DOE/PC/90042--T3

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

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QUARTERLY TECHNICAL REPORT

The main goal of this contract is to develop a catalyst and technology that produces C_4 directly from coal-derived syngas and that uses 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 third quarterly report for contract DE-AC22-91PC90042, covers the testing of various CeO_2 - and ZrO_2 -based catalyst systems designed to examine the effects of catalyst preparation and process variables. Testing of sol-gel ZrO_2 catalysts calcined at lower temperatures, which yield higher surface areas, indicates improved performance. Additional improvements are achieved with Ba or Cs addition, which increases the percentage of tetragonal ZrO_2 . The addition of water to the feed stream had a beneficial effect on selectivity.

RESEARCH RESULTS

Catalyst Preparation

The preparation of catalysts IS-1 through IS-6 was discussed previously.¹ Seven sol-gel catalysts were prepared during the period as indicated in Table 1. In addition, two CeO_2 catalysts, one commercial powder (IS-8) and one precipitated (IS-9) were prepared.

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Table 1**Preparation of Sol-Gel Catalysts**

Catalyst	Catalyst Description	Surface Area, m ² /g	Calcination Temp, C°
IS-7	3% Si-ZrO ₂	120	600
IS-8	Commercial CeO ₂ Powder ^a	2.3	—
IS-9	Precipitate CeO ₂ Powder ^b	69.9	500
IS-10	1% Ba-ZrO ₂	71.4	550
IS-11	ZrO ₂	81.0	500
IS-12	2% Ba-ZrO ₂	95.6	—
IS-13	ZrO ₂	59.6	550
IS-14	1% Cs-ZrO ₂	64.6	500
IS-15	2% Ba-ZrO ₂ ^c	79.9	450
IS-16	ZrO ₂	73.6	500

^a From W.R. Grace

^b Prepared by a method analogous to IS-1 (see quarterly report No. 1)

^c Prepared by spray-impregnating Ba(NO₃)₂ onto IS-11 to determine effects of the method of Ba incorporation

Catalyst Testing

The catalysts were tested in the laboratory catalyst test plant, which was described in Quarterly Report No 1.² The catalysts were activated to 450°C in flowing nitrogen in the laboratory test plant. The catalysts were then reduced at 600 psig and 450°C in flowing 1:1 H₂:CO for 4 hours. Conversion and selectivity were measured at three combinations of temperature, pressure, and space velocity. These operating conditions were selected to give intermediate conversions of 10 to 30%. A detailed summary of each successful run is given in the appendix.

Runs 2 to 10 were discussed previously.¹ Run 11 evaluated IS-7 to determine the effects of Si on a Sol-Gel ZrO₂ base. Run 12 evaluated higher conversion levels using the ZrO₂ catalyst (IS-5) calcined at 600°C. Runs 13 and 14 evaluated the effect of two forms of CeO₂ catalyst: IS-8 and IS-9. Runs 15

and 17 evaluated IS-10 and IS-12 to determine the effects of Ba addition at the 1% and 2% levels on the Sol-Gel ZrO_2 base. Run 16 used IS-11 to evaluate the effects of lower calcination temperature (500°C). Run 18 used IS-11 to evaluate the effects of a lower H_2 :CO ratio of 0.7:1. Run 19 used IS-14 to evaluate the effects of adding Cs. Run 20 used IS-11 to evaluate an alternative method of Ba addition to the Sol-Gel ZrO_2 base. Run 21 used IS-16 to evaluate the effects of water addition to the feed on a Sol-Gel ZrO_2 catalyst.

The CO conversion and isobutylene yield for Runs 11 to 20 (except run 12) at the conditions of 450°C , 1,200 psig, and 1,920 gas hourly space velocity (GHSV), is given in Table 2. These conditions generally provide the maximum CO conversion for each run. Runs 5 to 10 is also provided in Table 2 for a comparison. The description of the catalysts also given in Table 2 includes the composition, method of preparation, and calcination temperature for each catalyst tested. Data for Runs 12 and 21 are at different conditions, as discussed later in this report. The conversion and yield data were obtained at relatively short times on-stream (~ 11 hours). The extent of catalyst deactivation has not been determined.

The freshly precipitated CeO_2 catalyst, IS-9, is by far the most active but is poorly selective to isobutene. The catalyst primarily produces saturated by-products. The commercial CeO_2 , IS-8, had low surface area and little activity.

Earlier tests show that lowering the calcination temperature of precipitated catalysts produced higher surface areas, higher tetragonal content, higher activity, and higher yields.¹ The ZrO_2 sol-gel catalysts show a similar relationship. A comparison of Run 9 (ZrO_2 calcined at 600°C) and Run 16 (ZrO_2 calcined at 500°C) shows that with the decrease in temperature: the surface area almost doubles ($81 \text{ m}^2/\text{g}$ vs. $45 \text{ m}^2/\text{g}$); the tetragonal phase increased from 10 to 55%; and CO conversion increases (23.9 vs. 30.2%). However, the isobutylene yield remained essentially the same (2.23 vs. 2.21%).

The addition of Si (Run 11) lowered the activity and selectivity compared to an unmodified ZrO_2 catalyst. Addition of Ba (Runs 15, 17, and 20) or Cs (Run 19) increased the tetragonal content and decreased activity but had little effect on yield. The method of adding the Ba, by either a sol-gel preparation (Run 17) or by spray impregnation (Run 20), had no significant effect on catalyst performance.

Table 2
Conversion of CO at Standard Conditions

Run	Cat.	Description	Calcination Temp, °C	SA, m ² /g	Tet, %	CO Conv., %	iC4 =, Yld %
5	blank			—	—	0.4	—
6	IS-3	ZrO ₂ , precipitated	600°C	28	5	4.9	0.79
7	IS-4	ZrO ₂ , precipitated	550°C	35	5	15.3	1.56
8	IS-1	ZrO ₂ , precipitated	500°C	63	15	17.5	1.54
9	IS-5	ZrO ₂ , sol-gel	600°C	45	10	23.9	2.21
10	IS-6	1% Y-ZrO ₂ , sol-gel	600°C	71	19	26.4	1.69
11	IS-7	3% Si-ZrO ₂ , sol-gel	600°C	120	—	18.7	0.77
12	IS-5	ZrO ₂ , sol-gel	600°C	45	10	34.9	1.51
13	IS-8	CeO ₂ , commercial		2	—	4.6	0.00
14	IS-9	CeO ₂ , precipitated	500°C	70	—	43.2	0.75
15	IS-10	1% Ba-ZrO ₂ , sol-gel	550°C	71	64	24.6	1.54
16	IS-11	ZrO ₂ , sol-gel	500°C	81	55	30.2	2.23
17	IS-12	2% Ba-ZrO ₂ , sol-gel	500°C	96	64	23.0	2.24
18	IS-11	ZrO ₂ , s-g, 0.7 H ₂ :CO	500°C	81	55	25.2	1.89
19	IS-14	1% Cs-ZrO ₂ , sol-gel	500°C	65	57	25.0	2.27
20	IS-15	2%Ba on IS-11	450°C	80	—	24.4	2.18
21	IS-16	ZrO ₂ , sol-gel	500°C	74	—	21.9	2.26

An evaluation of the ZrO₂ catalyst (IS-5) at higher conversion conditions (450°C, 1,200 psig, 480 GHSV as shown in Run 12) versus standard conversion conditions (450°C, 1,200 psig, 1920 GHSV as shown in Run 9) did not significantly increase the yield of isobutene. The additional conversion produced mostly saturated products, such as isobutane. This result suggests that higher yields of isobutene may require catalysts with higher activity at constant conditions.

Run 18 evaluated the effects of a lower $H_2:CO$ ratio feed (0.7:1) on catalyst performance. Comparing feed ratios of Run 18 with that of Run 16 (1:1 $H_2:CO$), the lower ratio feed produced a lower activity and a lower selectivity to isobutene. However, the total yield of isobutene and heavies is much greater (4.25% vs. 3.04%). This result suggests improved efficiency of the coupling process.

Run 21 evaluated the effects of water addition. Periods 1 and 2 used dry feed, while Period 3 used feed saturated with water vapor. The first period of the run had a CO conversion of 23.6% and an isobutene yield of 2.26%. Holding conditions constant, Period 2 showed a slight decrease in conversion (22.2%) and a sharp drop in yield (1.52%). Passing the feed through a water saturator at 25°C added 0.07 vol-% water vapor to the feed during Period 3. All other conditions were held constant. The CO conversion decreased to 21.9%, but yield improved to 2.26%, which is the same as the initial value.

CONCLUSIONS

Adding components such as Ba, Cs, Y, or Si to the ZrO_2 catalysts decreases conversion. Acidic components (Si) decrease the selectivity to isobutene, neutral components (Y) have small effects on selectivity, and basic components (Ba, Cs) slightly increase selectivity. The addition of water vapor appears to stabilize selectivity. Lower $H_2:CO$ ratios appear to favor the coupling reaction and increase heavies (mostly isopentenes) production. Increasing conversion by increasing temperature primarily increases the production of saturates. The CeO_2 catalysts are very active but poorly selective for isobutene.

FUTURE WORK

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 synthesis gas conversion. Based on this understanding, further catalyst improvements can be developed.

In the next quarter, the plan is to evaluate the effect of H₂:CO ratio, water addition, and catalysts containing active metals, such as Co and Cu, and to evaluate the effect of these parameters on activity and selectivity. Lower H₂:CO ratios appear to favor the coupling reaction and will be extended to still lower (0.5:1) ratios. Water appears to stabilize catalyst performance, which could be a key process characteristic. The analysis of the catalyst performance indicates a need for yet greater activities. Both Cu and Co are known for activity in syngas reactions (methanol synthesis and Fischer-Tropsch, respectively) and may provide a needed activity increase.

REFERENCES

1. G.J. Gajda, Development of a Catalyst for Conversion of Syngas-Derived Materials to Isobutylene, Quarterly Report No. 2, Prepared for United States Department of Energy Under Contract No. DE-AC22-91PC90042, Oct. 1991.
2. P.T. Barger and G.J. Gajda, Development of a Catalyst for Conversion of Syngas-Derived Materials to Isobutylene, Quarterly Report No. 1, Prepared for United States Department of Energy Under Contract No. DE-AC22-91PC90042, Aug. 1991.

APPENDIX

Run Summaries

Run Summary	Run:	11
	Catalyst:	15-7

Period	1	2	3
Temperature, C	450	401	452
Pressure, psig	600	1200	1200
GHSV, hr-1	960	960	1920
Mass Balance, %	112.2	118.5	112.0
Conversions, %			
CO	16.15	10.14	18.74
H2	19.23	24.00	24.17
Selectivities, C mole %			
CO2	50.00	59.77	51.02
Hydrocarbon	50.00	30.23	48.98
HC Selectivities, C mole %			
Methane	33.33	61.54	43.75
Ethane	9.52	15.38	8.33
Ethylene	4.76	0.00	0.00
Propane	14.29	23.08	6.25
Propylene	7.14	0.00	6.25
I-Butane	9.52	0.00	8.33
N-Butane	0.00	0.00	8.33
I-butene	9.52	0.00	8.33
N-Eutenes	0.00	0.00	0.00
C5+	11.90	0.00	10.42

I-Butene Yield, C mole %	0.77	0.00	0.76
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Run Summary		Run:	12
		Catalyst: 15-5	

Period	1	2	3
Temperature, C	450	442	449
Pressure, psig	1200	1200	1200
GHSV, hr-1	1920	960	480
Mass Balance, %	113.6	133.7	126.4

Conversions, %			
CO	18.64	18.36	34.94
H2	21.33	31.34	35.79

Selectivities, C mole %			
CO2	53.54	60.81	50.00
Hydrocarbon	46.46	39.19	50.00

HC Selectivities, C mole %			
Methane	30.43	44.83	31.63
Ethane	8.70	6.90	8.16
Ethylene	4.35	0.00	2.04
Propane	13.04	20.69	12.24
Propylene	6.52	0.00	3.06
I-Butane	8.70	13.79	16.33
N-Butane	0.00	0.00	4.08
I-butene	17.39	13.79	8.16
N-Butenes	0.00	0.00	4.08
C5+	10.87	0.00	10.20

I-Butene Yield, C mole %	1.51	0.99	1.43
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Run Summary		Run:	13
		Catalyst:	15-8

Period	1	2	3
Temperature, C	450	401	451
Pressure, psig	600	1200	1200
GHV, hr-1	960	960	1920
Mass Balance, %	107.0	112.0	107.2

Conversions, %			
CO	2.47	1.33	4.59
H2	9.60	11.31	12.61

Selectivities, C mole %			
CO2	50.00	66.67	47.83
Hydrocarbon	50.00	33.33	52.17

HC Selectivities, C mole %			
Methane	66.67	100.00	58.33
Ethane	33.33	0.00	16.67
Ethylene	0.00	0.00	0.00
Propane	0.00	0.00	25.00
Propylene	0.00	0.00	0.00
1-Butane	0.00	0.00	0.00
N-Butane	0.00	0.00	0.00
1-butene	0.00	0.00	0.00
N-Butenes	0.00	0.00	0.00
C5+	0.00	0.00	0.00

1-Butene Yield, C mole %	0.00	0.00	0.00
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Run Summary	Run: 14
Catalyst: 15-9	

Period	1	2	3
Temperature, C	451	400	452
Pressure, psig	600	1200	1200
GHSV, hr-1	960	960	1920
Mass Balance, %	112.4	121.7	132.7

Conversions, %			
CO	17.36	29.24	43.17
H2	19.36	36.02	47.68

Selectivities, C mole %			
CO2	48.91	49.11	43.88
Hydrocarbon	51.09	50.89	56.12

HC Selectivities, C mole %			
Methane	29.79	37.21	44.87
Ethane	8.51	11.63	14.10
Ethylene	0.00	0.00	1.28
Propane	25.53	17.44	19.23
Propylene	0.00	6.98	3.85
I-Butane	17.02	0.00	2.56
N-Butane	0.00	4.65	5.13
I-butene	8.51	4.65	2.56
N-Butenes	0.00	0.00	0.00
C5+	10.64	17.44	6.41

I-Butene Yield, C mole %	0.75	0.69	0.62
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Run Summary Run: 15
Catalyst: 15-10

Period	1	2	3
Temperature, C	451	400	454
Pressure, psig	600	1200	1200
GHSV, hr-1	960	960	1920
Mass Balance, %	112.7	109.8	114.5

Conversions, %			
CO	21.90	16.35	24.58
H2	21.05	22.57	25.96

Selectivities, C mole %			
CO2	58.26	61.18	54.89
Hydrocarbon	41.74	38.82	45.11

HC Selectivities, C mole %			
Methane	35.42	30.30	38.33
Ethane	12.50	6.06	13.33
Ethylene	4.17	0.00	3.33
Propane	12.50	9.09	10.00
Propylene	0.00	0.00	0.00
I-Butane	8.33	0.00	13.33
N-Butane	0.00	0.00	0.00
I-butene	16.67	24.24	13.33
N-Butenes	0.00	0.00	0.00
C5+	10.42	30.30	8.33

I-Butene Yield, C mole %	1.52	1.54	1.48
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Run Summary Run: 16
Catalyst: IS-11

Period	1	2	3
Temperature, C	449	402	454
Pressure, psig	600	1200	1200
GHSV, hr ⁻¹	960	960	1920
Mass Balance, %	114.9	111.8	117.6
Conversions, %			
CO	25.46	16.34	30.18
H ₂	22.93	20.51	31.83
Selectivities, C mole %			
CO ₂	52.55	64.29	50.89
Hydrocarbon	47.45	35.71	49.11
HC Selectivities, C mole %			
Methane	27.69	36.67	32.53
Ethane	9.23	6.67	7.23
Ethylene	6.15	0.00	2.41
Propane	13.85	0.00	14.46
Propylene	4.62	0.00	3.61
1-Butane	6.15	13.33	14.46
N-Butane	0.00	0.00	0.00
1-butene	18.46	26.67	14.46
N-Butenes	6.15	0.00	4.82
C ₅ +	7.69	16.67	6.02

1-Butene Yield, C mole % 2.23 1.56 2.14

Run Summary	Run: 17
Catalyst: 15-12	

Period	1	2	3
Temperature, C	451	400	451
Pressure, psig	600	1200	1200
GHSV, hr ⁻¹	960	960	1920
Mass Balance, %	114.5	110.8	117.3

Conversions, %			
CO	24.25	12.35	22.95
H2	23.46	20.69	25.79

Selectivities, C mole %			
CO2	54.62	66.67	56.91
Hydrocarbon	45.38	33.33	43.09

HC Selectivities, C mole %			
Methane	27.12	33.33	39.62
Ethane	10.17	9.52	11.32
Ethylene	6.78	0.00	3.77
Propane	15.25	14.29	5.66
Propylene	5.08	0.00	0.00
I-Butane	6.78	0.00	7.55
N-Butane	0.00	0.00	0.00
I-butene	20.34	19.05	22.64
N-Butenes	0.00	0.00	0.00
C5+	8.47	23.81	9.43

I-Butene Yield, C mole %			
	2.24	0.78	2.24

Run Summary	Run: 18
	Catalyst: 15-11

Period	1	2	3
Temperature, C	449	401	449
Pressure, psig	600	1200	1200
GHSV, hr-1	960	960	1920
Mass Balance, %	114.8	112.4	113.6
Conversions, %			
CO	25.71	15.08	25.20
H2	20.86	16.28	28.59
Selectivities, C mole %			
CO2	46.95	61.11	51.88
Hydrocarbon	53.05	38.89	48.13
HC Selectivities, C mole %			
Methane	19.54	31.43	31.17
Ethane	6.90	5.71	5.19
Ethylene	2.30	0.00	2.60
Propane	10.34	0.00	11.69
Propylene	3.45	0.00	3.90
I-Butane	4.60	11.43	10.39
N-Butane	0.00	0.00	0.00
I-butene	13.79	22.86	15.58
N-Butenes	4.60	0.00	0.00
C5+	34.48	28.57	19.48

I-Butene Yield, C mole %	1.88	1.34	1.89
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Run Summary		Run: 19
		Catalyst: 15-14

Period	1	2	3
Temperature, C	451	400	451
Pressure, psig	600	1200	1200
GHV, hr-1	960	960	1920
Mass Balance, x	115.3	119.7	116.0
Conversions, %			
CO	23.30	16.98	24.95
H2	24.00	35.22	23.46
Selectivities, C mole x			
CO2	58.54	58.43	59.40
Hydrocarbon	41.46	41.57	40.60
HC Selectivities, C mole x			
Methane	37.25	24.32	37.04
Ethane	7.84	0.00	7.41
Ethylene	7.84	0.00	3.70
Propane	0.00	0.00	0.00
Propylene	5.88	0.00	5.56
1-Butane	7.84	0.00	14.81
N-Butane	0.00	0.00	0.00
1-butene	23.53	21.62	22.22
N-Butenes	0.00	0.00	0.00
C5+	9.80	54.05	9.26

1-Butene Yield, C mole x	2.27	1.53	2.25
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Run Summary		Run: 20
		Catalyst: 15-15

Period	1	2	3
Temperature, C	451	401	450
Pressure, psig	600	1200	1200
GHSV, hr-1	960	960	1920
Mass Balance, %	111.9	113.2	116.7

Conversions, %			
CO	19.27	13.26	24.36
H2	21.05	21.42	25.25

Selectivities, C mole %			
CO2	59.00	70.59	51.49
Hydrocarbon	41.00	29.41	48.51

HC Selectivities, C mole %			
Methane	36.59	45.00	33.85
Ethane	9.76	10.00	6.15
Ethylene	4.88	0.00	3.08
Propane	7.32	0.00	13.85
Propylene	0.00	0.00	4.62
1-Butane	9.76	0.00	12.31
N-Butane	0.00	0.00	0.00
1-butene	19.51	20.00	18.46
N-Butenes	0.00	0.00	0.00
C5+	12.20	25.00	7.69

1-Butene Yield, C mole %	1.54	0.78	2.18
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Run Summary Run: 21
Catalyst: 15-16

Period	1	2	3
Temperature, C	451	451	451
Pressure, psig	605	610	615
GH5U, hr-1	960	960	960
Mass Balance, %	115.0	118.0	114.6
Conversions, %			
CO	23.58	22.24	21.85
H2	22.57	23.77	22.32
Selectivities, C mole %			
CO2	56.00	54.70	53.45
Hydrocarbon	44.00	45.30	46.55
HC Selectivities, C mole %			
Methane	29.09	43.40	40.74
Ethane	10.91	7.55	3.70
Ethylene	3.64	3.77	3.70
Propane	5.45	5.66	5.56
Propylene	5.45	0.00	0.00
1-Butane	7.27	15.09	14.81
N-Butane	0.00	0.00	0.00
1-butene	21.82	15.09	22.22
N-Butenes	7.27	0.00	0.00
C5+	9.09	9.43	9.26

1-Butene Yield, C mole % 2.26 1.52 2.26

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