

LIQUEFACTION CONTRACTORS' REVIEW MEETING
September 3-5, 1991

ABSTRACT

TITLE: COBALT CATALYST DEVELOPMENT

AUTHORS: HAYIM ABREVAYA (principal investigator)
WILLIAM M. TARGOS

INSTITUTION: UOP
25 E. ALGONQUIN ROAD
DES PLAINES, IL 60017

CONTRACT NUMBER: DE-AC22-89PC89869

PERIOD OF PERFORMANCE: 09/01/89 TO 09/01/93

OBJECTIVE:

To elucidate the relationship between catalytic properties and the function of cobalt Fischer-Tropsch catalysts and to apply this fundamental knowledge in the development of a stable cobalt catalyst with low C_1+C_2 selectivity in slurry reactors.

ACCOMPLISHMENTS AND CONCLUSIONS:

Cobalt catalysts typically result in high methane selectivity. This high selectivity was verified by testing a reference cobalt catalyst. Researchers believe that methane selectivity can be minimized by careful control of cobalt crystallite size and cobalt-modifier interaction. This program shows that reverse micelle impregnation on a support can be used to design the size and composition of cobalt-containing crystallites. The selection of the right support material seems to be one of the key factors in the design of the catalytic properties.

PLANS:

- . A suitable support will be identified for cobalt catalysts.
- . Both known and new cobalt modifiers will be evaluated.

INTRODUCTION

Cobalt catalysts have three features that make them distinctly different than iron catalysts:

- . Higher specific activity relative to iron.
- . Low selectivity to CO_2 .
- . High methane selectivity.

Whether the second feature, i.e. the essential absence of water-gas-shift activity is a disadvantage or an advantage is not presently clear. In the absence of water-gas-shift activity, the high-pressure Fischer-Tropsch reactor volume can be fully used to convert essentially all of the CO to hydrocarbons. The higher activity of cobalt certainly seems to be one of its most attractive features; however, the catalytic properties need to be carefully tailored in order to lower the methane selectivity.

Work in various research laboratories showed the existence of several modifiers that can lower the methane selectivity with cobalt. Some researchers believe that another key factor for low methane formation is minimizing the formation of highly dispersed cobalt. Both cobalt-modifier interactions and cobalt crystallite size can be carefully controlled by reverse micelle impregnation, which is a patented UOP procedure. The merits of this procedure have been shown with ruthenium catalysts under DOE Contract DE-AC22-84PC70023.¹ The current work is investigating the application of reverse micelle impregnation to cobalt catalysts with the objective of developing a superior catalyst.

RESULTS AND DISCUSSION

Performance of Reference Cobalt Catalyst

An experimental cobalt catalyst (TC 211) prepared under DOE Contract DE-AC22-84PC70028 by Union Carbide's Molecular Sieve Division (Tarrytown, New York) was tested in this program. This catalyst was not prepared by reverse micelle impregnation, and therefore, it was considered a reference catalyst for this program. After the Molecular Sieve Division merged with UOP in 1989, all catalysts and intellectual property developed under the former contract was transferred to UOP.

The relation between $\text{CO}+\text{H}_2$ conversion and space velocity with the reference cobalt catalyst at 210 C and 21 atm with 2 H_2 : 1 CO feed gas is shown in Figure 1. A conversion level of about 85% was obtained at a space velocity of 2.0 NL/hr/g Co (normal liter per hour per gram cobalt). Similar conversion levels at comparable space velocities require significantly higher temperatures when iron catalysts are used; this result verifies that cobalt has much higher specific activity relative to iron.

During the same run, the methane selectivities at different $\text{CO}+\text{H}_2$ conversions with the reference cobalt catalyst at 210 C, 21 atm, 2 H_2 :1CO feed gas are shown in Figure 2. The selectivity to methane

increased as the conversion decreased below about 42%. During this interval, the H₂:CO usage ratio and the feed ratio were the same, and therefore the H₂:CO ratio at the outlet of the reactor was 2.0. This result indicates that the variation of selectivity is only related to the variation of conversion. Furthermore, a usage ratio of 2.0 verifies the essential absence of water-gas-shift activity with the cobalt catalyst. Above 42% conversion, the methane selectivity showed a slight decrease and was about 6.5% at 85 to 93% conversion. Iron catalysts result in much lower methane selectivities at this low temperature; therefore, this result verifies the high methane selectivities typically observed with cobalt catalysts.

The overall evaluation of the reference cobalt catalyst verifies that an important catalyst developmental need is selectivity improvement. This program is going to address the commonly observed selectivity problem in cobalt catalysts by application of the reverse micelle procedure.

Preparation of Cobalt Catalysts by Reverse Micelle Impregnation

A few different materials have been recently used as supports for the reverse micelle impregnation of cobalt. Desired intermediate-size crystallites of about 6 nm obtained on one of these supports are illustrated in the scanning transmission electron micrographs (STEM) of an experimental bimetallic cobalt catalyst (585R2655) in Figure 3. However, another support resulted in highly dispersed cobalt (585R2704), apparently because of the high metal-support interaction. These results indicate that selection of the right support material is important for the successful application of the reverse micelle impregnation procedure.

Individual crystallites in the experimental bimetallic cobalt catalyst 585R2655 were examined by energy dispersive x-ray analysis (EDX). Table 1 shows that the atomic ratio of the second component to cobalt did not show large variations among individual crystallites. These results verify that reverse micelle impregnation can be used to control crystallite size and composition with bimetallic cobalt catalysts.

Current efforts in this program are focusing on the identification of suitable activation treatments for reverse micelle-derived catalysts. These catalysts, as well as catalysts prepared on various supports, will be evaluated in the fixed-bed pilot plant. Promising catalysts will be later tested in the slurry pilot plant.

REFERENCES

1. Hayim Ar'evaya, et al., "The Development of a Stable Ruthenium Catalyst", Final Report, Contract DE-AC22-84PC70023, 1990.

Table 1

STEM EXAMINATION OF BIMETALLIC COBALT CATALYST

CRYSTALLITE	I SECOND : COMPONENT: COBALT ATOMIC RATIO, *100
1	0.6
2	0.79
3	1.4
4	2.1
5	0
6	0.65
7	0.64
8	0.50
9	0.31
10	1.4
11	0.38
12	2.2
13	0.65
14	0.51

FIGURE 1

**CO + H₂ Conversion and Space Velocity
with Reference Co Catalyst TC 211
210°C, 21 Atm, 2H₂:1CO Feed**

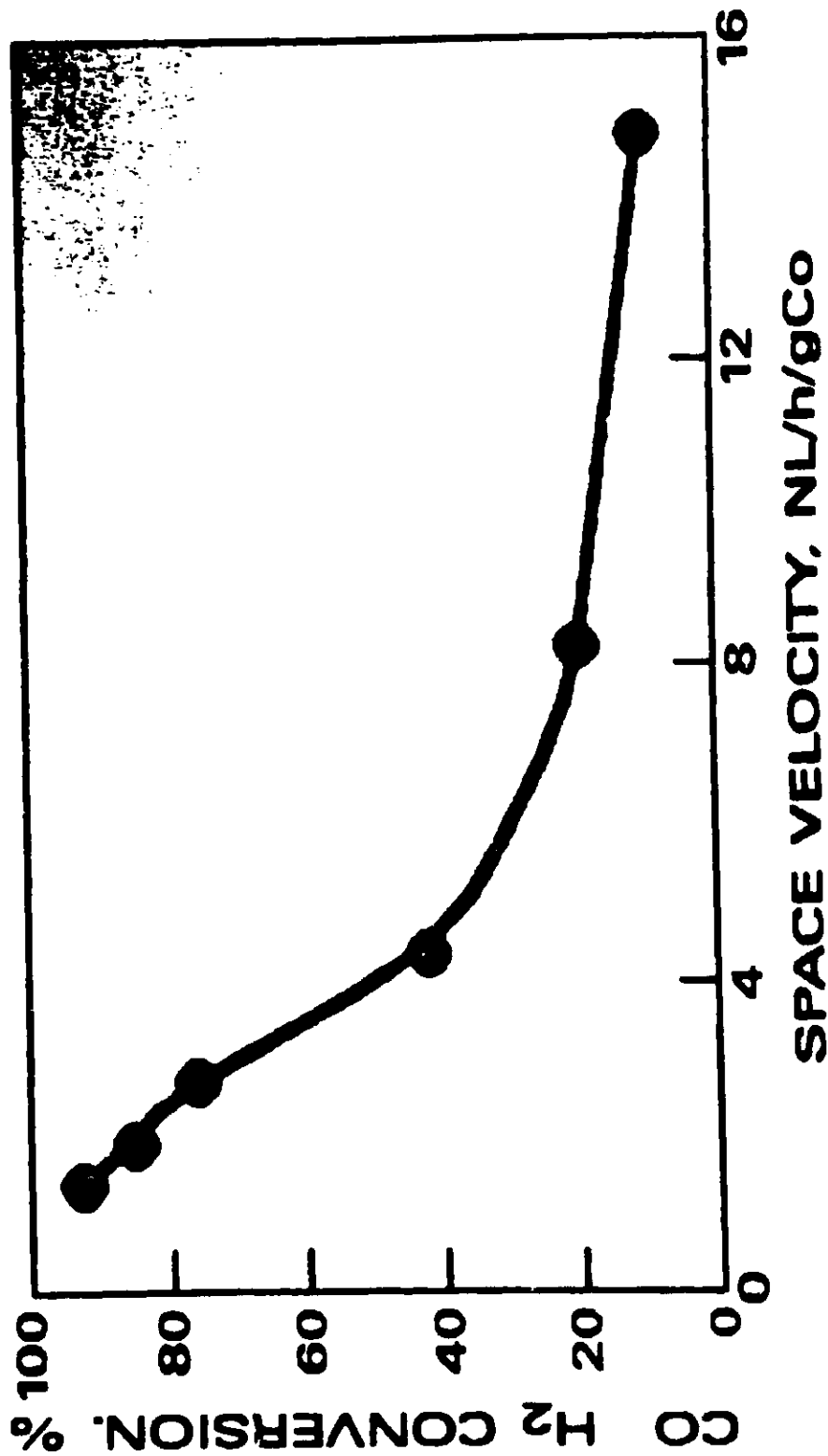


FIGURE 2

Methane Selectivity at Different Conversions with Reference Co Catalyst TC 211

210°C, 21 Atm, 2H₂:1CO

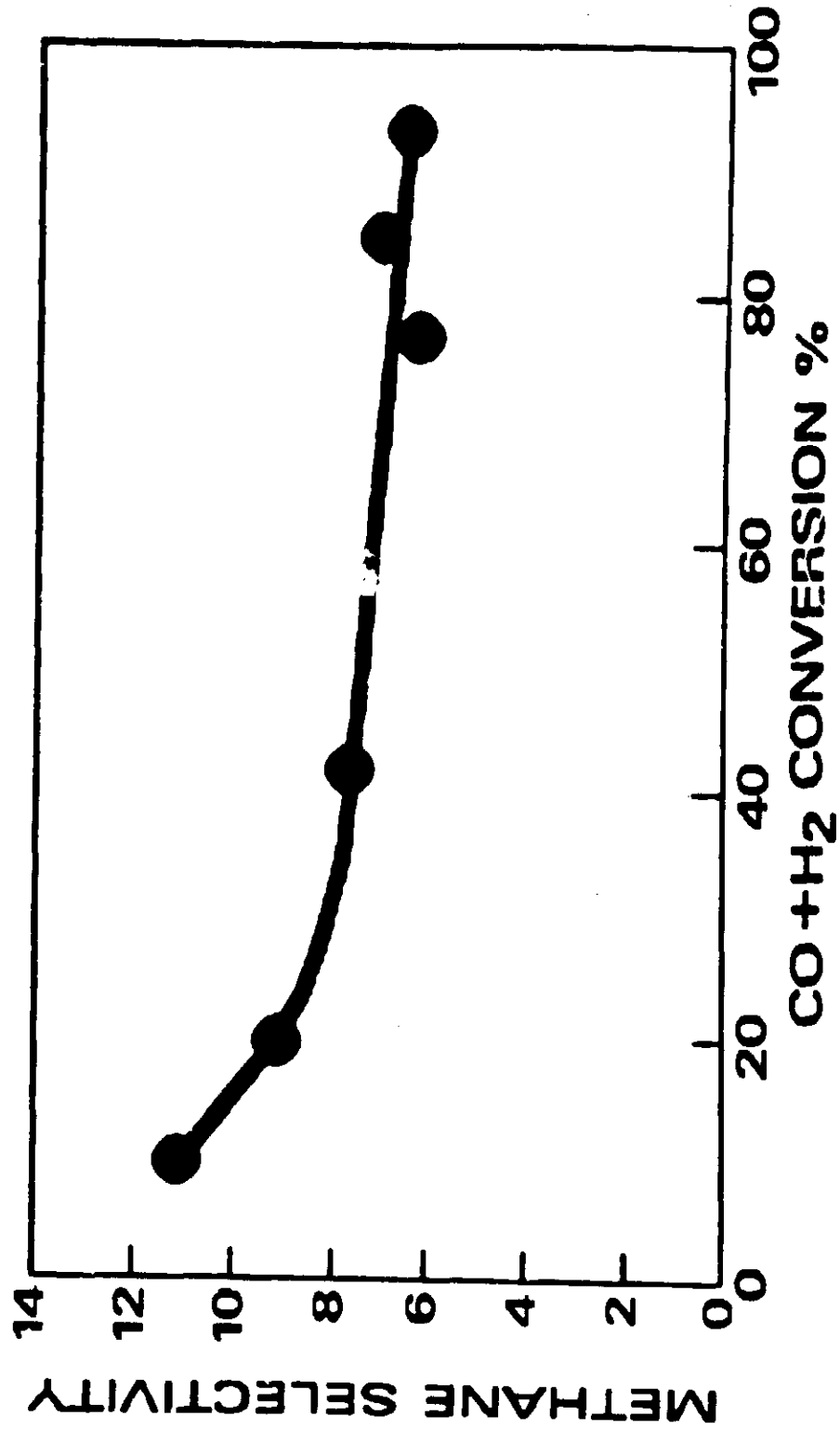


FIGURE 3

STEM MICROGRAPHS OF COBALT CATALYSTS



INTERMEDIATE SIZE

0.1 μm



HIGHLY DISPERSED