

5.3.4 Structural Isomerization

As mentioned earlier, the selectivity for isobutane in the C₄-fraction varied in the order Cs ~ Rb < K << Na < Li << H. Structural isomerization occurred primarily as a result of secondary reactions of olefins on the acid sites in the zeolites. As discussed in the previous section, formation of branched hydrocarbons from olefins can result from decomposition of oligomers formed on acid sites. Datka⁽¹⁰²⁾ has shown that the higher the concentration and strength of the acid sites in a zeolite, the more branched the olefin oligomers. Thus, a decomposition of the oligomer formed on the more acidic zeolites would result in the formation of more isoparaffins. Weeks and Bolton⁽¹⁰⁷⁾ have also demonstrated that the major products of 1-butene reaction on HY zeolite at 200 °C are isobutane and isopentane formed by the breakdown of polymeric compounds.

The formation of isobutane via a bifunctional mechanism, i.e., direct isomerization of n-butenes to isobutenes on acid sites followed by hydrogenation on metal sites, is less likely, since the former reaction is known to be very slow compared to the carbonium ion-type reactions such as olefin oligomerization.⁽⁶⁶⁾

In order to gain insight into possible mass transfer effects on structural isomerization, a plot was made of the fraction of isobutane in the C₄-fraction versus E_a at

constant conversion and is shown in Figure 5.4. Since the formation of isobutane involves acid sites and since RuHY has significantly greater number of acid sites than the other zeolite-supported catalysts, it may be expected that it would deviate from any trend established by the other catalysts. This appears to be the case, as is apparent in Figure 5.4. Thus a possible effect of diffusion on structural isomerization, represented by the line in Figure 5.4 for catalysts with comparable acid site concentrations cannot be completely ruled out. Steric factors may also influence olefin oligomerization in the presence of the larger cations such as K, Rb and Cs, thus inhibiting formation of the typical oligomer breakdown products such as isoparaffins.

There is also a good possibility that the nature of the alkali cations modified the properties of the acid sites. Certainly, the trend in selectivity for isobutane suggests this. Thus, at this time, it may be concluded that both modifications of the acid sites by the alkali cations and mass transfer effects may play a role in structural isomerization of olefins during CO hydrogenation.

Secondary acid-catalyzed reactions will be dealt with in more detail in the following chapter.

5.4 Conclusions

The results presented in this paper provide evidence that the nature of the cations used to neutralize the AlO_4^- groups of the zeolite can have a marked effect on the catalytic properties of ruthenium for CO hydrogenation in ion-exchanged zeolite-supported Ru catalysts. Although the nature of the neutralizing alkali cations in Y-zeolites has hardly any influence on the specific activity of the catalysts or on the overall chain growth probability, it has a pronounced effect on the olefin and branched hydrocarbon selectivities. Electronic and electrostatic field effects on reactions occurring on the metal particles may easily be ruled out. However, variations in the strength of the acid sites as a function of the nature of the neutralizing alkali cations as well as mass transfer limitations apparently play a major role in shaping the olefin and isoparaffin selectivities. Indeed, one probable reason for the variation of the olefin-to-paraffin ratio with the nature of the cation is the enhancement of olefin hydrogenation by a hydrogen transfer mechanism on the acid sites following the decomposition of oligomers adsorbed on these sites. Spillover hydrogen may also enhance this process of olefin hydrogenation on the acid sites. The selectivity for isobutane, suggested to be formed by the breakdown of branched oligomers, was found to decrease with increasing

cation radius. The variation in the strength of the acid sites generated during reduction as a function of the nature of the neutralizing alkali cations as well as steric factors are believed to have produced this effect. Finally, evidence suggests that the nature of the neutralizing cations in the zeolite can indirectly produce mass transfer effects during reaction as a result of effecting a uniform versus a shell distribution of Ru in the zeolites during catalyst preparation.

6.0 SECONDARY REACTIONS DURING CO HYDROGENATION ON ZEOLITE-SUPPORTED METAL CATALYSTS: INFLUENCE OF ALKALI CATIONS

6.1 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, coking, etc.

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⁽¹⁰⁸⁾ 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⁽¹⁷⁾ and Fe⁽¹⁸⁾, 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 significantly altered by secondary reactions. (8,14-15,19,109) Chen et al. (14-15), for example, have observed that, when CO hydrogenation is carried out over zeolite-supported Ru catalysts, the formation of iso-paraffins is enhanced with increasing concentration and acid strength of the zeolite hydroxyl groups.

In the study of CO hydrogenation on a series of Y-zeolite supported Ru catalysts reported in chapter 5, 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 chapter reports the results of a further study to determine the nature as well as activity and selectivity of those sites involved in the secondary reactions.

6.2 Experimental

6.2.1 Materials

Some of the zeolite-supported ruthenium catalysts described in previous chapters were used in this study. The catalyst containing the highest concentration of Brønsted acid sites, RuHY obtained after reduction of RuNH_4Y , was re-exchanged 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 ($\text{M} = \text{Li}, \text{Na}, \text{or Rb}$) with similar acid site concentrations following calcination to form MHY were prepared by ion-exchange of NH_4Y zeolite with the alkali nitrates and their composition determined by AA, as described in chapter 3. The results of this elemental analysis are given in Table 6.1 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.

6.2.2 Reaction studies

CO hydrogenation was carried out over the series of RuY catalysts at atmospheric pressure and in the 483-573 K temperature range. Details of the reaction and product .pa

Table 6.1 Elemental Analysis Results

Catalyst	Na/Al	M/Al*	NH ₄ /Al
NH ₄ Y	0.20	--	0.80
LiNH ₄ Y	0.16	0.24	0.60
NaNH ₄ Y	0.43	--	0.57
RbNH ₄ Y	0.16	0.22	0.62

* M = Li, Rb

analysis procedures have been reported in chapter 3.

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. Details of this reaction are also given in chapter 3.

6.3 Results and Discussion

6.3.1 CO Hydrogenation

In the 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 5.1). 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, the product composition indicated significant differences in olefin/paraffin ratios and iso-paraffin 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, iso-paraffins, 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 ~ Rb > K > Na > Li ~ H. Figure 6.1 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 iso-butane 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 iso-butane. 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 iso-butane 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 iso-butane), RuHY which had been re-exchanged with K^+ after Ru reduction in order to eliminate the Brønsted (H^+) sites, RuRbY (a catalyst producing essentially no iso-butane), and RuRbY followed in the catalyst bed by HY. The results listed in

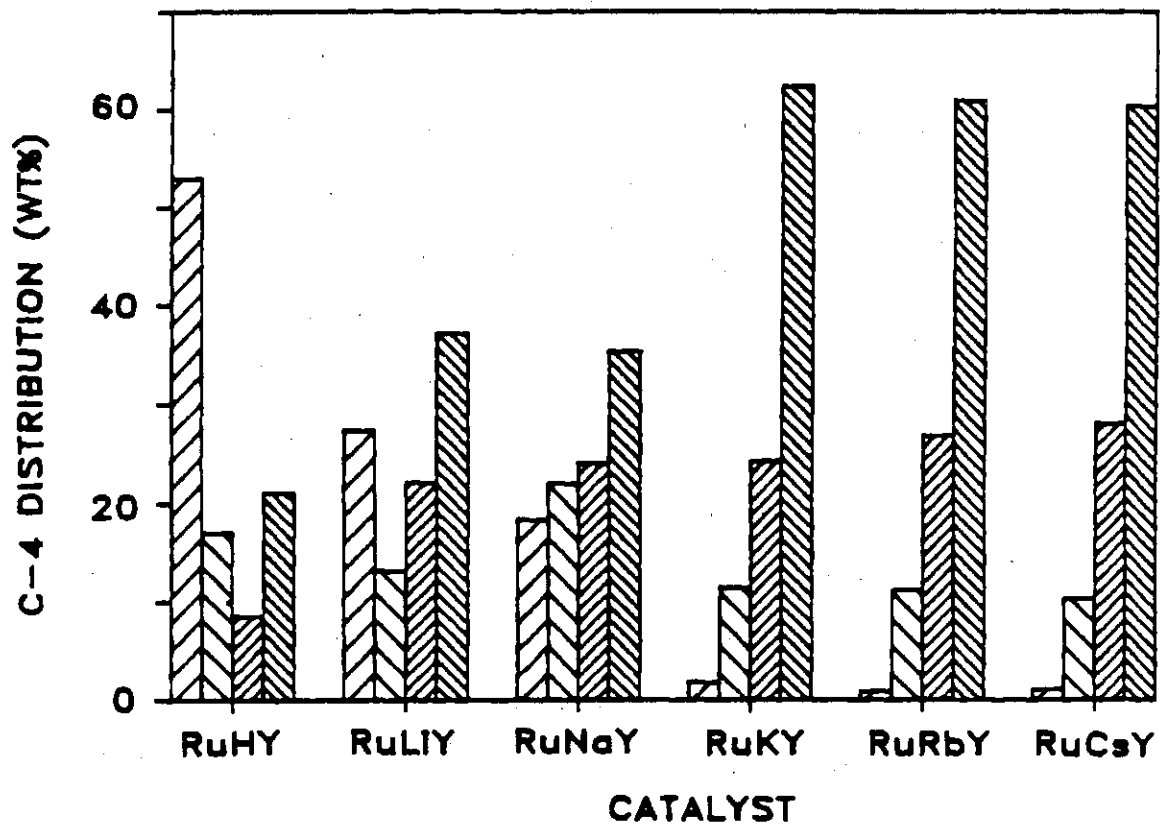


Figure 6.1 C₄-isomer distribution from CO hydrogenation over RuY-zeolites at 523 K;

- (/) Iso-butane
- (-) N-butane
- (|) 1-butene
- (X) 2-butenes

Table 6.2 show that at 523 K RuHY gave 53% iso-butane (based on the total amount of C_4). When the Brønsted acid sites in this catalyst were replaced by potassium cations, the iso-butane was no longer obtained and the propylene-to-propane ratio increased significantly. On the other hand, RuRbY yielded only very small quantities of iso-butane; however, when 0.2 g of HY was added at the tail end of the reactor bed in a separate layer, the iso-butane 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 iso-paraffins were obtained by Chen et al. (14) 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 iso-butane 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, 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

Table 6.2 Effect of Acidity on Olefin and Isobutane Selectivities^(a)

Catalyst	Propene/Propene 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, H₂/CO = 1.

(b) RuHY treated in 0.1 N K₂CO₃ solution after reduction.

(c) RuRbY and HY in separate layers.

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.

6.3.2 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 used in CO hydrogenation. The olefin reactions were first carried out over the non-acidic alkali form of the zeolites in the presence of either helium or hydrogen. Topchieva et al.⁽¹¹⁰⁾ 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, at 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 6.3). Thus, only double bond shift and cis-trans isomerization 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.⁽⁵⁸⁾ Several authors^(96,111-114) 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.^(96,114) It has been suggested that any activity of these zeolites is due to the presence of divalent cations such as Ca^{2+} ions which may be present as impurities.⁽¹¹¹⁾ 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.⁽¹¹²⁻¹¹³⁾ 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 6.3). 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.

Table 6.3 Butene Isomerization on Non-Acidic Alkali Zeolites*

	LiY	NaY	RbY
Conversion (%)	7.5	7.9	6.4
Activity [mol x 10 ⁻³ /(h)(g)]	1.9	2.0	1.6
cis/trans ratio	0.8	0.6	1.7

* Reaction Conditions: 523 K, 1 atm,
Flow rate = 100 ml/min,
1.5% 1-butene in He,
5 min of reaction.