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PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL
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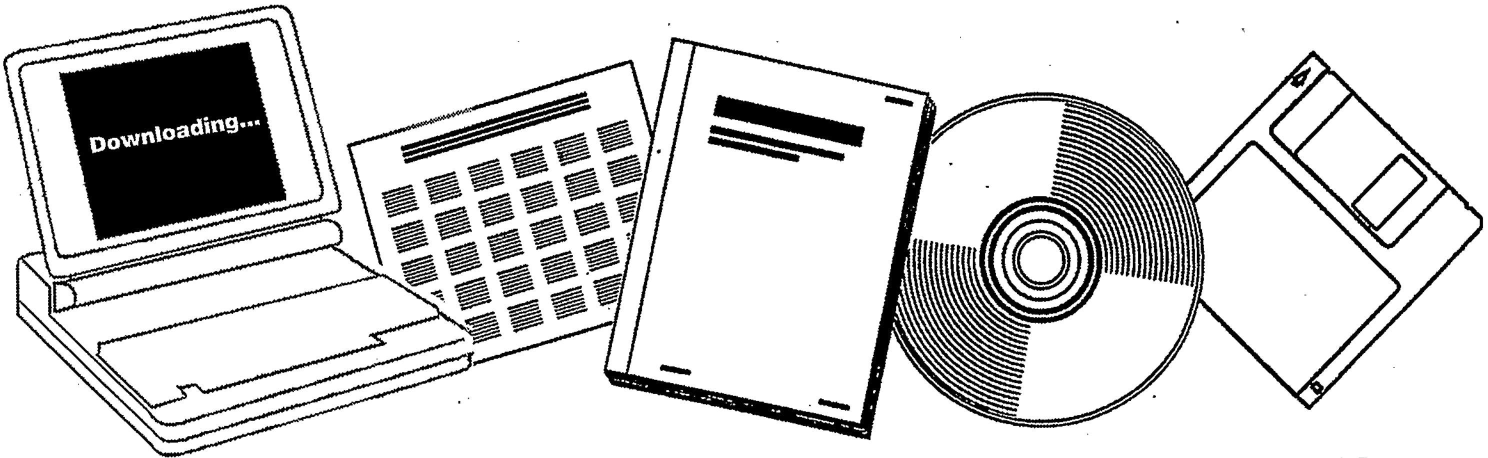

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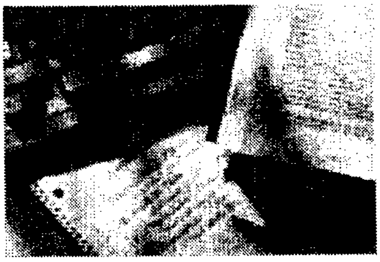

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CATION PROMOTION EFFECTS IN ZEOLITE-SUPPORTED F-T CATALYSTS

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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, H_2 chemisorption, carbon deposition, catalytic activity, chain growth probability, selectivity for CH_4, selectivity for olefins, and diffusion in the zeolite. Each of these items will be investigated for the catalysts proposed to be studied.

The main objectives of this study are:

1. To develop a better understanding of how neutralizing alkali cations in zeolites can affect F-T product selectivity over a supported metal
2. to illuminate the effect of these cations on

   a. chemisorption properties
   b. CO disproportionation
   c. the mechanism of CO hydrogenation
   d. the deactivation characteristics

3. to elaborate upon the effect of decreasing ionization potential of the alkali cations on the catalytic properties
4. To investigate the effects of Rb and Cs promotion, studied only superficially in the past.

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

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

II. SUMMARY OF PROGRESS

During this quarter, a series of alkali zeolites were prepared by partial exchange of NH_4Y and various alkali cations (Li^+, Na^+, Rb^+). These catalysts were characterized by atomic absorption and flame-emission spectroscopy. The concentration of NH_4^+ cations was determined by Kjeldahl analysis. The transformations of olefins (propylene and butene) over these catalysts were investigated under similar conditions as those used for CO hydrogenation over Y-zeolite supported Ru catalysts.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

1 - Catalyst Preparation and Characterization

Partially exchanged MHY zeolites (M = Li^+, Na^+, Rb^+) with similar acid site concentrations were prepared by ion-exchange of NH_4Y (strem chemicals) with the alkali nitrates (Alfa Products, ultrapure). In order to obtain the desired exchange levels of the alkali cations repeated contacts with dilute aqueous solutions of the alkali nitrate were used. The filtrates were analyzed each time by atomic absorption to determine the extent of ion-exchange. Finally the samples were washed several times with distilled water and then dried at 40°C for 48 hours.

A complete analysis of the dried samples was carried out using atomic absorption to determine the aluminum and alkali cation content of the zeolites. The sodium content was determined by flame-emission spectroscopy. A Kjeldahl analysis was used to determine the concentration of the residual NH_4^+ cation. The results of these analyses are given in Table 1. The acid site concentrations of the various MHY zeolite was about 55% of the exchangeable neutralizing cations.

2 - Reaction Studies

Experimental

The olefin (propylene and butene) reactions were carried out under similar conditions used previously for CO hydrogenation, i.e., in a continuous flow reactor operating at atmospheric pressure and 523 K. A pyrex reactor was used to eliminate the possible olefin reactions on the walls of a metallic reactor under the condition used in this study. The catalysts were first treated at 673 K for two hours under a hydrogen stream in order to decompose the ammonium cation and produce the protonic form zeolites, MHY (M = Li^+,Na^+, Rb^+). The reactor was then cooled down to reaction temperature (523 K). A flowrate of 100 ml/min of approximately 1% olefin in helium was used with a catalyst change of 0.1 g. Samples of the reactor outlet were analyzed by on-line gas chromatography after 5 minutes of reaction as during the CO hydrogenation experiments.

Since similar results were obtained whether hydrogen or helium was used as the diluting gas and since the main objective of this study was to investigate the acid-catalyzed reactions of olefins , helium was chosen to avoid any possible hydrogenation of the olefins on the thermocouple inserted in the reactor. Such reactions were found to be significant without the presence of a catalyst.

Results and Discussion

a. Propylene transformation

The catalytic activities for propylene reaction of the four zeolites used in this investigation are compared in Figure 1. The activities are expressed in moles of propylene converted per hour and per gram of catalyst. The selectivities obtained with each catalyst are listed in Table 1. Although the HY zeolite had a higher concentration of acid sites, its activity was much lower than that of LiHY. One may anticipate that because of the high concentration of acid sites and since acid-catalyzed reactions of hydrocarbons are always accompanied by carbon deposits, the deactivation rate of HY may be higher than on LiHY. However a study of the deactivation of these catalysts by varying the sampling time showed that the catalyst activities remained practically constant over the first 10 minutes of reaction and started to decrease from then onward. Thus, it may be suggested that the diluting effect of the lithium cations increases the acid strength of the remaining acid sites. However further studies are necessary to assess this effect of Li cations on the zeolite acidity.

Figure 1 shows also that the nature of the alkali cation has a significant effect on the zeolite activity for propylene reactions. The activity was markedly increased when Li^+ was the neutralizing cation. When Rb cations were present in the zeolite no activity for the propylene reactions was observed. In the products obtained from this reaction on HY, LiHY, and NaHY (Table 2) C_4, C_5 and C_6 hydrocarbons constitute more than 90% of the products in each group. The product distributions for these catalysts provide evidence that the olefin transformations proceed through an oligomerization-cracking mechanism coupled with hydrogen transfer leading to the formation of saturated hydrocarbons (1). Such reactions have been shown to be strongly dependent on the strength of the acid sites present in the zeolite (2). Furthermore, Datka (2) has also observed that the higher the strength of these acid sites, the more branched the oligomer intermediates, resulting in the formation of more isoparaffins. It may, thus, be concluded that the nature of the alkali cations present in the zeolite has a significant effect on the strength of the acid sites.

b. 1 - butene transformation

With 1-butene reaction on acidic zeolites two types of reactions may be distinguished: 1./ the oligomerization - cracking reactions of 1-butene leading to the formation of both lighter and heavier products as well as isobutane; 2./ the double bond and cis/trans isomerization. The first reactions follow the same mechanism as the propylene reactions and therefore are very much dependent on the strength of the acid sites in the zeolite. The cis/trans isomerization as well as double bond shift on the other hand proceed rapidly on week Bronsted acid sites.

The effect of the nature of the alkali cation present in the zeolite on the rate of each of these competing reaction is shown in Figure 2. The activities are expressed in moles of 1-butene converted per hour and per gram of catalyst. The product distributions obtained with the various catalysts are listed in Table 3. It may be noted that they are qualitatively similar to the product distributions obtained with propylene reactions, suggesting similar mechanisms to be operative for all olefin transformations on acid sites.

Considering separately the oligomerization - cracking activity (Figure 2), the same trend as in the case of propylene is observed with 1-butene. However the latter seems to be much more reactive than propylene. This may be due to its higher ability to form carbonium ions. As for the isomerization reactions (double bond shift and cis/trans isomerization), a reverse trend is observed, i.e., increasing activity from LiHY to RbHY. This is in contrast to results reported by Lombardo et al. (3) who showed that the activity was increased when Li^+ was substituted for Na^+ and decrease by K^+ substitution. However under the conditions used by these authors, only the isomerization reactions were taking place. Our results, in agreement with those of Dzwigaj et al., suggest that at least two types of acid sites may be involved in the double bond and cis/trans isomerization on the one hand and the oligomerization reactions on the other hand, accompanied by cracking and hydrogen transfer. The relative rates of the two types of reaction depends not on the overall concentration of acid sites but on the concentration of the strong acid sites. Since the isomerization reactions are much faster than the other reactions, a higher activity for isomerization is observed when all the sites are of the weak type, thus all available for this reaction as in the case of RbHY.

Figure 3 shows the C_4-isomer distribution obtained with the four catalysts. Except for the case of HY, the same trend of C_4-isomer distribution as a function of the neutralizing cations were found when CO hydrogenation was carried out over the RuY zeolites (4). The isobutane and butane concentrations may be taken as a measure of the oligomerization-cracking-hydrogen transfer reactions while the 2-butene concentrations represent a measure of the isomerization actitivty. The odd results obtained for HY, in spite of its higher concentration of acid sites cannot be fully explained at the present time. As noted in the previous section the exchange of only small amounts of alkali may increase the acid strength of the zeolite. Much higher concentrations of alkali cations are present in the case of RuY zeolites used in our study, so that such an effect was not observed.

This study establishes the importance of the secondary acid-catalyzed reactions of the primary olefinic products of CO hydrogenation over RuY zeolites in shaping the overall selectivities of these catalysts. It also provides strong evidence that the nature of the neutralizing alkali cations may have a significant effect on these reactions.

IV. FORECAST OF WORK

During the next quarter, a study of the possible phenomenon of hydrogen spillover and its effect on the possible olefin hydrogenation on the zeolite support will be carried out.

H_2 TPD experiments will be carried out to characterize the type of chemisorption of H_2 on Ru sites in order to establish the influence, via the effect on the zeolite acidity, of the nature of the neutralizing alkali cations on the Ru properties.

REFERENCES

1. Dzwigaj, S., Haber, J., and Romotowski, T., Zeolites, 4, 147 (1984).

2. Datka, Jr., in "Catalysis by Zeolites," (B. Imelik et al. Eds.), p. 121, Elsevier Sci. Publ. Co., Amsterdam, 1980.

3. Lombardo, E.A., Sill, G.A., and Hall, W.K., J. Catal. 22, 54 (1971).

4. Goodwin, J.G., Jr., and Oukaci, R., 9th Quarterly Report.

Table 1: Elemental Analysis Results

Catalyst	Na/Al	M/Al*	NH_4/Al
NH_4Y	0.20	--	0.76
$LiNH_4Y$	0.16	0.24	0.54
$NaNH_4Y$	0.43	--	0.51
$RbNH_4Y$	0.16	0.22	0.59

* M = Li, Rb

Table 2: Product Distribution from Propylene Reactions

Product	HY	LiHY	NaHY	RbHY
Propane	5.89	5.96	11.86	0
Isobutane	11.28	26.59	3.51	0
n-butane	0.16	0.17	0.00	0
1 butene + isobutene	13.90	9.75	19.91	0
trans-2-butene	8.18	7.16	14.64	0
cis-2-butene	4.91	4.40	8.78	0
Total C_5	25.76	23.31	21.96	0
Total C_6	29.93	22.66	19.3	0

Table 3: Product Distribution from 1-Butene Reactions

Product	HY	LiHY	NaHY	RbHY
Propane	0.07	0.0	0.0	0.0
Propylene	3.50	1.09	2.38	0.32
isobutane	12.01	24.97	5.91	0.26
n-butane	1.87	3.85	1.00	0.11
trans-2-butene	46.07	34.41	51.39	59.51
Cis-2-butene	28.92	20.33	32.37	38.20
Total C_5	2.79	7.19	4.77	1.46
Total C_6	4.76	8.16	2.17	0.14

FIGURE 1: Activity for Propylene Reactions

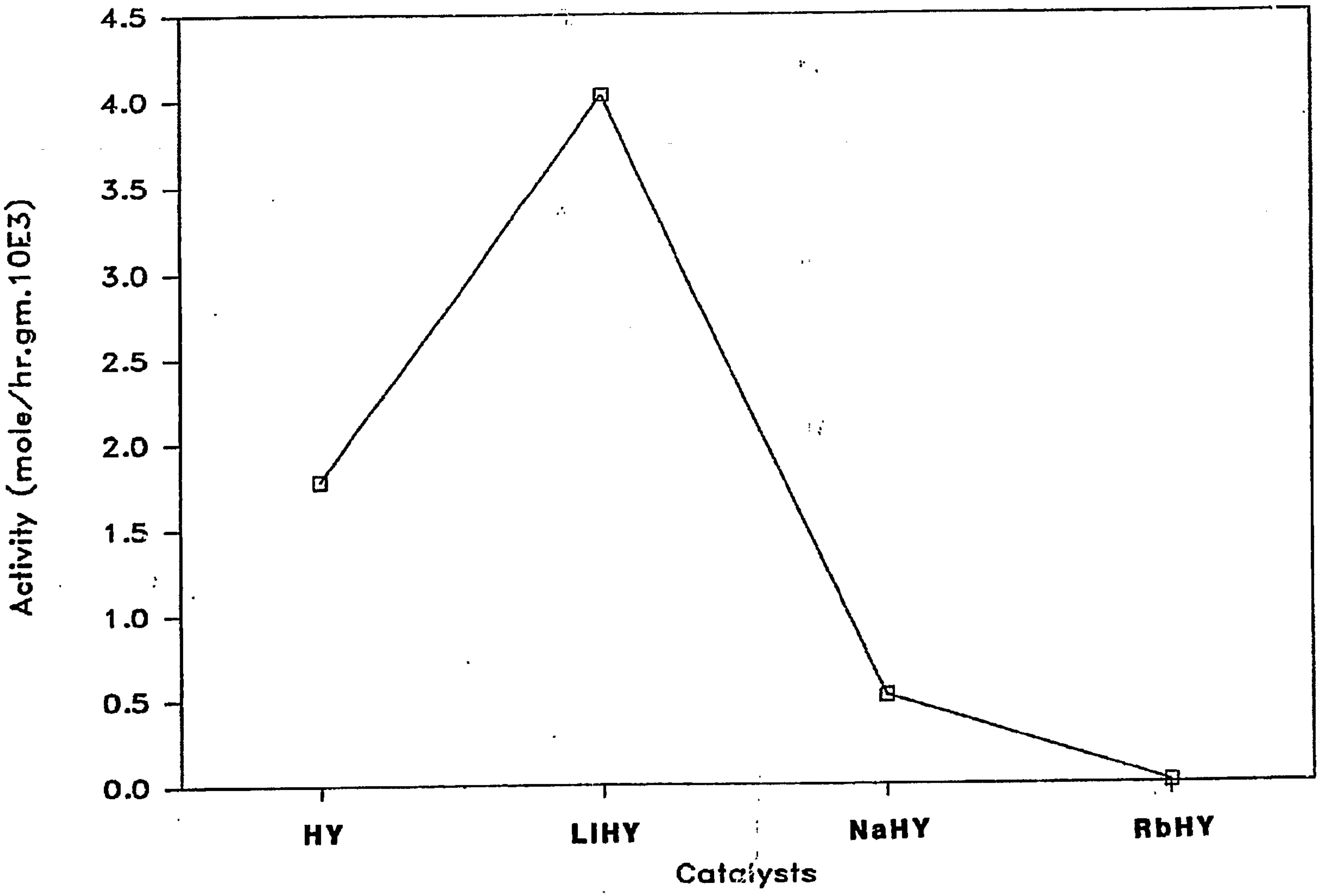


FIGURE 2: Activity for 1-Butene reactions

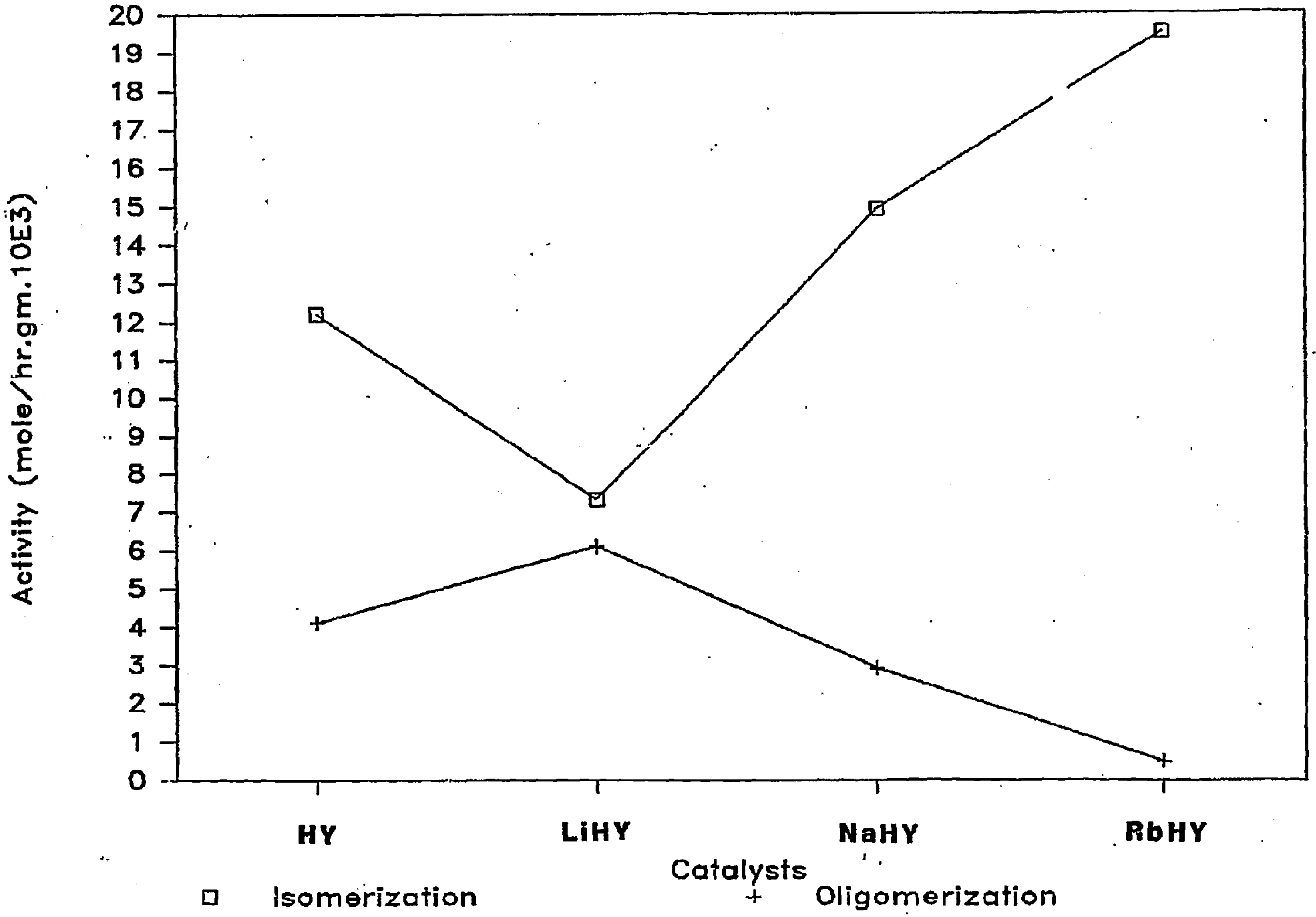
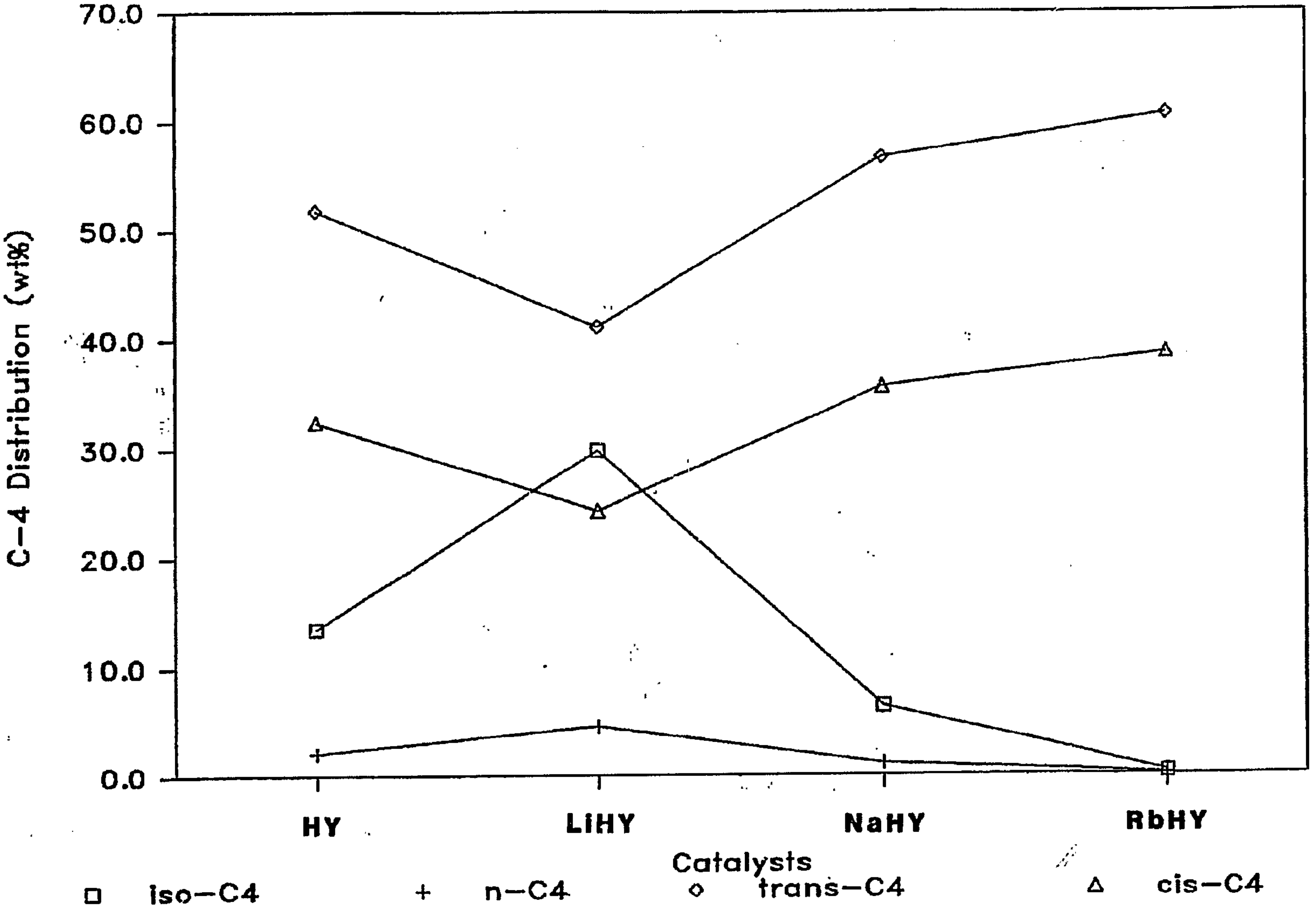


FIGURE 3: C−4 Product Distribution



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