# CATION PROMOTION EFFECTS IN ZEOLITE-SUPPORTED F-T CATALYSTS. 8TH QUARTERLY REPORT, JUNE 1985-AUGUST 1985

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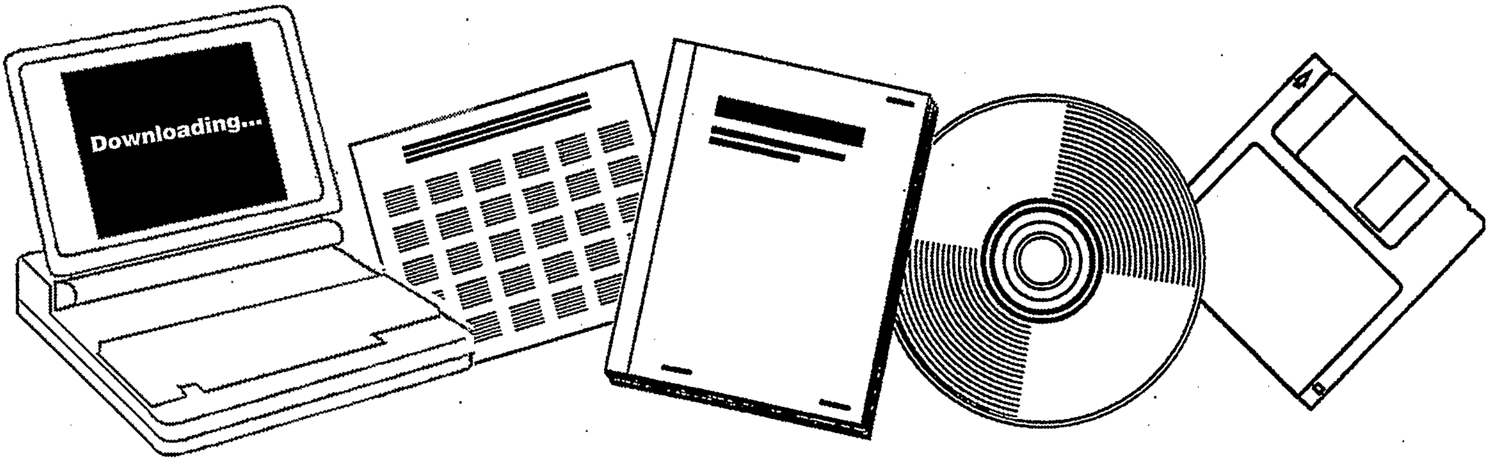

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# CATION PROMOTION EFFECTS IN ZEOLITE-SUPPORTED F-T CATALYSTS

8th Quarterly Report
June 1985 - August 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, $H_2$ chemisorption, carbon deposition, catalytic activity, chain growth probability, selectivity for $CH_4$, 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 catlaysts 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 ($Cs^+$, $Rb^+$, $K^+$, $Na^+$ and $Li^+$), 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 having uniform average Ru particle diameters and supported on Y zeolites containing various alkali cations ($Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$) have been investigated to determine the effect of the neutralizing cations on CO hydrogenation at atmospheric pressure and 200-300°C. The results of this investigation are discussed in the next section.

## III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

### Reaction Studies

CO hydrogenation has been carried over a new series of Y-zeolite supported Ru catalysts. The adsorption characteristics of these catalysts were discussed in detail in the 7th quarterly report. Table 1 and 2 give a summary of the results and the calculated average Ru particle sizes. The catalytic properties of these catalysts are described in detail in the following section.

### Catalytic Activity

The turnover frequencies for the various catalysts studied were calculated using the estimated site concentrations provided by the hydrogen chemisorption measurements. Because of the possible suppression of hydrogen chemisorption on zeolite supported catalysts prepared by ion-exchange, chemisorption measurements may not provide an exact measure of the metal dispersion or of the active ruthenium sites. Thus, the calculated TOF based on hydrogen chemisorption and summarized in Table 3 should be considered as maximum values. Table 3 compares the TOF's at 523 K and the apparent activation energies for CO conversion for the various catalysts. No significant effect of the nature of the neutralizing alkali-cations on TOF was found, and the TOF's do not differ markedly from that of Ru/$SiO_2$. With similar metal loadings, the concentration of the structural hydroxyl groups, formed during the reduction of the ruthenium ions in LiY, NaY, KY, RbY and CsY, should be comparable in all these catalysts. It is generally accepted that for alkali cation zeolites, exchange of sodium ions for smaller cations or larger ones produces a change in the electrostatic field inside the zeolites, and hence a change in the strength of their acid sites (1). The larger the charge-to-radius ratio, the greater would be the electrostatic field and the strength of acidity.

However, with monovalent cations such as $Li^+$, $Na^+$, $K^+$, $Rb^+$, and $Cs^+$, the variations in the acidity of the zeolite remain still too small to produce significant differences in the activities of these catalysts (2). However, the TOF obtained for RuHY is four times greater than that for the other catalysts. This high activity of RuHY cannot be attributed only to a metal particle size effect, since, as pointed out earlier, the crystallite size calculated from $H_2$ chemisorption was most probably overestimated. Assuming a similar dispersion to that found for RuNaY, the TOF for RuHY still remains greater by at least a factor of 2, suggesting a metal support interaction which increases the turnover number of Ru on HY zeolite.

Several workers have observed a similar trend of increasing activity for CO hydrogenation with increasing acidity of the support. Thus, Fajula et al. (3) found a higher activity for methanation on PdHY than on PdNaY catalysts. They suggested a participation of acid sites of the support in CO hydrogenation. Similarly, Arai (4) found that the activity for F-T reactions was higher on RhHY than on RhNaY. Vannice (5) has also suggested that an increase in the acidity of the support produces an increase in methanation activity of palladium. Similarly, Leith (6) found that when sodium ions in Y-zeolites were exchanged by multivalent cations or protons, a two-to-three fold increase in the specific activity of Ru resulted.

In all the works reviewed above, the enhancement of the activities of the metal, be it Pd, Rh or Ru, on the more acidic zeolites were attributed to an increase in the surface concentration of the less strongly bound carbon monoxide species, resulting from the electron deficient character of the supported metal which increases with the acidity of the support. Several workers have examined the infrared spectra of CO adsorbed on Pd (7), Rh (4), and Ru (8) catalysts and found evidence that an increase in strength of support acidity produces a shift to higher frequencies and an enhancement of bands assigned to linearly adsorbed CO. The presence of electron acceptor sites on the support, i.e., the acidic hydroxyl groups, produces some electron depletion at the metallic surface and hence a decrease in availability of d-electrons for back donation. These results are also consistant with the suggestions by Vannice (9) and Okuhara et al. (10) that a weakening of the metal-carbon monoxide bond, paralleled by an increase in hydrogen adsorption, results in a higher activity for CO hydrogenation.

## Selectivity

The term selectivity used in the present paper refers to the weight fraction of CO converted into a given hydrocarbon or a group of hydrocarbons. Table 4 compares the hydrocarbon product distributions obtained at 523 K on the various catalysts.

It is seen that for the different Y-zeolite-supported Ru the selectivity for $CH_4$ formation and the chain growth probability at a given temperature, are essentially the same regardless of the nature of the neutralizing alkali cations. Moreover, use of protons to neutralize the $AlO_4$-groups of the zeolite does not seem to produce any significant change in $CH_4$ selectivity or chain growth probability. Therefore, a fundamental difference exists between the influence of alkali cations when used as neutralizing cations in a zeolite framework and their effect when added as promoters. Indeed ~~in~~ the latter case, it has been repeatedly shown (11) that alkali promoters cause a shift to higher hydrocarbons at the expense of methane formation. Consequently, it may be concluded that, provided the zeolite type is conserved, neither the alkali cations nor the total acidity has a substantial effect on the product selectivities, at least at atmospheric pressure.

In studying CO hydrogenation over a series of Ru/zeolites, Jacobs et al. (12) reported that under typical Fischer-Tropsch conditions ($H_2/CO = 1/1$, GHSV $= 1800\ hr^{-1}$, $T \sim 523$ K), RuNaX gave a higher selectivity for higher hydrocarbons than RuNaY did. This behavior was explained on the basis of a stronger metal-support interaction in the case of RuNaY due to the fact that NaY is more acidic than NaX. However, in the present work, RuHY and RuNaY exhibited the same selectivity for $CH_4$ despite the higher acidity of the former catalyst. Therefore, our results cannot be fully explained in the same terms as those reported in reference (12). The possible linkage between $CH_4$ formation and the acidity of the support cannot be totally ruled out. Indeed, the correlation between the selectivity for methane and Si/Al ratio of the support (13) suggests that the relative amount of $CH_4$ is connected to the acid strength rather than the total acidity. Indeed, Barthomeuf (14) reported an excellent correlation between the acid strength of a series of zeolites and their Si/Al ratios. In addition, another important factor was stressed by this author: the nature of alkali cations as well as the partial or total decationization of a given zeolite induced a much less pronounced change in the acid strength than that brought about by a variation in Al content. This should explain why all our RuY zeolites gave almost the same selectivity for $CH_4$ and the same chain growth probability ($\alpha = 0.5$) regardless of the nature of the neutralizing cations.

## Olefin Fraction

The neutralizing cations in Y-zeolites were found to have a strong influence on the olefin-to-paraffin ratio ($C_3^=/C_3$) as illustrated at constant temperature in Table 4 and at constant CO conversion in Table 5. The $C_3^=/C_3$

ratio was highest when the larger alkali cations had been exchanged into the zeolite and followed more or less the sequence Cs > Rb > K > Na ~ Li > H. As pointed out in the previous sections, the acidic properties of the zeolites are expected to decrease, although not drastically, in the reverse order.

Leith (15) has also observed that the olefin selectivity of zeolite supported ruthenium in the hydrogenation of carbon monoxide is enhanced when potassium and cesium are exchanged into Y-zeolites. He interpreted his results in terms of a lowering of the hydrogenating activity of the metal, as a result of a decrease in the electron deficient character of the metal particles by the introduction of larger alkali cations into the support. However, this interpretation cannot fully account for these results, since, if significant electron transfer between the metal and the zeolites had occurred, one would expect an effect on both the activity and the product distribution. However, as pointed out in the previous sections, such effects were not observed.

Thus, the enhancement of the olefin selectivity in the presence of larger alkali cations may be due to other factors than the relative strength of acidity of the various catalysts. It has been suggested (16,17) that the electrostatic field inside the zeolite, the strength of which correlates with increasing charge-to-radius ratio (18) acts directly on the reacting molecules rather than on the metal. It has also been suggested by Barthomeuf (1) that a competition for reactant adsorption between the various sites present (cations, protons, and here metal sites) may affect the catalytic activity. It has been shown that the adsorption of hydrocarbons increases in the order Li < Na < K < Rb < Cs (7), thus suggesting an effect of the nature of the cation on the secondary hydrogenation of olefins. Further work is necessary for a better understanding of these phenomena.

## IV. FORECAST OF WORK

The activities planned for the next quarter are a completion of an investigation of the electrostatic field effect of the cations using other test reactions such as cyclopropane hydrogenolysis and benzene hydrogenation and a commencement of a more detailed study of the effect of Si/Al ratio, using the same zeolite structure (Y-zeolite) but varying the Si/Al ratio by dealumination.

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Table 1: Catalyst Characteristics Based on Hydrogen Chemisorption

| No. | Catalyst | Loading (wt%) | $H_2$ (irr.) (μmole/g.cat.) | D (%) | $\bar{d}_p$ (Å) |
|---|---|---|---|---|---|
| 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.) (μmol/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 |

Table 3: Catalytic Properties of Ru Catalysts at 523 K

| No. | Catalyst | CO Conversion (%) | TOF ($s^{-1}x10^3$) | $E_{CO}$ (kJ/mol) |
|---|---|---|---|---|
| 1 | RuHY | 8.3 | 40.5 | 74.5 |
| 2 | RuLiY | 3.4 | 10.7 | 67.3 |
| 3 | RuNaY | 4.8 | 10.5 | 66.1 |
| 4 | RuKY | 2.3 | 8.0 | 80.7 |
| 5 | RuRbY | 4.4 | 14.1 | 100.6 |
| 6 | RuCsY | 4.5 | 12.4 | 100.1 |

Table 4: Selectivities of Ru Catalysts at 523 K

| No. | Catalyst | Selectivity (wt%) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ | $C_3^=/C_3$ |
| 1 | RuHY | 34.3 | 13.7 | 19.1 | 17.1 | 12.3 | 3.5 | 1.1 |
| 2 | RuLiY | 33.4 | 14.3 | 21.8 | 17.6 | 11.8 | 1.1 | 2.8 |
| 3 | RuNaY | 36.9 | 14.8 | 20.9 | 15.1 | 9.8 | 2.4 | 2.3 |
| 4 | RuKY | 30.7 | 13.7 | 23.5 | 15.8 | 11.0 | 5.2 | 6.4 |
| 5 | RuRbY | 33.5 | 14.4 | 22.0 | 15.3 | 9.7 | 5.1 | 5.7 |
| 6 | RuCsY | 36.1 | 13.2 | 21.6 | 15.1 | 9.8 | 4.2 | 6.1 |

Table 5: Cation Effect on Selectivity at Constant CO Conversion

| Catalyst | T(K) | CO Conv. (%) | $C_1$ (wt%) | $C_3^{=}/C_3$ |
|---|---|---|---|---|
| RuHY | 503 | 4.5 | 23.4 | 2.3 |
| RuLiY | 533 | 4.5 | 38.3 | 2.0 |
| RuNaY | 523 | 4.8 | 36.9 | 2.3 |
| RuKY | 543 | 4.5 | 35.3 | 4.2 |
| RuRbY | 523 | 4.4 | 33.5 | 5.7 |
| RuCsY | 523 | 4.5 | 36.1 | 6.1 |

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