

7.0 SECONDARY REACTIONS DURING CO HYDROGENATION ON ZEOLITE-SUPPORTED METAL CATALYSTS: EFFECT OF SI/AL RATIO

7.1 Introduction

During the study investigating the effect of the nature of the neutralizing alkali cations on CO hydrogenation over Ru/Y-zeolites and the possible secondary reactions of the primary F-T products, it was established that the concentration and the acid strength of the protonic sites have a significant effect on acid-catalyzed reactions such as isomerization, oligomerization, cracking, hydrogen transfer, etc. Although the variation in the strength of the acid sites of the zeolite with the nature of the alkali cation was relatively small, the secondary acid-catalyzed reactions produced significantly different isomer distributions and different olefin-to-paraffin ratios depending on the nature of the alkali cations present in the zeolite.

The work being reported in the present chapter was undertaken to investigate further these secondary reactions over zeolite supports having a wider range of acidity strength. CO hydrogenation was carried out over zeolite-supported ruthenium catalysts using zeolites NaX, NaY, KL, and Na-mordenite which all have different Si/Al ratios. The reaction of butene on the various zeolites not containing

any metal and on the acidic forms of Y and mordenite zeolites was also carried out under temperature and pressure conditions similar to those used for CO hydrogenation. This was done in order to determine the activity of the constituent atoms or ions of the zeolite framework responsible for secondary reactions of the primary olefins formed during CO hydrogenation on the metal particles dispersed within these zeolites.

7.2 Experimental

7.2.1 Materials

Zeolite-supported Ru catalysts were prepared by ion-exchange of the zeolites NaX, NaY, KL and Na-mordenite with $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ following the same preparation method described in chapter 3. After decomposition under vacuum and reduction in hydrogen at 673 K, the resulting Ru catalysts were then characterized by atomic absorption, and chemisorption of hydrogen and carbon monoxide. The physical characteristics of these catalysts are given in chapter 4.

The zeolite NH_4Y and the ammonium form of the mordenite (NH_4 -mordenite) were also used for the olefin reactions.

7.2.2 Reaction Studies

CO hydrogenation was carried out as also described in chapter 3. To investigate further the effect of Si/Al ratio

on the possible support-catalyzed secondary reactions of the primary olefinic products from CO hydrogenation, olefin reactions were carried out on the zeolites NaX, NaY, KL, and Na-mordenite without Ru. Propylene and 1-butene transformations were used as model reactions under similar conditions to those of CO hydrogenation. Detailed description of these reactions and analysis procedures are also given in chapter 3.

The butene reaction was also carried out on the acidic forms of Y-zeolite and mordenite, i.e., the zeolites HY and H-mordenite being obtained after decomposition of the ammonium form at 673 K for two hours in flowing hydrogen. The deactivation characteristics of these zeolites for the olefin reactions were also investigated.

7.3 Results and Discussion

7.3.1 Catalyst activities for CO Hydrogenation

Table 7.1 compares the turnover frequencies (TOF) for CO conversion based on the estimated site concentrations provided by hydrogen chemisorption measurements. The calculated TOF's for CO conversion on RuKL and RuNa-mordenite should be considered as maximum values since some suppression of hydrogen chemisorption is suggested by the higher CO/H ratios obtained for these catalysts. Although

Table 7.1 Catalytic Properties of Ru/Zeolites for CO Hydrogenation^(a)

Catalyst	TOF ^(b) (s ⁻¹ × 10 ³)	E _a (kJ/mol)	Selectivity (wt%)				
			C ₁	C ₂	C ₃	C ₄	C ₅ ⁺
RuNaX	5.8	99.8	17.3	11.7	24.8	19.4	26.7
RuNaY	6.9	66.1	32.7	14.0	21.5	17.0	14.8
RuKY	7.8	80.7	30.7	13.7	23.5	15.8	16.2
RuKL	8.4	106.9	49.5	12.3	17.8	11.7	8.7
RuNaM ^(c)	8.0	116.4	56.0	16.6	12.3	9.9	5.2

(a) Reaction Conditions: 523 K, 1 atm, H₂/CO = 1, 5 min of reaction.

(b) Based on H₂ chemisorption results..

(c) M = Mordenite.

RuKY has the same Si/Al ratio as RuNaY, it is included in Table 7.1 since it allows a better comparison with RuKL which has a different Si/Al ratio but contains the same neutralizing cations.

It may be noted that, since all the catalysts used in this study have similar metal loadings, the concentration of the Brønsted acid sites formed during reduction of the Ru should be comparable for all the catalysts (see Chapter 2). It is well known that the higher the Si/Al ratio (for $\text{Si/Al} < 6$) of a zeolite, the stronger are its acid sites.⁽⁸⁷⁾ It has also been suggested that, due to possible interaction between the metal and the acidic hydroxyl groups of the support which materializes by a transfer of electrons from the metal to the support, an increasing acidity of this support may result in an increase in the activity of the metal for CO hydrogenation.^(23,55) Thus, using these arguments and the converse of the conclusion of Jacobs et al.,⁽²²⁾ the TOF for CO hydrogenation on Ru supported on zeolites of varying Si/Al would be expected to increase as the Si/Al ratio increases. However, the results presented in Table 7.1 suggest no such an effect of the support acidity on TOF, especially if the results obtained for RuKL and Ru-mordenite are corrected for the effect of suppression of hydrogen chemisorption on the calculated site concentrations. Similarly, an investigation of the effect of the nature of the neutralizing alkali cations on CO

hydrogenation over Y-zeolite-supported Ru catalysts has revealed that the nature of these cations and the resulting acidity of the Y-zeolite had hardly any effect on the intrinsic catalytic properties of the metal (see chapter 5). All the catalysts exhibited similar activities and chain growth probabilities, although the strength of the acid sites was found to vary with the nature of the alkali cation (see chapter 6). It was proposed that, under reaction conditions, the interaction of the primary olefinic products with the support Brønsted acid sites may act to disrupt any metal-support interactions which would otherwise exist. Similar interactions of olefins, electron-donating molecules, with the hydroxyl groups of such catalysts resulting in the interruption of the possible metal-support interactions have been suggested by Romannikov et al.⁽⁹⁸⁾ Thus, even in a wider range of acidity strength, as produced by the various Si/Al ratios, this process of interruption of the metal-support interactions under reaction conditions seems still possible. Previous studies of adsorption of H₂ and CO on similar catalysts,^(20,21) as well as the chemisorption results shown in Table 4.5, have revealed that the support acidity may affect the adsorption properties of the metal for the individual gases, at least at room temperature. Thus, while adsorption of the individual reactants appears to be affected by the strength of the acid sites of the zeolite, it may be concluded that this

parameter has hardly any effect on TOF for CO hydrogenation.

7.3.2 Catalyst Selectivities in CO Hydrogenation

The hydrocarbon distributions obtained at 523 K on the zeolite-supported Ru catalysts with different Si/Al ratios are also listed in Table 7.1, and the selectivity for methane formation at constant CO conversion (ca.1%) is shown in Figure 7.1. While the nature of the neutralizing cations in the zeolite has been shown not to affect the ASF distribution, an increase in Si/Al ratio caused the product selectivity to shift towards lower molecular weight hydrocarbons, especially methane. Jacobs et al.⁽²²⁾ also observed a similar trend in methane selectivity in their study of CO hydrogenation over a series of Ru/zeolites with different Si/Al ratios. Metal-support interactions were invoked to explain this behavior. Chen et al.⁽¹⁵⁾ found that the selectivity for methane appeared to correlate with the concentration of the residual neutralizing alkali cations in the zeolite. However, the variations they reported in hydrocarbon distribution may have been influenced by variations in metal particle size. Several other authors have also observed a certain dependence of CH₄ formation on support acidity. Fajula et al.⁽⁵³⁾ suggested a direct involvement of acidic sites in the methanation reaction path on zeolite-supported Pd catalysts, since they found that the selectivity for methane formation was directly related to

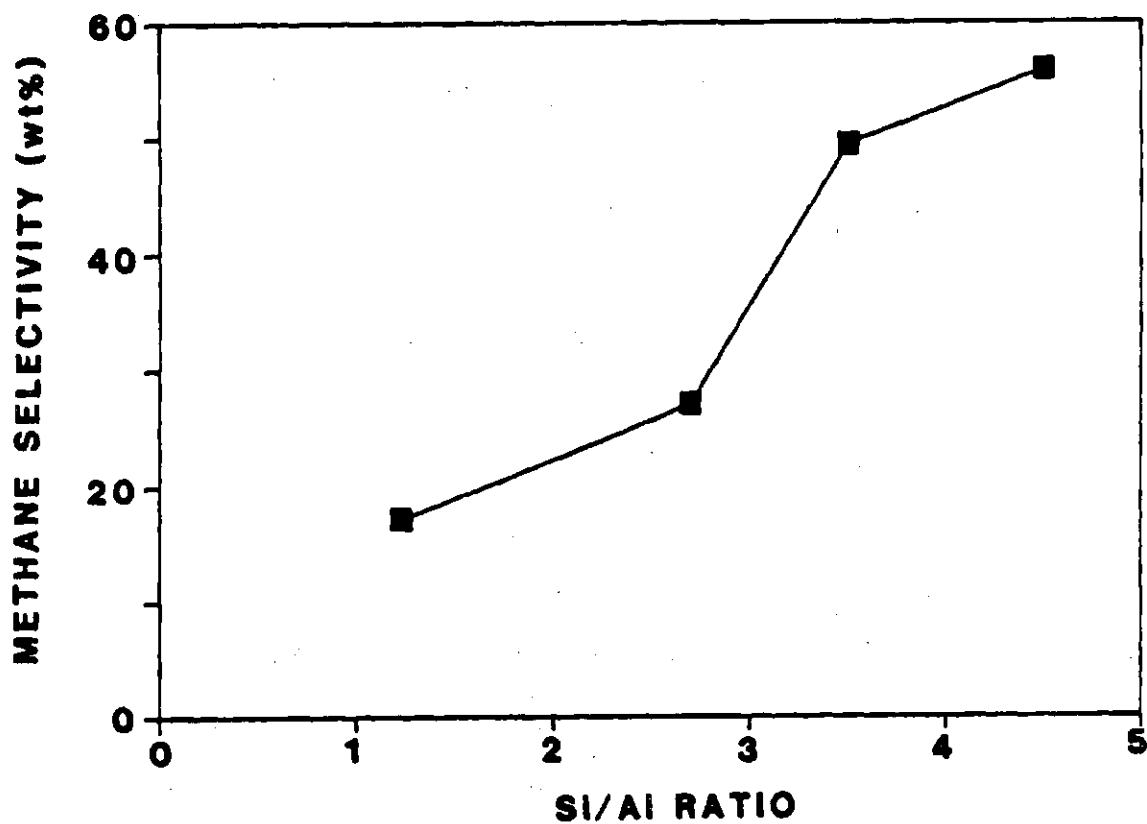


Figure 7.1 Effect of Si/Al Ratio on Selectivity for Methane at constant CO Conversion

the density of acidic sites at the surface of the support. Peuckert and Linden⁽¹²³⁾ also found for a series of Co/zeolites that the less acidic samples yielded much less methane than the others and attributed their results to metal-support interactions.

It is doubtful that this enhancement of methane formation with increasing acidity is a result of metal-support interaction alone, since it is hardly conceivable that a change in the electronic properties of the metal would not also affect the overall activity for CO hydrogenation. Methane can result from direct CO hydrogenation or from the decomposition of the primary hydrocarbon products either by hydrogenolysis reactions on the metal or by the competing reactions of cracking on the acidic support, which would obscure the metal action. Cracking reactions, being of the carbonium ion type, would be very much dependent on the strength of these acid sites. Thus, the effect of acidity on selectivity for methane formation may be related to the carboniogenic activity of the support, although methane may not be a primary product of hydrocarbon cracking. The various possible acid-catalyzed reactions result often in the formation of hydrogen-deficient carbonaceous materials which leads eventually to the deactivation of these catalysts. As will be shown in the following section dealing with the deactivation characteristics of HY and H-mordenite, the

greater the strength of the acid sites, the faster the catalyst deactivates. Consequently, more carbonaceous residues are expected to build up on the more acidic supports during CO hydrogenation. Spillover hydrogen may contribute to methane formation by hydrogenating some of the more reactive carbonaceous residues.

Two other parameters that were found previously (chapters 5 and 6) to be directly related to the carboniogenic activity of the support are the selectivities for olefins and isoparaffins represented by the propylene-to-propane ratio ($C_3^=/C_3^-$) and the iso-butane content of the C_4 -fraction, respectively. The $C_3^=/C_3^-$ ratio (Table 7.2), which may be taken as a measure of the catalyst activity for secondary olefin hydrogenation, was found to decrease with increasing Si/Al ratio and followed a reverse trend to that observed for methane and iso-butane selectivities. Figure 7.2 shows the plot of the $C_3^=/C_3^-$ ratio and of the selectivity for iso-butane obtained at constant CO conversion versus the Si/Al ratio, indicating that the same trend is observed whether the comparison is made at constant temperature or at constant CO conversion. The selectivity for iso-butane increased as would be expected with zeolite acidity strength since this is obviously the product of a secondary acid-catalyzed reaction. It may be noted that, due to the fact that potassium instead of sodium is used as the

Table 7.2 Effect of Zeolite Type on Selectivities for Olefins and Isoparaffins (a)

Catalyst	$C_3^= / C_3^-$ Ratio	i-C ₄ (%) ^(b)
RuNaX	13.6	0.0
RuNaY	4.2	20.2
RuKY	6.4	1.8
RuKL	3.8	12.3
RuNaM ^(c)	0.5	27.3

(a) Reaction Conditions: 523 K, 1 atm, H₂/CO = 1, 5 min of reaction.

(b) Iso-butane in C₄-fraction.

(c) M = Mordenite.

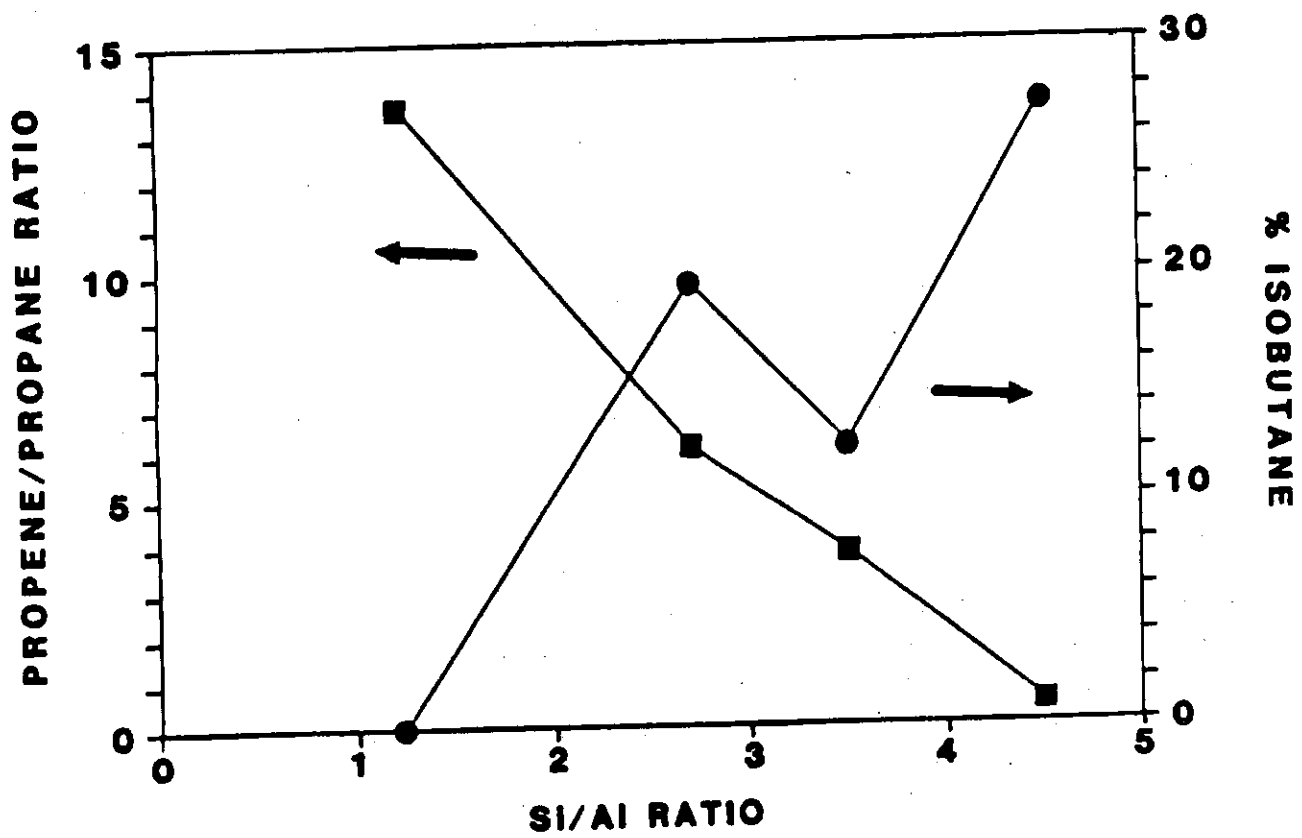


Figure 7.2 Effect of Si/Al Ratio on Selectivities for Olefins and Isoparaffins at Constant CO Conversion

Table 7.3 Effect of Acidity on Selectivity
at Constant CO Conversion (~ 1.5%)^(a)

	RuNaX	RuNaX+HM ^(b)	RuNaM ^(b)
C ₁	17.3	32.2	63.2
C ₂	11.7	10.7	16.6
C ₃	24.8	11.5	10.9
C ₄	19.4	28.9	7.3
C ₅ ⁺	26.7	16.7	2.0
C ₃ ⁼ /C ₃ ⁻	13.6	0.9	0.4
i-C ₄ (%) ^(c)	0.0	61.8	25.0

(a) Reaction Conditions: 1 atm, H₂/CO = 1,
5 min of reaction.

(b) M = Mordenite.

(c) Iso-butane in C₄-fraction.

neutralizing cation in L-zeolite, the effect of increasing Si/Al ratio on both the selectivities for isoparaffins and olefins is best illustrated when comparing RuKL to RuKY. Indeed, it has been shown (see chapter 6) that the nature of the neutralizing alkali cation in zeolites may have a significant effect on the strength of their acid sites and, hence, on both the C_3^-/C_3^- ratio and the selectivity for iso-butane.

Although there can be no doubts about the origin of the isoparaffins during CO hydrogenation on the more acidic Ru catalysts, the participation of the support in the secondary hydrogenation of the primary olefinic products may still be questioned. In order to elucidate this effect of the support acidity on both the selectivity for methane and the olefin-to-paraffin ratio, CO hydrogenation was carried out over RuNaX, the least acidic of all the catalysts, followed by a layer of H-mordenite (0.1 g) at the tail end of the reactor. Table 7.3 compares the hydrocarbon product distributions, the C_3^-/C_3^- ratios, and the iso-butane content of the C_4^- fractions obtained when CO hydrogenation was carried out over RuNa-mordenite, RuNaX and when RuNaX followed by HY. The methane fraction, although not reaching the level observed on RuNa-mordenite was practically doubled, the C_3^-/C_3^- dropped from 13.6 to 0.9, a value similar to that obtained with the mordenite catalyst, while 62% of the C_4^- fraction was in the form of iso-butane. From these results,

it may be suggested that the larger amounts of methane produced on the more acidic catalysts are rather the result of increasing cracking activity of the zeolite. In addition to cracking, an enhancement of various acid-catalyzed secondary reactions such as oligomerization, hydrogen transfer, etc., which are known to be favored with more acidic catalysts, (66,102,119) may be responsible for not only the increase in isoparaffin formation but also for higher olefin hydrogenation activity by hydrogen transfer. This paraffin formation process involving intermolecular hydrogen transfer has been shown to be one of the most dominant reactions of olefins in the presence of acidic zeolites, whether the olefin is a reactant or an intermediate. (62) Hydrogen spillover from the metal may also play an important role in the enhancement of the selectivity for paraffins with increasing acidity of the support. Increasing the strength of the acid sites would result in an increase in the concentration of strongly adsorbed olefins which would be equivalent to the appearance of additional olefin hydrogenation sites. An enhancement of the olefin hydrogenation reactions would also lead to a shift in the overall selectivity to lower molecular weight hydrocarbons, since any olefin formed on a F-T site has a greater chance of being intercepted by acid site on which it can be rapidly converted to a species inactive for further chain growth on another F-T site. The acid site concentration

exceeds significantly that of the metal sites on these catalysts, even if 100% dispersion of the metal is assumed with all metal sites active for hydrogenation reactions. For every $\text{Ru}(\text{NH}_3)_6^{3+}$ exchanged, the subsequent decomposition and reduction of the precursor leads to the formation of three acid sites. It is well known that the strength of such acid sites is a function of the Si/Al ratio. Given the catalytic properties of acid sites, it follows that with the more acidic catalysts a shift of the selectivity to lighter hydrocarbons is observed, accompanied by lower selectivities for olefins and greater iso-paraffin formation. There have been proposals that the neutralizing sodium cations also present may be active in olefin hydrogenation.⁽¹¹⁰⁾ However, as will be shown in the next section, these cations play no role as active sites under F-T reaction conditions.

Somewhat surprisingly the selectivity for iso-butane obtained with RuNa-mordenite was not significantly higher than that obtained with RuNaY. This may be explained by the fast deactivation characteristics of the strongest acid sites in RuNa-mordenite, as illustrated in the following section by the deactivation characteristics of H-mordenite. In addition, possible channel blocking by larger metal particles, may result in less acid sites being accessible to olefin molecules produced on the metal. This is, at least, what is suggested by the results obtained when CO hydrogenation was carried out on RuNaX-zeolite followed by

H-mordenite. In this case, the majority of the C₄-fraction was in the form of iso-butane, while on RuNa-mordenite only 25% was in the form of iso-butane (Table 7.3).

7.3.3 Olefin Reactions on the Zeolites without Ru

The metal Ru can contribute to the secondary hydrogenation and isomerization of the primary olefinic products of CO hydrogenation. In order to eliminate the effect of the metal on secondary reactions and to investigate the catalytic properties of the support alone for these reactions, 1-butene and propylene transformations, at the same temperature and pressure as CO hydrogenation, were carried out on the various zeolites with different Si/Al ratios in their alkali forms and not containing any metal. While all the zeolites were completely inactive for the propylene reaction, they exhibited relatively low activity for 1-butene isomerization reactions (see Table 7.4). Since these zeolites in their alkali forms have very few acid sites, mainly the hydroxyls terminating the zeolite crystal faces and some due to cation deficiencies within the zeolite framework, only double bond shift and cis-trans isomerization were observed. There was no evidence for oligomerization or skeletal isomerization of the 1-butene for which stronger acid sites are required. The differences in 1-butene conversion on the various zeolites shown in Table 7.4 do not follow a trend which may be associated with

Table 7.4 Activity and Selectivity of the Alkali Form of the Zeolites for 1-Butene Reaction (a)

Catalyst	Conversion (%)	Cis/Trans Ratio
NaX	25.0	0.74
NaY	8.5	0.60
KL	14.7	0.64
NaM ^(b)	11.2	0.64

(a) Reaction Conditions: 523 K, 1 atm,
1% 1-butene in hydrogen,
Flow rate = 100 ml/min
5 min of reaction.

(b) M = Mordenite.

any particular zeolite properties. If the hydroxyl groups on the external surface of the zeolite crystallites are effectively the sites responsible for the butene isomerization, these differences may be explained by possible differences in the size of the crystallites. The number of terminal hydroxyl groups has been shown to be a strong function of the zeolite crystallite diameter.⁽¹²⁴⁾ Finally, contrary to the suggestion by Topchieva et al.⁽¹¹⁰⁾ that the cations may exhibit significant activity for the hydrogenation of olefins when treated with hydrogen at high temperature, no hydrogenation activity was observed for any of the zeolites under these reaction conditions. The only products obtained from 1-butene reactions were cis- and trans-2-butenes, their ratio being almost the same for all the zeolites (Table 7.4). Similar results have been obtained when the nature of the cations in Y-zeolites was varied (see chapter 6). It may be concluded that the neutralizing alkali cations in the zeolite are inactive for any possible secondary reactions which may be observed during CO hydrogenation over zeolite-supported ruthenium catalysts. Thus, the only sites for these secondary reactions would be the metal sites on which the primary olefinic products are produced and the adjacent acid sites associated with the zeolite and produced during preparation of the ion-exchanged metal catalyst.