

THE EFFECT OF ACTIVATION AND PROMOTION ON A FISCHER-TROPSCH CATALYST

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INTRODUCTION

Since the late 1970's, an interest in the production of gasoline and other transportation fuels from synthesis gas has been renewed. A conceptual scheme for the production of gasoline from low-ratio synthesis gas is the two-stage method developed by Mobil [1]. In this process, mixtures of hydrogen and carbon monoxide are reacted in a slurry bubble column containing a conventional Fischer-Tropsch catalyst in the first stage. The product from this step is then sent to the second-stage reactor that contains the shape-selective zeolitic catalyst ZSM-5. One of the goals of the indirect liquefaction research program at the Pittsburgh Energy Technology Center is to investigate catalyst systems in the slurry phase that are potential candidates for the first-stage process. These catalyst systems should process low ratios (0.5/1 to 1/1 of H_2/CO) of synthesis gas to produce a high yield of light olefins and gasoline-range hydrocarbons.

Certain results in the literature indicate that synthesis gas conversions with iron-manganese oxide catalysts yield a suppressed C_1 -fraction and a large C_2 - C_4 light-hydrocarbon fraction that deviates from that predicted by Schulz-Flory kinetics [2,3]. A recent three-phase study with iron-manganese catalysts of various compositions found that hydrogenation of olefins occurred along with olefin isomerization reactions [4]. The C_2 - C_4 content of the hydrocarbon distribution followed Schulz-Flory kinetics and did not exceed the 56 weight percent maximum predicted by Schulz-Flory. Since these results with iron-manganese catalyst were not as good as those reported in the patent literature, two areas of interest -- catalyst activation and promotion -- were investigated with the intent of improving olefin selectivity and catalyst activity and stability.

In this study, the activation and promotion of a 21Fe/79Mn catalyst were investigated in a slurry reactor. The effects of the process parameters of temperature, pressure, and reducing gas composition on the activation step and on the subsequent catalyst activity and product selectivity were studied. Also, the alkali promotion of the iron-manganese catalyst with potassium carbonate was investigated. Slurry samples were taken at various times on stream, and the catalyst was analyzed by surface techniques so that the catalyst properties could be correlated with process results.

EXPERIMENTAL

The catalyst was prepared in a continuous, stirred precipitation reactor similar to a unit used by Kölbel and Ralek [5]. Nitrates of iron and manganese were reacted with ammonium hydroxide. Batches of the washed

and vacuum-dried coprecipitate were crushed, sieved through a 100-mesh screen, and homogenized by rolling. A portion of the total batch was further crushed and sieved through 325 mesh (44 μm). Catalyst for all the tests in this study was obtained from this portion. The fresh catalyst was about 14 weight percent iron and 52 weight percent manganese.

The slurry studies were conducted in a one-liter stainless steel stirred reactor as described elsewhere [6]. Typically, fifty-one grams of iron-manganese catalyst that were sieved through 325 mesh (44 μm) were placed in the reactor with the molten medium wax to make a 13.5 weight percent suspension based on unreduced catalyst weight. The high-boiling paraffinic wax (P-22 from Fisher Scientific Company) had an average carbon number of 28. The reactor system was sealed, cooled, leak-tested, and purged with helium. At the desired activation pressure, the temperature was increased to the desired activation temperature under a flow of helium. Isothermal conditions within the reactor were established by means of a sliding thermocouple in a thermowell in the reactor. The impeller was stopped and gas flow was decreased to a small amount, at which time the unexpanded slurry level was lowered to 0.5 liter by using the reactor pressure to force the excess wax through a dipleg and filter and into a heated wax trap. The impeller was then restarted, and once isothermal and isobaric conditions were reestablished, the inert flow was stopped and the activation gas was introduced. Unless specified, activation usually lasted for twenty-four hours. At the end of this activation, the liquid level was again readjusted, and the system pressure and temperature were adjusted to 200 psig and 275°C, respectively. Synthesis feed gas was introduced in increments over the next hour until a weight hourly space velocity (WHSV) of 1.21 hr^{-1} was reached. (WHSV is defined as grams of gas per hour per gram of charged catalyst.) Trap drainings, flows, and gas analyses were measured on a twenty-four hour basis for material balance determinations. Unless otherwise stated, tests in this study used a 1H₂:1CO feed gas.

The gaseous and liquid products were characterized by various analytical techniques. Gas exiting the reactor system was analyzed for hydrogen, carbon monoxide, carbon dioxide, nitrogen, and hydrocarbons up to C₈ by gas chromatography. The liquid condensate in the trapping system was collected and physically separated into an aqueous fraction and an oil fraction. The aqueous phase was analyzed by mass spectrometry to detect oxygenates, and the water content was determined by the Karl Fischer reagent technique. The liquid hydrocarbon samples were characterized by fluorescent indicator adsorption (FIA) ASTM D-1319 to determine the functionality of the liquid oil, and by bromine number ASTM D-1159 to check the olefin content. Infrared studies were also performed on the oil fractions. Relative amounts of terminal, trans-internal, and beta-branched-terminal olefins were determined by infrared spectral analysis. The wax fraction, which was dependent on the trapping system, and selected liquid oil samples for a particular period of time were also analyzed by gas chromatography with a capillary column.

Slurry samples were withdrawn from the reactor at various times on stream. The wax-encapsulated iron-manganese catalysts were characterized by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). A mild washing of the slurry-catalyst samples by sonication in toluene was performed before the XPS analysis. These washed samples still contained

slurry wax, but it was at a level that permitted XPS data acquisition while simultaneously preventing oxidation of the catalyst surface. The samples were then either spread onto holders or pressed into thin wafers for subsequent XPS data acquisition. Preliminary XPS data were also obtained from activation of an iron-manganese catalyst treated in situ with hydrogen in the XPS. These data were acquired from wafered samples after gaseous treatment at pressures near 1.5 atm and temperatures between 275°C and 450°C. Preliminary results of various activations with iron-manganese catalyst in a thermogravimetric analyzer (TGA) were also obtained.

RESULTS AND DISCUSSION

In a previous study with various iron-manganese catalysts [4], a standard activation with carbon monoxide was used. With the 21Fe/79Mn catalyst used in this study, the catalyst was activated with carbon monoxide as the base-line case at 2.25 WHSV, 275°C, and 200 psig for 24 hours. All activations were conducted in situ. Activation parameters investigated were temperature (275°C versus 300°C), pressure (0 psig versus 200 psig), and gas composition (CO, CO followed by H₂ -- Kölbel-type [3], synthesis gas, and hydrogen). Slurry reactor results for selected periods during a test are shown in Table 1. Synthesis process conditions for all the tests were 1.21 WHSV of 1H₂/1CO feed gas, 275°C, and 200 psig unless otherwise indicated. In the tests where carbon monoxide was used to reduce the catalyst, the carbon dioxide was monitored in the exit gas by an infrared detector. In all cases, after the beginning of the carbon monoxide reduction, the carbon dioxide concentration reached a maximum during the first two hours and thereafter asymptotically approached a zero concentration.

As in past work with iron-manganese catalysts, the functionality of the product in the base-line test SL-54 changed with time on stream. As seen in Table 1, the light olefin content decreased with synthesis time due to olefin hydrogenation. This is paralleled by FIA results on the liquid oil, which reveal that with time on stream, the oil becomes more paraffinic and less olefinic. Also with catalyst aging, the olefinic products exhibit more double-bond isomerization. If the 2-butene/1-butene ratio is used as an index for olefin isomerization, this ratio -- thus, isomerization -- increased in the C₄ fraction with time. Similarly, by infrared analysis of the liquid oils, the ratio of internal to terminal olefins also increased with time.

The catalyst in test SL-57 was activated identically to the base-line test except at 300°C. This higher temperature of activation increased the initial activity of the catalyst but also increased the deactivation rate of the catalyst. A lower pressure (0 psig) of activation was used in test SL-60, and this increased the initial activity over the base-line test. A Kölbel-type of activation in test SL-58 (CO treatment for 24 hours at 275°C and 200 psig, followed by H₂ treatment at 275°C and 200 psig) had activity results similar to those of the base-line test SL-54.

The trends in the product selectivity were the same for all the tests (see Table 1). With time on stream, the hydrocarbon selectivity shifted to a lighter fraction; the olefin content decreased; and a larger percentage of olefin isomers occurred. A minor exception is noted in the Kölbel-type

activation test, where the internal-to-terminal olefin ratios in both the gas and oil phases went through a minimum during the first part of the test.

The major differences in the activation studies occurred when the catalyst was activated at 275°C and 200 psig with hydrogen or synthesis gas (1H₂/1CO) as compared to carbon monoxide. No catalyst activity occurred with hydrogen activation, and only slight conversion (<2%) occurred with a synthesis gas activation. Investigating a higher iron-to-manganese ratio catalyst, Maiti et al. [7] claimed that a MnFe₂O₄ spinel and MnO were the major phases at hydrogen reduction temperatures below 300°C. The XPS information in the latter section will clarify this point.

The addition of a structural promoter to the 21Fe/79Mn catalyst was attempted to stabilize the activity and maintain a high light-gas olefin content. Schulz and Gokcebay [8] claimed that potassium addition to their iron-manganese catalysts reduced secondary olefin hydrogenation and isomerization reactions. Based on this, several batches of 21Fe/79Mn catalyst were impregnated with various amounts of potassium. Three different potassium levels were investigated: 0.1, 0.4, and 1.3 weight percent. Results are listed in Table 1. An activation with carbon monoxide at 2.25 WHSV, 275°C, and 0 psig for 24 hours was done in situ for each test.

As compared to test SL-60 that had an unpromoted catalyst, the activity of the 0.1% potassium catalyst was about the same except after 119 hours on stream, where the potassium-promoted catalyst had deactivated significantly. The 0.4 and 1.3 weight percent potassium-promoted catalysts had very high initial activities [50 mole percent (H₂ + CO)-conversion] but decreased after 200 hours on stream to values comparable to the unpromoted catalyst.

The hydrocarbon distribution for the unpromoted iron-manganese shifts to a lighter fraction with time and to a lower olefin content with a larger fraction of olefin isomers. The lowest loading of 0.1 weight percent potassium did not seem to change these trends. However, for the catalyst with the 0.4 weight percent potassium loading, the product distribution shifts to a higher carbon number with time. The percent olefinic product actually increases with time, and the internal/terminal olefin ratio decreases -- indicating less olefin isomerization. At the highest potassium loading in test SL-62, the hydrocarbon distribution is relatively constant and is shifted to higher molecular weights. The olefin content is high (85 weight percent), and the internal/terminal olefin ratio is about an order of magnitude less than with the unpromoted iron-manganese catalyst. With this iron-manganese catalyst, a high loading of potassium is evidently needed to prevent olefin hydrogenation and isomerization reactions. However, the product distribution is shifted so that only about 30 weight percent of the hydrocarbon product is C₂-C₄, rather than the 40 weight percent obtained with the unpromoted catalyst.

The XPS analysis of the wax-encapsulated iron-manganese catalysts determined the surface atomic ratios Fe/Mn and C/Mn (see Table 2). These results can be correlated with the activity of a catalyst during three-phase testing. For example, the (H₂+CO) conversion in SL-61 was negligible throughout the slurry run. Such inactivity is mirrored in the C/Mn ratios that are constant throughout the test and are lower than C/Mn for other slurry tests. In relation to test SL-61, XRD and in situ XPS results with

an unpromoted iron-manganese catalyst under hydrogen with temperatures ranging from 275°C to 450°C revealed that metallic iron was not produced. Instead, a solid solution of FeO-MnO and/or a Fe-Mn spinel is formed. Hence, the constant and low C/Mn ratio in SL-61 suggests that iron is not available for iron carbide formation during synthesis gas exposure, and thus, no conversion/activity is observed during the test.

The variations in the atomic ratios for slurry tests SL-54 through SL-60 are related to differences in the activation gas sequence and the activation parameters for the unpromoted iron-manganese catalyst. In general, the trend in these tests is for the Fe/Mn values to decrease with time on stream. Correspondingly, the C/Mn values increase with time on stream and can be related to carbon deposition as a function of time on stream and/or as a difference in the amount of slurry wax retained by the catalysts after toluene sonication. In all cases, the catalyst deactivated to some extent over the first 200 hours on stream. More specifically, an increased carbon content was found on the catalyst activated under carbon monoxide at 300°C (SL-57) compared to the catalyst activated under carbon monoxide at 275°C (SL-54) with synthesis time. This increased C/Mn ratio, as independently confirmed by TGA results, is probably related to an enhanced amount of iron carbide and/or carbon formation during the activation and usage stages of SL-57. Such enhancement paralleled the faster deactivation rate for SL-57. The corresponding C/Mn ratios for SL-58 show that H₂ reduction after CO exposure (Köbel-type activation) decreases the carbon content on the catalyst to levels below SL-57. Such a decrease may be related to greater formation of metallic Fe after the hydrogen reduction, as indicated by the high Fe/Mn ratio after 48 hours on stream.

Table 2 also reports XPS results from the potassium-promoted tests SL-62 through SL-64. In general, for these tests, the Fe/Mn ratio increases with time on stream, unlike results with the unpromoted catalysts. Also, the C/Mn ratio increases with time on stream. In all cases with the promoted catalyst, the potassium appears to enhance the surface iron concentration during a test. The potassium also appears to increase surface carbon deposition during a test. The catalyst in test SL-64 deactivated significantly during the experiment, and this could be related to the rapidly increasing C/Mn ratio during the test.

SUMMARY

The effects of various activations of an iron-manganese catalyst on synthesis gas conversion were investigated in a slurry reactor. Although the activation temperature and pressure did affect catalyst activity, olefin hydrogenation and isomerization reactions still appear to be significant in all cases. The activating gas composition had the most dramatic effect, with the catalyst exhibiting no activity after a hydrogen activation. Potassium promotion of the iron-manganese catalyst succeeded in increasing the activity and increasing the percentage of olefins in the light gas fraction. However, the hydrocarbon distribution was shifted to a higher average molecular weight. The XPS results of catalyst slurry samples at various process times were correlated with the catalytic process results to explain the particular catalyst performance.

DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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Table 1: Results of Activation and Promotion Studies.

Test	SL-54			SL-57			SL-58			SL-60			
Synthesis Time on Stream, hr [#]	47	118	142	191	47	119	167	43	115	187	48	120	204
CO-Conversion, mole percent	27.4	26.9	27.3	20.6	36.3	25.9	16.2	25.2	26.5	16.3	35.7	32.4	29.1
(H ₂ +CO)-Conversion, mole percent	29.8	27.5	29.0	24.1	38.3	29.2	15.8	25.0	25.5	19.7	35.6	33.1	30.1
Hydrocarbon Distribution, wt%													
CH ₄	8.0	8.8	8.4	9.2	6.8	9.1	14.0	8.9	9.4	10.7	6.9	7.2	7.8
C ₂ -C ₄	41.7	43.0	42.4	44.2	37.2	37.1	45.8	43.9	43.5	40.3	38.3	39.1	40.7
C ₅ +	50.2	48.2	49.2	46.6	56.0	53.8	40.2	47.2	47.1	49.1	54.8	53.7	51.5
Olefin Content C ₂ -C ₄ Fraction, wt%	76.5	70.8	70.7	69.4	74.2	62.2	50.5	73.5	71.9	63.9	76.8	72.3	68.8
Internal/Terminal-Olefin Ratio	1.1	1.5	1.7	1.9	0.94	2.3	--	2.1	1.6	1.9	0.67	1.1	1.8
2-Butene/1-Butene Ratio	0.30	0.45	0.53	0.56	0.29	0.69	1.0	0.35	0.30	0.55	0.21	0.30	0.44
Test	SL-63			SL-64			SL-62						
Potassium Loading, wt%		0.1			0.4				1.3				
Synthesis Time on Stream, hr [#]	48	119		46	118	187	47	119	191				
CO-Conversion, mole percent	32.9	14.6		56.3	32.9	18.0	59.5	40.5	30.4				
(H ₂ +CO)-Conversion, mole percent	32.8	15.2		50.2	29.5	18.6	50.0	33.9	25.9				
Hydrocarbon Distribution, wt%													
CH ₄	7.0	16.6		9.4	9.5	6.6	3.7	3.6	3.8				
C ₂ -C ₄	32.3	48.8		37.6	37.1	29.3	21.0	23.4	25.1				
C ₅ +	60.7	34.6		53.0	53.4	64.1	75.3	73.0	71.1				
Olefin Content C ₂ -C ₄ Fraction, wt%	65.4	45.4		65.2	67.4	69.3	83.8	84.8	85.9				
Internal/Terminal-Olefin Ratio	1.4	3.0		1.5	1.2	0.63	0.14	0.16	0.23				
2-Butene/1-Butene Ratio	0.50	0.25		0.45	0.33	0.11	0.03	0.04	0.05				

[#]Slurry Synthesis Conditions: 1.21 MHSV of 1H₂/1CO, 275°C, 200 psig.

Table 2: Fe/Mn and C/Mn Atomic Ratios from XPS Analysis of Iron-Manganese Slurry Catalysts Sampled From the Slurry Reactor After Specified Activation Step(s) and After Specified Times on Stream.

Slurry Test	<u>SL-54</u>	<u>SL-57</u>	<u>SL-58</u>	<u>SL-61</u>	<u>SL-60</u>	<u>SL-63</u>	<u>SL-64</u>	<u>SL-62</u>
Fe/Mn								
CO-Activation	0.23	0.30	0.34		0.16	0.18	0.29	
H ₂ -Activation			0.32	0.29				
~48 hours	0.22	0.20	0.43	0.29	0.16	0.20	0.53	0.16
~100 hours				0.29		0.28		
~200 hours	0.16	0.14	0.19		0.15		0.50	0.24
C/Mn								
CO-Activation	4	6	10		10	7	8	
H ₂ -Activation			6	6				
~48 hours	6	12	10	4	19	13	23	16
~100 hours				4		15		
~200 hours	7	28	16		52		59	34