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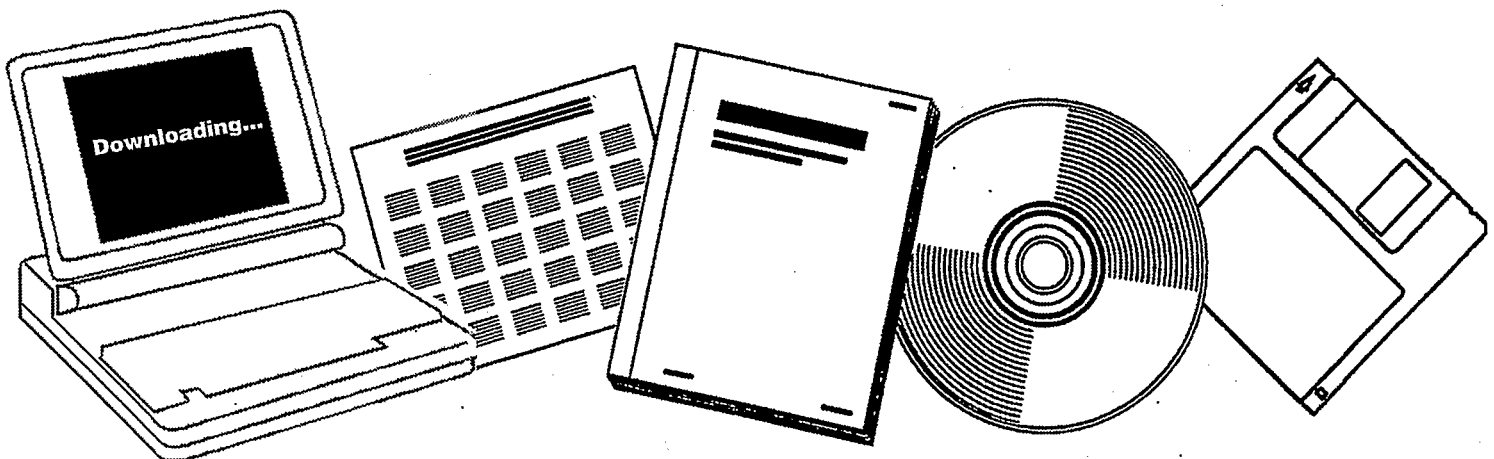
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**CATION PROMOTION EFFECTS IN  
ZEOLITE-SUPPORTED F-T CATALYSTS. SEVENTH  
QUARTERLY REPORT, MARCH 1985-MAY 1985**

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

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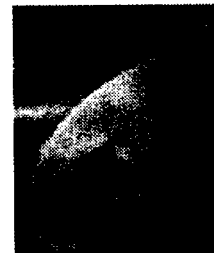
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CATION PROMOTION EFFECTS IN  
ZEOLITE-SUPPORTED F-T CATALYSTS

7th Quarterly Report  
March 1985 - May 1985

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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 upon 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, several series of catalysts have been prepared. These catalysts are mainly zeolite-supported Ru prepared using NaX, NaY, KL, X and Y zeolites containing a range of alkali cations ( $\text{Cs}^+$ ,  $\text{Rb}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{Li}^+$ ), and a series of dealuminated NaY zeolites. Preparation and characterization of these samples by means of gas volumetry and atomic absorption have been described in a previous quarterly report. Further investigations of surface and catalytic properties are under way.

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

A new series of ruthenium catalysts was prepared by the conventional ion exchange of Y zeolite containing various alkali cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ). Prior to reduction with hydrogen, the decomposition of the Ru-hexammine complex was carried out under vacuum using a slow heating rate ( $0.5 \text{ K sec}^{-1}$ ) up to 673 K. The samples were characterized by  $\text{H}_2$  and CO chemisorption. Much higher and more comparable dispersions were found for most of the catalysts

compared to those found after decomposition under flowing helium as discussed in previous reports.

Studies of CO hydrogenation at atmospheric pressure and 200-300°C have begun using this new series of Ru-zeolite catalysts.

### III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

#### Effect of Decomposition Method on Ru Dispersion

It has been frequently reported that highly dispersed ruthenium catalysts can be prepared by the conventional ion-exchange of sodium zeolites followed by pretreatment before hydrogen reduction either under flowing helium or by degassing under vacuum at 623 K (1). The heating rate was found to be the major factor affecting ruthenium dispersion. However, as reported previously (2), the decomposition of the Ru-hexammine complex under flowing helium produced highly dispersed ruthenium catalysts only when the neutralizing cation present in the zeolite was sodium. For Y zeolites containing other alkali cations ( $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ) rather low ruthenium dispersions were obtained under the same pretreatment conditions. In order to explore the effect of the decomposition method on ruthenium dispersion, a new series of ruthenium catalysts with the various alkali cations was prepared by decomposition under vacuum using a slow heating rate ( $0.5 \text{ K sec}^{-1}$ ) up to 673 K. The preparation method was exactly described in the 1st quarterly report except for this decomposition prior to reduction with hydrogen.

The samples were characterized by  $\text{H}_2$  and CO chemisorption following the method described in previous reports. The results of  $\text{H}_2$  and CO chemisorption for the various Ru catalysts are given in Tables 1 and 2. Except for RuHY, a comparison of the dispersions given in Table 1 with the CO/H ratios in Table 2 suggests that the dispersions of the ruthenium in the various Y-zeolites are

high and similar. The high average particle diameter calculated for RuHY could be a result of hydrogen chemisorption suppression due to the higher concentration of acidic hydroxyl groups in that zeolite. Indeed, it has been reported that suppression of irreversible hydrogen chemisorption could be significant for most zeolite-supported ruthenium catalysts prepared by ion-exchange, especially at high concentrations of strongly acidic hydroxyl groups (3). The high CO/H ratio for RuHY suggests that the Ru dispersion is in fact comparable to that of the other catalysts.

Comparing the dispersions given in Table 1 with those obtained after decomposition under flowing helium (2), these were much higher, except for RuNaY which gave a similar dispersion with either decomposition method. Gallezot (4) has reported that heating zeolite-supported metals in the presence of a gas may considerably enhance the mobility of the metal, leading to sintering. Minachev et al. (5) have shown that reduction of transition metals in zeolites is accompanied by migration of metal to the external surface of the zeolite crystals and that the reduction and migration process depends on factors such as the chemical nature of the cation, the degree of ion exchange, cation location and the thermal stability of structural hydroxyls. It has also been reported (6) that noble metals of Group VIII can agglomerate into larger particles in the presence of water vapor, and it has been suggested that only thoroughly degassed samples should be contacted with hydrogen. Thus, depending on the nature of the cation present, the decomposition of the ruthenium complex under flowing helium is believed to enhance the mobility of the metal and does not result in a thorough degassing of the sample, therefore leading to the formation of larger metal particles.



### Reaction Studies

CO hydrogenation studies have been started for this new series of Ru catalysts following the procedure described in the 4th quarterly report. The main results will be discussed in detail in the next quarterly report.

### IV. FORECAST OF WORK

During the next quarter, the reaction study of CO hydrogenation over the new series of RuY catalysts having uniform average Ru particle sizes will be completed and the results analyzed and written up.

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Table 1: Catalyst Characteristics Based on Hydrogen Chemisorption

No.	Catalyst	Loading (wt%)	H <sub>2</sub> (irr.) ( $\mu$ mole/g.cat.)	D. (%)	$\bar{d}_p$ ( $\text{\AA}$ )
1	RuHY	3.8	57	30	28
2	RuLiY	3.4	89	53	16
3	RuNaY	3.8	126	67	12
4	RuKY	3.2	83	52	16
5	RuRbY	3.6	87	49	17
6	RuCsY	3.7	102	56	15

Table 2: CO Chemisorption Results

No.	Catalyst	CO (irr.) ( $\mu$ mol/g.cat.)	CO/H	CO/Ru (Total)
1	RuHY	404	3.5	1.1
2	RuLiY	665	3.7	2.0
3	RuNaY	924	3.7	2.5
4	RuKY	567	3.4	1.8
5	RuRbY	640	3.7	1.8
6	RuCsY	725	3.6	2.0

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