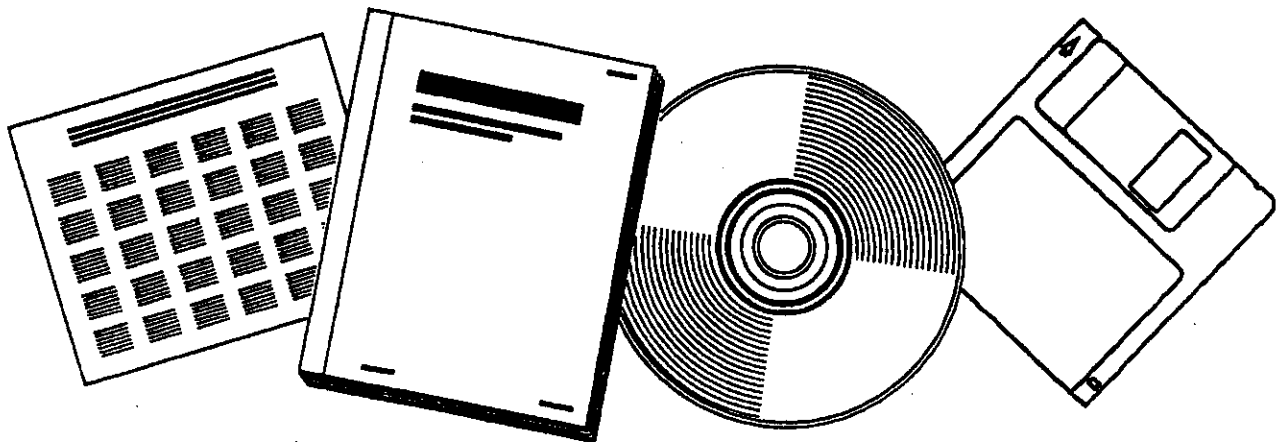**NTIS**
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IMPROVED FISCHER-TROPSCH SYNTHESIS CATALYSTS FOR INDIRECT COAL LIQUEFACTION. QUARTERLY TECHNICAL PROGRESS REPORT NO. 8, 1 JULY-30 SEPTEMBER 1987

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IMPROVED FISCHER-TROPSCH SYNTHESIS CATALYSTS
FOR INDIRECT COAL LIQUEFACTION

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SUMMARY

The monoruthenium cluster catalyst with a molecular sieve support and the tetraruthenium cluster catalyst with a sodium-Y zeolite support have been examined for Fischer-Tropsch Synthesis (FTS) performance at high pressure (6.9 MPa) in a slurry reactor and compared with conventional ruthenium with an alumina support and clean fused iron catalysts. Of the four catalysts tested, only the conventional ruthenium catalyst exhibited a chain growth factor of 0.88 and a methane selectivity of 6.6%, which are typical of slurry reactor results reported for iron catalysts under similar conditions. The other three catalysts tested showed low chain growth factors (ranging from 0.44 to 0.57) and high methane selectivity (ranging from 20 to 32%). We were not able to determine a chain growth probability factor for these catalysts in the wax range because the field ionization mass spectrometry (FIMS) results were inconclusive as a consequence of the presence of a very large (octacosane) solvent peak.

A cobalt catalyst with approximately 50% sulfur coverage was prepared and tested for FTS activity and selectivity at ambient pressure and compared with the FTS performance of the clean and fully sulfided cobalt catalysts. Although the results of sulfur treatment of the cobalt catalyst were not as striking as those for the fused iron catalysts, the introduction of sulfur caused a decrease in methane selectivity and an increase in olefin selectivity with only a moderate decline in activity.

EXPERIMENTAL RESULTS

Task 2: Medium-Level Sulfur Treatment of Co/Al₂O₃ Catalyst

The alumina-supported cobalt FTS catalyst was treated with H_2S until
sulfur was chemisorbed to a coverage of about one-half saturation. After
a more severe passivation procedure (exposure to 99.5% CO at 523 K), the
rate of sulfur adsorption at 425 K was slowed to about 0.4 monolayers per
hour in a recirculating stream of 30 ppm H_2S in 100-kPa H_2. After
reduction at 773 K, the catalyst was characterized by H_2 and CO
chemisorption and tested for FTS performance.

Task 3: FTS Testing of Clean and Sulfur-Treated Co/Al₂O₃ Catalysts

The medium-level sulfur-treated cobalt catalyst was examined for FTS
activity and product distribution with 1:1 H_2:CO synthesis gas at 100 kPa
and 525 K (Table 1). It showed reduced FTS activity relative to that of
the fresh cobalt catalyst but, unlike the sulfur-treated fused iron
catalyst, only a moderate decrease in methane selectivity. The olefin-
to-paraffin ratio for light hydrocarbons for the sulfur-treated cobalt
catalyst (3:1) was also lower than that for the medium-level, sulfur-
treated fused iron catalyst (20:1). Unlike the sulfur-treated fused iron
catalyst, which showed an increase in olefin selectivity relative to that
of the clean iron catalyst, the sulfur-treated cobalt catalyst showed a
decrease in light olefin selectivity compared to that of the clean cobalt
catalyst under similar conditions.

Task 4: Evaluation of Improved FTS Catalysts

The FTS activity and selectivity in the slurry phase were examined
for four catalysts: the allyl-derived Ru monomer on a molecular sieve
support, the aluminum-hydridocarbonyl-derived Ru_4 cluster catalyst on an
Na-Y zeolite support, a conventional Ru catalyst on alumina, and the
fused iron standard catalyst (Table 2). The reactor set-up was similar

Table 1

FIXED-BED FTS PERFORMANCE OF CLEAN AND SULFUR-TREATED
COBALT CATALYSTS

Catalyst	Temperature (K)	Pressure (MPa)	H_2/CO Ratio	Run Duration (h)	CO_2	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	Total	Chain Growth Factor[b]	Olefin to n-Paraffin Ratio[c]	Methane Selectivity[d]
Clean 10 wt% Co/Al$_2$O$_3$	573	0.1	1	20	33.79	112.44	9.66	14.67	8.94	4.56	2.81	1.54	0.89	0.51	0.34	278.09	0.38	3.8	45
	548	0.1	1	2	78.75	261.95	24.41	39.86	18.95	7.32	3.55	1.62	0.75	0.33	0.22	585.76	0.47	4.7	43
	548	0.1	1	26	29.99	86.67	15.17	12.82	6.67	2.91	1.78	0.93	0.52	0.28	0.18	221.12	0.54	10.6	43
High-Level Sulfur-Treated 10 wt% Co/Al$_2$O$_3$	548	0.1	1	21	2.75	2.88	1.02	0.69	0.28	0.14	0.08	0.06				9.69	0.49		32
Medium-Level Sulfur-Treated 10 wt% Co/Al$_2$O$_3$	523	0.1	1	23	21.639	103.57	9.42	16.65	9.53	5.44	3.15	1.73	1.00	0.49	0.29	284.03	0.56	0.21	39

[a] NGHSV = 600 h^{-1}; Product rate for each carbon number includes n-paraffins and α- and β-olefins; total product rate is on a carbon-atom basis.

[b] Average chain growth factor for C_{30} hydrocarbons.

[c] Average olefin to paraffin ratio for C_2 to C_4 hydrocarbons.

[d] C_1 rate/(total rate) × 100%.

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Table 2

FTS PERFORMANCE OF FUSED IRON, CONVENTIONAL
RUTHENIUM, AND RUTHENIUM CLUSTER CATALYSTS
IN A SLURRY REACTOR AT 7 MPa

Catalyst	Temperature (K)	Pressure (MPa)	H_2/CO Ratio	Run Duration (h)	Product Rate (nmol/s/g cat)					Chain Growth Factor[a]	Methane Selectivity[b]
					CO_2	C_1	C_2	C_3	C_4		
Clean Fused Iron	493	6.9	1	48	90.9	11.6	6.2	5.9	3.2	0.57	32
Ru$_4$/Na-Y Zeolite 0.61 wt% Ru	493	6.9	1	48	15.9	9.0	2.2	1.35	0.57	0.44	34
Ru/5A Molecular Sieve 0.37 wt% Ru	493	6.9	1	48	0.26	0.54	0.106	0.04	0.018	0.45	20
Conventional Ru/Al$_2$O$_3$ 0.50 wt% Ru	473	6.9	1	48	1.09	0.24	0.0063	0.022	0.019	0.88	6.6

[a] For C_2-C_4 fraction
[b] Estimated using chain growth factor for the C_2-C_4 fraction and assuming Anderson-Shultz-Flory product distribution.

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to that used by Huff and Satterfield.[1] In a 300-mL slurry reactor, 2 g
of powdered catalyst was used with 50 g of n-octocosane wax (n-$C_{28}H_{58}$,
99%, Alfa Chemical) with 1:1 $CO:H_2$ syngas at 60 atm and 483 K (10K) for
48 hours. The gas outlet was connected to a high temperature trap
(100°C). The hydrocarbon distribution of the product gas up through C_4
was directly analyzed periodically by capillary GC with flame ionization
detection (FID). Condensation in the sample lines precluded observation
of hydrocarbons above butane.

The liquid product distribution was analyzed by FIMS after the
synthesis run. We were unable to detect higher hydrocarbons from any of
these slurry runs because of the high concentration of the n-octocosane.

[1]G. A. Huff, Jr., and C. N. Satterfield, Ind. Eng. Chem. Fundam. 21,
479 (1982).

DISCUSSION

The results of the slurry reactor experiments neither deny nor
verify the hypothesis that the cluster catalysts can produce a narrowed
FTS product distribution. The FIMS analysis of slurry liquid samples at
the end of the experiments was not adequate even to resolve the high
molecular weight product distribution for the conventional catalysts, and
we could not have expected to measure the product distribution in the
C_{12+} range for the cluster catalysts. Additional slurry runs with much
longer reaction times (at least 200 hours) must be performed to test the
cluster hypothesis.