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

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

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QUARTERLY TECHNICAL 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 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 seventh quarterly report 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 low calcination temperature and mild reaction conditions (low temperature, low pressure and low space velocity). Testing of solvent-extracted sol-gel ZrO_2 catalysts indicates a decrease in isobutene yield. Lowering the reaction temperature, pressure and space velocity resulted in a small improvement in isobutene yield. Three extended runs demonstrated reasonable catalyst stability.

In view of the generally poor isobutene yields, the emphasis in this project will shift to isoalcohol production.

RESEARCH RESULTS

Catalyst Preparation

The preparation of catalysts IS-1 through IS-28 was discussed previously.^{1,2,3,4,5,6} Four sol-gel catalysts and three solvent extracted catalysts were prepared during the period, as indicated in Table 1.

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Table 1

Preparation of Catalysts

Catalyst	Catalyst Description	Surface Area, m ² /g	Calcination Temp, °C
IS-13	ZrO ₂	60	550
IS-29	1% Y-ZrO ₂ /n-C ₇ ^a	-	450
IS-30	1% Cs-ZrO ₂ /EtOH ^a	-	450
IS-31	1% Cs-ZrO ₂ /Me ₂ CO ^a	-	450
IS-32	ZrO ₂	95	475
IS-33	ZrO ₂	107	450
IS-34	ZrO ₂	122	425

^a Solvent Extracted

Catalyst Testing

The catalysts were tested in the laboratory catalyst test plant, described in Quarterly Report No 1.² The catalyst was activated to 400°C in flowing nitrogen in the laboratory test plant. The catalyst was then reduced at 600 psig and 400°C in flowing H₂:CO for 4 hr. The ratio of H₂ to CO 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 (10-30%). A detailed summary of each successful run is given in the appendix.

Runs 2-47 were discussed previously.^{1,2,3,4,5,6} Runs 48 through 59 were completed this quarter and are summarized in Table 2. Previous work indicated that lower catalyst calcination temperatures yield higher surface area catalysts and better isobutene yields.^{1,2} Runs 48 through 50 used catalysts that had been solvent extracted to remove sol-gel residue and permit lower calcination temperatures. However, the isobutene yields are below those from the reference catalyst in run 34.

Run 51 tested the effects of methanol addition to the feed. The products were dimethyl ether and methane. This completes the evaluation of potential recycle intermediates. None of the

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materials tested (ethylene, propylene, ethanol or methanol) yields isobutene when added to the feed to simulate recycle.

Runs 52 through 56 tested the effects of lower temperature and lower pressure on isobutene yield. Work by Maruya, et al., indicated high isobutene selectivities under mild conditions.⁷ By extending the calcination time, usable catalysts were obtained at calcination temperatures as low as 425°C. Comparison of run 34 with runs 52 through 56 indicates small improvements in the maximum isobutene yield. Lowering the H₂:CO from 2:1 to 1:1 reduced the isobutene yield due to more rapid deactivation.

Runs 57 through 59 were extended tests of catalyst performance to evaluate short-term stability. Run 57 shows high isobutane and low isobutene yields due to hydrogenation activity from the reactor internals. Runs 58 and 59 used a modified reactor to avoid the hydrogenation problem. Runs 58 and 59 indicate reasonable stability over the tested conditions. The isobutene yield as a function of time is given in Figures 1 and 2. The vertical lines represent condition changes. Plots of isobutene yield as a function of CO conversion are given in Figures 3 and 4. As can be seen from Figures 3 and 4, isobutene yield appears to reach a limit of about 4% as CO conversion increases. Thus any gains in selectivity at mild conditions are compensated by lower conversions and hence lower yields. As conversion increases with decreasing space velocity, the isobutene yield appears to converge to the same limit.

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Table 2
Conversion of CO at Maximum Isobutene Yield

Run	Cat.	Description	Feed H ₂ :CO Ratio	CO Conv., %	iC4 = Yld, %
34	IS-21	ZrO ₂ , sol-gel	2:1	21.3	2.33
48	IS-29	1% Y-ZrO ₂ , extracted	2:1	27.0	1.86
49	IS-30	1% Cs-ZrO ₂ , extracted	2:1	29.7	1.76
50	IS-31	1% Cs-ZrO ₂ , extracted	2:1	28.3	1.53
51	IS-13	ZrO ₂ , sol-gel	2:1	19.6	1.70
52	IS-13	ZrO ₂ , sol-gel	2:1	20.5	2.00
53	IS-32	ZrO ₂ , sol-gel	2:1	16.4	2.41
54	IS-33	ZrO ₂ , sol-gel	2:1	28.9	3.70
55	IS-34	ZrO ₂ , sol-gel	2:1	31.7	3.75
56	IS-33	ZrO ₂ , sol-gel	1:1	23.0	2.32
57	IS-21	ZrO ₂ , sol-gel	2:1	33.8	1.24
58	IS-32	ZrO ₂ , sol-gel	2:1	27.8	3.57
59	IS-33	ZrO ₂ , sol-gel	2:1	25.5	3.17

CONCLUSIONS

Reducing the catalyst calcination temperature increases the surface area and improves the isobutene yield. A limit is reached at 425°C calcination temperature. Using mild reaction conditions, isobutene selectivity can be slightly improved, but the overall yield tends to a limit of about 4% as CO conversion increases.

Addition of methanol to the feed results in the formation of methane and dimethyl ether. Thus intermediate recycle is not a viable option for Isosynthesis catalysts.

FUTURE WORK

In view of the low isobutene yield by direct synthesis and the failure of potential recycle intermediates to produce isobutene, no further work in Isosynthesis will be conducted. The research effort will shift to developing higher alcohol (IsoAlcohol) synthesis catalysts.

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