5.0 EFFECT OF GROUP IA CATIONS ON CO HYDROGENATION OVER RU/Y-ZEOLITES

5.1 Introduction

Earlier studies(20-21) have provided evidence that the adsorption stoichiometries and states of H_2 and CO on ruthenium can be significantly affected by the type of zeolite in which the metal is entrapped. Changes in activity and selectivity with the type of zeolite support have also been observed.(14-15,22) These changes have often been attributed to modifications of the electronic structure of the metal particles as a result of metal-support interactions. However, rather conflicting trends for these support effects have been repported.(8,22-23) In fact, this is not so surprising since, in addition to particle size effects, a large number of parameters may change the environment of the metal particles encaged in zeolites and hence their adsorption and catalytic properties. Some zeolite properties, such as acidity, depend on constituent atoms or ions of the zeolite framework.(94).

The present chapter discusses the results of an investigation of the influence of alkali neutralizing cations on CO hydrogenation over ion-exchanged zeolite-supported ruthenium catalysts.

5.2 Experimental

The series of Y-zeolite-supported Ru catalysts prepared by ion-exchange and decomposed under vacuum, and a silica-supported Ru sample were used for this study. The pretreatment and reduction conditions for these catalysts have been described in chapter 3 of this thesis and their characteristics from hydrogen and CO chemisorption are given in Tables 4.2 and 4.3.

Fischer-Tropsch synthesis was carried out at atmospheric pressure and 483-573 K using a 1:1 mixture of H_2/CO. Details of the reaction and product analysis procedures have been described in chapter 3.

5.3 Results and Discussion

5.3.1 Catalytic Activity

The turnover frequencies (TOF) for the various catalysts studied were calculated using the estimated site concentrations provided by hydrogen chemisorption measurements. Because of the possible suppression of hydrogen chemisorption on zeolite-supported catalysts prepared by ion-exchange, chemisorption measurements may not provide an exact measure of the metal dispersion and of the active ruthenium sites. Thus, the calculated TOF's based on hydrogen chemisorption and summarized in Table 5.1, should be considered as maximum values. Table 5.1 compares the TOF's at 523 K for CO conversion on the various catalysts. More detailed reaction data is given in Appendix B.

No significant effect of the nature fo the neutralizing alkali-cations on TOF was found, and the TOF's measured do not differ markedly from that of Ru/SiO_2. Having similar metal loadings, the concentration of the structural groups, formed during the reduction of the ruthenium ions in LiY, NaY, KY, RbY, and CsY, should be comparable in all these catalysts. This occurs since during ion-exchange, similar amounts of alkali cations, M^+ ($M^+ = Li^+$, Na^+, K^+, Rb^+, Cs^+) are replaced by Ru ions, as described in chapter 1. The reduction step leads then to the simultaneous formation of similar number of acid sites.

It is generally accepted that for alkali cation zeolites, exchange of sodium ions for smaller or larger cations produces a change in the electrostatic field inside the zeolite, and hence a change in the strength of their acid sites.(94-95) As shown in Table 5.2 adapted from reference (96), the larger the charge-to-radius ratio, the greater will be the electrostatic field, hence the stronger the acidity. Considering the results in Table 5.1 then, for monovalent cations such as Li^+, Na^+, K^+, Rb^+, and Cs^+, either the variation in the acidity of the zeolites remain too small to produce significant differences in the activity of supported Ru or, as will be discussed latter, the

Table 5.1 Catalytic Properties of Ru Catalysts at 523 K

Catalyst	CO conversion (%)	TOF ($s^{-1}x10^3$)	E_a (kJ/mol)
RuHY	8.3	40.5	74.5
RuLiY	3.4	10.7	67.3
RuNaY	3.1	6.9	66.1
RuKY	2.3	8.0	80.7
RuRbY	4.4	14.1	100.6
RuCsY	4.5	12.4	100.1
$RuSiO_2$	1.5	8.8	99.7

Table 5.2 Physical Parameters for the Various Cationic Y-Zeolites*

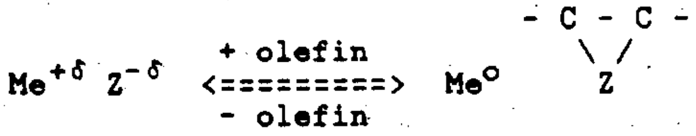
Zeolite	Ionic Radius (Å)	Electrostatic Field (V/Å)	Electrostatic Potential ($Å^{-1}$)
LiY	0.6	2.1	1.67
NaY	0.95	1.3	1.05
KY	1.33	1.0	0.75
RbY	1.48	0.8	0.67
CsY	1.69	0.6	0.59

* From Ref. (96)

olefinic products may "neutralize" the acid sites, rendering them ineffective for electronic interactions with the metal particles. However, the TOF obtained for RuHY is four-times greater than that for the other catalysts. This high activity of RuHY cannot be attributed only to an over estimation of metal particle size calculated from H_2 chemisorption. Assuming a similar dispersion to that for RuNaY, the TOF for RuHY still remains greater by at least a factor of 2. A possible metal-support interaction which increases the TOF of CO conversion on Ru sites in HY zeolite could be suggested.

Several workers have observed a similar trend of increasing activity for CO hydrogenation with increasing acidity of the support. Fajula et al.(73) found a higher activity for methanation on PdHY than on PdNaY catalysts. They suggested a participation of acid sites of the support in CO hydrogenation. Similarly, Arai(54) found that the activity for F-T reactions was higher for RhHY than for RhNaY. Vannice(55) has also suggested that increasing the acidity of the support produces an increase in methanation activity of palladium. Leith(23) reported that, when sodium ions in Y-zeolites were exchanged by multivalent cations or protons, a two-to-three fold increase in the specific activity of Ru resulted.

In all the works reviewed above, the enhancement of the activity of the metal, be it Pd, Rh, or Ru, in more acidic zeolites was attributed to an increase in the surface concentration of less strongly bound carbon monoxide species, resulting from an electron deficient character of the supported metal which increased with the acidity of the support. Several research groups have examined the infrared spectra of CO adsorbed on Pd(50), Rh(54), and Ru(20) catalysts and found evidence that an increase in strength of the support acidity produces a shift to higher frequency and an enhancement of bands assigned to linearly adsorbed CO. It has been suggested that the presence of electron acceptor sites on the support, i.e. the acidic hydroxyl groups, produces some electron depletion at the metallic surface and hence a decrease in the availability of d-electrons for back donation. These results are consistent with the suggestions by Vannice(26) and Okuhara et al.(97) that a weakening of the metal-carbon monoxide bond, paralleled by an increase in hydrogen adsorption, results in a higher activity for CO hydrogenation. However, such an interpretation for these results may be doubtful when one considers that the electron deficient character of the metal particles would also result in significant suppression of hydrogen chemisorption (18). In addition, Romannikov et al.(98), based on IR studies of co-adsorption of CO and 1-hexene,have suggested that in the presence of electron-donating molecules such as olefins, the electron-deficient character of the metal particles may disappear as a result of interactions of the olefin molecules with the electron-acceptor sites of the zeolite, i.e., the acidic sites. As olefins are one of the major primary products of CO hydrogenation, they would act to "neutralize" the acid sites of the zeolite, thus interrupting the interaction of these acid centers with the metal particles according to the scheme:



$$Me^{+\delta}\ Z^{-\delta}\ \underset{-\ \text{olefin}}{\overset{+\ \text{olefin}}{\Longleftrightarrow}}\ Me^{0}\quad \overset{-\,C\,-\,C\,-}{\overset{\backslash\ /}{Z}}$$

Thus, if such a mechanism is indeed operative, one must be cautious in trying to correlate the catalytic properties of a supported metal with IR results for CO adsorption alone. Such a phenomenon of adsorption "neutralization" would also explain why no effect of the nature of the neutralizing alkali cation on TOF was observed, even though these cations produce variations in the acid strength of the protonic sites, detected by the secondary acid-catalyzed reactions.

As for the higher activity observed for RuHY in CO hydrogenation, another interpretation may be proposed. It has been shown(45) that when Fischer-Tropsch reaction is carried out on a composite catalyst consisting of a physical mixture of CO hydrogenation component and an acid component (a zeolite), CO conversion is increased. This synergistic effect is provided by the presence of the acid sites of the zeolite which remove reaction intermediates formed on the F-T component by converting them to new species inert for further readsorption and chain growth on the metal sites. Thus, for RuHY, because of its higher concentration and strength of acid sites, the same "drainoff" mechanism must be in effect, resulting in the higher overall activity of this catalyst. However, this increase in activity is probably due in large part to the fact that the Ru particles were significantly larger in this catalyst. It is well known that TOF increases dramatically with Ru particle size in the range 1-4 nm.(14)

The apparent activation energy for CO conversion, E_a, varied with the neutralizing cation (Table 5.1). While the values of E_a for RuRbY and RuCsY were equal to that for Ru/SiO_2 and are comparable to common values in the literature, the values for the other zeolite-supported catalysts were significantly lower. Values as low as 66 KJ/mol suggest some possible mass transport limitations. An explanation can be offered to the cause of this variation in E_a. Figure 5.1 shows a plot of E_a versus the crystal ionic radius of the initial charge balancing cations of the zeolites used for catalyst preparation. Since the Ru exchange to give ca. 3 wt% is not the maximum exchange possible and the exchanging solution becomes depleted in Ru, it is suggested that Ru is initially more uniformly distributed throughout the zeolite crystallites for the small cation zeolites. Because of the limitations on the diffusion of $[Ru(NH_3)_6]^{3+}$ in the larger cation zeolites, Ru is probably less uniformly distributed and ion-exchanges preferentially in the external shell of the zeolite crystallites. This difference in distribution of the Ru, if true, would not seem to affect the % dispersion of the reduced metal but would affect the activation energy of reaction by introducing diffusion limitations on reactants and products for the zeolite catalysts having smaller neutralizing cations. E_a for RuHY is plotted versus the crystal ionic radius of NH_4^+ (1.43 Å), since Ru was initially exchanged with NH_4Y, and does not fall squarely on the relatively smooth curve through the results for the alkali zeolites. This is probably due to the fact that NH_4Y is fairly easy to decompose and possibly contained a mixture of H^+ and NH_4^+ neutralizing cations at the time of Ru exchange. This conclusion about possible diffusion limitations during reaction in RuHY, RuLiY, RuNaY, and RuKY is further confirmed by the non-linearity of the Arrhenius plots for these catalysts above 523K (see Appendix C for the various Arrhenius plots).

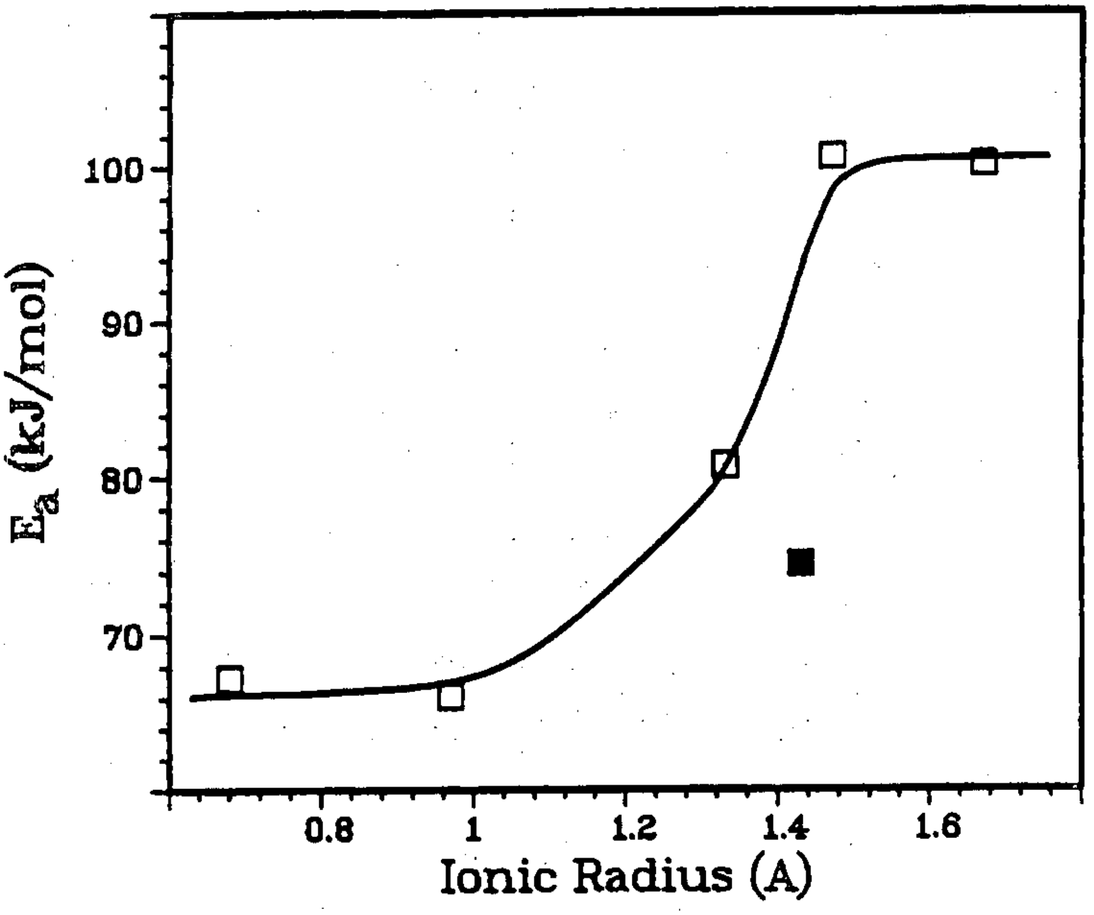


Figure 5.1 Variations in E_a with neutralizing cation radius; (■) RuHY

5.3.2 Methane Selectivity and Chain Growth Probability

The term selectivity used in the present paper refers to the weight percent of the total CO reacted which was converted into a given hydrocarbon or group of hydrocarbons. Table 5.3 compares the hydrocarbon product distributions obtained at 523 K on the various catalysts, and figure 5.2 gives the selectivity for CH_4 as a function of reaction temperature. The product selectivity shift towards lower molecular weight hydrocarbons, especially methane, with increasing temperature is consistent with the behavior of classical Fischer-tropsch catalysts and reflects the thermodynamics of the system.

It is seen that, for the different Y-zeolite-supported Ru catalysts, the selectivity for CH_4 formation and the chain growth probability at 523 K were essentially the same regardless of the nature of the neutralizing alkali cations. Moreover, use of protons to neutralize the AlO_4^- groups of the zeolite did not seem to produce any significant change in CH_4 selectivity or chain growth probability. Therefore, a fundamental difference exists between the influence of alkali cations when used as neutralizing cations in a zeolite framework and their effect when added as promoters. In the latter case, it has been repeatedly shown(6,34) that alkali promoters cause a shift to higher hydrocarbons at the expense of methane formation. Consequently, it may be

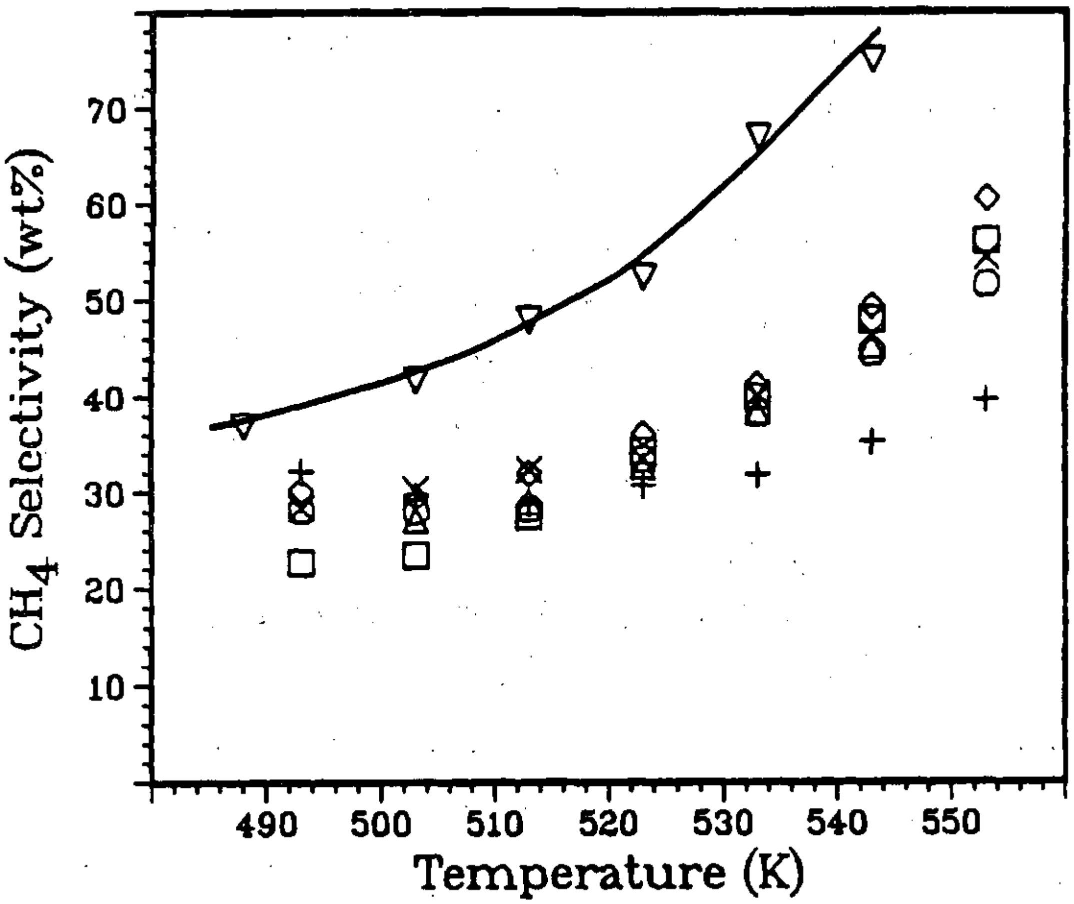


Figure 5.2 Methane Selectivity vs Temperature

(□) RuHY, (○) RuLiY, (△) RuNaY,
(+) RuKY, (×) RuRbY, (◇) RuCsY,
(▽) Ru/SiO$_2$

Table 5.3 Product Distribution at 523 K

Catalyst	Selectivity (wt%)					
	C_1	C_2	C_3	C_4	C_5	C_6
RuHY	34.3	13.7	19.1	17.1	12.5	3.5
RuLiY	33.4	14.3	21.8	17.6	11.8	1.1
RuNaY	32.7	14.0	21.5	17.0	10.9	3.9
RuKY	30.7	13.7	23.5	15.8	11.0	5.2
RuRbY	33.5	14.4	22.0	15.3	9.7	5.1
RuCsY	36.1	13.2	21.6	15.1	9.8	4.2

concluded that neither the nature of the group IA cations (H^+, Li^+, Na^+, K^+, Rb^+, Cs^+) nor the total acidity has a substantial effect on chain growth, at least at atmospheric pressure. There are some more pronounced differences at higher reaction temperatures; however, no cation effect appears to be indicated.

In studying CO hydrogenation over a series of Ru/zeolites, Jacobs et al.(22) reported that under typical Fischer-Tropsch conditions ($H_2/CO = 1/1$, GHSV = 1800 hr^{-1}, T ~ 523 K), RuNaX gave a higher selectivity for higher hydrocarbons than RuNaY did. This behavior was explained on the basis of a stronger metal-support interaction in the case of RuNaY due the fact that NaY is more acidic than NaX. However, in the present work, RuHY and RuNaY exhibited the same selectivity for CH_4 despite the higher acidity (greater number of acid sites) of the former catalyst. Therefore, our results cannot be fully explained in the same terms as those employed in reference (22). The possible linkage between CH_4 formation and the acidity of the support, however, cannot be totally ruled out. Indeed, the correlation between the selectivity for methane and Si/Al ratio of the support(15) suggests that the relative amount of CH_4 formed is connected to the acid strength of the support rather than the total acidity. Indeed, Barthomeuf(87) has reported an excellent correlation between the acid strength of a series of zeolites and their Si/Al ratios. In addition, another important factor was stressed by this author: the nature of alkali cations as well as the partial or total decationization (replacement of the alkali cations by H^+) of a given zeolite induces a much less pronounced change in the acid strength than that brought about by a variation in Al content. This should explain why all the ion-exchange RuY zeolites gave almost the same selectivity for CH_4 and the same chain growth probability (a = 0.5) regardless of the neutralizing cations.

4.3.3 Olefin Fraction

The C_3-fraction was selected for comparing the olefinic fractions yielded by the various catalysts, because, as expected(8,22), the C_2 fraction was mainly paraffinic and the olefin fractions of hydrocarbons having more than three carbon atoms were complicated by possible secondary isomerization reactions.

In order to compare the ability of these catalysts to produce unsaturated hydrocarbons, the following question must be addressed: under which experimental conditions should the comparison be made? Previous workers have considered several situations. King(8) insisted mainly on constant CO conversion. Using as many as 16 supported Ru catalysts and despite some scatter in experimental data, he reported a unique inverse correlation between CO conversion and $C_3^{=}/C_3^{-}$ ratio. Only very few samples did not fit the correlation. Kikuchi et al.(10) reported two different plots of $C_3^{=}/C_3^{-}$ vs CO conversion for Ru/Al_2O_3 and Ru/V_2O_3. However, the data obtained with Ru on other supports does not fit either correlation. McClory and Gonzalez,(11) using Ru/SiO_2 with various promoters, reported three types of comparisons where one of the following parameters was kept constant: temperature, CO conversion, or turnover number of CH_4 formation. They found that the first kind of comparisons leads to larger differences between the catalysts. Morris et al.(9) varied the space velocity such that a constant conversion (10%) could be achieved at a given temperature (493 K). In the present work, the comparison was carried out both at constant temperature (523 K) and at constant CO conversion.

The nature of the neutralizing cations in Y-zeolites was found to have a strong influence on the olefin-to-paraffin ratio ($C_3^{=}/C_3^{-}$), regardless of whether the comparison was made at constant temperature (Figure 5.3) or constant CO conversion (Table 5.4). Whether at constant temperature or conversion, the $C_3^{=}/C_3^{-}$ ratio was highest where the larger alkali cations had been exchanged into the zeolite and followed more or less the sequence Cs ~ Rb > K > Na > Li ~ H. The variation in the amount of isobutane in the C_4-fraction is included in Figure 5.3 and Table 5.4 as this reflects the secondary acid-catalyzed reactions which

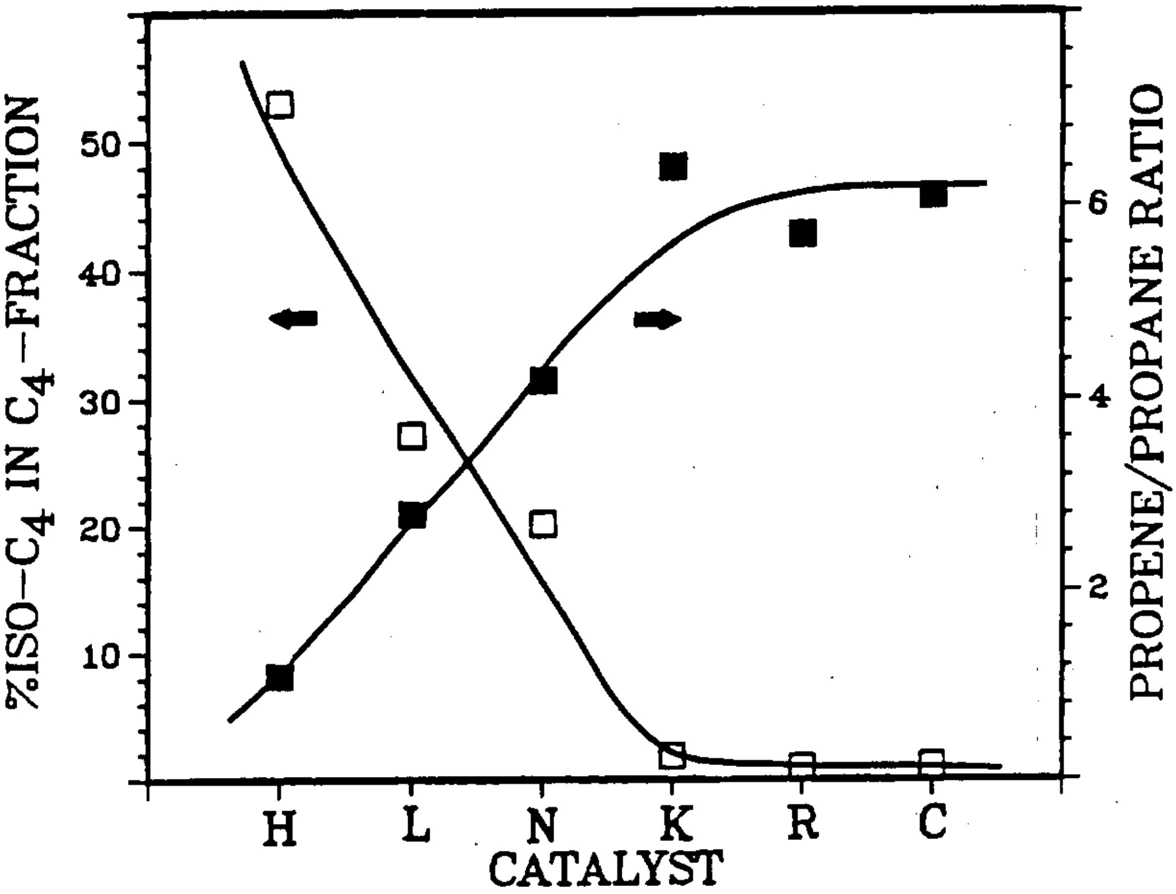


Figure 5.3 Effect of neutralizing cation on olefin and isobutane formation; Catalysts: (H) RuHY, (L) RuLiY, (N) RuNaY, (K) RuKY, (R) RuRbY, (C) RuCsY.

Table 5.4 Cation Effect on Selectivity at Constant CO Conversion (~ 4.5%)

Catalyst	T (K)	C_1 (wt%)	$C_3^=/C_3^-$	i-C_4 (%)*
RuHY	503	23.4	2.3	58.2
RuLiY	533	38.3	2.0	23.5
RuNaY	533	38.4	2.9	16.2
RuKY	543	35.3	4.2	2.1
RuRbY	523	33.5	5.7	0.9
RuCsY	523	36.1	6.1	1.1

* % isobutane in total C_4-fraction.

were enhanced in the order: Cs ~ Rb < K << Na < Li << H. These results indicate that the major primary hydrocarbon products formed under the reaction conditions described above were olefins which could undergo either direct secondary hydrogenation on metal sites or secondary acid catalyzed reactions. Furthermore, the nature of the alkali cations in the zeolite was found to have a considerable effect only on these secondary reactions, since the activity and chain growth probability remained practically constant whatever the nature of these cations.

Leith(56) has also observed that the olefin selectivity of zeolite-supported ruthenium in the hydrogenation of carbon monoxide is enhanced when potassium and cesium are exchanged into Y-zeolites. He interpreted his findings in term of a lowering of the hydrogenation activity of the metal as a result of a decrease in the electron-deficient character of the metal particles brought about by the introduction of larger alkali cations into the support. However, this interpretation cannot fully account for these results, since, if the electron deficient character of the metal varied with the nature of the alkali cation, one would also anticipate an effect on both activity and chain growth probability. Except for RuHY which had a higher activity, no such effect was observed. Thus, one must look to other parameters which might possibly affect the olefin selectivity through changes in the nature of the alkali cation.

Ru particle size effects can certainly be ruled out completely since the hydrogen and carbon monoxide chemisorption results show that the dispersions of all the catalysts used in this study were similar, on the order of 50 to 60%. Furthermore, Kellner and Bell(99) have shown that the ratio $C_3^=/C_3^-$ is not dependent on particle size for dispersions below about 70%.

It has also been suggested(100-101) that the hydrogenation activity of zeolite-supported metals may be enhanced under the action of the electrostatic field inside the zeolite acting directly on the reacting molecules rather than on the metal. As can be seen in Table 5.2, the difference in electrostatic field between LiY- and NaY-zeolites is much more important than between NaY and any other alkali Y-zeolite. Thus, if the electrostatic field were to have a major effect on the secondary reactions, one would expect to see a much more significant difference in olefin selectivities between RuLiY and RuNaY and a less pronounced difference between RuNaY and the catalysts containing the larger alkali cations. However, this was not the case, since RuHY, RuLiY and RuNaY had almost the same selectivity for olefins, and the $C_3^=/C_3^-$ ratios were two to three times higher for RuKY, RuRbY and RuCsY. As pointed out previously, the polarizing power of the cations or the electrostatic field generated by them may have an effect on the strength of the Brønsted acid sites which would increase with decreasing cation radius.(95) Although the variations in the strength of these acid sites with the nature of the cation are not significant enough to produce an electronic effect on the metal particles, they still may play an important role in the acid-catalyzed reactions. Thus, if the primary products of CO hydrogenation desorb mainly as olefins, as the results in table 7 seem to indicate, these olefins may readsorb on metal sites to be further hydrogenated to paraffins. The rate of this reaction would remain unaffected by the nature of the alkali cations if the electronic structure of the metal particles is itself unchanged by the latter.

Olefins may also adsorb on the acid sites and undergo carbonium ion-type reactions. The most important proton-catalyzed reactions of olefins are isomerization, oligomerization, polymerization, disproportionation, paraffin formation via hydrogen transfer, cracking, and coke formation. The rate of these reactions are influenced by the concentration and the acid strength of the hydroxyl groups present in the zeolite.(66,102) Thus, the decrease of the olefin-to-paraffin ratio with decreasing cation radius, paralleled by an increasing acidity strength, may be partly explained by a second olefin hydrogenation mechanism, i.e., the enhancement of hydrogen transfer reactions catalyzed by acid sites. Formation of paraffins by similar hydrogen transfer reactions have been observed in propylene polymerization over silica-alumina(103) and various olefin reactions on zeolites.(102,104-106) These studies of acid-catalyzed olefin reactions have demonstrated that the interaction of the acidic hydroxyl groups with the adsorbed olefins is accompanied by olefin oligomerization. At temperatures higher than 370 K, the olefin oligomers decompose by a disproportionation mechanism to produce gaseous paraffins and some polyene species which remain on the zeolite.(102) The gaseous paraffins produced from this oligomer decomposition are rich in isobutane and isopentane.

However, it is doubtful that the decrease in the $C_3^=/C_3^-$ ratio with decreasing cation radius can be accounted for completely by an enhancement of the hydrogen transfer reactions as well as the disproportionation reactions of olefins with increasing support acidity. Otherwise, one would expect the hydrocarbon distribution with carbon number to be more different for RuHY, RuLiY, and RuNaY than for RuRbY and RuCsY. In addition, even though RuHY has a much larger concentration of acid sites than the other catalysts, it did not produce a $C_3^=/C_3^-$ ratio that was significantly out of line.

An important effect of mass transport limitations on the $C_3^=/C_3^-$ ratios due to a uniform versus shell distribution of Ru in the zeolite cannot be ruled out . The value of the activation energy can be used as an inverse measure of diffusion resistance during reaction. Figure 5.4 shows a plot of the $C_3^=/C_3^-$ ratio versus E_a for the zeolite supported catalysts at constant conversion. This plot suggests a significant effect of diffusion on this ratio. Since hydrogenation of olefins is easy even during CO hydrogenation, the increase in residence time of olefins following their formation results in an increased probability for readsorption on the metal sites and hydrogenation. However, this interpretation is still not sufficient to explain the decrease of $C_3^=/C_3^-$ ratio with cation radius, since it has also been shown (see next chapter) that when all the protonic sites are replaced by K^+ in RuHY, the $C_3^=/C_3^-$ ratio increases from a low value of 2.6 to 16.9 for similar conversions. Such a result points again to the participation of acid sites in olefin hydrogenation.

It is thus suggested that, in addition to secondary hydrogenation on metal sites, the primary olefinic products may be hydrogenated significantly on the acid centers, the hydrogen being supplied not only by hydrogen transfer from adsorbed olefins but also by hydrogen spillover from the metal to the support.

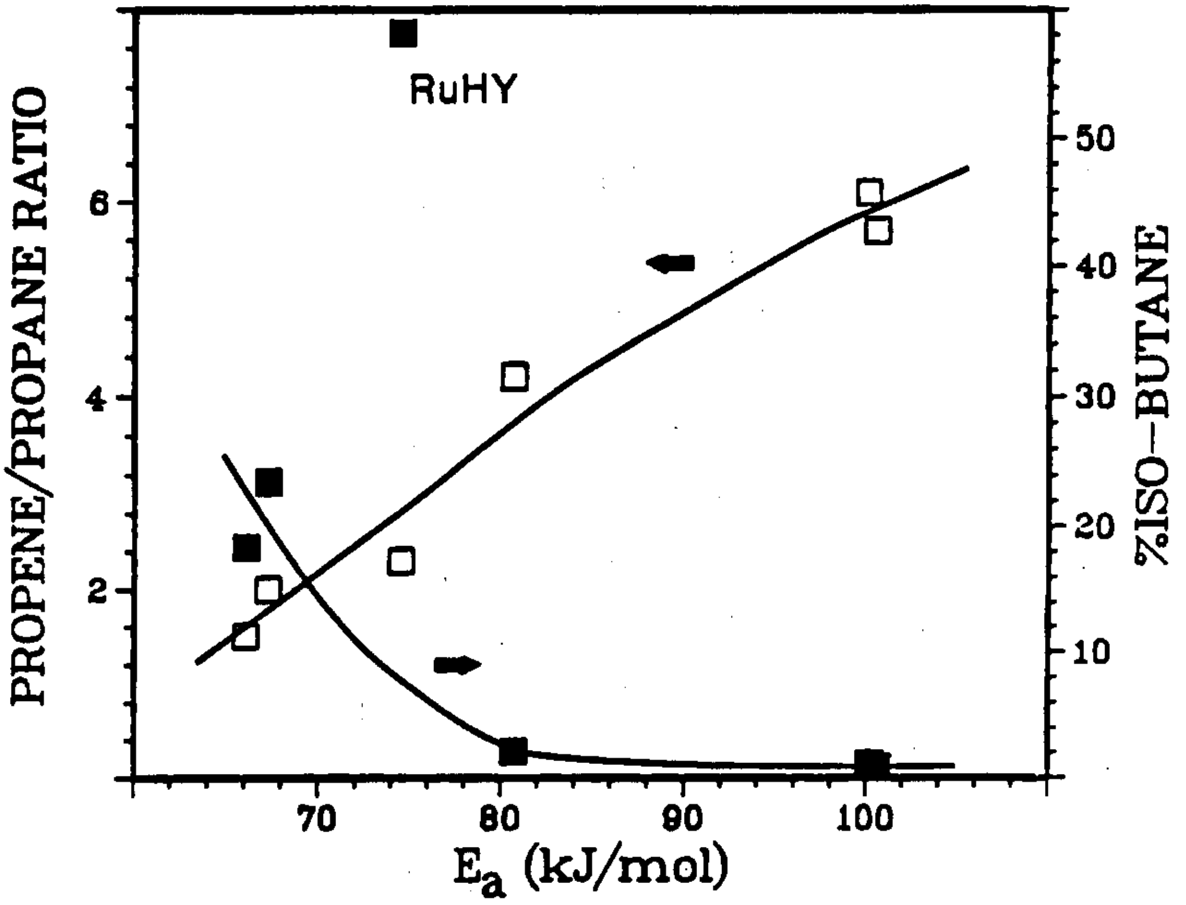


Figure 5.4 Variation of $C_3^=/C_3^-$ Ratio and i-C_4-fraction With E_a at Constant Conversion