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Development of a Catalyst for Conversion
of Syngas-derived Materials to Isobutylene
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QUARTERLY TECHNICAL REPORT

The objective of this program is to develop an improved catalyst and process for the conversion of synthesis gas to isobutylene. The research will identify and optimize the key catalyst and process characteristics that give improved performance for CO conversion by a non-Fischer-Tropsch process.

INTRODUCTION

The need for development of alternate fuels in the United States is a national priority. Gasoline reformulation has also become a priority throughout the refining industry. Eliminating aromatics, olefins, and butanes from gasoline to meet the new environmental regulations will significantly lower the octane of the gasoline pool if other high-octane blending components are not available to replace them. In most proposed new gasoline formulations, the addition of oxygenates, such as methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), or tertiary amyl methyl ether (TAME), is being considered to maintain an acceptable octane.

The production of the ethers (MTBE and ETBE) will ultimately be limited by the availability of isobutylene (iC_4). Traditional commercial routes for producing iC_4 are unable to meet the large growth in demand anticipated for fuel ethers.

Developing a process to take advantage of the vast coal reserves of the United States by converting the coal to oxygenated gasoline blending components would be desirable. The technology

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already exists for making methanol from coal-derived syngas. Numerous commercial processes are also available to make MTBE from methanol and iC_4^- . A new technology that can be used to make iC_4^- from syngas would complement the syngas-to-methanol process and help to ease the anticipated shortages of iC_4^- . The main goal of this research is to develop a catalyst and technology that produce iC_4^- directly from coal-derived syngas and are capable of using a lower (0.5 to 1.0) $H_2:CO$ ratio.

This report covers the preliminary catalyst testing designed to verify literature data and to shake down the catalyst test unit.

RESEARCH RESULTS

A laboratory catalyst test system, diagrammed in Figure 1, was constructed. The system consists of:

- A gas feed section for the 1:1 $H_2:CO$ or nitrogen feeds with flow rates set by a metering valve
- A liquid feed section with flow rates set by a metering valve
- The reactor, rated for 2,250 psig at 550°C
- An on-line GC system for analyzing oxygen-containing products and heavier (C_4+) hydrocarbons
- A liquid trap for collecting the heavier product for mass balance and more detailed analysis
- A gas sample tube for collecting the gaseous products for analysis by off-line GC
- A gas flow measuring system for determining the effluent gas volume, which, combined with the gas analysis, is used for mass balance

The first catalyst, IS-1, was prepared following a similar procedure to the one used by Deflin.¹ Ammonium hydroxide was added to a solution of zirconyl chloride to precipitate the ZrO_2 catalyst. The precipitate was filtered, washed with distilled water to remove residual chloride, and dried at 150°C. The dried catalyst was calcined at 500°C for 2 hr in flowing air. The calcined catalyst had a surface area of 63 m^2/g .

The catalyst was placed in the reactor and activated to 450°C in flowing nitrogen. Then the catalyst was reduced at 600 psig and 450°C in flowing 1:1 $H_2:CO$ for 4 hr. A series of tests (DOE Run 1) at various temperatures, pressures, and space velocities was completed. The results are presented in Tables 1, 2, and 3.

Table 1 compares results at constant temperature and space velocity as a function of pressure. The conversion of CO and H₂ increases with pressure. Total C₄ selectivity increases with pressure but shifts toward increasing paraffin content. Table 2 compares results at constant pressure and space velocity as a function of temperature. The conversion of CO and H₂ increases with temperature. The selectivity to hydrocarbons increases, as does the paraffin-to-olefin ratio, with increasing temperature. Table 3 compares results at constant temperature and pressure as a function of space velocity. As expected, CO and H₂ conversion decreases with increasing space velocity. Carbon dioxide selectivity is essentially constant, and the paraffin-to-olefin ratio decreases with increasing space velocity. This data provide a baseline for future catalyst comparisons.

Table 1
Effects of Pressure on the Performance of a
ZrO₂ Isosynthesis Catalyst

	Periods		
	2	3	4
Temperature, °C	450	450	450
Pressure, psig	300	600	1,200
H ₂ /CO, molar	1.0	1.0	1.0
CO GHSV, cc/cc cat/hr	960	970	960
CO conversion, %	6.3	13.6	20.9
Selectivity, % C			
CO ₂	67.7	53.6	54.5
C ₁	19.4	17.4	19.1
C ₂ - C ₃	12.9	10.1	10.9
iC ₄	0	5.8	7.3
iC ₄ =	0	5.8	3.6
nC ₄ + nC ₄ =	0	0	0
C ₅ + + C ₅ + =	0	7.2	4.5

Table 2
Effects of Temperature on the Performance of a
ZrO₂ Isosynthesis Catalyst

	Periods		
	6	4	5
Temperature, °C	353	450	500
Pressure, psig	1,200	1,200	1,200
H ₂ /CO, molar	1.0	1.0	1.0
CO GHSV, cc/cc cat/hr	960	960	960
CO conversion, %	1.7	20.9	42.3
Selectivity, % C			
CO ₂	87.5	54.5	45.3
C ₁	12.5	19.1	21.3
C ₂ - C ₃	0	10.9	17.9
iC ₄	0	7.3	10.5
iC ₄ =	0	3.6	0
nC ₄ + nC ₄ =	0	0	3.0
C ₃ + + C ₃ + ⁻	0	4.5	1.9

Table 3
Effects of Space Velocity on the Performance of a
ZrO₂ Isosynthesis Catalyst

	8	4	7
Temperature, °C	450	450	450
Pressure, psig	1,200	1,200	1,200
H ₂ /CO, molar	1.0	1.0	1.0
CO GHSV, cc/cc cat/hr	540	960	2,100
CO conversion, %	36.8	20.9	16.7
Selectivity, % C			
CO ₂	48.8	54.5	49.4
C ₁	17.5	19.1	15.7
C ₂ - C ₃	10.1	10.9	11.1
iC ₄	11.1	7.3	9.0
iC ₄ =	3.7	3.6	9.0
nC ₄ + nC ₄ =	1.8	0	0
C ₃ + + C ₃ + ⁻	6.9	4.5	5.6

FUTURE WORK

This section discusses work in the first year of a three-year contract.

Catalyst Formulation

The preliminary evaluation of catalysts will consist of two phases. In the first phase of catalyst evaluation, materials that have been previously reported for the selective production of branched C_4 products from syngas, such as IS-1, will be reproduced and tested. The testing will provide a base of catalyst performance data that can be used for the direct comparison of different catalyst systems. In the next quarter, the effects of calcination temperature, (450°C to 600°C) and catalyst additives, (Y, Na, Li, and Cs) on ZrO_2 -based catalysts will be evaluated.

In the second phase of catalyst testing, new formulations will be evaluated to identify approaches for the development of a catalyst with performance exceeding that of previously described materials. Specific performance factors to be emphasized are catalyst activity and selectivity to C_4 branched products rather than C_1 - C_3 lights and saturated by-products. The primary goal will be to identify relationships between catalyst properties and performance for syngas conversion. Based on this understanding, further catalyst improvements can be developed.

Many of the previous reports of catalysts for the conversion of syngas to branched C_{4+} products indicate that C_1 compounds, methane or methanol, are primary by-products. These by-products suggest that the initial C-C bond formation is a slow step in the overall process. Thus, a multistage process using C_2 or C_3 intermediates formed in a first stage as feed to an isosynthesis second stage may be much more efficient than a single-stage system.

The use of new methods for the preparation of metal oxide catalysts with improved properties, such as regulated crystallite size, increased uniformity throughout the metal oxide particle, and increased surface area, is another approach that will be investigated. Various precipitation methods for the control of the metal oxide structure, the use of sol-gel technology for the preparation of metal oxide materials and supported metal oxide catalysts will be examined to achieve these goals.

Elucidation of Reaction Mechanism

An understanding of the reaction pathways occurring over the catalyst is important for the development of improved catalysts. Therefore, experiments will be carried out to probe the mechanism of syngas conversion over the best catalysts found in the first phase of catalyst screening. The emphasis of these studies will be to obtain practical mechanistic data sufficient to guide the development of further catalyst improvements. Experiments that can be used for the elucidation of specific aspects of the reaction pathway include testing at high space velocity, spiking experiments and ^{13}C labeling.

Process Concepts

The final goal is to identify potential process configurations that result in either improved activity or selectivity to the desired branched C_4 olefin or alcohol products. Approaches to be evaluated include recycle of $\text{C}_1\text{-C}_3$ unsaturated intermediates, such as alcohols, aldehydes, and olefins, ($\text{C}_2\text{-C}_3$) and multistage processes. Examples of multistage processes concepts include the conversion of $\text{C}_1\text{-C}_3$ intermediates formed over the syngas conversion catalyst to C_4 branched compounds and the initial conversion of syngas to methanol and higher linear alcohols followed by a separate aldol condensation step to give the desired branched products. One such multistage process would use a first-stage catalyst to selectively produce linear higher alcohols from syngas, such as the recently discovered MoS_2 -based catalysts that operate by a Fischer-Tropsch-type mechanism. A portion of the methanol and normal propanol that are produced over this first-stage catalyst is then passed over dehydrogenation-aldol coupling catalyst in the second stage to produce branched C_4 products.

REFERENCES

1. M. Deflin, J. C. Lambert, and P. E. Dejaifve, Canadian Patent 1,226,875 (1987).

FIGURE 1
LABORATORY CATALYST TEST SYSTEM

UOP 1011-20

APPENDIX

Run Summaries

Run Summary		Run:		Catalyst:		1	
						15-1	
Period	1	2	3	4	5	6	7
Temperature, C	400	450	450	450	500	353	448
Pressure, psig	300	300	500	1200	1200	1200	1200
GHSV, hr-1	950	950	950	950	950	950	2100
Mass Balance, %	105.1	108.4	109.3	114.7	128.2	105.1	110.3
Conversions, %							
C0	2.29	6.29	13.61	20.87	42.25	1.56	16.70
H2	4.92	9.03	17.37	24.00	44.15	2.73	20.95
Selectivities, C mole %							
C02	81.82	67.74	53.62	54.55	45.32	87.50	49.44
Hydrocarbon	18.18	32.26	46.38	45.45	54.68	12.50	50.56
HC Selectivities, C mole %							
Methane	100.00	60.00	37.50	42.00	39.04	100.00	31.11
Ethane	0.00	20.00	6.25	6.00	12.33	0.00	4.44
Ethylene	0.00	20.00	6.25	4.00	0.00	0.00	4.44
Propane	0.00	0.00	9.38	12.00	18.49	0.00	13.33
Propylene	0.00	0.00	0.00	0.00	2.05	0.00	0.00
I-Butane	0.00	0.00	12.50	16.00	19.18	0.00	17.78
N-Butane	0.00	0.00	0.00	0.00	5.48	0.00	0.00
I-butene	0.00	0.00	12.50	8.00	0.00	0.00	17.78
N-Butenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C5+	0.00	0.00	15.63	10.00	3.42	0.00	11.11

8	451	1200	540	117.7	108.8
9	451	1200	540	117.7	108.8
10	451	1200	540	117.7	108.8
11	451	1200	540	117.7	108.8
12	451	1200	540	117.7	108.8
13	451	1200	540	117.7	108.8
14	451	1200	540	117.7	108.8
15	451	1200	540	117.7	108.8
16	451	1200	540	117.7	108.8
17	451	1200	540	117.7	108.8
18	451	1200	540	117.7	108.8
19	451	1200	540	117.7	108.8
20	451	1200	540	117.7	108.8
21	451	1200	540	117.7	108.8
22	451	1200	540	117.7	108.8
23	451	1200	540	117.7	108.8
24	451	1200	540	117.7	108.8
25	451	1200	540	117.7	108.8
26	451	1200	540	117.7	108.8
27	451	1200	540	117.7	108.8
28	451	1200	540	117.7	108.8
29	451	1200	540	117.7	108.8
30	451	1200	540	117.7	108.8
31	451	1200	540	117.7	108.8
32	451	1200	540	117.7	108.8
33	451	1200	540	117.7	108.8
34	451	1200	540	117.7	108.8
35	451	1200	540	117.7	108.8
36	451	1200	540	117.7	108.8
37	451	1200	540	117.7	108.8
38	451	1200	540	117.7	108.8
39	451	1200	540	117.7	108.8
40	451	1200	540	117.7	108.8
41	451	1200	540	117.7	108.8
42	451	1200	540	117.7	108.8
43	451	1200	540	117.7	108.8
44	451	1200	540	117.7	108.8
45	451	1200	540	117.7	108.8
46	451	1200	540	117.7	108.8
47	451	1200	540	117.7	108.8
48	451	1200	540	117.7	108.8
49	451	1200	540	117.7	108.8
50	451	1200	540	117.7	108.8
51	451	1200	540	117.7	108.8
52	451	1200	540	117.7	108.8
53	451	1200	540	117.7	108.8
54	451	1200	540	117.7	108.8
55	451	1200	540	117.7	108.8
56	451	1200	540	117.7	108.8
57	451	1200	540	117.7	108.8
58	451	1200	540	117.7	108.8
59	451	1200	540	117.7	108.8
60	451	1200	540	117.7	108.8
61	451	1200	540	117.7	108.8
62	451	1200	540	117.7	108.8
63	451	1200	540	117.7	108.8
64	451	1200	540	117.7	108.8
65	451	1200	540	117.7	108.8
66	451	1200	540	117.7	108.8
67	451	1200	540	117.7	108.8
68	451	1200	540	117.7	108.8
69	451	1200	540	117.7	108.8
70	451	1200	540	117.7	108.8
71	451	1200	540	117.7	108.8
72	451	1200	540	117.7	108.8
73	451	1200	540	117.7	108.8
74	451	1200	540	117.7	108.8
75	451	1200	540	117.7	108.8
76	451	1200	540	117.7	108.8
77	451	1200	540	117.7	108.8
78	451	1200	540	117.7	108.8
79	451	1200	540	117.7	108.8
80	451	1200	540	117.7	108.8
81	451	1200	540	117.7	108.8
82	451	1200	540	117.7	108.8
83	451	1200	540	117.7	108.8
84	451	1200	540	117.7	108.8
85	451	1200	540	117.7	108.8
86	451	1200	540	117.7	108.8
87	451	1200	540	117.7	108.8
88	451	1200	540	117.7	108.8
89	451	1200	540	117.7	108.8
90	451	1200	540	117.7	108.8
91	451	1200	540	117.7	108.8
92	451	1200	540	117.7	108.8
93	451	1200	540	117.7	108.8
94	451	1200	540	117.7	108.8
95	451	1200	540	117.7	108.8
96	451	1200	540	117.7	108.8
97	451	1200	540	117.7	108.8
98	451	1200	540	117.7	108.8
99	451	1200	540	117.7	108.8
100	451	1200	540	117.7	108.8

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