Fischer-Tropsch Co/Ru Catalyst Development

by

R. R. Frame and H. B. Gala

UOP
Des Plaines, Illinois

Contract No.: DE-AC22-89PC89869

Period of Performance: September 1989 - September 1993

Abstract

The objective of this contract is determining whether a benefit can be obtained from incorporating a small amount of ruthenium (Ru) into a supported cobalt (Co) catalyst for slurry autoclave processing and whether a low methane-producing catalyst can result. Recent work on this contract has centered on the development of high-activity Co-based Fischer-Tropsch catalysts supported on a steamed and acid-washed Y zeolite. The preparation, characterization, and performance evaluation of these catalysts is reviewed.

These catalysts are prepared by the impregnation of Co and other metals onto a steamed and acid-washed Y zeolite followed by calcination and reduction. Manganese, zirconium, and sometimes Ru are used in addition to Co. The support, method of impregnation, and use of zirconium and manganese in addition to Co are integral parts of the supported catalyst developed under a previous DOE contract to a division of Union Carbide that is now part of UOP. The support was chosen because the steaming procedure creates many pores in the 50 to 100 Å diameter range, a size considered ideal for supporting Co crystallites for Fischer-Tropsch reaction.

Catalyst physical properties are described. The most active catalyst is one containing 28 wt-% Co (no Ru). Its properties are discussed in detail as are the results of STEM analysis before and after reduction.

Most performance evaluations were done in a fixed-bed pilot plant although in one case a catalyst was evaluated in a slurry autoclave plant. Performance comparisons of the previously developed catalyst (8 wt-% Co) and the new catalysts are presented. These data show that catalyst activity increased with Co level up to at least 28 wt-% Co. With this high level of Co, the incorporation of a small amount of Ru did not produce a more active catalyst. In fact, the one such catalyst evaluated to date was not conversion stable. Included in the performance summaries are comparisons of the light product selectivities of the new catalyst and those obtained from the earlier 8 wt-% Co catalyst.

Finally, the two runs, fixed-bed and slurry autoclave reactors, performed with fresh samples of one of the new catalysts are compared.

Fischer-Tropsch Cobalt-Ruthenium Catalyst Development

UOP 2148-1

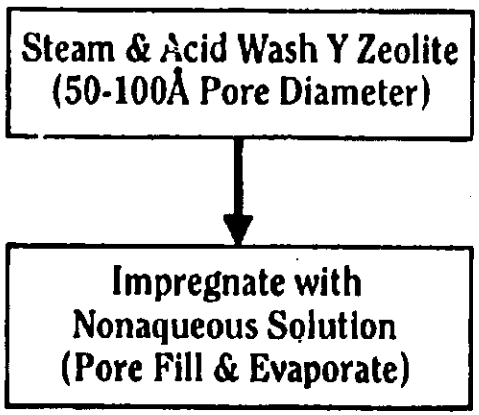
Objective of the Contract

- Develop Cobalt-Based F-T Catalyst for Methane-Derived Synthesis Gas

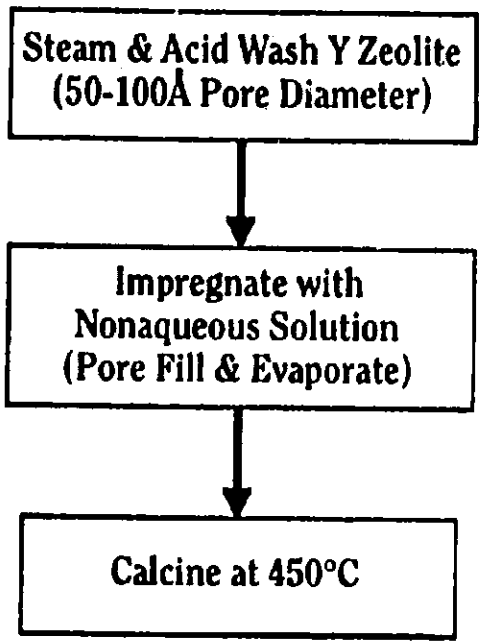
Catalyst Preparation Method

Steam & Acid Wash Y Zeolite
(50-100Å Pore Diameter)

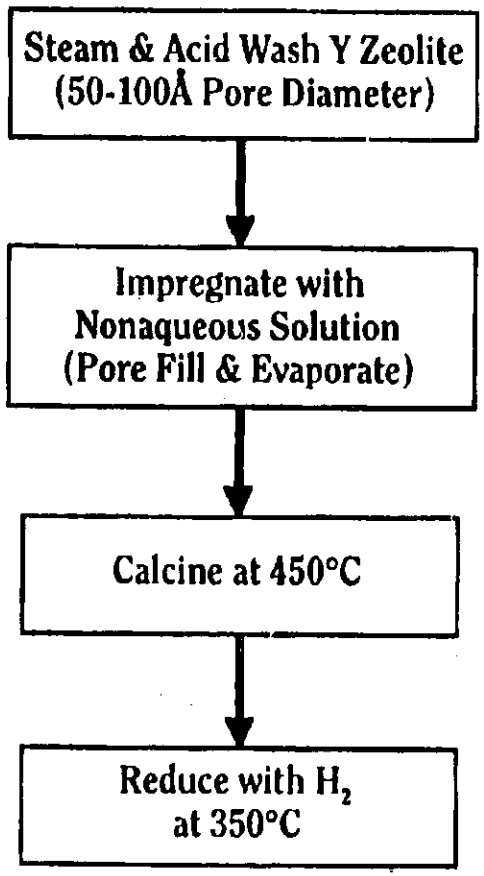
Catalyst Preparation Method



Catalyst Preparation Method



Catalyst Preparation Method



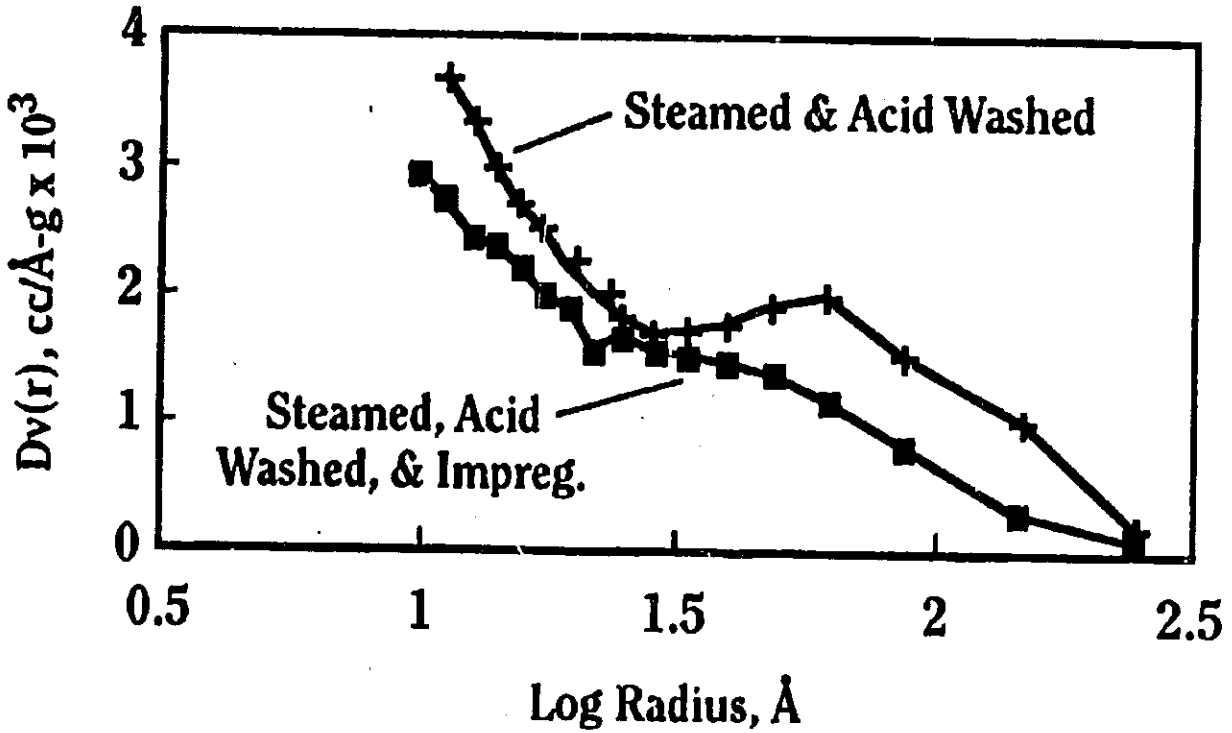
Comparison of Cobalt Catalysts

Catalyst	Metals, wt-% Co	Mn	Zr	Wt Tested, g
Best from Previous Contract (DE-AC22-81PC40077)	8.3	1.3	1.0	13
Best from Current Contract (DE-AC22-89PC89869)	28.7	1.9	1.1	6

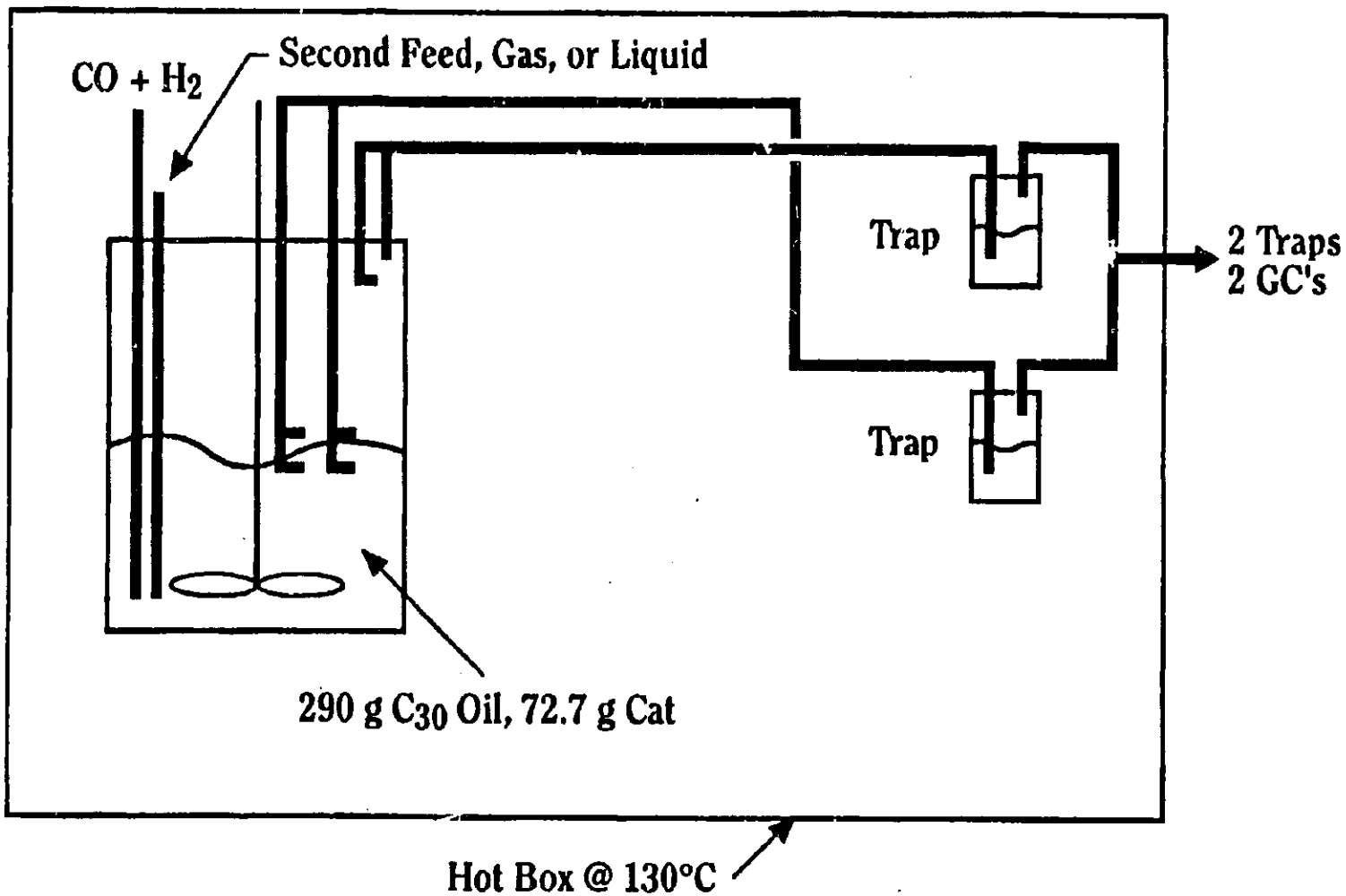
Influence of Acid Wash on Support Properties

Support Description	Before Acid Wash	After Acid Wash
Surface Area, m^2/g	574	588
Pore Volume, cc/g	0.50	0.55
Aluminum, % Removed	—	90
X-Ray Diff., % Crystal	84.5	87.0

Support Pore Size Distribution Before and After Impregnation



Schematic of Slurry Autoclave Plant



UOP 2145-27
UOP 2148-14

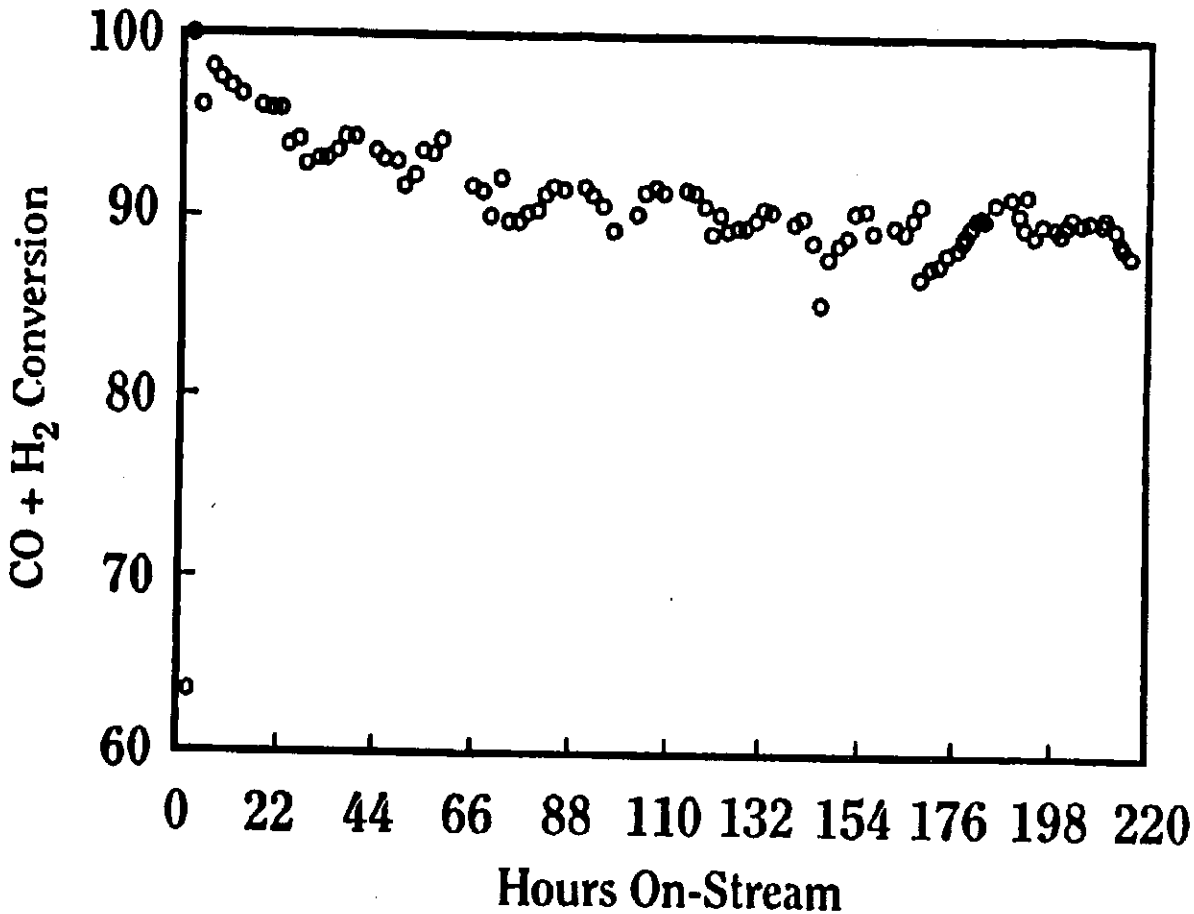
Catalyst Screening Conditions

Reactor	Fixed Bed with Quartz Diluent
Reactor Loading, g	13 Catalyst & 160 Diluent *or* 6.5 Catalyst & 167 Diluent
Feed, molar	2 : 1, H_2 : CO
Feed Rate, NL/hr·g Co	4.9, Downflow
Inlet Temperature,°C	211
Pressure, psig	287

Performance Overview of Cobalt Catalysts

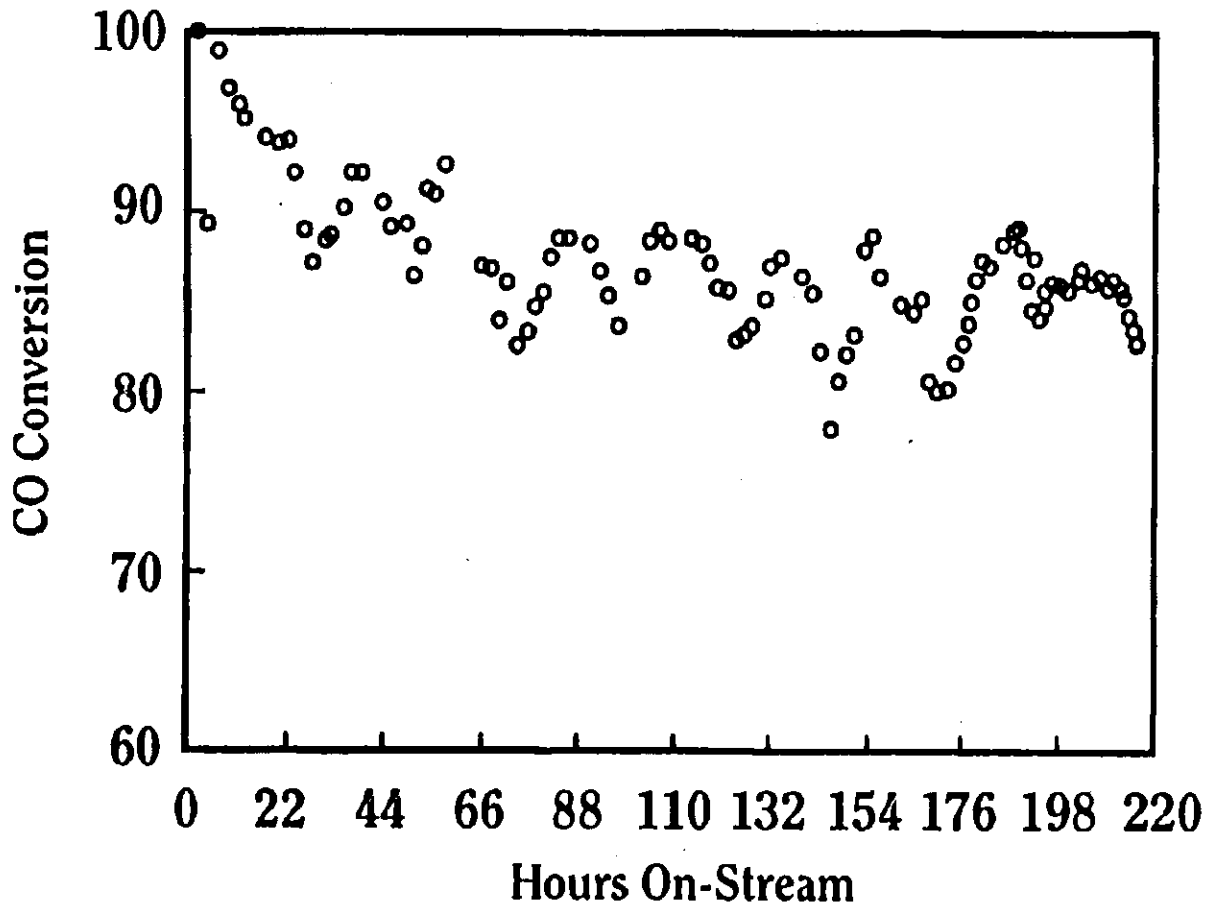
Catalyst	Temp., °C		CO Conv., %	Selectivities, mol-%		
	Inlet	Max.		C_1	C_2	$C_2^=$
Best from Previous Contract (13 g Loading)	211	212	50	8.5	1.0	0.1
Best from Current Contract (6 g Loading)	211	232	85	10.0	1.5	0.1

Syngas Conversion for Co Catalyst

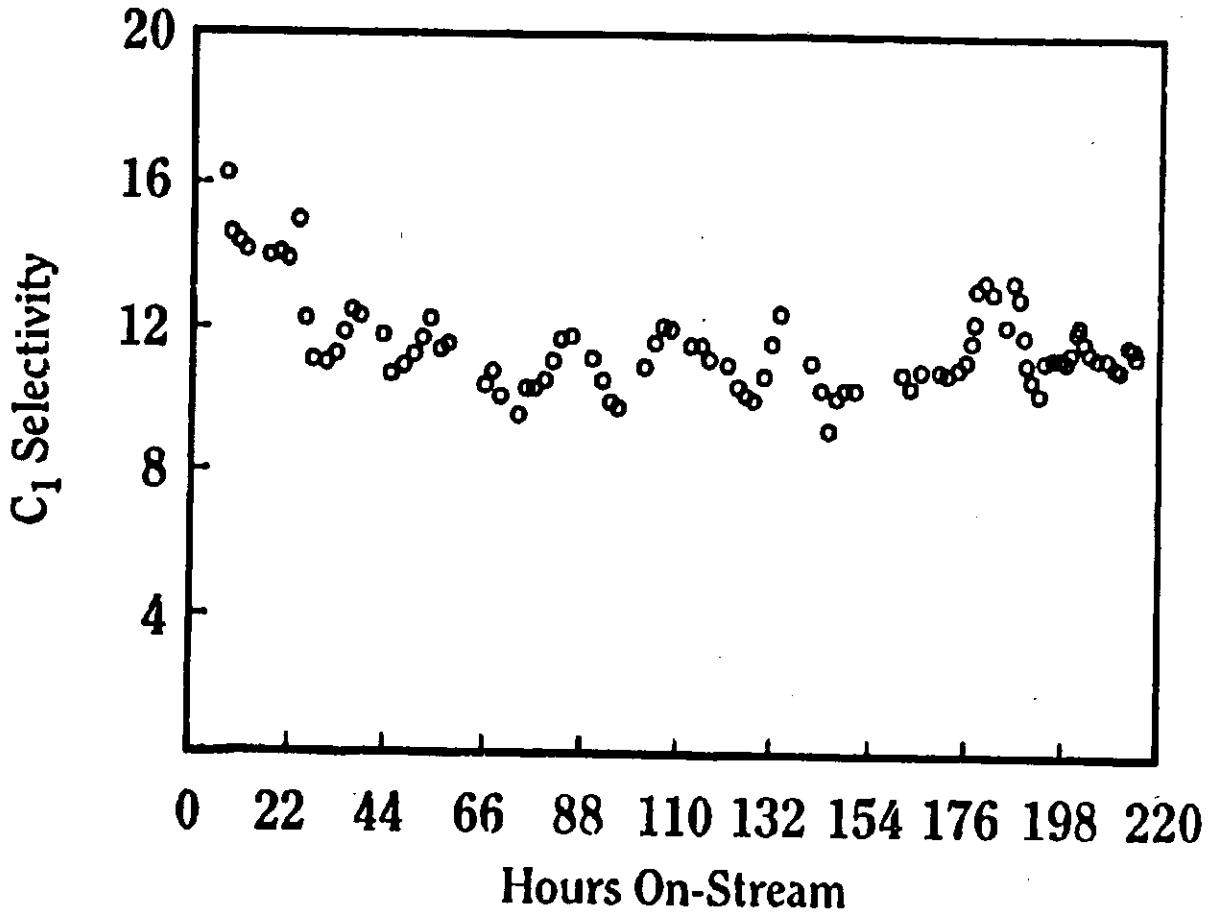


UOP 2148-9

Co Conversion for Co Catalyst

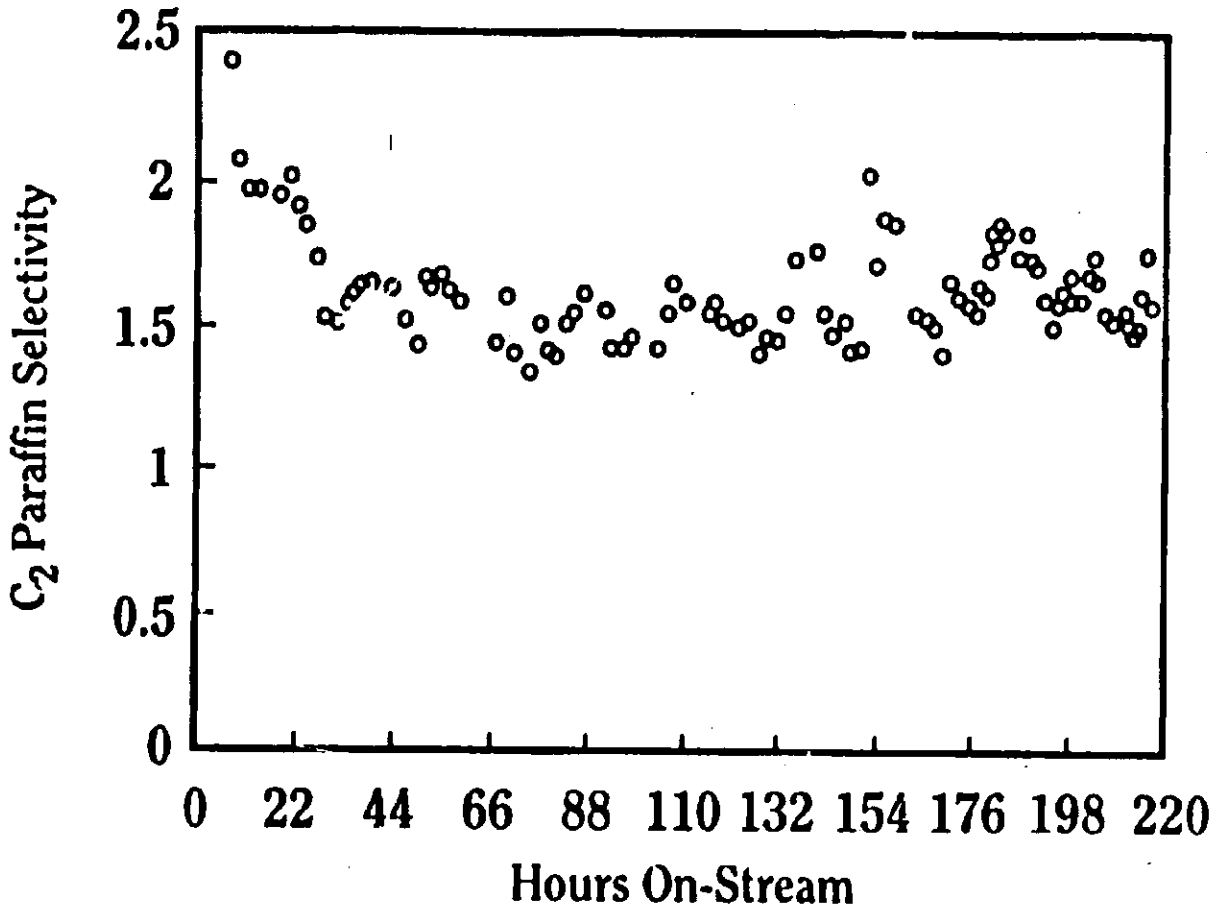


Methane Selectivity



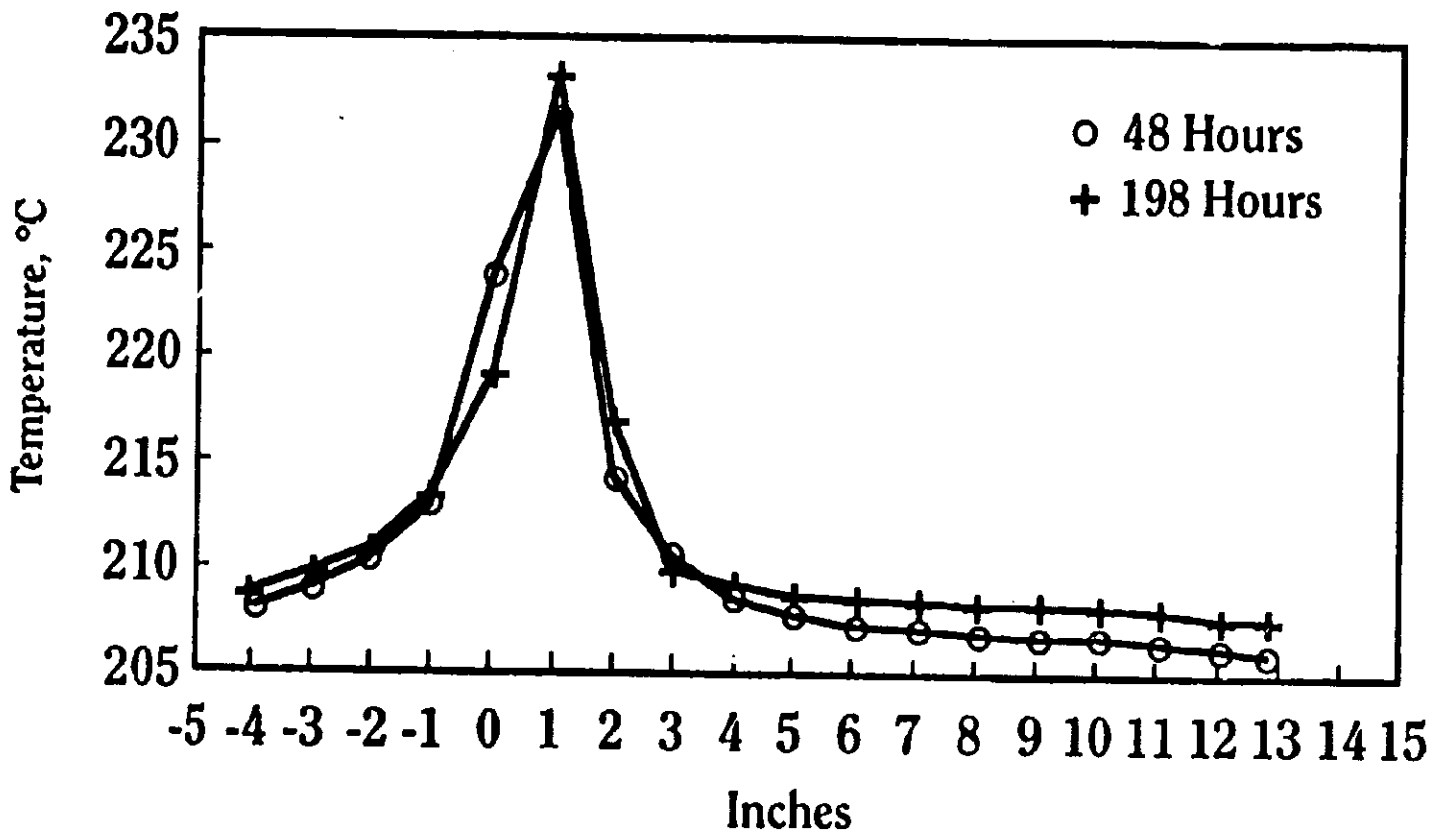
UOP 2148-11

Ethane Selectivity



UOP 2148-12

Temperature Profiles in the Reactor



UOP 2148-13

Autoclave Evaluation of Co Catalyst

Catalyst	Reactor	Reactor Loading	Temp., °C
17% Co on Steamed & Washed Y Zeolite Bound with 25% Silica	Fixed-Bed	18 g Cat* 160 g Quartz	Inlet = 211 Max = 218
	Autoclave	18 g Cat* 290 g Oil	221

* 18 g Bound Contains 13 g Catalyst

Performance Overview of Co Catalyst

Catalyst	Reactor	CO Conv., %	Selectivities, mol-%		
			C_1	C_2	$C_2^=$
17% Co on Steamed & Washed Y Zeolite Bound with 25% Silica	Fixed-Bed	55	11	2.1	0.1
	Autoclave	58	10	1.9	0.1

Conclusions

- Extremely Active, High-Co Catalyst Developed for Slurry Bubble Processing
- Low Ru in High Co Catalyst Does Not Enhance Activity

Future Work

- Autoclave Run with 27% Co Catalyst and Full Product Characterization