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

Author:
Gregory J. Gajda

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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 the Technical Progress Report No. 4 for contract DE-AC22-91PC90042, covers the testing of various ZrO_2 -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 1 or 2% cesium (Cs) addition indicates decreased stability at a $H_2:CO$ ratio of 0.5. The addition of cobalt (Co) or copper (Cu) to the base ZrO_2 catalyst results in a small activity gain, but a selectivity loss. This gain in Cu catalyst activity is mostly due to increased methane production. The Co catalyst shifts selectivity toward saturated products. The addition of water to the feed stream had a beneficial effect on stability. The addition of a basic clay had no effect on the activity or selectivity.

RESEARCH RESULTS

Catalyst Preparation

The preparation of catalysts IS-1 through IS-16 was discussed previously.^{1,2} One sol-gel catalyst was prepared during this reporting period, as were several spray-impregnated catalysts and one mixed catalyst (Table 1).

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TABLE 1
PREPARATION OF SOL-GEL CATALYSTS

Catalyst	Catalyst Description	Surface Area, m ² /g	Calcination Temp., °C
IS-14	1 % Cs-ZrO ₂	64.6	500
IS-16	ZrO ₂	73.6	500
IS-17	2 % Cs-ZrO ₂	110	500
IS-18	50 % IS-16 + 50 % Basic Clay	-	-
IS-19	1 % Cu-ZrO ₂ *	71.9	450
IS-20	1 % Co-ZrO ₂ *	71.9	450

* Prepared by spray-impregnating nitrate salt onto IS-16

Catalyst Testing

The catalysts were tested in the laboratory catalyst test plant as described in Quarterly Report No 1.² The catalyst was activated by flowing nitrogen over the catalyst at 450°C in the laboratory test plant. The catalyst was then reduced at 600 psig and 450°C in a H₂ and CO environment for 4 hr. Catalyst reduction was conducted at various of H₂ to CO ratios. 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 22 through 30 were completed this quarter and are summarized in Table 2. Run 21 is a standard test using the standard catalyst (IS-16). Runs 23, 29 and 30 were used to evaluate the effects

of adding a basic clay, copper or cobalt to the standard sol-gel catalyst (IS-16) calcined at 500°C. The basic clay was added in Run 23 to determine if increased basicity would improve Isosynthesis performance. Comparison of Runs 23 and 21 shows that the addition of the basic clay had little effect on the performance. Copper and cobalt were added to the catalyst to try to increase the activity for CO conversion. Comparing Runs 29 and 21, conversion increased slightly but selectivity dropped with copper addition for a slightly lower yield of isobutene. In Runs 30 and 21, conversion increased, but selectivity to isobutene dropped sharply using cobalt; the result was an initially lower isobutene yield. With continuing time-on-stream, the conversion and selectivity converged toward the unmodified catalyst, possibly as a result of gradual coking of the cobalt function.

The 2% Cs-ZrO₂ catalyst (IS-17) was used in a series of tests to evaluate the effect of feed H₂/CO ratio on CO conversion and *i*C₄ = yield. The initial test at 1:1 H₂/CO (Run 22) can be compared with Run 21 with the standard catalyst (IS-16). The conversion of the IS-17 catalyst in Run 22 is slightly higher, but selectivity to isobutene is much lower; the result was a reduced isobutene yield. The IS-17 catalyst was then tested at 0.5:1 H₂/CO in Run 24. Conversion and isobutene yield were both lower at the lower feed ratio, and conversion appeared to be deactivating.

Previous work has demonstrated a stabilizing effect of water addition³. The IS-17 catalyst was tested at the lower feed ratio (0.5 H₂:CO) and saturated with water at room temperature in Run 25. The addition of water had a moderate effect, but deactivation continued.

An attempt to raise conversion by increasing the reactor temperature resulted in plugging the reactor. When the reactor was opened, several of the steel spacer screens used to position the catalyst in the reactor were found to be eroded and covered with coke. The screens appear to have reacted with the feed at higher temperatures.

To check for an adverse effect caused by the screens, Run 25 was repeated (at 0.5 H₂:CO) with non metallic spacers (run 26). This run showed a greater influence of water on stabilization of the catalyst, but conversion and yield were still lower than at 1:1 H₂/CO feed ratio. Finally, a run was

conducted at constant test conditions (475°C, 600 psig, 960 GHSV) to evaluate the stability at the lower feed ratio (Run 28). Conversion decreased steadily. The run was divided into periods during which the GC analysis was taken, as indicated in the run sheets. No water was present during Periods 1 through 3. Adding water to the feed in Periods 4 through 10 did not stop or significantly slow the deactivation rate.

To determine if this effect was caused by the catalyst, the 1 % Cs-ZrO₂ catalyst (IS-14) was tested at the lower (0.5:1) feed ratio (Run 27). With water present, the conversion and yield were lower, at 0.5:1 H₂/CO compared to 1:1 H₂/CO in Run 19, but the catalyst was relatively stable. This result implies that the poor conversion and yield performance is due to the lower feed ratio.

CONCLUSIONS

The addition of Cu, Co, or basic clays to the ZrO₂ catalysts has little effect on CO conversion or isobutene selectivity. In general, unmodified zirconia appears to give the best isobutene yield. Lower H₂/CO ratios appear to increase the rate of deactivation and, at 0.5:1 H₂/CO, significantly decrease the CO conversion and isobutene yield.

FUTURE WORK

Previous work has demonstrated only two factors that consistently lead to improved catalyst performance: surface area and percent tetragonal zirconia content. In the next quarter, we will attempt catalyst modifications to increase these two parameters. Specifically, the addition of Y or La is reported to stabilize zirconia at close to 100% tetragonal content⁴.

In view of the stability problems experienced at low H₂/CO feed ratios, higher ratios will be investigated for possible activity, selectivity, and stability improvements. The effect of H₂/CO ratio and water addition will also be investigated. Catalysts containing phase stabilizers, such as Y and La, will be investigated next quarter.

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., %	iC4= Yield, %
19	IS-14	1 % Cs-ZrO ₂ , sol-gel	1:1	65	57	25.0	2.27
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
23	IS-18	50 % IS-16 + hydrotalcite	1:1	-	-	25.8	2.23
24	IS-17	2 % Cs-ZrO ₂ , sol-gel	0.5:1	110	68	15.7	1.14
25	IS-17	2 % Cs-ZrO ₂ , sol-gel	0.5:1	110	68	17.5	1.13
26	IS-17	2 % Cs-ZrO ₂ , sol-gel	0.5:1	110	68	12.6	1.17
27	IS-14	1 % Cs-ZrO ₂ , sol-gel	0.5:1	65	57	17.8	1.71
28	IS-17	2 % Cs-ZrO ₂ , sol-gel	0.5:1	110	68	13.1	0.57
29	IS-19	1 % Cu-ZrO ₂ , sol-gel	1:1	72	-	27.9	2.17
30	IS-20	1 % Co-ZrO ₂ , sol-gel	1:1	72	—	28.7	1.43

REFERENCES

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

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APPENDIX

DETAILED RUN SUMMARY

Run Summary

Run: 22
Catalyst: 15-17

Period	1	2	3
Temperature, °C	440	400	450
Pressure, psig	600	1200	1200
GHSV, hr ⁻¹	900	900	1000
Mass Balance, %	160.8	115.4	113.4
Conversions, %			
CO	23.13	16.39	19.24
H2	85.61	73.64	21.78
Selectivities, C mole %			
CO2	53.33	62.79	53.33
Hydrocarbon	46.67	37.21	46.67
HC Selectivities, C mole %			
Methane	24.49	25.00	30.61
Ethane	12.24	6.25	8.16
Ethylene	4.08	0.00	4.08
Propane	18.37	0.00	6.12
Propylene	6.12	0.00	6.12
I-Butane	8.16	12.50	8.16
N-Butane	0.00	0.00	0.00
I-butene	16.33	25.00	16.33
N-Butenes	0.00	0.00	0.00
C5+	10.20	31.25	20.41
Oxygen Balance, %	114.29	168.75	114.29
I-Butene Yield, C mole %	1.76	1.52	1.50
i-C4H8/CH4, C-molar	0.67	1.00	0.53

Period	1	2	3
Temperature, °C	450	400	450
Pressure, psia	600	1,200	1,200
GHSV, hr ⁻¹	900	900	1,020
Mass Balance, %	115.6	143.3	117.1
Conversions, %			
CO	25.79	16.74	26.33
H ₂	25.09	72.63	25.61
Selectivities, C mole %			
CO ₂	55.40	61.25	53.47
Hydrocarbon	44.60	38.75	46.53
HC Selectivities, C mole %			
Methane	29.03	25.81	31.34
Ethane	9.68	6.45	5.97
Ethylene	3.23	0.00	2.99
Propane	4.84	9.68	4.48
Propylene	4.84	0.00	4.48
I-Butane	6.45	0.00	11.94
N-Butane	0.00	0.00	0.00
I-butene	19.35	25.81	17.91
N-Butenes	6.45	0.00	5.97
C ₅ +	16.13	32.26	14.93
Oxygen Balance, %	124.19	158.06	114.93
I-Butene Yield, C mole %	2.23	1.67	2.19
i-C ₄ H ₈ /CH ₄ , C-molar	0.67	1.00	0.57

Run Summary	Run: 24
	Catalyst: 15-17

Period	1	2	3
Temperature, °C	451	450	450
Pressure, psia	600	1210	1220
GHSV, hr ⁻¹	960	960	1920
Mass Balance, %	112.4	110.1	111.1
Conversions, %			
CO	15.71	8.08	12.03
H2	27.17	23.06	25.83
Selectivities, C mole %			
CO2	60.91	63.64	57.14
Hydrocarbon	39.09	36.36	42.86
HC Selectivities, C mole %			
Methane	32.56	30.00	33.89
Ethane	9.30	10.00	11.11
Ethylene	4.65	0.00	5.56
Propane	6.98	15.00	8.33
Propylene	6.98	0.00	0.00
I-Butane	9.30	0.00	11.11
N-Butane	0.00	0.00	0.00
I-butene	18.60	20.00	11.11
N-Butenes	0.00	0.00	0.00
C5+	11.63	25.00	13.89
Oxygen Balance, %	155.81	175.00	133.33
I-Butene Yield, C mole %	1.14	0.59	0.57
i-C4H8/CH4, C-molar	0.57	0.67	0.29

Run Summary

Run: 25
Catalyst: 15-17

Period	1	2	3	4
Temperature, °C	450	400	449	430
Pressure, psia	600	1000	1000	1000
GHSV, hr ⁻¹	960	960	1020	960
Mass Balance, %	114.0	117.9	109.7	177.5
Conversions, %				
CO	17.49	16.22	31.25	86.49
H ₂	30.85	44.11	21.11	90.94
Selectivities, C mole %				
CO ₂	59.68	52.07	43.21	62.38
Hydrocarbon	40.32	47.93	51.79	37.62
HC Selectivities, C mole %				
Methane	32.00	41.38	31.03	47.08
Ethane	12.00	12.24	6.90	16.62
Ethylene	4.00	3.45	6.90	0.62
Propane	12.00	10.34	10.34	20.31
Propylene	6.00	5.17	0.00	1.85
I-Butane	8.00	6.90	13.79	2.46
N-Butane	0.00	0.00	0.00	4.92
I-butene	16.00	6.90	13.79	0.00
N-Butenes	0.00	0.00	0.00	0.00
C5+	10.00	8.62	17.24	6.15
Oxygen Balance, %	148.00	108.62	93.10	165.85
I-Butene Yield, C mole %	1.13	0.54	0.59	0.00
i-C ₄ H ₈ /CH ₄ , C-molar	0.50	0.17	0.44	0.00

Run Summary

Run: 26
Catalyst: 15-17

Period	1	2	3	4
Temperature, °C	450	450	451	474
Pressure, psig	600	1220	1215	1215
GHV, hr-l	960	960	1020	960
Mass Balance, %	112.3	115.5	120.5	146.3
Conversions, %				
CO	12.55	13.11	16.20	24.36
H2	23.06	30.84	30.59	38.14
Selectivities, C mole %				
CO2	61.63	52.08	59.13	50.44
Hydrocarbon	38.37	47.92	40.87	49.56
HC Selectivities, C mole %				
Methane	27.27	41.30	29.79	24.78
Ethane	6.06	13.04	8.51	7.08
Ethylene	6.06	4.35	4.26	1.77
Propane	9.09	6.52	6.33	7.96
Propylene	0.00	6.52	6.33	2.65
i-Butane	12.12	8.70	8.51	21.24
n-Butane	0.00	0.00	0.00	3.54
i-Butene	24.24	8.70	25.53	10.62
n-Butenes	0.00	0.00	0.00	7.08
C5+	15.15	10.87	10.64	13.27
Oxygen Balance, %	160.61	108.70	144.68	101.77
i-Butene Yield, C mole %	1.17	0.55	1.69	1.23
i-C4H8/CH4, C molar	0.89	0.21	0.86	0.43

Run Summary

Run: 27
Catalyst: 15-14

Period	1	2	3
Temperature, °F	449	461	449
Pressure, psia	6.00	12.15	12.10
GHSV, hr ⁻¹	900	900	1920
Mass Balance, %	119.1	119.7	118.7
Conversions, %			
CO	17.81	19.00	17.23
H ₂	29.79	25.92	31.12
Selectivities, C mole %			
CO ₂	64.80	73.53	62.30
Hydrocarbon	35.20	26.47	37.70
HC Selectivities, C mole %			
Methane	31.82	38.89	34.78
Ethane	9.09	0.00	8.70
Ethylene	4.55	0.00	4.35
Propane	6.82	16.67	6.52
Propylene	0.00	0.00	0.00
I-Butane	9.09	0.00	8.70
N-Butane	0.00	0.00	0.00
I-butene	27.27	44.44	26.09
N-Butenes	0.00	0.00	0.00
C ₅ +	11.36	0.00	10.87
Oxygen Balance, %	184.09	277.78	165.22
I-Butene Yield, C mole %	1.71	1.18	1.69
i-C ₄ H ₈ /CH ₄ , C-molar	0.86	1.14	0.75

	Run Summary				Run: 28		Catalyst: IS-17	
	1	2	3	4	5	6	7	8
Period	475	475	475	475	473	474	475	476
Temperature, C	605	605	600	600	605	605	610	610
Pressure, psig	960	960	960	960	960	960	960	960
GHSV, hr ⁻¹	151.7	113.1	111.3	109.6	107.6	106.7	150.8	105.1
Mass Balance, %								
Conversions, %								
CO		13.06	11.40	9.91	8.49	8.05		3.48
H2		28.26	25.56	24.44	18.90	18.60		12.80
Selectivities, C mole %								
CO2		52.75	54.43	52.94	48.28	47.27		52.17
Hydrocarbon		47.25	45.57	47.06	51.72	52.73		47.83
HC Selectivities, C mole %								
Methane		41.86	44.44	43.75	40.00	37.93		54.55
Ethane		9.30	11.11	6.25	6.57	6.90		0.00
Ethylene		4.65	5.56	6.25	0.00	0.00		0.00
Propane		13.95	16.67	18.75	10.00	10.34		0.00
Propylene		0.00	0.00	0.00	0.00	0.00		0.00
I-Butane		9.30	11.11	12.50	13.33	13.79		0.00
N-Butane		0.00	0.00	0.00	0.00	0.00		0.00
I-butene		9.30	11.11	12.50	13.33	13.79		0.00
N-Butenes		0.00	0.00	0.00	0.00	0.00		0.00
C5+		11.63	0.00	0.00	16.67	17.24		45.45
Oxygen Balance, %		111.63	119.44	112.50	93.33	89.66		109.09
I-Butene Yield, C mole %		0.57	0.58	0.58	0.59	0.59		0.00
i-C4H8/CH4, C-molar		0.22	0.25	0.29	0.33	0.36		0.00

Period	9	10
Temperature, C	474	475
Pressure, psig	610	610
GHSV, hr ⁻¹	960	960
Mass Balance, %	102.4	120.7
Conversions, %		
CO	1.83	2.05
H ₂	12.20	72.12
Selectivities, C mole %		
CO ₂	66.67	66.67
Hydrocarbon	33.33	33.33
HC Selectivities, C mole %		
Methane	100.00	100.00
Ethane	0.00	0.00
Ethylene	0.00	0.00
Propane	0.00	0.00
Propylene	0.00	0.00
I-Butane	0.00	0.00
N-Butane	0.00	0.00
I-butene	0.00	0.00
N-Butenes	0.00	0.00
C ₅ +	0.00	0.00
Oxygen Balance, %	200.00	200.00
I-Butene Yield, C mole %	0.00	0.00
i-C ₄ H ₈ /CH ₄ , C-molar	0.00	0.00

Run Summary

Run: 29
Catalyst: 15-19

Period	1	2	3
Temperature, °F	449	403	450
Pressure, psig	610	1210	1200
GHSV, hr ⁻¹	960	960	1000
Mass Balance, %	117.6	114.9	120.6
Conversions, %			
CO	27.90	24.82	30.38
H2	27.19	29.65	31.75
Selectivities, C mole %			
CO2	51.95	55.56	55.95
Hydrocarbon	48.05	44.44	44.05
HC Selectivities, C mole %			
Methane	40.54	78.33	62.16
Ethane	5.41	0.00	2.70
Ethylene	5.41	0.00	2.70
Propane	4.05	0.00	4.05
Propylene	4.05	0.00	0.00
I-Butane	5.41	0.00	5.41
N-Butane	0.00	0.00	0.00
I-butene	16.22	13.33	16.22
N-Butenes	5.41	0.00	0.00
C5+	13.51	8.33	6.76
Oxygen Balance, %	108.11	125.00	127.03
I-Butene Yield, C mole %	2.17	1.47	2.17
i-C4H8/CH4, C-molar	0.40	0.17	0.26

Run Summary

Run:

30

Catalyst: 15-20

Period	1	2	3
Temperature, °F	450	450	450
Pressure, psia	610	1210	1210
GHSV, hr ⁻¹	960	960	1000
Mass Balance, %	119.5	110.5	120.2
Conversions, %			
CO	28.67	23.41	30.60
H2	25.96	23.35	29.20
Selectivities, C mole %			
CO2	49.38	61.60	50.58
Hydrocarbon	50.63	38.40	49.42
HC Selectivities, C mole %			
Methane	24.69	33.33	27.06
Ethane	9.88	4.17	7.06
Ethylene	0.00	0.00	0.00
Propane	14.81	0.00	17.65
Propylene	3.70	6.25	3.53
i-Butane	14.81	8.33	14.12
n-Butane	4.94	0.00	4.71
1-butene	9.88	16.67	14.12
n-Butenes	4.94	0.00	0.00
C5+	12.35	31.25	11.76
Oxygen Balance, %	97.53	160.42	102.35
i-Butene Yield, C mole %	1.43	1.50	2.14
i-C4H8/CH4, C-molar	0.40	0.50	0.52

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