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CATION PROMOTION EFFECTS IN ZEOLITE-SUPPORTED F-T CATALYSTS. FIFTH QUARTERLY REPORT, SEPTEMBER-NOVEMBER 1984

PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL
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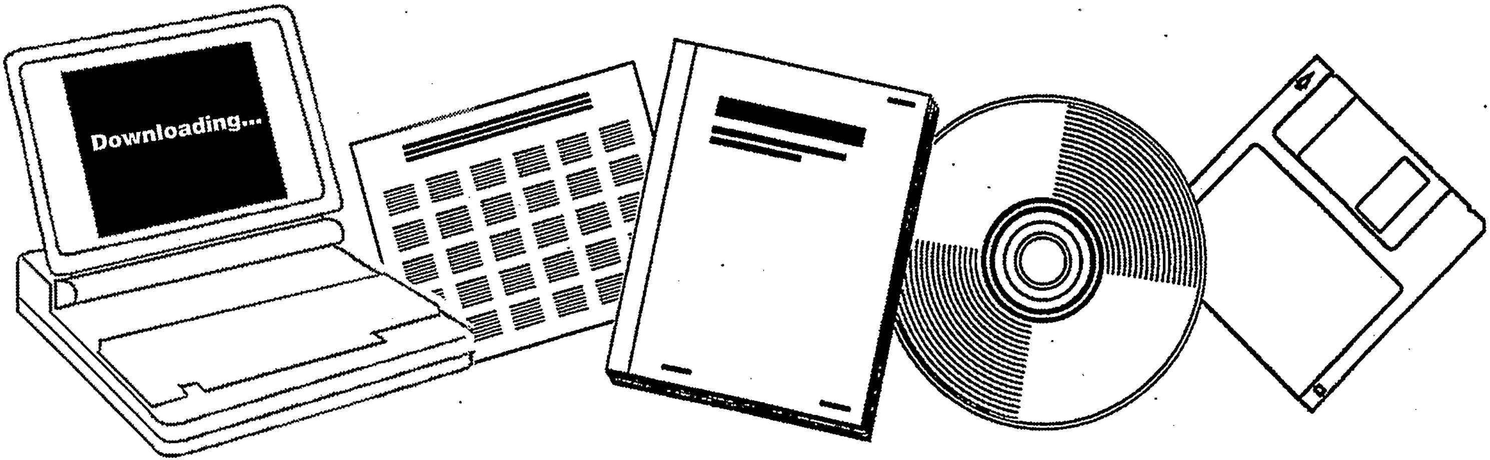

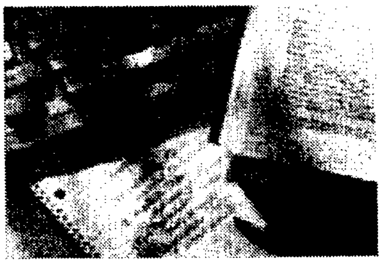

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CATION PROMOTION EFFECTS IN ZEOLITE-SUPPORTED F-T CATALYSTS

5th Quarterly Report
September 1984 - November 1984

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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 neutalizing 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 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 (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

During this quarter, September 1 to November 30, 1984, we have concentrated our efforts mainly on the characterization of the various catalysts under study, by selective hydrogen and carbon monoxide chemisorption. The results obtained from these measurements point to the need to use other techniques such as XRD and TEM in order to fully characterize these catalysts before trying to correlate the results from the CO hydrogenation experiments with the chemisorption properties of the various catalysts.

During the same period, further CO hydrogenation experiments have been performed at atmospheric pressure and in the temperature range 220-300°C. Also, TGA studies of ammonia adsorption are under progress in order to determine the effect of alkali cations on the acid strength of the various catalysts.

III DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Catalyst Characterization

The ruthenium catalysts under study (Ru/NaY, LiY, KY, CsY, RbY, HY, NaX, KL, NaMordenite), all prepared by ion-exchange, were characterized by selective gas chemisorption at 25°C. The hydrogen chemisorption measurements were used to calculate the metal surface area, particle size, and dispersion as described in the 2nd quarterly report. The amounts of irreversibly chemisorbed hydrogen were used in these calculations since this quantity has been shown to best reflect the stoichiometry of H/Ru(s) = 1(1). However, H_2 chemisorption alone may not be very reliable for characterization when the metal is highly dispersed on acidic supports such as zeolite-supported ruthenium prepared by ion-exchange(2). With such supports the suppression of hydrogen chemisorption may be significant. Therefore carbon monoxide chemisorption at 25°C was also carried out on the same samples, after desorption of H_2 at 420°C under vacuum. The same procedure as for the H_2 adsorption measurements was used. CO chemisorption has also been shown to be inadequate for surface area determination, since the stoichiometry of CO adsorption on Ru is determined by the metal particle size.(3,4) However, CO chemisorption can serve to compare relative metal dispersions and the presence of H_2 chemisorption suppression since less support effects are evident in CO adsorption. From considerations of CO/H and CO/$Ru_{(total)}$ ratios, it is possible to tell whether suppression of hydrogen chemisorption took place on the Ru catalysts.

The results of H_2 and CO chemisorption for the various Ru catalysts are given in Tables 1 and 2. The average particle diameters, estimated by hydrogen chemisorption, were larger than the free diameter of the major zeolite cavities for all except the NaY-supported ruthenium. Several interpretations can be found in the literature to explain such large particle sizes. First, if some metal exists as large particles on the external surface of the zeolite, an average metal particle diameter larger than the size of the zeolite pores would be calculated from chemisorption even though most of the metal may exist as very small particles inside the zeolite. Such a situation has been observed by TEM for highly dispersed Ru/NaY catalysts(1). The error introduced by large particles deposited on the external surface can be aggravated by a significant collapse of the zeolite support and encapsulation of the metal. However, this has been shown not to be generally the case for most zeolites(5). Also, localized destruction of the lattice to form cracks and holes was observed by Verdonck et al(6). Thus filling of these voids by Ru metal would result in large particle sizes being measured. Encapsulation of the metal could also occur by another phenomenon. Gustafson and Lunsford(7) suggested that in the presence of H_2 the mobility of Ru is increased, resulting in the agglomeration of Ru in several adjacent unit cells where the particles may be connected through the windows of the zeolite framework. This would render some of the metal particles inaccessible to hydrogen adsorption. This behavior would be expected to be more significant for the KL and NaMordentie due to their straight channel framework.

The final explanation for these high calculated ruthenium particle sizes is that the suppression of irreversible hydrogen chemisorption could be significant for most zeolite-supported Ru prepared by ion-exchange, resulting in an overestimation of the average particle diameters. The CO/H chemisorption ratio has been shown to be a good indication of H_2 chemisorption suppression (2). In the absence of such suppression, the CO/H ratio was found to be between 2.5 and 4 for highly dispersed Ru$^{(4)}$. In cases where the suppression of hydrogen chemisorption was significant, ratios as high as 12 were found$^{(2)}$. From a consideration of the CO/H ratio it was shown that the suppression of hydrogen chemisorption increases as the Si/Al ratio of the zeolite support increases for ion-exchanged Ru catalysts. The presence and strength of acidic hydroxyl protons which is correlated with the Si/Al ratio are suggested to be the reason for hydrogen chemisorption suppression. As can be seen in Table 2 and Figure 1 where the Ru/CO ratios are plotted against the Si/Al ratios of the zeolite, except for the Ru supported on NaY, the CO/H ratios suggest little or no H_2 chemisorption suppression. However, this suppression cannot be ruled out completely, especially for the ruthenium catalysts dispersed onto highly acidic zeolite supports, i.e., RuHY, RuKL and RuNaMordenite. Indeed, the CO/H ratios were also found in previous studies$^{(4,8)}$ to be a function of particle size. These ratios decreased from about 5 to 1.5 as the average diameter increased from 10 to 100Å.

A plot of CO/H ratio versus average particle size (Figure 2) suggests that the metal particle sizes for RuNaM, RuRbY and RuHY are overestimated due, most probably, to suppression of hydrogen chemisorption. However, a consideration of the CO/Ru$_{(total)}$ ratios, which are less than unity, suggests that the ruthenium is not highly dispersed in these catalysts as compared to RuNaY. The large particle size obtained for RuNaX cannot be explained by trhe suppression of hydrogen chemisorption due to metal-support interactions as this type of catalysts did not usually exhibit any H_2 chemisorption suppression(8). In this case encapsulation of the metal in the zeolite pores and large particles on the external surface of the zeolite could be responsible for the suppression of hydrogen chemisorption and the high average particle diameter which results from it. For the other RuY catalysts with the various alkali cations, the average particle size is believed to be overestimated due to hydrogen chemisorption suppression, the amount of which varies with the degree of metal-support interaction. This metal-support interaction is believed to be a function of the nature of the alkali cation. TGA studies of ammonia adsorption are being carried out in order to determine the effect of alkali cations on the acid strength of the various catalysts. Further characterization of these catalysts by physical techniques such as XRD and TEM are also required in order to estimate more accurately the effect of the zeolite type and of the various cations in the Y zeolites on the chemisorption properties of these catalysts.

IV. FORECAST OF WORK

During the next quarter, the characterization of the various catalyst will be continued using

1. X-ray diffraction
2. repetition of H_2 and CO chemisorption on selected catalysts
3. TGA studies of ammonia adsorption

The CO hydrogenation experiments will be continued. a more complete interpretation of the results obtained from these experiments will be reported in the next quarterly report.

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Table 1: Characteristics Based on Hydrogen Chemisorption

Catalyst	H_2 (irr.) (μmole/g)	S (m^2Ru/g)	d (Å)	D (%)
3.21% RuHY	32	3.15	42	20
3.11% RuLiY	66	6.49	20	43
3.11% RuNaY	98	9.64	13	64
3.16% RuKY	78	7.67	17	50
3.20% RuRbY	32	3.15	42	20
3.17% RuCsY	54	5.31	24	34
3.15% RuNaX	21	2.06	63	13
3.16% RuKL	64	6.29	20	41
3.15% RuNaM	36	3.54	36	23
1.83% $RuSiO_2$	48	4.72	16	53

Table 2: CO Chemisorption

Catalysts	Si/Al Ratio	CO(in) (μmole/g)	CO/H_{ir}	CO/Ru_T
RuHY	2.41	138	2.1	0.4
RuLiY	2.41	420	3.2	1.4
RuNaY	2.41	795	4.3	2.6
RuKY	2.41	237	1.5	0.8
RuRbY	2.41	166	2.6	0.5
RuCsY	2.41	290	2.7	0.9
RuNaY	1.23	78	1.8	0.25
RuKL	3.0	400	3.1	1.3
RuNaM	4.52	275	3.8	0.9

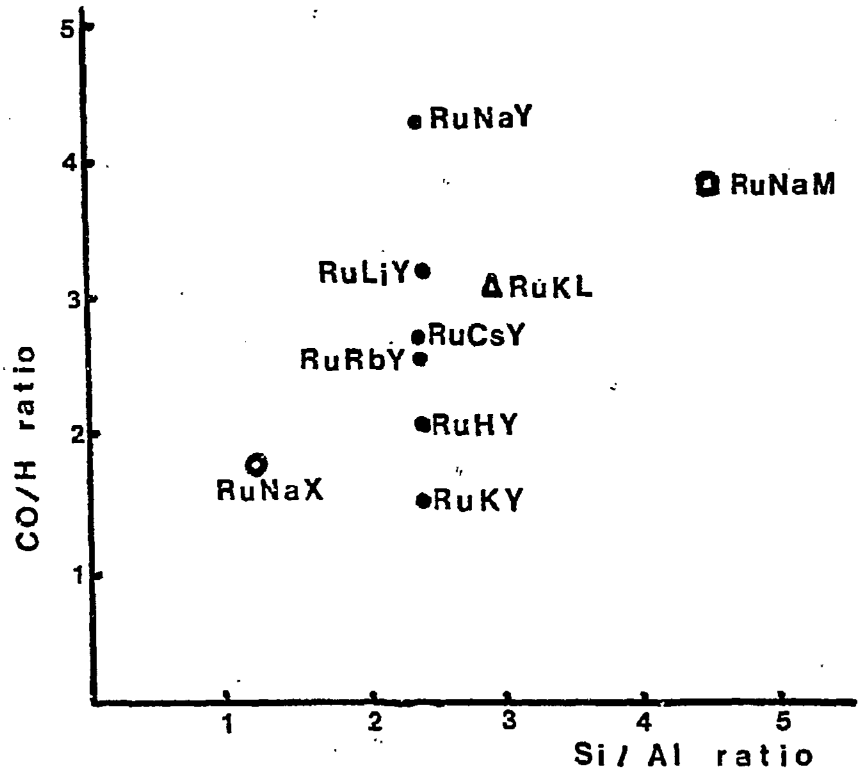

Figure 1: CO/H vs Si/Al ratio of the zeolite

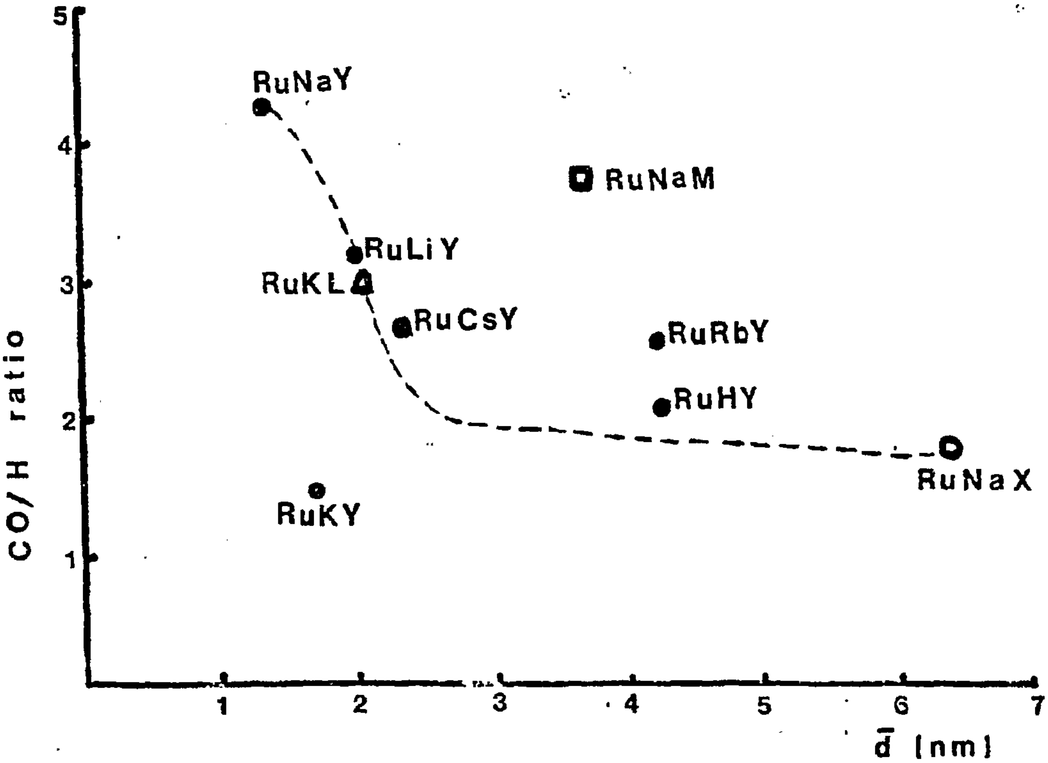

Figure 2: Effect of average Ru particle size on CO/H ratio

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