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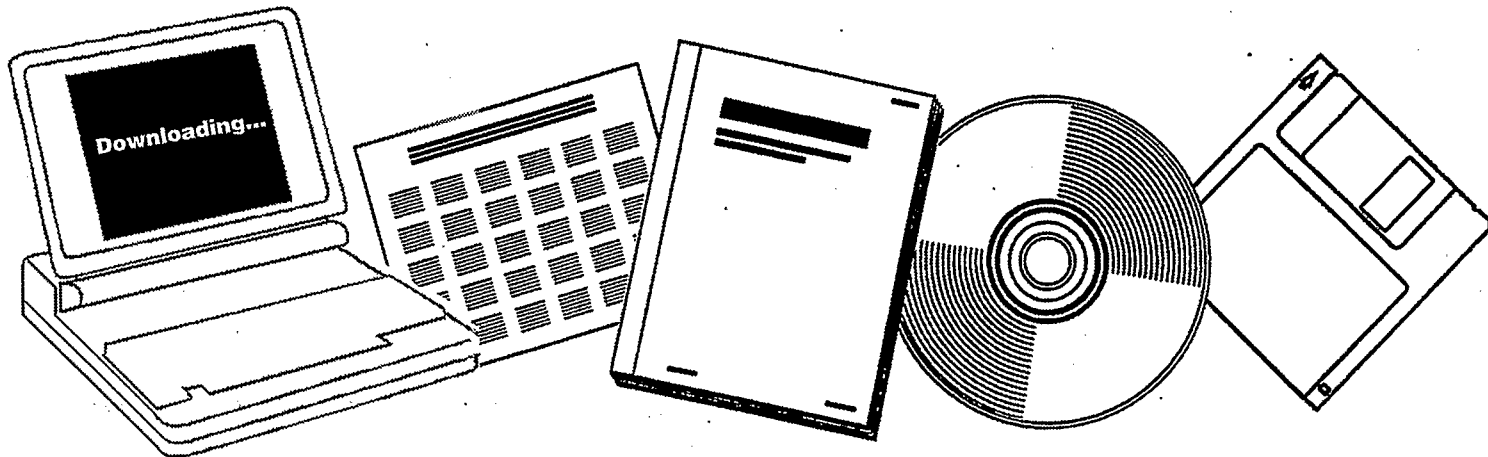
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**CATION PROMOTION EFFECTS IN
ZEOLITE-SUPPORTED F-T CATALYSTS. SIXTH
QUARTERLY REPORT, DECEMBER 1984-FEBRUARY
1985**

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

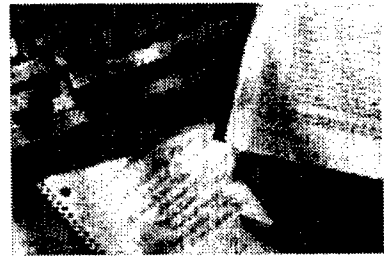
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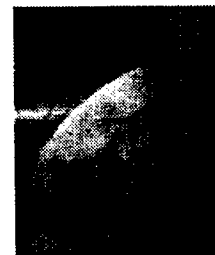
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CATION PROMOTION EFFECTS IN
ZEOLITE-SUPPORTED F-T CATALYSTS

6th Quarterly Report
December 1984 - February 1985

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March 1985

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I. OBJECTIVE AND SCOPE OF WORK

An investigation into zeolite-supported F-T catalysts begun under Grant #DE-FG22-81PC40774 (Office of Fossil Energy, D.O.E.) has produced results which suggest that alkali cations, remaining in a zeolite and serving to neutralize the structure, act to promote higher hydrocarbon formation. It appears that the F-T metal must be highly dispersed throughout the zeolite in the vicinity of these cations for this promotion effect to take place. This effect is also highly dependent upon alkali cation concentration.

The current research involves a study of the promotion effects of the neutralizing alkali cations on CO hydrogenation (under typical F-T conditions) over zeolite-supported Ru catalysts. Ru is a useful, model catalyst for the study of such promotion of this synthesis. First, alkali promotion has been found to have a great effect on product selectivity over Ru. Second, Ru does not form any stable carbides, thereby removing this complicating factor. Third, Ru is relatively easy to reduce to the metallic state. Fourth, Ru is the F-T metal easiest to keep inside zeolite crystallites. Fifth, under typical conditions, there is little oxygenated hydrocarbon formation or skeletal isomerization of the hydrocarbons over Ru. Thus, the neutralizing cations in the zeolite support should affect CO hydrogenation over Ru possibly by affecting: CO chemisorption, H₂ chemisorption, carbon deposition, catalytic activity, chain growth probability, selectivity for CH₄, selectivity for olefins, and diffusion in the zeolite. Each of these items will be investigated for the catalysts proposed to be studied.

The main objectives of this study are:

1. To develop a better understanding of how neutralizing alkali cations in zeolites can affect F-T product selectivity over a supported metal

2. to illuminate the effect of these cations on
 - a. chemisorption properties
 - b. CO disproportionation
 - c. the mechanism of CO hydrogenation
 - d. the deactivation characteristics
3. to elaborate upon the effect of decreasing ionization potential of the alkali cations on the catalytic properties
4. To investigate the effects of Rb and Cs promotion, studied only superficially in the past.

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

This investigation should provide a more fundamental understanding of the involvement of alkali cations in determining the catalytic properties of zeolite-supported metals for CO hydrogenation.

II. SUMMARY OF PROGRESS

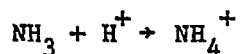
During this quarter, December 1, 1984 - February 28, 1985, the TGA studies of ammonia adsorption carried out to determine the effect of alkali cations and Si/Al ratio of the various ion exchanged zeolites on the surface acidity has been completed. The results obtained from these measurements are presented in the following section.

Also, during this quarter a new batch of ruthenium catalysts has been prepared. The same preparation method as described in the 1st quarterly report has been used except for the decomposition step prior to reduction with hydrogen. It has been frequently reported in the literature that the Ru-hexamine complex can be decomposed either under flowing helium or by degassing under vacuum at 673 K, the rate of heating being the major factor controlling the metal dispersion. However, as observed in the previous report, the first method (i.e. decomposition under flowing helium) produced rather low dispersed Ru-catalysts, except for the Ru/NaY catalyst. So, the Ru samples are decomposed under vacuum using a slow heating rate (0.5 K s^{-1}) upto 673 K in order to achieve higher metal dispersions. The characterization of these samples by H_2 and CO chemisorption is under progress. However, much higher dispersion was found for most of the catalysts characterized to date than for those decomposed under flowing helium.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

TGA STUDIES OF AMMONIA ADSORPTION

The ammonia adsorption can be used to measure the surface acidity of zeolites. During the adsorption, ammonia molecules react with the protons of surface hydroxyl groups and form ammonium ions.



Ammonia adsorption in zeolites has been studied extensively^(1,2,3). The amount of adsorption of ammonia is related to the number of surface acid sites⁽²⁾. The strength of acid sites can be determined by changing the partial pressure of ammonia^(4,5). Only strong acid sites can adsorb the

ammonia at low partial pressures. Another way to determine the strength of acidity is to evacuate the ammonia at different temperatures after adsorption. At higher temperatures, only strong acid sites can retain the ammonia. The remaining amount of ammonia after desorption is the amount of the acidity corresponding to a certain range of acid strength⁽²⁾.

The temperature range of ammonia adsorption is from 150°C to 500°C. In order to eliminate the physical adsorption of ammonia, a minimum temperature of 150°C is necessary⁽¹⁾.

1 - Experimental Procedure

The ammonia adsorption study was carried out in a TGA system (Figure 1) consisting of a Cahn RG-2000 beam microbalance and a flow system.

Linde electronic grade ammonia gas was used in this study. 50 mg of samples were used.

The reduced RuMZ (M=H, Li, Na, K, Rb, and Cs. Z=X, Y, L, and M) catalyst samples were then reduced at 400°C in a H₂ stream flowing at 30 cm³/min. The heating rate to 400°C was 1°C/min. The reduction at maximum temperature lasted one hour. Then the sample was cooled down to 100°C in flowing He with a flow rate of 30 cm³/min. The adsorption temperatures were in a range of 100°C to 400°C. Adsorption was started at the low temperature limit. After equilibrium was reached, the temperature was increased by increments of 100°C. Adsorption isobars were obtained at a partial pressure of ammonia of 277 torr. The adsorption isotherm at 195°C was obtained by varying the ammonia and helium flow rates.

The zeolite samples without Ru metal were first dried at 420°C in flowing helium. The adsorption of ammonia was started right after drying. The adsorption experimental procedure for the zeolite samples was the same as that of the Ru catalyst samples. The experimental conditions are listed in Table 1.

Table 1: Experimental Conditions of Ammonia Adsorption

Samples	NH ₃ Rate cm ³ /min	He Rate cm ³ /min	Purge Gas cm ³ /min	Heating Rate °C/min
RuMZ	5	5 - 150	5 (He)	1
MZ	5	5 - 150	5 (He)	5

*Note: M = metal cations, M=NH₄, Li, Na, K, Rb, and Cs
Z = zeolites, Z = X, Y, L, and M.

2. Results and Discussion

In order to check the amount of physically adsorbed ammonia, the surface coverage of ammonia was calculated by assuming a diameter of 3.65 nm for the ammonia molecules. The surface coverage of ammonia was compared with the nitrogen adsorption results. As shown in table 2, the surface coverage of ammonia at 200°C is about only 12-30% of a monolayer of nitrogen adsorption. This indicates that there is no ammonia physically adsorbed at this temperature.

Table 2: Surface Coverage of N₂ and NH₃

Sample	N ₂ (m ² /gm) at -195°C	NH ₃ (m ² /gm) at 200°C	NH ₃ /N ₂
HY	923.42	263.7	0.286
LiY	761.92	139.0	0.182
NaY	740.65	125.9	0.170
KY	757.29	111.9	0.148
CsY	487.78	92.7	0.190
NaY20	801.81	115.7	0.144
NaY40	839.96	110.3	0.131
NaY60	778.70	98.4	0.126

- Effect of Ion Exchange in Aqueous Solution

The surface acidity of zeolites is strongly dependent upon the type of cations present in the zeolite lattice as well as the extent of cation site occupancy. During the ion exchange process, the surface acidity may be modified during the exchange in aqueous solution. In order to study the influence of the aqueous solution, two samples NaYW and NaYN were prepared. The NaYW sample is prepared by stirring the NaY in water at 50°C for 18 hours. The NaYN was obtained by pretreating the NaY with a NaNO₃ aqueous solution at the same condition as NaYW sample. The results shown in figures 2 and 3 indicate that the adsorption amount on only NaYW was significantly higher than on the original NaY. The amount adsorbed on NaYW is higher than that adsorbed on NaYN. The higher adsorption amount may be caused by the Na cations being replaced by protons. During the process, part of the Na⁺ cations may be exchanged by protons from H₂O molecules in the aqueous solution, and this would result in an increase in the number of acid sites. For the NaYN sample, the original Na cations can be exchanged by both protons and the Na cations in the solution, while on the NaYW sample the original Na cation can only be exchanged with protons. Thus the NaYW contains more protons than NaYN, and the adsorption amount consequently increases.

The acid sites which are created during aqueous treatment are mostly strong acid sites. As shown in figure 3, the adsorption isotherm of NaYW is parallel to the isotherm therefore the difference of adsorption amount between the two isotherms stayed constant in the entire experimental pressure range.

- Effect of Preparation of Zeolite-Supported Ru Metals

The zeolite-supported Ru samples had higher adsorption amounts than the corresponding zeolites (Figures 2 and 3). This is a result of the ion-

exchange preparation method. During the catalysts preparation, the neutralizing cations were exchanged with Ru amine ions. Each ruthenium amine ion has a valence of 3 and it can replace three alkali cations.

After ion exchange, the catalysts were heated under vacuum. The ruthenium amine decomposed into ruthenium ions and ammonia, and reduced by NH_3 . These samples were also reduced again in H_2 . During the reduction process, the Ru ions were reduced to Ru metal, and protons were introduced to balance the charge of the zeolite framework. Therefore, acid sites were created. This resulted in a higher adsorption amount on the zeolite-supported Ru samples than on the zeolites.

Based on ion exchange stoichiometry, a calculation was carried out to determine the increase in the number of acid sites on Ru/MZ samples. The calculated and the experimental results at 195°C in pure ammonia are listed on Table 3.

As shown in Table 3 and as would be expected, the experimental results are lower than the calculated values. At 195°C , some acid sites are too weak to adsorb ammonia, so that the experimental results are lower than the calculated ones. For the Ru/NaX sample, the experimental result was much lower than the calculation. This may be caused by the larger metal particles, which were too large to exist inside the zeolite cavities. Therefore, a smaller amount of acid sites was created during the preparation process. By comparing the adsorption isotherms of Ru/MZ to the corresponding isotherms of zeolites, one can notice the shape of adsorption isotherm of both zeolite and zeolite-supported Ru samples are almost the same (Figure 3). This means that the acid sites created during the reduction process are mostly strong sites, resulting in a small change in the isotherm shape.

Table 3: Number of Acid Sites Created
During Preparation of Ru/MZ

Sample	Metal Loading	Particle size (Å)	Calculated mmol/gm	Experimental mmol/gm (195°C)
RuHY	3.21%	42	0.0	0.0
RuLiY	3.11%	20	0.92	0.75
RuNaY	3.11%	13	0.92	0.84
RuKY	3.16%	17	0.94	0.75
RuRbY	3.20%	42	0.95	
RuCsY	3.17%	24	0.94	1.10
RuNaY	1.00%		0.31	0.45
RuNaY20	1.20%	10.6	0.36	0.59
RuNaY40	1.13%		0.34	
RuNaY60	1.21%	17.7	0.36	0.37
RuNaX	3.15%	63	0.93	0.10
RuNaM	3.15%	36	0.93	
RuKL	3.16%	20	0.94	0.80

- THE INFLUENCE OF NEUTRALIZING CATIONS

The results of ammonia adsorption on alkali-cation exchanged Y zeolites and on zeolite-supported Ru samples are shown in figures 4 to 7. As the results show, the adsorption amount on both the zeolite and the zeolite-supported Ru samples increased as the cation size decreased. This means that the number of acid sites increases as the cation radius decreases. The adsorption isotherms progressively become flattened as the cation size decreases.

Earlier studies showed that the Bronsted acidity is generated by the exchange of multivalent ions, while exchanged alkali cations do not generate this acidity⁽⁶⁾. Ward studied the adsorption of pyridine on alkali and alkaline earth cation forms Y zeolites by infrared spectra⁽⁷⁾. He found that alkaline cation forms are Bronsted acids whereas the alkali forms are not. Since the alkali cations do not generate the acidity, the changes in both the number of acid sites and the shape of adsorption isotherms may be caused by the changes in the electrostatic field of the zeolites. Using Ward's data⁽⁷⁾, the electrostatic field and the adsorption amount were plotted as shown in figure 8. As shown in the figure, the change of adsorption amount is directly related to the change of electrostatic field. When the cations are present in zeolite framework, the electrostatic field caused by the electrostatic potential of the cations produces a polarizing action, which tends to draw the bonding electrons of hydroxyl groups away from the hydrogen atom towards the oxygen atom. Therefore, the O-H bond of hydroxyl group becomes weaker and the O-H group becomes more acidic. The polarizing action increases with increasing electrostatic field, consequently the acid strength of the hydroxyl group increases^(8,9). A similar result was reported by Ward from the adsorption of pyridine on alkali cation Y zeolites forms⁽⁷⁾. He reported that

the frequency of Bronsted acid absorption band decreased linearly with increasing electrostatic field. The population of Bronsted acid sites also increases with the electrostatic field.

When Na cations are exchanged by Li cations which have higher electrostatic potential, the electrostatic field of zeolite is increased. The stronger electrostatic field produces an increase in both acid strength and Bronsted acid site population. Therefore, the adsorption amount increases and the acid strength distribution becomes narrower, thus giving a flattened adsorption isotherm. When larger cations are exchanged, the electrostatic field becomes weaker, causing a decrease in both acid strength and number of Bronsted acid sites. So that the adsorption amount decreases and the slope of the adsorption isotherm increases (Figures 5 and 7).

The HY and Ru/HY samples gave the higher adsorption amount of ammonia (Figures 4 to 7). In the hydrogen Y zeolite, protons are present in the zeolite framework to balance the charge⁽¹⁰⁾. These protons are also the acid sites. Thus the total number of acid sites of HY is higher than those of the alkali cation Y zeolites. Consequently, the ammonia adsorption amount of HY and Ru/HY is the highest.

The adsorption amount on RuHY is almost the same as that on HY. during catalyst preparation, some neutralizing protons were replaced by ruthenium amines. After reduction, the ruthenium ions are reduced into the metal forms, and new protons produced during the reduction process serve to neutralize the charge in the zeolite framework. Therefore, there is no change in the number of protons, and the adsorption amount is the same.

As shown on figure 8, the adsorption at high temperature, which represents the strongest acid sites, is less affected by the change in electrostatic field than adsorption at low temperature. Thus the weak acid

sites are affected most. The adsorption on Ru/MY systems changes less than on the zeolites. When the Ru metal is present in the zeolite cavities, the electrostatic field distribution inside the zeolite might be modified. Because of the conduction effects of the metal particles, the gradient of electrostatic field inside the zeolite would be reduced. A more uniform field would result. Thus, stronger acid sites are produced.

The relative adsorption amounts (adsorption amount of MY or Ru/MY/NaY or Ru/NaY) and the relative electrostatic field (R.E.F.) were plotted in figure 9. As shown in the figure, there is no linear relationship between the relative adsorption amounts and the relative electrostatic field. For most samples, the decrease in the adsorption amount is almost parallel to the decrease in the electrostatic field except for RuKY and RuCsY. This phenomenon may be explained by the conductor effects of the Ru metals. For the KY and CsY, the neutralizing cations are located on the walls of the large cavities^(11,12). Hence the local electrostatic field inside the supercages is already stronger than the overall. While, the conductor effects of the metal particles further strengthen the local field. Under the influence of the strong local field, the number of Bronsted acid sites has less change than the overall field. Thus the change in the adsorption amount is small for the HY, LiY, RuHY and RuLiY. The situation is different since the protons and Li cations can penetrate into the sodalite cages and are well shielded. Therefore the field inside the supercages would be lower than the overall field, and results in a lower increase in the adsorption amount. As shown in the figure, the zeolites and the zeolite-supported Ru systems have almost the same adsorption amount. Since the polarizing action in these zeolites is so strong, the number of the adsorption sites almost reaches the maximum.

Therefore, the conductor effects of the metal particle could not create more adsorption sites.

- INFLUENCE OF SI/AL RATIO

The Si/Al ratio of zeolites is an important factor on the surface acidity. In order to study the influence of Si/Al ratio, the ammonia adsorption was carried on a series of dealuminated Y zeolites and a series of different types of zeolites with different Si/Al ratio. Ammonia adsorption was also carried out on these zeolites with Ru metal.

- Effects of Dealumination

The adsorption results on dealuminated Y and dealuminated Ru/Y are shown in figures 10 to 13. As the adsorption isotherms show in figures 11 and 13, the adsorption amount of ammonia decreased with increasing degree of dealumination of both zeolites and Ru/Y samples. The isotherm curves are also flatter as the degree of dealumination increases. The change in the shape of the adsorption isotherm indicates that the dealumination had more effect on the weak acid sites than on the strong ones. In a study of n-butylamine adsorption on EDTA dealuminated Y zeolites, Beaumont and Barthomeuf^(13,14) have reported that the weak acidity decreased with aluminum content while the number of strong acid sites remained constant until the aluminum content was below 35 atoms per unit cell. Then the number of strong acid sites decreased with decreasing aluminum content. They suggested that the cations with the weakest acidity were eliminated first during EDTA extraction. Similar results have been reported by other investigators⁽¹⁵⁾.

Plotting the adsorption amount vs Al content, our results show a similar behavior. The adsorption at high temperature remains almost the same while the adsorption at lower temperature decreases with the Al content.

The decrease in adsorption amount seems not only to be related to the change in the electrostatic field, but also to be related to the aluminum content. The results show that the adsorption amount on NaX is higher than that on NaY. Since the NaY has a higher electrostatic field (1.3 V/Å) than NaX (0.8 V/Å)^(7,16), the higher adsorption amount of NaX could not be a result of the electrostatic field. The aluminum content may be the major factor. The results show that the adsorption amount decreases with aluminum content (Figure 14). During dealumination, the number of acid sites decreases with decreasing aluminum content. Hence, the adsorption amount decreases. The cation content also decreases with the aluminum content. The reduction in cation content should reduce the cation-ammonia interaction, which causes the adsorption amount to fall down.

As shown in figure 14, the change in the adsorption amount at low aluminum content (below 40 Al atom per unit cell) is less than at high aluminum content. This is caused by the increase in the acid strength coefficient α_0 . The α_0 is a measure of the interaction between the acid sites. When the aluminum content is high, the acid sites can interact with each other, therefore the acid strength decreases and the α_0 has a lower value. When aluminum atoms are partially removed from the zeolite framework, the Al tetrahedra are diluted by the Si tetrahedra. The distance between the acid sites increases and the interaction between the acid sites is reduced. This later causes an increase in the acid strength and α_0 increases⁽¹⁷⁾. When the aluminum content is below 28 Al atoms per unit cell for X and Y zeolites, the acid strength is at its maximum^(13,14). The increase in acid strength causes less change in the adsorption amount at lower aluminum content.

The dealuminated Ru/NaY systems have the same behavior. As shown in figure 14, the adsorption curves of zeolite-supported Ru metals have similar

shape as those of the zeolites alone. This phenomenon indicates that the change in acidic properties of metal/zeolite systems is independent of the supported metals.

- Effect of Type of Zeolites

Figures 15 and 16 show the adsorption results of ammonia on different types of zeolites which have different Si/Al ratio. The results indicate that the total number of acid sites increases as the Si/Al ratio decreases. But the strong acidity increases with increasing Si/Al ratio. The shape of the adsorption isotherms is flattened with increasing Si/Al ratio. Earlier studies^(14,17,18) showed that the acid strength increased with the Si/Al ratio because of less interactions between the acid sites. The increase in the strength of acidity causes an increase in the adsorption amount.

By comparing figure 17 and 18, one can notice that the adsorption amount increases with the Si/Al ratio on different type of zeolites. But the adsorption amount on dealuminated Y zeolites decreases as the Si/Al ratio increases. The different behavior may be caused by the different framework of the zeolites structure. The X and Y zeolites have the same three dimensional framework, but the mordenite and L have different two dimensional frameworks⁽¹⁹⁾. The different framework structure would result in a different arrangement of cation and aluminum positions, which can change the electrostatic field inside the zeolites as well as the polarizing action. Therefore, the surface acid sites are different, so are the adsorption amounts. For the X and Y zeolites, the structure is the same, therefore the behavior is the same.

The adsorption on KL and Ru/KL are lower than expected, which may be caused by the different type of cation. The potassium cation has a lower

electrostatic potential than sodium cation, so that a weaker electrostatic field is expected to result. Consequently, the surface acidity decreases with the weaker field. Since the change of the field mainly affects the weaker acid sites, this causes a greater decrease in the adsorption amount at low temperatures. The adsorption at high temperatures is less affected.

3. SUMMARY

From the ammonia adsorption results, it can be concluded that the surface acidity of zeolites and Ru/Zeolites is mainly dependent upon the electrostatic field of the zeolites and the aluminum content.

For alkali cation exchanged Y zeolites, the surface acidity is dependent upon the electrostatic field. When the cations with strong electrostatic potentials are exchanged, the electrostatic field increases as well as the polarizing action. The latter changes the non-acidic hydroxyl groups into acidic hydroxyl groups and results in an increase of the acid strength. Vice versa, the decrease in the electrostatic potential of the cations would reduce the electrostatic field. Hence, both acid sites and acid strength are reduced.

For dealuminated Y zeolites, the aluminum content is the governing factor. The dealumination reduces the aluminum content as well as the number of acid sites, therefore, reducing the adsorption amounts.

The structure of the zeolite also affects the surface acidity. The different framework structure of zeolite would change the electrostatic field inside the zeolites, causing a change in the surface acidity and the acid strength. The number of acid sites and the acid strength decrease with Si/Al ratio for the same type of zeolite. On different types of zeolites, the number of acid sites and the acid strength increases with the Si/Al ratio.

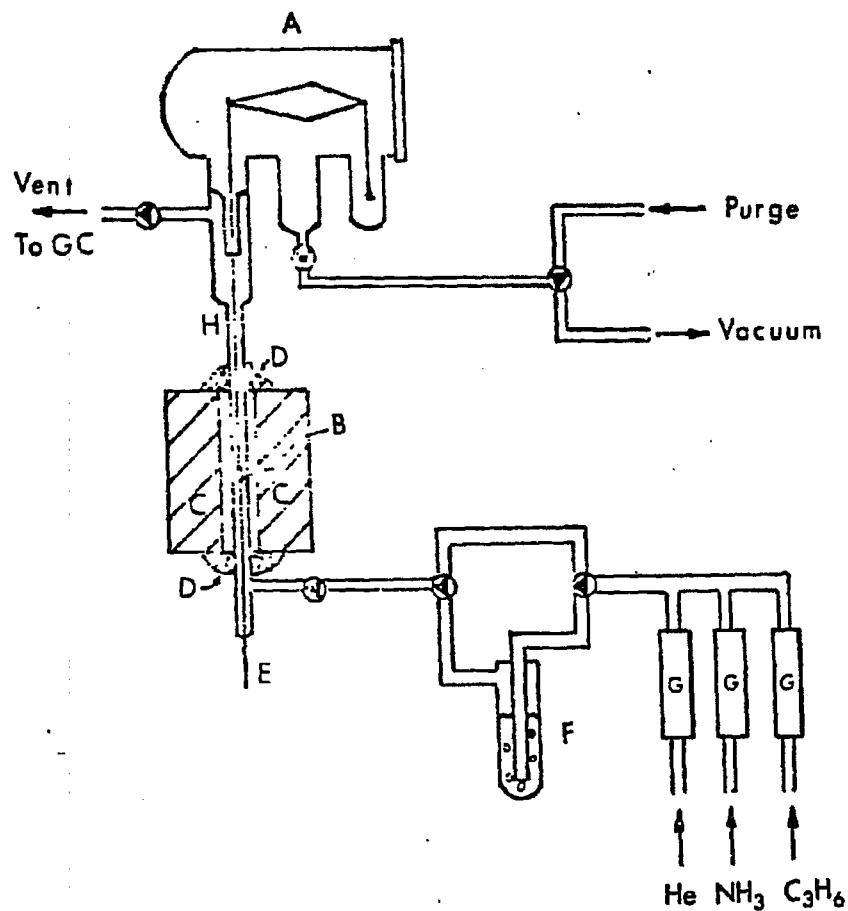
The ruthenium metal/zeolite systems have identical behavior as the corresponding zeolites, except for the total number of acid sites. The higher adsorption amount on Ru/MZ systems is a result of the ion exchange preparation method. The results indicate that the acid sites which are created by this preparation method are predominantly strong acid sites. The identical behavior of zeolites and Ru metal/zeolites indicates that the supported metal has no effect on the surface acidity of the supports.

IV. FORECAST OF WORK

During the next quarter, the characterization of the new catalysts prepared by decomposing the Ru-hexammine complex under vacuum will be continued using H₂ and CO chemisorption and X-ray diffraction when necessary. The CO hydrogenation experiments will be continued using these newly prepared catalysts.

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|------------------|------------------|
| A. Microbalance | E. Thermocouple |
| B. Sample Bucket | F. Saturator |
| C. Heater | G. Rotameter |
| D. Glass Wool | H. Hangdown Tube |

Figure 1: TGA Apparatus

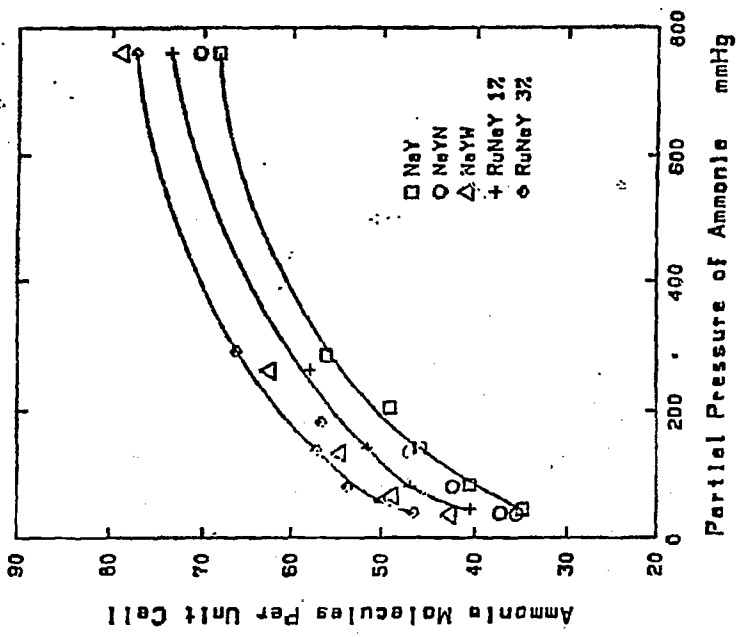


Figure 3: Ammonia Adsorption on NaY and RuNaY at 195°C

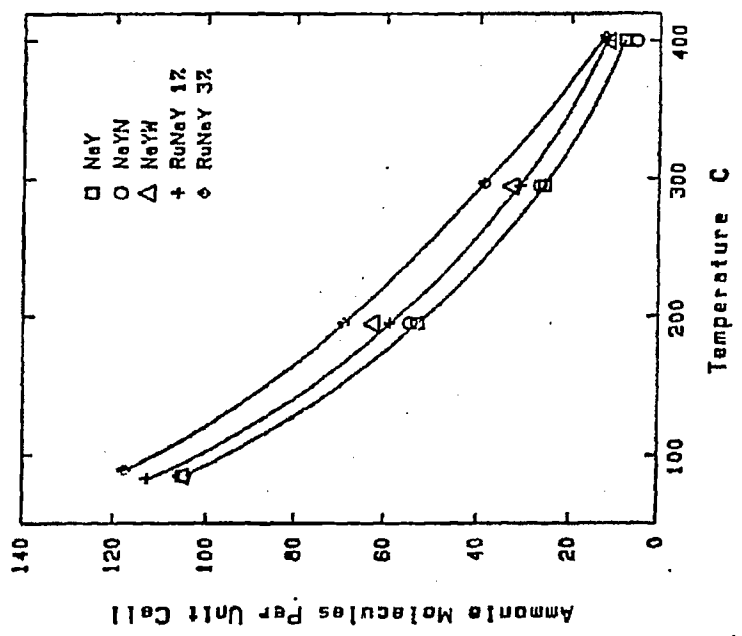


Figure 2: Ammonia Adsorption on NaY and RuNaY at 277 mm Hg partial pressure of ammonia

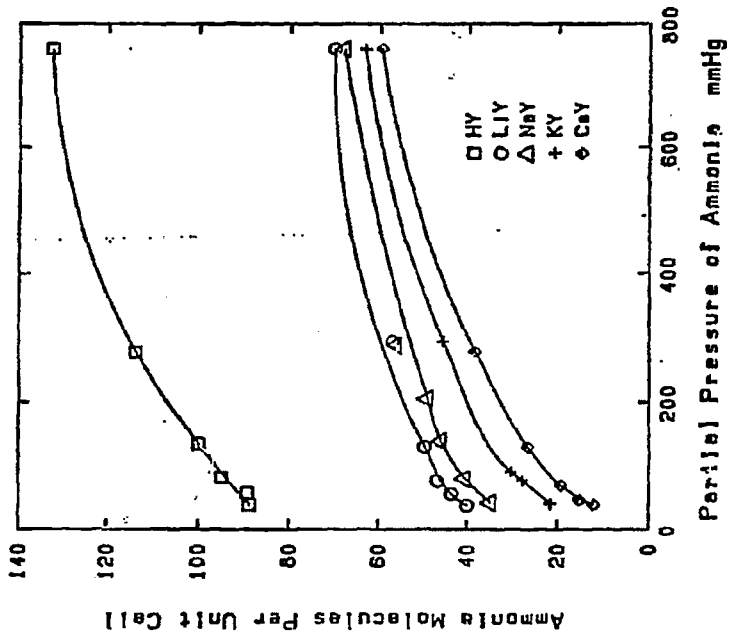


Figure 5: Ammonia Adsorption on Alkali Cation Forms γ at 195°C

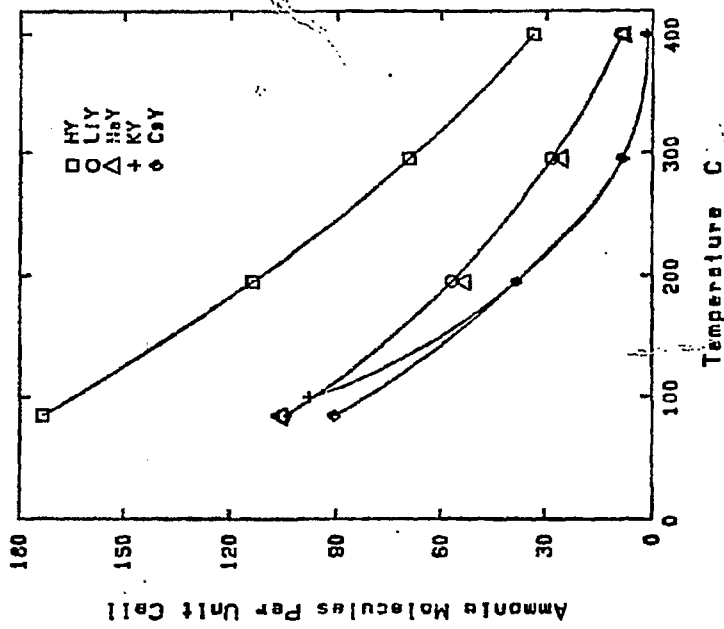


Figure 4: Ammonia Adsorption on Alkali Cation Forms γ at 277 mm Hg Partial Pressure of Ammonia

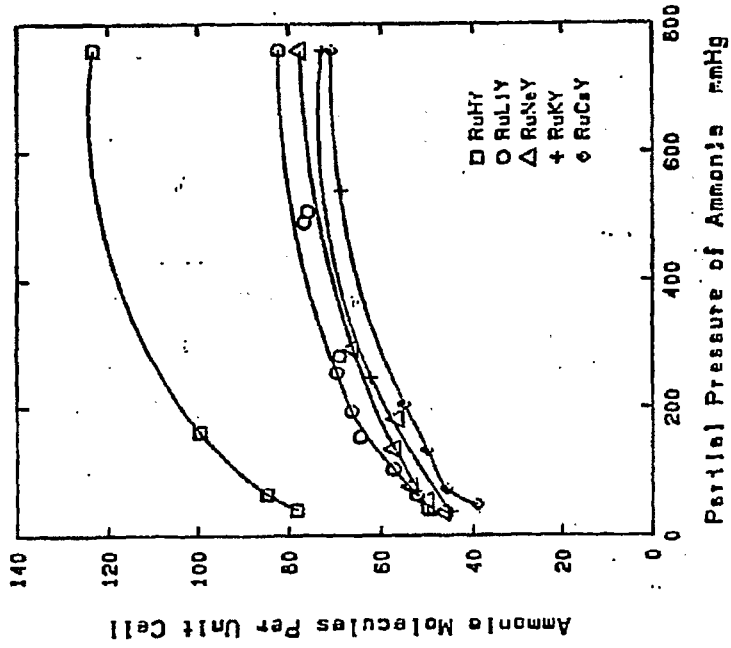


Figure 7: Ammonia Adsorption on Alkali Cation Forms Ru/HY at 195°C

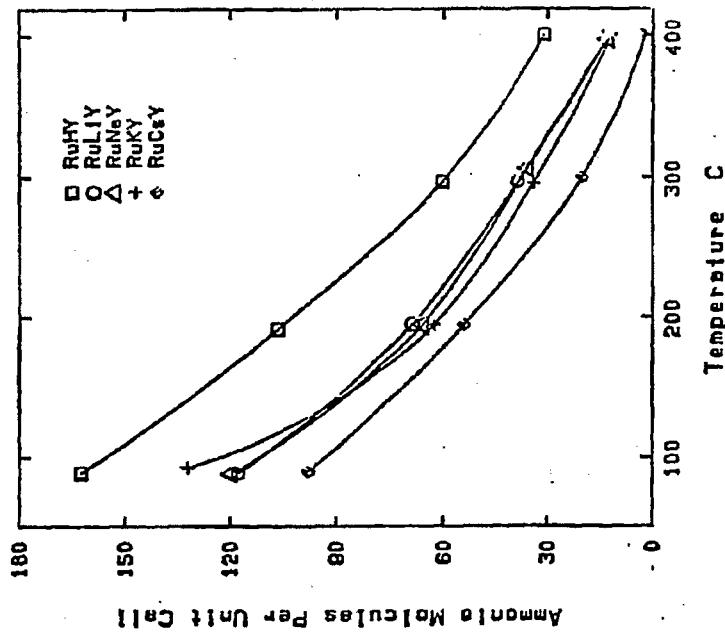


Figure 6: Ammonia Adsorption on Alkali Cation Forms Ru/HY at 277 mm Hg Partial Pressure of Ammonia

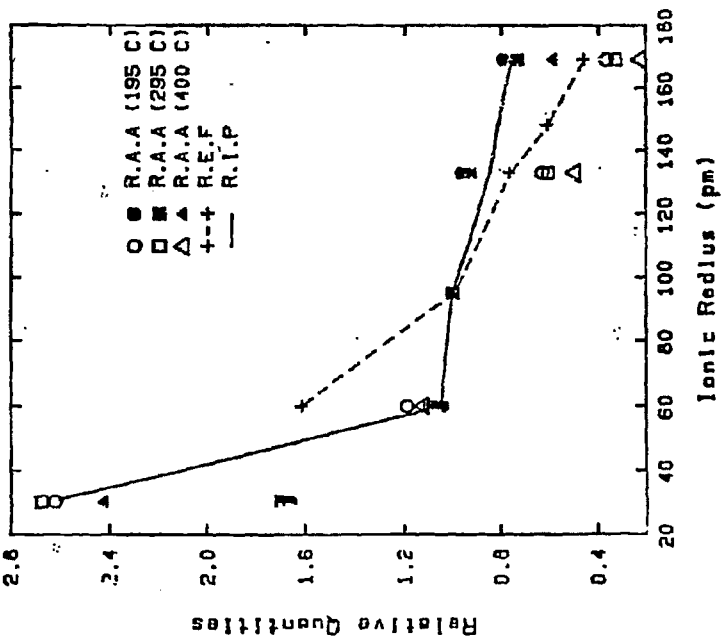


Figure 9: Relationship between the Cation Radius and the Relative Adsorption Amount
 (open points - zeolites, filled points - Ru/HZ)
 R.A.A - relative Adsorption Amount
 R.E.F - Relative Electrostatic Field
 R.I.P - Relative Electrostatic Potential

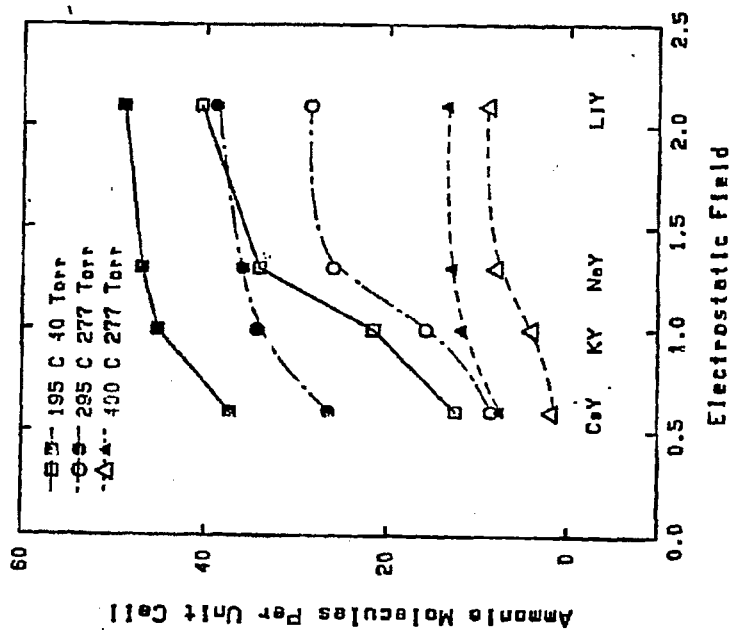


Figure 8: Relationship of the Electrostatic Field and the Adsorption Amount
 (open points - zeolites, filled points - Ru/HZ)

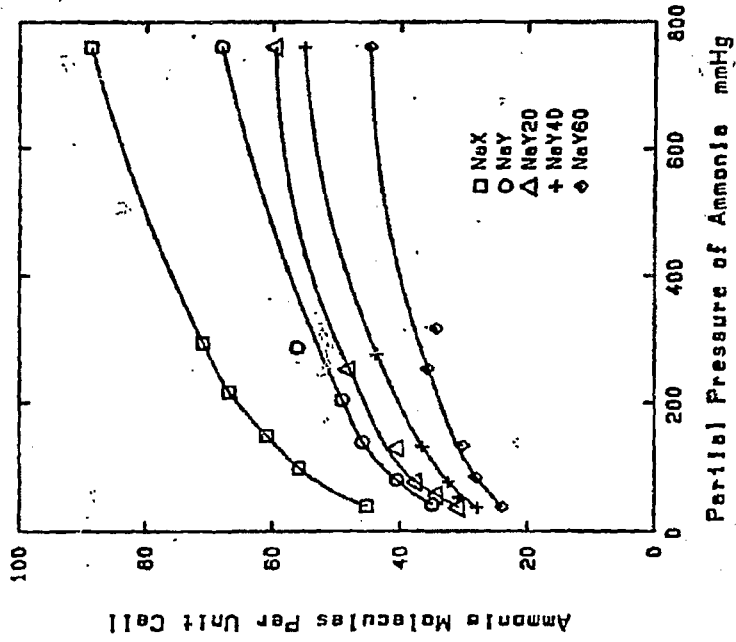


Figure 11: Ammonia Adsorption on Dealuminated NaY at 195°C

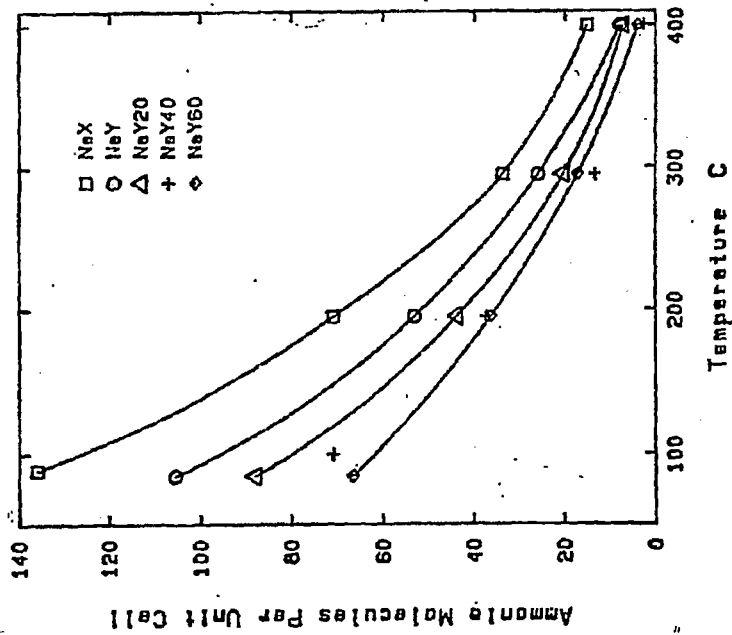


Figure 10: Ammonia Adsorption on Dealuminated NaY at 277 mm Hg Partial Pressure of Ammonia

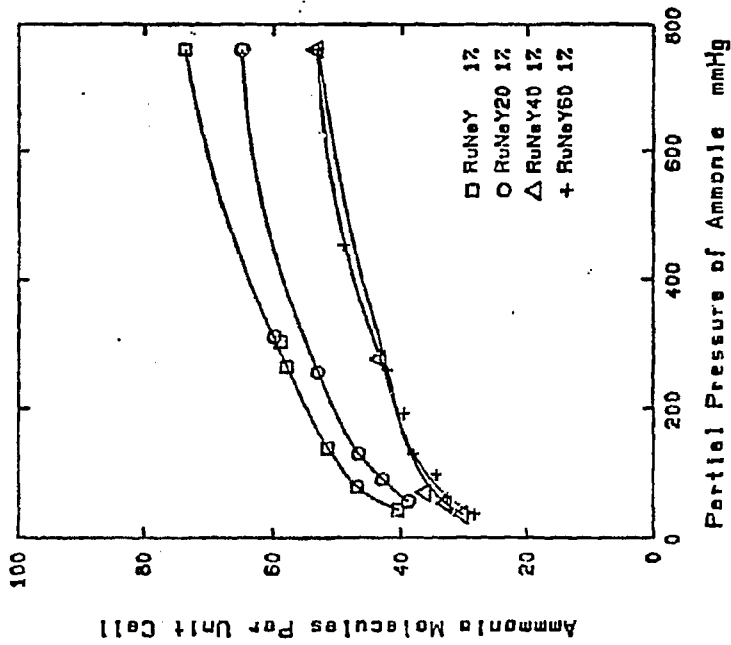


Figure 13: Ammonia Adsorption on Dealuminated Ru/NaY at 195°C

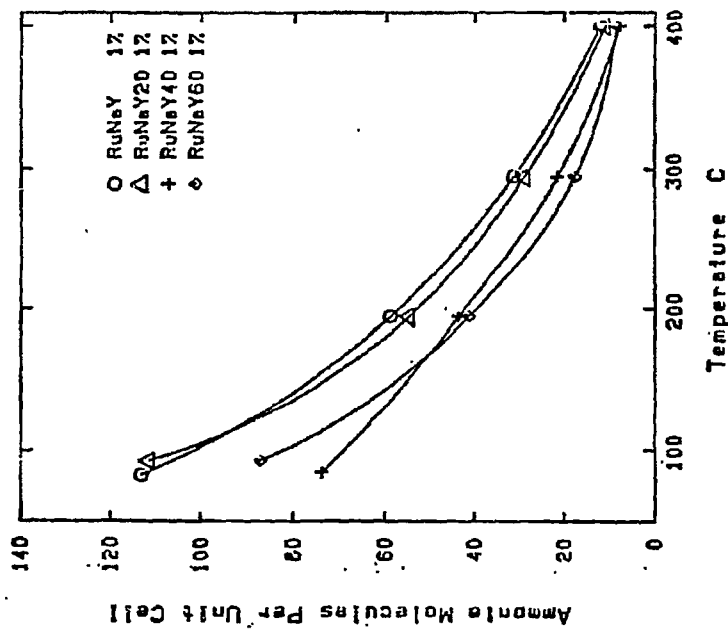


Figure 12: Ammonia Adsorption on Dealuminated Ru/NaY at 277 mm Hg Partial Pressure of Ammonia

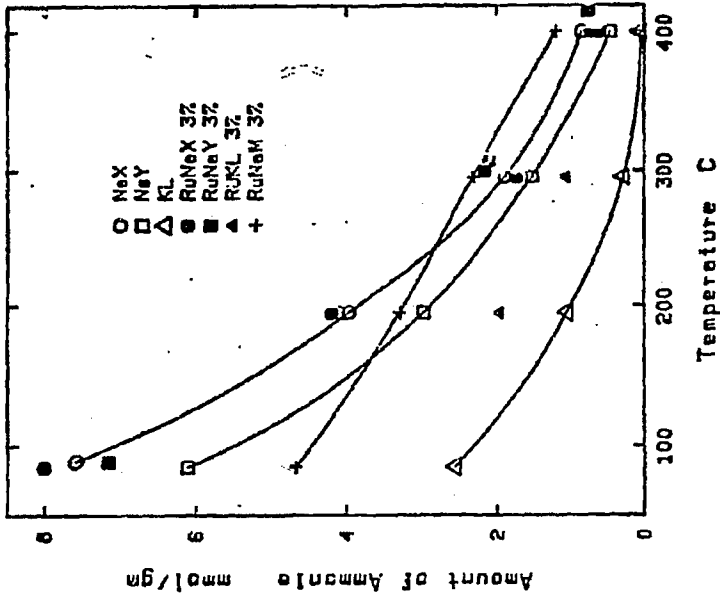


Figure 15: Ammonia Adsorption on Different Type of Zeolites and Metal/zeolite Systems At 277 mm Hg Partial Pressure of Ammonia (open points - zeolites, filled points - Ru/MZ)

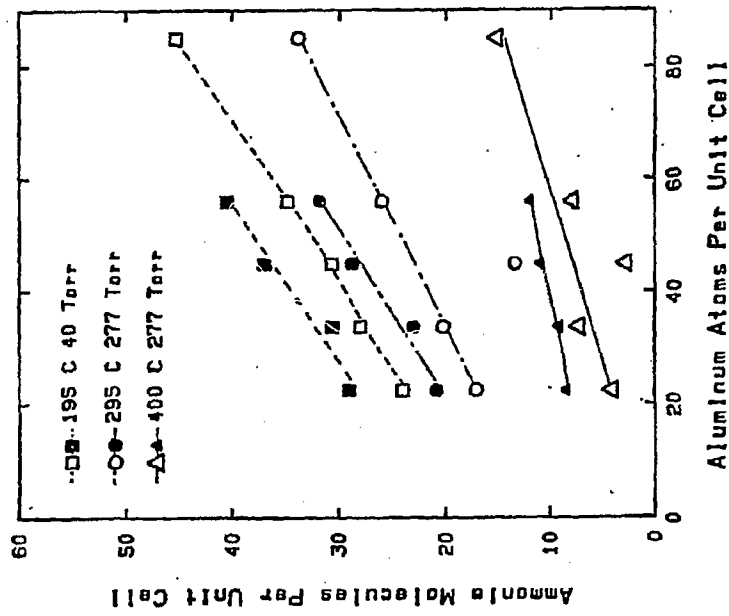


Figure 14: Relationship between the Aluminum Content and the Adsorption Amount (open points - zeolites, filled points - Ru/MZ)

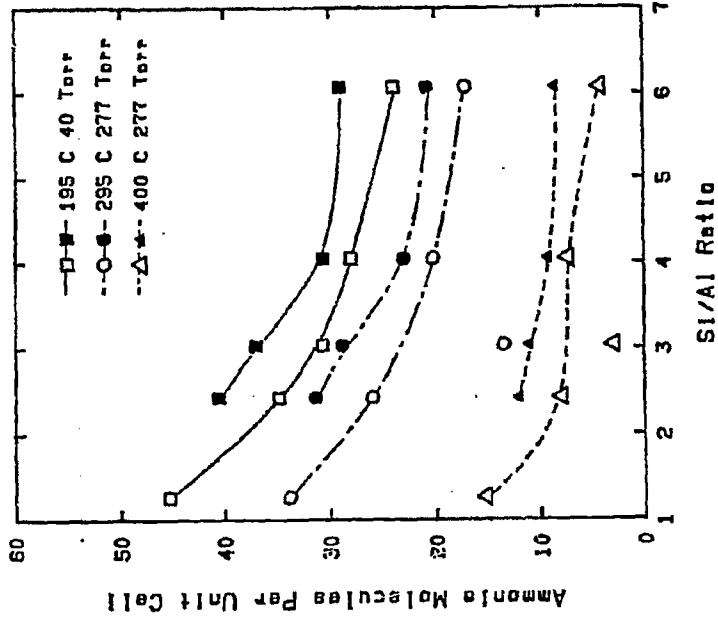


Figure 17: Relationship between the Si/Al Ratio and the Adsorption Amount of Dealuminated NaY and Ru/NaY (open points - zeolites, filled points - Ru/HZ)

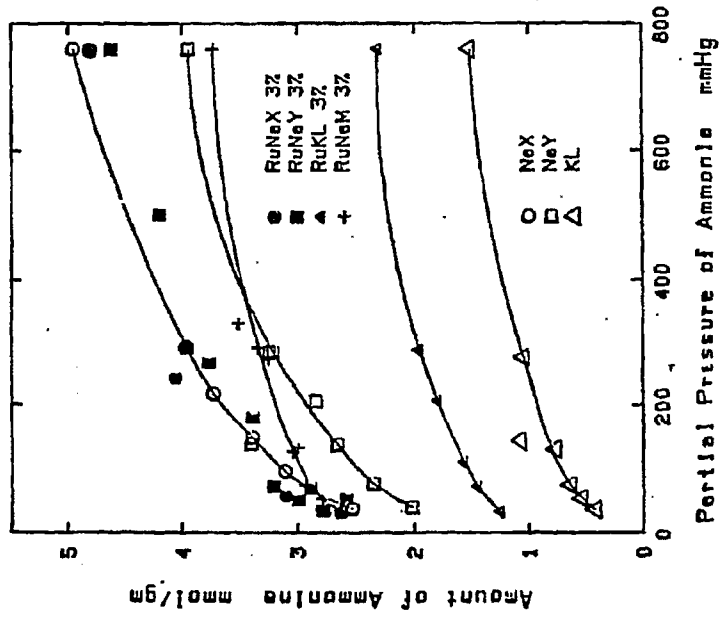


Figure 16: Ammonia Adsorption on Different Type of Zeolites and Metal/Zeolite Systems At 195°C (open points - zeolites, filled points - Ru/HZ)

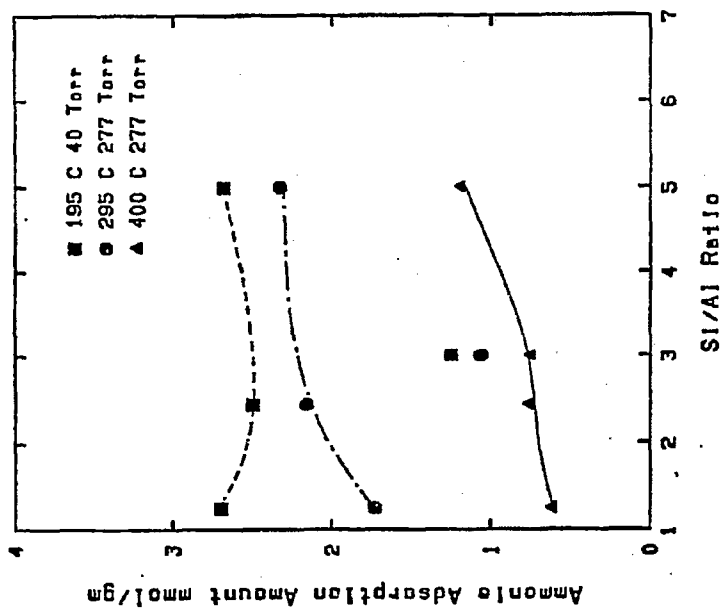


Figure 18: Relationship between the Si/Al Ratio and the Adsorption Amounts on Different Types of Zeolites and Ru/Zeolites

(open points - zeolites, filled points - Ru/MZ)

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