weight of alumina was 1:1, such that the volume of solution was approximately 2.5 times the pore volume of the catalyst. Two impregnation steps were used, each to load 12.5% of Co by weight. After the second impregnation/drying step, the catalyst was calcined under air flow at 350 °C. The 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 again at the same conditions as used previously.

2.2. Catalyst characterization

2.2.1. XANES spectroscopy

The electronic structure of sulfur, following catalyst poisoning was investigated by XANES in fluorescence mode near the S K-edge at the Soft X-ray Microcharacterization Beamline (SXRMB) at the Canadian Light Source, Inc. The used catalyst sample, after COS 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 [36].

2.2.2. Temperature programmed hydrogenation

To characterize the sulfur exposed and un-poisoned catalysts, the end-of-run catalyst fixed in wax product was transferred to an air-free environment (inert chamber); moreover, the typical Soxhlet extraction procedure was avoided. Instead, the catalyst sample was diluted with hot ortho-xylene to remove the high molecular weight FT-wax fractions. It was not possible to completely remove the FT-wax from the catalyst particles by this method. However, the remaining wax acts as a protective barrier for the air-sensitive catalyst particles. Extracted catalyst was treated mildly with $1\%O_2/N_2$ at 200 °C for 2 h to remove the wax product formed from FTS, prior to characterization by temperature programmed hydrogenation (TPH) measurements.

Temperature programmed hydrogenation (TPH) profiles of un-poisoned and COS poisoned catalysts were recorded using a Zeton-Altamira AMI-200 unit equipped with a thermal conductivity detector (TCD). The TPH was performed using a 10% H_2/Ar gas mixture and referenced to argon at a flow rate of 30 cm^3/min. The catalyst samples were heated from 50 to 850 °C at a heating ramp of 10 °C/min.

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.*, rewax, 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 (± 1 °C) using a temperature controller.

The catalyst (~12.0 g of 63–106 μm) was loaded into a fixed-bed reactor for ex-situ reduction at 350 °C and atmospheric pressure for 12 h using a gas mixture of H_2/He (60 NL/h) with a molar ratio of 1:3. The reduced catalyst (~10.0 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, 2.0 MPa, $H_2/CO = 2$, and a stirrer speed of 750 rpm. The co-fed COS was delivered to the CSTR by using a cylinder containing 15 ppm COS (balance hydrogen), a certified mixture purchased from Scott-Gross. Siltek/Sulfinert deactivated stainless steel tubing was used from the cylinder regulator to the reactor to prevent sulfur adsorption to the gas tube. The Siltek/Sulfinert coating is the most inert substrate available for the transfer of low levels of polar and non-polar compounds, especially traces of organosulfur and mercury compounds.