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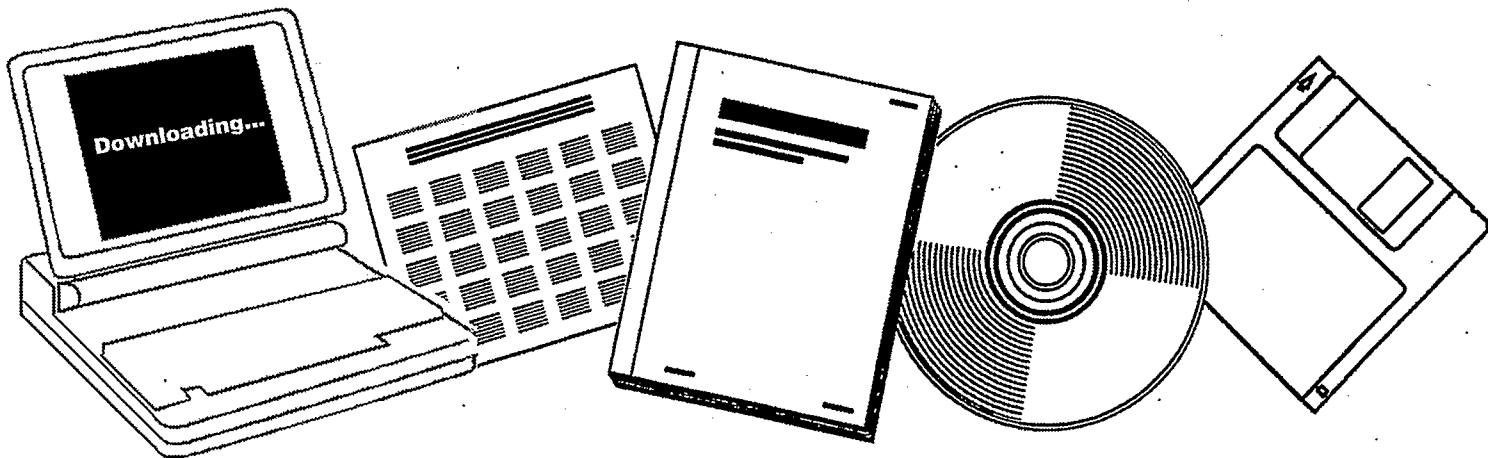
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CATION PROMOTION EFFECTS IN ZEOLITE-SUPPORTED F-T CATALYSTS

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

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ZEOLITE-SUPPORTED F-T CATALYSTS

3rd Quarterly Report
March 1984 - May 1984

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I. OBJECTIVE AND SCOPE OF WORK

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

The current research involves a study of the promotion effects of the neutralizing alkali cations on CO hydrogenation (under typical F-T conditions) over zeolite-supported Ru catalysts. Ru is a useful, model catalyst for the study of such promotion of this synthesis. First, alkali promotion has been found to have a great effect on product selectivity over Ru. Second, Ru does not form any stable carbides, thereby removing this complicating factor. Third, Ru is relatively easy to reduce to the metallic state. Fourth, Ru is the F-T metal easiest to keep inside zeolite crystallites. Fifth, under typical conditions, there is little oxygenated hydrocarbon formation or skeletal isomerization of the hydrocarbons over Ru. Thus, the 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 on 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 the 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, March 1, 1984, to May 30, 1984, our efforts have been concentrated on three main tasks:

- Surface analysis of dealuminated zeolite by means of ESCA:

A series of dealuminated NaY zeolites was studied by ESCA. NaY zeolite was dealuminated using an aqueous solution of H_4EDTA . Changes in surface compositions and chemical states as a result of dealumination are reported. ESCA data indicated that aluminum and sodium are preferentially removed from

the external surface of the zeolite during dealumination. This is presumably due to diffusional limitations of EDTA molecules into the internal cavities of the zeolite particles. It was found also that the Al_{2p} binding energies of Nafaujasite type zeolites are an increasing function of Al/Si ratios of the zeolites. This illustrates the effects of Madelung potential on the chemical states of the framework aluminum atoms.

- Adsorptive properties of dealuminated and alkali-exchanged zeolite:

Adsorption isobars of cyclopropane, cyclohexane and benzene have been performed in the temperature range 25-120°C using a TGA system. The results were explained on the basis of variations of void volumes and heat of adsorption as well as chemical interactions.

- Catalytic properties: CO hydrogenation:

Several runs of CO hydrogenation have been carried out at atmospheric pressure over the following catalysts:

3% Ru/NaY

1% Ru/20% dealuminated zeolite

1% Ru/40% dealuminated zeolite

1% Ru/60% dealuminated zeolite

The main results and interpretation will be discussed in the next paragraph.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

III.1 Surface analysis of dealuminated and alkali-exchanged Y zeolites by ESCA.

Thermal stability of zeolites is of great importance for their commercial applications. It has been reported that removal of framework aluminum of the zeolites may result in greater thermal stability (1-3). Dealumination of zeolites can be achieved by either acid leaching (4) or by chemical extraction

with chelating ligands (5). Recent attention has been focused on understanding of the surface properties of dealuminated zeolites (6-7).

The samples were dealuminated using ethylenediaminetetra-acetic acid (EDTA). Changes in chemical states of the dealuminated zeolites were correlated with surface composition, structure, and cation of the zeolites. Homogeneity of the dealumination by EDTA is also reported.

ESCA spectra were recorded on an LHS-10 system with a DS4X data system. A magnesium anode (Mgk = 1253.6eV) operated constantly at 13.0kV and 20.0mA was utilized for the entire analysis. Surface compositions of all the samples were estimated based on Leybold-Heraeus sensitivity factors (8) and all the binding energies (BE's) were referenced to the Si_{2p} line (Si_{2p} - 103.0eV) of the zeolite samples (9).

All of the zeolite samples were obtained from Strem Chemicals. Dealuminated NaY samples were prepared in an aqueous solution of H₄EDTA refluxed at 90°C for 24 hours with continuous stirring. Following dealumination samples were washed with hot water to wash out soluble products and then dried at 60°C overnight. The amounts of H₄EDTA added to the solution were equivalent to 20%, 40% and 60% of the stoichiometric aluminum in the NaY zeolite. The amount of aluminum removed is believed to be close to the stoichiometric ratio between NaY and H₄EDTA in the solution (2) and, therefore, the bulk Al/Si ratio of the dealuminated samples were calculated based on complete consumption of H₄EDTA during the dealumination reactions.

ESCA data of the synthetic zeolites are summarized in Table 1. ESCA results for similar samples have also been reported elsewhere by other researchers (7, 9-13). The data in Table 1 is presented here for comparison with dealuminated samples. It should be noticed that the C_{1s}BE's from contamination are scattered between 284 and 286eV. This suggests that the C_{1s}

line may not be suitable as a binding energy reference. Rather, a BE of one of the major components of the zeolites, Si_{2p} , should be used as an internal BE reference.

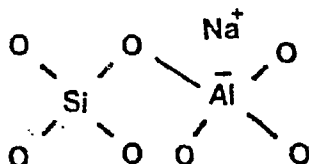
As indicated in Table 1, the surface Al/Si and cation/Si ratios are significantly lower than the bulk stoichiometric ratios of the zeolites; a result in good agreement with a number of recent publications (7, 10-13). Also, the surface Al/Si ratios are slightly greater than the surface cation/Si ratios. This may be due either to imperfect crystallinity of the zeolite particles or to replacement of cations by protons which are not detectable by ESCA.

Surface aluminum deficiency of synthetic zeolites has been reported recently (10-13), but the mechanism for the "natural" dealumination is not fully understood. It is of great interest to compare the ESCA data of these synthetic zeolites and those of the zeolite samples after dealumination with H_4EDTA . As shown in Table 2, ESCA data indicate that the % of surface Al removed exceeds the calculated % bulk dealumination. This suggests a preferential removal of Al from the external surface during the dealumination reactions, presumably due to diffusional limitations of H_4EDTA molecules into the internal cavities of the zeolite particles. Comparison of the ESCA data in the present study and the results from recent publications (6-7) indicates a good agreement (Figure 1).

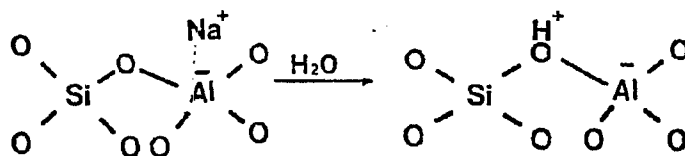
A plot of surface vs. bulk Al/Si ratios for all the zeolites under consideration is given in Figure 2. The dashed line in the plot represents the 1 to 1 equivalent between surface and bulk Al/Si ratios. It is clear that all the non-dealuminated zeolites exhibit somewhat a deficiency in surface aluminum concentration. In the dealuminated samples, the surface aluminum deficiencies are even more pronounced. Another interesting feature of the

ESCA data is the relationship between surface cation/Si and surface Al/Si ratios, as shown in Figure 3. It is apparent that the results for all the zeolites can be easily fitted by a straight line. This line, however, deviates from the 1 to 1 ratio line between cation and aluminum for perfect zeolite crystals (dashed line). HY does not fall on the same line as the other samples since the cations in HY are not measurable by ESCA.

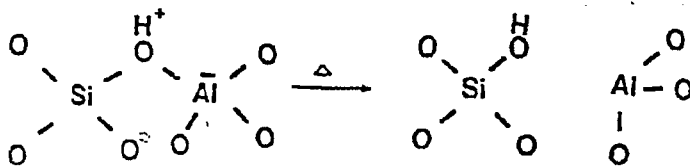
Deviation of the straight line in Figure 3 from the theoretical line may be related to the termination of the zeolite crystals on the external surface. The cation sites in zeolites may be represented by the following schematic, in which cations such as Na^+ are associated with the framework aluminum atoms, i.e.



The cation sites on the external surface may be more accessible to ion exchange with water molecules during washing, i.e.



During the drying or calcination step, the following reactions may occur (14, 15),



In both cases, the measurable amount of cations by ESCA will be decreased.

ESCA data indicate that the amount of cations detected by ESCA is directly proportional to the amount of aluminum atoms present, regardless of the preparation procedures of the zeolites (synthetic or dealuminated). Because of the surface sensitive nature of ESCA, only the outmost cage and the external surface can be seen. Thus, the ESCA results suggest that either the cation sites at the crystal termination positions are occupied with protons or the termination aluminum atoms are tri-coordinated. A uniform distribution of aluminum will give an amount of aluminum at the terminated positions proportional to the amount of aluminum present.

Changes in chemical state of Al among various Na faujasite zeolites were also studied. As shown in Figure 4, the Al_{2p} BE's are an increasing function of surface Al/Si ratio, probably caused by the modification of the Madelung potential resulting from variations in Al/Si ratios (12-13). This is possibly the reason for increasing acidity as a result of dealumination. Results for

the other zeolites in the present study do not fall into this trend for Na faujasites. The variation in BE observed for these other zeolites (Table 2) are probably due to effects of the different cations (H^+ , Rb^+ , vs. Na^+) and crystal structures (faujasite vs. NaZ modenite).

Several conclusions can be drawn from this ESCA study of dealuminated NaY zeolites:

1. During dealumination, Al and cations are preferentially removed from the external surface, probably due to diffusional limitations of H_4EDTA into the internal cavities of the zeolites.
2. Within the sampling zone of ESCA, the aluminum atoms are uniformly distributed. The Al crystal termination position is probably either neutralized by protons or it tri-coordinated.
3. Dealumination causes a variation in chemical state of the framework aluminum atoms, evidence of changing crystal potential as a result of dealumination.

These results have been the subject of an oral communication given in collaboration with Dr. Shyu and Skopinski (from Leybold-Heraeus Vacuum Products, Inc.) at the 6th Symposium on Applied Surface Analysis (University of Dayton, Ohio, June 6-8, 1984).

III.2 Adsorptive properties of dealuminated and alkali-exchanged Y zeolite.

Adsorption isobars of cyclopropane, cyclohexane and benzene have been determined in the temperature range 25-120°C. The adsorbed quantities of gases have been measured by following the weight changes in TGA system using a Cahn microbalance. Several interesting features have been obtained.

Figure 5 shows, as an example, several adsorption isobars of benzene. The alkali-exchanged zeolite (NaY, LiY, KY, RbY, CsY) give rise to a set of

parallel straight lines. This is explained mainly on the basis of a blocking effect which increases when the alkali-cation radius increases. Thus at a given temperature the quantity of adsorbed gas is lessened as the void volume decreases. On the other hand, the 60% dealuminated NaY zeolite exhibits a different trend. The reason lies in the fact that the heat of adsorption decreases upon dealumination. This means that the interaction adsorbent-adsorbate is weakened and the surface is more easily depopulated when the temperature is raised.

It is also worthy to note that at a given temperature and regardless of the sample under study, more benzene is adsorbed than cyclohexane. This is due to the specific interaction of benzene π -bond system with the adsorbent.

III.3 Catalytic properties: CO hydrogenation.

CO hydrogenation in typical Fischer-Tropsch synthesis conditions have been carried out using Ru supported on NaY and a series of dealuminated zeolites. The experimental conditions are:

- Pressure: 1atm
- Temperature: 220-300°C
- Mixture: CO/H₂ = 1
- Catalyst Weight: 0.2-0.3 g
- Space Velocity: 5000h⁻¹
- Product Analysis: GC with TCD and FID detectors

Although this study is not yet very advanced, the first results show already a significant influence of dealumination on catalytic properties of Ru in Fischer-Tropsch synthesis. Two major features may be reported.

- Increasing amounts of CH_4 are obtained when percentage of dealumination increases. This may be related to the general trend reported in an earlier work between CH_4 formation on one hand and the metal-support interaction on the other. Indeed it was reported that Ru/NaY prepared by vapor impregnation produced much less methane than the one prepared by ion-exchange. Likewise, in this case, since dealumination generates stronger acidic sites, it may be assumed that Ru on increasingly dealuminated zeolite interacts more and more strongly with the support.- The second features which is not yet fully interpreted is the slow decrease in intrinsic activity as more dealumination takes place. Interpretation of this result needs the knowledge of metallic particle sizes which are not yet available.

More comprehensive picture of the effect of dealumination on CO hydrogenation properties of Ru will be certainly included in the forthcoming quarterly report.

IV. FORCAST OF WORK

In the next quarter the following tasks are planned:

- Continuation of CO hydrogenation studies in order to fully delineate the role of dealumination. Effects of alkali cations and zeolite structure will also be studied.
- Continuation of adsorption study by means of both TGA and gas volumetry.
- Surface study of some zeolites loaded Ru by ESCA.

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Table 1. ESCA Data of Commercial Zeolites

Samples	Binding Energies (eV)					Atomic Ratios			
	<u>O_{1s}</u>	<u>C_{1s}</u>	<u>Al_{2s}</u>	<u>Al_{2p}</u>	<u>Na_{1s}</u>	Cation/Si		Al/Si	
						<u>Bulk*</u>	<u>Surface**</u>	<u>Bulk</u>	<u>Surface</u>
NaX	532.0	285.6	119.8	75.0	1073.1	0.833	0.661	0.833	0.764
NaY	532.0	284.7	119.5	74.65	1073.0	0.417	0.367	0.417	0.397
HY	532.0	285.9	119.25	74.40	1072.5	--	0.031	0.417	0.370
RbY	531.9	284.7	--	74.52	--	0.417	0.322	0.417	0.379
NaZ	532.2	284.9	119.4	74.56	1072.9	0.200	0.180	0.200	0.191

* Bulk ratios were estimated based on the stoichiometry of the zeolites.

** Surface ratios were estimated based on the ESCA data corrected with LH sensitivity factors.

TABLE 2. ESCA DATA OF DEALUMINATED ZEOLITE SAMPLES

SAMPLES	BINDING ENERGIES (EV)*						% AL REMOVED**
	<u>Na 1s</u>	<u>O 1s</u>	<u>C 1s</u>	<u>Si 2s</u>	<u>Al 2s</u>	<u>Al 2p</u>	
NAY	1073.0	532.0	284.7	154.2	119.50	74.65	0
20% DEAL. NAY	1072.7	532.2	284.5	154.1	119.25	74.40	34.3
40% DEAL. NAY	1072.6	532.2	285.0	154.0	119.10	74.20	73.6
60% DEAL. NAY	1072.6	532.3	283.9	154.0	119.10	74.15	79.3

* ALL BE'S ARE REFERENCED TO Si_{2p} (= 103.0 EV).

** ESTIMATED BASED ON ESCA ATOMIC RATIOS

Figure Captions

Figure 1.

Comparison surface spectroscopic data of the dealuminated NaY zeolites with those in the literature.

(a) A plot of surface Na/Si ratios vs. bulk Na/Si ratios

(b) A plot of surface Al/Si ratios vs. bulk Al/Si ratios

Figure 2.

A plot of surface Al/Si ratios vs. bulk Al/Si ratios for a series of zeolites.

Figure 3.

A plot of surface cation/Si ratios vs. a surface Al/Si ratios for a series of zeolites.

Figure 4.

A plot of Al_{2p} binding energies of the sodium form of faujasite type zeolites as a function of surface Al/Si ratio.

Figure 5.

Benzene adsorption isobars.

Fig. 1

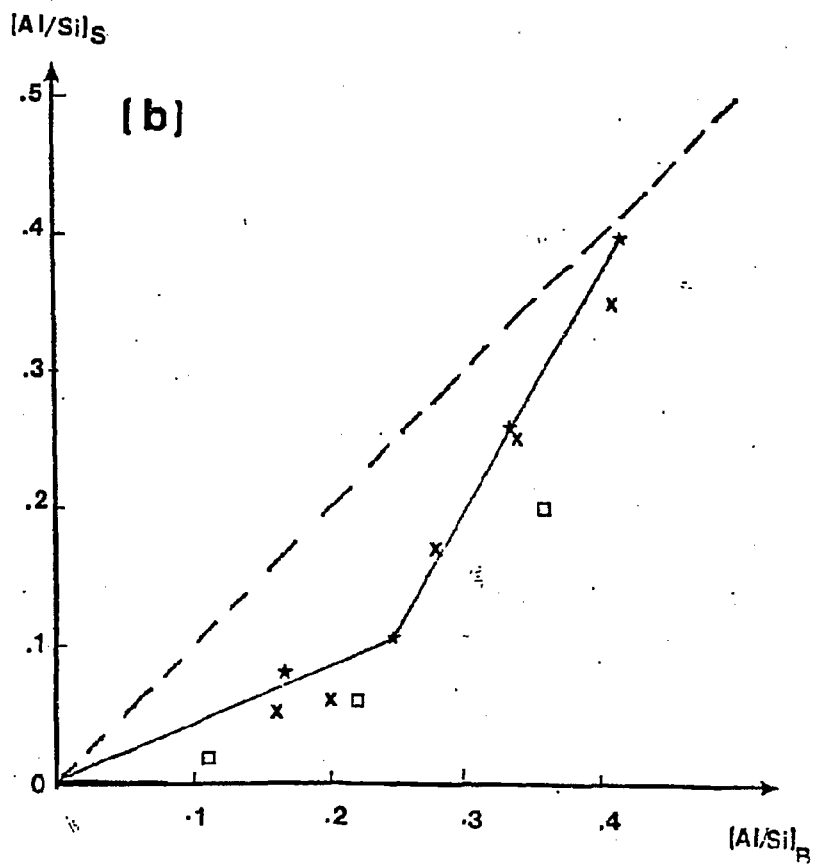
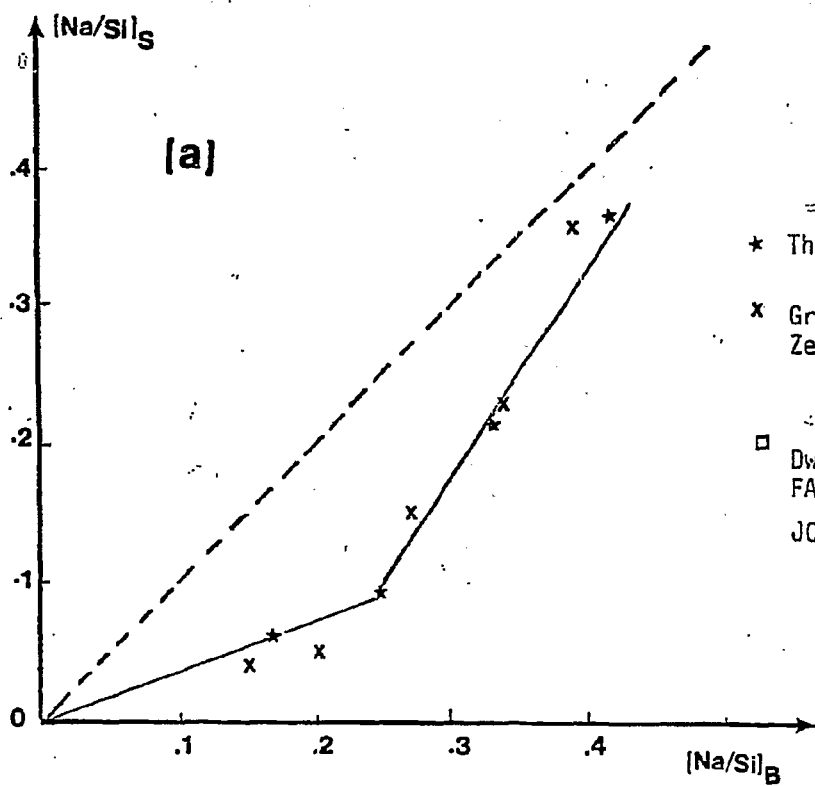
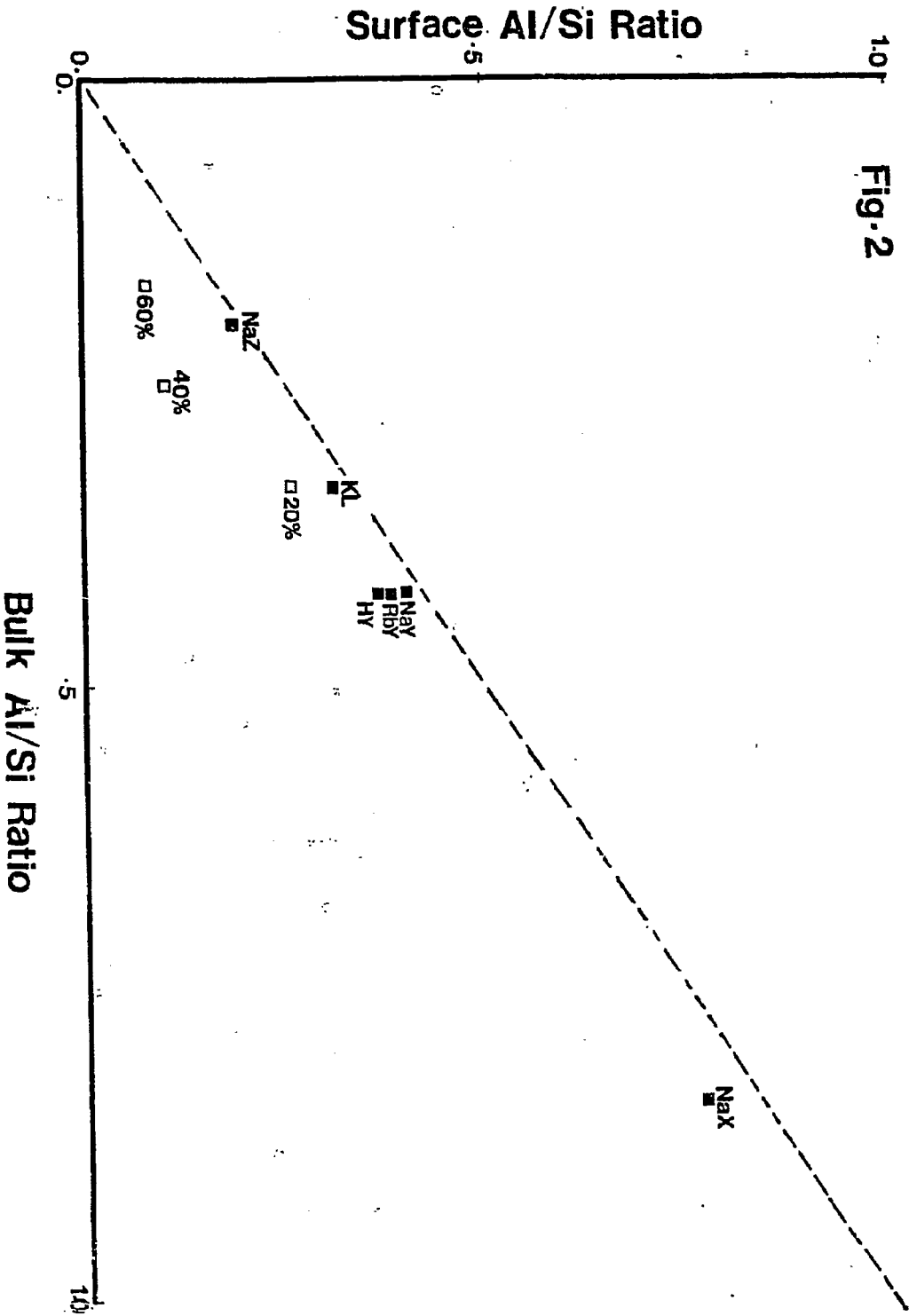
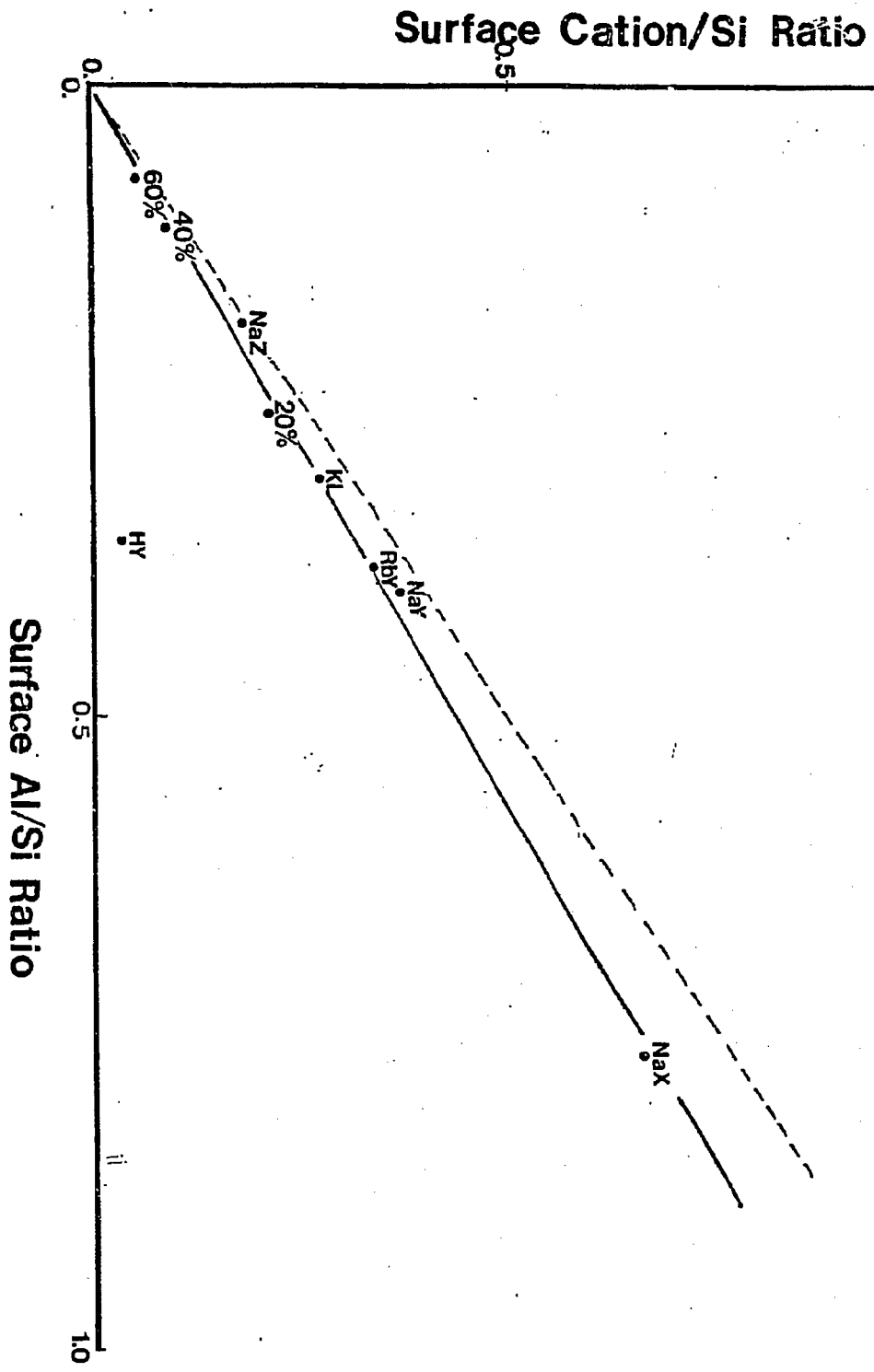
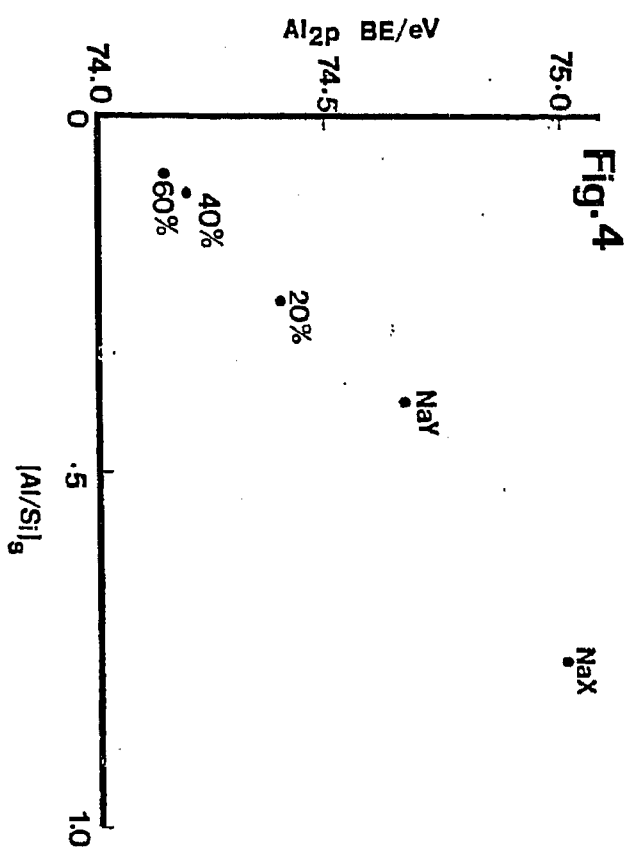


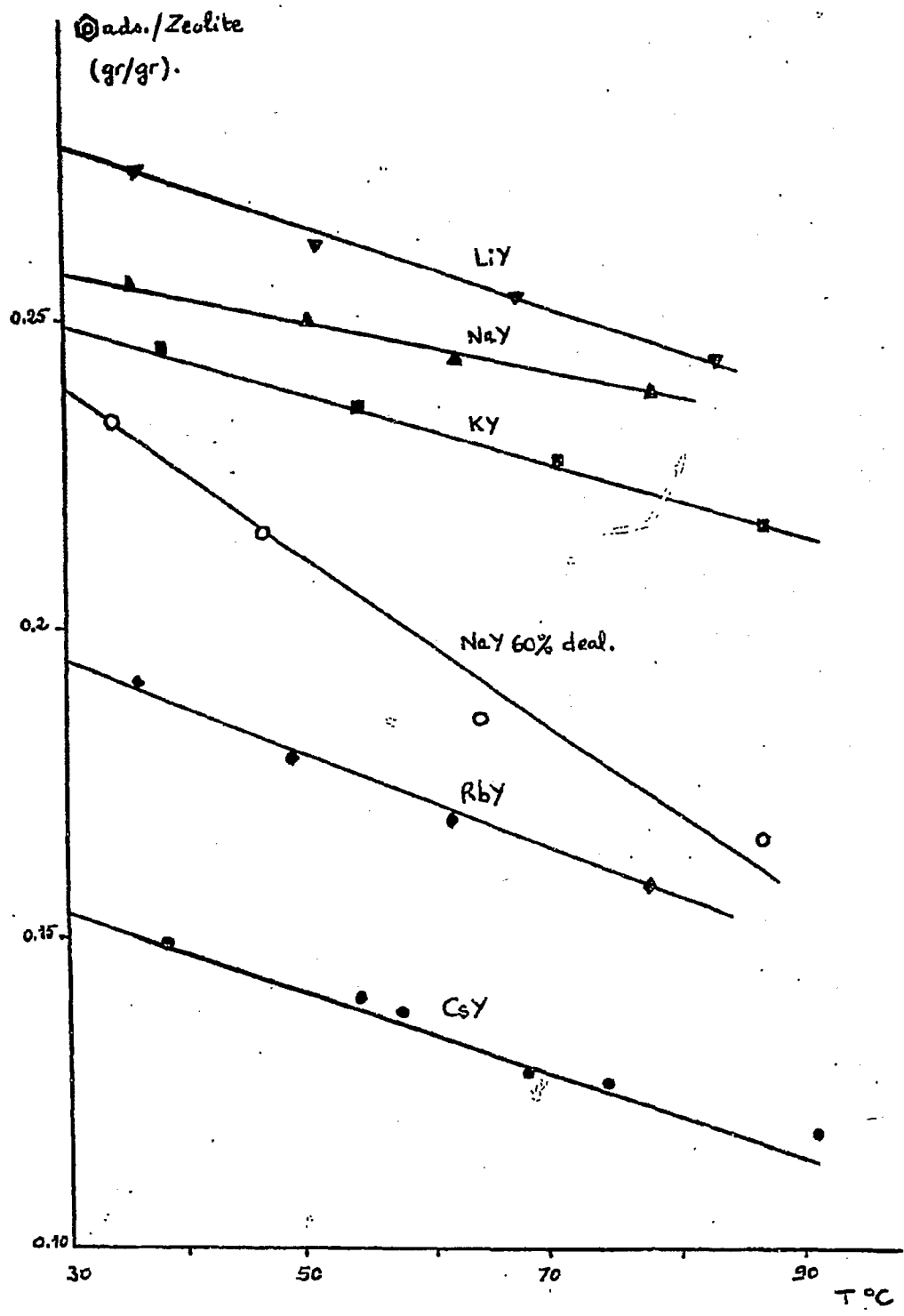
Fig. 2



1.0 Fig. 3







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