Journal of Catalysis 337 (2016) 80–90

Contents lists available at ScienceDirect

Journal of Catalysis

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

Fischer–Tropsch synthesis: Effect of ammonia on supported cobalt catalysts

Venkat Ramana Rao Pendyala [a], Gary Jacobs [a], Clement Bertaux [a], Syed Khalid [b], Burtron H. Davis [a,*]

[a] Center for Applied Energy Research, University of Kentucky, 2540 Research Park Drive, Lexington, KY 40511, USA
[b] NSLS, Brookhaven National Laboratories, Brookhaven Ave., Upton, NY 11973, USA

ARTICLE INFO

Article history:
Received 23 September 2015
Revised 11 January 2016
Accepted 12 January 2016

Keywords:
Fischer–Tropsch synthesis
Effect of ammonia
Supported cobalt catalysts
EXAFS/XANES
Deactivation
Product selectivity

ABSTRACT

The effect of ammonia in syngas on the performance of various supported cobalt catalysts (i.e., Al_2O_3, TiO_2 and SiO_2) was investigated during Fischer–Tropsch synthesis (FTS) using a continuously stirred tank reactor (CSTR). The addition of ammonia (10 ppmv NH_3) caused a significant deactivation for all supported cobalt catalysts, but the rate of deactivation was higher for the silica-supported catalysts relative to the alumina and titania-supported catalysts used in this work. Ammonia addition had a positive effect on product selectivity (i.e., lower light gas products and higher C_5+) for alumina and titania-supported catalysts compared to ammonia free conditions, whereas, the addition of ammonia increased lighter hydrocarbon (C_1–C_4) products and decreased higher hydrocarbon (C_5+) selectivity compared to ammonia-free synthesis conditions for the silica-supported catalyst. For alumina and titania-supported catalysts, the activity almost recovered with mild *in-situ* hydrogen treatment of the ammonia exposed catalysts. For the silica-supported catalyst, the loss of activity is somewhat irreversible (i.e., cannot be regained after the mild hydrogen treatment). Addition of ammonia led to a significant loss in BET surface area and changes in pore diameter (consistent with pore collapse of a fraction of pores into the microporous range as described in the literature), as well as formation of catalytically inactive cobalt support compounds for the silica-supported catalyst. On the other hand, the pore characteristics of alumina and titania-supported catalysts were not significantly changed. XANES results of the ammonia exposed silica-supported catalysts further confirm the formation of cobalt-support compounds (cobalt silicates).

1. Introduction

Fischer–Tropsch synthesis (FTS) is a key industrial process to catalytically convert syngas (a mixture of CO and H_2) to liquid hydrocarbons and chemicals via a surface polymerization reaction [1,2]. In comparison with traditional petroleum-derived liquid hydrocarbons, the FTS liquid hydrocarbons are free of sulfur and aromatic pollutants [3–5], which make them ideal candidates for the synthesis of clean transportation fuels. Syngas can be produced from various carbonaceous sources [6–8], such as natural gas, coal, biomass, and shale gas, through steam reforming, partial or autothermal oxidation, or gasification processes. Therefore, the FTS process is of prominent interest to both academia and industry. The Fischer–Tropsch (FT) reaction was shown to be catalyzed by certain transition metals including Ru, Fe, and Co [1]. Ru-based catalysts are highly active, but the Ru resource is scarce and expensive; thus, it is not used commercially [4]. Co-based FTS catalysts are usually preferred for certain applications (e.g., GTL) because these catalysts are more active per weight of metal, more stable toward deactivation by water (a by-product of the FTS reaction), have lower activity for the competing water–gas-shift (WGS) reaction, and produce a higher fraction of linear long-chain paraffins and less oxygenates than Fe-based catalysts [9–12].

Gasification and reforming are processes in which a carbon source (biomass, coal, petcoke or natural gas) is converted to synthesis gas in the presence of oxygen and/or steam. This synthesis gas (or syngas) can then be converted to transportation fuels via Fischer–Tropsch 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 [13]. Coal, which originates from biomass, typically contains all of the same inorganic impurities as found in biomass [14]. Hence, technologies for the removal of these impurities have already been developed in connection with large-scale CTL plants. However, these plants normally operate with iron catalysts while most BTL concepts to date are based on cobalt catalysts. Iron and cobalt catalysts share the sensitivity toward some, but not all, of

---

* Corresponding author. Fax: +1 859 257 0302.
E-mail address: burtron.davis@uky.edu (B.H. Davis).

http://dx.doi.org/10.1016/j.jcat.2016.01.026

the impurities commonly found in coal and biomass-derived synthesis gas.

The effect of sulfur was investigated in an earlier study [15]. Very low levels of sulfur (<250 ppbv) may increase the CO conversion and sulfur levels up to 438 ppbv did not exhibit a poisoning effect. On the other hand, irreversible deactivation was observed at higher concentrations (>500 ppbv). Similar findings were observed by Pansare and Alison [16]; they did not observe any detectable deactivation if the synthesis gas contained 50 ppbv H_2S, while higher concentrations ($\geqslant$300 ppbv) caused significant and irreversible deactivation. Only few studies have reported the effect of ammonia on cobalt and iron-based FT catalysts in the open literature. In a recent investigation [17], we reported the effect of ammonia over a typical Fe-based catalyst; the Fe catalyst was quite resistant to high levels of ammonia, regardless of whether ammonia gas or ammonium hydroxide was used. Up to 200 ppmw, NH_3 was not found to either significantly deactivate the Fe catalyst or measurably change the Fe catalyst selectivity. To date, the effect of ammonia over cobalt catalysts has been less clear; some researchers have reported no effect [18,19], while others have reported an immediate impact on catalytic activity [20–24]. Claeys et al. [18] reported that co-feeding of up to 25% NH_3 in the synthesis gas did not affect FT activity, and similar findings were observed by Borg et al. [19] with 4.2 ppmv of ammonia. Poisoning studies of cobalt-based FTS catalysts by means of nitrogen-containing compounds such as NH_3 and HCN have been previously published [20–22]. In one study, cobalt catalysts were rapidly but reversibly deactivated by HCN and NH_3 [20]. Syntroleum workers showed that cobalt catalysts can be deactivated by as much as 16–38%, depending on the type and level of N-containing poison [22]. An Exxon patent [25] claims that a combined concentration of 100 ppb of NH_3 and HCN in synthesis gas will result in a catalyst half-life of only 4 days for supported cobalt catalysts in a slurry reactor. However, the patent also indicates that the catalyst can be rejuvenated by hydrogen treatment to restore the initial activity.

In our previous investigation [23], we reported the effect of ammonia over a Pt-promoted Co/alumina catalyst by varying the ammonia (NH_4OH) concentration from 1 to 1200 ppmw, and the percentage of drop relative to initial conversion was virtually identical at all of the ammonia concentrations (1–1200 ppmw) explored. The effect of ammonia for a Pt–Co/alumina catalyst had a negative effect on CO conversion and a positive effect on selectivity (i.e., lower methane and higher C_5+), whereas, the Co/SiO_2 and Pt–Co/SiO_2 catalysts showed negative effects on both CO conversion and product selectivity [24]. The aim of the present study was to investigate the effect of ammonia (10 ppmv NH_3) on various supported (alumina, silica and titania) cobalt catalysts. All the supported cobalt catalysts exhibited a negative effect on CO conversion but there is a positive effect on product selectivity for alumina and titania supported catalysts. To investigate the reason for the negative effect on product selectivity for the silica supported catalysts, the catalysts were withdrawn from the reactor prior to and following exposure to ammonia during the FTS reaction, and the samples were investigated using standard H_2 TPR and EXAFS and XANES spectroscopic techniques. Particular attention was also paid to the capability of each catalyst to recover its activity following a period of exposure to ammonia.

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 [26], 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.

PQ silica CS-2133 was also used as a support for cobalt FTS catalysts. An aqueous incipient wetness impregnation (IWI) method was used to load cobalt nitrate (cobalt nitrate hexahydrate, $Co(NO_3)_2{\cdot}6H_2O$, Sigma Aldrich, 99.95%) to the support. To obtain a cobalt loading of 20 wt.%, multiple impregnation steps were applied, due to the limited solubility of the cobalt nitrate salt. Following cobalt addition, the resulting slurry was dried at 80–100 °C in a rotary evaporator following each impregnation step. The solid obtained was dried at 120 °C overnight and calcined at 350 °C under flowing air for 4 h.

0.2% Pt–10% Co/TiO_2 catalyst was prepared by a single step slurry impregnation method using Degussa P-25 TiO_2 (72% anatase, 50 m^2/g, calcined at 350 °C for 4 h) with cobalt nitrate hexahydrate solution. The sample was dried at 120 °C for 16 h and calcined under airflow at 350 °C for 4 h. 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.

Due to the lower surface area (50 m^2/g) of titania support, a loading of 10% of Co is used in order to obtain smaller Co clusters, whereas alumina and silica supports have higher surface areas 140 and 327 m^2/g, respectively. Due to the higher surface areas of alumina and silica supports, higher cobalt loadings were used. A loading of 0.5% Pt is typical for the 25% Co/Al_2O_3 research catalysts for facilitating the reduction of cobalt oxides strongly interacting with the support [27,28]. Due to the lower surface area of titania, a loading of 10% of Co was used in order to obtain Co clusters of similar size [27]. However, since excessive Pt is known to promote excessive chain termination [29], a similar Pt/Co ratio was used to facilitate the strongly interacting cobalt oxides with titania. Thus, the weight percentage was decreased to 0.2% Pt for the case of 10% Co/TiO_2. Standard silica supported cobalt catalysts that are air calcined exhibit a weak interaction between cobalt oxides and silica [27,28]. No Pt is usually necessary to promote cobalt oxide reduction; therefore, it was not added to the Co/silica catalysts in the current contribution.

2.2. Catalyst characterization

To characterize the ammonia-exposed catalysts, the end-of-run catalyst along with wax 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 300 °C for 4 h to remove the wax product formed from FTS, prior to characterization of temperature programmed reduction (TPR) measurements. In a very recent study, Keyvanloo et al. [30] also followed similar procedure for the wax extraction.

2.2.1. BET surface area and porosity measurements

BET surface area and porosity measurements of the calcined and ammonia pre-treated alumina, titania and silica supported-