XPS/MICROREACTOR STUDIES OF BIFUNCTIONAL F-T CATALYSTS

T.G. Kinisky, T.M. Schear, J.G. Miller and J.A. Rabo

DE-AC22-84PC70028, IMPROVED CATALYSTS FOR LIQUID HYDROCARBON FUELS FROM SYNGAS

Union Carbide Corporation / UOP
Tarrytown Laboratory

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PIs (Authors): T.G. Kinisky[1], T.M. Schear[1], J.G. Miller[2], and J.A. Rabo[2]

INSTITUTION/ORGANIZATION:
1. Union Carbide Corporation
Central Scientific Laboratory
Tarrytown, NY 10591
(914) 789-2706.

2. UOP
Tarrytown Technical Center
Tarrytown, NY 10591

CONTRACT NO: DE-AC22-84PC70028

OBJECTIVE:

The objectives of this program are to develop and optimize new catalysts with improved activity, selectivity, and stability for the conversion of syngas to motor fuels with molecular sieve-containing catalysts, and to define economic value for the optimum process/catalyst system.

ABSTRACT:

Characterization of bi-functional F-T catalysts consisting of cobalt supported on the molecular sieve TC-123 and promoted with X9 and X11 was preformed using a microreactor system attached directly to a x-ray photoelectron spectrometer. X-ray photoelectron spectroscopy (XPS) was used to monitor changes in the chemical state of the cobalt oxide species as a function of reduction and syngas reaction conditions.

The as-synthesized cobalt chemical state was found to be predominately Co_3O_4 on unpromoted Co TC-123. The addition of X9 or X9 and X11 resulted in Co(2+) oxide being the predominate specie. Reduction in hydrogen at 320psi and 350°C revealed that only a portion of the total cobalt is reduced to the metallic state with the percent reduction being a function of the additives. Reaction of hydrogen reduced catalysts with syngas resulted in additional reduction of the cobalt to the metallic state. Reduction of cobalt in syngas was studied as a function of promoter (X9 versus X9+X11), temperature (240C, 260C, and 280C), and syngas composition (CO/H_2= 2, 1, and 0.5).

OBJECTIVES OF CURRENT CONTRACT

- Develop and Optimize New Catalysts with Improved Activity, Selectivity, and Stability for the Conversion of Syngas to Motor Fuels with Molecular Sieve-Containing Catalysts.
- Define Economic Value for Optimum Process/Catalyst System.

OBJECTIVE OF THIS STUDY

- Provide Catalyst Characterization to Further Understand the Role of the Metal, Promoters, Molecular Sieve, and Processing Conditions on F-T Activity and Lifetime.

OUTLINE

I. Catalysts Studied

II. Goals

III. XPS/Microreactor

IV. Characterization

   A. As-synthesized

   B. Hydrogen Treatment

      1. Effect of Time and Promoters

   C. Syngas Reaction

      1. Product Analysis

      2. Effect of Promoters, Time, Temperature, and Syngas Composition

V. Summary

CATALYSTS

- Cobalt loaded molecular sieve (TC-123) with promoters X9 and X11.

    - Co TC-123
    - Co/X11 TC-123
    - Co/X9/X11 TC-123

PROMOTER EFFECTS ON Co/TC-123
FISCHER-TROPSCH CATALYSTS

CONDITIONS: 260, 1.5:1 H_2:CO, 500 psig, 300 GHSV

Catalyst	Co/TC-123		$Co/X_{11}/TC-123$		$Co/X_{11}/X_9/TC-123$
Conversion	73		81		77
C_1	26.0	→	12.2		10.0
C_2–C_4	14.3		10.4		11.0
C_5–350°F	26.2		29.6		29.0
350–650°F	22.3		30.1		27.9
650°+	11.2		17.7		22.0
C_5+	59.7	→	77.4		79.0
Stability (% Loss/Hr)	.2	→	.02	→	.007

GOAL

- Monitor the Chemical State of the Cobalt Following Treatment Under Simulated Processing Conditions.
  - ✓ Cobalt Chemical State As-synthesized.
  - ✓ Effect of Promoters and Time on Cobalt Processed Under Reduction Conditions.
  - ✓ Effect of Promoters, Temperature, Time, and Syngas Composition on Cobalt Processed Under Reaction Conditions.

X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)
+ MICROREACTOR

X-RAY PHOTOELECTRON SPECTROSCOPY (XPS or ESCA)

- Surface sensitive technique.
- Can detect all elements with the exception of H and He.
- Chemical state identification:
  Oxidation states, chemical bonding, etc.
- Requires ultra-high vacuum analysis chamber.

XPS Instrument: Perkin-Elmer, Physical Electronics
Model 550.

XPS STUDIES
As-Synthesized

- The surface concentrations of Co, X9, and X11 were found to be similar to the bulk concentrations.
- The chemical state of the cobalt was different depending upon the presence of promoters. The Co TC-123 cobalt was mainly Co (+2) and (+3), while the cobalt of the promoted catalysts had a higher level of Co (+2).

XPS
Hydrogen Treatment

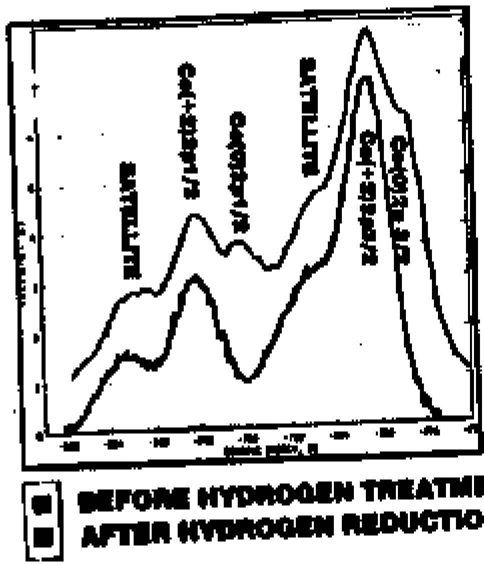
Objective: Examine the chemical state changes in cobalt following hydrogen treatment.

Parameters: Time and Promoters

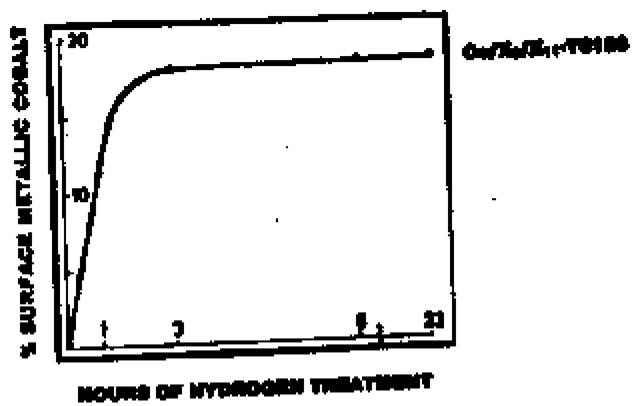
Conditions: 320 psi hydrogen, 350 C, 50 ml/min

ACTIVATION

TYPICAL Co 2p XPS SPECTRUM OF $Co/X_8/X_{11}$-TC123 CATALYST



PERCENT SURFACE METALLIC COBALT VS TIME OF HYDROGEN TREATMENT



Hydrogen Treatment: Effect of Promoters
Surface (XPS) vs. Bulk (Oxygen Titration)

	---------- % Cobalt Metal ----------	
	XPS (surface)	O2 Titration (bulk)
Co TC-123	<3	3
Co/X11 TC-123	15	17
Co/X9/X11 TC-123	22	21,23

!!!!! EXCELLENT AGREEMENT BETWEEN SURFACE (XPS) AND BULK (O2 TITRATION) !!!!!

XPS
Syngas Reactions

Objective: Monitor changes in the chemical state of the cobalt under simulated reaction conditions.

Parameters: Effect of promoters, time, temperature, and syngas composition.

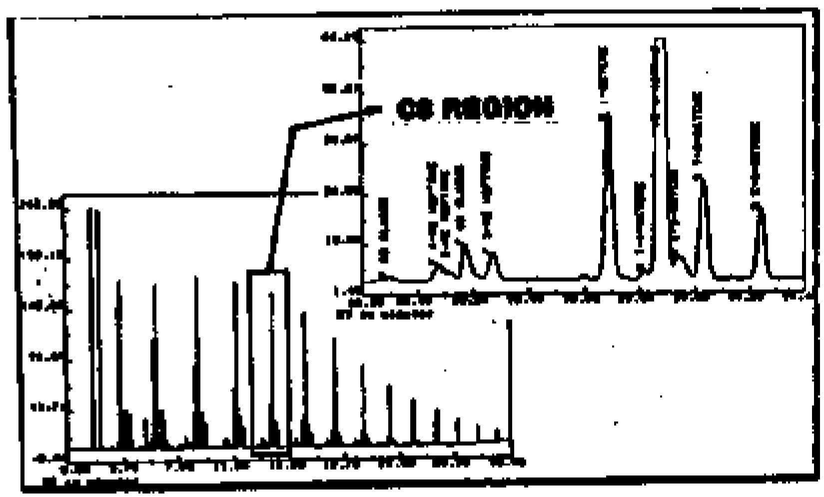
Conditions: 300 psi, GHSV=600

Catalyst Performance
Microreactor/Product Analysis

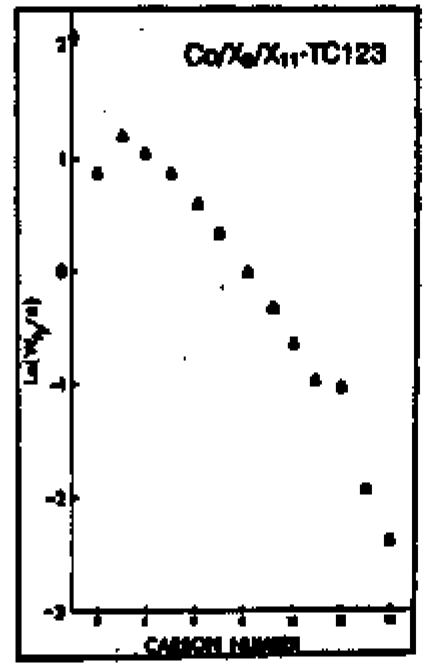
- A gas chromatograph attached to the reactor was used to monitor product composition.

- Schulz-Flory plots, olefin to paraffin ratios (C4), and relative activity measurements were determined for each catalyst run.

GC FLAME IONIZATION CHROMATOGRAM OF PRODUCTS OBTAINED FROM THE ACTIVATED $Co/X_8/X_{11}$-TC123 CATALYST DURING REACTION WITH SYNGAS



SCHULZ- FLORY PLOT

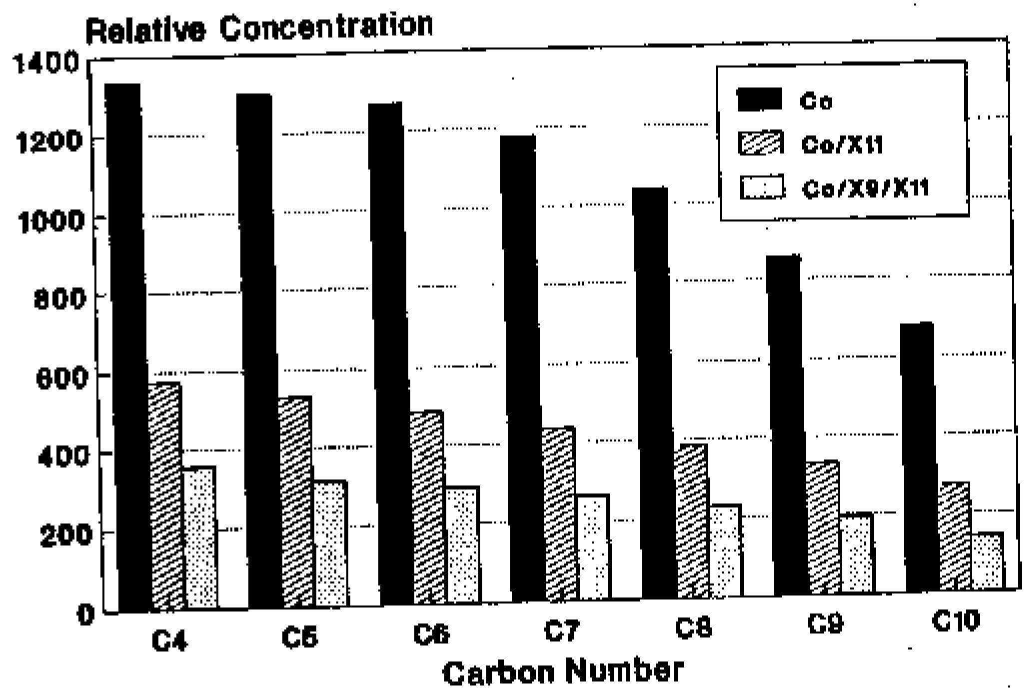


XPS/SYNGAS REACTION
Effect Of Promoter

	---- % Co Metal ----			
	Hydrogen	Syngas	P/O (C4)	Relative Activity
Co	<3	**83**	1.00	3.2
Co/X11	15	**21**	0.34	1.8
Co/X9/X11	22	**25**	0.36	1.0

Conditions: 240C; 50:50; 6 hrs.

Product Distribution
Effect of Promoter



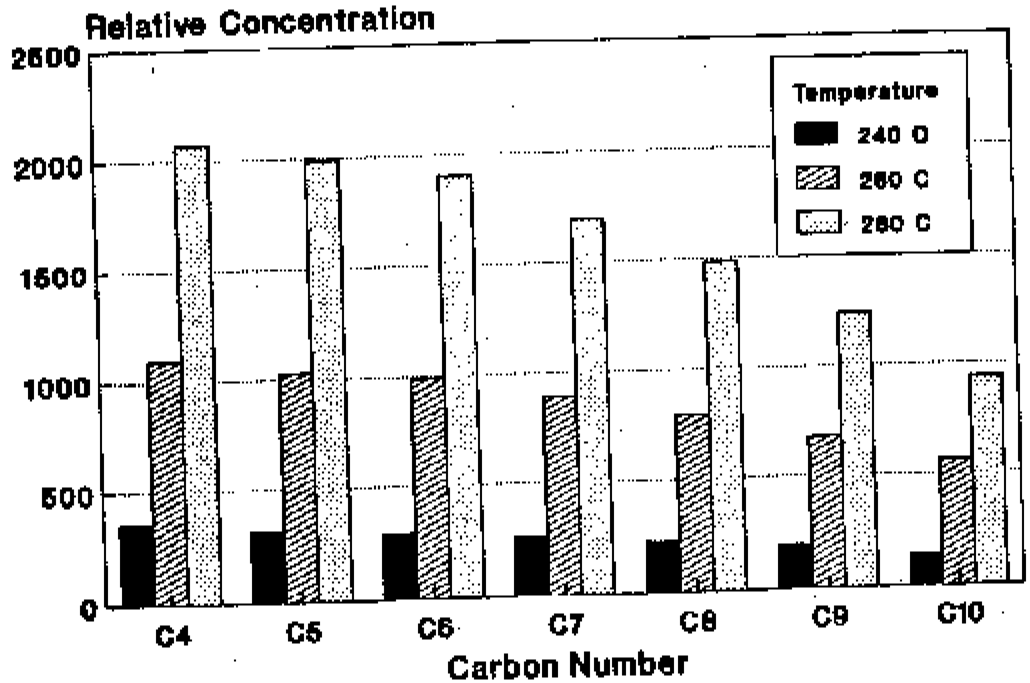
240C; 50:60; 320 psi; 600 GHSV

XPS/SYNGAS REACTION
Effect of Temperature

	% Co Metal (from syngas)	P/O (C4)	Relative Activity
240C	2.7	0.36	1.0
260C	4.1	0.47	3.1
280C	12.6	0.59	5.6

Co/X9/X11 TC-123; 50:50; 6hrs.

Product Distribution
Effect of Temperature



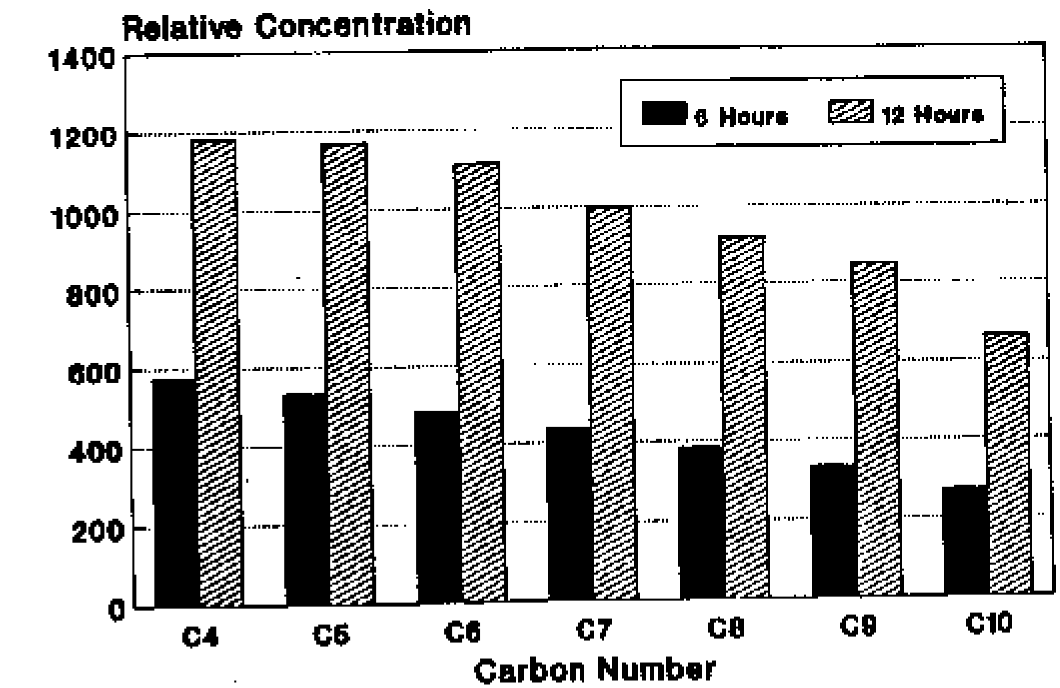
Co/X9/X11 TC-123; 50:50; 600 GHSV; 6 Hrs

XPS/SYNGAS REACTION
Effect of Time

	% Co Metal	P/O (C4)	Relative Activity
6 Hrs.	21	0.34	1.0
12 Hrs.	45	0.60	2.3

SAMPLE: Co/X11 Catalyst; 240C; 50:50

Product Distribution
Effect of Time



Co/X11 TC-123; 240C; 50:50; 320 psi

XPS/SYNGAS REACTION

Effect of Syngas Composition

Hydrogen:CO (vol:vol)	% Cobalt Metal (from syngas)	P/O (C4)	Relative Activity
66:33	5.9	15.41	3.6
50:50	13.6	0.61	2.9
33:66	30.6	0.24	1.0

Co/X11 TC-123; 260C; 6 hrs.

SUMMARY

- The presence of the X11 and X9 promoters effect the extent of cobalt reduction to cobalt metal following treatment in hydrogen. This may be due to differences in the cobalt chemical state (Co_3O_4 vs. CoO; Co^{2+} vs Co^{3+}) after calcination.
- Upon exposure to syngas (after hydrogen pretreatment), further reduction of cobalt to the metallic state is observed. The extent of initial reduction in syngas is influenced by promoters, time, temperature, and syngas composition.

SUMMARY (Con't)

- In comparison to the other variables examined (time, temp., syngas), the presence of promoters had the greatest influence on the extent of the initial cobalt reduction upon exposure of the catalyst to syngas. This result indicates a strong interaction between the cobalt and the promoters.

- The promoters slow the rate of cobalt reduction to the metallic state in the early stages of syngas reaction. It is believed that this reduces cobalt metal sintering relative to unpromoted catalysts. This in turn results in better catalyst lifetime and enhanced performance.

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Catalyst Preparation

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