Catalysis Letters 22 (1993) 283–288

Unusual reactions on a cobalt-based Fischer–Tropsch catalyst

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Received 20 April 1993; accepted 30 August 1993

A cobalt-based Fischer–Tropsch catalyst, after 125 days of continuous synthesis, was found to have retained excessive amounts of synthesis products and was not pyroforic in air. Upon resuming synthesis, unusual reactions were observed for about 20 h. Carbon monoxide conversion was quantitative. The major product was methane, with a fairly flat distribution of paraffins and isoparaffins. Excessive end gas volumes and the presence of isoparaffins suggest that hydrocracking of the waxes deposited in the catalyst pores may have been the major reaction. Later, "normal" synthesis occurred. Catalyst activity measurements indicated a successful regeneration by the events.

Keywords: Fischer–Tropsch synthesis; Co catalyst; wax accumulation; air exposure; hydrocracking; catalyst regeneration

1. Introduction

We wish to report some unusual reactions observed during the course of our studies of the Fischer–Tropsch (FT) synthesis. We will briefly describe the sequence of events which have led to these observations, and we also report on our limited efforts seeking an understanding of the events.

The original objective of the work was to find out, how the catalytic properties of a Co,Mg/diatomaceous earth catalyst are influenced by the temperature of the pH-controlled precipitation. For the first commercial Co,Mg,Th/diatomaceous earth catalyst the Co, Mg and Th were precipitated from hot solution at a fast rate [1]. In our previous work, we studied the metal–support interactions in Co,Mg/silica catalysts, which also included diatomaceous-earth supported catalysts [2,3]. We have reported, that cobalt silicate can form during the catalyst preparation if the precipitation occurs in the presence of a reactive silica support [2,3]. The present work was aimed at finding out the properties of the catalyst which was precipi-

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tated at room temperature. This report is not intended to describe our results related to our objectives. However, it will give sufficient details of our work to provide background information. The focus of the report will be a description and characterization of the unusual events.

2. Experimental

Catalyst preparation. To a solution of 30.9 g of $Co(NO_3)_2 \cdot 6H_2O$ and of 16.0 g $Mg(NO_3)_2 \cdot 6H_2O$, which was stirred at room temperature, was added a solution of 17.9 g Na_2CO_3 in 150 ml water within a minute. Stirring continued for 5 min when 25 g of Filter-Cel (Manville Corp.) was added. The mixture was then vacuum-filtered and worked up similarly as described for catalysts precipitated at 80–85°C [2]. The cobalt content of the dried catalyst was calculated as 17% assuming quantitative cobalt uptake. The magnesium content, determined by inductively coupled plasma spectroscopy, was 0.66%.

Analytical methods. A previous report [2] gives details of the nitrogen sorption analyses for surface area and pore size distribution and of the IR analyses for cobalt silicate determination.

Catalyst evaluation. The catalyst was evaluated in a 3/4″ i.d. carbon steel reactor that was part of an automated catalyst evaluation unit. A more detailed description of the unit and of the analytical system was reported previously [2,4]. The catalyst charge was 6 g as 3.25–2.8 mm granules. It was reduced at 380°C for 2 h in a hydrogen stream. During the first 116 days of testing, the feed had the following composition: 17.0% CO, 34.1% H_2, 48.8% N_2. After the 116th day, the feed composition was changed to 15.6% CO, 39.8% H_2, 44.6% N_2 (H_2 : CO ratio 2.55 : 1) for the rest of the experimentation. The space velocities were 0.34 WHSV (g feed/g cat h) or 114 VHSV (v/v) during the first 116 days, and 0.35 WHSV or 124 VHSV using the hydrogen-rich feed. The pressure was 158 kPa during the first 113 days and 205 kPa during the remainder of the experimentation. On the 46th and 89th days, catalyst regenerations were carried out under atmospheric hydrogen at 350°C. Except for periods of temperature dependence studies, attempts were made to maintain identical CO conversion levels by compensating for the slow catalyst activity declines by slight increases in the temperature, and later by an increase of the pressure. Excluding the periods of the temperature dependence studies, the reaction temperature ranged between 187 and 195°C; the CO conversion between 79% and 60%, and the growth factor between 0.82 and 0.72.

Oxygen treatment of an active catalyst. In this experiment, a different catalyst was used, which was precipitated at 85°C. The catalyst was charged into the reactor, reduced and tested for hydrocarbon synthesis as described above (17–34–49 feed composition, 156 kPa, 192°C, 0.34 WHSV). After three days of reaction, the synthesis gas flow was replaced by nitrogen purge and the reactor was cooled down to room temperature. Then small doses of air were bled into the nitrogen purge.

This caused a very exothermic reaction in the top of the catalyst bed. GC analyses of the inlet and effluent gas streams revealed quantitative uptake of the oxygen. In spite of the small size of the doses, temperature excursions to 70–80°C occurred. The reactor was allowed to cool down before the air-dosing was continued. The exotherm slowly moved down in the catalyst bed. When the exotherm ceased and the reactor effluent showed the presence of oxygen, the air-dosing was stopped. The reactor was heated up to 192°C under nitrogen purge, and the synthesis was resumed. The catalyst activity (CO conversion and alpha value) remained the same as before the start of the oxygen treatment.

3. Results and discussion

IR analysis of the catalyst did not show a band at 1034 wavenumber. This indicates that cobalt silicate did not form during catalyst preparation [2,3]. As anticipated, an active catalyst was obtained after a short reduction at 380°C. Nitrogen sorption measurements showed 69 m^2/g surface area and 0.19 cm^3/g pore volume for the unreduced catalyst. For comparison, a catalyst of similar elemental composition, but made by precipitation at 85°C in the presence of the support, had a surface area of 74 m^2/g and a pore volume of 0.10 cm^3/g [2]. The higher surface area in this latter catalyst is believed to originate from the different chemistry of the precipitation: both basic cobalt carbonate and cobalt silicate were shown to form in this latter case [2].

As outlined in section 2, the catalyst was extensively evaluated in an experiment lasting for 125 days. At this point, the reactor was cooled down to room temperature under nitrogen purge, and the catalyst was removed from the reactor. Surprisingly, it was not pyroforic, as observed in many other experiments. The catalyst weight was 10.5 g versus the initial 6.0 g unreduced catalyst charge, suggesting waxy hydrocarbon accumulation in the pores. Although it is well known that FT catalysts accumulate waxes, it seems to be unusual to have this large amount of waxes retained. The pore structure and the wetting characteristics of the catalyst may have played a role.

Since the recovered catalyst appeared to be indifferent to air, after about 4 h of air exposure it was recharged into the reactor and synthesis was resumed without any catalyst activation step. For about a 20 h period, very surprising observations were made. The four capillary chromatograms taken during this period are shown in fig. 1, and the analysis results are given in table 1. The findings are summarized below:

(1) Extremely high catalytic activity was indicated by the quantitative CO conversion (see table 1).

(2) The product distribution was unusual. The major product was methane. Olefins were absent. For example, there were no peaks at 4.24, 6.62, 7.05 and 7.35 min retention times in fig. 1, where propene, 1-butene, cis-2-butene and trans-

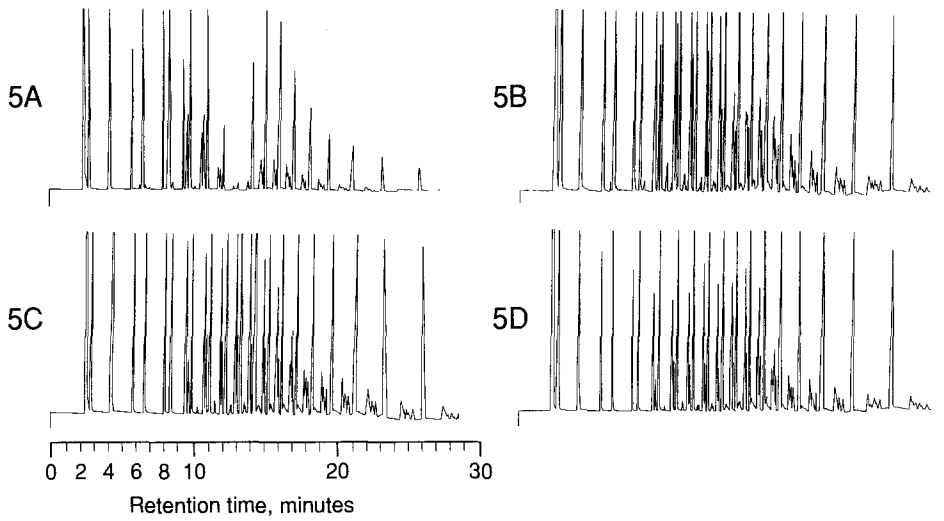

Fig. 1. Chromatograms of hydrocarbon products after catalyst exposure to air. Some product identifications: 2.43 min = methane; 2.84 min = ethane; 4.37 min = propane; 6.00 min = isobutane; 6.82 min = *n*-butane; 8.29 min = isopentane; 8.79 min = *n*-pentane.

2-butene appear, respectively, during regular syntheses. Isoparaffins formed in substantial quantities, mostly C_4 to C_9 isoparaffins. For example, large amounts of isobutane, isopentane, 2-methylpentane and 3-methylpentane were observed at 5.99, 6.27, 9.80 and 10.02 min retention, respectively. During normal synthesis, isobutane forms at trace level only; the other branched paraffin concentrations are also low. However, as the carbon number increased, the branched to normal paraffin ratios in fig. 1 more and more resembled those found during normal synthesis. Looking at the overall product distributions, no similarity can be recognized with the Schulz–Flory type distributions. In analyses A, C and D (see table 1), the C_8 to C_{16} hydrocarbons showed shallow maxima at C_{11}–C_{12}.

(3) We regularly measured the volume of the end-gases by a wet test meter and calculated the gas contraction with the knowledge of the feed rate. During "normal" synthesis conditions, the gas contraction reasonably correlates with the CO conversion [1]. During this unusual 20 h period, the treatments did not indicate contraction. There must have been a gas source other than the feed. The only explanation to the extra gas source can be the hydrocracking of the waxes present in the catalyst pores. The observed isoparaffins in the products also seem to lend support to the postulation that hydrocracking occurred. Hydrocracking is known to produce an enrichment in branched molecules [5].

(4) While analysis A showed substantial quantities of water as expected from FT synthesis or methanation, analyses B, C and D showed very little water (see table 1). In the GC charts, we looked for signs of unidentified peaks that could represent oxygenated products (alcohols, etc.) but have not found any. Thus, we are unable to account for the oxygen of the CO, with the exception of analysis A. This brings up the question, what happened to the carbon monoxide.

Table 1
Product analyses after re-charging air-exposed catalyst [a]

Parameter, product	Analysis results, values			
	sample A	sample B	sample C	sample D
hours after re-charge	0.1	1.5	5.0	7.0
temperature (°C)	201	198	187	186
CO conversion (%)	100	100	100	100
selectivity to H_2O [b] (%)	~ 80	~ 10	~ 5	~ 2
selectivity to CO_2 (%)	4	0.1	0.1	0.1
hydrocarbons in wt% [c]				
C_1	72.0	55.2	59.8	57.8
C_2	7.2	9.0	5.1	4.0
C_3	5.0	6.1	3.0	2.4
C_4	3.5	4.0	2.3	1.9
C_5	2.9	2.8	1.8	1.7
C_6	2.2	2.6	2.0	1.8
C_7	1.3	2.5	2.2	2.0
C_8	0.4	2.5	2.5	2.3
C_9	trace	2.4	2.7	2.5
C_{10}	0.6	1.8	2.9	2.7
C_{11}	1.2	1.5	3.0	3.2
C_{12}	0.9	1.7	2.7	3.9
C_{13}	0.8	1.7	2.1	3.7
C_{14}	0.7	1.6	1.6	2.5
C_{15}	0.4	1.1	1.4	1.6
C_{16}	0.3	1.2	1.5	1.7
$>C_{16}$	0.5	2.3	1.6	1.9

[a] The conversion and selectivity data were derived from GC analyses on a Porapak QS column with TC detection and on a fused silica capillary with FID detection. The chromatograms on the fused silica capillary are shown in fig. 1.

[b] Assuming one mole of water from one mole of carbon monoxide. Crude estimates; we were not set up for quantitation of water.

[c] Normalized for the detected hydrocarbons. Our analytical system was not set up for the detection of $>C_{18}$ hydrocarbons which were probably also present.

About 20 h after re-starting the reaction, the synthesis conditions returned to "normal". Table 2 presents the product analyses obtained during this period. Table 2 also includes the product analyses before the unusual events for comparison. It can be recognized, that the unusual events resulted in a catalyst regeneration, as revealed by the increased CO conversion, increased growth factor and substantially decreased methane selectivity.

We hypothesize, that some oxygen may have diffused slowly to the active catalyst surface during the exposure of the catalyst to air, and that chemisorbed oxygen may have modified the catalyst. To learn about the possible role of oxygen on the catalytic properties, an experiment was carried out by controlled exposure of an

Table 2
Catalyst performance data before and after the unusual events [a]

Days	CO conv.(%)	Methane selectivity		CO_2 sel. (%)	Growth factor
		carbon (%)	percent of theoretical [b]		
118	76.2	13.2	306	1.9	0.792
119	74.0	15.0	332	2.0	0.787
125–126	unusual events				
127	83.9	9.0	269	1.8	0.817
128	84.4	8.7	282	1.7	0.824
143	70.9	8.8	250	1.5	0.812

[a] Under identical reaction conditions: 191°C; 205 kPa; 15.6% CO, 39.8% H_2, 48.8% N_2 feed composition; 0.35 WHSV.
[b] The found methane value compared to the value calculated with the growth factor using the Schulz–Flory equation.

active catalyst to air as described in section 2. Surprisingly, the catalyst remained active for synthesis after the exposure. However, "normal" synthesis was found; the unusual reactions did not occur. It should be realized that this experiment was not a reproduction of the original: the catalyst, its experimental history and the mode of exposure to oxygen greatly differed.

The experiment leading to the unusual reactions should be reproducible. However, a complete reproduction would require extraordinary efforts because of the four months experimentation. The observation of the unusual reactions may be anticipated after much shorter reaction time, if the pores of an active, wax-retaining catalyst are filled up with waxes before room temperature air exposure.

Acknowledgement

The outstanding technical assistance of D.J. Schumacher is gratefully acknowledged.

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