Chemisorption of C3 hydrocarbons on cobalt silica supported Fischer–Tropsch catalysts

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Chemisorption of propene and propane was studied in a pulse reactor over a series of cobalt silica-supported Fischer–Tropsch catalysts. It was shown that interaction of propene with cobalt metal particles resulted in its rapid autohydrogenation. The reaction consists in a part of the propene being dehydrogenated to surface carbon and CH\textsubscript{x} chemisorbed species; hydrogen atoms released in the course of propene dehydrogenation are then involved in hydrogenation of remaining propene molecules to propane at 323–423 K or in propene hydrogenolysis to methane and ethane at temperatures higher than 423 K. The catalyst characterization suggests that propene chemisorption over cobalt catalysts is primarily a function of the density of cobalt surface metal sites. A correlation between propene chemisorption and Fischer–Tropsch reaction rate was observed over a series of cobalt silica-supported catalysts. No propane chemisorption was observed at 323–373 K over cobalt silica-supported catalysts. Propane autohydrogenolysis was found to proceed at higher temperatures, with methane being the major product of this reaction over cobalt catalysts. Hydrogen for propane autohydrogenolysis is probably provided by adsorbed CH\textsubscript{x} species formed via propane dehydrogenation. Propene and propane chemisorption is dramatically reduced upon the catalyst exposure to synthesis gas (H\textsubscript{2}/CO = 2) at 323–473 K. Our results suggest that cobalt metal particles are probably completely covered by carbon monoxide molecules under the conditions similar to Fischer–Tropsch synthesis and thus, most of cobalt surface sites are not available for propene and propane chemisorption.

KEY WORDS: cobalt catalysts; Fischer–Tropsch synthesis; olefin readsorption; autohydrogenation; hydrogenolysis.

1. Introduction

Fischer–Tropsch (FT) synthesis produces a wide range of hydrocarbons from synthesis gas. The renewed interest to FT synthesis is primarily due to its use in the conversion of natural gas to more valuable long-chained hydrocarbons. Owing to their high activity and selectivity, cobalt-supported catalysts have been found particularly suitable for the production of higher hydrocarbons [1–3].

The mechanism of FT synthesis represents linear polymerization of adsorbed CH\textsubscript{x} monomers formed, by hydrogenation of adsorbed CO molecules [2,3]. It has been suggested [3] that chain growth proceeds via the addition of surface methylene species to adsorbed alkyl groups, which can undergo β-hydrogen abstraction to form linear α-olefins or hydrogen addition to form n-paraffins. It has been shown that n-paraffins and α-olefins are the primary products of FT polymerization, and that the reaction kinetics and hydrocarbon selectivity normally obey an Anderson–Schulz–Flory (ASF) distribution. The secondary reactions, however, lead to deviations from ASF statistics, which are generally attributed to readsorption of α-olefins produced by the FT reaction. It has been shown that the readsorbed olefins could be either hydrogenated or reinserted into the polymerization sequence. The rate of hydrogenation to the rate of olefin reinsertion ration depends on a number of parameters, e.g. the pressure of carbon monoxide, hydrogen and water [4]. Olefin hydrogenation leads to n-paraffins, which are terminal products of FT synthesis, whereas olefin reinsertion into the polymerization network reverses the predominant chain termination pathway by reinitiating the surface chain growth. As the result, the chain termination probability is reduced, while the paraffin to olefin ratio and selectivity to higher hydrocarbons are increased. Readsoption of olefins becomes more influential with increasing bed residence time and carbon monoxide conversion. The effect of olefin readsorption on the selectivity of FT synthesis has been confirmed by olefin co-feeding experiments [5,6] with the highest rate of reinsertion observed for C2 and C3 olefins [7]. Propene hydrogenation as a model reaction of secondary olefin readsorption and hydrogenation has been studied by Aaserud [8] and Schanke [9]. It has been found that lower activity of the catalysts in propene hydrogenation favors propene readsorption and leads to a higher C5+ selectivity in FT reaction.

Only chemisorption of methane and ethene has been extensively studied on transition metals, while studies of propene chemisorption have been mostly limited to...
monocrys... was studied previously [10–13]. Carbon-13 NMR shows [14] that at elevated temperatures propylidyne decomposes over Pt catalysts via dehydrogenation to surface carbon. Besides molecular desorption and hydrogen production from propene dehydrogenation over Pt(111), a small amount of propane was detected over 280 K, which is probably due to self-hydrogenation of the olefin [15].

Overall, despite the fact that olefin readsoption seems to be at the heart of the FT synthesis mechanism, very few studies have addressed the detailed mechanism of C3+ olefins chemisorption and reaction over cobalt-supported catalysts. The present paper is focused on adsorption and reaction of propene and propane over cobalt silica-supported FT catalysts in a pulse reactor. The objective of the work is to obtain new insights into the mechanism of propene and propane interaction with cobalt-supported FT catalysts at different conditions. For a series of cobalt silica supported catalysts, the data on propene chemisorption are discussed alongside with the results of catalyst characterization and compared with the catalytic performance in FT synthesis.

2. Experimental

2.1. Catalyst preparation

Cobalt-supported catalysts were prepared using impregnation of silica (Cab–o–Sil M5, \( S_{\text{BET}} = 230 \, \text{m}^2/\text{g} \)) with aqueous solutions of cobalt nitrate or acetate and are labeled as CoN and CoAc, respectively. Prior to impregnation, silica support was agglomerated by wetting in distilled water. Following the impregnation stage, the catalysts were dried overnight at 373 K and then calcined in flowing air at 373–673 K. The temperature ramp was 1 IC/min. The cobalt content and temperatures of catalyst calcination are shown in table 1. Prior to chemisorption experiments and FT catalytic tests, the catalysts were reduced in a flow of hydrogen at 673 K for 5 h. Further details of catalyst preparation and characterization are available from Ref. [16].

2.2. Catalyst characterization

The surface area of the catalysts was measured by nitrogen adsorption using BET method. Cobalt dispersion was measured by X-ray diffraction, the powder diffraction patterns of oxidized cobalt catalysts were recorded using a Siemens D5000 diffractometer (Cu(K\(\alpha\)) radiation). The average crystallite size of CoO was calculated according to the Scherrer equation [17] using a (440) peak at 20 = 65.344°.

Cobalt reducibility was evaluated from X-ray photoelectron spectra (XPS). XPS surface analyses were performed using a VG ESCALAB 220XL spectrometer. The Al(K\(\alpha\)) nonmonochromatized line (1486.6 eV) was used for excitation with a 300 W-applied power. The analyzer was operated in a constant pass energy mode (\( E_{\text{pass}} = 40 \, \text{eV} \)) and the binding energies were referenced to the Si 2p core level (103.6 eV) of the SiO2 support. The powdered catalyst was pressed as thin pellets onto a steel block. In situ reduction of the cobalt catalysts was carried out in pure hydrogen at 673 K for 5 h in the reactor cell of the preparation chamber attached to the analysis chamber of the spectrometer, whilst the spectroscopic measurements were carried out under vacuum better than 10⁻⁷ Pa.

2.3. FT catalytic measurements

The carbon monoxide hydrogenation was carried out in a fixed bed microreactor at atmospheric pressure. The catalyst was crushed and sieved to obtain catalyst grains between 0.05 and 0.2 mm in diameter. After the reduction, a flow of premixed synthesis gas with the molar ratio of H\(_2\)/CO = 2 was introduced into the reactor. The reaction temperature was 463 K. The carbon monoxide contained 5% of nitrogen, which was used as an internal standard for calculating carbon monoxide conversion. The gas transfer lines were kept at 423 K to avoid possible condensation of the reaction products. The reaction products were analyzed on-line by gas chromatography using a Hewlett-Packard 5890 Series II Gas Chromatograph with a 13X molecular sieve column and a thermal conductivity detector for the analysis of H\(_2\), N\(_2\), CO, CO\(_2\) and CH\(_4\). C\(_1\)–C\(_{18}\) hydrocarbons were separated on a packed 10% CP-Sil5 column on Chromosorb WHP and analyzed by a flame-ionization detector.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Co content, wt.%</th>
<th>( S_{\text{BET}} ), m(^2)/g</th>
<th>( T_{\text{calcination}} ), K</th>
<th>( d_{\text{CoO}_4} ) (XRD), nm</th>
<th>Co dispersion, %</th>
<th>Relative amount of metallic Co after reduction (XPS), %</th>
<th>Estimated number of cobalt metal sites, ( \mu \text{mol/g} )</th>
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<td>CoNl</td>
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