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CATION PROMOTION EFFECTS IN ZEOLITE-SUPPORTED F-T CATALYSTS. 9TH QUARTERLY REPORT, SEPTEMBER-NOVEMBER 1985

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

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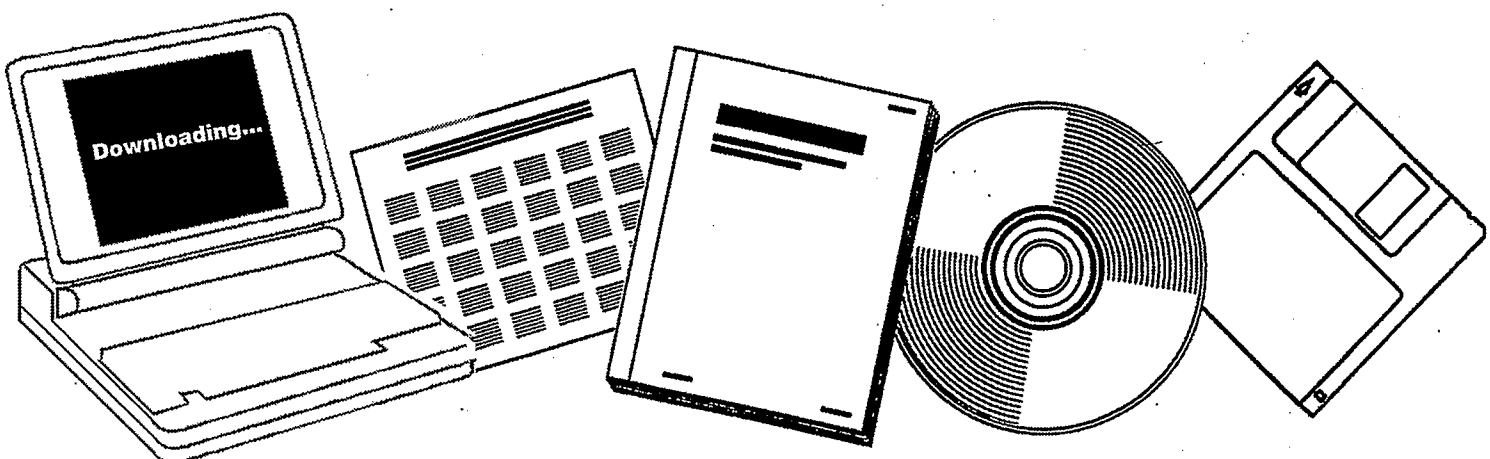

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CATION PROMOTION EFFECTS IN ZEOLITE-SUPPORTED F-T CATALYSTS

9th Quarterly Report
September 1985 - November 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, 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

The effect of zeolite acidity on the isomer distribution in the products of CO hydrogenation over ion-exchanged zeolite-supported Ru catalysts was investigated with various alkali cations (Li^+,Na^+,K^+,Rb^+,Cs^+). The transformation of olefins (propylene and butene),under similar conditions as those of CO hydrogenation, were also investigated in order to understand the effect of the various constituents of the support, i.e., the hydroxyl groups and the alkali cations, on the possible secondary reactions of the primary products of F-T synthesis.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Experimental: reaction studies

CO hydrogenation, at atmospheric pressure and in the 483-573 K temperature range, was carried out in a tubular microreactor with a 1:1 mixture of H_2 and CO flowing at 2.4 ℓ /h. The products were analyzed by gas chromatography after five miutes of reaction.This five minute reaction period was followed by a 40 minute hydrogen treatment of the catalyst in order to obtain reproducible results in successive runs. Details of the reaction procedure and product analysis have been reported in previous quartely reports.

In order to compare the isomerization and olefin hydrogenation activity of the various alkali-cation Y zeolites without ruthenium, but-1-ene isomerization and propylene hydrogenation were carried out as test reactions under similar conditions to those of CO hydrogenation, i.e., in a continuous flow reactor operating at atmospheric pressure and 523 K. The same reaction system was used. The catalysts were treated at 573 K for one hour under a hydrogen stream before cooling to reaction temperature. For the but-1-ene isomerization reaction a flowrate of 100 ml/min of 1% butene in hydrogen was used with a catalyst charge of about 0.1 g. As for propylene hydrogenation, a reaction mixture of $He:H_2:C_3H_6$ of 60:39:1 was used at the same flowrate with similar catalyst charges. Samples of the reactor outlet were analyzed on-line by gas chromotography after 5 minutes reactions as during the CO hydrogenation experiments. The GC column used in this study (SP-1700) permitted full analysis of the C_4-fraction in the hydrocarbon products. The only drawback of this column is that the separation of but-1-ene and isobutene could not be achieved. Although the C_5- and C_6- fractions were also able to be analyzed in

detail, the results were less accurate owing to the small quantities of these products. Only a global analysis of the C_5^- and C_6^- fractions is reported where appropriate.

Results and discussion

Olefin transformation over alkali cation Y zeolites (without Ru)

The catalytic activities for but-1-ene isomerization of some of the zeolites used in this investigation are compared under the reaction conditions outlined in the previous section. The activities are expressed in moles of but-1-ene converted per hour and per gram of catalyst. These activities together with the selectivities obtained with each catalyst are listed in Table 1. The selectivities for each reaction, double bond shift and cis-trans isomerization, are defined as the ratio of cis-but-2-ene to trans-but-2-ene, and the ratio of trans-but-2-ene to but-1-ene. The cis/trans ratios, however, do not represent the initial selectivities as they are usually defined in the literature. From this table, it can be seen that the cis/trans ratios remain practically unchanged with the nature of the neutralizing cation, approaching the equilibrium value. In Table 2 are listed the specific activities of the various zeolites for propylene hydrogenation. While with most alkali cation-type zeolites the propylene reacted mainly to form propane, with the hydrogen-type zeolite, the reaction of propylene gave a more complex product distribution which was found to be the same whether the reaction was carried out in the presence of hydrogen or in a helium atmosphere. From Table 2 it is seen that the alkali cation zeolites did not show appreciable catalytic activity for olefin hydrogenation. The relatively higher activity obtained for CsY might be due to the possible presence of impurities brought about by the cesium nitrate used in the preparation of this catalyst. The product

distribution obtained with HY resembles the one obtained when but-1-ene was reacted over the same catalyst. The product distributions obtained with both reactions are compared in Table 3. With but-1-ene transformation on HY, traces of methane and C_2- hydrocarbons were also detected, suggesting some cracking activity.

The isomerization of n-butene over zeolites, which can involve double bond shifts, cis-trans isomerization and skeletal isomerization are considered to involve a common intermediate, the secondary butyl carbonium ion (2,3). It has also been reported (2-4) that Group IA Y zeolites have very low activity for carbonium ion reactions. It has been suggested that the possible activity of these zeolites is due to the presence of divalent cations such as Ca^{2+} ions (2) which are normally found as impurities in these catalysts. Furthermore, partial decationization by simple washing with distilled water and possible replacement of the alkali cation by protons from the water was found to result in appreciable catalytic activity for the isomerization of olefins (4). Whatever the origin of the carboniogenic activity, the substitution of the Na^+ ions by other alkali cations was found to result in substantial effects on the acid catalyzed reactions. The activity was markedly increased when Na^+ was replaced by Li^+, while it decreased when it was exchanged by K^+, Rb^+, or Cs^+ (2,5). As can be seen in Table 1, the zeolites used in this study had a significant activity for the isomerization of butenes which was found also to increase with decreasing cation radius, suggesting an effect of the nature of the cation on the acid strength of the hydroxyl groups present in these zeolites. In this series of experiments, CsY did not exhibit a marked difference from Na Y in its ability to isomerize but-1-ene. However, it may be noted from Table 2 that CsY had also a suprisingly high activity for propylene hydrogenation while RbY and KY had no measurable activity for this reaction.

Thus, as pointed out above, the high activity of CsY can only be attributed to the presence of metal impurities such as iron. This would also explain its high activity for but-1-ene isomerization since reduction of metal ions during the hydrogen treatment would result in the formation of more acidic hydroxyl groups than would normally be expected in the zeolite. It may also be noted that when a more acidic zeolite such as HY is used, the isomerization of but-1-ene is accompanied by the formation of secondary products such as isobutane, and other saturated and olefinic hydrocarbon species of lower and higher carbon numbers. These are the products of various secondary rections such as oligomerization, polymerization, cracking, hydrogen transfer, etc., which are known to be favored with the more acidic catalysts.(6)

Propylene hydrogenation over the various alkali Y zeolites was carried out mainly to determine whether the support was active for this reaction and olefin hydrogenation in general. In the study of CO hydrogenation over Ru deposited in these zeolites, it was observed that the $C_3^= / C_3^-$ ratio increased with increasing cation radius and this behavior could not be correlated with any of the intrinsic catalytic properties of the metal. Furthermore, it has been suggested by other researchers that the alkali cations in the zeolite play an important role as adsorption centers for hydrocarbons and that the nature of the alkali cation may influence significantly the hydrocarbon adsorption properties of these zeolite (7). Topchieva et al (8) have suggested that the cations may exhibit significant activity for the hydrogenation of olefins when treated with hydrogen at high temperatures. However, in our experiments, we failed to observe any appreciable hydrogenation activity with most of the zeolites. KY and RbY were relatively inactive, while the higher activity of CsY can only be attributed to the presence of impurities. The activity displayed by NaY and LiY for this

reaction is believed to be insignificant to affect markedly the olefin/paraffin ratio under CO hydrogenation conditions. However, the transformation of propylene over HY zeolite in both hydrogen and helium atmospheres, like the transformation of but-1-ene over this zeolite (Table 3) led to the formation of normal- and iso-paraffins, even in the absence of hydrogen. These results provide strong evidence that the olefins may be hydrogenated via a hydrogen transfer mechanism on the acid sites. The presence of isobutane and isopentane suggests also that the formation of branched hydrocarbons may result from a breakdown of olefin oligomers formed on the acid sites followed by their hydrogenation by this hydrogen transfer mechanism. Furthermore, since independently of the nature of the reactant olefins similar product distributions were obtained, it can be concluded that common intermediates forming on the acid sites react to give such product distributions.

Similarly, Venuto et al. (9) have observed that when ethylene is passed over REX at 213 ^{o}C, low molecular weight gaseous paraffins are formed. Shepard, et al. (10) have reported that hydrogen transfer reactions occur over silica-alumina in propylene polymerization. The transformation of olefins over zeolites in general have been extensively investigated (11-16). From the various studies, it may be concluded that while isomerization of n-olefins (double bond shift and cis-trans isomerization) takes place readily on weak acid sites (Lewis or Bronsted sites), stronger acid site are required for the oligomerization reactions. Further reactions of the intermediate oligomer, such as disproportionation, paraffin formation via an intermolecular hydrogen transfer meachanism, often accompanied by the formation of polycyclic aromatic compounds and coke formation, and cracking reactions are also observed at higher temperatures or with still stronger acid sites. It appears from these

studies and our results that the nature of the reaction products is independent of the nature of the reactant olefin molecules but dependent only on the oligomer intermediates formed on the acid sites. A significant aspect of these studies is that these acid-catalyzed reactions provide a second mechanism for the hydrogenation of olefins other than the coventional metal-catalyzed hydrogenation. Furthermore, it was established that the isoparaffins are the breakdown products of the oligomer intermediate rather than skeletal isomerization products of the corresponding linear olefins since isobutane and isopentane are formed similarly whatever the reactant olefin. This is confirmed by Chevalier, et al. (17) who showed that the isomerization of n-butenes to isobutenes is a very slow reaction due to the fact that it involves the formation of a primary carbenium ion intermediate. As for the variations in isoparaffin selectivities, Datka (14) has also shown that the higher the concentration and strength of the acid sites present in the zeolite, the more branched the oligomer intermediate resulting in the formation of more isoparaffins. Thus, the yield of isoparaffins from the transformation of olefins on acid catalysts can be taken as a measure of the oligomerization, disproportionation, and hydrogen transfer activity of these catalysts.

Transformation of primary olefinic products from CO hydrogenation.

The olefin-to-paraffin ratio as represented by the propylene/propane ($C_3^=/C_3^-$) ratio and the C_4-isomer distribution are chosen here to analyze the transformation over the zeolite support of the primary olefinic products obtained from CO hydrogenation over the various ruthemium catalysts. In the previous quarterly report, the activities and overall selectivities of the various Ru/Y zeolites have been reported. Figure 1 shows the C_4-isomer distribution at 523 K obtained for the same catalysts. The selectivity for isobutane was found to decrease with increasing cation radius. Figure 1 shows

also that β-olefins constituted the major part of the C_4-olefins and their concentration varied in the reverse order to that of isobutane. However, only small variations in but-1-ene and n-butane were observed with increasing cation radius.

The results listed in Table 4 show that at 523 K RuHY gave 53% isobutane (based on the total amount of C_4). When this catalyst was exchanged after reduction with a dilute solution of K_2CO_3, in order to replace H^+ by K^+ the isobutane was no longer obtained and the $C_3^=/C_3^-$ ratio increased to 16.9. On the other hand, RuRbY yielded only very small small quantities of isobutane, but, when 0.2g of HY was added at the tail end of the reactor bed in a separate layer, the isobutane content of the C_4-fraction increased to 30%,and the $C_3^=/C_3^-$ ratio dropped from 6.4 to 4.1 (Table 4).

In the light of what has been established with the studies of olefin transformations on zeolite and in connection with the results shown in Table 4, it may be concluded that the hydrocarbon products of CO hydrogenation over supported ruthemium catalysts are mainly, if not totally, desorbed as olefins, probably α-olefins, which can then undergo secondary reactions on the acid sites or to a lesser extent hydrogenation on the metal sites. Indeed, in the case of RuHY, when all the protonic sites are replaced by K^+, the $C_3^=/C_3^-$ ratio increases from the low value of 2.6 to 16.9 for similar conversions (Table 4). The results obtained when the products of CO hydrogenation over RuRbY were passed through a layer of HY also provided strong evidence that the primary olefinic products can undergo subsequent isomerization, oligomerization, as well as hydrogenation, on the acid sites provided by the zeolite.

As shown in Figure 1, when CO hydrogenation was carried out over RuY zeolites exchanged with various neutralizing cations, the selectivity for

isobutane was found to decrease with increasing cation radius. When supports with very low acidity, SiO_2 or NaX, were used, no isobutane was detected. However, with the exception of RuHY, all the other zeolite-supported catalysts studied here are expected to have had the same number of acidic sites, since they all had similar metal loadings. Thus, the extent of the recations leading to isobutane is not just a function of the acid site concentration. So, the variation in acid strength with the nature of the alkali cations must be responsible for these variations in isobutane selectivity. It can also be seen in Figure 1 that the β-olefins decrease as the isoparaffins increase, thus pointing to competitive reaction paths for the transformation of the primary olefins depending on the acid strength of the zeolite.

It may also be observed that in most cases where isobutane was produced in large quantities, the isobutane/n-butane ratio was much in excess of the equilibrium value of 1.2 at the reaction temperature of 523 K (18). Okuda, et al. (19) have also reported isoparaffin/n-paraffin values in excess of the equilibrium values when F-T synthesis was carried out on zeolite-supported Ru-Pt catalysts. This reinforces the proposition that isoparaffins are formed mainly via disproportionation reactions of olefin oligomers formed on the acid sites, since a bifunctional path of acid catalyzed skeletal isomerization of n-olefins to iso-olefins and their subsequent hydrogenation on metal sites would be restricted by equilibrium.

IV. FORECAST OF WORK

During the next quarter, an investigation of the electrostatic field effect of the cations using cyclopropane hydrogenolysis as a test reaction will be completed. The preparation and characterization of a new series of Ru catalysts using dealuminated Y-zeolites will be carried out.

REFERENCES

1. Jacobs, P.A., in "Carboniogenic Activity of Zeolites,"p.88,Elsevier Sci. Publ. Co., Amsterdam (1977).

2. Lombardo, E.A., Sill, G.A., and Hall, W.K., J. Catal. 221971).

3. Lombardo, E.A., Sill, G.A., and Hall, W.K., Adv. Chem. Ser. 102, 346 (1971).

4. Abbot, J., and Wojciechowski, B.W., J. Catal.90, 270 (1984).

5. Yashima, T., Susuki, H., and Hara, N., J. Catal. 33, 486 (1974).

6. Guisnet, M., in "Catalysis by Acids and Bases," (B. Imelik et al. Eds.) p. 283, Elsevier Sci. Pub. Co., Amsterdam, 1985.

7. Barthomeuf, D., in "Catalysis by Zeolites," (B. Imelik et al. Eds.), p. 55, Elsevier Sci. Pub. Co., Amsterdam, 1980.

8. Topchieva, K.V., Zhdanov, S.P., Rosolovskaya, E.N., Shaknovskaya, O.L., and Samuelvich, N.N., Russ. J. Phys. Chem. 48, 1459 (1974).

9. Venuto, P.B., Hamilton, L.A., and Landis, P.S., J. Catal. 5, 484 (1966).

10. Shephard, F.E., Rooney, J.J., and Kemball, C., J. Catal. 1, 379 (1962).

11. Eberly, P.E., Jr., J. Phys. Chem. 71, 1717 (1967).

12. Weeks, T.J.,Jr., and Bolton, A.P., J. Chem. Soc., Farad. I, 70, 1676 (1974).

13. Weeks, T.J., Jr., Angel, C.L., Ladd, I.R., and Bolton, A.P., J. Catal. 33, (1974).

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

15. Bein, T., Plath, P.J., and Schulz-Ekloff, G., React. Kinet. Catal. Lett., 26,153 (1984).

16. Dzwigaj, S., Haber, J ., and Romotowski, T., Zeolites, 4,174 (1984).

17. Chevalier, F., Guisnet, M., and Maurel, R., Proc. Int. Congr. Catal. 6th, London, 1977, Vol. 1, p. 478.

18. Rossini, F.D., in "Physical Chemistry of Hydrocarbons," (A. Farkas, Ed.), Vol. 1, p. 363, Acad. Press, 1950.

19. Okuda, O., Tatsumi, T., Fujimoto, J., and Tominaga, H., Chem Soc. Japn., Chem. Lett., 1153 (1983).

Table 1
Activities and Selectivities of Y-Zeolites with Various Alkali Cations for But-1-ene Isomerization at 523 K

Catalyst	Activity (mole $h^{-1}g^{-1}x10^3$)	Trans-2-Butene / 1-Butene	Cis-2-Butene / Trans-2-Butene
CsY	15.3	0.58	0.80
RbY	4.7	0.15	0.65
NaY	15.5	0.60	0.72
LiY	19.7	1.04	0.75
HY	25.8	2.24	0.62
Equilibrium ratios*		3.37	0.59

*From Ref. (18).

Table 9: Activities of Y-Zeolites with Various Alkali Cations for Propylene Hydrogenation

Catalyst	Conversion (% C_3H_6)	Activity (mole $h^{-1}gx10^3$)
HY	37.4	16.4
LiY	1.1	0.71
NaY	0.4	0.25
KY	< 0.1	--
RbY	< 0.1	--
CsY	12.9	7.5

Table 3 : Product Distributions in Reactions of Propylene and 1-Butene over HY-zeolites at 523 K

Product	Selectivity (mole %)		
	1%C_3H_6 (in H_2+He)	1%C_3H_6 (in He)	1%C_4H_8 (in H_2)
C_1+ C_2	---	---	traces
Propane	12.3	12.2	0.2
Propylene	---	---	2.5
Isobutane	17.6	17.5	7.8
Butane	0.3	0.3	34.9
1-Butene	17.2	14.0	---
2-Butenes	12.5	10.0	48.6
Isopentane	13.2	13.2	2.7
C_5+C_6	26.9	32.7	3.2

Table 4: Effect of Acidity on Olefin Fraction and C_4-isomer Distribution from CO Hydrogenation at 523 K over RuY-Zeolites

Catalyst	C_4-isomer in C_4-products					
	$C_3^=/C_3^-$	iso-C_4^-	n-C_4^-	1-$C_4^=$	2-$C_4^=$	cis/trans
RuHY	1.1	53.0	17.1	8.7	21.2	0.62
RuHY(K)[a]	16.9	0	8.0	27.6	64.4	0.90
RuRbY	6.4	1.4	8.7	29.8	60.1	0.61
RuRbY+HY[b]	4.1	30.6	11.1	17.9	40.3	0.58

(a) RuHY treated in 0.1 N K_2CO_3 solution after reduction

(b) RuRbY and HY in separate layers

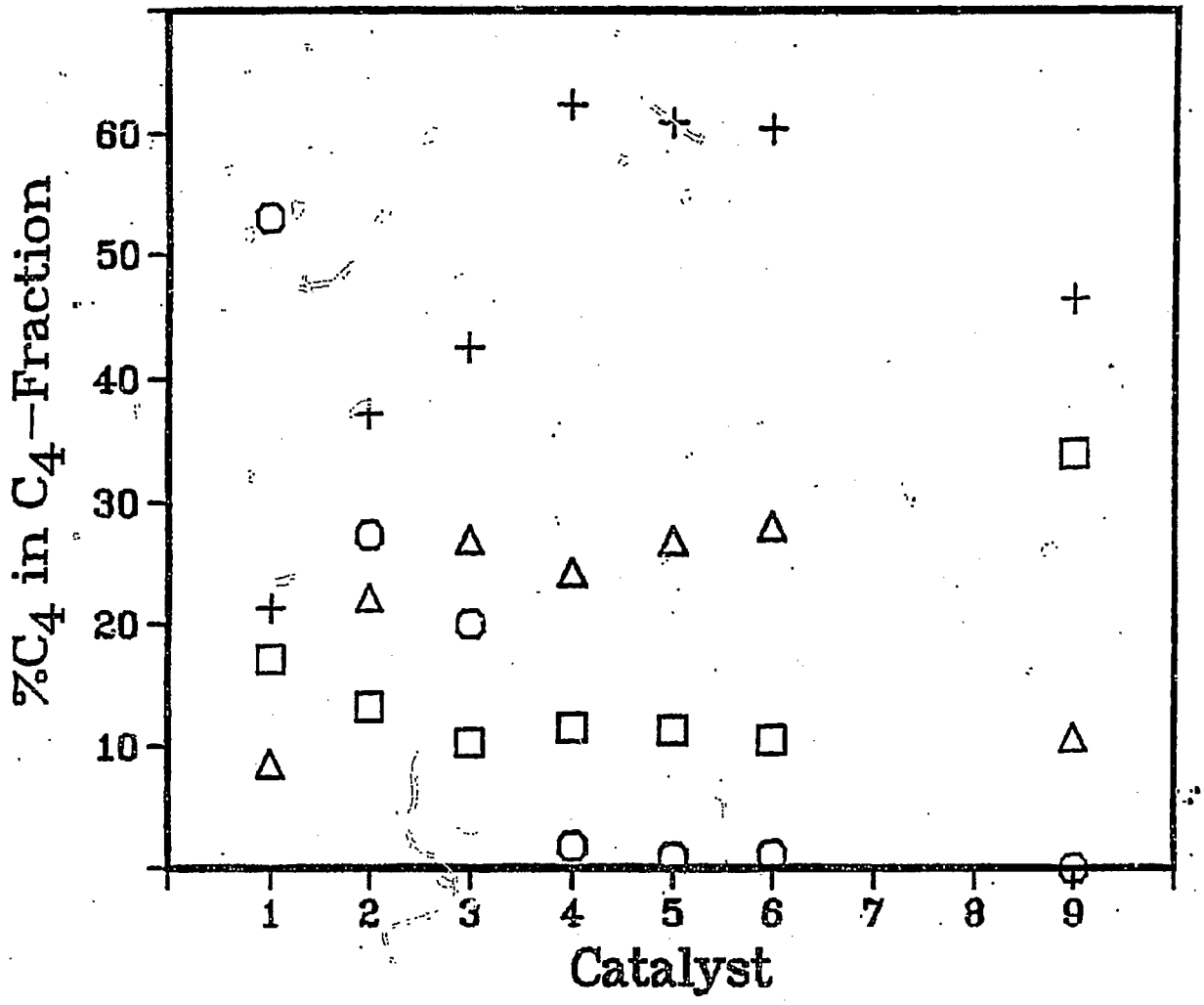
FIGURE CAPTIONS

Figure 1: C_4-isomer distribution at 523 K from CO hydrogenation over Ru-alkali cation zeolites

- ○ iso-butane
- + 2-butenes
- □ n-butane
- △ 1-butene

Catalysts: 1: RuHY, 2: RuLiY, 3: RuNaY
4: RuKY, 5: RuRbY, 6: RuCsY,
9: $RuSiO_2$

Figure 1. C_4– Isomer Distribution At 523 K



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