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Effect of Si/Al Ratio on Secondary Reactions during CO Hydrogenation on Zeolite-Supported Metal Catalysts

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The effect of zeolite acidity on the product distribution in CO hydrogenation over ion-exchanged zeolite-supported Ru catalysts was investigated 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 conditions similar to those used for CO hydrogenation, were investigated in order to understand the effect of zeolite acidity on possible secondary reactions of the primary olefinic products of Fischer–Tropsch (F–T) synthesis. The results of this study establish the importance of the bifunctional nature of the zeolite-supported F–T catalysts in modifying catalyst selectivity. This modification is achieved as a result of secondary reactions of the primary olefinic F–T products on the acid sites of the zeolite, generated during catalyst preparation. Depending on the strength of the acid sites, a function of the Si/Al ratio, various competitive reaction paths can be observed for the transformation of the olefinic compounds.

I. INTRODUCTION

CO hydrogenation over conventional Fischer–Tropsch (F–T) catalysts leads to the formation of a wide range of products. Many studies carried out in this field have been aimed at developing highly selective catalysts for the conversion of syn gas to fuels and chemical feedstocks (*1*, *2*). Several approaches have been attempted in order to circumvent the Anderson–Schultz–Flory (ASF) chain growth probability which characterizes most CO hydrogenation (*3*). 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 depending on the zeolite used (*4–7*). This behavior of the composite catalysts has been attributed to the carboniogenic activity and the shape-selective character exhibited by zeolites. 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. Zeolite-supported F–T metal catalysts have also been found to be as effective as the composite catalysts in limiting the F–T product distribution (*1*). In this case, the narrow product distribution was attributed mainly to the physical constraints exerted by the pore size. Secondary isomerization and cracking of the F–T products over the acid sites present inside the zeolite support were ruled out. However, a number of studies of CO hydrogenation over supported ruthenium catalysts, using various zeolites as supports and various methods of catalyst preparation, have demonstrated that the acidity of the zeolite may have a pronounced effect on the isomer distribution of the hydrocarbon products formed by F–T synthesis (*8–12*). In addition, in a more recent study investigating the effect of the nature of the neutralizing alkali cations on CO

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hydrogenation over Ru/Y-zeolites and the possible secondary reactions of the primary F–T products (*13, 14*), it was established that the concentration and the acid strength of the protonic sites had a significant effect on acid-catalyzed reactions such as isomerization, oligomerization, cracking, and hydrogen transfer. 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 present work 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 have Si/Al ratios ranging from 1.4 to 5.5. The reaction of butene on the various zeolites containing no metal and on the acidic forms of mordenite and Y-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.

II. EXPERIMENTAL

Materials

Zeolite-supported Ru catalysts were prepared by ion exchange of the zeolites NaX, NaY, KL (Strem Chemicals), and Na-mordenite (Norton) with $Ru(NH_3)_6Cl_3$ (Strem Chemicals) following the same preparation method as described in Ref. (*13*). An elemental analysis of the zeolites used in this study, as determined by atomic absorption, is given in Table 1 in the form of unit cell composition. After decomposition under vacuum and reduction in hydrogen at 673 K, the resulting Ru catalysts were then characterized by atomic absorption and by chemisorption of hydrogen and carbon monoxide. The characterization procedures have been described in Ref. (*13*).

TABLE 1

Unit Cell Composition of the Dehydrated Zeolites

Zeolites	Composition
NaX	$Na_{80}(AlO_2)_{80}(SiO_2)_{112}$
NaY	$Na_{52}(AlO_2)_{52}(SiO_2)_{140}$
KL	$K_{7.9}(AlO_2)_{7.9}(SiO_2)_{28.1}$
Na-mordenite	$Na_{7.4}(AlO_2)_{7.4}(SiO_2)_{40.6}$

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

Reaction Studies

CO hydrogenation was carried out in a tubular microreactor where the prereduced catalyst (0.25 g) was first re-reduced in a hydrogen stream at 673 K for 2 h before cooling to reaction temperature. The reaction was carried out at atmospheric pressure and 483–573 K using a 1 : 1 mixture of H_2 and CO flowing at 2.4 liters/h. A sample of the effluent gas was analyzed on-line by gas chromatography after 5 min of reaction. This time was found to be sufficient to establish the product distribution. The hydrogen bracketing technique, which consisted of a 40-min hydrogen treatment of the catalyst after every 5-min reaction period, was used to maintain a clean metallic surface. A detailed description of the reaction and product analysis procedures has also been reported in Ref. (*13*).

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 conditions similar to those of CO hydrogenation, i.e., in a continuous flow microreactor operating at atmospheric pressure and 523 K. A flow rate of 100 ml/min of a reactant mixture of 1% olefin in hydrogen was used. Products from the reactor were also analyzed on-line by gas chromatography after 5 min of reaction, following the same procedure as that used for the CO hydrogenation product analysis. Before the reaction, the zeolite (0.1 g) was first heated up to 673 K for 2 h under flowing hydrogen to eliminate any water present.

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 2 h in flowing hydrogen. The deactivation characteristics of these zeolites for the olefin reactions were also investigated.

III. RESULTS AND DISCUSSION

Catalyst Characterization

The results of H_2 chemisorption for the zeolite-supported Ru catalysts, used to calculate metal particle sizes and dispersions, are given in Table 2. The Si/Al ratios of the zeolite supports, calculated from the AA analysis results, are also listed in Table 2 since they represent the major variable in this study. The CO/H ratios are also included in the same table as they serve as a measure of suppression at room temperature of hydrogen chemisorption (*15*). The CO/H ratios obtained for RuKL and RuNa-mordenite suggest actually a significant suppression of hydrogen chemisorption on these catalysts. Such results would be expected for these two catalysts since the acid strength of the hydroxyl groups formed on the support, which is correlated with the Si/Al ratio of the zeolite (*16*), has been shown to play an important role in hydrogen chemisorption suppression for zeolite-supported ruthenium catalysts prepared for ion exchange (*15*). This would partly explain the higher particle sizes calculated from H_2 chemisorption for these two catalysts. Any agglomeration of Ru in the zeolite channels may render some portions of the metal particles inaccessible to adsorption. Such behavior would also result in an overestimation of the particle sizes calculated from H_2 chemisorption.

TABLE 2

Catalyst Characteristics

Catalyst	Ru (wt %)	Si/Al ratio	H_2(irr.)[a] (μmol/g·cat.)	D[b] (%)	d_p[b] (Å)	$(CO/H)_{irr}$[c] ratio
RuNaX	3.0	1.4	80	54	16	—
RuNaY	3.8	2.7	126	67	12	3.7
RuKY	3.2	2.7	83	52	16	3.4
RuKL	3.2	3.5	53	36	24	5.0
RuNaM[d]	3.2	5.5	39	26	32	4.3

[a] Irreversible H_2 chemisorption.

[b] Dispersion (D) and particle size (d_p) from H_2 chemisorption.

[c] From CO and H_2 chemisorption measurements at room temperature.

[d] M, mordenite.

TABLE 3

Catalytic Properties of Ru/Zeolites for CO Hydrogenation[a]

Catalyst	TOF[b] ($s^{-1} \times 10^3$)	Selectivity (wt%)				
		C_1	C_2	C_3	C_4	C_5^+
RuNaX	5.8	17.3	11.7	24.8	19.4	26.7
RuNaY	6.9	32.7	14.0	21.5	17.0	14.8
RuKY	7.8	30.7	13.7	23.5	15.8	16.2
RuKL	8.4	49.5	12.3	17.8	11.7	8.7
RuNaM[c]	8.0	56.0	16.6	12.3	9.9	5.2

[a] Reaction conditions: 523 K, 1 atm, $H_2/CO = 1$, 5 min of reaction.

[b] Based on H_2 chemisorption results.

[c] M, mordenite.

Catalyst Activities for CO Hydrogenation

Table 3 compares the turnover frequencies (TOF) for CO conversion based on the estimated site concentrations provided by hydrogen chemisorption measurements. The calculated TOFs 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 RuKY has the same Si/Al ratio as RuNaY, it is included in Table 3 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 (*13*). It is well known that the higher the Si/Al ratio (for Si/Al < 6) of a zeolite, the stronger are its acid sites (*16*). 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 (*17, 18*). Thus, using these arguments and the converse of the conclusion of Jacobs *et al.* (*19*), 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 3 suggest no such 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 (*13*). 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 (*14*). 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.* (*20*). 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 H_2 and CO on similar catalysts (*15, 21*), as well as the chemisorption results shown in Table 2, 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.

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 3, and the selectivity for methane formation at constant CO conversion (ca. 1%) is shown in Fig. 1. While the nature of the neutralizing cations in the zeolite has been shown not to affect the ASF

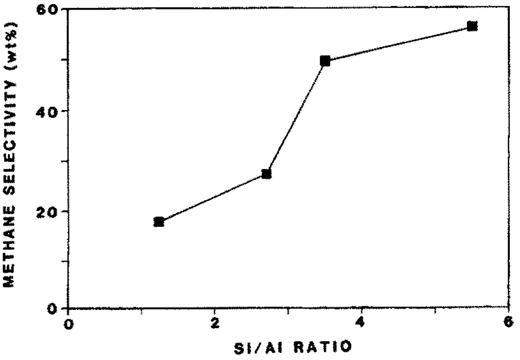

FIG. 1. Effect of Si/Al ratio on selectivity for methane at constant CO conversion.

distribution (*13*), an increase in Si/Al ratio caused the product selectivity to shift toward lower-molecular-weight hydrocarbons, especially methane. Jacobs *et al.* (*19*) 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.* (*10*) found that, for Ru/zeolites prepared by ion exchange, the selectivity for methane appeared to correlate with the concentration of the residual neutralizing alkali cations in the zeolite. Although the differences they reported in hydrocarbon distribution may have been influenced by variations in metal particle size, the trend of their results did not deviate much from that of the present results. In another study of CO hydrogenation on a similar series of Ru/zeolite catalysts, but prepared by vapor impregnation with $Ru_3(CO)_{12}$, Chen *et al.* (*22*) have also observed a trend of increasing methane formation with increasing Si/Al ratio of the support. Variations in metal particle size may also account for some of the differences observed. Since this preparation method does not result in the formation of acid sites on the support, hardly any metal–support interactions should be expected, nor any secondary reactions on the support. Several other authors have also observed a certain dependence of CH_4 formation on support acidity. Fajula *et al.* (*23*) 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 the density of acidic sites at the surface of the support. Peuckert and Linden (*24*) 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 interactions 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 is 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 (*13, 14*) 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 isobutane content of the C_4 fraction, respectively. The $C_3^=/C_3^-$ ratio (Table 4), 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 trend opposite to that observed for methane and isobutane selectivities. Figure 2 shows the plot of the $C_3^=/C_3^-$ ratio and of the selectivity for isobutane obtained at constant CO conversion versus the Si/Al ratio, indicating that the same trend is ob-

TABLE 4

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, $H_2/CO = 1$, 5 min of reaction.

[b] Isobutane in C_4 fraction.

[c] M, mordenite.

served whether the comparison is made at constant temperature or at constant CO conversion. The selectivity for isobutane 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 neutralizing cation in L-zeolite, the effect of increasing Si/Al ratio on the selectivities for both isoparaffins and olefins is best illustrated when comparing RuKL to RuKY. Indeed, it has been shown (*14*) 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 isobutane.

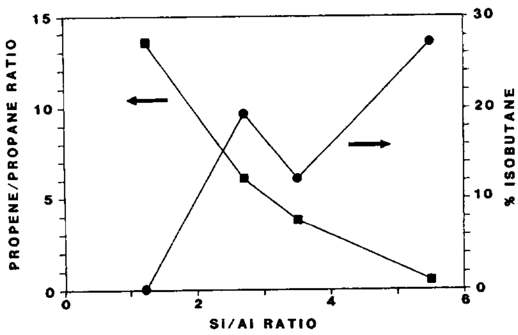

FIG. 2. Effect of Si/Al ratio on selectivities for olefins and isoparaffins at constant CO conversion.

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 5 compares the hydrocarbon product distributions, the $C_3^=/C_3^-$ ratios, and the isobutane content of the C_4 fractions obtained when CO hydrogenation was carried out over RuNa-mordenite, Ru NaX, and when RuNaX was 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-based catalyst, while 62% of the C_4 fraction was in the form of isobutane. 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. Although catalytic cracking in itself would not result in methane formation, it leads to an in-

TABLE 5

Effect of Acidity on Selectivity at Constant CO Conversion (ca. 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, $H_2/CO = 1$, 5 min of reaction.

[b] M, mordenite.

[c] Isobutane in C_4 fraction.

creased formation of carbonaceous deposits. In the presence of hydrogen provided by spillover from metal sites these carbonaceous deposits may be hydrogenated to methane. In addition to cracking, an enhancement of various acid-catalyzed secondary reactions such as oligomerization and hydrogen transfer, which are known to be favored with the more acidic catalysts (*25–27*), may be responsible for not only the increase in isoparaffin formation but also the 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 (*28*). 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 an 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 $Ru(NH_3)_6^{3+}$ exchanged, the subsequent decomposition and reduction of the precursor lead to the formation of three acid sites. Since the Ru loadings were approximately the same, the concentrations of acid sites introduced into the catalysts were constant. However, 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 isoparaffin formation. There have been proposals that the neutralizing sodium cations also present may be active in olefin hydrogenation (*29*). However, as is shown in the next section, these cations play no role as active sites under F–T reaction conditions.

Somewhat surprisingly the selectivity for isobutane 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 fewer 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 C_4 fraction was in the form of isobutane, while on RuNa-mordenite only 25% was in the form of isobutane (Table 5).

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 6). Since these zeolites in their alkali forms have very few

TABLE 6

Activity and Selectivity of the Alkali Form of the Zeolites for 1-Butene Reaction[a]

Catalyst	Conversion (%)	Isobutane (%)	*cis/trans* ratio
NaX	25.0	0	0.74
NaY	8.5	0	0.60
KL	14.7	0	0.64
NaM[b]	11.2	0	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.

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 6 do not follow a trend which may be associated with 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 (*30*). Finally, contrary to the suggestion by Topchieva *et al.* (*29*) that the cations may exhibit significant activity for the hydrogenation of olefins when treated with hydrogen at high temperatures, no hydrogenation activity was observed for any of the zeolites under these reaction conditions. The only products obtained from 1-butene reaction were *cis*- and *trans*-2-butenes, their ratio being almost the same for all the zeolites (Table 6). Similar results have been obtained when the nature of the cations in Y-zeolites was varied (*14*). 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.

Deactivation Characteristics of H-mordenite and HY-zeolite

Since the selectivity for isobutane 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 isobutane 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 (*14*). 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 Figs. 3 and 4). It can be seen that the activity for isobutane formation on H-mordenite, which was initially much higher than that 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 Figs. 3 and 4 to 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 ac-

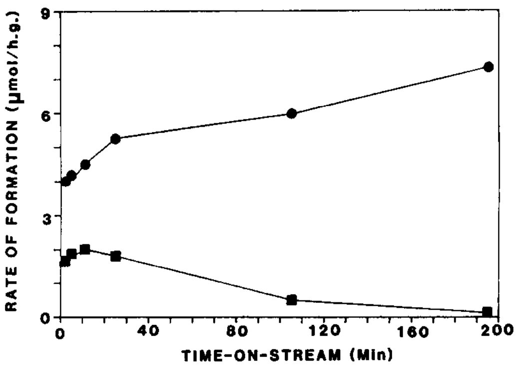

FIG. 3. Isobutane (■) and *cis*-2-butene (●) formation rates vs time-on-stream on HY.

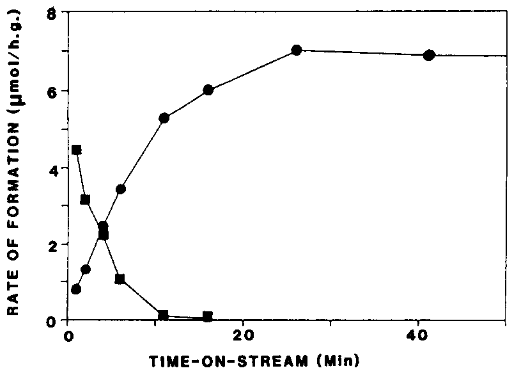

FIG. 4. Isobutane (■) and *cis*-2-butene (●) formation rates vs time-on-stream on H-mordenite.

tivities 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

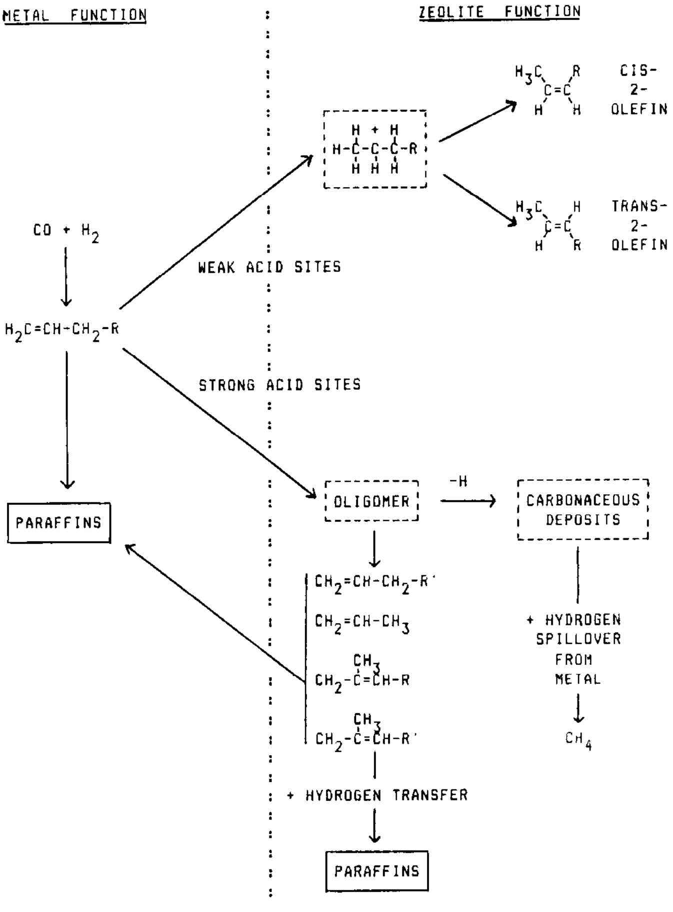

FIG. 5. Reaction scheme for CO hydrogenation on zeolite-supported metal catalysts.

the presence of strong acid sites, to double-bond migration and *cis–trans* isomerization which can occur even on very weak acid sites (*26, 27*). 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 mordenite are already in an advanced deactivation state, resulting in poorer selectivities for isoparaffins.

IV. CONCLUSIONS

This work, like the previous studies (*13, 14*), 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, as illustrated schematically in Fig. 5, 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. 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.

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