

6.3.3 Olefin Reactions over Partially-Exchanged HY-Zeolite

When zeolite-supported Ru catalysts are prepared by ion-exchange of Ru with alkali zeolites, the subsequent decomposition and reduction of the precursor leads to the formation of three Brønsted acid sites for each metal atom involved. Since only these Brønsted acid sites appear to be involved in the transformations of the primary olefinic products of CO hydrogenation, an indirect effect of the nature of the remaining alkali cations on these olefin reactions can be best investigated with a set of partially exchanged alkali Y-zeolites having similar concentrations of Brønsted acid sites but no metal sites. Such acid-site containing alkali zeolites were found to exhibit considerable activity for both propylene (Table 6.4) and 1-butene reactions (Tables 6.5-6.6). Activity for the reaction of propylene, expressed in moles of propylene converted into hydrocarbons per hour and per gram of zeolite, declined with increasing atomic number of the alkali cation (Figure 6.2). The activity was markedly increased when Li^+ was the neutralizing cation. When Rb cations were present in the zeolite no activity for propylene reaction was observed.

It is important to note that LiHY was even more active than HY even though HY has a higher concentration of Brønsted acid sites. One might anticipate that, because of the high concentration of acid sites and since acid-

Table 6.4 Propylene Reaction on HY and Partially-Exchanged HY-Zeolites*

	HY	LiHY	NaHY	RbHY
Conversion (%)	7.1	16.1	2.1	<0.1
	Product Distribution (wt%)			
Propane	5.9	6.0	11.9	0.0
Iso-Butane	11.3	26.6	3.5	0.0
Butane	0.2	0.2	0.0	0.0
1-Butene+Isobutene	13.9	9.7	19.1	0.0
Trans-2-Butene	8.2	7.2	14.6	0.0
Cis-2-Butene	4.9	4.4	8.8	0.0
Total C ₅	25.8	23.3	22.0	0.0
Total C ₆	29.9	22.7	19.3	0.0

* Reaction Conditions: 523 K, 1 atm,
 1% Propylene in Helium,
 Flow rate = 100 ml/min,
 5 min of reaction.

Table 6.5 1-Butene Reaction on HY and Partially-Exchanged HY-Zeolites*

	HY	LiHY	NaHY	RbHY
Conversion to products (%)	65.3	53.7	71.5	80.0
Unrecovered Butene (%)	21.9	40.4	13.4	3.8
Activity [mol x 10 ⁻³ /(h)(g)]	21.8	23.5	21.2	20.9
	Product Distribution (wt%)			
Propane + Propylene	3.6	1.1	2.4	0.3
Iso-Butane	12.0	25.0	5.9	0.3
Butane	1.9	3.8	1.0	0.1
Trans-2-Butene	46.1	34.4	51.4	59.5
Cis-2-Butene	28.9	20.3	32.4	38.2
Total C ₅	2.8	7.2	4.8	1.5
Total C ₆	4.8	8.2	2.2	0.1

* Reaction Conditions: 523 K, 1 atm, 1% 1-butene in Helium, Flow rate = 100 ml/min, 5 min of reaction.

Table 6.6 Low Temperature Butene Isomerization*

	HY	LiY	NaY	RbY
Conversion (%)	35.1	39.8	28.0	7.4
Activity [mol x 10 ⁻³ /h.g.]	8.7	9.9	7.0	1.8
cis/trans ratio	1.5	1.6	1.5	2.6

* Reaction Conditions: 313 K, 1 atm,
Flow rate = 100 cc/min,
1% 1-butene in He,
5 min of reaction.

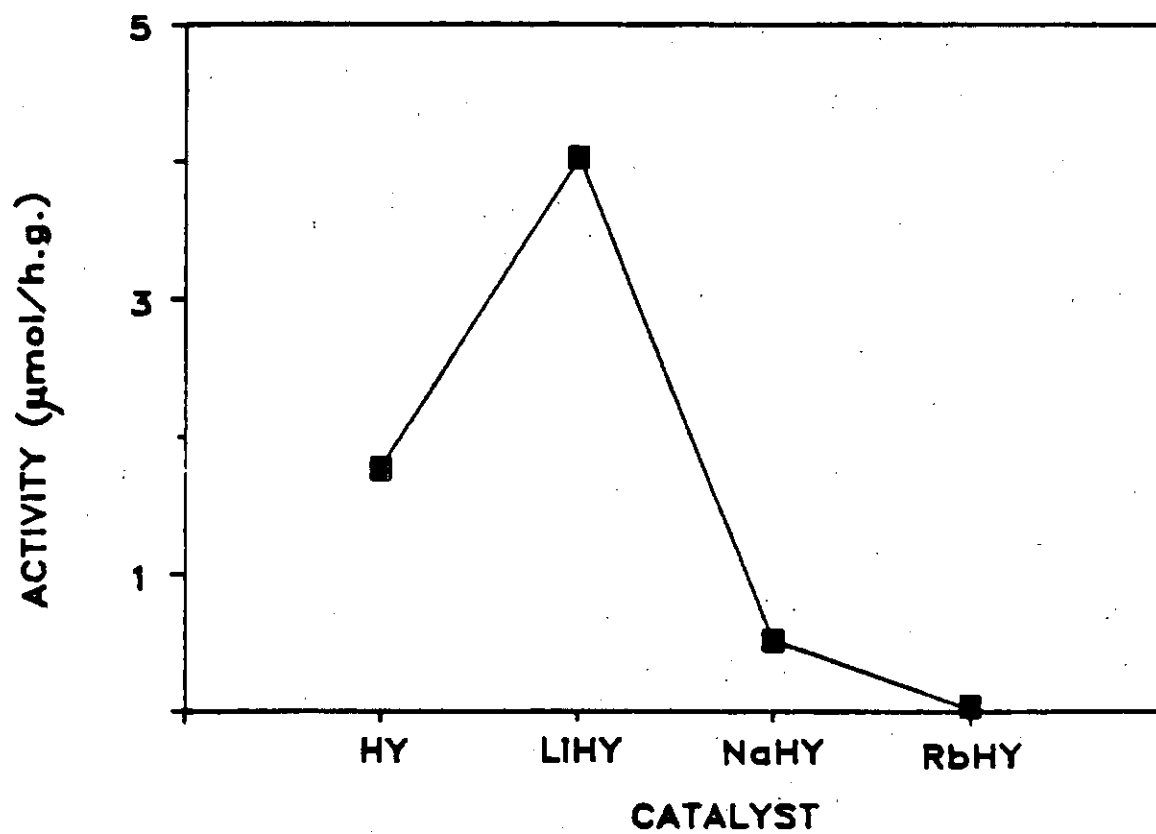


Figure 6.2 Effect of nature of neutralizing cations in Y-zeolites on the activity for propylene reactions at 523 K.

catalyzed reactions of hydrocarbons are always accompanied by carbon deposits, the deactivation rate of HY may be higher than that of LiHY. However, a study of the deactivation of these catalysts by varying the sampling time of the products showed that the catalyst activities remained practically constant during the first 10 minutes of reaction. This somewhat surprising effect of lithium on the zeolite activity for propylene reaction and also for 1-butene reaction was, thus, a real effect and not just due to rapid deactivation of the HY zeolite. O'Donoghue and Barthomeuf,⁽¹¹⁵⁾ studying a series of HY-zeolites partially exchanged with Li, K, and Rb cations using 2-propanol dehydration and infra-red spectroscopy, found also that LiHY-zeolites have higher acid catalytic activity than HY. They suggested that the acidic strength of the remaining hydroxyl groups increases when protons are replaced by Li cations due to their high polarizing power acting on the OH groups through the lattice. Other increases in the strength of the Brønsted acid sites have also been observed on partial dehydroxylation of HY-zeolites.⁽¹¹⁶⁻¹¹⁸⁾ Unfortunately, no completely satisfactory explanation of acidic strength derivation has yet been proposed.

The selectivities obtained with each catalyst for propylene reaction are listed in Table 6.4. In this reaction on HY, LiHY, and NaHY, C₄, C₅, and C₆ hydrocarbons constituted more than 90% of the products, with a high

proportion in each group in the form of iso-paraffins. These product distributions provide evidence that the olefin transformations under the reaction conditions used in this work proceed through an oligomerization-cracking mechanism coupled with hydrogen transfer leading to the formation of a wide range of both saturated and unsaturated hydrocarbons. Several investigations of olefin reactions on solid acid catalysts such as zeolites have arrived at similar conclusions. (104-107, 119-121) Such reactions have also been shown to be strongly dependent on the strength of the acid sites present in the zeolite. (102) Moreover, Datka (102) has also observed that the greater the strength of these acid sites the more branched the oligomer intermediates. This results in the formation of more iso-paraffins. It may be suggested that the effect of the nature of the neutralizing alkali cations on both the activity and selectivity of the zeolite for propylene reactions reflects the significant influence that these cations may have on the strength of the Brønsted acid sites present in the zeolite. In agreement with the findings of O'Donoghue and Barthomeuf, (115) the LiHY-zeolite apparently had the strongest acid sites and RbHY the weakest.

This acidic series of zeolites was very active for 1-butene reaction under the reaction conditions used (Table 6.5). Two categories of reactions may be distinguished for

1-butene reaction on acidic zeolites. The oligomerization reaction of 1-butene, followed by a number of other reactions which include cracking, intermolecular hydrogen transfer, etc, leads to the formation of a wide range of hydrocarbon products. These reactions follow the same mechanism as that for propylene or any other olefin transformation over an acidic zeolite and are therefore very much dependent on the strength of the acid sites and the reaction temperature. (102,104-107,119-121) The second category of reactions involved in butene transformation on acidic catalysts involves double bond shift and cis/trans isomerization. These reaction steps are known to proceed rapidly even on weak Brønsted acid sites.

The effect of the nature of the alkali cations present in the zeolite on the rate of each of these competing reactions is shown in Figure 6.3. The activities are expressed in moles of 1-butene converted per hour and per gram of catalyst either to 2-butenes (isomerization) or other products excluding the 2-butenes (lumped here under the term oligomerization). LiHY again appeared to be the catalyst most active for the acid-catalyzed oligomerization reactions. The activity for these reactions, as in the case of the propylene reactions, also declined with increasing atomic number of the alkali cation. However, 1-butene seemed to be much more reactive than propylene. This may be due to its greater ability to form carbonium ions. As for

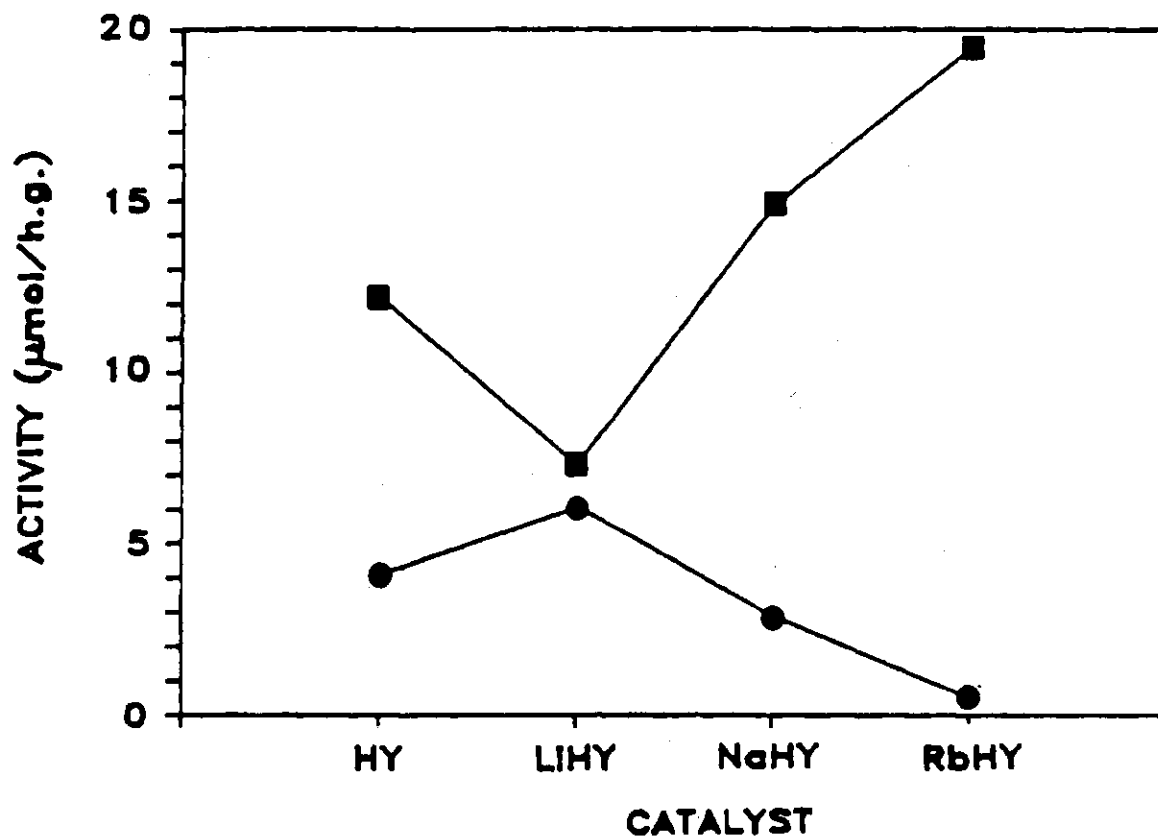


Figure 6.3 Effect of nature of neutralizing cations in Y-zeolites on the activity for 1-butene reactions at 523 K; (■) Isomerization, (●) Oligomerization-Cracking.

the isomerization reactions (double bond shift and cis/trans isomerization), a reverse trend was observed, i.e., increasing activity from LiHY to RbHY. This is in contrast to results reported by Lombardo et al.⁽¹¹²⁾ who showed that the activity was increased when Li^+ was substituted for Na^+ and decreased by K^+ substitution. However, under the conditions used by these authors, only the isomerization reactions were taking place. When 1-butene reaction was carried out at 313 K instead of 523 K, where the isomerization reactions were not disturbed by the oligomerization of butene, the activity was found to decline with increasing atomic number of the alkali cation present in the zeolite (Table 6.6), in agreement with the results of Lombardo et al.⁽¹¹²⁾

The high temperature results (Figure 6.3), in agreement with those of Dzwigaj et al.,⁽¹¹⁹⁾ suggest that a distribution of sites with varying acid strengths is involved in the transformation of 1-butene. The double bond and cis-trans isomerization can occur on sites of any strength while the oligomerization reactions accompanied by cracking and hydrogen transfer can only take place on the strong acid sites. Hence, the individual rates of the various competing reactions would depend not only on the overall concentration of acid sites but also on the acid strength distribution of these sites. The individual rates of the various reactions are not necessarily alike. The

rapid isomerization of 1-butene to 2-butene is an easy reaction which involves only an intramolecular rearrangement. On the other hand, the formation of the other hydrocarbon products from the reaction of 1-butene on strong acid sites involves a complex sequence of steps which include carbon-carbon bond formation and breaking. Moreover, the primary reaction step preceding this sequence of surface reactions has been shown by Weeks et al.⁽¹²¹⁾ to be the isomerization of 1-butene to 2-butene. The rate of formation of 2-butenes has, therefore, to be much faster than the rate of formation of all the other products. A higher relative activity for isomerization would be observed when most of the sites are of the weak type and hence available for this reaction, as in the case of RbHY.

Other parameters, such as steric factors, fast deactivation of the acid sites, and transport phenomena, may also be partly responsible for this distorted kinetic picture of the 1-butene reaction on the various zeolites. Olefin reactions on strong acid sites involve also the formation of oligomers which are tightly bound to the surface and constitute the hydrogen reservoir for hydrogenation of olefins on the acid sites. Subsequent hydrogen transfer accompanied by cracking results in the formation of paraffins, the dehydrogenation process being associated with a buildup of bulky hydrogen-deficient

polymeric materials. These unsaturated residues cannot diffuse out of the zeolite pores because of either their size or their strong interaction with the catalyst surface. (104,121) The net result would obviously be the blocking of active sites by these residues which contribute to the rapid deactivation of the catalyst. (102) Hence only part of the acid sites may participate in the reaction of olefins on the zeolites with the strongest acid sites. This is supported by the high amount of unrecovered 1-butene, determined by mass balance of reactants and products, which must have been strongly and irreversibly adsorbed in the zeolite cavities in the case of LiHY, HY, and NaHY (see Table 6.6). Finally all these olefin reactions are very fast and therefore may well be diffusion limited. The various zeolites did not exhibit significant differences in total activity for 1-butene conversion (Table 6.5). This is probably due to the fact that such high conversions, close to equilibrium, were manifested. At this reaction temperature of 523 K used for comparison to the CO hydrogenation results, the rate may have been limited by diffusion of the reactants and products in the zeolite pore network. Hence, the observed overall rate of reaction would actually be a measure of the rate of diffusion of reactants and products, with reaction equilibrium established in the zeolite pores. An Arrhenius plot indicates that this is in fact the case.

The product distributions obtained with the various catalysts are listed in Table 6.5. It may be noted that they are qualitatively similar to the product distributions obtained with propylene reactions, suggesting similar mechanisms for all olefin transformations on acid sites. The changes in the product distributions with the nature of the cation reflect obviously changes in the acid strength distribution. Figure 6.4 shows the distribution of C₄ products from 1-butene reaction. Except for the case of HY, this distribution is qualitatively similar to that realized during CO hydrogenation over the comparable zeolite-supported Ru catalysts (Figure 6.1). Of course, during CO hydrogenation over the Ru catalysts there was much more n-butane due to the possibility of secondary hydrogenation on the metal sites. The iso-butane and n-butane concentrations from 1-butene reaction in the absence of Ru may be taken as a measure of the oligomerization-cracking-hydrogen transfer reactions, the 2-butene concentrations representing a measure of the isomerization activity. This provides evidence that the primary olefinic products desorbing from F-T metal sites are being readsorbed on the acid sites where they can undergo a number of transformations as illustrated schematically by the butene molecule in Figure 6.5.

LiHY, somewhat surprisingly, produced the greatest

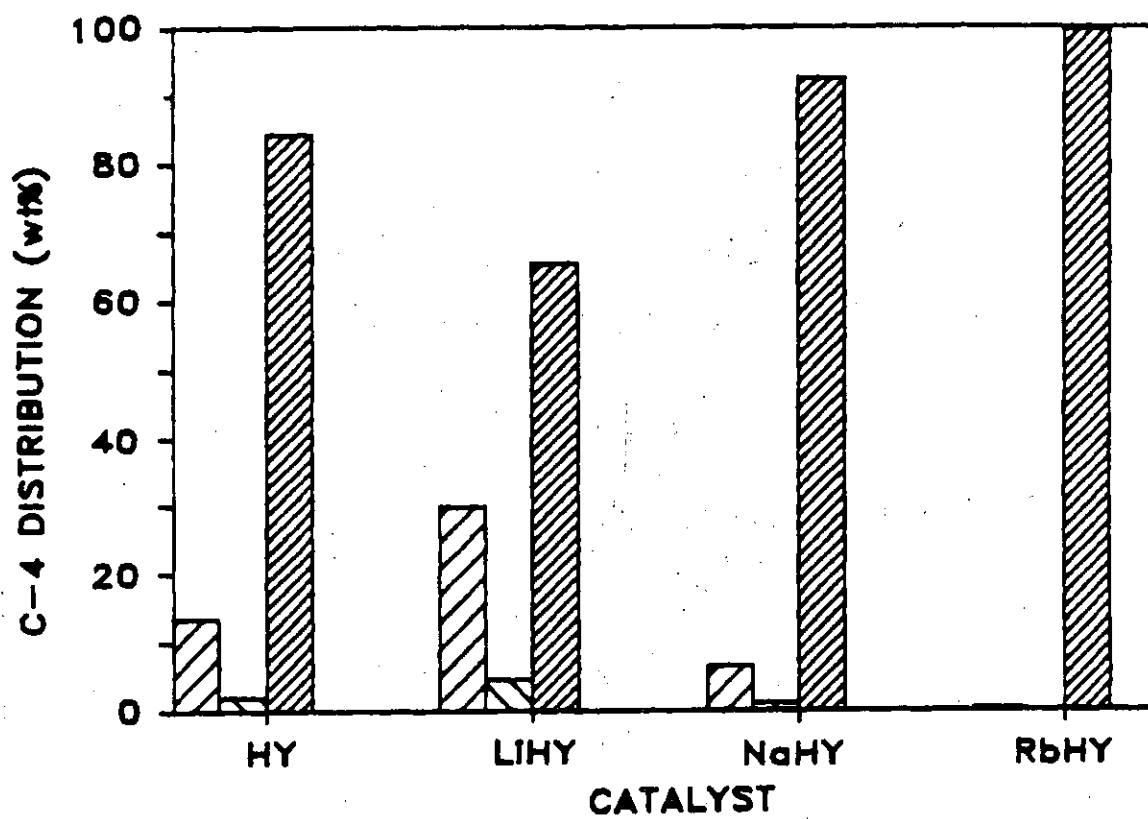


Figure 6.4 C₄-isomer distribution from 1-butene reactions over partially-exchanged HY-zeolites at 523 K;

(▨) Isobutane, (▩) N-butane, (▧) 2-butenes.

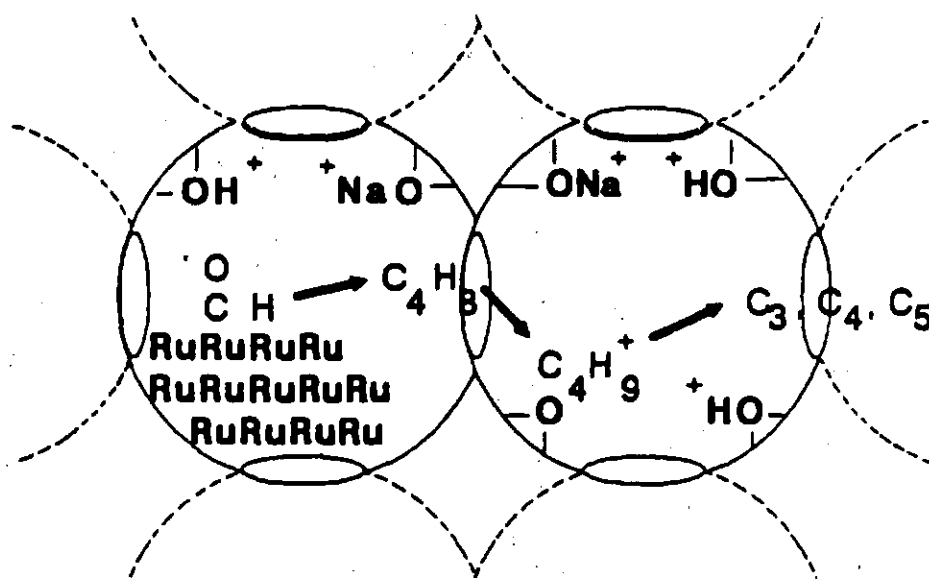


Figure 6.5 Secondary reactions in RuNaY prepared by ion-exchange.

fraction of iso-butane indicating a strong effect of Li on the acid sites. This was not the case during CO hydrogenation on the LiY-zeolite-supported catalyst. However, in that catalyst, Li constituted only 15% of the exchangeable cations while Na constituted 55%. Such small concentrations of Li may not be sufficient to increase significantly the strength of the acid sites formed in the zeolite. In fact, the sodium may alter large number of acid sites in the opposite direction. Moreover, the concentration of acid sites in the zeolite-supported Ru catalysts was much lower than in the partially-exchanged alkali zeolites used for the olefin reactions.

HY produced a lower fraction of iso-butane in the C₄ products during 1-butene reaction than RuHY during CO hydrogenation. This may be explained by the fact that the reaction of 1-butene under the conditions used is probably, as suggested earlier, diffusion limited. During CO hydrogenation diffusion does not represent a major problem since all the reactant, 1-butene, would be produced within the zeolite pores, in the proximity of the secondary reaction sites (see Figure 6.5). In addition, during the 1-butene reaction study, part of the 1-butene may have first reacted on the external weak acid sites of the zeolite, forming 2-butenes which may leave the catalyst bed without necessarily going through the zeolite pores. Finally, the olefin reactions were carried out in the absence of hydrogen

and possible hydrogen spillover from Ru which may also explain some of the apparent differences observed for 1-butene reaction over HY and the same reaction happening during CO hydrogenation over RuHY. The chromatographic column used to separate the hydrocarbon products was unfortunately not able to separate 1-butene from iso-butene. Thus, if the latter was formed, as is usually the case during these olefin reactions, it would not have been distinguished. In the presence of activated hydrogen, any iso-butene formed would be able to be hydrogenated to isobutane, hence increasing the concentration of the latter in the C₄-fraction.

Another significant aspect of these olefin reaction studies in relation to the CO hydrogenation results is that they provide further evidence that the primary olefinic products may be hydrogenated on strong acid sites, via an intermolecular hydrogen transfer mechanism. The presence of iso-butane and iso-pentane in the products of olefin reactions in the absence of hydrogen, whatever the reactant olefin, 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, and not necessarily by direct skeletal isomerization of the corresponding linear olefins. (107) It may also be observed that, as in most cases

where iso-butane is produced in large quantities, the iso-butane/n-butane ratio is much in excess of the equilibrium value of 1.2 at the reaction temperature of 523 K. (122) Okuda et al. (19) have also reported iso-paraffin/n-paraffin values much greater than the equilibrium value for F-T synthesis on zeolite-supported Ru-Pt catalysts. This reinforces the proposition that isoparaffins are formed mainly via the cracking of olefin oligomers formed on the acid sites, since a bifunctional mechanism involving an acid-catalyzed skeletal isomerization of n-olefins to iso-olefins and their subsequent hydrogenation on metal sites would be restricted by equilibrium.

6.4 Conclusion

This study establishes the importance of the secondary acid-catalyzed reactions of primary olefinic products of CO hydrogenation in shaping the overall selectivities of RuY-zeolite catalysts. It also provides strong evidence that the neutralizing alkali cations, while playing no role as active sites, may have a significant effect on these reactions by affecting the strength of the Brønsted acid sites formed in the zeolite. Competitive reaction paths for the transformation of primary olefinic products on the acid sites may be involved, the relative importance of each depending on the acid strength of the sites. These secondary

reactions include isomerization, oligomerization, cracking, hydrogenation via hydride transfer, etc. All these reactions, under the CO hydrogenation conditions, result in the rapid conversion of the primary olefins to isomeric compounds which are essentially inert for further chain growth by readsorption on the metal sites.