Catalyst	Dispersion, %	*S.A.	Treatment Procedure
		m ² /g	
37 RuNaY	65.5	9.56	a-b-c-d-e-f-g
1.5% RuNaY	55.3	4.03	a-b-c-d-g
0.76% RuNaY	77.4	2.86	a-b-c-d-e-f-g
0.19% RuNaY	95.8	0 •89	a-b-c-d-e-f-g
17 Ru/NaY	77	4.12	h-b-g
3.86% Ru/SiO ₂	26	4 .88	1-c-d-g

Table 1 Catalyst Characterization Data

a. Prepared by ion-exchange with $Ru(NH_3)_6Cl_3$.

b. Decomposed in vacuum at 1° C/min up to 400° C.

c. H_2 reduction at 450°C ($P_{H_2} = 0.2$ atm).

d. H_2 adsorption at 25°C.

e. Desorption at 400°C for 2 hr.

f. CO adsorption at 25°C.

g. Exposed to air at room temperature.

h. Prepared by $Ru_3(CO)_{12}$ vapor phase deposition.

i. Prepared by RuCl₃•H₂0 wet impregnation.

* Ruthenium metal surface area, determined by H_2 chemisorption at 25°C.

Table 2 Kinetic Parameters for Ethane Hydrogenolysis on Ruthenium Catalysts

Catalyst E	a (kcal/mol) ⁺	Temp. Range (^o C)	N 160°C 10 ^{3%}	(H ₂ Rate Order)	m (C ₂ H ₆ Rate Order)	ln A
3% RuNaY	38.9	162 - 179	2 •93	-2 •0	0.8	37.7
1.5% RuNaY	38.5	173 - 191	0.66	-2.0	1.1	36.8
0.76% RuNay	32.1	160 - 178	5° C	-2.2	8 •0	29 .8
0.19% RuNaY	30.4	170 - 192	2.6	-1.6	6*0	28.9
1% Ru/NaY	33.7	173 - 194	6° E	-1 -6	0.8	35.0
3.86% Ru/S102	31.8	156 - 183	1.9	-2.21	0.66	28.4

Molecules/Ru surface atom.sec, the feed composition was 6% C_2H_6 , 15.6% H_2 , 78.4% He.

+1 kcal = 4.186 kJoule

<u>12</u>1



Figure 1. Arrhenius plots for ethane hydrogenolysis. Feed composition: 6% ethane, 15% hydrogen, 79% helium.



Figure 2. Arrhenius plots for cyclopropane hydrogenolysis on ruthenium supported on different supports. Feed composition: 3% cyclopropane, 20% hydrogen, 77% helium.



Figure 3. Influence of temperature on selectivity S₂ in the hydrogenolysis of cyclopropane.







Figure 5. Arrhenius plots for propane hydrogenolysis. Feed composition: 3% propane, 20% hydrogen, 77% helium.



Influence of temperature on selectivity S₅ in the propane hydrogenolysis for ruthenium catalysts with varying dispersion, D. Figure 6.

THE INFLUENCE OF THE SUPPORT ON K PROMOTION OF Ru FOR THE FISCHER-TROPSCH SYNTHESIS

C.H. Yang, Y.W. Chen, J.G. Goodwin, Jr., and I. Wender

Abstract

An investigation of the effect of the support on the K promotion of Ru F-T catalysts has been made. The support was found to play a great role in determining the modification in selectivity able to be obtained by promotion.

INTRODUCTION

Ruthenium is known as a good hydrogenation catalyst and has been found to have the highest Fischer-Tropsch (F-T) activity among Group VIII transition metals in producing linear hydrocarbons at high pressure and moderate temperature. Supported Ru, such as Ru/SiO_2 and Ru/Al_2O_3 , has been used to produce gaseous and liquid hydrocarbons, (1-3) but such catalysts have been found to give a poor selectivity for olefins and to produce methane as the major product at temperature higher than 260°C. Recent studies have shown that significant improvements in the catalytic selectivity in the F-T synthesis at low pressure can be obtained by metal-support interactions (4) or by alkali promotion (5) of the Ru.

Potassium and potassium salts" have long been used to enhance the activity and the selectivity for both olefinic and long chain hydrocarbons of Fe catalysts. For Ru, such K promotion has been found to activate the chemisorption of dinitrogen and thus increase the activity of ammonia synthesis at low temperatures and pressures. (6) It has been suggested that this occurs by electron donation to the catalytic metal. Activation of Ru by K promotion has been found to be considerable for both ammonia synthesis and CO hydrogenation reactions if a conductive support, such as graphite, is used. It has been inferred that an electron conductor may facilitate the transfer of electrons from the potassium to the ruthenium. (6 - 8) Earlier research reported that the addition of K to the Ru had no significant effect in changing the catalytic properties of the metal, either supported or non-supported. (9,10) However, Okuhara et al. (5) have recently found that the presence of K in a carbonyl-derived, highly dispersed Ru catalyst enhanced the preferential formation of C2-C5 olefins at 260°C but at the same time depressed the activity of the reaction.

This paper reports the results of an investigation into the effect of the support on the influence of K addition on the hydrocarbon selectivity of the Ru metal in the F-T reaction. In this study, different classes of Ru catalysts were prepared using traditional SiO₂ and Al₂O₃ supports, SMSI titania, graphite, and zeolite Y supports.

EXPERIMENTAL.

The titania support was from Degussa, and SiO₂ and NaY supports were from Strem Chemicals. The catalysts were prepared by impregnation of the supports with an aqueous solution of RuCl₃. 3H₂O or by ion-exchange of the NaY zeolite with Ru(NH₃)₆Cl₃. All the impregnated samples were made by the incipient wetness technique. These catalysts were dried in air at 40°C for 50 hours. Ru/Al₂O₃ and Ru/graphite were also obtained from Strem Chemicals. The addition of potassium was made by an impregnation of K₂CO₃ solution to the Ru catalysts followed by drying.

The standard pretreatment used for all the samples consisted of a stepwise heating procedure to 400°C in flowing hydrogen (50 cc/min). The samples were held at 400°C in hydrogen flow for at least 2 hours before cooling to the chosen reaction temperature in the range 250°C to 325°C.

* refer to all different forms of potassium, designated as K in this study.

Kinetic studies were carried out in two similar microreactor systems. The product gas was transferred from the reactor to the sampling valve of the G.C. via a heated transfer line and was analyzed either by a Hewlett-Packard 5750 or by a Perkin-Elmer Sigma 115 Gas Chromatograph equipped with TCD, FID, and Porapak Q columns.

The reactant gases used were $H_2(99.999\%)$, He(99.997%), and a H_2/CO mixture $(H_2/CO = 1, 99.9\%)$ which were further purified by passing through traps to remove water and metal carbonyl contaminants before passage through the reactors.

The steady state reaction rate was measured after catalyst stabilized. A Hydrogen Bracketing Technique was used in which the reactant stream was replaced by a pure H₂ flow after short reaction periods so as to maintain a clean metal surface. For all the samples studied, the catalytic activities were measured after 30 minutes of reaction and calculated from CO conversions based on CO flow rates coupled with carbon balances on the product stream. The CO conversion was kept below 5% to minimize the effects of heat transfer and concentration gradients. Typical F-T reaction conditions were applied to a variety of supported Ru catalysts at H₂/CO = 1 , 1 atm pressure, and a space velocity G.H.S.V. of 1800 hr⁻¹.

RESULTS AND DISCUSSION

The catalystic activities and the distributions of hydrocarbons for the various Ru catalysts are presented in Table 1 for a reaction temperature of 280°C. The specific rate of CO conversion for the unpromoted 5 wt% Ru catalysts was found to increase in the sequence: $TiO_2 < Al_2O_3$, $SiO_2 < NaY < graphite.$ The high activity of graphite-supported Ru is consistant with the result found in the literature for graphite-supported Fe in the synthesis reaction. (11) This behavior is probably due to the fact that graphite can enhance electron transfer to the metal. The Ru/TiO_2, although having the lowest activity in the series, shows high yields of olefins while methane formation is greatly reduced, as expected. It is obvious that the SMSI behavior is responsible for this superiority in olefin production.

In each case, the addition of K significantly enhanced the fraction of olefinic products (C_2-C_4) for the impregnated Ru catalysts. On the other hand, the rate of the synthesis is decreased by this addition. However, the selectivity of methane formation does not change markedly upon K addition.

The effect of temperature on methane and olefin fractions formed over these Ru catalysts is shown in Figures 1 and 2, respectively. Methane formation normally increases with increasing temperature of the reaction, since the possibility of hydrogenation of the primary surface complex is expected to be greater at higher temperature. A trend towards a decreasing fraction of olefins with an increasing temperature is also to be expected. It is apparent (Figure 2) that methane formation is not affected by the addition of K to the Ru catalysts in the temperature range 250°C to 325°C, except for Ru/Al₂O₃. On the other hand, the C₂-C₄ olefin fraction for all the promoted catalysts examined was found to remain essentially independent with increasing temperature. This behavior indicates that the presence of potassium atoms in the vicinity of Ru crystallites may have deactivated some active Ru sites for olefin hydrogenation.

The formation of liquid hydrocarbons (C5+) over the SiO2- and Al2O3supported Ru catalysts were also greatly enhanced by K promotion (Table 1). The hydrocarbon distribution from the F-T reaction over these catalysts can be fitted into the Anderson-Schulz-Flory equation. The chain growth probabilities calculated both from the slope and from the intercept of the fitted straight line are given in Table 2, designated as P_s and P_1 , respectively. Obviously, the addition of K has promoted chain growth on both SiO2- and Al2O3- supported Ru. However, it has no effect on higher hydrocarbon formation for the SMSI Ru/TiO2 catalyst.

CATALYSTS
Ru
6
PROPERTIES
CATALYTIC
TABLE 1:

-	H2/C0 = 1 Temp = 280°	C GHSV = 1	$800 \text{ hr}^{-1} \text{ P} = 1 \text{ a}$	Ē		
	Rate	H	Selectivity (wt)	%)	п С2 С2	۳ وی
Catalyst	(µmol/sec.gCata.)	СН _ф	.c2-c4 (ole%)	c5+	\mathbf{c}_{2}	5
5% Ru/S102	1.54	64.5	31.0(55) ^a	4.6	0.47	4.0
2.1%K,5% Ru/S102	0.15	62.3	32.6(87)	0.0	11.85	4.2
5% Ru/AL ₂ 0 ₃	1.08	49.1	43.0(61)	7.9	0.66	5.1
2.5%K, 5% Ru/A203	0.29	40.2	38.5(98)	21.2	22.40	53.5(
57 Ru/T102	1.34	33.1	49.5(68)	17.4	1.26	7.6
1.9%K, 5% Ru/TiO2	0.94	29.3	52.3(88)	18.4	4.90	20.8(
5% Ru/graphite	3.42	78.2	21.5(4)	0.3	0.05	0.0
2.5%K, Ru/graphite	1.37	65.3	37.7(85)	. 0	0.73	130.4
5% RuNaY (IW)b	3.13	86.7	13.1(5)	0.2	0.1	ł
2.5%K, 5% RuNaY	1.20	87.5	11.6(42)	. 6.0	0.43	1
3% RuNay (IE) ^c	2.96	89.2	10.8(22)	0	0.20	1.2
1.8XK, 3X RuNaY	2.24	95.7	4.3(18)	0	0.17	1.54
						in the second seco

Values in parenthesis are the wt% fraction of olefins in the C_2-C_4 total fraction. (a)

(b) by incipient wetness.

(c) by ton-exchange.







Figure 2 Temperature Dependence of CH₄ Formation.

PROBABILITY	OF	CHAIN	GROWTH	ACCOF	DING	TO
ANDER	50N-	-SCHULZ	Z-FLORY	PLOT	a	•

	Probability -		
Catalyst	Pi	Ps	
Ru/S102	0.39	0.38	
K- Ru/S102	0.45	0.44	
Ru/Al ₂ 03	0.41	0.42	
$K-Ru/Al_20_3$	0.53	0.53	
Ru/TiO ₂	0.50	0.50	
K- Ru/TiO2	0.50	0.50	

a. Reaction at 280°C, $H_2/CO = 1$, and $GHSV = 1800 \text{ hr}^{-1}$

Both ion-exchanged and impregnated RuNaY catalysts produced predominantly methans. The addition of K increased the olefin fraction by an order of magnitude for the impregnated RuNaY but it had no effect for that of the ion-exchanged catalyst. Since the ion-exchanged RuNaY is highly dispersed (> 60%) and with Ru predominantly inside the zeolite crystal, the Ru, therefore, is probably not accessible to the impregnated potassium salt. This can also be verified by comparing the activation energy of the reaction for both the unprompted and the promoted catalysts. It was found that the activation energy for CO conversion decreased between 20 to 50% after K addition for all the Ru catalysts except ion-exchanged RuNaY. For ion-exchanged RuNaY, it remained unchanged (ca. 22 Kcal/ gmole). It has been postulated that the addition of K decreases the activation energy of the F-T reaction on Fe by causing a lowering of the local ionization energy in the vicinity of an adsorbed K atom. (12)

The most significant change in hydrocarbon selectivity was found on graphite -supported Ru catalysts. The unpromoted Ru/graphite produces essentially only paraffins in the C₂-C₄ range while the K-Ru/graphite produced mainly olefins, surprisingly 82% of the total C₂-C₄ hydrocarbons produced was propylene. Previous research of K promotion on the Ru₃(CO)₁₂/Al₂O₃ catalyst has indicated that the maximum propylene produced from the F-T synthesis was 42% in total C₂-C₄ hydrocarbons. (5) The fact that the graphite is an electron conductor may be involved in this effect. Ozaki (6) and Sagert and Poutesu (7) have suggested that the electron density of the transition metal may have increased when it is supported on graphite. Addition of K to the Ru/graphite probably enhanced this effect.

CONCLUSION

The addition of a potassium promoter can greatly affect the catalytic properties of Ru in the F-T reaction, depending on the support chosen. It enhances olefin formation and higher hydrocarbon production for the traditional Al_2O_3 - and SiO₂-supported Ru. On Ru/graphite at 1 atm, it preferentially promotes propylene formation. Potassium enhances by about 20% the olefin production over Ru/TiO₂ in the temperature range 250°C to 325°C. As a result of alkali promotion of the Ru catalysts, the clefin fraction of the C₂-C₄ hydrocarbons produced becomes a weak function of the reaction temperature. Further study is needed to delineate the promoter-matal-support interactions.

LITERATURE CITED

- (1) Vannice, M.A., J. Catal. <u>37</u>, 449 (1975).
- (2) King, D.L., J. Catal. <u>51</u>, 386 (1978).
- (3) Karn, F.S., Shultz, J.F., and Anderson, R.B., Ind. Eng. Chem., Prod. Res. Develop. <u>4</u>, 275 (1965).
- (4) Vannice, M.A., and Garten, R.L., J. Catal. <u>63</u>, 255 (1980).
- (5) Okuhara, T., Kobayaski, K., Kimura, T., Misono, M., and Yoneda, Y., J. C. S. Chem. Comm. 1114 (1981).
- (6) Ozaki, A., Acc. Chem. Res. <u>14</u>, 16 (1981).
- (7) Sagert, N. H., and Poutesu, R. M. L., Can. J. Chem. <u>51</u>, 4031 (1973).
- (8) Vannice, M.A., Jung, H.-J., Walker, P.L., Jr., Moreno-Castilla, C., Mahajan, O.P., paper presented at the AICHE 88th National Meeting, Fuels and Petrochemicals Division, Philadelphia, June 1980.
- (9) Pichler, H., Adv. Catal. <u>4</u>, 289 (1952).
- (10) McVicker, G.B., and Vannice, M.A., J. Catal. <u>63</u>, 25 (1980).
- (11) Ino, T., Watanabe, H., Kikuchi, E., and Morita, Y., Bulle. Sci. Eng. Res. Lab., Waseda Daigaku <u>94</u>, 40 (1981).
- (12) Paol, Z., Ertl, G., and Lee, S.B., Appli. Surf. Sci. 8, 231 (1981).

EFFECT OF PREPARATION METHOD ON THE CATALYTIC PROPERTIES OF ZEOLITE-SUPPORTED RUTHENIUM IN THE FISCHER-TROPSCH SYNTHESIS

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ABSTRACT

Three preparation techniques [incipient-wetness using a solution of RuCl₃, vapor-impregnation by Ru₃(CO)₁₂, and ion-exchange with Ru(NH₃)₆Cl₃] have been used to prepare NaY zeolite supported ruthenium catalysts. The effect of these preparation methods on the activity and product selectivity of the Ru catalysts in the Fischer-Tropsch synthesis was examined at temperatures in the range of 220-320°C, a pressure of 1 atm, a CO/H₂ ratio of 1, and flow rates in the range GHSV = 1800-3600 hr⁻¹.

It was found that there is a good inverse correlation of turnover numbers for CO conversion to the CO/H adsorption ratio, suggesting that the relative availability of adsorbed H₂ and CO determines catalyst activity during reaction. Selectivity in the F-T synthesis was greatly influenced by the preparation method and metal loading. Catalysts prepared by incipient wetness produced mainly methane. Catalysts prepared by vapor impregnation had the bast selectivities for higher hydrocarbons and olefins even though they had the smallest average Ru particle sizes.

The observed changes in adsorption, activity, and selectivity with preparation method appear to result from differences produced in metal location in/on the zeolite, metal particle size, and zeolite-metal interactions.

I. INTRODUCTION

Ruthenium has been recognized as one of the best catalysts 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 FT catalysts, such as Fe and Co, and is not converted to a carbide under FT reaction conditions. The use of zeolite supports for FT synthesis is of particular interest since these supports offer several advantages over conventional supports, such as: (i) ability to maintain high metal dispersion, (ii) metal-zeolite interactions, (iii) bifunctional catalysis, and (iv) shape selectivity.

Various preparation techniques exist which enable one to prepare zeolitesupported metals having different physical and chemical properties. This paper reports on an investigation into the effect of these techniques on the catalytic properties of NaY-supported Ru for CO hydrogenation.

II. EXPERIMENTAL

Materials

Synthetic zeolite NaY, $RuCl_3$ °1.5 H_2O , $Ru(NH_3)_6Cl_3$, and $Ru_3(CO)_{12}$ were obtained from Strem Chemicals, Inc. All gases used were UHP grade from Air Products.

Preparation and Pretreatment

Three preparation techniques, incipient-wetness (I.W.), ion-exchange (I.E.), and vapor impregnation (V.I.), were used to introduce Ru on or into the NaY zeolite support. The incipient-wetness catalysts were prepared from

RuCl₃·1.5 H_20 dissolved in distilled water at a concentration sufficient to yield the proper metal loading when impregnating each gram of the support with 0.7 cm³ of solution. After the impregnation, the samples were dried overnight in air at 40°C.

For preparing the ion-exchanged catalysts, $Ru(NH_3)_6Cl_3$ was dissolved in a weakly acidic hydrochloride solution (pH = 4.5). This solution was then mixed with NaY 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 $40^{\circ}C$.

The vapor-impregnated catalysts were prepared via the vapor phase of $\operatorname{Ru}_3(\operatorname{CO})_{12}$. NaY zeolite was calcined in vacuo at 450°C to remove water. The impregnation then took place in an evacuated, sealed pyrex cell held at a temperature of 80°C. This temperature ensured that the vapor pressure of $\operatorname{Ru}_3(\operatorname{CO})_{12}$ was high enough for reasonably rapid adsorption on the zeolite but not high enough to cause decomposition of the carbonyl. A more detailed procedure is given elsewhere.⁽²⁻³⁾

After preparation, catalysts prepared by incipient-wetness were reduced in flowing hydrogen by heating to 420° C at 0.5° C/min and holding at that temperature for 2 hours. The ion-exchanged and vapor-impregnated catalysts were decomposed slowly under vacuum (ca. 3×10^{-7} zesr.) by heating to 420° C (0.5° C/min) and holding for 2 hours. The catalysts were then reduced in pure hydrogen at 420° C for two hours.

Characterization

The reduced samples were characterized by A.A., I.R., and H2 and CO

chemisorption measurements. The Ru metal loadings of the catalysts were determined by a Perkin Elmer 380 Atomic Absorption Spectrophotometer using the method of Fabec.⁽⁴⁾

The gas chemisorption measurements were made at ambient temperature in a glass adsorption system capable of achieving a vacuum of ca. 3×10^{-7} torr. The initial point on the isotherm required 1 day for equilibrium. Equilibrium was attained for each additional point of the first isotherm and usually required 2-4 hours. 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⁽⁵⁾ and Wilson and Hall.⁽⁶⁾ A second isotherm was measured after evacuation of the sample for 2-3 min. 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.

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 stopcocks at both ends to provide gas flow in and out. The catalyst was ground slightly in an agate mortar and then compressed under 3 x 10^4 psi into a selfsupporting 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, using a Perkin Elmer 683 grating infrared spectrophotometer, in the range 1500-2500 cm⁻¹ with a resolution of 2 cm⁻¹.

Fischer-Tropsch

Kinetic 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

catalyst particles were sieved and only 100-120 mesh were used. The reactant gases used were H_2 (99.999%), He (99.997%), and a H_2/CO mixture (H_2/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 react any oxygen to water. 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 Products were separated using a 6 ft. x 1/8 in. stainless Chromatograph. 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 The hydrogen bracketing technique, which gave the catalyst a 40 min. 180°C. 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, both 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.

III. RESULTS AND DISCUSSIONS

H₂ and CO Chemisorption

In recent reported studies, Ru metal surface areas and particle sizes have been measured by selective gas adsorption, X-ray line broadening, electron microscopy and related techniques. However, when high dispersions of Ru or any other metals are present in supported metal catalysts, it becomes impossible to use X-ray line broadening and exceedingly difficult to use electron microscopy methods for determination of catalyst dispersion. Also, H₂ chemisorption may not be a reliable for characterization due to the suppression of chemisorption on electron-deficient Ru.⁽⁷⁾ CO chemisorption is typically an accurate method for characterization not because the stoichiometry may change as the Ru particles become smaller.⁽⁸⁾ In addition, suppression of H₂ and CO chemisorption on SMSI catalysts is known to occur.⁽⁹⁾ However, even with all the possible difficulties, H₂ chemisorption still remains the best overall method to determine Ru metal surface area in highly dispersed Ru catalysts.

In this study, the Ru surface areas were calculated from the hydrogen adsorption measurements, assuming a stoichiometry of $H_{irr}/Ru = 1$ and an average Ru area of 8.17 Å².⁽¹⁰⁾ The average Ru crystallite sizes, d, were calculated using the relationship $d = \frac{5}{5 \cdot \rho}$, where ρ is the density of the metal, S the surface area of Ru per gram of Ru, and the assumption is made that the particles are cubes of edge size, d, with five sides exposed to the gas phase. The resultant relationships between Ru metal loading and average particle size for Y-zeolite supported Ru prepared by different methods are given in Figure 1. The average particle size for catalysts prepared by ionexchange was found to be independent of Ru concentration (below 3 wt%) and had

values between 1 and 1.5 nm, about the size of the zeolite supercages. In contrast to the ion-exchanged catalysts, catalysts prepared via vapor impregnation by $Ru_3(CO)_{12}$ had average particle diameters of 1 nm, which were also independent of metal loading. The average particle size for the catalysts prepared by incipient-wetness using an aqueous solution of $RuCl_3$ was found to vary linearly with Ru metal loading. The Ru^{+3} in the $RuCl_3$ solution used was probably in its hydrated form and, thus, too bulky to enter the zaolite pores. Most of the Ru, therefore, ended up on the limited external surface of the zeolite granules in these catalysts. Consequently, an increase in metal loading resulted in an increase in metal sintering due to its high concentration on the external zeolite surface.

The reduction of ion-exchanged RuY zeolite samples has been studied by several researchers.⁽¹¹⁻¹⁵⁾ Most of these researchers have agreed that when an ion-exchanged sample is evacuated and heated slowly to 400° C prior to H₂ reduction, the average Ru particle size is ca. 1 nm. However, when H₂ is present during the dehydration procedure, the average particle size is ca. 2 nm. Our results are in agreement with these conclusions.

Some of the average particle sizes for the ion-exchanged catalysts in this study were larger than the free diameter of the zeolite supercages. These results can be rationalized in two ways. The first explanation, proposed by Verdonck et al.,⁽¹⁵⁾ involves the localized destruction of the lattice by H_20 to form cracks and holes. Filling of these voids by Ru metal could result in average particle sizes greater than the free diameter of zeolite. The second explanation, suggested by Gustafson and Lunsford,⁽¹²⁾ is that in the presence of hydrogen the mobility of Ru is increased resulting in an agglomeration of the metal in several adjacent supercages such that the particles are connected through the 12-membered windows. Based on earlier

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T.E.M. results,⁽¹⁶⁾ most of the Ru is inside the zeolite framework and the largest particles are concentrated on the external zeolite surface. The presence of even a relatively few large particles is able to significantly increase the average particle size calculated.

In our study of the Ru/NaY catalysts prepared from $Ru_3(CO)_{12}$, all the average particle sizes at different metal loadings were found to be exclusively around 1 nm. The differences in average particle size found for the ion-exchanged and the vapor-impregnated catalysts may be due to one or both of the following explanations: (i) The presence of residual water in ion-exchanged catalysts results in a bimodal distribution.⁽¹⁵⁾ Since the zeolite is precalcined in a vacuum before introducing the Ru in the vaporimpregnated catalysts, less residual water is present during decomposition and reduction than in the ion-exchanged catalysts. The Ru remains highly dispersed in the supercage and, hence, produces a more mono-dispersed system. (11)The greater concentration of Na in the vapor-impregnated catalysts results in a lower acidity for the zeolite, thereby suppressing interactions between the oxygen atoms of the zeolite and the ruthenium. For ion-exchanged catalysts, the Na atoms have been exchanged with Ru(NH3)63+ cations during preparation. Upon reduction, the zeolite is gradually transformed into a partial hydrogen zeolite having a strong oxidizing agent (-OH group). The possible existence of metal-support interactions might cause the ruthenium to be in a higher oxidation state than the presumed value of Evidence for an interaction between the oxygen atoms of alumina and zero. ruthenium has been presented by Kellner and Bell⁽¹⁷⁾ using infrared spectroscopy and Clausen and Good⁽¹⁸⁾ using Mossbauer Spectroscopy. Electrondeficient Pd, resulting from interaction with OH groups in NaY, has also been reported. (19) Formation of electron-deficient surface species could suppress

hydrogen adsorption to a certain extent, since highly electron-deficient matals do not appreciably interact with hydrogen. (20) This would result in overestimation of the average particle size in the ion-exchanged catalysts.

Comparing the stolchiomatry of irreversible CO chemisorption to that of H_2 shows some very interesting differences (see Figure 2). The CO/H ratio (molecule of CO per atom of hydrogen strongly adsorbed) has a value of 2-3 for vapor-impregnated catalysts, while the CO/H ratio has a value of 4-5 for ion exchanged catalysts having average Ru particle diameters less than 1.6 nm. This ratio decreases rapidly as particle size increases. The CO/H ratio for the incipient-wetness catalysts is independent of average particle size in the range above 5 nm and has a value of about 1.5. CO/H ratios greater than unity, in the absence of H_2 chemisorption suppression, imply multiple CO chemisorption to form surface species of the form $Ru(CO)_2$, $Ru(CO)_3$, and even $Ru(CO)_4$.⁽¹²⁾ It can be surmised that multiple chemisorption should take place on low coordinated metal surface sites. As the particle size increases, the fraction of surface atoms of low coordination number decreases.⁽²²⁾ This explains the decrease in the CO/H ratio with increasing average particle size.

The difference in CO/H ratios for ion-exchanged and vapor-impregnated catalysts having similar dispersions is probably due to matal-zeolite interactions. Eased on IR results, it appears that Ru matal in ion-exchanged catalysts is probably more electron-deficient than Ru in vapor-impregnated catalysts.⁽²⁴⁻²⁵⁾ This would result in some hydrogen suppression for the ion-exchanged catalyst. Indeed, it has been found⁽²³⁾ that there is a measurable amount of hydrogen suppression for the ion-exchanged Ru/NaY catalysts. However, suppression of CO chemisorption appears not to be significant. Therefore, the CO/H chemisorption ratios for the ion-exchanged catalysts are

higher than those for the vapor-impregnated catalysts with the same metal dispersions.

Infrared Spectroscopy

Carbon monoxide chemisorption on supported ruthenium has been extensively studied by IR.⁽²⁴⁻³¹⁾ The IR bands observed have not yet been completely assigned. However, most researchers⁽³¹⁻³⁵⁾ agree that smaller metal particles are less throughly reduced or are more modified by the proximity to the structural oxygen of the oxide support. As can be seen in Figure 3, CO chemisorbed on the vapor-impregnated catalyst absorbs at lower wavenumbers than that on the ion-exchanged catalysts. The difference in the wavenumbers reflects differences in the ruthenium particle sizes and quite likely the effect of the zeolite on the electronic structure of the metal particle. (2,24-25) Reduction of Ru has been shown to produce a decrease in the CO vibrational frequency, corresponding to a decrease in electron deficiency of the metal atoms.⁽²⁶⁾ In an IR study of Pd supported on NaY, Chukin et al.⁽¹⁹⁾ found higher frequencies than normal for CO adsorbed on reduced Pd. They ascribed this result to the interaction of the metal with strongly acidic OH groups via a donor-acceptor mechanism.

Considering both the chemisorption and IR results, it is possible that, for ion-exchanged catalysts, partial migration of free electrons from metal atoms to the proton of the strongly acidic OH groups results in the formation of a charge-transfer complex:

 $\frac{\delta + \delta - H}{H - 0 < zeolite}$

The presence of Na⁺ cations in vapor-impregnated catalysts neutralizes the strongly acidic sites:

Ru--Na-O<zeolite

and results in less interaction of the Ru with the zeolite.

The electron-deficient character of Ru for the ion-exchanged catalysts should be more than that for the vapor-impregnated catalysts. Although we are still not able to obtain CO peaks with IR for the incipient-wetness catalysts due to low Ru surface area and IR opacity of the samples, the electronic state of the Ru should be the same as bulk metal due to its large particle size and location primarily on the external zeolite surface. ESCA studies of a Ru/NaY catalyst prepared by the incipient-wetness method support this idea.⁽³⁶⁾

Reaction Studies

All fresh, reduced catalysts were given the pretreatment described earlier. The primary hydrocarbon products produced under all reaction conditions were α -olefins and normal paraffins. The oxygen released in conjunction with the synthesis of hydrocarbons appeared as water and small amounts of carbon dioxide. Trace amounts of methanol were also detected at low temperatures. The term "percentage total conversion of CO" refers to the conversion of CO to hydrocarbons through pentane and to CO₂. All turnover numbers were based on irreversible hydrogen chemisorption on the fresh catalysts. The steady state refers to a time frame of about 30-200 min. after the start of the reaction. All designated initial reaction data were taken 5 min. after the start of the reaction. By using a hydrogen-bracketing technique, activities were reproducible to within a few percent after the

catalysts became stabilized. Maintaining the catalysts in hydrogen for prolonged periods was also determined to have no effect on catalyst activity.

Particle Size Effects:

As can be seen in Figure 4, the turnover number of the ion-exchanged Ru catalysts was found to increase with increasing average metal particle size in the range of 1 to 3 nm. For the incipient-wetness catalysts, turnover number was constant as average particle size varied above 3 nm. A smooth curve can in fact be fit to the points from both the ion-exchanged and incipient-wetness Selectivity for methane decreased significantly with increasing catalysts. metal loading for the ion-exchanged catalysts (see Figure 5). This was less true for the catalysts prepared by the incipient-wetness techinque, which had an anomalously high methane selectivity. King⁽³⁷⁾ also found the latter result for unsupported Ru. ESCA studies have indicated that catalysts prepared by incipient-wetness method have the same properties as bulk Ru.⁽³⁶⁾ Catalysts prepared by the vapor-impregnation method, however, exhibited greater selectivities for C_2-C_4 olefins and higher hydrocarbons than the other catalysts. In addition, their turnover numbers were much greater than those of ion-exchanged catalysts having similar dispersions of Ru.

The trend of decreasing turnover number with decreasing particle size in the range of 1-4 nm is in agreement with the data of $Jacobs^{(38)}$ for Ru/NaY and King⁽³⁷⁾ for Ru/Al₂O₃ and Ru/SiO₂, both data sets being over smaller ranges of particle size than the one of this study. Moreover, they were not able to prepare catalysts having average particle sizes less than 1 nm. For the sake of comparison with the present results for ion-exchanged and incipient-wetness catalysts, the results reported by Kellner and Bell⁽³³⁾ for Ru/Al₂O₃ have also

been replotted in Figure 6. It is evident that the data follow similar trends and that the slopes of straight lines fitted to each data set are nearly identical. We did not find the sharp decrease in activity for the highly dispersed Ru catalysts (% dispersion > 75) reported by Kellner and Bell.⁽³³⁾

When one compares the CO/H ratios for irreversible chemisorption at 25°C for the various catalysts (Figure 2) to their turnover numbers (Figure 4) one finds a good inverse correlation: the greater the CO/H ratio for a given catalyst, the lower its turnover number for CO conversion. This result suggests that, under reaction conditions, hydrogen may possibly compete more successfully with CO for adsorption sites on vapor-impregnated catalysts than on ion-exchanged catalysts having similar dispersions. Such an effect would lead to the expectation that higher specific activities should occur on the vapor-impregnated catalysts, which is in fact the case. However, contrary to what would be expected, the selectivity for methane was much less.

Jung⁽³⁹⁾ and Bartholomew et al.⁽⁴⁰⁾ have reported that the larger the CO/H adsorption ratio on a catalyst, the higher its selectivity to C_2^+ hydrocarbons. They hypothesized that small metal crystallites which interact strongly with the support produce hydrogen-poor hydrocarbons (compared to methane) simply because the crystallite surfaces during reaction are deficient in hydrogen. Our results did not indicate for NaY-supported Ru any such relationship between selectivity and CO/H adsorption ratio. However, it was found that the selectivity is a function of both the preparation method and the metal loading, as reported by King.⁽³⁷⁾ More surprisingly, the vapor-impregnated catalysts were very active and produced larger amounts of higher hydrocarbons than the other catalysts. This finding does not support the particle size dependent reaction mechanism proposed by Nijs and Jacobs.⁽⁴¹⁾

Significant amounts of isobutane were also observed for the ion-exchanged catalysts but were absent for the vapor-impregnated ones.⁽⁴²⁾ (see Table 1). In the ion-exchanged catalysts, Na⁺ cations have been replaced by trivalent $\operatorname{Ru}^{3+}(\operatorname{NH}_3)_6$. Following decomposition and reduction, three Bronsted acid sites will be produced for each Ru atom reduced. The iso-butane formation would appear to be due to the presence of these Bronsted acid sites in the ion-exchanged catalysts following reduction, which produces bifunctional catalytic properties.

It has been found that the catalytic behavior of vapor-impregnated Ru catalysts depends strongly on the level of CO conversion.⁽⁴³⁾ Amelse et al.⁽⁴⁴⁾ found the same result for iron alloy catalysts and discovered that this result correlates to a high activity for the water-gas shift reaction. Those catalysts having the higher water-gas shift activities produced the higher olefin selectivities and also had greater abilities for the incorporation of olefins into the growing chains. The dependence of catalytic behavior for the vapor-impregnated catalysts on CO conversion seems to to be similarly correlated to a high activity for the water-gas shift reaction. For zeolite-supported Ru, it has been found that the lower the acidity the higher the activity in the water-gas shift reaction.⁽³⁷⁾ The vapor-impregnated catalysts would obviously have the lowest acidity.

Reaction Temperature Effects:

As can be seen in Figures 7 and 8, the turnover number for CO and the methane selectivity increased with increasing reaction temperature for all the catalysts. However, the selectivity for methane increased more significantly for the ion-exchanged catalysts. The olefin fraction in C_2-C_4 , on the other

hand, decreased with increasing reaction temperature in all cases (see Figure 9). This is consistent with results cited in the literature. (38,45,46)

The selectivity changes observed on variation of the reaction temperature are not just due to thermodynamics. It can be shown that the Gibb's free energies of reaction for the formation of higher molecular weight hydrocarbons in the F-T synthesis are more negative and decrease more rapidly with decreasing temperature than those of lower molecular weight hydrocarbons for F-T conditions (220-320°C). Thus, the formation of a smaller fraction of CH_A as the temperature is decreased would be expected. However, the formation of paraffins are thermodynamically favored at F-T temperatures. Since the relative differences between the Gibb's free energies of the paraffins and olefins become less as temperature decreased, it has been suggested that this should result in an increase in the olefin fraction as reaction temperature is decreased.⁽⁴⁷⁾ However, such an explanation cannot possibly explain the formation of olefin fractions which exceed those of the paraffins. The greatest variance in the olefin fraction probably results from differences in various kinetic steps. It is suggested that olefins are primary products in F-T and their fraction decreases with increasing temperature due to an increase in hydrogenation activity.(48)

The same activation energies noted in Figure 7 and Table 2 for these three catalysts indicate that diffusion effects were not significant in this study at any temperature.

Reduction Temperature Effects:

The influence of the reduction temperature on the activity is shown in Figure 10. For the ion-exchanged catalysts, the activity decreases slightly

with increasing reduction temperature. This has been attributed by Jacobs et $a1.^{(49)}$ to the sintering of the metal particles. The lower activity at 250° C is probably due to an incomplete reduction.

Contrary to the results found for the ion-exchanged catalysts, the activity for the incipient-wetness catalysts increased with increasing reduction temperature. This may be due to an effect of residual chlorine. XPS and SIMS studies on unsupported Ru and FeRu alloys have shown that Ru metal indeed retains substantial amounts of chlorine after reduction of RuCl₃ to the metal.⁽⁵⁰⁾ Koopman et al.⁽⁵¹⁾ have examined the effect of reduction temperature on RuCl₃/SiO₂ and have found the metal surface area to be increased at higher temperatures due to the removal of traces of chlorine from the Ru surface. This would result in an increased specific activity following higher reduction temperatures.

Catalyst Stability:

In the reaction temperature range 200-300°C, it was found that the activities and selectivities are reproducible when going up and down with the temperature on using the hydrogen bracketing technique. Carbon deposition was also found to be reversible in that the carbon deposited at high tempertures could be hydrogenated at lower temperatures and vice versa.

Catalyst life tests for Ru/NaY were performed and are plotted in Figure 11. All catalysts were very stable and suffered only a slight decrease in the first 30 min. of reaction. Accompanying activity loss, selectivity shifted to higher hydrocarbons as shown in Figure 12. After 30 hours of continuous reaction, the catalysts were hydrogen treated at the reaction temperature and the experiment repeated. The phenomena described in Figure 11 and 12 were

thus found to be completely reproducible. This is in excellent agreement with the results reported by Deutzenberg et al. (52) for Ru/Al203 and Mijs and Jacobs⁽⁴¹⁾ for ion-exchanged Ru/NaY. These results indicated that the selectivity shift to higher hydrocarbons with reaction time is not due to the sintering of Ru metal. M js and Jacobs (41) concluded that at the beginning of FT synthesis some surface carbon is formed which is easily hydrogenated to. methane but which does not initiate chain growth. Another species is gradually formed later on which can initiate chain growth. The rate at which this species is formed decreases when the catalyst support is more acidic. The formation of this second species is enhanced by the presence of water. The difference in activation energies between initial and steady state found here (Table 2) possibly suggests that slightly different reaction mechanisms may exist, i.e., as a result of an increase in water present, since little deactivation is seen.

CONCLUSIONS

The results presented in this study indicate that, using different preparation techniques, one is able to change greatly the chemical and physical proparties of Ru/NaY catalysts. The CO/H ratio had a value of 2-3 for chemisorption on vapor-impregnated catalysts at ambient temperature, while the CO/H ratio of ion-exchanged catalysts had a value of 4-5 for average Ru particle diameters less than 1.6 nm. This ratio decreased rapidly as particle size increased. The CO/H ratio for the incipient-watness catalysts was independent of average particle size in the range above 5 nm and had a value of about 1.5. These modifications in the nature and stoichiometry of CO and

 H_2 adsorption occur presumably because of different site geometries and/or the interaction of the metal with the zeolite.

The specific activity of supported ruthenium prepared by the ion-exchange method was found to increase with increasing average metal particle size in the range 1-3 nm. For the incipient-wetness catalysts specific activity was constant as average particle size varied above 3 nm. Catalysts prepared by the vapor-impregnation method exhibited a much higher activity than ionexchanged catalysts having similar average particle sizes. A general pattern is evident, namely, increasing specific activity with decreasing CO/H adsorption ratio, suggesting that the relative availability of adsorbed H₂ and CO determines catalyst activity during reaction.

Selectivity in CO/H_2 reaction over Ru/NaY was influenced by the preparation method and metal loading. Selectivity for methane decreased with increasing metal loading for the ion-exchanged catalysts. This was less true for the catalysts prepared by the incipient-wetness technique, which had an anomalously high methane selectivity. The vapor-impregnated catalysts exhibited much higher selectivities for C_2 -C₄ olefins and higher hydrocarbons than the other two catalysts.

It is hypothesized that, for ion-exchanged catalysts, partial migration of electronic charge from the metal atom to the proton of strongly acidic OH groups lead to the formation of a charge transfer complex. Possibly, because of the presence of these acid sites in the ion-exchanged catalysts, iso-butane is also able to be formed. As a result of the neutralization of the zeolite structure by only Na⁺ cations in vapor-impregnated catalysts, the electrondeficient character of Ru in those catalysts appears to be negligible. Catalysts prepared by the incipient-wetness method have the same electronic state of the Ru as bulk metal since they have large Ru particles located on

the external zeolite surface which apparently do not interact with the zeolite. It is interesting to note that the catalysts containing Ru highly dispersed, and in large part inside the zeolite structure (ion-exchanged and vapor-impregnated catalysts), have the best selectivities for higher hydrocarbons. Considering the case of the vapor-impregnated catalysts, this selectivity for higher hydrocarbons should not be due only to a strong metalzeolite interaction.

On the basis of this and previous studies, it appears that the observed changes in adsorption, activity, and selectivity with preparation method and metal dispersion are probably the result of differences in the location of the metal, average metal particle size, and interaction between the metal and the zeolite.

REFERENCES

- 1. Vannice, M.A., J. Catal. <u>37</u>, 449 (1975).
- 2. Goodwin, J.G., and Naccache, C., J. Mol. Catal. 14, 259 (1982).
- 3. Gallezot, P., Coudurier, G., Primet, M., and Imelik, B., in "Molecular Sieves II," ed. by J.R. Katzer, ACS Symp. Ser. 40, 144 (1977).
- 4. Fabec, J.L., submitted for publication.
- 5. Benson, J.E., and Boudart, M., J. Catal. 4, 704 (1965).
- 6. Wilson, G.R., and Hall, W.K., J. Catal. 17, 190 (1970).
- 7. Payne, V.L., Ph.D. Thesis, University of Illinois at Urbana-Champaign, 1982.
- 8. Yang, C.-H., and Goodwin, J.G., Jr., React. Kinet. and Catal. Lett. 20, 13 (1982).
- 9. Vannice, M.A., and Garten, R.L., J. Catal. 63, 255 (1980).
- 10. Dalla Betta, R.A., J. Catal. <u>34</u>, 57 (1974).
- 11. Elliott, D.J., and Lunsford, J.H., J. Catal. 57, 11 (1979).
- 12. Gustafson, B.L., and Lunsford, J.H., J. Catal. 74, 393 (1982).
- 13. Federson, L.A., and Lunsford, J.H., J. Catal. 61, 39 (1980).
- Pearce, J.R., Mortier, W.J., and Uytterhoeven, J.B., J. Chem. Soc., Farad. Trans. I, <u>75</u>, 1395 (1979).
- Verdonck, J.J., Jacobs, P.A., Gent, M., and Poncelet, G., J. Chem. Soc., Farad. Trans. I, <u>76</u>, 403 (1980).
- 16. Goodwin, J.G., Jr., unpublished results.
- 17. Kellner, C.S., and Bell, A.T., J. Catal. 71, 296 (1981).
- 18. Clausen, C.A., III, and Good, M.L., J. Catal. <u>38</u>, 92 (1975).
- Chukin, G.D., Laundau, M.V., and Druglikov, V.Y., in "Preceeding of the Sixth International Congress on catalysis," ed. by G.C. Bond, P.B. Wells, and F.C. Tompkins, p. 688, The Chemical Society, London, (1977).
- 20. Cusumano, J.A., Dalla Betta, R.A., and Levy, R.B., "Catalysis in Coal Conversion," Academic Press, New York, (1978), p. 32.
- 21. Kobayashi, M., and Shirasaki, T., J. Catal. 28, 289 (1978).

- 22. Della Betta, R.A., J. Fnys. Chem. 79, 2519 (1975).
- 23. Wang, H.-T., Chen, Y.-W., and Goodwin, J. G., Jr. in preparation.
- 24. Goodwin, J. G., Jr. and Naccache, C., J. Catal. 64, 482 (1980)
- 25. Goodwin, J. G., Jr., and Naccache, C., Appl. Catal. 4, 145 (1982).
- 26. Sheppard, N., and Nguyen, T.T., in "Advances in Infrared and Raman Spectroscopy," Vol. 5, ed. by R.J.H. Clark and R.E. Hester, Chap. 2, p. 66 (1978).
- 27. Blackmond, D.G., and Goodwin, J.G., J. Chem. Soc., Chem. Comm., 125 (1981).
- 28. Ekerdt, J.G., and Bell, A.T., J. Catal 58, 170 (1979).
- 29. Kuzentsov, V.L., and Bell, A.T., J. Catal. 65, 374 (1980).
- Yamaski, H., Kobori, Y., Naito, S., Onishi, T., and Tamaru, K., J. Chem. Soc., Farad. Trans. I, <u>77</u>, 2913 (1981).
- 31. Dalla Betta, R.A., J. Phys. Chem. 79, 2519 (1975).
- 32. Brown, M.F., Gonzalez, R.D., J. Phys. Chem. 80, 1731 (1976).
- 33. Kellner, C.S., and Bell, A.T., J. Catal. 75, 251 (1982).
- 34. Eossi, A., Garbassi, F., Petrini, G., and Zanderighi, L., J. Chem. Soc., Farad. Trans. I, <u>78</u>, 1029 (1982)
- 35. Vedrine, J.C., Dufaux, M., Naccache, C., Imelik, B., J. Chem. Soc., Farad. Trans. I, <u>74</u>, 440 (1978).
- 36. Shyu, J.Z., Hercules, D. M., and Goodwin, J. G., Jr. manuscript in preparation.
- 37. King, D.L., J. Catal. 51, 386 (1978).
- 38. Jacobs, P.A., in "Catalysis by Zeolites," ed. by Imelik, B., Naccache, C., Ben Taarit, Y., Vedrine, J.C., Coudurier, G., and Praliaud, H., P. 293, Elsevier, Amsterdam, (1980).
- 39. Jung, H.J., Fh.D. Thesis, The Pennsylvania State University, 1981.
- 40. Eartholomew, C.H., Pannell, R.B., and Butler, J.L., J. Catal. <u>65</u>, 335 (1980).
- 41. Mijs, H.H., and Jacobs, P.A., J. Catal. <u>66</u>, 401 (1980).
- 42. Ghen, Y.W., Wang, H.T., and Goodwin, J.G., Jr., manuscript in preparation.
- 43. Goodwin, J.G., Jr., Chen, Y.W., and Wang, H.T., "Site Activities of Zeolite-Supported Ru for CO hydrogenation," 4th Quarterly Report, DOE, January 1982.
- 44. Amelse, J.A., Schwartz, L.H., and Butt, J.B., J. Catal. 72, 95 (1981).
- 45. Kellner, C.S., and Bell, A.T., J. Catal. 67, 175 (1981).
- 46. Kellner, C.S., and Bell, A.T., J. Catal. 70, 418 (1981).
- 47. Castner, D.G., Blackadar, R.L., and Somorjai, G.A., J. Catal. <u>66</u>, 257 (1980).
- 48. Biloen, P., private communication.
- 49. Jacobs, P.A., Nijs, H.H., Verdonck, J.V., and Uytterhoeven, J.B., Prep. Div. Petrol. Chem., ACS, 23, 469, (1978).
- 50. Ott, G.L., Delgass, W.N., Winogard, N., and Baltinger, W.E., J. Catal. <u>56</u>, 174 (1979).
- 51. Koopman, P.G.T., Kieboom, A.P.G., and van Bekkum, H., J. Catal. <u>69</u>, 172 (1981).
- 52. Dautzenberg, F.N., Helle, J.N., Van Santen, R.A., and Verbeek, H., J. Catal. 50, 8 (1977).

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·.	Effect of	Preparation	Mathods	on	Isobutane	Formation	6	250 ⁰ C	
. *							•	•	
		•		•	•	· ·.		•	

Catalyst	Freparation Mathod	$\frac{1 - C_4}{\text{total } C_4} (wt%)$
		······································
27 Ru/NaY	incipient-wetness	0
4Z Ru/NaY	incipient-wetness	Ó
0.5% Ru/Nay	10n-exchange	ca. 14
37 Ru/NaY	ion-exchange	18
0.5% Ru/NaY	Vapor-impregnation	0
12 Ru/NaY	vapor-impregnation	0

TABLE 1

TABLE 2

Preparation Effects on Activation Energy

Prep. Method	wtZ Ru	Initial ⁽¹⁾ E _{act} (kcal/mole)	Steady State ⁽²⁾ E _{act} (kcal/mole)
	•		
Incipient-Wetness	2	21	24
Ion-Exchange	3	16.7	· 23
Vapor-Impregnation	1	15.8	22

(1) 5 min. after start of reaction

(2) 30 min. after start of reaction



RU METAL LOADING (WT%)

FIGURE 1:

Effect of Matal Loading on Average Ru Particle Diameter

📑 I.W. **O** 1.E. **△** v.1.



PARTICLE SIZE DIAMETER (A)







FIGURE 4: Particle Size Effect on Turnover Number over Ru/NaY (Reaction Conditions: 250° C, 1 atm, $H_2/CO = 1$, GHSV = 1800)

□ 1.E. ○ 1.W. △ V.I.



FIGURE 5: Effect of Ru Metal Loading on the Selectivity for Methane (Reaction Conditions: 250° C, 1 atm, $H_2/CO = 1$, GHSV = 1800)

□ I.E. ○ I.W. △ V.I.



FIGURE 6: Effect of Dispersion on the Specific Activity for Methane Over Supported Ru Catalysts

	Catalyst	<u>T(⁰K)</u>	P (atm)	H_2/CO	Source
	Ru/A1203	523	4	2	King ⁽³⁷⁾
0	Ru/NaY	523	1	1	This Study
Δ	Ru/Al ₂ 0 ₃	498	10	3.	Kellner and Bell(33)
	Ru/A1203	478	1	2	Kellner and Bell(33)

SPECIFIC ACTIVITY (MMOLE/G.SEC



1000/TEMP. (1/K)



: Arrhenius Plot for Zeolite-Supported Ru Catalysts

🖸 I.E.	(3% Ru)
O I.W.	(2% Ru)
▲ V.I.	(1% Ru)





□ I.E. ○ I.W. △ V.I. 166



FIGURE 9: Reaction Temperature Effect on Selectivity for Olefins (Reaction Conditions: 1 atm, $E_2/CO = 1$, GESV = 1800)

☐ I.E. ○ I.W. △ V.I.





○ 1.w.



(Reaction Conditions: 250°C, 1 atm, H₂/CO = 1, GHSV = 1800) I.E. I.W.

° **∆ v.i.**





(Reaction Conditions: 250° , 1 atm, $H_2/CO = 1$, GHSV = 1800)

FISCHER-TROPSCH SYNTHESIS OVER ZEOLITE-SUPPORTED Ru CATALYSTS DERIVED FROM Ru3(CO)12

Y .- W. Chen, H .- T. Wang, J. G. Goodwin, Jr., and W. K. Shiflett

ABSTRACT

A set of zeolite-supported Ru catalysts were prepared from $\operatorname{Ru}_3(\operatorname{GO})_{12}$ using zeolites NaX, NaY, KL, and NaMordenite. These catalysts were characterized and studied under Fischer-Tropsch conditions in order to determine their unique properties and the effect of the zeolite support. For comparison, a catalyst using SiO₂ as a support was also used. Ru₃(CO)₁₂ did not appear to be able to diffuse into NaX. Overall, the best catalyst in terms of high Ru dispersion, low methane selectivity, and high olefin selectivity was Ru/NaY. The type of zeolite used as the support had a strong effect on methane selectivity. This method of preparation, compared to the ion-exchange method, is much superior in producing low yields of methane and high yields of olefins.

INTRODUCTION

Supported carbonyl complexes are currently receiving wide attention both for their potential application as an important new class of catalysts and for their utility as models for more traditional types of heterogeneous catalysts.(1) There have been four techniques used to adsorb metal carbonyl complexes on inorganic supports: (i) wet impregnation, ⁽²⁾ (ii) extraction, ⁽³⁾ solvated metal atom dispersion (SMAD),⁽⁴⁾ and (iv) (111) vaporimpregnation.⁽⁵⁻⁷⁾ While silica, alumina, and other metal oxides have been widely used as supports for transition-metal carbonyl complexes, the use of zeolite supports has been fairly limited. Due to their high surface area. shape-selective character, acidic nature, and well-defined structure, zeolites can play an important role in Fischer-Tropsch catalysis. (8-10) . The high surface area allows a high degree of metal dispersion in the zeolite, while the acidity and shape-selectivity can significantly affect the selectivity of the catalyst. In addition, using zeolites as the support may better preserve the original $Ru_3(CO)_{1,2}$ metal cluster character.⁽⁵⁾

Ruthenium has been shown to be one of the most active FT catalysts.⁽¹¹⁾ Several researchers⁽¹²⁻¹⁴⁾ have reported that highly dispersed catalysts prepared from $\operatorname{Ru}_3(\operatorname{CO})_{12}$ are much more active and selective for $\operatorname{C}_2-\operatorname{C}_4$ olefins and higher hydrocarbons in atmospheric pressure F-T synthesis than those prepared from RuCl_3 . In contrast, Ferkul et al.⁽¹⁵⁾ found that methane was the primary product for $\operatorname{Ru}_3(\operatorname{CO})_{12}$ -derived catalysts supported on $\operatorname{Al}_2\operatorname{O}_3$, SiO_2 , and NaY zeolite. In addition, they reported that catalyst activities decreased in the following order: $\operatorname{Ru}/\operatorname{Al}_2\operatorname{O}_3 > \operatorname{Ru}/\operatorname{NaY} > \operatorname{Ru}/\operatorname{SiO}_2$. The $\operatorname{Ru}/\operatorname{Al}_2\operatorname{O}_3$ catalyst was also very active for carbon dioxide hydrogenation.

The present studies were undertaken to investigate the effect of zeolite supports on the catalytic properties of ruthenium catalysts prepared from

Ru₃(CO)₁₂. These catalysts utilized as supports zeolites NaX, NaY, KL and NaMordenite. A silica-supported catalyst was also used for comparison.

EXPERIMENTAL

Catalyst Preparation

Synthetic zeolites (NaX, NaY, KL), SiO₂, and Ru₃(CO)₁₂ were obtained from Strem Chemicals, Inc. NaMordenite (NaM), a synthetic large port mordenite, was obtained from the Norton Company. The supports were heated under vacuum at 450° C prior to their impregnation by vapor-phase Ru₃(CO)₁₂. This impregnation process took place in an evacuated, sealed Pyrex cell held at a temperature of 80° C. The detailed procedure is well documented elsewhere.⁽⁶⁻⁷⁾ The supported complex was then decomposed on heating (0.5° C/min) to 420° C and holding at this temperature for 2 h under a vacuum of 10^{-5} Pa.

Characterization

The decomposed catalysts were found to be in a completely reduced state, and subsequent reduction in H_2 was unnecessary. Thus, following decomposition under vacuum, H_2 and CO chemisorption measurements were carried out. After the chemisorption of H_2 was measured, the catalyst was heated under vacuum for 2 h at 420°C to completely desorb the hydrogen. The chemisorption measurements were carried out at room temperature in a glass adsorption system capable of achieving a dynamic vacuum of ca. 10^{-5} Pa. Total chemisorbed H_2 or CO was determined by extrapolation of the linear part of the first isotherm to zero pressure. 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 these two isotherms gave the amount of irreversibly chemisorbed hydrogen or carbon monoxide. Metal loadings were determined by atomic absorption.

FT Reaction

The kinetic data at a total pressure of 101 kPa were gathered using a 3/8 in. (1 in = 2.54 cm) stainless steel microreactor containing approximately 0.4 g of catalyst. Gases used were H_2 (99.999%), He (99.997%), and a H_2/CO mixture ($H_2/CO=1$, 99.9%), which were further purified by passage through Drierite and 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 the oxygen as water. All gases were obtained from Air Products. 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 115 Gas Chromatograph equipped with TCD and FID. Products were separated using a 6 ft x 1/8 in. (1 ft = 30.48 cm) stainless-steel column packed with Porapak Q. A 0.5 cm³ sample was injected into the column which was held at 50°C for 2 min and then programmed at 15°C/min to 200°C. This permitted the separation of products up through C_8 . The previously decomposed catalysts were reduced overnight in flowing H_2 at 300°C prior to the measurement of the reaction kinetics. Product samples were taken after 30 min of reaction. Based on catalyst life studies, 30 min of reaction was sufficient to establish the product distribution. No problem with product hold-up in the zeolite support was observed at 1 atm for reaction times of 30 min or more. All reported results were obtained through a range of ascending and descending reaction temperatures. The bracketing technique, (11) which gave the catalyst a 30 min exposure to H₂ after every

kinetic measurement, was used to maintain a clean Ru surface and to give reproducible, consistent kinetic results. The CO conversion was kept below 5% to minimize the effects of heat and mass transfer and secondary reactions.

RESULTS AND DISCUSSIONS

The solvent used,⁽¹⁶⁾ support OH groups,⁽¹⁷⁾ and water physically adsorbed on the support⁽¹⁸⁾ have been found to affect the properties of supported metals derived from organometallic compounds. In this study, the alkali-zeolites were calcined in vacuum at 420°C and did not contain any free water. Because these supports were in the unexchanged alkali form, they also had very low concentrations of OH groups. In addition, no solvent was used in the vapor impregnation preparation process.

The results of H, and CO chemisorption for the various Ru catalysts are given in Table 1. The average metal particle diameters, as estimated by H2 chemisorption, were larger than the free diameter of the major zeolite cavities for all except the NaY-supported catalyst. These results can be interpreted in four possible ways. The first explanation, proposed by Verdonck et al., (19) involves the localized destruction of the lattice to form cracks and holes. Filling of these voids by Ru metal would result in large particle sizes being measured. The second explanation, suggested by Gustafson and Lunsford, (20) is that in the presence of H₂ 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 behavior would be expected to be more significant for the KL and NaMordanite due to their straight channel frameworks. The third explanation is that the suppression of irreversible hydrogen chemisorption might occur. Takasu et al.⁽²¹⁾ have reported that, as metal particle size

TABLE 1

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CATALYST CHARACTERISTICS

Support	Si/Al ratio	Metal Loading (wt%)	H ₂ (irr.) (µmole/g)	CO (irr.) (µmole/g)	CO/H (irr.)	ā (Å)	۶D
NaX	1.2	0.75	3.7±2.0	46±2.0	ca. 6.8	85	10
	1.2	0.27	5	55	ca. 5.6	22	37
NaY	2.4	1.3	58	274	2.4	9	9 0
KL	3	1.4	32	220	3.5	18	45
NaM	5	0.74	18	105	3.0	18	48
sio ₂		0.43	19	111	2.9	9	90

decreases, the adsorption energy of hydrogen on metal particles also However, a study by chemisorption and transmission electron decreases. microscopy (TEM) of catalysts prepared from Ru3(CO)12/NaY showed that for a highly dispersed Ru catalyst (ca. 100%) there was no indication of Ho chemisorption suppression at ambient temperature, and the use of irreversible H₂ chemisorption at room temperature was appropriate for determining average particle diameters.⁽²²⁾ The CO/H chemisorption ratio can be a significant indicator of H₂ chemisorption suppression.⁽²³⁾ In the absence of such suppression, the CO/H ratio normally takes on values between 2.5 and 4 for highly dispersed Ru.⁽²⁴⁾ As can be seen in Table 1, the ratios for Ru supported on NaY, KL, NaM, and SiO2 suggest little or no H2 chemisorption suppression on those catalysts. The large values of CO/H found for Ru/NaX are probably a consequence of errors associated with the measurement of small amounts of H_2 chemisorption rather than H_2 chemisorption suppression. Α fourth explanation is that the presence of even a few very large particles on the external surface of the zeolite is able to skew the average metal particle diameter calculated from chemisorption to a size larger than the zeolite pores, even though most of the metal may exist as very small particles inside It can be concluded, then, that for Ru supported on NeY, KL, the zeolite. NaM, and SiO₂, the average particle diameters calculated should be relatively The large average diameters found for Ru/KL and Ru/NaM probably accurate. reflect the fact that some metal is encapsulated in the zeolite pores and some exists as large particles on the external zeolite surfaces. Such a situation has been observed by TEM for even highly dispersed Ru/NaY catalysts. (22)

A miscalculation of the average particle size for Ru/NaX, resulting in a gross over estimation of average Ru particle size, can be ruled out. Ru can be totally reduced in catalysts prepared by this method, thus no decrease in

 H_2 chemisorption can be related to incomplete reduction. In addition, no H_2 chemisorption suppression is exhibited by zeolite-supported Ru prepared from $Ru_3(CO)_{12}$. Furthermore, where H_2 chemisorption suppression exists (zeolite-supported Ru prepared by ion exchange), no suppression is seen when the zeolite support has a low Si/Al ratio (as in the case for NaX).⁽²³⁾ Activity and selectivity results, compared to previous results for zeolite-supported Ru,⁽¹⁴⁾ confirm the conclusion based on the H_2 chemisorption results that Ru/NaX has a relatively low Ru dispersion.

The average particle size, as calculated from H_2 chemisorption, for NaXsupported catalysts was found to increase monotonically with increasing Ru loading. Such an increase in particle size with loading is typical of zeolite-supported Ru where Ru is deposited primarily on the external surface of the support.⁽¹⁴⁾ Since NaX has the same structure and cage dimensions as NaY but approximately twice as much Na, one may assume that most of the Ru was on the external surface of NaX due to the inhibition of diffusion of $Ru_3(CO)_{12}$ into the zeolite by a larger number of cations in the cage openings. The particle size obtained for the SiO₂-supported sample is comparable to the results of Kellner and Bell⁽²⁵⁾ for Ru/SiO₂ prepared by impregnation with a solution of Ru₃(CO)₁₂.

After several cycles of FT synthesis with hydrogen-bracketing, the catalytic properties of these catalysts were stabilized. The activity increased during this stabilization period and was accompanied by a shift to higher hydrocarbons. Such an increase in activity during the initial reaction period is not observed for Ru catalysts in general and seems to be unique for catalysts prepared from $Ru_3(CO)_{12}$.

The catalytic properties of these catalysts at steady state are shown in Tables 2 and 3. The primary hydrocarbon products under reaction conditions

TABLE 2

CATALYTIC PROPERTIES(a) OF Ru CATALYSTS

			· .	•	•	
Support	Metal Loading	CO Turnover No. x 10 ³	<u>Activity</u> umole	µmole_	E _{CO}	(b) a
	(wt%)	(site ⁻¹ sec ⁻¹)	g cat. sec	g Ru sec	(kcal/mole)	
NaX	0.75	40	0.296	39.5	21	0.42
NaY	1.3	5	0.580	44.6	23	0.76
KL .	1.4	4	0.252	18.0	23	0.64
NaM	0.74	8	0.280	37.8	22	0.60
SiO2	0.43	2	0.076	17.6 ·	24	0.54

(a) Reaction conditions: 1 atm, 250° C, H₂/CO=1, GHSV=2700 h⁻¹

(b) Chain-growth probability

were methane, a-olefins, and normal paraffins. Trace amounts of acetaldehyde and methanol were detected and increased with increasing Si/Al ratio of the supports. Interestingly, no correlation between the reaction rate and support Si/Al ratio was observed. Significant selectivities for olefins and carbon dioxide (see Table 2 and 3) were, however, an important feature. Previous

Support	Metal Loading	R _{CO(3)} /R _{CO(1)} (c)	co	2/CH4 ^(d)	R _{CO2} /R _{HC} (e)		
	(wt%)		250 ⁰ C	280 ^o C			
NaX	0.75	0.74	1.3	0.5	1.0		
Nay	1.3	1.25	2.1	0.8	0.6		
KL	1.4	1.31	8.2	4 •1	1.3		
NaM	0.74	1.14	5.3	3.7	1.2		
sio ₂	0.43	1.30	4.0	1.5	1.2		

- (c) The ratio of the reaction rate in the 3rd cycle to that in the 1st cycle
- (d) Weight basis
- (e) The ratio of rate of carbon consumption for CO_2 formation to that for hydrocarbon formation

results in the literature^(26,27) have indicated that, in the FT synthesis, the weight ratio of CO_2/CH_4 is less than unity for Ru catalysts, in contrast to the present findings.

Results from this study indicate that r_{CO_2}/r_{HC} ratios (where r_{HC} is the rate of carbon atom incorporation in hydrocarbons) were greater than unity at 250°C, except for the Ru/NaY catalyst, and decreased with increasing reaction Since one mole of CO converted to any type of non-oxygenate temperature. gives one mole of H_20 or CO_2 as a by-product, the maximum possible r_{CO_2}/r_{HC} that can be obtained via conversion of all the H_20 to CO_2 by the water-gas shift reaction is unity. Therefore, any r_{CO_2}/r_{HC} ratio greater than one indicates the occurrence of the Boudouard reaction which provides another route for CO₂ formation. Our results are in good agreement with those reported by Gkuhara et al., (13) who found that catalysts prepared from $Ru_3(CO)_{12}/Al_2O_3$ were more active for CO_2 formation than ones prepared from RuCl₃/Al₂0₃. In contrast to these results, Ferkul et al.⁽¹⁵⁾ reported that, for the catalysts derived from Ru3(CO)12, the production of methane was In addition, they found that CO₂ formation was significantly predominant. suppressed. The different results may be due to the high temperature of reaction (375°C) and the high conversion (80%) used in the study, which possibly resulted in secondary reactions such as hydrogenolysis.⁽²⁸⁾ In our study, the CO conversion was kept below 5% to limit effects due to the watergas shift reaction as well as other secondary reactions.

As can be seen in Table 2, on a per gram Ru basis, specific activity decreases in the order NaY > NaX, NaM > KL, SiO₂. The lower turnover number

TABLE 3

PRODUCT SELECTIVITY (C1-C5) OF Ru CATALYSTS (wt%)

	•							-	
Support	Metal Loading (wt %)	c ₁	c ₂	c [*] 2	c ₃	c ₃	с ₄	c ₄	с ₅ +
NaX	0.75	42	7	4	1	16	9	4	17
NaY	1.3	18	5	2	0	39	6	4	26
KL	1.4	38	4	4	1 ·	21	5	5	22
NaM	0.74	42	5	3	1	17	5	5	22
sio ₂	0.43	28	5	5	1	29	7	7	18

Reaction Conditions: 1 atm, 250°C, $H_2/CO = 1$, GHSV = 2700 h⁻¹

(TON) in the case of NaY-supported Ru is compensated by the higher Ru surface area. The high TON observed on the NaX supported catalyst is likely due to its large average Ru particle size.^(8,14,35) No significant effect of the support on TON was found in this study for similarly dispersed catalysts.



Figure 1: Temperature Dependence of Methane Formation



Figure 2: Temperature Dependence of C2-C4 Formation



Figure 3: Temperature Dependence of Olefin Formation in C_2-C_4 Fraction

The activation energies for CO conversion over these various catalysts center around 23 kcal/mole and are quite consistent with values reported previously.^(27,30-31) The hydrocarbon distribution was able to be fitted to the Anderson-Schulz-Flory equation. It was found that the chain-growth probabilities in this study, based on the C_3-C_7 distribution, were much higher than those for ion-exchanged Ru/NaY catalysts⁽¹⁴⁾ and Ru/Al₂O₃ catalysts⁽²⁵⁾ having similar metal loadings. The chain growth probability decreased slightly with increasing reaction temperature in the range 240-300°C.

The effects of reaction temperature on the methane, C_2-C_4 hydrocarbon, and C_2-C_4 olefin fractions over these catalysts are shown in Figures 1, 2, and 3, respectively. Methane formation increased with increasing temperature of reaction, as expected. A trend towards increasing methane formation with increasing Si/Al ratio of the support was also observed, except for the NaXsupported Ru catalyst. For Ru deposited on the external surface of NaY, the selectivity is shifted to methane.^(14,32) The results for the NaX-supported catalysts in this study are in accord with the previous conclusion that the Ru is primarily in the form of large particles on the external surface.

It is interesting to note that C_2-C_4 hydrocarbon formation is only slightly decreased with increasing temperature in the range 220-300°C. It can be concluded that the increase in methane formation with temperature comes mainly from a decrease in the formation of liquid hydrocarbons (C_5^+) and is almost independent of C_2-C_4 formation. Over the samples studied, the fraction of olefins in C_2-C_4 was nearly 3 times greater than that for comparable, similarly dispersed NaY-supported Ru catalysts prepared by ion-exchange.⁽¹⁴⁾ The selectivity for propylene was as high as 40% of all hydrocarbons (including CH_4) at a reaction temperature of 250°C. It seems appropriate to ascribe the C_2-C_4 olefin formation to a property of Ru resulting from the method of preparation rather than to just a particle size effect, since the ion-exchanged catalysts previously studied⁽¹⁴⁾ had approximately the same particle sizes but exhibited quite different selectivities.

As shown in Figure 3, the formation of olefins decreased with increasing temperature and Si/Al ratio of the zeolite support, except in the case of Ru/NeX. However, the zeolite support appeared to exert only a relative weak effect upon the ability to make olefins. Of greater importance for olefin selectivity appears to be factors influenced by the method of preparation.

Thus, Ru/SiO₂ prepared by vapor impregnation exhibited a similar olefin selectivity as zeolite-supported Ru. A previous study of Ru/NaY catalysts has shown the effect that preparation method can have on this selectivity.⁽¹⁴⁾ Of the three preparations methods employed, vapor impregnation produced catalysts having the greatest selectivities for olefins.

The relationship between selectivity and the nature of the catalyst may be attributed to the effect of metal dispersion, metal location in/on the zeolites, metal precursor species, and properties of the zeolite support. The extent to which each of these factors play a role is unknown and must await further investigation. In principle, the acidity of alkali zeolites is essentially nil and therefore independent of the Si/Al ratio.⁽³³⁻³⁴⁾ The concentration of residual alkali cations, however, may affect the catalytic properties of Ru metal.⁽²³⁾ Finally the TON number is a strong function of average Ru metal particle size in the catalyst.

CONCLUSIONS

The results presented in this study indicate that the activity and selectivity for CO hydrogenation of zeolite-supported ruthenium catalysts prepared from $Ru_3(CO)_{12}$ are strongly influenced by the nature of the support. The properties of these catalysts differ significantly from those of incipient-wetness and ion-exchanged Ru catalysts. On the basis of specific activity (per g of Ru) and selectivity for olefins and higher hydrocarbons, the most effective support was NaY. This catalyst had a smaller average metal particle size than ion-exchanged Ru/NaY catalysts previously studied.⁽¹⁴⁾ In addition, the selectivity for methane was decreased and that for olefins was greatly increased for the carbonyl-based catalyst.

Surprisingly, $\operatorname{Ru}_3(\operatorname{CO})_{12}$ did not appear to be able to diffuse into NaX, even though it was able to diffuse easily into NaY. This resulted in significantly poorer dispersions of Ru on NaX. Average particle size was a function of metal loading. It is suggested that the extra Na cations in NaX were able to act as a barrier for $\operatorname{Ru}_3(\operatorname{CO})_{12}$ diffusion during preparation. From the dispersions and selectivities obtained for KL-and NaMordenitesupported catalysts, it can be assumed that, while diffusion of $\operatorname{Ru}_3(\operatorname{CO})_{12}$ was not rapid, a significant amount of $\operatorname{Ru}_3(\operatorname{CO})_{12}$ was able to migrate into these zeolites.

Finally, excluding Ru/NaX because of its poor dispersion of Ru in the zeolite, the catalytic selectivity for methane appeared to be a function of Si/Al ratio. However, due to the difficulty in getting Ru/KL and Ru/NaM as well dispersed as Ru/NaY, it is difficult to say whether this variation in methane selectivity was a true function of Si/Al ratio or was, in fact, a function of a related property such as alkali cation type and concentration as previously found for zeolite-supported Ru prepared by ion exchange.⁽²³⁾ Selectivity for C_2-C_4 olefins was not a strong function of zeolite type.

These results point out that, for zeolite-supported F-T catalysts, a number of parameters (metal particle size, particle location, Si/Al ratio, alkali type and concentration, etc.) play major roles in determining catalytic properties.

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REFERENCES

- 1 A.K. Smith and J.M. Basset, J. Mol. Catal. 2, 229 (1977).
- 2 A. Brenner and D.A. Hucul, JACS 102, 2484 (1980).
- 3 J.M. Stencel, J.R. Kiehl, L.J. Douglas, C.A. Spitler, J.E. Crawford, and G.A. Melson, Colloids and Surfaces, in press.
- 4 K. Matsuo, and K.J. Klabunde, J. Catal. 73, 216 (1982).
 - 5 J.G. Goodwin, Jr., and C. Naccache, Appl. Catal. 4, 145 (1982).
 - 6 J.G. Goodwin, Jr., and C. Naccache, J. Mol. Catal. 14, 259 (1982).
 - 7 P. Gallezot, G. Coudurier, M. Primet, and B. Imelik, ACS Symp. Series 40, 144 (1977).
 - 8 P.A. Jacobs, in <u>Catalysis by Zeolites</u>, ed. by Imelik, B., et al. p. 293, Elsevier, Amsterdam (1980).
 - 9 H.H. Nijs, P.A. Jacobs, J.J. Verdonck, and J.B. Uytterhoeven, in Growth and Properties of Metal Clusters, ed. by Bourdon, J., p. 479, Elsevier, Amsterdam (1980).
- 10 C. Naccache and Y. Ben Taarit, Pure Appl. Chem. 52, 2175 (1980).
- 11 M.A. Vannice, J. Catal. 37, 449 (1975).
- 12 G.B. McVicker and M.A. Vannice, J. Catal. 63, 25 (198).
- 13 T. Okuhara, K. Kobayashi, T. Kimura, M. Misono, and Y. Yoneda, JCS Chem. Comm., 1114 (1981).
- 14 Y.W. Chen, H.T. Wang, and J.G. Goodwin, Jr., J. Catal., in press.
- 15 H.E. Ferkul, D.J. Stanton, J.D. McCowan, and M.C. Baird, JCS Chem. Comm., 955 (1982).
- 16 K. Matsuo and K.J. Klabunde, Organ. Chem. 47, 843 (1982).
- 17 M. Deeba and B.C. Gates, J. Catal. 67, 303 (1981).
- 18 A.K. Smith, F. Hugues, A. Theolier, J.M. Basset, R. Ugo, G. M. Zanderighi, J.L. Bilhou, V.B. Cougnol, and W.F. Graydon, Inorg. Chem. <u>18</u>, 3104 (1979).
- 19 J. J. Verdonck, P.A. Jacobs, M. Genet, and G. Poncelet, JCS Farad. Trans. I <u>76</u>, 403 (1980).
- 20 B.L. Gustafson and J.H. Lunsford, J. Catal. 74, 393 (1982).
- 21 Y. Takasu, T. Akimaru, K. Kashara, Y. Matsuda, H. Miura, and I. Toyoshima, JACS <u>104</u>, 5249 (1982).

- 22 J.G. Goodwin, Jr., J. Catal. 68, 227 (1981).
- 23 Y.W. Chen, H.T. Wang, and J. G. Goodwin, Jr., Zeolites, in press.
- 24 C.-H. Yang and J.G. Goodwin, Jr., React. Kinet. Catal. Lett. 20, 13 (1982).
- 25 C.S. Kellner and A.T. Bell, J. Catal. 75, 251 (1982).
- 26 P.A. Jacobs, J. Verdonck, R. Nijs, and J.B. Uytterhoeven, Adv. Gnem. <u>178</u>, 15 (1979).
- 27 J.G. Ekerdt and A.T. Bell, J. Catal. 58, 170 (1979).
- 28 Y. Kobori, H. Yamaski, S. Naito, T. Onishi, and K. Tamaru, JCS Farad. Trans. I <u>78</u>, 1473 (1982).
- 29 C.N. Satterfield and G.A. Huff, Jr., Can. J. Chem. Engr. 60, 159 (1982).
- 30 P.K. Agrawal, J.R. Katzer, and W.H. Manogue, J. Catal. 74, 332 (1982).
- 31 H. Knozinger, Y. Zhao, B. Tesche, R. Barth, R. Epstein, B.C. Gates, and J.P. Scott, JCS Farad. Discus <u>72</u>, 53 (1981).
- 32 D. Ballivet-Tkatchenko and I. Tkatchenko, J. Mol. Catal. 13, 1 (1981).
- 33 D. Barthomeuf, J. Fhys. Chem. <u>83</u>, 249 (1979).
- 34 S. Hocevar, and B. Drzaj, J. Catal. 73, 205 (1981).
- 35 D.L. King, J. Catal. <u>51</u>, 386 (1978).

SUPPORT EFFECTS ON CO HYDROGENATION OVER RU/ZEOLITE CATALYSTS

Y. W. Chen, H. T. Wang, and James G. Goodwin, Jr.

ABSTRACT

Hydrogenation of carbon monoxide at 101.3 kPa has been studied over a series of ion-exchanged Ru catalysts supported on NaX, NaY, KL, NaMordenite, and HY zeolites. The type of zeolite had pronounced effects on the activity and selectivity of the Ru. The specific activity would appear to be related to the dispersion of reduced ruthenium in the zeolite. Methane selectivity, however, seems to be strongly influenced by the type and concentration of alkali cations remaining in the ion-exchanged zeolite. These cations appear to promote chain growth much as traditional alkali promoters would, though perhaps more indirectly. Due to bifunctional properties of the zeolitesupported catalysts, a significant fraction of C_4 was in the form of isobutane. Formation of isobutane seems to be related to either the Si/Al ratio in the zeolites or the concentration of the remaining alkali cations, but not In addition, H_2 chemisorption at $25^{\circ}C$ was to the OH concentration. increasingly suppressed as the Si/Al ratio of the zeolite support increased. Both the formation of isobutane and the suppression of H_2 chemisorption may be related to the acid strength of the OH groups present, which is a function of the Si/Al ratio of the zeolite.

Recent studies have shown that ruthenium catalysts are very active for the water-gas shift,⁽¹⁾ ammonia synthesis,⁽²⁻³⁾ hydrogenation of benzene,⁽⁴⁾ hydrogenolysis of propane, (5) higher alcohol synthesis, (6) Kolbel-Engelhardt reaction,⁽⁷⁾ and Fischer-Tropsch synthesis.⁽⁸⁾ In the Fischer-Tropsch synthesis, ruthenium has the ability to produce hydrocarbons up to heptane 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 except in hydrocracking catalysts. 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 large surface area allows a high degree of metal dispersion in the zeolite. While acidity, cation exchange properties, and shape-selectivity can the significantly affect the selectivity of the catalysts.

In assessing metal-support interactions, it is important to consider both electronic effects, where the support can donate or extract charge density from the metals, and bifunctional effects, where sites on the support and on the metal particles act somewhat independently on the reactants and intermediates. The behavior of transition metals in zeolites is complex and not fully understood at this time. Jacobs et al.(9,10) have reported 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 $300^{\circ}C$.
Accompanying this decrease in Si/Al ratio was also a shift in product selectivity towards higher hydrocarbons. Few results on F-T activities and selectivities were given. Fajula et al.⁽¹¹⁾ have reported that the activity for methanation on Pd/HY is much higher than that on Pd/NaY catalyst. They concluded that interactions between the partially hydrogenated reactant species and the acid groups on the support result in an enhancement of the reaction rate.

The present studies were undertaken to investigate the effects of various aspects of zeolite supports on Ru catalysts for the Fischer-Tropsch synthesis. These catalysts were supported on NaX, NaY, KL, NaMordenite, and HY. II EXPERIMENTAL

Materials

The zeolites were obtained from Strem Chemicals (NaX, NaY and KL) and Norton (NaZeolon = large port NaMordenite). The composition and properties of the zeolites are listed in Table 1. HY was prepared by ion-exchanging of NaY to form NH_4Y . The extent of exchange was 84%. The Ru zeolites were prepared by a conventional ion-exchange technique using $Ru(NH_3)_6Cl_3$ which was obtained from Strem Chemicals.

For preparing the ion-exchanged catalysts, Ru(NH3)6C13 was dissolved in a weakly acidic hydrochloride solution (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. 4 x 10^{-5} Pa.) by heating to 420° C (0.5°C/min) and holding at that temperature for two hours. Otherwise, the catalysts were decomposed under flowing H_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. During the decomposition procedure the NHAY support was converted to HY.

Catalyst Characterization

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. 4×10^{-5} Pa. Total chemisorption of hydrogen or carbon monoxide was determined by extrapolation of the linear part of the first isotherm to zero pressure. 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 phyisorbed). The differences 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. 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 207 MPa 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 Studies

Kinetic measurements were made at 101.3 kPa total pressure using a 3/8 in. (1 in. = 2.54 cm) stainless steel tubular reactor containing approximately 0.3 g of catalyst. The reactant gases used were H_2 (99.999%), He (99.997%), and a H_2/CO mixture ($H_2/CO = 1$, 99.9% pure), 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 from Air Products. The flow rate of each gas was controlled by a micro-metering valve and measured by a bubbleflow meter. 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 (1 ft. = 30.48 cm) packed with Porapak Q and were detected by a thermal conductivity detector. A 0.5 cm³ gas sample was injected into the column and its temperature was held at 50°C for 2 min. The column oven was then programmed to go to 180°C at 15°C/min. The hydrogen bracketing technique, which gave the catalyst a 30 min. H2 exposure after every kinetic measurement, did an exceptionally good job of maintaining a clean Ru surface and yielded reproducible initial activities and selectivities. In order to make sure that there was no hydrocarbon produced due to the mixing of pure H_2 and the reaction mixture by gaseous diffusion during the initial period of each reaction run, both 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. Reproducibility of results was ±3%.

III. RESULTS AND DISCUSSIONS

Infrared Spectroscopy

The IR investigation of CO adsorption on these Ru zeolite catalysts at 25° C produced spectra similar to those previously reported and discussed.^(12, 36) 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

ESCA spectra from the reduced catalysts indicated a fairly complex structure. In all cases, there 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 possibly located in the sodalite cages, small reduced Ru particles, and small reduced Ru particles, probably located in the super cages, which appeared to be affected strongly by the zeolite.⁽¹³⁾ An in-depth

discussion of these results will be given in a series of upcoming articles.^(33,34)

Chemisorption

From H_2 chemisorption at 25°C, average Ru particle diameters and dispersions were calculated (Table 2). 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. Since the stoichiometry of CO adsorption on Ru is determined by the metal particle size, ⁽¹⁴⁾ 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 2 would seem to indicate that the Ru dispersions in the various catalysts were similar and probably on the order of 70-90%.

Catalytic Activity

The F-T synthesis was carried over a range of temperatures. Table 3 shows typical results for the various catalysts at a reaction temperature of 250°C. As can be seen in Table 3, 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 as a result of various degrees of hydrogen chemisorption suppression at 25°C. However, these specific rates

should vary approximately in the same way as the turnover number (T.O.N.) since these catalysts appear to have similar dispersions as measured by CO chemisorption.

Jacobs et al.^(9,10) reported that for catalysts prepared by ion-exchange of $Ru(NH_3)_6Cl_3$ with a wide variety of zeolites the activity for methanation decreased with increasing Si/Al ratio of the zeolite support, provided the temperature of reduction was only 300°C. Due to the high metal loading used (5.6 wt% Ru), the Ru was not highly dispersed in these catalysts. This is indicated by the fact that the CO/Ru ratios were less than unity.

Coughlan et al.⁽¹⁵⁻¹⁸⁾ previously reported the exchange of $[Ru(H_2O)_6]^{3+}$ into several zeolites. They⁽¹⁷⁾ reported that the turnover number for the hydrogenation of benzene increased smoothly with increasing metal surface area and was independent of the type of the zeolite. Their catalysts were prepared, however, at a pH of 6.5, where $[Ru(H_2O)_6]^{3+}$ is unstable and polymerized hydroxy species are known to occur.⁽¹⁹⁾ This would result in the formation of large Ru particles on the external surface of the zeolite support. King⁽²⁰⁾ did not see any differences between the specific activities of NaX and NaY supported Ru catalysts for CO hydrogenation. The starting material was $Ru(NO)(NO_3)_3$ and a high metal loading was used in his catalysts. As a result, the formation of large Ru metal particles on the external surfaces of the zeolites would have been likely. In addition, the reaction was not operated in a differential mode and secondary reactions were probably also significant.

In this study, the observed differences in specific activity do not seem to be related to any of the known characteristics of the zeolites, such as Si/Al ratio, OH concentration, and remaining alkali concentration. The differences might be due to the particle size effect or the degree of

reduction of the Ru. From an intensive study of Ru/NaY catalysts,⁽²¹⁾ it has been found that turnover number is a strong function of average particle size. However, based on the CO chemisorption results, we hypothesize that the average particle size of all the catalysts in this study are approximately the same. Therefore, the particle size would seem not to be the only important variable affecting activity.

Suzuki et al.⁽²²⁻²³⁾ have reported that the activity of zeolite-supported Ni for several reactions is proportional to the dispersion of reduced nickel. The degree of nickel ion reduction and the dispersion state of the reduced nickel were found to be affected by the type of zeolite support and the extent of nickel exchange. It is well known that one of the main factors determining the metallic dispersion is the strength of interactions between the metallic particles and the support. In the case of zeolite carriers, the electron-deficient character of small metallic particles has been shown, by XPS and IR, for several Pd/NaY⁽²⁴⁾ and Pt/NaY⁽²⁵⁾ catalysts. This was explained by the withdrawal of electrons from the metal particles by electronacceptor sites of the support. In a recent paper, Fajula et al. (11) found the activity for methanation on Pd/HY to be much higher than that on Pd/NaY catalysts. They postulated that methanation on supported palladium proceeds mainly through direct CO hydrogenation with the participation of acid sites on the support. In this study, however, no differences were found in the rate of CO conversion over the ruthenium catalysts under F-T conditions which followed changes in OH concentration. It must be concluded therefore that rate of reaction is a complex function of a number of factors, such as: particle size, zeolite-metal interaction, etc.

Catalytic Selectivity

Olefin Fraction

The data in Table 3 show that the olefin fraction of C_2-C_4 hydrocarbons was approximately constant for all the supports used. 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 calculation of the C_2-C_4 olefin fraction was much greater.

Methane

There were very large differences in the selectivity for methane. Since particle size has been found not to be a factor in determining this quantity in NaY zeolite-supported Ru, (21) one must look to characteristics of the zeolite supports which might affect it. Three of the most likely candiates Si/Al ratio, OH concentration in the reduced catalysts, and the are: concentration and type of alkali cations remaining after ion-exchange. One or more of these characteristics might cause a given effect on selectivity by affecting the Ru directly via some type of metal-support interaction or by interacting directly with primary or secondary reaction products. These characteristics are related by the equation

$$N_{\rm H} = \frac{1}{r+1} N - N_{\rm Na}$$

where

NH

f N_{Al} $N_{\rm H}$ = est. concentration of OH groups (moles/g) N_{A1} = concentration of Al in zeolite (moles/g)

N_{Na} = concentration of Na⁺ remaining (moles/g)
N = total concentration of Si and Al (moles/g)
f = fraction of exchange of Na⁺ or K⁺ by Ru cations

= Si/Al ratio

r

Thus, the Si/Al ratio, concentration of OH groups, and remaining alkali cation concentration are complex functions of each other. Figure 1 shows a plot of methane selectivity versus Si/Al ratio. As can be seen, Si/Al ratio does not appear to correlate very well to the results found. Figure 2 shows a plot of methane selectivity versus estimated OH concentration resulting from reduction of the Ru cations, as calculated from the amount of Ru exchanged and the assumption of the formation of 3 OH groups per Ru cation reduced. For the HY supported catalyst, 84% of the cations present were assumed to be H⁺. The OH concentration too does not appear to greatly affect methane selectivity. However, methane selectivity appears to be a strong function of the concentration of the residual neutralizing alkali cations (Figure 3). 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 3 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. This is in fact, what is observed for RuKL. 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 that line. However, the

seeming effect of these cations may be produced in quite a different manner than that of regular alkali promotion. In addition, it is possible that these cations may act in an indirect manner upon the Ru, affecting such things as the electro-static field in the zeolite.

While the NaM-supported Ru exhibited the greatest amount of hydrogen chemisorption suppression at ambient temperature, it also gave the highest selectivity for CH_4 of the alkali-containing zeolite based catalysts. These results point out the complexity of the F-T system of reactions and the difficulty in applying adsorption characteristics of a catalyst at lower temperatures to the understanding of events occurring on the catalyst surface at F-T conditions. It is thus more important to understand the quality of the catalyst that gives rise to the H₂ chemisorption ability and how it may affect other surface steps during F-T than to understand such an isolated event, since it is the relative rates of reaction of the various steps (adsorption, surface reaction, desorption) which determine product selectivity. More work is needed before such an understanding is possible.

Isobutane

A significant fraction of C_4 was in the form of iso-butane for a number of the catalysts. Due to bifunctional properties of zeolite-supported catalysts,⁽²⁶⁻²⁸⁾ it is not surprising that branched hydrocarbons would be found in the product stream. However, as can be seen in Figure 4, OH concentration did not appear to play a role in producing iso-butane. Both the Si/Al ratio (Figure 5) and residual alkali concentration (Figure 6) seemed to be related to the formation of iso-butane if one neglects RuHY due to relatively large Ru particles formed. King⁽²⁰⁾ 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. Based on a previous study of the effect of preparation method on the F-T properties of NaY-supported Ru, (21) only catalysts prepared by ion-exchange produced isobutane. Catalysts prepared by vapor impregnation with Ru₃(CO)12 and having similar Ru dispersions as the ion-exchanged catalysts, the same Si/Al ratio, higher concentrations of Na⁺, and no significant concentration of OH groups did not produce any isobutane. Thus, the Si/Al ratio, by itself, does not directly affect this production. However, since the acid strength of the OH groups increases with an increase in the Si/Al ratio, it is suggested that this combination of presence of OH groups and their strength may influence the formation of isobutane. It has also been suggested that this combination may be the cause of H_2 chemisorption suppression.⁽³⁵⁾ The relationship of isobutane formation to residual alkali concentration may be only coincidental, due to the fact that, for the same Ru loading, the residual alkali concentration decreases as the Si/Al ratio increases. This is because, for higher Si/Al ratios, the initial alkali cation concentrations are less.

The role of mass transport in polyfunctional catalysis has been considered in detail by Weisz⁽²⁹⁾. Diffusional kinetics are likely to be particularly important for the production of iso-butane in the present system. The formation of iso-butane can be described by the following mechanism

(Ru) + H₂ > Isobutane (zeolite) _____isobutene 1 - butene < $(Ru) \div H_2$ 🛸 n-butane

203 -

Weisz⁽²⁹⁾ has derived a general criterion to check for the absence of mass transport limitations, and many researchers^(27,28,30) have used this criterion with zeolite catalysts. Therefore, Weisz's criterion⁽²⁹⁾ was applied to give an indication of the presence or absence of mass transport limitations in this study. The criterion for the absence of mass transport limitations is:

$$\Phi = \frac{dn}{dt} \frac{1}{[B]} \frac{R^2}{eq} \ll 1$$

From the observed conversion, the rate of isobutane formation per unit volume of catalyst was calculated to be 0.5×10^{-8} moles sec⁻¹cm⁻³. Due to the complexity of the C₄ species, we were not able to calculate [B]_{eq} exactly. The maximum possible concentration was estimated to be about 50% of isobutane; for steady state operation, [B]_{eq} would be thus about 0.25×10^{-8} moles cm⁻³. The effective diffusivity of isobutene in NaY has been reported to be 1.0×10^{-6} cm²sec⁻¹ at 250° C,⁽³¹⁾ and the radii of the zeolite particles were about 0.01 cm (100-120 mesh). Applying Weisz's criterion, one obtains $\phi >> 1$ indicating that the reaction was probably substantially constrained by diffusion limitations. In this study the residence time of 1butene in a zeolite particle would have been approximately,

$$t = \frac{L^2}{2D} = \frac{(0.02)^2}{(2) (1.0 \times 10^{-6})} = 200 \text{ (sec)}.$$

This is long enough to produce the isomerization reaction within the same zeolite particle.

The observed reaction temperature effect on isobutane selectivity can be interpreted by the assumption of competing reactions, as shown in the following scheme:



Selectivity would be dependent upon the relative effectiveness factors, which are determined by diffusion criteria. Isobutane formation normally decreases with increasing temperature of the reaction, as can be seen in Figure 5. Since the hydrogenation activity of Ru is expected to be greater at higher temperatures and the residence time of 1-butene is decreased with increasing temperature, the isomerization activity is greatly reduced at higher temperatures.

CONCLUSIONS

A series of ion-exchanged zeolite-supported Ru catalysts have been studied. The results of this study suggest that the type of zeolite support has pronounced effects on the activity and selectivity of Ru for CO hydrogenation. The specific activity appears to be related in part to the dispersion of reduced ruthenium in the zeolite. The degree of ruthenium ion reduction and the dispersion of the reduced ruthenium are probably affected by the type of zeolite support. Olefin selectivity does not seem to vary greatly with the different supports. Methane selectivity, however, appears to be strongly related to the concentration of the alkali cations remaining in the zeolite. As far as is known, this is the first time that chain growth promotion in F-T synthesis by the neutralizing alkali cations in zeolites has been suggested. It is not yet known whether this is due to direct or indirect interaction.

Formation of iso-butane is perhaps related to either the Si/Al ratio or the concentration of remaining alkali cations, but it is not related to the OH concentration. It is suggested, however, that this formation may be related to the acid strength of the OH groups present, which is a function of the Si/Al ratio. Although CO diffusion does not significantly affect the specific activity of CQ conversion, the diffusion of 1-butene plays an important role in the formation of iso-butane.

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 catalyst preparation methods,⁽²¹⁾ pretreatment conditions, etc., may cause different factors to be important in determining catalytic properties.

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REFERENCES

1.	Verdonck, J.J., Jacobs, P.A., and Uytterhoeven, J.B., JCS Chem. Comm., 181 (1979).
2.	Urabe, K., Shiratori, K., and Ozaki, A., J. Catal. 72, 1 (1981).
3.	Shiflett, W. K., and Dumesic, J.A., I&EC Fund. 20, 246 (1981).
4.	Romannikov, V.N., Ione, K. G., and Pedersen, L.A., J. Catal. <u>66</u> , 121 (1980).
5.	Galvagno, S., Schwank, J., and Gubitosa, G., JCS Faraday Trans. I <u>78</u> , 2509 (1982).
6.	Kiennemann, A. Jenner, G., Bagherzadah, E., and Deluzarche, A., I&EC Prod. Rev. and Devel. <u>21</u> , 418 (1982).
7.	Gustafson, G. L., and Lunsford, J.H., J. Catal. 74, 393 (1982).
·8.	Nijs, H.H., and Jacobs, P.A., J. Catal. <u>66</u> , 401 (1980).
9.	Jacobs, P.A., Nijs, H. H., Verdonck, J. V., and Uytterhoeven, J. B., Preprints Div. Petrol. Chem. ACS 23, 469 (1978).
10.	Jacobs, P.A., Nijs, H. H., Verdonck, J.V., and Uytterhoeven, J.B., in Hydrogen Synthesis from Carbon Monoxide and Hydrogen, ed. by E. L. Kugler and F. W. Steffgen, Adv. Chem. Series, ACS, <u>178</u> , 15 (1979).
11.	Fajula, F., Anthony R. G., and Lunsford, J.H., J. Catal. 73, 237 (1982).
12.	Blackmond, D. G., and Goodwin, J. G., Jr., J.C.S. Chem. Comm., 125 (1981).
13.	Shyu, J. Z., PhD dissertation, University of Pittsburgh, 1983.
14.	Yang, CH., and Goodwin, J. G., Jr., Kin. and Cat. Lett.20, 13 (1982).
15.	Coughlan, B., Carroll, W. M., and McCann, W.A., Chem & Ind., 527 (1976).
16.	Coughlan, B., Narayanan, S., McCann, W. A., and Carroll, W. M., Chem & Ind., 125 (1977).
17.	ibid, J. Catal. <u>49</u> , 97 (1977).
18.	Coughlan, B., and McCann, W. A., JCS Farad. Trans. I 75, 1969 (1979).
19.	Harzion, A., and Navon, G., Inorg. Chem. <u>19</u> , 2236 (1980).
20.	King, D. L., J. Catal. <u>15</u> , 386 (1978).
21.	Chen, Y. W., Wang, H. T., and Goodwin, J. G., Jr., J. Catal., in press.

- 22. Suzuki, M., Tsutsumi, K., and Takahashi, H., Zeolites 2, 185 (1982).
- 23. ibid, <u>2</u>, 193 (1982).
- 24. Chukin, G. D., Laundau, M.V., Druglikov, V. Y., et al., in "Proceedings of the Sixth International Congress on Catalysis", ed. by G. C. Bond, P. B. Wells, and F. C. Tompkins, The Chemical Society, London (1977), p. 668.
- 25. Tri, T. M., Massardier, J., Gallezot, P., and Imelik, B., Preprints 7th Int. Congr. Catal., Tokyo (1980), p. Al6.
- 26. Rao, V.U.S., and Gomley, R. J., Hydrocarbon Processing, p. 139, November 1980.
- 27. Chang. C. D., Lang, W. H., and Silvestri, A. J., J. Catal. <u>56</u>, 268 (1979).
- 28. Caesar, P. D., Brennan, J. A., Garwood, W. E., and Ciric, J., J.Catal. <u>56</u>, 274 (1979).
- 29. Weisz, P. B., Adv. Catal. 13, 137 (1962).
- 30. Keering, J., Kotter, M., and Riekert, L., Chem. Engr. Sci. <u>37</u>, 581 (1982).
- 31. Hsu, L. K. P., and Haynes, H. W., Jr., AIChE Journal 27, 81 (1981).
- 32. Breck, D. W., Zeolite Molecular Sieves, John Wiley & Sons, New York, 1974. pp.49, 163.
- 33. Shyu, J.Z., Hercules, D.M., and Goodwin, J.G., Jr., manuscript in preparation.
- 34. Shyu, J.Z., Hercules, D.M., and Goodwin, J.G., Jr., manuscript in preparation.
- 35. Wang, H.T., Chen, Y.W., and Goodwin, J.G., Jr., Zeolites, in press
- 36. Goodwin, J.G., Jr., and Naccache, C., J. Catal. 64, 482 (1980).

TABLE 1

CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES OF THE ZEOLITES (32)

Zeolite	Chemical Composition	Si/Al Ratio	Dlameter of Free Apertures (nm)	Void Volyme (cm ³ /cm ³)
NaX	$Na_{86}[(A10_2)_{86}(S10_2)_{106}].264H_20$	1.23	0.74	0-50
NaY	$Na_{56}[(A10_2)_{56}(S10_2)_{136}] -250H_2^{0}$	2 .41	0.74	0 •48
KL	K9[(AI02)9(S102)27].22H20	3.0	0.71	0.32
NaMordenite	Na8.7[(A102)8.7(S102)39.3] •24H20	4 . 52	0.67 x 0.70	0 •28

Catalyst	_* d ₂₂	D [*]	CO/Hir	CO _{ir} /Ru _T
÷	Р (пт)	(%)		
2.5% RuNaX	1.0		2.98	2 .47
3.1% RuNaY	1.6	51	4.59	2.24
2.8% Ru KL	2.6	. 32	9.88	316
2.2% RuNaM	3.9	22	12	2.64
		•		•

TABLE 2

CATALYST CHARACTERISTICS BASED ON CHEMISORPTION

*determined from irrev. H₂ chemisorption

TABLE 3

Catalyst	-r _{CO} (mole/sec.g cat)	CH4 (wt.%)		01e. Frac. in $C_2 - C_4$ (wt. %)
2.5% RuNaX	2.46	47		0.49
3.1% RuNaY	1.21	- 73		0.53
3.0% RuHY	1.23	97	ca.	0.59
2.8% RuKL	2.20	54		0.56
2.27 RuNaM	1.06	83	ca.	0.38

EFFECT OF THE SUPPORT ON F-T SYNTHESIS

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).



Methane Selectivity versus Catalyst S1/Al Natio

Figure 1:







Methane Selectivity versus Residual Alkali Cation Concentration Figure 3:



Figure 4: Iso-butane Selectivity versus OH Concentration







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