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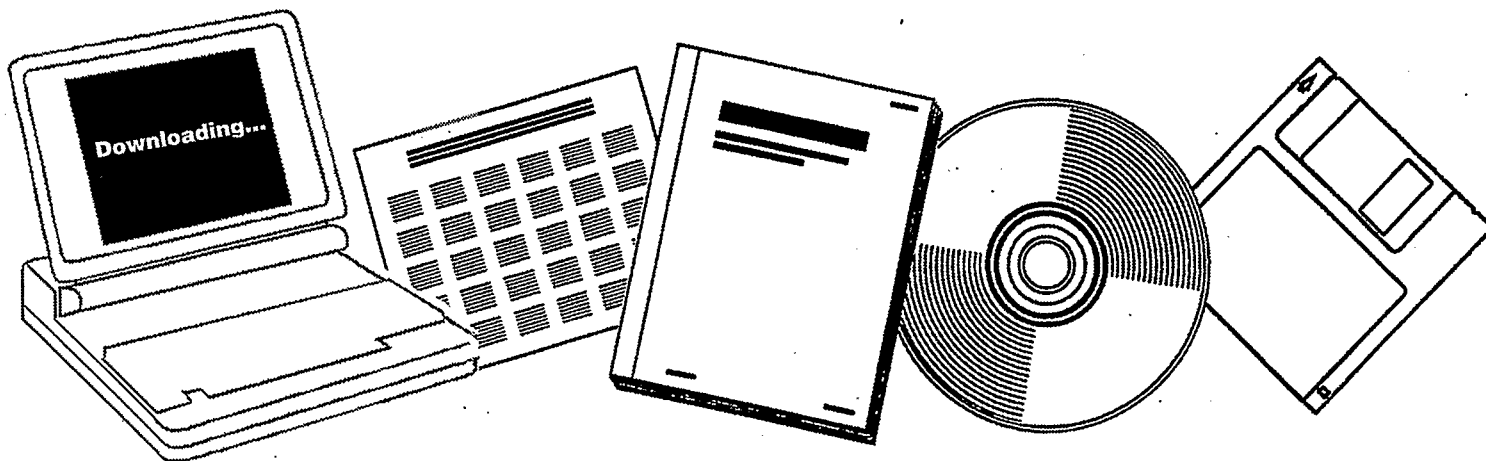
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**CATION PROMOTION EFFECTS IN  
ZEOLITE-SUPPORTED F-T CATALYSTS. FIRST  
QUARTERLY REPORT, SEPTEMBER-NOVEMBER 1983**

**PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL  
AND PETROLEUM ENGINEERING**

**DEC 1983**



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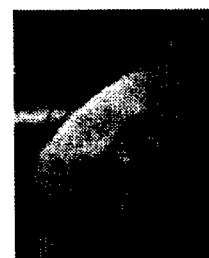
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DE84 004676

CATION PROMOTION EFFECTS IN  
ZEOLITE-SUPPORTED F-T CATALYSTS

1st Quarterly Report  
September 1983 - November 1983

James G. Goodwin, Jr.  
A. Sayari

Department of Chemical and Petroleum Engineering  
University of Pittsburgh  
Pittsburgh, PA 15261

December 1983

Prepared for the U. S. Department of Energy  
under Grnt No. DE-FG22-83PC60805

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## I. Objective and Scope of Work

An investigation into zeolite-supported F-T catalysts begun under Grant #DE-FG22-81PC40774 (Office of Fossil Energy, D.O.E.) has produced results which suggest that alkali cations, remaining in a zeolite and serving to neutralize the structure, act to promote higher hydrocarbon formation. It appears that the F-T metal must be highly dispersed throughout the zeolite in the vicinity of these cations for this promotion effect to take place. This effect is also highly dependent upon alkali cation concentration.

The current research involves a study of the promotion effects of the neutralizing alkali cations on CO hydrogenation (under typical F-T conditions) over zeolite-supported Ru catalysts. Ru is a useful, model catalyst for the study of such promotion of this synthesis. First, alkali promotion has been found to have a great effect on product selectivity over Ru. Second, Ru does not form any stable carbides, thereby removing this complicating factor. Third, Ru is relatively easy to reduce to the metallic state. Fourth, Ru is the F-T metal easiest to keep inside zeolite crystallites. Fifth, under typical conditions, there is little oxygenated hydrocarbon formation or skeletal isomerization of the hydrocarbons over Ru. Thus, the neutralizing cations in the zeolite support should affect CO hydrogenation over Ru possibly by affecting: CO chemisorption, H<sub>2</sub> chemisorption, carbon deposition, catalytic activity, chain growth probability, selectivity for CH<sub>4</sub>, selectivity for olefins, and diffusion in the zeolite. Each of these items will be investigated for the catalysts proposed to be studied.

The main objectives of this study are:

1. to develop a better understanding of how neutralizing alkali cations in zeolites can affect F-T product selectivity over a supported metal

2. to illuminate the effect of these cations on
  - a. chemisorption properties
  - b. CO disproportionation
  - c. the mechanism of CO hydrogenation
  - d. the deactivation characteristics
3. to elaborate on the effect of decreasing ionization potential of the alkali cations on the catalytic properties
4. to investigate the effects of Rb and Cs promotion, studied only superficially in the past.

In order to accomplish these objectives, catalysts will be prepared and studied by gas volumetry, temperature programmed desorption, IR spectroscopy, catalytic reaction, and thermogravimetry. These catalysts will be zeolite-supported Ru prepared variously using NaX, NaY,  $\text{NH}_4\text{Y}$ , KL, NaMordenite, X and Y zeolites containing a range of alkali cations ( $\text{Cs}^+$ ,  $\text{Rb}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ), and a series of dealuminated NaY zeolites.

This investigation should provide a more fundamental understanding of the involvement of alkali cations in determining the catalytic properties of zeolite-supported metals for Co hydrogenation.

## II. Summary of Progress

During the first quarter of the project, a research team has been assembled. A flow TGA system has been constructed, and construction of a high pressure reaction system has begun. In addition, a series of zeolite-supported ruthenium catalysts have been prepared by an ion-exchange technique. Characterization of these catalysts by means of atomic absorption, TGA, X-ray diffraction, and selective adsorption has begun.

### III. Detailed Description of Technical Progress

#### Personnel

Dr. Abdelhamid Sayari, from the University of Tunis, has been recruited as a post-doctoral fellow to assist the P.I. (Professor James G. Goodwin, Jr.). Dr. Sayari started to work full-time on this project November 1, 1983. Mr. Tian, who is a visiting scholar from the People's Republic of China, has started TGA studies by means of the flow microbalance system. Mr. Feng, an M. S. student, will be in charge of H<sub>2</sub> and CO adsorption measurements.

#### Equipment Design and Fabrication

A micro-reactor system is being constructed for performing high pressure Fischer-Tropsch synthesis from syngas. This reaction system will allow us to carry out F.T synthesis in the range pressure of 1-20 atm.

Another similar system is being designed for light hydrocarbon hydrogenolysis studies. Ethane, propane and cyclopropane hydrogenolyses on Pt/SiO<sub>2</sub> and Pt/NaY (1) and on Ru/SiO<sub>2</sub> and Ru/NaY (2,3) has been investigated. The results seem to indicate a zeolite electrostatic field effect on certain catalytic properties. Since the catalysts to be studied with consist of Ru supported on various zeolites (Mordenite, KL, NaX, NaY, MY (M=Li, K, Rb, Cs), and NaY with different Si/Al ratios), they should have different electrostatic field strengths. Hydrogenolysis of hydrocarbons especially the small and distorted cyclics such as cyclopropane should provide useful information concerning this effect of electrostatic field.

The flow microbalance system was constructed in order to study the deactivation kinetics and mechanism of the catalysts under F.T. conditions related to carbon deposition. This will be done by monitoring the time-on-

stress weight variation of the catalysts. The microbalance system is also be used for some analytical purposes. Catalysts are submitted to redox cycles under different conditions for characterization purposes (metal loading, ease of oxidation/reduction).

### Catalyst Preparation

Ruthenium catalysts are being prepared by ion-exchange of hexamine ruthenium (III) chloride. Zeolite Y samples having alkali cation other than sodium are being prepared by the same technique using NaY and an aqueous solution of the desired alkali species. Origins of starting materials are summarized in Table 1.

TABLE 1

<u>Chemical</u>	<u>Origins</u>
LiNO <sub>3</sub>	Alfa Products, ultrapure
KNO <sub>3</sub>	Alfa Products, ultrapure
RbNO <sub>3</sub>	Alfa Products 99%
CsNO <sub>3</sub>	Alfa Products 99.9%
NaY	Strem Chemicals
NaX	Strem Chemicals
KL	Strem Chemicals
Ru(NH <sub>3</sub> ) <sub>6</sub> Cl <sub>3</sub>	Strem Chemicals

#### a. Preparation of MY (M = Li, K, Rb, Cs)

In order to obtain the maximum exchange levels of M<sup>+</sup>, NaY is first vigorously stirred at room temperature for 18 hours in 100 ml an aqueous solution containing twofold equivalent excess of MnO<sub>3</sub>. Repeated contacts and higher temperatures were used in the case of the large sized cations especially Rb and Cs. Table 2 shows the experimental conditions of the different ion-exchange steps (IES).

TABLE 2

<u>Zeolite/IES</u>	<u>Step 1</u>	<u>Step 2</u>	<u>Step 3</u>
LiY	18 h RT*	-	-
KY	18 h RT	4 h 60°C	-
RbY	18 h RT	4 h 80°C	4 h 80°C
CsY	18 h RT	4 h 80°C	4 h 80°C

\* room temperature

All the MY samples are washed several times with deionized water and then dried at 40°C for 18 hours.

b. Preparation of Ru-Z (Z = NaY, MY, NaX, KL)

The Ru (NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> is dissolved in acidic hydrochloric solution (pH = 4.5). This solution is then mixed with the required amount of a given zeolite and stirred continuously for 50 hours at room temperature. Excess solution is used for this purpose to maintain approximately a constant pH during ion-exchange. The solid is then thoroughly washed in deionized water several times and dried in air for 24 hours at 50°C.

Before their reduction, the Ru samples are decomposed under pure helium flowing at 60 cm<sup>3</sup>/min. The temperature was raised from ambient to 420°C at 0.5°Cmin<sup>-1</sup> and held for 4-5 hours. The samples are then reduced at 420°C for 2 hours with hydrogen flowing at the same rate. Helium (Air Products, UHP) is purified by passing through a heated copper trap to remove oxygen traces and then through a molecular sieve trap to remove water. Hydrogen is passed through an Engelhard Deoxo purifier followed by molecular sieve trap before contracting the catalysts.



#### IV. FORECAST OF WORK

In the next quarter of this project we will focus on cyclopropane hydrogenolysis. Since it appears that this reaction is very sensitive to structural and electronic properties of zeolite supported metal catalysts, it should be an excellent probe for the catalytic behavior of our supported ruthenium and the zeolite electrostatic field effect. Cyclopropane adsorptive properties of zeolites will also be studied by means of the microbalance system. These properties will be correlated with the hydrogenolysis activity. As far as the preparation of catalysts is concerned, ruthenium supported on NaY previously dealuminated at different levels will be prepared. Construction of the high pressure, F-T reaction system will be completed and CO hydrogenation studies will begin.

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