

Report 1

ZEOLITE SUPPORTED Ru IN THE F-T SYNTHESIS:
EFFECT OF ZEOLITE TYPE

J. Goodwin
University of Pittsburgh

ZEOLITE SUPPORTED Ru IN THE F-T SYNTHESIS: EFFECT OF
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James G. Goodwin, Jr., Y.-W. Chen, H.-T. Wang
and J. Z. Shyu

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

ABSTRACT

The effect of zeolite supports on the properties of Ru F-T catalysts has been studied. Ion-exchanged Ru catalysts were prepared using NaX, NaY, HY, KL, and NaMordenite have been characterized by IR, ESCA, and chemisorption and studied under F-T synthesis. The suppression of hydrogen chemisorption was found to be a strong function of the Si/Al ratio. Methane selectivity, however, seemed to be strongly influenced by the type and concentration of alkali cations remaining in the ion-exchanged zeolite. Some important factors which may affect the properties of a zeolite-supported metal catalyst are listed.

INTRODUCTION

Ruthenium has been recognized as one of the best metals for the Fischer-Tropsch synthesis (1). It has the ability to produce significant amounts of higher hydrocarbons even at a pressure of only one atmosphere. In addition, it is considerably easier to reduce than other Fischer-Tropsch metals, such as Fe and Co, and is not converted to a carbide under F-T reaction conditions. While silica, alumina, and other metal oxides have been widely used as supports for transition metals, the use of zeolite supports has been fairly limited. Due to their high surface area, shape selective character, acidic nature, ion-exchange properties, and well-defined structure, zeolites have a great potential in Fischer-Tropsch catalysis. The high surface area allows a high degree of metal dispersion in the zeolite, while the acidity, cation-exchange properties, and shape-selectivity can significantly affect the selectivity of the catalysts.

It has been reported by Jacobs et al. (2) that, for Ru ion-exchanged with a wide variety of zeolites, the activity for methanation increased by a factor of three as the Si/Al ratio of the zeolite support decreased, provided the temperature of reduction was only 300°C. Accompanying this decrease in Si/Al ratio was also a shift in product selectivity towards higher hydrocarbons. Due to the high metal loading used, the Ru was not very highly dispersed in these catalysts. Few results on F-T activity and selectivities were given.

The present studies were undertaken to further investigate the effect of the type of zeolite support on Ru catalysts in Fischer-Tropsch synthesis. These catalysts were supported on NaX, NaY, KL, NaMordenite, and HY.

EXPERIMENTAL

The zeolites were obtained from Strem Chemicals (X, Y and L types) and Norton (NaZeolon = large port Na Mordenite). The composition of the dehydrated zeolite was X: $\text{Na}_{36}(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}$ Y: $\text{Na}_{56}(\text{AlO}_2)_{56}(\text{SiO}_2)_{135}$ L: $\text{K}_9(\text{AlO}_2)_9(\text{SiO}_2)_{27}$ M: $\text{Na}_8(\text{AlO}_2)_8(\text{SiO}_2)_{40}$. HY was prepared by ion-exchange of NaY to form NH_4Y which was then calcined at 538°C . The extent of exchange was 84%.

For preparing the ion-exchanged catalysts, $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ was dissolved in a weakly acidic hydrochloride solution ($\text{pH} = 4.5$). This solution was then mixed with the zeolite and stirred continuously for 50 hours at ambient temperature. Excess solution was used to maintain an approximately constant pH during ion-exchange. After the ion-exchange reaction, the catalysts were filtered and washed several times in deionized water and dried in air overnight at 40°C . The catalysts were usually decomposed slowly under vacuum (ca. 3×10^{-7} torr.) by heating to 420°C ($0.5^\circ\text{C}/\text{min}$) and holding at that temperature for 2 hours. These catalysts were then reduced in pure hydrogen at 420°C for two hours. Otherwise, the catalysts were decomposed under flowing E_2 by heating slowly in a stepwise fashion to 420°C and holding for two hours. No significant differences in catalytic behavior were found to result from these different decomposition procedures.

The reduced catalysts were characterized by H_2 and CO chemisorption (static gas volumetry), A.A., IR, and ESCA. The gas chemisorption measurements were conducted at ambient temperature in a glass adsorption system capable of achieving a vacuum of ca. 3×10^{-7} torr. Total chemisorption of hydrogen or carbon monoxide was determined by extrapolation of the linear part of the first isotherm to zero pressure, corresponding to

the method described by Benson and Boudart (3) and Wilson and Hall (4). A second isotherm was measured after evacuation of the sample for 2-3 minutes following the first isotherm. The second isotherm provided a measure of the reversibly bound hydrogen or carbon monoxide (both chemisorbed and physisorbed). The difference between the two isotherms gave the amount of irreversibly chemisorbed hydrogen or carbon monoxide.

The Ru metal loadings of the catalysts were determined by A.A. using the method of Fabec (5). I.R. spectroscopy was used to study CO adsorption on Ru. The I.R. cell was constructed of pyrex and had KCL windows. The cell had vacuum stopcock valves at both ends to provide gas flow in and out. The catalyst was ground slightly in an agate mortar and then compressed under 3×10^4 psi into a self-supporting disc having a diameter of 2.5 cm and a weight between 30 and 50 mg. Following catalyst pretreatment and adsorption of CO, spectra were recorded at 25°C. ESCA data were taken via a sealable probe of catalysts which had been reduced but not exposed to air. An AEI ES200 ESCA spectrometer with an Al anode was used.

Reaction measurements were made at 1 atm total pressure using a 3/8 in. stainless steel tube reactor containing approximately 0.5 g of catalyst. The reactant gases used were H₂ (99.999%), He (99.997%), and a H₂/CO mixture (H₂/CO = 1, 99.9%), which were purified by passing through drierite and 5A molecular sieve traps to remove water and metal carbonyl contaminants. Prior to passage through the molecular sieve trap, the hydrogen was passed through a Deoxo unit to remove oxygen. The flow rate of each gas was controlled by a micro-metering valve and measured by a rotameter. The product gas was transferred from the reactor to the sampling valve of the gas chromatograph via a heated transfer line and was analyzed by a Perkin Elmer Sigma 1 Gas Chromatograph. Products were separated using a 6 ft. x 1/8 in. stainless

steel column packed with Porapak Q and were detected by T.C.D.. A 0.5 cm³ gas sample was injected into the column while its temperature was held at 50°C for 2 min. The column oven was then temperature programmed at 15°C/min to 180°C. The bracketing technique, which gave the catalyst a 40 min. H₂ exposure after every kinetic measurement, did an exceptionally good job of maintaining a clean Ru surface and giving reproducible results. In order to make sure that there was no hydrocarbon produced due to the mixing of pure H₂ and the reaction mixture by gaseous diffusion during the initial period of each reaction run, the H₂ and reaction mixture flows were separated by a short flow of He. The CO conversion was kept below 5% to minimize the effects of heat and mass transfer and secondary reactions.

RESULTS AND DISCUSSION

The IR investigation of CO adsorption of these Ru zeolite catalysts at 25°C produced spectra similar to those previously reported (6). These results showed that, in general, as the Si/Al ratio of the support increased the frequency of the absorbed CO also tended to increase indicating weaker CO chemisorption. The one case that deviated slightly from this trend was that of RuKL. It is felt that the slight deviation to lower CO vibrational frequencies was due to presence of K⁺ in the L zeolite as opposed to Na⁺ in all the other zeolites studied. This would seem to be reasonable given the relatively greater ability of K compared to Na to destabilize CO in alkali promoted F-T catalysts.

ESCA spectra from the reduced catalysts indicated a fairly complex structure. In all cases these were 3 resolvable peaks in the Ru 3p_{3/2} region. In general, the ESCA data did not show a great difference among the various catalysts. From the results, one could conclude that in every case

very small particles of Ru were predominately present and were in a number of different environments. The resulting species seemed to be the following: cationic Ru under the strong influence of the electrostatic field of the zeolite, small reduced Ru particles interacting with the support, and small reduced Ru particles, probably located in the super cages, which were affected strongly by the alkali cations present.

From H_2 chemisorption at $25^\circ C$, average Ru particle diameters and dispersions were calculated (Table 1). It would appear that as the Si/Al ratio of the zeolite support increases larger average particle diameters result. However, it becomes apparent from a consideration of the CO/H ratios that suppression of hydrogen chemisorption took place on the Ru catalysts with higher Si/Al ratios (it is impossible for 1 Ru atom to bond to 12 CO ligands). The amount of such suppression was directly related to the Si/Al ratio (Figure 1). Since the stoichiometry of CO adsorption on Ru is determined by the metal particle size (7), it is difficult to use CO to determine metal surface areas. However, CO chemisorption can at least serve to compare relative metal dispersions. The CO/Ru_T ratios in Table 1 would seem to indicate that the Ru dispersions in the various catalysts were similar and probably on the order of 70 - 90%.

The F-T synthesis was carried over a range of temperatures. Table 2 shows typical results for the various catalysts at $250^\circ C$. As can be seen in Table 2, the specific rate of reaction of CO varied by a factor of 2. Specific rate is used due to the uncertainty in the determination of the number of Ru surface sites; however, based on the discussion in the previous paragraph, these specific rates should vary, approximately in the same way as the turnover number (T.O.N.) The observed differences in specific rate do not seem to be related to any of the known characteristics of the zeolite, such

as: Si/Al ratio, OH concentration, alkali concentration. From an intensive study of RuNaY catalysts (8), it has been found that T.O.N. is a strong function of average particle size. While other factors may have also been important, particle size would seem to have played a principal role. On the other hand, selectivity did not seem to be greatly influenced by the size of the Ru particles.

Table 2 also shows that the olefin fraction in the C₂-C₄ hydrocarbons is approximately constant. The values that deviate the most from 0.53 do so due to the fact that mostly methane was produced in those cases, hence the error in determination of the quantities used to calculate the C₂-C₄ olefin fraction was much greater.

There were very large differences in the selectivity for methane. Since particle size is not a factor in determining this quantity, one must look to characteristics of the zeolite supports which might affect it. Three of the most likely candidates are: Si/Al ratio, OH concentration in the reduced catalysts, and the concentration and type of alkali cations remaining after ion-exchange. These characteristics might cause a given effect by affecting the Ru directly in some type of metal-support interaction or by interacting directly with primary or secondary products. Figure 2 shows a plot of methane selectivity versus Si/Al ratio. As can be seen, Si/Al ratio does not appear to correlate very well. Figure 3 shows a plot of methane selectivity versus OH concentration. This concentration too does not appear to greatly affect this selectivity. However, methane selectivity appears to be a strong function of alkali concentration. (Figure 4). This should not be surprising considering that alkali species are well known promoters of the F-T synthesis and tend to increase chain growth probability and, thereby, to decrease the methane selectivity. The only catalyst that deviates greatly from the linear

relationship in Figure 4 is RuKL. This deviation is most likely due to the fact that this zeolite contains K^+ instead of Na^+ like the others. If Na in a zeolite does have a promotion function, then K should have an even greater one since most results in the literature show K compounds to be better promoters of chain growth than Na compounds. In fact the result for RuKL lies well below the line connecting the points for the other catalysts and has a much lower methane selectivity than it would if it were on the line.

A significant fraction of C_4 was in the form of iso-butane for a number of the catalysts. OH concentration did not appear to play a role in producing this compound. Both the Si/Al ratio and alkali concentration seemed to be related to the formation of iso-butane, but it is impossible, at this time, to suggest that one is more important than the other. King (9) explored F-T synthesis over a group of Ru catalysts having NaX, NaY, and silica-alumina as supports. He found that the Si/Al ratio appeared to be important in affecting the fraction of iso-butane formed. Our results are in accord with his.

CONCLUSIONS

A series of ion-exchanged zeolite-supported Ru catalysts have been studied, and the following conclusions can be drawn:

- H_2 chemisorption suppression becomes important as the Si/Al ratio of the zeolite increases.
- Specific activity may be related primarily to the Ru particle size distribution.
- Methane selectivity appears to be strongly related to the concentration of the alkali cations remaining.
- Olefin selectivity does not seem to vary greatly with the different supports.

- Formation of iso-butane is perhaps related to either the Si/Al ratio or the concentration of the remaining alkali but not to the OH concentration.

As far as is known, this is the first time that chain growth promotion in F-T by the neutralizing alkali cations in the zeolite has been suggested.

It is important to keep in mind that there are a large number of factors which may affect the properties of a zeolite-supported metal. Some of them are: metal particle size and geometry, metal reducibility, location of metal, pore structure, OH concentration and strength, Lewis acidity, neutralizing cations present and their concentration, interaction of the metal with the zeolite (OH's, L.A. sites, cations, structural oxygen), defect structure, and presence of impurities. Different preparation methods (8), pretreatment conditions, etc., may cause different factors to be important in determining catalytic properties.

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REFERENCES

1. M. A. Vannice, *J. Catal.* 37, 449 (1975).
2. P. A. Jacobs, J. Verdonck, R. Nijs, and J. B. Uytterhoeven, in Hydrocarbon Synthesis from Carbon Monoxide and Hydrogen, ed. by E. L. Kugler and F. W. Steffgen, *Adv. in Chem. Series 178*, A.C.S., 1979, pp 15-23.
3. J. E. Benson and M. Boudart, *J. Catal.* 4, 704 (1965).
4. G. R. Wilson and W. K. Ball, *J. Catal.* 17, 190 (1970).

5. J. L. Fabec, submitted for publication.
6. D. G. Blackmond and J. G. Goodwin, Jr., J.C.S. Chem. Comm., 125 (1981).
7. C.-H. Yang and J. G. Goodwin, Jr., Kin. and Cat. Lett., in press.
8. Y.-W. Chen, H.-T. Wang, and J. G. Goodwin, Jr., manuscript in preparation.
9. D. L. King, J. Catal. 51, 386 (1978).

TABLE 1
CHARACTERISTICS BASED ON CHEMISORPTION

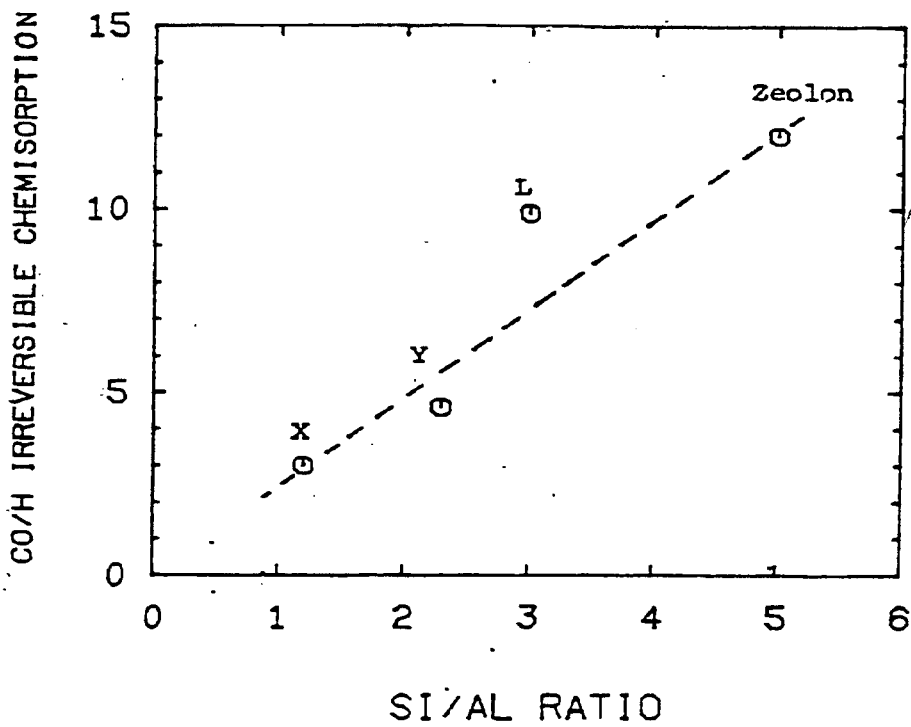
Catalyst	\bar{d}_p^* (A)	D^* (%)	CO/H _{ir}	CO _{ir} /Ru _T
2.5% RuNaX	10	83	2.98	2.47
3.1% RuNaY	16	51	4.59	2.24
3.0% RuHY	-	-	-	-
2.8% Ru KL	26	32	9.88	3.16
2.2% RuNaM	39	22	12	2.64

* determined from irrev. H₂ chemisorption

TABLE 2
EFFECT OF THE SUPPORT ON F-T SYNTHESIS

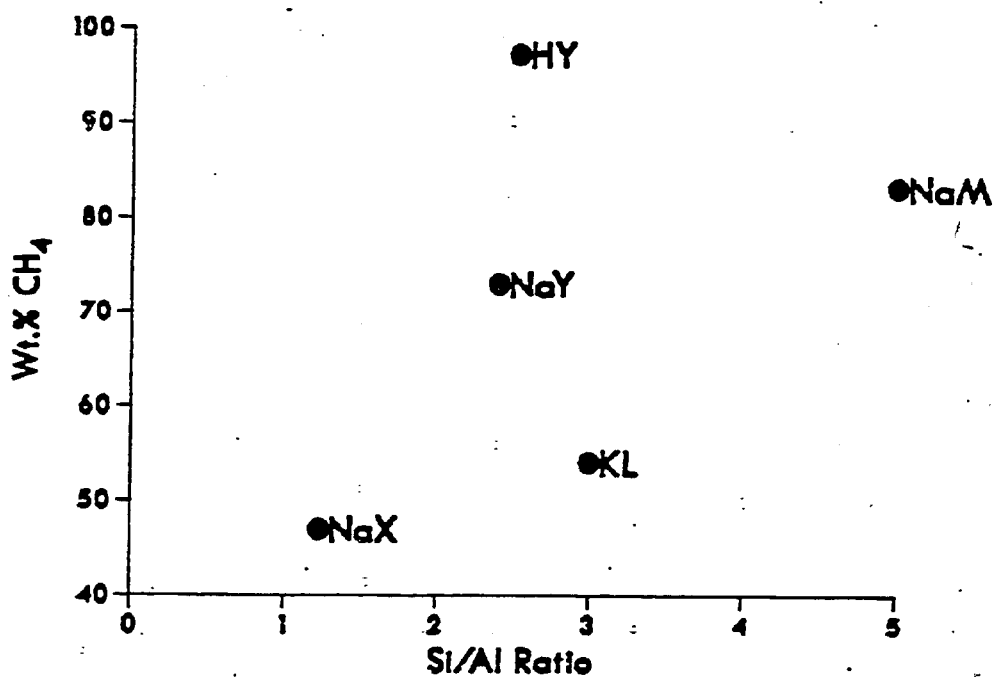
Catalyst	$-r_{CO}$ (mole/sec·g cat.)	CH ₄ (wt.%)	Ole. frac. in C ₂ -C ₄
2.5% RuNaX	2.46	47	0.49
3.1% RuNaY	1.21	73	0.53
3.0% RuHY	1.23	97	~ 0.59
2.8% RuKL	2.20	54	0.56
2.2% RuNaM	1.06	83	~ 0.38

Reaction conditions: 250°C, H₂/CO = 1, 1 atm, GHSV = 1800 hr⁻¹
 Products det. by T.C.D. through C₅ (little HC above C₅).



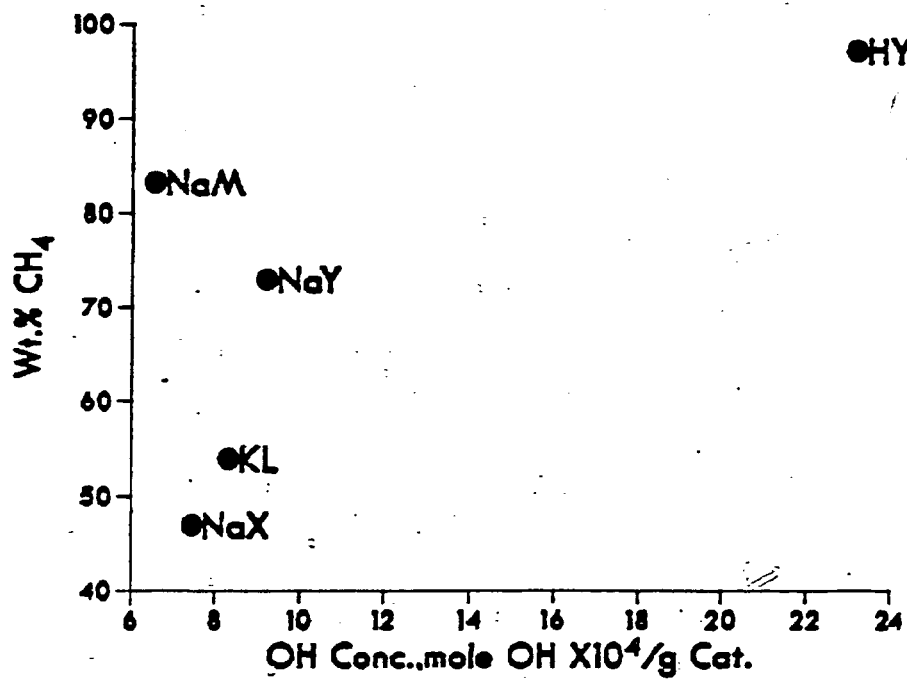
Variation in $(CO/H)_{ir}$ with Si/Al Ratio of Support
catalysts prep. by ion-exchange

FIGURE 1



Methane Selectivity vs. Si/Al Ratio for Ru/Z(I.E.)
(Reaction at 250°C)

FIGURE 2



Methane Selectivity vs. OH Concentration for Ru/Z(I.E.)

(Reaction at 250°C)

FIGURE 3

Dr. Richard R. Schehl
U.S. Dept. of Energy
Pittsburgh Energy Tech. Center
P.O. Box 10940
Pittsburgh, PA 15236

Mr. Edward Schmetz
U.S. Dept. of Energy
Div. of Coal Liq. Technology
FE-43 F-311GTN
Washington, DC 20545

Dr. Russell C. Schulz
UOP-Process Division
20 UOP Plaza
Des Plaines, IL 60016

Dr. Abolghasem Shamsi
U.S. Dept. of Energy
Pittsburgh Energy Tech. Center
P.O. Box 10940
Pittsburgh, PA 15236

Mr. Andrew G. Sharkey, Jr.
U.S. Dept. of Energy
Pittsburgh Energy Tech. Center
P.O. Box 10940
Pittsburgh, PA 15236

Dr. John Shen
U.S. Dept. of Energy
FE-34 E-328 GTN
Washington, DC 20545

Dr. William Slegier
Brookhaven National Laboratory
Building 526
Upton, NY 11973

Dr. Dennis N. Smith
U.S. Dept. of Energy
Pittsburgh Energy Tech. Center
P.O. Box 10940
Pittsburgh, PA 15236

Dr. Fred W. Steffgen
U.S. Dept. of Energy
Pittsburgh Energy Tech. Center
P.O. Box 10940
Pittsburgh, PA 15236

Dr. John M. Stencil
U.S. Dept. of Energy
Pittsburgh Energy Tech. Center
P.O. Box 10940
Pittsburgh, PA 15236

Dr. Richard A. Strehlow
Oak Ridge National Lab.
P.O. Box X
Oak Ridge, TN 37830

Mr. Gregory J. Thompson
UOP - Process Division
20 UOP Plaza
Des Plaines, IL 60016

Dr. Richard Tischer
U.S. Dept. of Energy
Pittsburgh Energy Tech. Center
P.O. Box 10940
Pittsburgh, PA 15236

Mr. Thomas Torkos
U.S. Dept. of Energy
Pittsburgh Energy Tech. Center
P.O. Box 10940
Pittsburgh, PA 15236

Dr. Anthony G. Vickers
UOP-Process Division
20 UOP Plaza
Des Plaines, IL 60016

Dr. Sterling E. Voltz
Mobil Research & Development
12 Billingsport Rd.
Paulsboro, NJ 08066

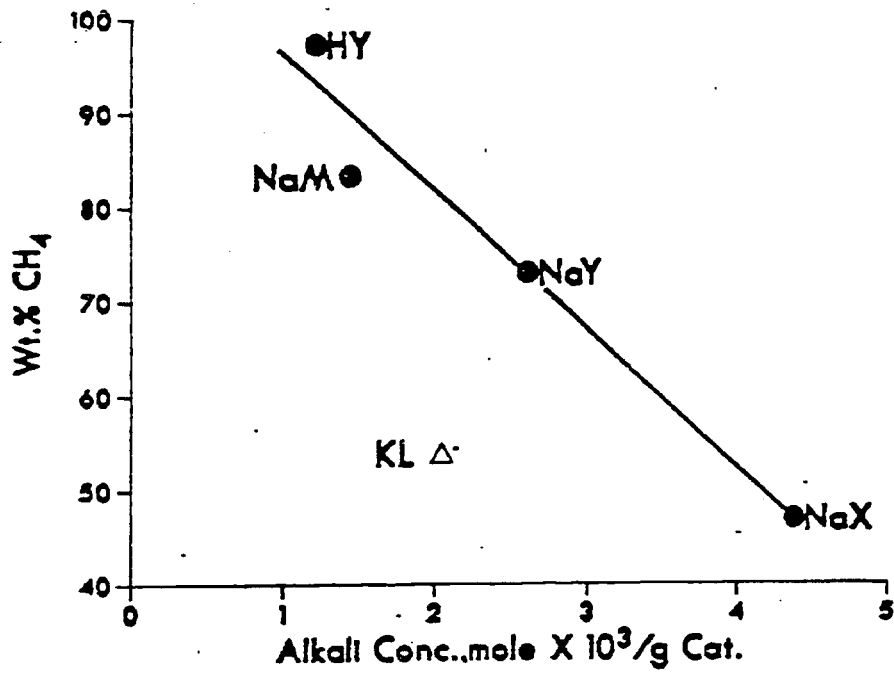
Dr. Charles H. Waide
Brookhaven National Lab.
Building 120
Upton, NY 11973

Dr. Irving Wender
University of Pittsburgh
Dept. of Chemical Engineering
1249 Benedum Hall
Pittsburgh, PA 15261

Dr. Chau-Hwa Yang
University of Pittsburgh
Dept. of Chem. & Petroleum
Engineering
1249 Benedum Hall
Pittsburgh, PA 15261

Dr. C. L. Yang
Union Carbide Corporation
Tarrytown, NY 10591

Mr. Michael F. Zarochak
PETC/US Dept. of Energy
P.O. Box 10940
Pittsburgh, PA 15236



Methane Selectivity vs. Alkali Conc. in Ru/Z(I.E.)
 (Reaction at 250°C)

FIGURE 4