

Synthesis Gas Conversion With a Transition Metal-Zeolite Catalyst

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INTRODUCTION

Recently, much interest has been generated in the synthesis of hydrocarbon fuels from low ratio hydrogen-to-carbon monoxide mixtures using indirect liquefaction catalysts. Studies have shown that a low $H_2:CO$ ratio synthesis gas is produced by the more efficient, second generation gasifiers (1). One of the objectives of the catalyst research program of the U. S. Department of Energy/Pittsburgh Energy Technology Center is to investigate various indirect liquefaction catalyst systems that are capable of using low ratio synthesis gas mixtures.

Of particular interest are catalysts that exhibit shape-selective properties. With the advent of the Mobil methanol-to-gasoline process, ZSM-5 and other medium pore zeolite systems have been investigated (2,3,4). Work at PETC has involved the direct conversion of low ratio hydrogen-to-carbon monoxide synthesis gas to liquid fuels via transition metal-zeolite combinations. In past experimentation, cobalt and iron, either promoted or unpromoted, have been investigated in tubular microreactors or in bench-scale mixed reactors. Due to the interesting preliminary results obtained with a Co-Th-ZSM-5 catalyst, a process variable study with this catalyst system was undertaken.

EXPERIMENTAL

The catalyst was prepared by physically mixing the transition metal-promoter coprecipitate with the zeolite. Cobalt-thoria in a ratio of about 10/1 was coprecipitated from a solution of the nitrates of these metals with sodium carbonate, washed, dried, and sieved through 200 mesh. The ammonium form of ZSM-5 was fabricated according to information in the patent literature (5). The dried NH_4 -ZSM-5 with a silica/alumina ratio of 30/1 was then sieved through 200 mesh, mixed with the dried coprecipitate, and rolled overnight for intimate mixing. Initially this mixture was pelleted for testing. However, due to the frangibility of the pellets, further testing was conducted with catalyst that was extruded with Catapal SB alumina and dried. The structural integrity of the extrudates was greatly enhanced by the alumina binder. Microreactor tests of the pelleted versus the extruded catalyst indicated that the addition of the alumina binder did not significantly affect the catalyst behavior. Extrudates were 1/8-inch-diameter cylinders with random lengths of approximately 1/8-inch, and the final catalyst composition was 12.5 percent cobalt, 1.2 percent thoria, 10-15 percent alumina, and the remainder ZSM-5.

The studies were carried out in a mixed reactor system as described by Berty (6). The catalyst extrudates were loaded into a 2-inch-diameter basket and supported by a stainless steel screen. Impeller speed was 1240 rpm. An outer furnace heated the reactor, while excellent bed temperature control was obtained by a modification that involved the installation of a coil in the reactor head through which air could flow for faster heat removal.

The schematic of the system is shown in Figure 1. Synthesis gas is stored in large gas holders at ambient conditions. The gas is then boosted to high pressures after going through a silica gel trap for dehumidification and an activated carbon trap to remove sulfur impurities. The high-pressured gas is stored in a bank of aluminum cylinders rather than carbon steel cylinders to prevent carbonyl formation. Before entering the system, the gas is again flowed through an activated carbon trap. The flow is metered and controlled by a mass flow meter, and hydrogen can be blended with the $\text{1H}_2\text{:1CO}$ synthesis gas via a similar apparatus. Products exit the reactor via a downward sloping heated line (200°C) and enter a hot trap (200°C) where heavy hydrocarbons, if produced, are condensed. Lighter products are condensed in water-cooled or air-cooled traps. The product gas is metered by a wet test meter and can be directed to an on-line gas chromatograph that can analyze hydrocarbons up to C_8 .

The catalyst was brought to synthesis conditions in an identical manner for each test. Initially the reactor was pressurized to 300 psig with hydrogen. The activation procedure began by flowing hydrogen at 1000 hr^{-1} space velocity over the catalyst while rapidly heating to 200°C . After maintaining this temperature level for two hours, the catalyst was heated to 350°C for twenty-one hours under the hydrogen flow. It has been reported in the literature that a 350°C reduction greatly enhances the hydrogen adsorption capacity of a cobalt catalyst (7). Afterwards, the catalyst temperature was reduced to 250°C and then the pressure was decreased to 100 psig. At these conditions the synthesis gas flow rate was incrementally increased over an hour until the design space velocity for the test was reached. Care was taken at this critical point so that temperature runaway did not occur. After this induction step, the pressure was increased to operating conditions, and afterwards the temperature was increased (10°C/hr) to synthesis conditions. Trap drainings, flow, and gas analyses were performed on a 24-hour basis for a material balance determination. All tests in this study used a $\text{1H}_2\text{:1CO}$ feed gas.

The gaseous and liquid products were characterized by various techniques. Product gas exiting the system was analyzed for hydrocarbons up to C_8 by gas chromatography. Liquid hydrocarbon samples, after a physical separation from the aqueous phase, were characterized by simulated distillation ASTM D-2887, fluorescent indicator adsorption ASTM D-1319, and bromine number ASTM D-1159. The aqueous fraction was analyzed by mass spectroscopy, and the water content was determined by the Karl Fischer reagent technique.

RESULTS AND DISCUSSION

To determine if deactivation would be a problem in the study, one of the first experiments in the process variable scan was a life test conducted at 280°C , 300 psig, and 1000 hr^{-1} space velocity of $\text{1H}_2\text{:1CO}$ synthesis gas. Data listed in Table 1 for test 1-39 at different times on stream indicate that catalyst deactivation is significant. The initial high ($\text{H}_2\text{+CO}$) conversion of 83.8 percent decreases after 417 hours on stream to 56.6 percent. The hydrocarbon product distribution also shifts to a lighter fraction with time, as noted by the increase in percent CH_4 (23.4 to 42.4) and by the decrease in $\text{C}_5\text{+}$ weight percent (61.0 to 38.5), which corresponds to the decreasing liquid product yield. The functionality of the liquid oil was constant throughout the test, with a high olefin (76) and low paraffin (20) and aromatic (4) percentages. Aqueous analyses indicated that +99 percent of this fraction was water. It

was concluded from this test that deactivation was a key factor, and subsequently all comparisons would be done after the same time on stream using a different catalyst charge for each test.

Test 1-42 was conducted to elucidate the role of the zeolite function of the bifunctional catalyst at the lower temperature of 280°C. Coprecipitated cobalt and thorium were added in the same proportion as the ZSM-5 based catalyst to calcined Catapal SB gamma alumina, and the mixture was then extruded with uncalcined alumina. When this test is compared to 1-39, the conversion versus time curves are almost identical, indicating that the Fischer-Tropsch component, Co-Th, is responsible for the synthesis activity of the catalyst and also is the functional component deactivating with time. However, the hydrocarbon distribution is different in each case, with the alumina based cobalt-thorium yielding a heavier product than the ZSM-5 based catalyst. This is evidenced in Table 1 by the greater wax fraction in the hydrocarbons with the alumina based catalyst (10.3 percent versus 1.8 percent) and less of the liquid oil fraction boiling in the gasoline range, as determined by simulated distillation (68 percent versus 89 percent).

The functionality of the liquid product oils indicates that more olefins are produced with the ZSM-5 based catalyst than with the alumina based catalyst. Proton NMR studies of the oils indicate that the ZSM-5 based catalyst produces a high degree of branching, whereas the alumina based catalyst product is linear. Also, β -olefins with negligible α -olefins are formed with the ZSM-5 based catalyst, whereas the opposite occurs with the alumina based catalyst.

The effect of reaction temperature was observed in four separate tests at 260°, 280°, 300°, and 320°C at process conditions of 300 psig and 4000 hr⁻¹ space velocity. Results are listed in Table 1. With an increase in temperature, the hydrocarbon distribution shifts to a lighter product, as indicated by the increasing CH₄ fraction, the decreasing C₅⁺ fraction, and the increasing fraction boiling in the gasoline-range. Also interesting is the functionality of the product oil. With a decrease in reaction temperature from 280°C, the olefin/paraffin ratio decreases and approaches a paraffinic product, which is characteristic of cobalt catalysts, thus indicating that at the lower temperature (< 260°C), the zeolite function does not significantly influence the reaction mechanism. The test at 300°C yielded an oil fraction not too different functionally from the 280°C test. However, at 320°C, a significant amount of aromatics was formed (46%), which can be attributed to the acid-catalyzed reactions within the zeolite framework at the higher temperature. No hydrocarbons above a carbon number of 12 were formed.

Unfortunately, at the elevated temperatures, the rate of deactivation is quite significant, as seen in Figure 2. As expected, initial conversions are greater at the higher temperatures, but the rate of deactivation is also greater at the higher reaction temperatures. Accelerated carbon or coke formation at the higher temperature could explain the rapid deactivation.

The effect of the promoter thorium can be determined by comparing test 1-57 (12.5% Co-ZSM-5) and test 1-41 (12.5% Co-1.2% ThO₂-ZSM-5), which are at the same process conditions. The thorium increases the activity of the cobalt-ZSM-5, as evidenced by the conversion data. Liquid products are more olefinic with the promoted catalyst. Also, the thorium shifts the product to a heavier hydrocarbon distribution, as noted by the decrease in the methane fraction, the increase in the C₅⁺ fraction, and the increase in the wax fraction.

The effects of different methods of catalyst pretreatment, which included calcination in air of only the zeolite component before mixing and extrusion, calcination in air of the total extruded catalyst, and chemically treating the zeolite before mixing and extrusion, were investigated. After the standard activation procedure and at process conditions of 4000 hr⁻¹ space velocity, 300 psig, and 280°C, the activities of all catalysts tested, as characterized by conversion, were identical. A catalyst air-calcined at 350°C exhibited similar results to an uncalcined catalyst activated in hydrogen at 350°C, and no major differences existed between the calcination of only the zeolite component as compared to calcination of the total catalyst.

Three tests with Co-Th-ZSM-5 were conducted at identical process conditions, with the only difference being the calcination temperatures of the respective catalysts: 538°C (test 2-6), 450°C (test 2-2), and no calcination (test 1-41). The simulated distillation results in Table 1 indicate that a lighter gasoline range liquid product is formed after the two higher temperature calcinations, although the conversions and liquid oil yields for all three tests are very similar. The aromatic fraction in the liquid oil increases (2, 7, and 10 percent) with the increasing temperature of calcination. Calcination evidently increases the strength of the acid sites in the zeolite component, and this leads to a greater aromatic formation.

In another comparison, the ZSM-5 component was exchanged with HCl (test 1-54) rather than the usual NH₄Cl exchange (test 1-41) with the purpose of increasing the strength of the acid sites. The uncalcined zeolites were then individually mixed with equal amounts of cobalt - thorium and extruded. Each catalyst was tested in a Berty reactor as in the previous preparative work: a space velocity of 4000 hr⁻¹ with 1H₂:1CO synthesis gas, 280°C, and 300 psig. Results indicate the activity of both catalysts was the same with time on stream. However, the product selectivity for the two catalysts was different. The product from the HCl-exchanged catalyst was much lighter than that from the NH₄Cl-exchanged catalyst, as seen by the difference in gasoline-range hydrocarbons (89 versus 70 percent). Although the functionality of the liquid product is still high in olefin content for both catalysts, the aromatic content from the HCl-exchanged catalyst was higher (11 percent) than that from the NH₄Cl-exchanged catalyst (2 percent).

SUMMARY

From this study with the promoted transition metal-zeolite combination, several conclusions can be made. At medium temperature and with a low H₂:CO ratio synthesis gas, the cobalt-thorium-ZSM-5 synthesizes a highly branched olefinic product. Deactivation at these conditions can be attributed to the Fischer-Tropsch component of the catalyst. As the higher optimum temperature for the catalytic activity of the zeolite component is approached, a high fraction of aromatics is formed in the liquid product. The effect of the addition of the promoter thorium to the transition metal-zeolite catalyst is to increase olefin production and to increase the amount of liquid hydrocarbon formation. A pretreatment step (calcination or chemical), which does not alter the synthesis activity of the catalyst, activates the acid sites of the zeolite component and thus increases production of aromatics.

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. Process Conditions and Synthesis Results

CFSTR Test No.	1-39	1-39	1-39	1-42	2-10	1-41	1-44	1-43	1-57	2-6	2-2	1-54
Hours on Stream	33	201	417	33	37	40	32	33	37	36	36	38
Space Velocity, hr ⁻¹	1000	1000	1000	1000	4000	4000	4000	4000	4000	4000	4000	4000
Temperature, °C	280	280	280	280	260	280	320	320	280	280	280	280
(H ₂ +CO) Conversion	83.8	67.9	56.6	80.5	25.9	61.4	66.7	54.8	55.4	64.4	66.7	63.7
H ₂ Conversion	93.3	87.1	76.0	91.7	33.9	77.9	82.3	68.8	72.9	82.5	84.8	82.3
Hydrocarbon Distribution, wt%												
CH ₄	23.4	34.5	42.4	22.5	17.6	18.1	38.8	65.5	26.5	20.0	18.5	21.2
C ₂ H ₆ +C ₂ H ₄	3.9	5.4	6.1	4.1	2.4	3.1	5.7	9.7	4.0	3.9	3.2	3.1
C ₃ H ₈ +C ₃ H ₆	5.9	6.4	7.8	5.9	5.1	5.2	5.2	5.2	7.4	4.9	4.0	3.7
C ₄ H ₁₀ +C ₄ H ₈	4.0	3.8	5.2	4.6	4.6	6.0	6.9	5.1	7.7	3.7	3.6	6.5
C ₅ +	61.0	49.6	38.5	52.6	54.7	62.9	43.3	14.5	54.4	66.4	70.0	65.4
Wax	1.8	0.3	0	10.3	15.6	4.8	0.1	0	0	1.1	0.8	0
Liquid Oil Product Composition, wt%												
Aromatics	4	2	2	2	3	2	4	46	4	10	7	11
Olefins	76	83	80	43	36	82	74	25	29	72	76	68
Saturates	20	15	18	55	61	16	22	29	67	18	17	21
Liquid in Gasoline												
Range (BP < 204°C), wt%	89	85	90	68	58	70	91	95	85	85	85	89
Liquid Yield, gm oil/ gm cat-hr	0.13	0.08	0.05	0.09	0.13	0.39	0.27	0.07	0.27	0.41	0.42	0.38

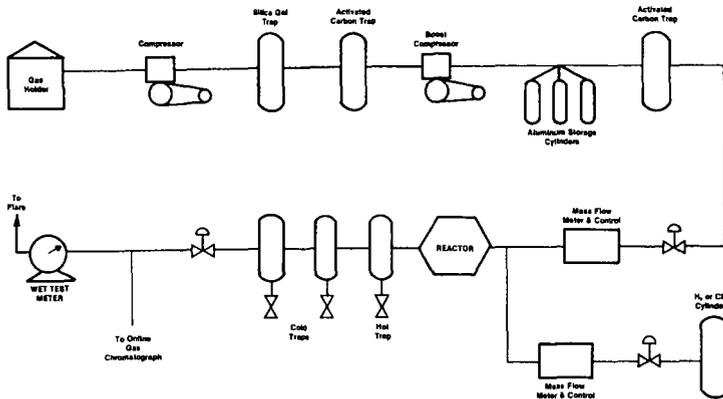


FIGURE 1. SCHEMATIC OF REACTOR SYSTEM

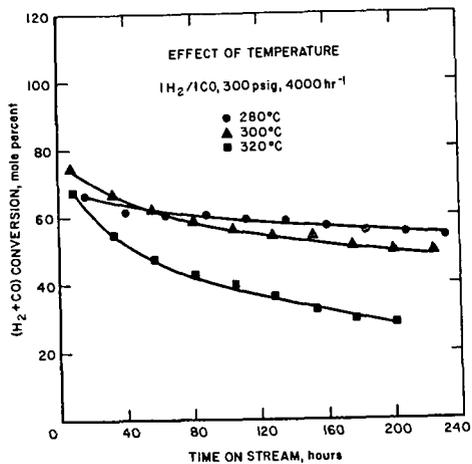


FIGURE 2. EFFECT OF REACTION TEMPERATURE ON CONVERSION WITH TIME