

7.3.4 Deactivation Characteristics of H-mordenite and HY-zeolite

Since the selectivity for iso-butane obtained when CO hydrogenation was carried out over RuNa-mordenite was found to be not significantly different from that obtained on RuNaY, it was suspected that the fast deactivation of the strong acid sites on the mordenite-based catalyst was the reason for not obtaining higher iso-butane yields on that catalyst. In order to investigate the deactivation characteristic of the acid sites present in these two zeolites, 1-butene reaction was carried out on the acidic form of these zeolites, HY and H-mordenite. The yield of isoparaffins from the transformation of olefins on acid sites can be taken as a measure of the oligomerization, polymerization, hydrogen transfer, and cracking activity of these catalysts. Therefore, the formation rate of isobutane on H-mordenite and HY-zeolite is chosen here to illustrate the deactivation characteristics of these two catalysts (see Figures 7.3 and 7.4). It can be seen that the activity for isobutane formation on H-mordenite, which was initially much higher than on HY, dropped rapidly to zero in the first few minutes of reaction, while on HY, a relatively constant activity was maintained for a much longer period.

The rates of formation of cis-2-butene on both HY and H-mordenite are included in Figures 7.3 and 7.4 to

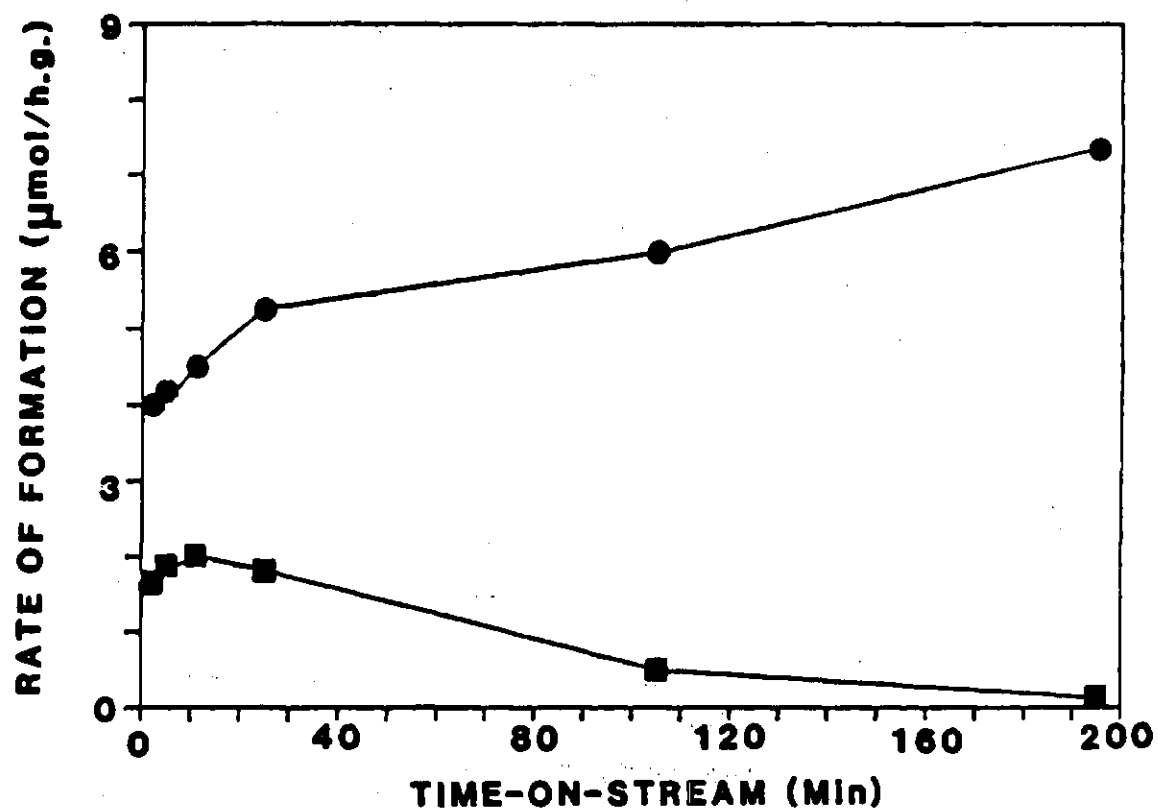


Figure 7.3 Iso-butane (■) and Cis-2-butene (●) Formation Rates vs Time-on-Stream on HY

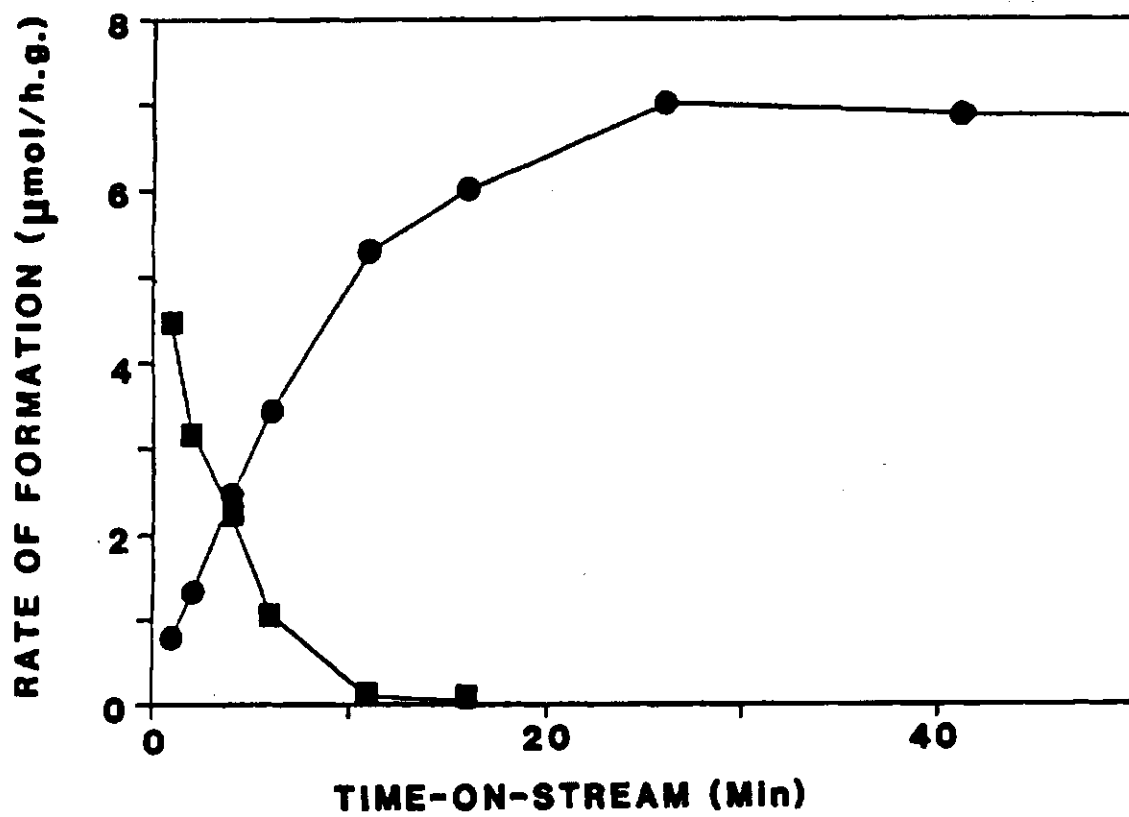


Figure 7.4 Iso-butane (■) and Cis-2-butene (●) Formation Rates vs Time-on-Stream on H-mordenite

illustrate how the isomerization activity varies with time-on-stream. Although the cis/trans ratio remained practically constant at its equilibrium value over the whole reaction period, the catalyst activities for isomerization increased as the oligomerization-cracking reactions decreased. After less than 10 min of reaction, the reaction path on H-mordenite, shifted completely from the oligomerization-cracking reaction path, usually observed in the presence of strong acid sites, to double bond migration and cis-trans isomerization which can occur even on very weak acid sites. (102,119) It may also be observed that even after several hours of reaction, the activity of both catalysts for isomerization was still at its highest value, suggesting that the protons which serve as reaction sites for the isomerization reactions can be furnished by the carbonaceous residues forming during reaction.

These results, suggest that the strong acid sites, active for the oligomerization and cracking reactions of olefins, deactivate much more rapidly in mordenite than in Y-zeolites. Therefore, when the results of CO hydrogenation over the various zeolite-supported catalysts are compared after 5 min of reaction, it may be assumed that the strong acid sites on zeolites such as the mordenite are already in an advanced deactivation state, resulting in poorer selectivities for isoparaffins.

7.4 Conclusion

This work has established that the bifunctional nature of the zeolite-supported F-T catalysts can play a significant role in the selectivities of these catalysts in CO hydrogenation. The acidity of the zeolite has hardly any effect on TOF for CO hydrogenation, suggesting that the electronic properties of the metal are unaffected by the acidity strength of the support under reaction conditions. Hence, proposals about metal-support interactions being responsible for variations in product selectivities from CO hydrogenation on zeolite-supported F-T catalysts seem unlikely. Instead, acid sites in the zeolite can account for selectivity differences introduced as a result of secondary reactions of the primary olefinic F-T products, such as isomerization, oligomerization, cracking, hydrogen transfer, and coke formation. As illustrated schematically in Figure 7.5, the relative importance of these acid-catalyzed reactions is a function of the strength of the zeolite acid sites, which itself is a function of the Si/Al ratio of the zeolite. These secondary reactions which convert rapidly the primary F-T products are at the origin of the major variations in the selectivities of the zeolite-supported F-T catalysts with the zeolite acidity.

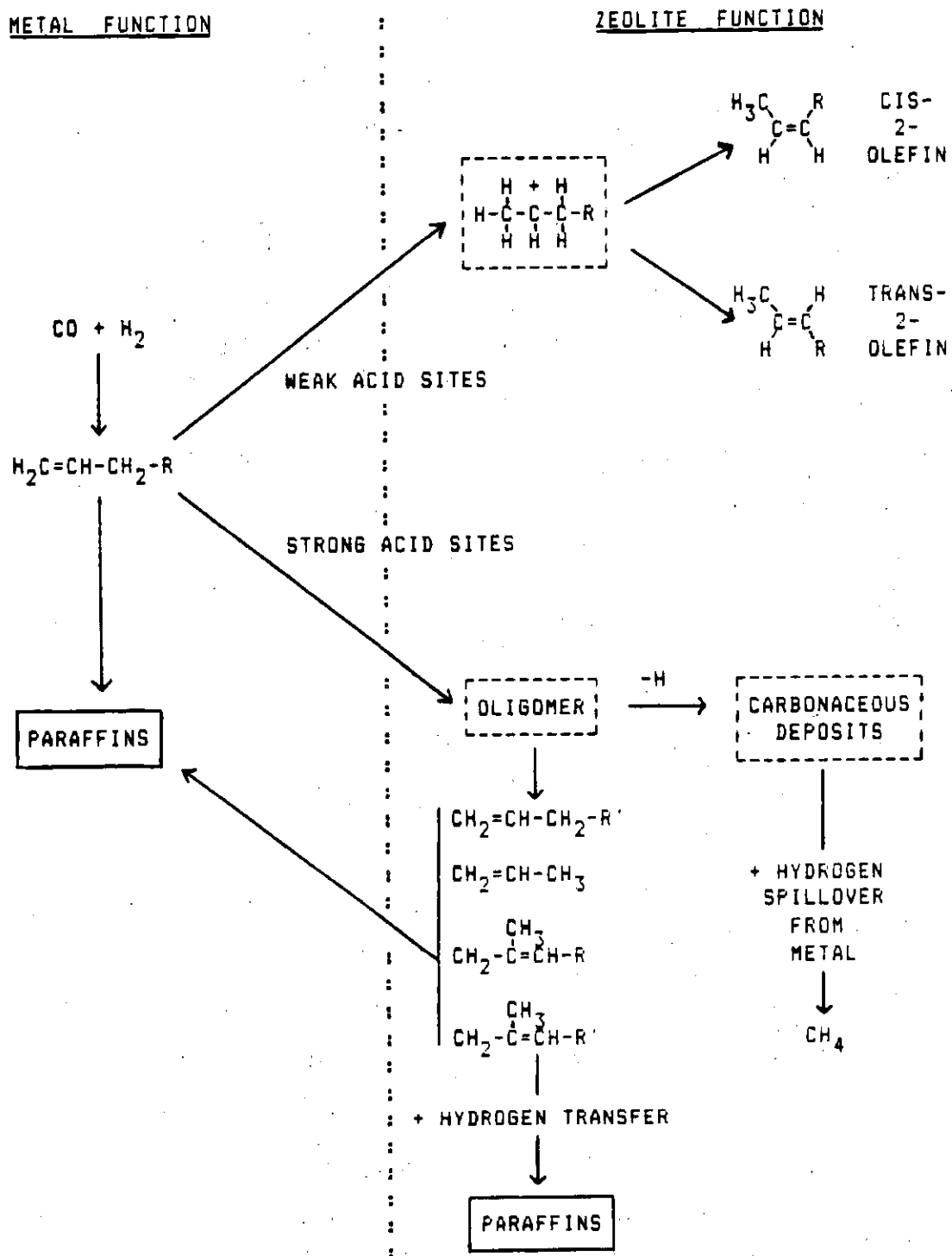


Figure 7.5 Reaction Scheme for CO Hydrogenation on Ru/Zeolites

7.0 SUMMARY

Zeolites offer enormous potential in the search for means by which the product selectivity of F-T catalysts may be controlled. Besides their shape-selective properties, their ion-exchange capabilities permit preparation of highly dispersed zeolite-supported metal catalysts having also acid sites. The properties of these acid sites can be varied and adapted to specific needs by changing the nature and concentration of the neutralizing cations.

Previous results for zeolite-supported Ru prepared by ion-exchange suggested a possible effect of the nature and concentration of the neutralizing cations in the zeolite on the catalytic properties of the metal. The interpretation of these results were complicated by the fact that a series of zeolites with different Si/Al ratios and different Ru particle sizes was used. In this study, a series of RuY catalysts prepared from NH_4Y , LiY, NaY, KY, RbY, and CsY zeolites by ion-exchange with ruthenium hexammine chloride and having comparable metal particle diameters were used to investigate the role of the neutralizing cations in CO hydrogenation.

In order to prepare catalysts with similar metal dispersions, the influence of the decomposition/reduction method on metal dispersion of Y-zeolite-supported Ru catalysts prepared by ion-exchange was studied.

Decomposition of the metal precursor using a dynamic high vacuum resulted in higher dispersions of the metal than found when decomposition was carried out in flowing inert gas. This is especially the case for Y-zeolites containing neutralizing cations other than sodium or potassium. This appears to be related to the more efficient removal of water from the zeolite under vacuum as well as the uniformity of Ru distribution in the zeolite crystallites.

Using catalysts with similar metal dispersions, it was found that the nature of the group IA cations has little effect on chemisorptive properties and on the activity and chain growth probability in CO hydrogenation on Ru. However, the nature of the cations produced changes in secondary reactions of primary olefinic products as a result of differences produced during catalyst preparation in Ru distribution in the zeolite crystallites and of modifications in the acid sites generated during reduction of the Ru.

The effect of neutralizing cations on the secondary reactions of the primary products from CO hydrogenation over ion-exchanged zeolite-supported Ru catalysts was further investigated using zeolites having the different alkali cations (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) but no metal sites. The transformation of olefins (propylene and butene) on the zeolites, under similar conditions to those used for CO

hydrogenation, was 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, cracking, and hydrogen transfer.

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 molecular weight of the alkali cation used.

The effect of zeolite acidity on the product distribution in CO hydrogenation over ion-exchanged zeolite-supported Ru catalysts was investigated further using zeolites with different Si/Al ratios. CO hydrogenation over RuNaX , RuNaY , RuKL , and RuNa -mordenite and the transformation of 1-butene on the zeolites without the metal, under similar conditions to those used for CO

hydrogenation, were studied in order to understand the effect of the Si/Al ratio on possible secondary reactions of the primary olefinic products of F-T synthesis. In conclusion, this study has established the importance of the bifunctional properties of zeolite-supported F-T catalysts in modifying catalyst selectivity. This modification is achieved by varying the strength of the zeolite acid sites which are the most important active centers for secondary reactions of the primary olefinic F-T products. Depending on the strength of the acid sites, a function of the Si/Al ratio and the remaining group IA cations, various competitive reaction paths can be observed for the transformation of the olefinic compounds, resulting in particular product distributions.