2

CONTRACT TITLE AND NUMBER:
Development of a Catalyst for Conversion of Syngas-derived Materials to Isobutylene
DE-AC22-91PC90042

Date: September 10, 1993
Technical Progress Report No.: 5
Reporting Period: 3/31/92-6/30/92

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

Author:
Gregory J. Gajda

Contract Period: March 15, 1991 to March 14, 1994

TECHNICAL PROGRESS REPORT

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 using a lower H_2/CO ratio (0.5 to 1.0). 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 Quarterly Report No. 5 for contract DE-AC22-91PC90042, covers the testing of various zirconia (ZrO_2) and bismuth oxide (Bi_2O_3) based catalyst systems designed to examine the effects of catalyst preparation and process variables, especially the H_2/CO ratio. Testing of sol-gel ZrO_2 catalysts with lanthanum (La) or yttrium (Y) addition indicates a decrease in isobutene yield. An attempt to increase catalyst surface area by impregnating Zr on a sol-gel SiO_2 catalyst was unsuccessful. A Bi_2O_3 catalyst was very low in activity as a result of complete reduction to Bi metal. Increasing the H_2/CO ratio to 2:1 slightly increased the isobutene yield and improved catalyst stability.

RESEARCH RESULTS

Catalyst Preparation

The preparation of catalysts IS-1 through IS-20 was discussed previously.[1-4] Four sol-gel catalysts and one precipitated catalyst were prepared during the period (Table 1).

TABLE 1

PREPARATION OF CATALYSTS

Catalyst	Catalyst Description	Surface Area, m^2/g	Calcination Temp., °C
IS-17	2% Cs-ZrO_2	110	500
IS-21	ZrO_2	88.0	500
IS-22	5% Y-ZrO_2	123.0	500
IS-23	8% La-ZrO_2	119.0	500
IS-24	15% Zr-SiO_2	514.0	650
IS-25	Bi_2O_3*	-	500

* Precipitated

Catalyst Testing

The catalysts were tested in the laboratory catalyst test plant as described in Quarterly Report No 1.[2] The catalyst was activated to 450°C in flowing nitrogen and then reduced at 600 psig and 450°C in flowing H_2/CO for 4 hr. The H_2/CO ratio varied in some tests. Conversion and selectivity were measured at three combinations of temperature, pressure, and space velocity. These operating conditions were selected to give intermediate conversions (10 to 30%). A detailed summary of each successful run is given in the appendix.

Runs 2-30 were discussed previously.[1-4] Runs 31 through 38 were completed this quarter and are summarized in Table 2. Run 31 is a repeat of Run 28 but with water vapor used from the start of the run. At 0.5:1 H_2/CO, the isobutene yield is much higher (1.16 vs. 0.57%) with the added water and closer to the yield achieved at 1:1 H_2/CO in Run 22 (1.76%).

Runs 32 through 34 further investigate the effects of water vapor and feed H_2/CO ratio. Run 32 compared a new batch of sol-gel zirconia (IS-21) with the previous batch (IS-16). The test was conducted at 1:1 H_2/CO with no added water vapor. Comparing Run 32 with Run 21 (IS-16), the CO conversions and isobutene yields are similar (2.28 vs. 2.26%). Run 33 repeated Run 32 but with water vapor added. Comparing Run 33 with Run 32, the initial isobutene yield is much lower (1.53 vs. 2.28%), but data at the remaining periods give similar isobutene yields with (Run 33) or without (Run 32) water vapor added (see run sheets in the Appendix). This result suggests that the addition of water vapor may accelerate the aging or line-out process.

Run 34 compares the catalyst using 2:1 H_2/CO without water. A comparison of Run 34 with Run 32 gives a similar initial isobutene yield (2.33 vs. 2.28%). However, comparing the data at the third standard condition (450°C, 1200 psig, 1920 GHSV) gives a much higher isobutene yield for 2:1 H_2/CO than 1:1 H_2/CO (2.27 vs. 1.49%). This result, which suggests that the higher feed ratio slows or prevents the aging process, is consistent with the faster deactivation rates seen with low (0.5:1 H_2/CO) feed ratios.[4] In view of the better results, further testing will be conducted at 2:1 H_2/CO without water addition.

Runs 35 and 36 used the addition of Y or La to try to increase the tetragonal zirconia content of the sol-gel catalyst. The stabilizing effects of Y or La were reported by Mercera, et al.[5] The addition of La (Run 35) or Y (Run 36) had a generally negative effect on the isobutene yield. The yield for La is 1.13%, and the yield for Y is 1.14% compared to the unmodified zirconia with an isobutene yield of 2.33%. The yields were stable at the remaining test conditions and remained lower than the unmodified catalyst. In general, additives to zirconia have had minimal beneficial effects on the catalyst (Table 3). No further additive testing is planned for the isosynthesis program.

Run 37 tested the possible effect of surface area on performance. In general, the surface area of the sol-gel zirconia catalysts increases with decreasing calcination temperature but appears to reach a limit of about 100 m^2/g. To exceed this limit, a catalyst was prepared by impregnating a high-surface-area sol-gel silica support with zirconyl nitrate solution and calcining. The final catalyst (IS-

24) had a surface area of 514 m^2/g. Testing in Run 37 was disappointing: CO conversion was low, and no isobutene was formed. The high calcination temperature may have caused the zirconia to react with the silica to form a low-activity complex. Alternative methods to support zirconia and achieve high surface area will be attempted.

An interesting observation is that all the good isosynthesis catalysts (thoria [ThO_2], zirconia [ZrO_2], ceria [CeO_2]) are also good oxide ion conductors. Catalyst IS-25 was prepared by precipitating Bi_2O_3 from bismuth nitrate solution. The Bi_2O_3 is also known as a good oxide ion conductor and could test the relationship between isosynthesis catalysts and oxide ion conductors. Unfortunately, Run 38 produced poor conversion and no isobutene. Analysis of the reactor contents indicated that the Bi_2O_3 was reduced to Bi metal before achieving any significant CO conversion.

TABLE 2

CONVERSION OF CO AT STANDARD CONDITIONS

Run No.	Catalyst	Description	Feed H_2:CO Ratio	SA, m^2/g	% Tetragonal Phase	CO Conv., %	*i*C4= Yield, %
21	IS-16	ZrO_2, sol-gel	1:1	74	—	21.9	2.26
22	IS-17	2% Cs-ZrO_2, sol-gel	1:1	110	68	23.1	1.76
28	IS-17	2% Cs-ZrO_2, sol-gel	0.5:1	110	68	13.1	0.57
31	IS-17	2% Cs-ZrO_2, sol-gel	0.5:1	110	68	17.1	1.16
32	IS-21	ZrO_2, sol-gel	1:1	88	75	23.9	2.28
33	IS-21	ZrO_2, sol-gel	1:1	88	75	21.8	1.53
34	IS-21	ZrO_2, sol-gel	2:1	88	75	21.3	2.33
35	IS-23	8% La-ZrO_2, sol-gel	2:1	119	74	24.4	1.13
36	IS-22	5% Y-ZrO_2, sol-gel	2:1	123	63	23.7	1.14
37	IS-24	15% Zr-SiO_2, sol-gel	2:1	514	-	1.5	0.00
38	IS-25	Bi_2O_3, precipitated	2:1	-	—	2.2	0.00

CONCLUSIONS

Increasing the H_2/CO feed ratio to 2:1 increases the performance of the zirconia catalysts. Addition of La or Y to the catalyst has negative effects on the isobutene yield. Bi_2O_3 is inactive for syngas conversion due to ready reducibility to Bi metal. Supporting Zr on silica achieves high surface area, but low CO conversion, possibly due to the formation of a low-activity complex.

TABLE 3

EFFECT OF ADDITIVES TO ZIRCONIA CATALYSTS ON ISOBUTENE YIELD

Additive	Isobutene Yield, %
None	2.26
1% Y	1.69
3% Si	0.77
1% Ba	1.54
2% Ba	2.24
1% Cs	2.27
2% Cs	1.76
1% Cu	2.17
1% Co	2.14

FUTURE WORK

Previous work has demonstrated only one factor which consistently leads to improved catalyst performance: surface area. In the next quarter we will attempt catalyst modifications to increase surface area by supporting zirconia on high surface area supports and lowering calcination temperatures.

In view of the low isobutene yields achieved to date, a recycle process would be required. In the next quarter we will examine the effects of adding various possible intermediates (ethylene, propylene and ethanol) to the syngas feed.

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.

3. G.J. Gajda, Development of a Catalyst for Conversion of Syngas-Derived Materials to Isobutylene, Quarterly Report No. 3. prepared for United States Department of Energy under Contract No. DE-AC22-91PC90042, Jan. 1992.

4. G.J. Gajda, Development of a Catalyst for Conversion of Syngas-Derived Materials to Isobutylene, Quarterly Report No. 4. prepared for United States Department of Energy under Contract No. DE-AC22-91PC90042, Dec. 1992.

5. P. D. L. Mercera, et al., Appl. Catal., 78, 79-96, (1991).

APPENDIX

DETAILED RUN SUMMARY

Run Summary Run: 31
Catalyst: IS-17

Period	1	2	3	4	5	6	7
Temperature, C	450	450	448	448	448	447	448
Pressure, psig	610	605	610	610	610	610	605
GHSV, hr-1	960	960	960	960	960	960	960
Mass Balance, %	118.8	110.4	112.1	109.6	107.2	140.7	110.2
Conversions, %							
CO	17.05	11.06	10.66	9.83	6.91	6.94	6.04
H2	44.68	21.88	23.01	22.44	12.80	91.55	17.44
Selectivities, C mole %							
CO2	57.63	52.63	48.65	48.53	50.00	42.86	41.86
Hydrocarbon	42.37	47.37	51.35	51.47	50.00	57.14	58.14
HC Selectivities, C mole %							
Methane	32.00	38.89	34.21	34.29	43.48	30.00	32.00
Ethane	12.00	11.11	10.53	5.71	8.70	10.00	8.00
Ethylene	4.00	5.56	5.26	5.71	8.70	0.00	8.00
Propane	12.00	8.33	15.79	17.14	0.00	15.00	12.00
Propylene	6.00	0.00	0.00	0.00	0.00	0.00	0.00
I-Butane	8.00	11.11	10.53	11.43	0.00	0.00	0.00
N-Butane	0.00	0.00	0.00	0.00	0.00	0.00	0.00
I-butene	16.00	11.11	10.53	11.43	17.39	20.00	0.00
N-Butenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C5+	10.00	13.89	13.16	14.29	21.74	25.00	40.00
Oxygen Balance, %	136.00	111.11	94.74	94.29	100.00	75.00	72.00
I-Butene Yield, C mole %	1.16	0.58	0.58	0.58	0.60	0.79	0.00
I-C4H8/CH4, C-molar	0.50	0.29	0.31	0.33	0.40	0.67	0.00
I-C4H8/C4s, C-molar	0.67	0.50	0.50	0.50	1.00	1.00	0.00
I-C4s/C4s, C-molar	1.00	1.00	1.00	1.00	1.00	1.00	0.00
Isosynthesis Profile	0.71	0.89	0.67	0.80	1.00	0.80	0.00

Run Summary — Run: 32 — Catalyst: IS-21

Period	1	2	3	4	5	6
Temperature, C	449	400	450	450	450	450
Pressure, psig	610	610	1,210	1,210	1,210	1210
GHSV, hr-1	960	960	1920	1920	1920	1920
Mass Balance, %	112.4	100.2	111.1	111.5	111.6	112.2
Conversions, %						
CO	23.91	8.97	24.16	19.85	20.30	19.37
H2	22.39	13.28	25.61	21.70	21.51	21.33
Selectivities, C mole %						
CO2	57.14	68.18	51.08	50.94	50.46	47.12
Hydrocarbon	42.86	31.82	48.92	49.06	49.54	52.88
HC Selectivities, C mole %						
Methane	31.48	57.14	37.70	42.31	44.44	40.00
Ethane	11.11	14.29	9.84	7.69	7.41	7.27
Ethylene	7.41	0.00	3.28	3.85	3.70	3.64
Propane	5.56	0.00	9.84	0.00	0.00	10.91
Propylene	5.56	0.00	4.92	5.77	5.56	0.00
I-Butane	7.41	0.00	13.11	15.38	14.81	14.55
N-Butane	0.00	0.00	0.00	0.00	0.00	0.00
1-Butene	22.22	28.57	13.11	15.38	14.81	14.55
N-Butenes	0.00	0.00	0.00	0.00	0.00	0.00
C5+	9.26	0.00	8.20	9.62	9.26	9.09
Oxygen Balance, %	133.33	214.29	113.11	103.85	101.85	89.09
1-Butene Yield, C mole %	2.28	0.81	1.49	1.50	1.49	1.49
1-C4H8/CH4, C-molar	0.71	0.50	0.35	0.36	0.33	0.36
1-C4H8/C4s, C-molar	0.75	1.00	0.50	0.50	0.50	0.50
I-C4s/C4s, C-molar	1.00	1.00	1.00	1.00	1.00	1.00
Isosynthesis Profile	1.00	2.00	0.94	1.78	1.78	1.33

Run Summary — Run: 33 — Catalyst: IS-21

Period	1	2	3	4
Temperature, C	400	400	400	400
Pressure, psig	600	1,000	1,000	1,000
GHSV, hr-1	900	900	1,500	1,500
Mass Balance, %	111.1	104.1	115.3	116.7
Conversions, %				
CO	21.84	10.54	21.83	21.00
H2	27.75	6.04	21.64	21.27
Selectivities, C mole %				
CO2	60.53	61.27	49.52	52.21
Hydrocarbon	39.47	38.73	50.48	47.79
HC Selectivities, C mole %				
Methane	37.78	38.89	38.98	44.44
Ethane	13.33	11.11	10.17	7.41
Ethylene	4.44	0.00	3.39	3.70
Propane	0.00	0.00	5.08	0.00
Propylene	6.67	0.00	5.08	5.56
I-Butane	8.89	0.00	6.78	14.81
N-Butane	0.00	0.00	0.00	0.00
I-butene	17.78	22.22	13.56	14.81
N-Butenes	0.00	0.00	0.00	0.00
C5+	11.11	27.78	16.95	9.26
Oxygen Balance, %	153.33	172.22	98.31	109.26
I-Butene Yield, C mole %	1.53	0.86	1.49	1.49
I-C4H8/CH4, C-molar	0.47	0.57	0.35	0.33
I-C4H8/C4s, C-molar	0.67	1.00	0.67	0.50
I-C4s/C4s, C-molar	1.00	1.00	1.00	1.00
Isosynthesis Profile	1.09	2.00	0.86	1.78

Run Summary — Run: 34 — Catalyst: 16-21

Period	1	2	3	4	5	6	7
Temperature, F	451	404	[illegible]	450	451	451	477
Pressure, psig	605	1,210	1,210	1,210	1,210	1210	1210
GHSV, hr -1	980	[illegible]	[illegible]	[illegible]	[illegible]	1920	1920
Mass Balance, %	110.3	[illegible]	110.3	[illegible]	113.3	217.5	116.1
Conversions, %							
CO	27.33	18.98	30.11	29.07	26.69	29.33	35.96
H2	15.58	15.16	17.93	33.93	18.65	32.57	23.32
Selectivities, C mole %							
CO2	52.13	57.14	49.06	42.86	47.87	45.78	38.69
Hydrocarbon	47.87	42.86	50.94	57.14	52.13	54.22	61.31
HC Selectivities, C mole %							
Methane	33.33	33.33	40.74	36.54	44.90	40.00	41.67
Ethane	13.33	7.41	11.11	7.69	8.16	4.44	7.14
Ethylene	8.89	0.00	3.70	3.85	4.08	0.00	2.38
Propane	6.67	11.11	5.56	11.54	0.00	6.67	10.71
Propylene	0.00	0.00	0.00	0.00	0.00	0.00	3.57
I-Butane	8.89	14.81	14.81	15.38	16.33	17.78	19.05
N-Butane	0.00	0.00	0.00	0.00	0.00	0.00	4.76
I-butene	17.78	14.81	14.81	15.38	16.33	8.89	4.76
N-Butenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C5+	11.11	18.52	9.26	9.62	10.20	22.22	5.95
Oxygen Balance, %	108.89	133.33	96.30	75.00	91.84	84.44	63.10
I-Butene Yield, C mole %	2.33	1.20	2.27	2.56	2.27	1.41	1.05
i-C4H8/CH4, C-molar	0.53	0.44	0.36	0.42	0.36	0.22	0.11
i-C4H8/C4s, C-molar	0.67	0.50	0.50	0.50	0.50	0.33	0.17
i-C4s/C4s, C-molar	1.00	1.00	1.00	1.00	1.00	1.00	0.83
Isosynthesis Profile	0.92	1.60	1.45	1.33	2.67	2.40	1.20

Run Summary — Run: 35 — Catalyst: IS-23

Period	1	2	3	4	5	6
Temperature, C	451	401	449	449	450	452
Pressure, psig	600	1,200	1,200	1,200	1,200	1200
GHSV, hr-1	9000	18000	19,00	19,00	19,00	19,20	
Mass Balance, %	113.11	100.2	111.2	113.6	115.1	197.9
Conversions, %						
CO	24.36	16.67	28.01	27.42	29.70	29.03
H2	17.63	15.47	20.96	20.13	21.00	86.77
Selectivities, C mole %						
CO2	55.81	60.16	55.00	52.53	50.46	51.11
Hydrocarbon	44.19	36.84	45.00	47.47	49.54	48.89
HC Selectivities, C mole %						
Methane	39.47	47.62	48.89	51.06	50.00	47.73
Ethane	15.79	9.52	8.89	8.51	7.41	9.09
Ethylene	10.53	0.00	4.44	4.26	3.70	4.55
Propane	0.00	0.00	0.00	0.00	0.00	0.00
Propylene	0.00	0.00	0.00	0.00	0.00	0.00
I-Butane	10.53	0.00	17.78	17.02	22.22	18.18
N-Butane	0.00	0.00	0.00	0.00	0.00	0.00
I-butene	10.53	19.05	8.89	8.51	7.41	9.09
N-Butenes	0.00	0.00	0.00	0.00	0.00	0.00
C5+	13.16	23.81	11.11	10.64	9.26	11.36
Oxygen Balance, %	126.32	171.43	122.22	110.64	101.85	104.55
I-Butene Yield, C mole %	1.13	1.17	1.12	1.11	1.09	1.29
I-C4H8/CH4, C-molar	0.27	0.40	0.18	0.17	0.15	0.19
I-C4H8/C4s, C-molar	0.50	1.00	0.33	0.33	0.25	0.33
I-C4s/C4s, C-molar	1.00	1.00	1.00	1.00	1.00	1.00
Isosynthesis Profile	0.80	2.00	2.00	2.00	2.67	2.00

Run Summary Run: 36
Catalyst: IS-22

Period	1	2	3
Temperature, C	452	399	453
Pressure, psig	610	1210	1205
GHSV, hr-1	960	960	1920
Mass Balance, %	112.5	111.1	235.3
Conversions, %			
CO	23.65	15.90	18.52
H2	17.36	15.88	97.49
Selectivities, C mole %			
CO2	56.63	60.00	100.00
Hydrocarbon	43.37	40.00	0.00
HC Selectivities, C mole %			
Methane	41.67	40.91	
Ethane	11.11	0.00	
Ethylene	11.11	0.00	
Propane	0.00	0.00	
Propylene	0.00	0.00	
I-Butane	11.11	18.18	
N-Butane	0.00	0.00	
I-butene	11.11	18.18	
N-Butenes	0.00	0.00	
C5+	13.89	22.73	
Oxygen Balance, %	130.56	150.00	
I-Butene Yield, C mole %	1.14	1.16	
I-C4H8/CH4, C-molar	0.27	0.44	
I-C4H8/C4s, C-molar	0.50	0.50	
I-C4s/C4s, C-molar	1.00	1.00	
Isosynthesis Profile	1.00	0.00	

Run Summary Run: 37
Catalyst: IS-24

Period	1	2	3
Temperature, C	450	399	449
Pressure, psig	605	1210	1210
GHSV, hr-1	960	960	1920
Mass Balance, %	104.6	106.5	104.6
Conversions, %			
CO	1.48	5.16	2.95
H2	2.75	2.91	4.69
Selectivities, C mole %			
CO2	40.00	5.56	30.00
Hydrocarbon	60.00	94.44	70.00
HC Selectivities, C mole %			
Methane	100.00	11.76	71.43
Ethane	0.00	0.00	28.57
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	88.24	0.00
Oxygen Balance, %	66.67	5.88	42.86
I-Butene Yield, C mole %	0.00	0.00	0.00
i-C4H8/CH4, C-molar	0.00	0.00	0.00
I-C4H8/C4s, C-molar	0.00	0.00	0.00
I-C4s/C4s, C-molar	0.00	0.00	0.00
Isosynthesis Profile	0.00	0.00	0.00

Run Summary Run: 38
Catalyst IS-25

	1	2	3
Period			
Temperature, C	448	399	450
Pressure, psig	610	1210	1205
GHSV, hr-1	960	960	1920
Mass Balance, %	102.5	104.9	143.3
Conversions, %			
CO	2.17	0.89	6.73
H2	4.42	4.85	58.51
Selectivities, C mole %			
CO2	42.86	33.33	13.64
Hydrocarbon	57.14	66.67	86.36
HC Selectivities, C mole %			
Methane	100.00	100.00	21.05
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	78.95
Oxygen Balance, %	75.00	50.00	15.79
I-Butene Yield, C mole %	0.00	0.00	0.00
I-C4H8/CH4, C-molar	0.00	0.00	0.00
I-C4H8/C4s, C-molar	0.00	0.00	0.00
I-C4s/C4s, C-molar	0.00	0.00	0.00
Isosynthesis Profile	0.00	0.00	0.00