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Development of a Catalyst for Conversion
of Syngas-derived Materials to Isobutylene
DE-AC22-91PC90042

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Contractor:
UOP
50 E. Algonquin Rd.
Des Plaines, IL 60017-5016

Author:
Gregory J. Gajda

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QUARTERLY TECHNICAL REPORT

Gasoline reformulation has become a priority throughout the refining industry. 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 will be unable to meet the large growth in demand anticipated for fuel ethers.

Developing a process in which coal could be converted to oxygenated gasoline blending components would take advantage of the vast coal reserves in the United States. The technology 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 could 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 contract is to develop a catalyst and technology that will produce iC_4 directly from coal-derived syngas and that is capable of utilizing a lower (0.5 to 1.0) $H_2:CO$ ratio. 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.

This report, which is the second quarterly report for contract DE-AC22-91PC90042, covers the testing of various ZrO_2 -based catalyst systems designed to examine the effects of catalyst

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preparation and process variables. Testing of precipitated ZrO_2 powders indicates improved performance at lower calcination temperatures, which yield higher surface areas. Additional improvements are achieved with a sol-gel catalyst despite a lower surface area. The addition of 1% Y to the sol-gel catalyst had a small detrimental effect on selectivity.

RESEARCH RESULTS

Catalyst Preparation

The first catalyst, IS-1, was prepared following the general procedure used by Deflin, et al.¹ The catalyst was prepared by using ammonium hydroxide to precipitate ZrO_2 from a solution of zirconyl chloride. 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 $63 \text{ m}^2/\text{g}$. Three additional calcination temperatures were also used. Calcining the dried catalyst at 450°C produced catalyst IS-2 with a surface area of $74 \text{ m}^2/\text{g}$. Similarly, calcining at 600°C produced catalyst IS-3 with a surface area of $28 \text{ m}^2/\text{g}$, and calcining at 550°C produced catalyst IS-4 with a surface area of $35 \text{ m}^2/\text{g}$. Two sol-gel catalysts were also prepared: IS-5, a pure ZrO_2 calcined at 600°C with a surface area of $45 \text{ m}^2/\text{g}$, and IS-6, a 1% Y- ZrO_2 catalyst calcined at 600°C with a surface area of $71 \text{ m}^2/\text{g}$.

Catalyst Testing

The catalysts were tested in the laboratory catalyst test system, described in Quarterly Report No 1.² The catalyst was activated 450°C in flowing nitrogen in the laboratory test system. The catalyst was then reduced at 600 psig and 450°C in flowing 1:1 H_2 :CO for 4 hr. Conversion and selectivity were measured at three combinations of temperature, pressure, and space velocity. These operating conditions were selected to give intermediate conversions (10-30%). A detailed summary of each successful run is given in the appendix.

Runs 2-4 were aborted because of coking problems. Sulfiding of the reactor prior to Run 5 appears to have cured the problem. Run 5 is a blank run to demonstrate the low background activity (0.4% CO conversion). Runs 6-8 are tests of precipitated ZrO_2 catalysts calcined at 600°C (IS-3), 550°C (IS-4), and 500°C (IS-1), respectively. Run 9 is a sol-gel ZrO_2 catalyst calcined at 600°C (IS-5) for comparison with Run 6, and Run 10 is a 1% Y- ZrO_2 sol-gel catalyst calcined at 600°C (IS-6) for comparison with Run 9.

The CO conversion for Runs 5-10 at the conditions of 450°C, 1,200 psig, and 1,920 GHSV, generally the maximum CO conversion conditions for each run, is given in Table 1. In general, the conversion increases with increasing surface area for the precipitated ZrO₂'s but is systematically higher for the sol-gel catalysts. The 1% Y-ZrO₂ catalyst has the highest conversion. The selectivity to iC₄ versus CO conversion is plotted in Figure 1. In general, the selectivity decreases with increasing conversion, except at low conversion where little iC₄ is produced. The sol-gel ZrO₂ catalyst is more selective than the precipitated catalysts, but the 1% Y-ZrO₂ catalyst is less selective (as a result of increased CH₄ production). The combination of high activity and selectivity for the sol-gel ZrO₂ catalyst gives an iC₄ yield of 2.2%, which is comparable to the best literature values for an unmodified ZrO₂ of 1.7% reported by Deflin, et al.¹

Table 1
Conversion of CO at Standard Conditions

Catalyst	Description	Run	Surface Area	CO Conversion
blank		5	—	0.4
IS-3	ZrO ₂ , 600°C	6	28	4.9
IS-4	ZrO ₂ , 550°C	7	35	15.3
IS-1	ZrO ₂ , 500°C	8	63	17.5
IS-5	ZrO ₂ , sol-gel, 600°C	9	45	23.9
IS-6	1% Y-ZrO ₂ , sol-gel, 600°C	10	71	26.4

FUTURE WORK

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 C₄ products from synthesis gas, 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 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

Figure 1

I-C4= Selectivity vs. CO Conversion

selectivity to C₄ branched products rather than C₁-C₃ lights and saturated by-products. The primary goal will be to identify relationships between catalyst properties and performance for synthesis gas conversion. Based on this understanding, further catalyst improvements can be developed.

The use of new methods for the preparation of metal oxide catalysts with improved properties such as regulation of crystallite size, increased uniformity throughout the metal oxide particle, and increased surface area is another approach that will be investigated. Variation of precipitation methods for the control of the metal oxide structure, the use of sol-gel technology for the preparation of metal oxide materials (such as IS-5), and supported metal oxide catalysts will be examined to achieve these goals.

In the next quarter, we plan to evaluate the effect of basic catalyst additives (Na, Ba, Cs) on ZrO₂-based catalysts. Literature reports claim improved selectivity for more basic catalysts.¹ In addition, the testing of sol-gel catalysts calcined at lower temperatures and the evaluation of CeO₂ catalysts are planned.

REFERENCES

1. M. Deflin, J. C. Lambert, and P. E. Dejaive, Canadian Patent 1,226,875 (1987).
2. P. T. Barger and G. J. Gajda, Quarterly Report No. 1, (1991).

APPENDIX
Run Summaries

Run Summary Run: 5
Catalyst:blank

Period	1	2	3	4
Temperature, C	401	451	502	502
Pressure, psig	610	1235	1210	1205
GH5U, hr-1	960	960	960	960
Mass Balance, %	131.5	124.9	108.4	105.1
Conversions, %				
C0	0.21	0.41	0.41	0.82
H2	3.26	4.80	2.57	6.87
Selectivities, C mole %				
C02	100.00	50.00	50.00	50.00
Hydrocarbon	0.00	50.00	50.00	50.00
HC Selectivities, C mole %				
Methane		100.00	100.00	100.00
Ethane		0.00	0.00	0.00
Ethylene		0.00	0.00	0.00
Propane		0.00	0.00	0.00
Propylene		0.00	0.00	0.00
I-Butane		0.00	0.00	0.00
N-Butane		0.00	0.00	0.00
I-Butene		0.00	0.00	0.00
N-Butenes		0.00	0.00	0.00
C5+		0.00	0.00	0.00

Run Summary	Run:	6
	Catalyst:	15-3

Period	1	2	3
Temperature, C	451	400	454
Pressure, psig	605	1200	1200
GHSV, hr-1	960	960	1920
Mass Balance, %	145.7	142.8	141.6

Conversions, %			
CO	7.55	2.71	4.88
H2	11.15	5.18	13.48

Selectivities, C mole %			
CO2	50.00	0.00	0.00
Hydrocarbon	50.00	100.00	100.00

HC Selectivities, C mole %			
Methane	26.32	30.77	25.00
Ethane	10.53	0.00	8.33
Ethylene	42.11	0.00	0.00
Propane	0.00	0.00	12.50
Propylene	0.00	0.00	0.00
I-Butane	0.00	0.00	16.67
N-Butane	0.00	0.00	0.00
I-butene	21.05	30.77	16.67
N-Butenes	0.00	0.00	0.00
C5+	0.00	38.46	20.83

Run Summary Run: Catalyst: 15-4 7

Period	1	3	4	5	6	7
Temperature, C	450	452	452	452	452	452
Pressure, psig	600	1200	1200	1205	1200	1200
GHSV, hr-1	960	1920	1920	1920	1920	1920
Mass Balance, %	102.4	134.7	131.4	130.2	135.2	129.0
Conversions, %						
C0	11.15	15.28	15.92	14.84	14.04	14.26
H2	15.37	17.69	16.33	17.08	19.23	18.07
Selectivities, C mole %						
C02	52.63	48.10	48.78	51.32	54.69	53.42
Hydrocarbon	47.37	51.90	51.22	48.68	45.31	46.58
HC Selectivities, C mole %						
Methane	33.33	21.95	23.81	27.03	31.03	29.41
Ethane	7.41	4.88	4.76	5.41	0.00	5.88
Ethylene	0.00	0.00	0.00	0.00	0.00	5.88
Propane	11.11	7.32	7.14	8.11	10.34	8.82
Propylene	0.00	0.00	0.00	0.00	0.00	0.00
I-Butane	14.81	9.76	9.52	10.81	13.79	11.76
N-Butane	0.00	0.00	0.00	0.00	0.00	0.00
I-butene	14.81	19.51	19.05	21.62	27.59	23.53
N-Butenes	0.00	0.00	0.00	0.00	0.00	0.00
C5+	18.52	36.59	35.71	27.03	17.24	14.71

Period	1	2	3
Temperature, C	451	400	452
Pressure, psig	600	1200	1200
GHSV, hr-1	960	960	1920
Mass Balance, %	112.3	101.3	116.6
Conversions, %			
C0	15.10	0.00	17.47
H2	12.35	0.00	19.56
Selectivities, C mole %			
C02	50.65		50.55
Hydrocarbon	49.35		49.45
HC Selectivities, C mole %			
Methane	26.32		28.89
Ethane	10.53		4.44
Ethylene	31.58		0.00
Propane	7.89		6.67
Propylene	0.00		0.00
I-Butane	0.00		8.89
N-Butane	0.00		0.00
I-butene	10.53		17.78
N-Butenes	0.00		0.00
C5+	13.16		33.33

Run Summary	Run:	9
	Catalyst: IS-5	

Period	1	2	3
Temperature, C	451	401	457
Pressure, psig	600	1200	1200
GHSV, hr-1	960	960	1920
Mass Balance, %	115.6	122.8	110.2
Conversions, %			
CO	22.41	15.57	23.94
H2	16.26	24.46	21.42
Selectivities, C mole %			
CO2	41.32	49.32	46.92
Hydrocarbon	58.68	50.68	53.08
HC Selectivities, C mole %			
Methane	15.49	18.92	24.64
Ethane	5.63	5.41	5.80
Ethylene	22.54	37.84	2.90
Propane	0.00	0.00	13.04
Propylene	4.23	0.00	4.35
I-Butane	5.63	0.00	11.59
N-Butane	0.00	0.00	0.00
I-butene	11.27	10.81	17.39
N-Butenes	0.00	0.00	5.80
C5+	35.21	27.03	14.49

Run Summary		Run: Catalyst:15-6		10
Period	1	2	3	
Temperature, C	453	403	452	
Pressure, psig	600	1200	1200	
GHSV, hr-1	960	960	1920	
Mass Balance, %	120.9	119.3	123.7	
Conversions, %				
CO	24.48	16.13	26.37	
H2	24.35	24.95	49.80	
Selectivities, C mole %				
CO2	49.61	60.00	52.00	
Hydrocarbon	50.39	40.00	48.00	
HC Selectivities, C mole %				
Methane	24.62	33.33	30.00	
Ethane	6.15	6.67	6.67	
Ethylene	6.15	0.00	3.33	
Propane	4.62	0.00	5.00	
Propylene	4.62	0.00	5.00	
I-Butane	6.15	13.33	13.33	
N-Butane	0.00	0.00	0.00	
I-Butene	12.31	13.33	13.33	
N-Butene	12.31	0.00	6.67	
C5+	23.08	33.33	16.67	

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