2.1.2 Product Selectivity Control

In recent years, the use of zeolites in F-T synthesis has produced significant deviations from the normal ASF behavior. For instance, the use of composite catalysts, consisting of physical mixtures of an F-T catalyst and a zeolite, has been demonstrated to limit the normal hydrocarbon chain growth and to promote substantial aromatic formation in the gasoline range.(45-48) This behavior of the composite catalysts was attributed to the carboniogenic activity and the shape selective character exhibited by the zeolite. It was established that the zeolite serves to intercept the F-T intermediates in the chain growth process and convert them by acid-catalyzed reactions into hydrocarbons inactive for further chain growth.

Another approach used to modify the ASF polymerization mechanism consists of entrapping metals, such as Ru(17) and Fe,(18) active in F-T synthesis, inside zeolite pores. The metal-zeolite catalysts were found to be as effective as the composite catalysts in limiting the chain growth of the F-T products.

2.2 Zeolite-Supported Metals

Besides the molecular dimensions and the uniformity of the zeolite pore network which give these materials their shape-selective properties, zeolites have also a number of other features which makes them attractive for F-T synthesis. One of the main advantages of zeolites over conventional supports such as alumina is their ion-exchange properties. Zeolites, owing to the isomorphous substitution of trivalent aluminum for tetravalent silicon in the lattice, have a net negative charge which is neutralized by cations. These can be exchanged with other cations of a different nature. This ion-exchange capability permits preparation of highly dispersed zeolite-supported metals under controlled pretreatment conditions. Furthermore, by changing the nature of the remaining neutralizing cations and the degree of exchange, the properties of the metal catalyst may be changed as desired.

During the preparation of metal-zeolite catalysts by ion-exchange with a transition metal ion, alkali cations M^+ are replaced by metal complex ions, such as $[Ru(NH_3)_6]^{3+}$ for Ru/zeolite catalysts:

$$\begin{aligned} &\{m[Ru(NH_3)_6]^{+3} \;+\; 3mCl^-\} \;+\; \{nM^+\ [Y]^{n-}\} \;{-}{-}{-}{-}{>} \\ &\qquad \{m[Ru(NH_3)_6]^{3+}\ (n-3m)M^+\ [Y]^{n-}\} \;+\; 3mMCl \end{aligned} \tag{2-6}$$

The reduction leads then to the simultaneous formation of acid sites as illustrated in Figure 2.2 where the complex ion $[Ru(NH_3)_6]^{3+}$ is shown as Ru^{3+} for simplicity. Depending on the concentration and strength of the acid sites, metal-support interactions may be expected to be more or less

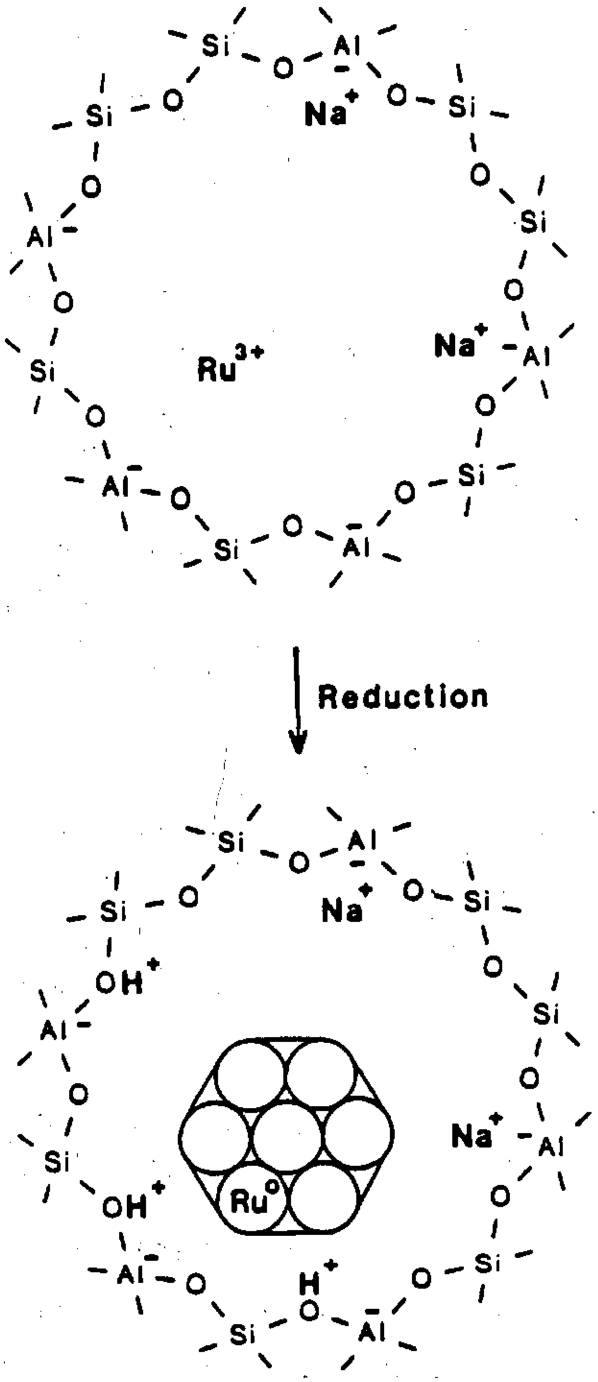


Figure 2.2 Reduction Scheme of Ion-Exchanged Ru/Zeolites

significant, thereby inducing changes in the adsorption and catalytic properties of the zeolite-supported metals. For instance, various metals have been found to lose their ability to chemisorb H_2 when highly dispersed on zeolites.(21,49) In a recent detailed investigation of the chemisorption properties of Ru supported on a series of zeolites of different acidities, Wang et al.(21) have observed significant suppression of hydrogen chemisorption for certain catalysts, while CO adsorption was apparently not suppressed. It was established that Ru catalysts prepared by vapor impregnation do not exhibit this hydrogen chemisorption suppression while the ones prepared by ion-exchange do. The major difference between the two preparation methods lies in the formation of acidic hydroxyl groups in the ion-exchanged catalysts, as illustrated in Figure 2, while in the catalysts prepared by vapor impregnation, the zeolite does not undergo any chemical changes and possess little acidity. Increasing the strength of the acidic hydroxyl groups by increasing the Si/Al ratio resulted also in larger CO/H ratios indicative of significant hydrogen chemisorption suppression. Among the possible interpretations proposed by the various authors are that the highly dispersed metal loses its metallic properties including those important for chemisorption, or that a partial electron transfer from the metal atoms to electron-acceptor sites of the zeolite support results in suppression of hydrogen chemisorption. In light of IR studies of CO adsorbed on PdY, PtY, and zeolite-supported Ru, an influence of the acidity of the zeolite support on the electronic structure of the metal particles has been demonstrated.(20,49-52) Evidence has been provided that the greater the acidity of the support, the greater the electron-deficient character of the metal.

There seems to be some good evidence that the acidity of zeolites used as supports for F-T active metals has a pronounced effect not only on selectivity but also on the catalyst activity. Indeed, several workers have observed a trend of increasing activity for CO hydrogenation with increasing acidity of the support.(23,53-55) The enhancement of the activity of the metal as well as changes in selectivity in more acidic zeolites were explained in most cases by metal-zeolite interactions which give an electron-deficient character to the supported metal in the more acidic supports.

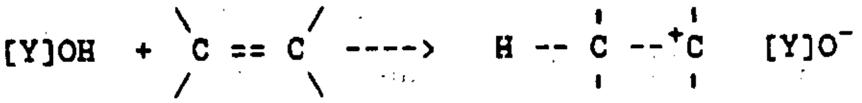
Besides the zeolite acidity, a large number of parameters may change the environment of metal particles entrapped in zeolites and hence their catalytic properties. When an F-T metal is exchanged into a zeolite, at relatively low loadings (for example 3%), a great proportion of the neutralizing cations remain in the zeolite and constitute part of the environment of the metal particles. In view of the well known effects on selectivity of alkali promoters in conventional F-T catalysts,(24-25) the remaining neutralizing cations in the zeolite might be also expected to influence the metal properties for CO hydrogenation over zeolite-supported F-T catalysts. Indeed, Chen et al.(15) investigating the effect of the Si/Al ratio of zeolite supports on the catalytic properties of Ru in F-T synthesis found the methane selectivity to correlate best with the concentration of the neutralizing sodium cations remaining in the zeolites. In addition, when potassium was the neutralizing cation as in the case of RuKL, a much lower methane selectivity than in the case of the sodium neutralized zeolites was observed. These findings were in agreement with the classical behavior of alkali promoters in F-T catalysts which are known to shift the selectivity towards the heavier products as their basicity increases, with a subsequent decrease in methane formation. The selectivity towards products of higher molecular weight in F-T synthesis on iron catalysts promoted with Group I alkali has been reported to depend on the relative basicity of the promoter, thus increasing in the order Li, Na, K, and Rb.(34) The olefin selectivity is also enhanced in the same order.

In the study reported by Chen et al.(15), no effect of the nature or concentration of the alkali cations remaining in the zeolite on the olefin fraction was observed and the interpretation of their results were complicated by the fact that a series of zeolites with different Si/Al ratios and different structures was used. It may also be noted that to date, except for one study reported recently by Leith,(56) the effect of the nature of the neutralizing alkali cations on the adsorption and catalytic properties of Group VIII metals exchanged in zeolites has never been investigated.

2.3 Zeolite-Catalyzed Reactions

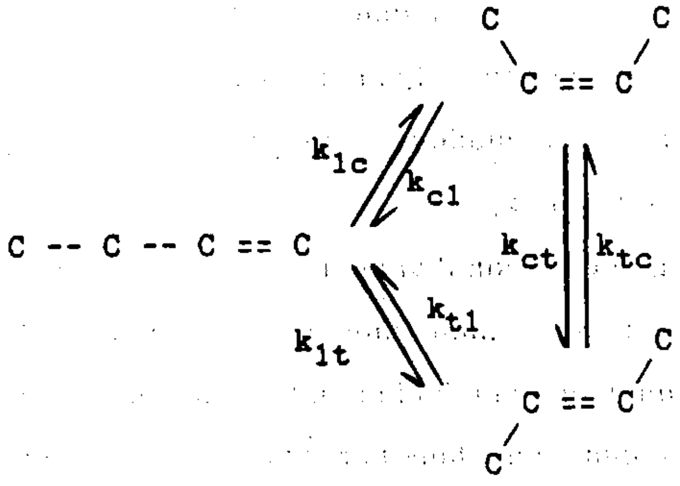
Since olefins tend to be the major primary hydrocarbon products in CO hydrogenation over transition metals, a number of secondary reactions on the zeolite support may also be expected to significantly modify product selectivity. Depending on the concentration and strength of the acid sites formed during catalyst preparation and the reaction conditions, these acid-catalyzed secondary reactions may include isomerization, oligomerization, cracking, hydrogen transfer, polymerization, cyclization, aromatization, or coking.

Acid-catalyzed transformations of olefins have been extensively studied since they represent one of the most important routes for most hydrocarbon conversions. Numerous books and reviews on the subject can be found in the literature.(57-65) It is generally accepted that acid-catalyzed reactions of olefins proceed through a carbonium ion intermediate formed by protonation of an olefin by a Brønsted acid site:(57)



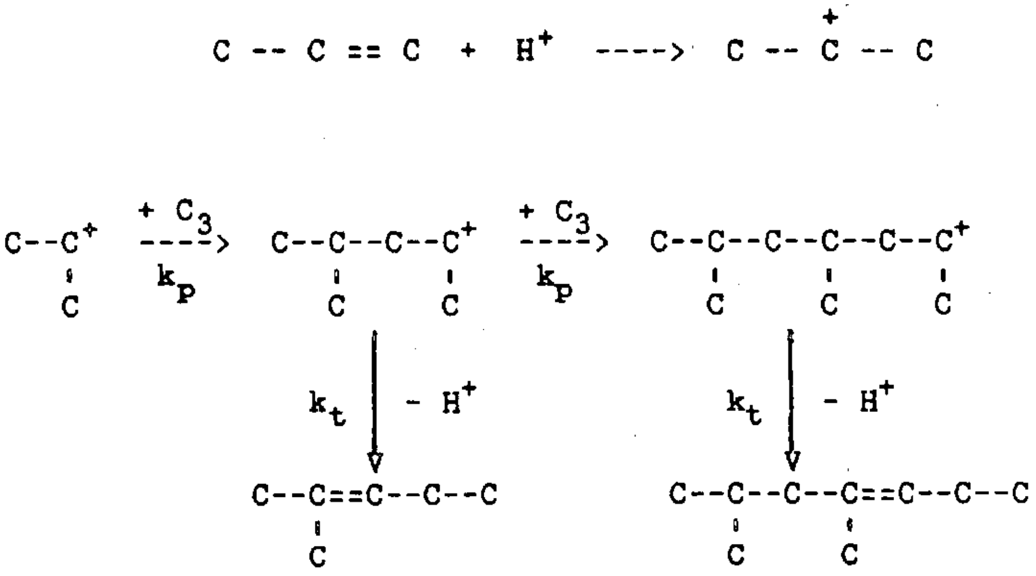
$$[Y]OH + \mathrm{C{=}C} \longrightarrow H\text{--}C\text{--}{}^{+}C \quad [Y]O^{-}$$

These carbonium ion intermediates are positively charged, highly reactive surface species which, depending on the strength of the active site and the reaction conditions, can undergo all types of reactions. Under mild conditions and weak acidity, only the simplest of all acid-catalyzed reactions of olefins, isomerization, may take place. The latter involves double-bond migration and cis-trans isomerization, as illustrated in the following scheme for n-butene isomerization:



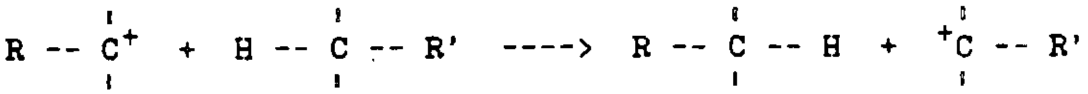
where the k's are rate constants for the reactions of 1-butene to cis-2-butene and trans-2-butene and the reaction of these latters two species to form each other. The rate of the overall reaction, i.e., butene isomerization, if carried out under conditions where no side reactions can occur, may serve as a relative measure of the acid strength of the zeolite active sites.(66)

Other olefin transformations such as oligomerization and polymerization may be expected to occur as the acid strength of the zeolite increases and/or under more severe reaction conditions, especially higher temperatures. These reactions also proceed via carbonium ion intermediates,(57) as illustrated for propylene reaction in the following scheme:



$$C{-}{-}C{=}{=}C + H^+ \longrightarrow C{-}{-}\overset{+}{C}{-}{-}C$$

where k_p and k_t are the rate constants of propagation and termination, respectively. Secondary cracking and hydrogen transfer reactions may be significant when these oligomerization reactions are carried out on zeolites.(58,62) The hydrogen transfer reactions would obviously provide a second mechanism for the formation of paraffins on zeolite-supported metal catalysts. This reaction can be represented schematically as follows:



$$R -- \overset{|}{\underset{|}{C^{+}}} + H -- \overset{|}{\underset{|}{C}} -- R' \text{ ----> } R -- \overset{|}{\underset{|}{C}} -- H + {}^{+}\overset{|}{\underset{|}{C}} -- R'$$

A number of other olefin reactions which all fit the carbonium ion theory may be observed on zeolite-supported catalysts which contain acid sites. An important side reaction which is a consequence of the hydrogen transfer reactions is coke formation on the catalyst surface. This reaction accompanies most hydrocarbon reactions on zeolites. Obviously, various parameters such as the nature of neutralizing Group IA cations remaining in the zeolite support, the degree of ion-exchange, the silicon-to-aluminum ratio of the zeolites, which all may influence the strength of the acid sites, may directly or indirectly affect olefin transformations. Thus, it is worthwhile to assess the effect of these parameters when products are produced such as those from CO hydrogenation.

2.4 Diffusion in Zeolites

The kinetics of certain reactions occurring within a zeolite pore network may be partially controlled by diffusion, since most zeolite pores are uniform and of sizes characteristic of simple organic molecules. Diffusion in zeolites is in the limit of the Knudsen region that Weisz called the "configurational regime".(67) Thus, for hydrocarbon diffusion in zeolites, the diffusivities are usually very small (10^{-8} - 10^{-10}).(68-72) Furthermore, it takes only a small amount of strongly adsorbed material to block the zeolite channels and, hence, have a strong effect on diffusivity. For instance, little intracrystalline polymerization is observed inside H-mordenite, while considerable amounts of polymers are formed in HY-zeolites.(58) Thus, the space available in the zeolite cavities may determine the rate of propagation and the molecular weight of the polymer.

3.0 EXPERIMENTAL

3.1 Materials

The zeolites NaY and NH_4Y (80% exchanged), NaX and KL were obtained from Strem Chemicals. The NH_4- and Na-mordenite were obtained from Norton.

3.1.1 Preparation of Fully-Exchanged Alkali Zeolites

Extensive ion exchange of NaY with alkali nitrates (Alfa Products, ultrapure) was carried out in order to obtain MY (M = Li, K, Rb, Cs) zeolites with an exchange level as high as possible. NaY was vigorously stirred at room temperature for 18 hours in an aqueous solution containing a twofold equivalent excess of MNO_3. Repeated contacts and higher temperatures were used in the case of the large sized cations. Finally, the MY samples were washed several times with distilled water and then dried at 323 K.

3.1.2 Preparation of Zeolite-Supported Ru Catalysts

The Ru-loaded zeolites (LiY, NaY, KY, RbY, CsY, NH_4Y, NaX, KL, Na-mordenite) were prepared by ion-exchange with $Ru(NH_3)_6Cl_3$ (Strem Chemicals) which had been first dissolved in a very dilute hydrochloric acid aqueous solution (pH = 4.5). Subsequently, the solution was mixed with the required amount of a given zeolite and stirred continuously for 50 hours at room temperature. The solid was then filtered, thoroughly washed with deionized water in order to free it of Cl ions, and dried in air for 48 hours at 323 K.

The resulting ruthenium catalyst precursors were then decomposed under vacuum, while heating at 0.5 K min^{-1} up to 673 K. This temperature was maintained for 4-5 hours. The samples were then reduced for one hour in hydrogen (approximately 400 torr) at that maximum temperature. As it will be shown in the next chapter, this decomposition method using vacuum results in higher dispersions of the metal than that resulting from decomposition under flowing helium. This is especially the case when the ruthenium-zeolites contain large-sized cations such as Rb and Cs.

3.1.3 Preparation of $RuSiO_2$

In order to compare properties of Ru/zeolite catalysts with a more conventional system, one silica-supported Ru sample was prepared following the ion-exchange method recently reported by Gay.(73) A calculated amount of $RuCl_3$-$1.5H_2O$ (Strem) was dissolved in 6 ml H_2O per gram of SiO_2 used and added to the SiO_2 (Strem Chemicals) under vigorous shaking. 0.8 ml of hydrazine hydrate (Fisher Scientific) per gram silica was then added slowly in order to generate in situ Ru(II) ammine species.(74) The mixture was stirred continuously for several hours, then washed with cold 1M ammonia solution (Fisher Scientific), and dried at 373 K for three hours. The sample was then decomposed in helium flowing at 60 cm^3/min. The temperature was also ramped at 0.5 K/min from ambient to 673 K where it was held for 4-5 hours. This pretreatment was followed by a 2 hour reduction in hydrogen flowing at the same rate. UHP grade (Air Products) helium was further purified by passing it through a heated copper trap to remove oxygen traces and then through a molecular sieve trap to remove water. Hydrogen was passed through an Engelhard Deoxo purifier followed by a molecular sieve trap before contacting the catalyst.

3.1.4 Preparation of Partially-Exchanged Alkali Y-Zeolites

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 hours.