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Fischer–Tropsch synthesis: Mössbauer investigation of iron containing catalysts for hydrogenation of carbon dioxide

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ABSTRACT

CO_2 hydrogenation was investigated with a doubly promoted (Cu, K) silica containing iron catalyst. Hägg carbide (χ-Fe_5C_2) is the dominant phase obtained under CO activation conditions at 543 K and 0.1 MPa and it was stable under FTS conditions typical for coal or biomass derived syngas using a H_2/CO ratio of 1:1 for at least ~100 h TOS. An Fe-phase change occurs (χ-$Fe_5C_2 \rightarrow Fe_3O_4$) after switching from H_2:CO:N_2 (1:1:2) to H_2:CO_2 (3:1). The distribution of hydrocarbon products changes significantly after switching to H_2:CO_2 (3:1), but then it slowly transformed to normal FTS products, albeit with over 3 times higher methane selectivity compared to FTS using H_2:CO:N_2 (1:1:2). A correlation was obtained between the rate of FTS and the % of Fe carbide indicating that iron carbide is the active phase for CO_2-based FT synthesis. Irrespective of conditions (i.e., either H_2:CO:N_2 = 1:1:2 or H_2:CO_2 = 3:1) and the Fe phase, the methane selectivity appears to primarily depend on the H_2/CO ratio.

1. Introduction

Fischer–Tropsch synthesis (FTS) involving the hydrogenation of CO to hydrocarbons is currently attracting renewed interest as a key technology for the production of clean transportation fuels and chemicals [1–3]. In contrast, carbon dioxide hydrogenation has received much less attention. However, several recent studies have indicated that carbon dioxide can be hydrogenated into fuels and chemicals [4–6]. Basically, the pathway for CO_2 hydrogenation to hydrocarbons can be categorized into two groups: (i) CO_2 hydrogenation to hydrocarbons via methanol synthesis [7,8]; and (ii) CO_2 hydrogenation to hydrocarbons via FTS conducted using iron based catalysts [9–13]. Unlike iron, cobalt catalysts do not exhibit significant water-gas shift (WGS) activity; hence, several researchers have proposed that cobalt is not as active as iron for the hydrogenation of CO_2, since reverse WGS was deemed to be important for converting CO_2. By the principal of microscopic reversibility, it was postulated that a catalyst that facilitates a forward reaction should also catalyze the reverse reaction. In fact, the principal applies to equilibrium, and away from equilibrium, other factors must also be considered [14].

Iron based catalysts are nevertheless considered to be ideally suited for CO_2 hydrogenation due to intrinsic WGS and reverse WGS activity [15]. In general, it is recognized that iron-based FTS catalysts typically contain carbidic iron and iron oxides after activation and during FTS. Much work has been devoted to studying the nature of working FTS catalysts using XRD, Mössbauer spectroscopy, and magnetic measurements [13,16–18]. Earlier studies suggest that surface carbidic iron species are the active phases for FTS; however, the exact identity of the active phase(s) remains controversial. Riedel et al. [19] reported that the activity and selectivity change during FTS with iron when switching from H_2:CO = 2:1 to H_2:CO_2 = 3:1 synthesis gas [19]. Surprisingly, the authors observed that only the Fe_5C_2 carbide phase was present in the used catalyst, even after being at steady state during FTS using H_2/CO_2 syngas for a long period of time. Fiato et al. [4] showed that, using iron-based catalysts, the selectivity to C_5^+ hydrocarbons for CO_2 hydrogenation H_2:CO_2 = 3:1 was comparable to that produced with conventional H_2:CO = 2:1 based feed stock. Lee et al. [20] started with metallic iron catalysts, and observed the formation of oxidized Fe species (Fe_3O_4) along with hexagonal χ-Fe_5C_2 carbide and θ-Fe_3C carbides during hydrogenation of CO_2. However, the authors [20] did not observe any oxides when the catalyst contained manganese as a promoter, and it was speculated that an outer surface shell enriched in manganese exhibited higher resistance to bulk oxidation. In this work, the effect of switching from H_2:CO:N_2 = 1:1:2 to H_2:CO_2 = 3:1 during FTS on the Fe phase composition was defined using Mössbauer spectroscopy. Catalyst samples were withdrawn from the continuously stirred tank reactor (CSTR) just after activation, while the H_2:CO:N_2 = 1:1:2

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was being replaced by H_2:CO_2 = 3:1 and afterwards, when H_2/CO_2 reached the steady state ratio of 3:1. Mössbauer data indicate that the Fe phase changes from carbide to magnetite after switching the synthesis conditions from H_2:CO:N_2 = 1:1:2 to H_2:CO_2 = 3:1.

2. Experimental

2.1. Catalyst preparation

The iron catalyst employed in this study was prepared by a continuous precipitation method. Ferric nitrate solution was obtained by dissolving $Fe(NO_3)_3{\cdot}9H_2O$ in distilled and deionized water, and then tetraethylorthosilicate was added to provide the desired Fe:Si ratio. The mixture was stirred vigorously until the tetraethylorthosilicate had hydrolyzed. A flow of the tetraethylorthosilicate and iron nitrate mixture was added to a CSTR precipitation vessel together with a stream of 30% ammonium hydroxide that was added at a rate to maintain a pH of 9.0. By maintaining the slurry pH at 9.0 and an average residence time of 6 min, a base catalyst material containing iron and silicon was obtained. The slurry from the CSTR was filtered with a vacuum drum filter and the solid was washed twice with deionized water. The final filter cake was dried at 383 K for 24 h in an oven with flowing air. For this study, the Fe:Si catalyst base powder was then impregnated with the amount of aqueous K_2CO_3 and $Cu(NO_3)_2$ solution needed to produce the desired composition [Fe:Si:K:Cu = 100:4.6:10.0:2.0 atomic ratio]. The catalyst was dried at 383 K overnight with good mixing followed by impregnation and calcination at 623 K in air flow for 4 h.

2.2. Reaction testing

The FTS experiments were carried out using a 1 l CSTR (Fig. 1) equipped with a magnetically driven stirrer with turbine impeller, a gas-inlet line, and a vapor outlet line with a SS fritted filter (2 micron) placed external to the reactor. A tube fitted with a SS fritted filter (0.5 micron) extends below the liquid level of the reactor for withdrawing reactor wax (designated rewax) to maintain a nearly constant liquid level in the reactor. Another SS dip-tube (1/8 in. OD), extending to the bottom of the reactor, was used to withdraw catalyst/wax slurry from the reactor at different synthesis times. The gases were pre-mixed in a 500 ml mixing vessel before entering the reactor. Polywax 3000 (PW3000, polyethylene fraction with average molecular weight of 3000) purchased from Baker Petrolite, Inc. was used as the start-up solvent.

Typically 20.0 g of iron catalyst (140 mesh) was added to melted (413 K) Polywax 3000 (310 g) in the CSTR. Prior to reaction, the catalyst was activated in situ using a CO flow (3 sl/h/g Fe) at 543 K and 0.1 MPa for 24 h. At the end of the activation period, a sample of activated catalyst was withdrawn via the slurry withdrawal dip-tube of the CSTR. Then, the reactor temperature was dropped to 523 K and the pressure was increased to 2.06 MPa. The total feed rate was adjusted to 3.0 sl/h/g Fe with the composition of H_2:CO:N_2 being 1:1:2. N_2 was used as balancing gas to maintain a constant flowrate when the feed ratio was changed. After reaching a pseudo-steady-state CO conversion, the feed mixture (H_2:CO:N_2 = 1:1:2) containing CO was replaced with CO_2 and the N_2 was replaced with H_2 (H_2:CO_2 = 3:1). The conversions of CO, H_2 and CO_2 were obtained by GC analysis (HP Quad series Micro-GC equipped with thermal conductivity detectors) of the product gas mixture. The reaction products were collected in three traps maintained at different temperatures – a hot trap (473 K), a warm trap (373 K) and a cold trap (273 K). The products were separated into different fractions (rewax, wax, oil and aqueous) and analyzed separately using a HP 5890 GC with capillary column DB-5 for oil and wax samples and a HP 5790 GC with Porapak Q packed column for aqueous samples. The rewax is accumulated heavier hydrocarbon products that were withdrawn from the reactor through a SS fritted 0.5 micron filter. The wax, on the other hand, are lighter hydrocarbon products obtained during FT synthesis and collected in a warm trap at 373 K. Catalyst/rewax slurry was withdrawn at different reaction times via the dip-tube after sufficient purging. In a typical catalyst slurry sampling procedure, about 10 g of catalyst slurry was purged, and discarded, and then 5–7 g of catalyst slurry was collected as a representative sample from the reactor. The sample bottles containing the catalyst slurry were filled with inert Ar and shipped to Wichita State University for Mössbauer analysis.

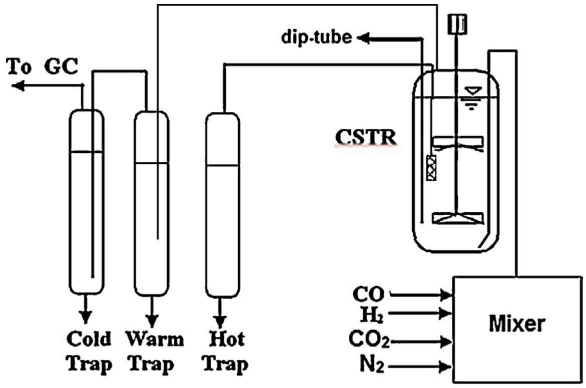

Fig. 1. CSTR Fischer–Tropsch synthesis reactor system.

2.3. Mössbauer spectroscopic measurements

Mössbauer spectra were collected in transmission mode by a standard constant acceleration spectrometer (MS-1200, Ranger Scientific). A radiation source of 50 mCi ^{57}Co in Rh matrix was used and the spectra were obtained using a gas detector. All samples were investigated at room temperature as well as at cryogenic temperatures (liquid He), typically over a velocity range of ±10 mm/s. The structural analysis of the samples was done by least-squares fitting of the Mössbauer spectra to a summation of hyperfine sextets. Details about the least-squares fitting procedure are described elsewhere [21].

3. Results and discussion

Initially, the carburized high α-Fe catalyst was exposed to syngas with inert nitrogen balancing gas, H_2:CO:N_2 (1:1:2) at 523 K and 2.09 MPa. Fig. 2 illustrates the H_2 and CO conversions with time-on-stream. The catalyst exhibits steady CO conversion of ca. 83% for more than 100 h TOS. As shown in Fig. 3, the selectivity to methane (6.0, C%) and C_5^+ (75, C%) remained essentially the same during the course of FT synthesis using syngas (H_2:CO:N_2 = 1:1:2). However, the selectivity to hydrocarbons changed abruptly after switching from CO containing feed (H_2:CO:N_2 = 1:1:2) to the one containing CO_2 (H_2:CO_2 = 3:1). The CO_2 syngas mixture (H_2:CO_2 = 3:1) tended to produce lighter hydrocarbons but the product spectrum slowly moved toward heavier products with time on-stream (TOS) (Fig. 3). It should be mentioned that for a given catalyst, the CO_2 conversion did not change significantly with reaction time. On the other hand, the initial low selectivity to CO (Fig. 3) increased with increasing TOS, approaching a value of 35% after 400 h TOS. The selectivity to methane decreased with increasing TOS from 20 to 10% for the hydrogenation of CO_2; however, the sum of the other lighter products (C_2–C_4) remained essentially constant. Furthermore, the heavier hydrocarbons represented by C_5^+ dropped from 75 to 47% after switching to H_2:CO_2 = 3:1 and then increased slowly and steadily with increasing TOS. Under steady-state conditions,