Secondary Reactions during CO Hydrogenation on Zeolite-Supported Metal Catalysts: Influence of Alkali Cations

RACHID OUKACI,[1] JEFFREY C. S. WU, AND JAMES G. GOODWIN, JR.[2]

*Department of Chemical and Petroleum Engineering, University of Pittsburgh,
Pittsburgh, Pennsylvania 15261*

The effect of neutralizing cations on the secondary reactions of the primary products from CO hydrogenation over ion-exchanged zeolite-supported Ru catalysts was investigated using zeolites with different alkali cations (Li^+, Na^+, K^+, Rb^+, Cs^+). The transformation of olefins (propylene and butene) on the zeolites without the metal, under conditions similar to those used for CO hydrogenation, was also studied in order to understand the effect of the various constituents of the support, i.e., the Brønsted acid sites generated during catalyst preparation and the alkali cations, on possible secondary reactions of the primary olefinic products. It was established that secondary acid-catalyzed reactions of these primary products can play a major role in shaping product selectivity during CO hydrogenation over zeolite-supported catalysts. Depending on the concentration and the strength of the acid sites, various competitive reaction paths can be observed for the transformation of the olefinic compounds. These include isomerization, oligomerization, polymerization, and cracking.

The strength of the acid sites was found to be a strong function of the nature of the neutralizing alkali cations remaining in the zeolite. The presence of Li^+ produced the strongest acid sites resulting in more oligomerization over LiHY than even HY. Acid site strength decreased with the molecular weight of the alkali cation used. © 1987 Academic Press, Inc.

I. INTRODUCTION

Since olefins tend to be the primary products in CO hydrogenation over transition metals, possible secondary reactions can significantly modify product selectivities. Such secondary reactions can include hydrogenation, hydrogenolysis, CO insertion, and chain propagation. These reactions may all be possible on the same metal sites responsible for the formation of these primary products. In addition, if an acidic support is used with the F–T (Fischer–Tropsch) metal, a number of carbonium ion-type reactions may result. Depending on the strength of the acid sites, these reactions may include isomerization, oligomerization, hydrogen transfer, cracking, polymerization, cyclization, aromatization, and coking.

These secondary acid-catalyzed reactions of the primary olefinic products may play a major role in altering the hydrocarbon product distribution obtained by F–T synthesis. Egiebor and Cooper (1) found that a high proportion of the olefins produced on silica-supported F–T catalysts are in the form of internal olefins. They showed that these internal olefins are formed by secondary reactions of 1-olefins on the Brønsted acid sites of the silica support. The use of zeolites as supports for metals, such as Ru (2) and Fe (3), active in F–T synthesis has suggested a possible effect of zeolites in limiting the chain growth of the F–T products. It has also been demonstrated that, due to the bifunctional properties of zeolite-supported catalysts, the isomer distribution of the hydrocarbons formed by F–T synthesis may be signifi-

[1] Permanent address: CERHYD, Route de Sidi-Moussa, Dar-El-Beida, Algiers, Algeria.
[2] To whom all correspondence should be addressed.

cantly altered by secondary reactions (4–8). Chen *et al.* (5, 6), for example, have observed that, when CO hydrogenation is carried out over zeolite-supported Ru catalysts, the formation of isoparaffins is enhanced with increasing concentration and acid strength of the zeolite hydroxyl groups.

In a recent study of CO hydrogenation on a series of Y-zeolite-supported Ru catalysts prepared by ion exchange (9), it was found that the nature of the alkali cation used to neutralize the zeolite had little effect on the properties of the metal for the primary reaction of CO. These cations, however, appeared to exert a major influence on the secondary reactions of the primary products formed on these zeolite-supported catalysts.

This paper reports the results of a further study to determine the nature as well as the activity and selectivity of those sites involved in the secondary reactions.

II. EXPERIMENTAL

Materials

Alkali cation (Li, K, Rb, and Cs) Y-zeolites were prepared by ion exchange of NaY zeolite (obtained from Strem Chemicals) with alkali nitrates (from Alfa Products). A series of zeolite-supported Ru catalysts was prepared by ion exchange of Ru with NH_4Y, LiY, NaY, KY, RbY, and CsY zeolites. The preparation, pretreatment, reduction, and characterization procedures for all these catalysts have been described elsewhere (9).

The catalyst containing the highest concentration of Brønsted acid sites, RuHY obtained after reduction in $RuNH_4Y$, was reexchanged with a dilute solution of K_2CO_3 in order to replace the protons by potassium cations and thereby decrease significantly the zeolite acidity.

Partially exchanged MNH_4Y zeolites (M = Li, Na, or Rb) with similar acid site concentrations following calcination to form MHY were prepared by ion exchange of NH_4Y zeolite (80% exchanged, obtained

from Strem Chemicals) with the alkali nitrates. 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 filtrate was 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 323 K for 48 h. A complete analysis of the dried samples was carried out by atomic absorption to determine the aluminum and alkali cation contents of the zeolites. The sodium content was determined by flame-emission spectroscopy. The results of this elemental analysis are given in Table 1 as ratios of the exchangeable cation. The acid site concentration, represented by the ammonium cation-to-aluminum ratio and determined by difference, was equivalent to about 60% of the exchangeable neutralizing cations in the MHY series.

The Si/Al ratio of the various zeolites was determined using ^{29}Si MAS solid-state NMR. The spectra were recorded at 59.627 MHz on a Bruker MSL300 instrument. The Si/Al values of the zeolites, included in Table 1, were calculated using the intensities of the NMR signals. The AA analysis gave similar results. As shown in Fig. 1, the Si/Al ratio of the parent zeolite, NH_4Y, was not altered during ion exchange with MNO_3 (M = Li, Na, or Rb) salts.

Reaction Studies

CO hydrogenation was carried out over the series of RuY catalysts at atmospheric

TABLE 1

Elemental Analysis Results

Catalyst	Si/Al^a	Na/Al	M/Al^b	NH_4/Al
NH_4Y	2.48	0.20	—	0.80
$LiNH_4Y$	2.45	0.16	0.24	0.60
$NaNH_4Y$	2.44	0.43	—	0.57
$RbNH_4Y$	2.48	0.16	0.22	0.62

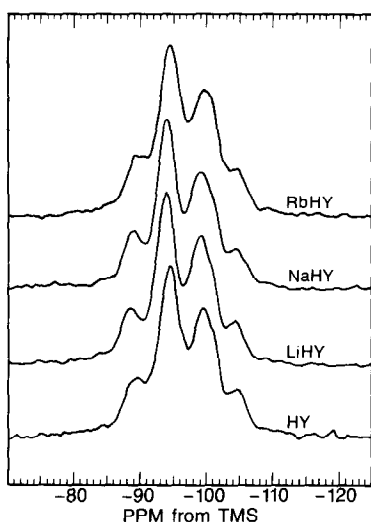^{a} From MAS NMR spectra (see Fig. 1).
^{b} M = Li, Rb.

FIG. 1. ^{29}Si MAS NMR spectra of the acidic zeolites.

the ammonium cation and produce the protonic-form zeolites HY and MHY (M = Li, Na, or Rb). The same pretreatment procedure was also followed in the case of the alkali-form zeolites LiY, NaY, and RbY. The reactor was then cooled down to a reaction temperature of 523 K, chosen in order to compare the properties of these zeolites with those of the zeolite-supported Ru catalysts for CO hydrogenation. A flow rate of 100 ml/min of a reactant mixture containing approximately 1% olefin in helium was used with a catalyst charge of 0.1 g. Samples of the reactor outlet were analyzed by on-line gas chromatography after 5 min of reaction, as during the CO hydrogenation experiments.

pressure and in the 483- to 573-K temperature range. Details of the reaction and product analysis procedures have been reported in Ref. (9).

To investigate the catalytic properties of the zeolite supports for olefin reactions at the temperature and pressure used in CO hydrogenation but without any intrusion from the presence of Ru, olefin (propylene and 1-butene) transformations were carried out over the alkali form and the partially exchanged Y-zeolites as well as HY-zeolite in a quartz microreactor. The catalysts were first pretreated at 673 K for 2 h under a hydrogen stream in order to decompose

III. RESULTS AND DISCUSSION

CO Hydrogenation

In the previous study of CO hydrogenation over this series of Y-zeolite-supported Ru catalysts prepared by ion exchange, it was found that the nature of the neutralizing alkali cations had little effect on chain growth probability and CO TOF (turnover frequency) (see Table 2). Since ASF (Anderson–Schultz–Flory) chain growth probability and CO TOF are functions of metal-catalyzed reaction, it was concluded that, under reaction conditions the alkali cations exert little effect on the basic catalytic properties of the supported Ru. However,

TABLE 2

Catalytic Properties^a of Zeolite-Supported Ru Catalysts (9)

Catalyst	Dispersion (%)	TOF ($s^{-1} \times 10^{-3}$)	Selectivity (wt%)					
			C_1	C_2	C_3	C_4	C_5	C_6
3.8% RuHY	30	40.5	34.3	13.7	19.1	17.1	12.3	3.5
3.4% RuLiY	53	10.7	33.4	14.3	21.8	17.6	11.8	1.1
3.8% RuNaY	67	6.9	32.7	14.0	21.5	17.0	10.9	3.9
3.2% RuKY	52	8.0	30.7	13.7	23.5	15.8	11.0	5.2
3.6% RuRbY	49	14.1	33.5	14.4	22.0	15.3	9.7	5.1
3.7% RuCsY	56	12.4	36.1	13.2	21.6	15.1	9.8	4.2

^{a} Reaction conditions: 523 K, 1 atm, H_2/CO = 1, 5 min of reaction.

the product composition indicated significant differences in olefin/paraffin ratios and isoparaffin formation. It was suggested that acid sites generated in the zeolite during reduction of the ion-exchanged Ru were the source of secondary reactions of the primary olefinic products leading to the formation of both paraffins, isoparaffins and internal olefins. The $C_3^=/C_3^-$ ratio was highest where the larger alkali cations had been exchanged into the zeolite and followed the sequence: $Cs \sim Rb > K > Na > Li \sim H$. Figure 2 shows a plot of the various components in the C_4 fraction as the nature of the neutralizing alkali cation was varied. As can be easily seen, the isobutane and 2-butene compositions varied strongly and inversely as the nature of the alkali cation was varied. RuHY produced a majority of the C_4 fraction in the form of isobutane. The presence of the heavier alkali cations (K, Rb, Cs) in the RuY catalysts resulted in high selectivities for 2-butenes and negligible activities for isobutane formation. These results suggest an important role for the acid sites and a possible role for the alkali cations in affecting these reactions.

In order to better understand this apparent role of the acid sites, a study was made of CO hydrogenation over a series of catalysts. This series included RuHY (the catalyst producing the highest selectivity for isobutane), RuHY which had been reex-
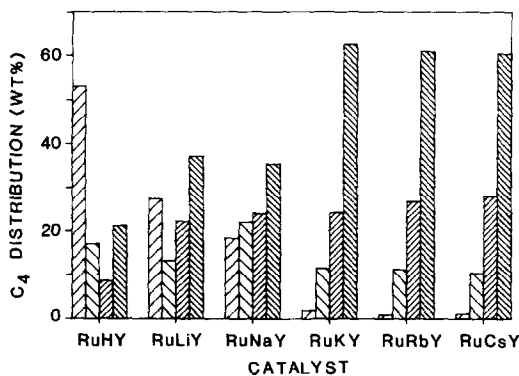
TABLE 3

Effect of Acidity on Olefin and Isobutane Selectivities[a]

Catalyst	Propene/propane ratio	Isobutane (wt% in C_4)
RuHY	1.1	53.0
RuHY(K)[b]	16.9	0.0
RuRbY	6.4	1.4
RuRbY + HY[c]	4.1	30.6

[a] Reaction conditions: 523 K, 1 atm, $H_2/CO = 1$.
[b] RuHY treated in 0.1 N K_2CO_3 solution after reduction.
[c] RuRbY and HY in separate layers.

changed with K^+ after Ru reduction in order to eliminate the Brønsted (H^+) sites, RuRbY (a catalyst producing essentially no isobutane), and RuRbY followed in the catalyst bed by HY. The results listed in Table 3 show that at 523 K RuHY gave 53% isobutane (based on the total amount of C_4). When the Brønsted acid sites in this catalyst were replaced by potassium cations, the isobutane was no longer obtained and the propylene-to-propane ratio increased significantly. On the other hand, RuRbY yielded only very small quantities of isobutane; however, when 0.2 g 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.

Similar high olefin-to-paraffin ratios and no isoparaffins were obtained by Chen et al. (5) when they carried out CO hydrogenation over zeolite-supported Ru catalysts prepared by vapor impregnation and containing no Brønsted acidity. However, lower olefin fractions and significant amounts of isobutane were also observed with ion-exchanged catalysts which contained Brønsted acid sites formed during the decomposition and reduction of the ruthenium.

These results provide strong evidence that the hydrocarbon products of CO hydrogenation over zeolite-supported ruthenium catalysts are mainly, if not totally,

FIG. 2. C_4 Isomer distribution from CO hydrogenation over RuY-zeolites at 523 K. (▨) Isobutane, (◣) n-butane, (▨) 1-butene, (◨) 2 butenes.

desorbed as olefins which can then undergo secondary reactions on the acid sites or to a lesser extent hydrogenation on the metal sites. Hydrogenation on the acid sites seems also to play a major role in the olefin fraction obtained. Furthermore, the rates of these acid-catalyzed reactions seem to be strongly dependent not only on the concentration of Brønsted acid sites but also on the nature of the cations occupying the remaining exchange sites in the zeolite framework.

Olefin Reactions over Alkali Y-Zeolites

The catalytic properties for olefin reactions of the zeolite supports containing no metal were investigated under the same conditions of temperature and pressure as those used in CO hydrogenation. The olefin reactions were first carried out over the nonacidic alkali form of the zeolites in the presence of either helium or hydrogen. Topchieva et al. (10) have suggested that zeolites in the alkali form may exhibit significant activity for the hydrogenation of olefins when treated with hydrogen at high temperatures. However, under the reaction conditions used in our experiments, the fully exchanged alkali zeolites exhibited no activity for propylene reaction. Even under hydrogenation conditions, no hydrogenation activity was observed.

The same zeolites showed also relatively low activities for 1-butene reaction, producing only 2-butenes as products regardless of whether the reaction was run in helium or in hydrogen (see Table 4). Thus, only double-bond shift and cis/trans isom-

TABLE 4

Butene Isomerization on Nonacidic Alkali Zeolites[a]

	LiY	NaY	RbY
Conversion (%)	7.5	7.9	6.4
Activity [mol × 10^{-3}/(h)(g)]	1.9	2.0	1.6
cis/trans Ratio	0.8	0.6	1.7

[a] Reaction conditions: 523 K, 1 atm, flow rate = 100 ml/min, 1.5% 1-butene in He, 5 min of reaction.

erization were involved in 1-butene conversion. It is commonly accepted that such reactions are proton-catalyzed, involving a common intermediate, the secondary butyl carbonium ion (11). Several authors (12–16) have also reported that Group IA Y-zeolites have very low or no activity for carbonium ion reactions since no Brønsted acidity can be detected (15, 16). It has been suggested that any activity of these zeolites is due to the presence of divalent cations such as Ca^{2+} ions (12) which may be present as impurities. However, partial decationization by simple washing with distilled water and replacement of some of the alkali cations by protons from the water has been found to result in appreciable catalytic activity for the isomerization of olefins (13, 14). Since hydroxyl groups are required to terminate the zeolite crystal faces, they may serve as active sites for double-bond isomerization, which requires only weak acidity. This would explain why no major difference could be detected between the catalytic activities of the various alkali zeolites investigated in this study (Table 4). Since no activity for propylene reactions and only relatively low butene isomerization activity were observed, it may be concluded that the alkali cations do not play any significant role as secondary reaction sites during CO hydrogenation.

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 of and reduction in the precursor lead to the formation of three Brønsted acid sites for each metal atom involved. Since only these Brønsted acid sites appear to be strongly 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

TABLE 5

Propylene Reaction on HY and
Partially Exchanged HY-Zeolites[a]

	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
Isobutane	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

[a] Reaction conditions: 523 K, 1 atm, 1% propylene in helium, flow rate = 100 ml/min, 5 min of reaction.

acid sites but no metal sites. Such acid site-containing alkali zeolites were found to exhibit considerable activity for both propylene (Table 5) and 1-butene reactions (Tables 6 and 7). Activity for the reaction of propylene, expressed in moles of propylene converted into hydrocarbons per hour and per gram of zeolite, declined with the increasing atomic number of the alkali cation (Fig. 3). 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.

TABLE 6

1-Butene Reaction on HY and
Partially Exchanged HY-Zeolites[a]

	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 × 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
Isobutane	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

[a] Reaction conditions: 523 K, 1 atm, 1% 1-butene in helium, flow rate = 100 ml/min, 5 min of reaction.

TABLE 7

Low-Temperature Butene Isomerization[a]

	HY	LiHY	NaHY	RbHY
Conversion (%)	35.1	39.8	28.0	7.4
Activity [mol × 10^{-3}/(h)(g)]	8.7	9.9	7.0	1.8
cis/trans Ratio	1.5	1.6	1.5	2.6

[a] Reaction conditions: 313 K, 1 atm, flow rate ≈ 100 cc/min, 1% 1-butene in He, 5 min of reaction.

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-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 min 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 (17), studying a series of HY-zeolites partially exchanged with Li, K, and Rb cations using 2-propanol dehydration and infrared spectroscopy, found also that LiHY-zeolites
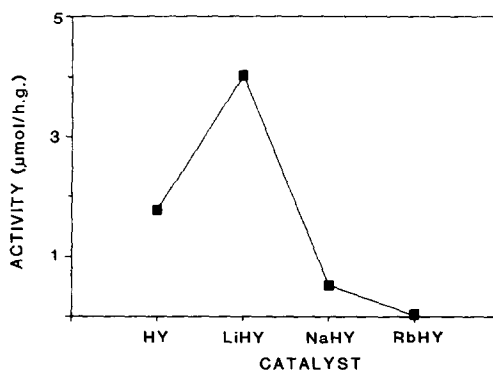

FIG. 3. Effect of nature of neutralizing cations in Y-zeolites on the activity for propylene reactions at 523 K.

have a 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 (18–20). 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 5. In this reaction on HY, LiHY, and NaHY, C_4, C_5, and C_6 hydrocarbons constituted more than 90% of the products, with a high proportion in each group in the form of isoparaffins. 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 (21–28). Such reactions have also been shown to be strongly dependent on the strength of the acid sites present in the zeolite (22). Moreover, Datka (22) 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 isoparaffins. It may be suggested that the effect of the nature of the neutralizing alkali cations on both the activity and the 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 (17), 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 reac-

tion conditions used (Table 6). 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 and intermolecular hydrogen transfer, 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 (21–28). 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 Fig. 4. The activities are expressed in moles of 1-butene converted per hour and per gram of catalyst to either 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
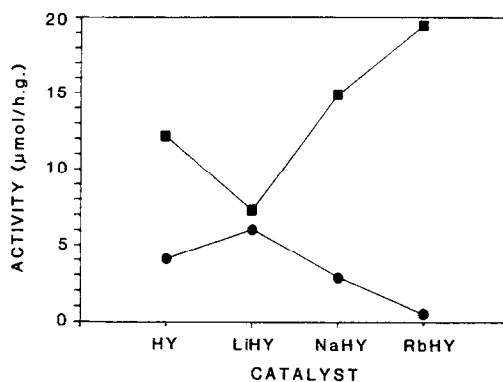

FIG. 4. Effect of nature of neutralizing cations in Y-zeolites on the activity for 1-butene reactions at 523 K. (■) Isomerization, (●) oligomerization-cracking.

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 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. (13) 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 the increasing atomic number of the alkali cation present in the zeolite (Table 7), in agreement with the results of Lombardo et al. (13).

The high-temperature results (Fig. 4), in agreement with those of Dzwigaj et al. (21), suggest that a distribution of sites with varying acid strengths is involved in the transformation of 1-butene. The double-bond and cis/trans isomerizations can occur on sites of any strength while the oligomerization reactions accompanied by cracking and hydrogen transfer can take place only 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. (25) to be the isomerization of 1-butene to 2-butene. The rate of formation of 2-butenes must, therefore, 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 (25, 26). The net result would obviously be the blocking of active sites by these residues which contribute to the rapid deactivation of the catalyst (22). 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). 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). 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 hydroge-

nation 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 of reaction data recorded over a wide range of temperatures exhibited a linear behavior at the lowest temperatures, giving an activation energy comparable to values reported in the literature (11). However, the slope of the Arrhenius plot decreases above 400 K, perhaps indicating that diffusion processes may be limiting.

The product distributions obtained with the various catalysts are listed in Table 6. 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 5 shows the distribution of C_4 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 (Fig. 2). Of course, during CO hydrogenation over the Ru catalysts there was much
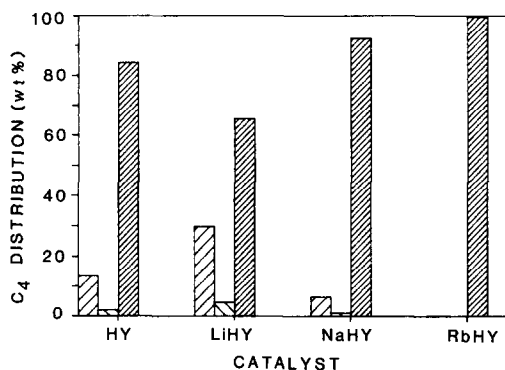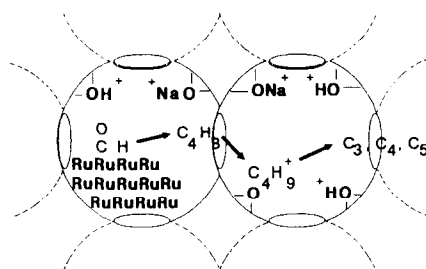

FIG. 6. Secondary reactions in RuNaY prepared by ion exchange.

more n-butane due to the possibility of secondary hydrogenation on the metal sites. The isobutane 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 Fig. 6.

LiHY, somewhat surprisingly, produced the greatest fraction of isobutane 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 numbers of acid sites in the opposite direction. Moreover, the concentration of acid sites in the zeolite-supported Ru catalysts was much lower than that in the partially exchanged alkali zeolites used for the olefin reactions.

HY produced a lower fraction of isobutane in the C_4 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 condi-

FIG. 5. C_4 isomer distribution from 1-butene reactions over partially exchanged HY-zeolites at 523 K. (▨) Isobutane, (◪) n-butane, (▨) 2-butenes.

tions 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 Fig. 6). 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 isobutane. 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 isobutane formed would be able to be hydrogenated to isobutane, hence increasing the concentration of the latter in the C_4 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 isobutane and isopentane 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 (24). It may also be observed that, as in most cases where isobutane is produced in large quantities, the isobutane/n-butane ratio is much in excess

of the equilibrium value of 1.2 at the reaction temperature of 523 K (29). Okuda et al. (7) have also reported isoparaffin/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 isoolefins and their subsequent hydrogenation on metal sites would be restricted by equilibrium.

IV. CONCLUSIONS

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, and hydrogenation via hydride transfer. 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.

REFERENCES

1. Egiebor, N. O., and Cooper, W. C., *Appl. Catal.* **17**, 47 (1985).
2. Nijs, H. H., Jacob, P. A., and Uytterhoeven, J. B., *J. Chem. Soc. Chem. Commun.*, 180 (1979).

3. Ballivet-Tkatchenko, D., and Tkatchenko, I., *J. Mol. Catal.* **13**, 1 (1981).

4. King, D. L., *J. Catal.* **51**, 386 (1978).

5. Chen, Y. W., Wang, H. T., and Goodwin, J. G., Jr., *J. Catal.* **83**, 415 (1983).

6. Chen, Y. W., Wang, H. T., and Goodwin, J. G., Jr., *J. Catal.* **85**, 499 (1984).

7. Okuda, O., Tatsumi, T., Fujimoto, K., and Tominaga, H., *Chem. Lett.,* 1153 (1983).

8. Tatsumi, T., Shul, Y. G., Sugiura, T., and Tominaga, H., *Appl. Catal.* **21**, 119 (1986).

9. Oukaci, R., Sayari, A., and Goodwin, J. G., Jr., *J. Catal.* **102**, 126 (1986).

10. Topchieva, K. V., Zhdanov, S. P., Rosolovskaya, E. N., Shakhnovskaya, O. L., and Samulevich, N. N., *Russ. J. Phys. Chem.* **48**, 1459 (1974).

11. Jacobs, P. A., "Carboniogenic Activity of Zeolites." Elsevier, Amsterdam, 1977.

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

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

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

15. Benesi, H. A., and Winquist, B. H. C., *Adv. Catal.* **27**, 97 (1978).

16. Ward, J. W., *J. Catal.* **10**, 34 (1968).

17. O'Donoghue, E., and Barthomeuf, D., *Zeolites* **6**, 267 (1968).

18. Hopkins, P. D., *J. Catal.* **12**, 325 (1968).

19. Jacobs, P. A., Leeman, H. E., and Uytterhoeven, J. B., *J. Catal.* **33**, 17 (1974).

20. Jacobs, P. A., Declerck, L. J., Vandamme, L. J., and Uytterhoeven, J. B., *J. Chem. Soc. Faraday Trans. 1* **71**, 545 (1975).

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

22. Datka, J., *in* "Catalysis by Zeolites" (B. Imelik *et al.*, Eds.), p. 121. Elsevier, Amsterdam, 1980.

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

24. Weeks, T. J., Jr., and Bolton, A. P., *J. Chem. Soc. Faraday Trans. 1* **70**, 1676 (1974).

25. Weeks, T. J., Jr., Angel, C. L., Ladd, I. R., and Bolton, A. P., *J. Catal.* **33**, 256 (1974).

26. Venuto, P. B., Hamilton, L. A., and Landis, P. S., *J. Catal.* **5**, 484 (1986).

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

28. Langner, B. E., *J. Catal.* **65**, 416 (1980).

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