JOURNAL OF CATALYSIS **142**, 531–539 (1993)

The Effect of Dealumination on Zeolite-Supported Ru Catalysts

JEFFREY C. S. WU, RACHID OUKACI, AND JAMES G. GOODWIN, JR.[1]

Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261

Received July 9, 1992; revised March 11, 1993

The physical and catalytic properties of a series Ru/dealuminated Y-zeolite catalysts prepared by ion exchange have been investigated in order to better understand the effect of the Si/Al ratio of a zeolite on the catalytic properties of a supported metal. Dealumination up to 52% was shown not to have affected the crystallinity of the zeolite. The reduced Ru catalysts exhibited increased metal dispersions, as measured by H_2 chemisorption, with increased zeolite dealumination. Turnover frequency (TOF) for CO hydrogenation vs Si/Al ratio showed a volcano shape. Maximum TOF occurred at a Si/Al ratio of about 5. While the overall product distribution was unaffected by Si/Al ratio, an increase in the selectivity for iso-C_4 with increasing dealumination indicated that secondary reactions of the F–T primary products were enhanced by the presence of stronger acid sites. It is well known that the concentration of acid sites in a dealuminated Y-zeolite decreases with increasing Si/Al ratio, while the strength of the acid sites increases and reaches a maximum for Si/Al $\approx$ 4.5. Since overall chain growth probability was not apparently affected by dealumination of the zeolite support, it is suggested that the increase in overall activity for CO hydrogenation on the dealuminated Ru catalysts may have been primarily due to an enhancement in secondary reactions as a result of the increase in acid strength lessening readsorption of olefinic primary products on Ru CO hydrogenation sites.

I. INTRODUCTION

Earlier studies of CO hydrogenation over zeolite-supported Ru catalysts carried out in this laboratory have provided evidence that the various constituents of the zeolite support may have significant effects on both the activity and the selectivity of supported metals for this reaction (*1–3*). A study of a series of RuY catalysts prepared by ion exchange from NH_4Y, LiY, NaY, RbY, and CsY zeolites indicated that the nature of the Group IA cation has only a small effect on the specific activity of the catalyst or the overall chain growth probability but has a pronounced effect on the olefin and branched hydrocarbon selectivities (*1*). This effect was attributed to the secondary acid-catalyzed reactions of the primary olefinic products of CO hydrogenation. The nature of the alkali cation affected the strength of the Brønsted acid sites formed in the zeolite during the reduction process of the catalyst (*1, 2*).

In another study we reported on the effect of zeolite acidity on the catalytic properties for CO hydrogenation of another series of ion-exchanged zeolite-supported Ru catalysts using zeolites with different Si/Al ratios, i.e., RuNaX, RuNaY, RuKL, and RuNa–mordenite (*3*). The importance of the bifunctional nature of these catalysts in modifying selectivity for CO hydrogenation was demonstrated. Depending on the strength of the acid sites of the zeolite, a function of the Si/Al ratio, various competitive secondary reaction paths were suggested for the primary olefinic products of CO hydrogenation. However, the interpretation of these results was complicated by the fact that a series of zeolites with different Si/Al ratios but also different framework structures was used.

Dealumination of zeolites can result in a

---

[1] To whom correspondence should be addressed.

0021-9517/93 $5.00

change in the Si/Al ratio while maintaining the original framework structure of the zeolite. The acidity of the zeolite is modified by dealumination since it is a function of Si/Al ratio (*4*, *5*). Certain physical properties of the zeolites, such as pore volume and thermal stability, may also be modified (*6–13*). This paper reports on the results of the investigation of the effect of dealumination on the physical properties as well as the catalytic properties for CO hydrogenation of a series of Ru/dealuminated Y-zeolite catalysts.

II. EXPERIMENTAL

The parent zeolite NH_4Y was obtained from Strem Chemicals. Using the method employed by Skeels and Breck (*10*) and Garralón *et al.* (*14*), the zeolite was dealuminated to different degrees at relatively mild conditions using an aqueous fluorosilicate solution. A zeolite–water slurry containing about 10–25 g of zeolite per 100 ml of water was preheated to 75–95°C. The system was buffered with a neutral salt, ammonium acetate. Typically, a 1 *M* solution of $(NH_4)_2SiF_6$ was added to the slurry at a rate of 0.005 moles of $(NH_4)_2SiF_6$ per minute per mole of aluminum present in the zeolite. Depending on the exchange percentage sought, the amount of $(NH_4)_2SiF_6$ used was $1–15 \times 10^{-4}$ moles per gram of zeolite. These concentrations and the addition rate maintained the reaction pH at about 6. After adding the $(NH_4)_2SiF_6$ solution, the slurry mixture was allowed to react at 75–95°C for 1 to 3 hr, then washed several times with distilled water and dried in the air at room temperature.

The crystallinity of the dealuminated zeolites was examined by X-ray diffraction (XRD). Solid State MAS (magic angle spinning) NMR of ^{29}Si was used to measure the homogeneity of the Si atoms in the tetrahedral structure of the dealuminated zeolites and also to determine the Si/Al ratio. ^{27}Al MAS-NMR was also performed on the highly dealuminated zeolites in order to probe for the presence of extra-framework Al. The total amount of Al in the dealuminated zeolites was measured by atomic absorption (AA). The void volume of zeolite was measured by the N_2 BET method at liquid nitrogen temperature (77.4 K).The parent and dealuminated zeolites were calcined at 500°C in flowing air (hydrocarbon free grade) for 10 hr before measuring the void volume.

The Ru-loaded dealuminated zeolites were prepared by ion exchange with a $Ru(NH_3)_6Cl_3$ solution. The detailed procedure for the preparation of such zeolite-supported Ru catalysts can be found elsewhere (*1*). The Ru catalysts were reduced by heating up to 400°C (0.5°C/min) under vacuum and then holding for 1 hr in static H_2 at that temperature. Such a technique has been shown to result in highly dispersed, reduced Ru catalysts. Static H_2 chemisorption was carried out to measure the metal dispersion and particle size. The detailed H_2 chemisorption procedure is described elsewhere in the literature (*1*). The Ru loading of the reduced catalysts was determined by atomic absorption.

CO hydrogenation was carried out in a tubular microreactor made from $\frac{1}{4}$-in.-ID stainless steel tubing (1 in. = 2.54 cm). The prereduced catalyst (0.1 g) was mixed with an equal weight of SiO_2 to improve the heat dissipation in the catalyst bed. The physically mixed catalyst was loaded into the reactor and then rereduced under flowing H_2. The temperature was ramped from ambient to 400°C at 2°C/min and held for two hours before cooling to reaction temperature.

CO hydrogenation was carried out at atmospheric pressure using a 1 : 1 mixture of H_2/CO flowing at 2.4 l/min. Reaction periods of 5 min were used with H_2 bracketing for 50 min between each reaction period. The initial reaction temperature was 250°C. In all cases, the catalysts were observed to be stable after two 5-min reaction periods. Data were acquired after stability was achieved. The reaction temperature was varied from 210 to 270°C in order to determine the apparent activation energy. The effluent gas was analyzed by on-line gas

TABLE 1

Characteristics of Dealuminated Y Zeolites

Zeolite	Si/Al[a]	Extracted Al[b] (%)	Acid conc.[c] (Al/unit cell)	Void volume[d] (ml/g)
HY-2	2.5	0	55	0.32
HY-3	3.3	19	44	0.33
HY-4	4.7	35	35	0.24
HY-5	5.8	52	26	0.22

[a] Si/Al framework ratio by ^{29}Si solid-state MAS NMR.

[b] Percentage of Al extraction measured by Al AA.

[c] Based on the amount of extracted Al[b].

[d] Void volume measured by N_2 BET at 77.4 K.

chromatography at the end of each 5-min reaction period. A description of the reaction and product analysis procedures can be found elsewhere (*1*).

III. RESULTS

Characterization of the Dealuminated Zeolites

Table 1 provides the characteristics of the parent and the dealuminated zeolites. The number in the zeolite identification represents the first digit of the Si/Al ratio. The Si/Al ratio was estimated from the ^{29}Si MAS-NMR spectra of the parent Y zeolite and the three dealuminated zeolites by using the equation (*11*)

$$\mathrm{Si/Al} = \frac{\sum_{n=0}^{4} I_{\mathrm{Si}(n\,\mathrm{Al})}}{\sum_{n=0}^{4} \frac{n}{4} I_{\mathrm{Si}(n\,\mathrm{Al})}},$$

where I = intensity of peak and n = number of Al atoms to which the Si atom is linked via oxygen in the zeolite structure (0, 1, 2, 3, or 4).

In zeolite Y, Si atoms can have five different surroundings, namely, Si surrounded by zero Al atoms, by one, by two, by three, and by four. Theoretically, five different Si peaks should be observed in ^{29}Si NMR. However, only four peaks were observed in the parent zeolite Y because the amount of Si surrounded by four Al atoms was negligible. This is consistent with other results in the literature (*11*, *15*). The peaks were slightly shifted to the right for the dealuminated zeolites. This phenomenon has also been observed by Thomas and Klinowski (*15*). With extent of dealumination, the intensities of the first peak, Si(0 Al), and the second peak, Si(1 Al), increased while the intensities of the third peak, Si(2 Al), and the fourth peak, Si(3 Al), decreased. Most of the Si was at Si(0 Al) and Si(1 Al) positions in the framework of the dealuminated zeolites. Since only peaks for tetrahedral Si were observed, no significant amount of defect Si structures appear to have been present. That is, most dealumination was accomplished by replacing one Al with one Si.

The percentage dealumination of the zeolites between 19 and 52%, as determined by AA, are also given in Table 1. The theoretical concentration of acid sites is represented by the number of Al atoms in a unit cell. The void volumes indicate that most extracted aluminum, which was generated during the dealumination procedure, was removed except for the zeolites with the highest levels of dealumination. The void volumes of HY-4 and HY-5, the most dealuminated zeolites, suggest that some extracted alumina possibly plugged some pores, thus, reducing the void volume. However, the ^{27}Al NMR results do not show any presence of extra-

TABLE 2

Characteristics of Catalysts

Catalyst	Ru[a] (wt%)	H_2 uptake[b] (μmole/g)	Dispersion[c] (%)	d_p[d] (Å)
RuHY-2	3.2	32	20	45
RuHY-3	3.3	43	27	33
RuHY-4	3.8	59	31	29
RuHY-5	3.7	67	36	25

[a] Metal loading measured by Ru AA.

[b] Difference between reversible and irreversible H_2 chemisorption extrapolated to zero pressure.

[c] Metal dispersion calculated from H_2 uptake, $H/Ru_s = 1$.

[d] Average Ru particle diameter calculated from H_2 chemisorption using method described in (*1*).

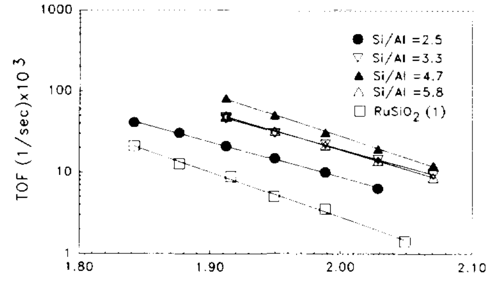

FIG. 1. Arrhenius plots of CO hydrogenation on dealuminated zeolite-supported Ru catalysts.

framework Al. The shapes of the BET isotherms indicate that the pore structure of these dealuminated zeolites remained the same as that of the parent zeolite. The X-ray diffractograms of the parent and the dealuminated Y zeolites indicate that the crystallinity was maintained in the dealuminated zeolites.

Chemisorption Characterization of the Ru/Zeolites

Table 2 gives the metal dispersions and average particle sizes of the zeolite-supported Ru catalysts based on H_2 chemisorption. The Ru dispersion increased with the level of dealumination.

CO Hydrogenation

Table 3 gives the results of CO hydrogenation at 230°C. The apparent activation energies were determined from Arrhenius plots (Fig. 1) using a least-squares method. Results for a typical Ru/SiO_2 catalyst are also presented in Fig. 1 for comparison. Turnover frequencies (TOF) were calculated based on metal dispersion determined from H_2 chemisorption. Figure 2 shows that the TOF of CO hydrogenation on the zeolite-supported Ru catalysts went through a maximum as Si/Al ratio increased. The overall product distribution and chain growth probability, α, for CO hydrogenation at 230°C was unaffected by variations in Si/Al ratio of the zeolite (see Table 3).

For this series of catalysts, the percentage of C_4 branched products (isobutene + isobutane) in the C_4 fraction was found to be almost independent of CO conversion (Fig. 3). In fact, the distribution of C_4 isomers in total C_4 was also found to be almost un-

TABLE 3

Ru/Y CO Hydrogenation

Catalyst[a]	Conversion[b] (%)	TOF[c] (1/sec) × 10^3	Selectivity (wt%)						E_a (kJ/mole)
			C_1	C_2	C_3	C_4	C_5	C_6	
RuHY-2	0.7	10	38	9	19	19	9	5	86 ± 6
RuHY-3	1.4	22	45	13	18	14	6	4	84 ± 2
RuHY-4	2.6	30	37	11	17	18	10	7	101 ± 7
RuHY-5	2.1	21	37	12	18	18	9	5	91 ± 1

[a] Physical mixture of catalyst + SiO_2.

[b] Reaction conditions: 230°C, $H_2/CO = 1$, 1 atm, 5-min. reaction.

[c] Based on H_2 chemisorption results.

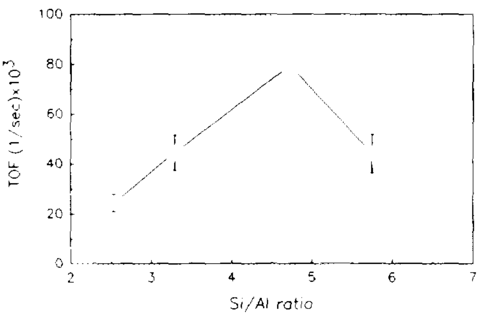

FIG. 2. Effect of Si/Al ratio on TOF of CO hydrogenation at 250°C and 1 atm.

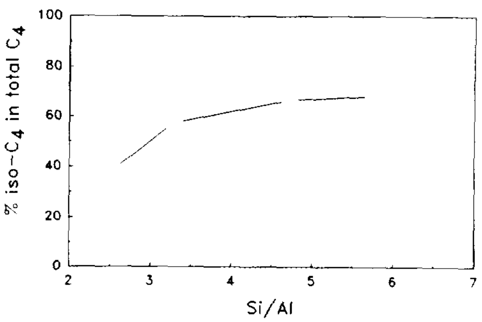

FIG. 4. Effect of Si/Al ratio on iso-C_4 produced during CO hydrogenation at 230°C and 1 atm.

changed within the range of reaction temperatures used. Figure 4 shows how the percentage of isobutene and isobutane in the C_4 fraction increased as the Si/Al ratio increased.

The olefin/paraffin ratio can indicate the primary olefin selectivity in CO hydrogenation as well as the degree of hydrogenation during secondary reactions (*1*, *2*). Figure 5 shows the effect of Si/Al ratios on the olefin/paraffin ratios for both linear and branched C_4 products.

IV. DISCUSSION

Metal Dispersion and Particle Size

As seen in Table 2, the average particle diameters of the Ru/zeolites were larger than the upper limit of the supercage diameter (13 Å). Gustafson and Lunsford (*16*) suggested that the Ru particles may agglomerate through the 12-member ring windows of several adjacent supercages. Thus, H_2 adsorption may be blocked due to metal particles filling zeolite supercages. During the initial reduction from the precursor-form of the catalysts, some of the ruthenium may also have migrated to the external surface where large particles could be formed. If some metal existed as large particles on the external surface of zeolite crystallites, an average particle diameter larger than the diameter of zeolite pore would be calculated from H_2 chemisorption, even though most of the metal was in the pores. Such a distribution of metal particles between the pore system and the external zeolite surface has been previously demonstrated by TEM for Ru in zeolites (*17*).

Another possible explanation could be the suppression of irreversible hydrogen chemi-

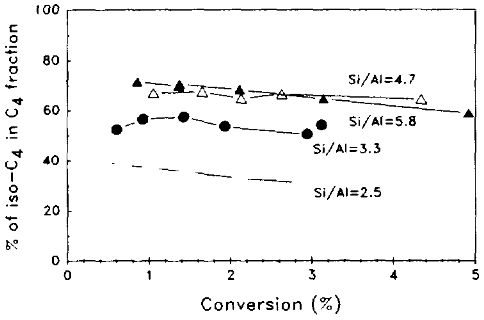

FIG. 3. Effect of CO conversion on secondary reactions in CO hydrogenation over Ru supported on zeolites with different Si/Al ratios.

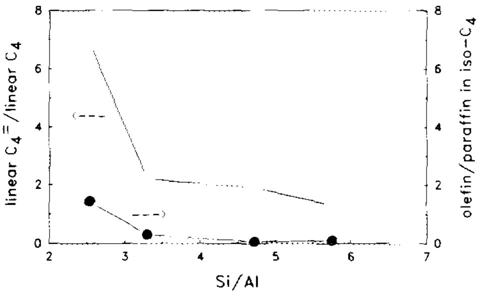

FIG. 5. Effect of Si/Al ratio on olefin formation during CO hydrogenation at 230°C and 1 atm.

sorption. Wang *et al.* (*18*) and Oukaci *et al.* (*1*) compared CO and H_2 chemisorption and observed that a significant suppression of hydrogen chemisorption appeared to occur on Ru/zeolite catalysts prepared by the ion-exchange method, and an interaction of the zeolite hydroxyls with Ru was suggested as a possible cause. If this happened in our catalysts, the average metal particle size would be overestimated. In all likelihood, it is a combination of the above factors which acts to yield an overestimation of the Ru average particle sizes. Thus, the particle sizes listed in Table 2 should be considered to be maximum values.

It appears that Ru agglomeration was reduced as the zeolite was dealuminated more. Table 2 shows that the metal dispersion of the catalysts increased with increasing Si/Al ratio. As the zeolite was dealuminated to a greater extent, the density of exchangeable sites (tetrahedral Al) became lower, thus making these sites more separated within the zeolite crystallites. Thus, after ion exchange, the metal precursor cations would have been possibly more isolated from each other, and this may have resulted in less metal sintering during H_2 reduction. In addition, since it is well known that the acid strength of H^+ occupied sites increases with dealumination of HY zeolite up to Si/Al ratio of about 5, interaction of the exchange sites with Ru cations or the reduced Ru atoms may also have reduced the amount of metal migration and sintering during reduction.

Catalyst Activity

Metal particle size should have had a minimal effect on the activity results since CO hydrogenation is known to be only slightly structure-sensitive. Furthermore, the range of average particle size is not wide (25–45 Å). The influence of shape selectivity on the reaction should have also been insignificant since Y zeolite was used and the framework structure was well maintained after dealumination (as determined by XRD) with little pore blockage (as determined by BET).

As seen in Table 3 and Fig. 1, the TOFs for CO hydrogenation over the dealuminated catalysts were higher than that over the non-dealuminated catalyst (RuHY-2). If there were a suppression of hydrogen chemisorption in the Ru/dealuminated zeolites, the values of TOF would be lower than those in Table 3. However, even if we assume that all the zeolite catalysts had identical dispersions as RuHY-2 or RuHY-5, the two extreme dispersions, the TOF for CO hydrogenation on the most dealuminated catalyst would still be at least a factor of three times higher than that on RuHY-2. Obviously, the increase in TOFs for Ru/dealuminated zeolite catalysts was not simply an underestimation of dispersion caused by the suppression of hydrogen chemisorption.

Another important difference between these catalysts was their acidic nature. The void volumes (Table 1) show that some residue alumina probably remained in the highly dealuminated zeolites. Such extra-framework aluminum could serve as Lewis acid sites (*7*). However, the ^{27}Al NMR results indicate, as shown also by Garralón *et al.* (*14*), that the $(NH_4)_2SiF_6$ dealumination procedure produced very little extra-framework Al. Zi and Yi (*13*), based on pyridine adsorption studies, also found that acid sites of dealuminated zeolites are mainly Brønsted-type acid sites. Furthermore, the pretreatment temperatures used in our studies were maintained below conditions where one would expect to generate Lewis acidity. Thus, the Lewis acid sites of our catalysts, if they existed at all, were overshadowed by the large amount of Brønsted acid sites. Because the structural Al content in the dealuminated Y zeolites was less than that in the parent Y zeolite, the concentrations of acid sites would have also been smaller (Table 1). There is unfortunately no obvious technique which allows a direct determination of either the type, the strength, or the concentration of acid sites on zeolite-supported metal catalysts. All the conventional techniques such as IR and TPD used to measure these parameters on "pure" zeolites rely on adsorption of base molecules (pyridine, NH_3, and others) which are also very reactive on metals, such as Ru, whether in the reduced or oxidized state. However, it is well known that the strength of the acid sites in Y zeolites increases with decreasing Al content for the Si/Al range 2.5–5.0 (*4, 5, 15*).

Previous reports (*19–22*) have shown an increase in activity for CO hydrogenation with increasing acidity of the support. Leith (*22*) suggested that the increase in activity was due to an increase in electron deficiency of the metal crystallites owing to an electron transfer to the electron-acceptor sites of the support. By this explanation, the electron-deficient character of the supported metal would be higher the higher the acidity of the zeolite support. Such an explanation fits what is seen by IR for CO adsorption on Ru supported in zeolites having different Si/Al ratios and having acid sites present (*23*). Vannice (*21*) and Okuhara *et al.* (*24*) have suggested that a weakening of the bound CO species, paralleled by an increase in H_2 adsorption, would result in a higher activity for CO hydrogenation. However, at least at 25°C, there may be more suppression of hydrogen chemisorption than CO chemisorption on Ru/zeolite catalysts (*1, 16*). In addition, variations in zeolite–metal interactions large enough to affect activity significantly would be expected to also influence primary product selectivity which does not appear to have been the case.

Another possible explanation is that the acid sites act to convert primary olefinic reaction products from CO hydrogenation to paraffinic species relatively inert for further readsorption on the metal sites (*1*). Consequently, more metal sites would be available for CO hydrogenation, since they would be less involved in readsorption of primary olefinic products, and the activity of the catalysts, thus, would be enhanced. In HY and dealuminated HY cases where there is a high concentration of strong acid sites, such a mechanism may well be in effect.

However, such an enhancement for CO hydrogenation would be affected not only by the strength of acidity but also by the concentration of acid sites. As the Si/Al ratio increases, the concentration of acid sites decreases. However, up to a Si/Al ratio of approximately 5, such a decrease in concentration is compensated by an increase in acid site strength. The acid site strength, however, is essentially constant for Si/Al > 5. As the zeolite is further dealuminated, the number of strong acid sites decreases. Thus, fewer acid sites would be available to compete for adsorption of reaction intermediates and to convert them to less reactive paraffinic species. This declining density of acid sites would also have an impact upon any electron transfer from the metal to the support which might be expected to become weaker because the metal crystallites would be surrounded by fewer acid sites. Based on the above arguments, the activity would be expected to go through a maximum as the zeolite is dealuminated, as was seen. Figure 2 shows that the TOF first increased with Si/Al ratio up to about 4.5, then decreased for the higher Si/Al ratio.

Product Selectivity

The lack of effect of Si/Al ratio on the overall product distribution or on the chain growth probability, α, is rather surprising. In a previous study of CO hydrogenation over a series of zeolite-supported Ru catalysts having different Si/Al ratios (1.4–5.5) but also different framework structures (X, Y, L, and mordenite), it was found that the product selectivity shifted towards lower-molecular-weight hydrocarbons, especially methane, as the Si/Al ratio increased (*3*). However, for a series of Y-zeolite-supported Ru catalysts with similar number of acid sites, the nature of the neutralizing alkali cations in the zeolite had no effect on the chain growth probability, while producing significant changes in secondary reactions of primary olefinic products (*1*). Such changes were interpreted in terms of the possible modifications of the acid sites present in the zeolites by the nature of the alkali cations. The lack of effect on chain growth probability suggested that, as in the present study, electronic and electrostatic field effects on reactions occurring on the metal paticles could be ruled out. Other phenomena may have been involved in affecting the chain growth probability of the X-, Y-, L-, and mordenite-supported Ru catalysts (*3*) since not only the Si/Al ratios but also the framework structures of the zeolite were different. Diffusion, steric effects, residence times within zeolite pores, probability for readsorption of primary products, etc., may have had significant effects on the product distribution.

Since secondary reactions of olefinic products of CO hydrogenation, such as isomerization, oligomerization, and cracking, are acid-catalyzed (*1–3*), they also would be influenced by the concentration and strength of acid sites in the Ru/dealuminated zeolites. The Brønsted acidity of Y zeolite can be probed by certain hydrocarbon reactions. DeCanio *et al.* (*7*) found that a normal HY zeolite exhibited much less activity (TOF based on number of Al atoms in the zeolite) than that of a dealuminated zeolite Y for methanol dehydration and cumene dealkylation. Mirodatos *et al.* (*25*) explained the selectivity change for *n*-decane cracking on a series of dealuminated HY zeolites as due to a variation in the electrostatic field caused by decreasing Al in the faujasite. The acidic nature of zeolite-supported Ru catalysts was also suggested to be a factor in the product distribution of CO hydrogenation (*1–3*). Using 1-butene and propylene reactions over a series of partially exchanged alkali Y-zeolites having similar concentration of Brønsted acid sites but different types of alkali cations, Oukaci *et al.* (*2*) found a correlation between the relative strength of the acid sites and the secondary reactions of primary olefinic F–T products. The strength of the acid sites is a strong function of the neutralizing cations in the zeolite as well as of the Si/Al ratio of the zeolite.

One measure of Brønsted acidity is the yield of branched products in CO hydrogenation since these are the products of acid-catalyzed reactions and since any other type of acidity, namely Lewis acidity, may be excluded under the pretreatment conditions used. Figure 4 shows that the percentage of isobutane and isobutene in C_4 products increased with increasing Si/Al ratio and leveled off when the Si/Al ratio was greater than 4. Previous results (*1*) showed that only linear C_4 products of CO hydrogenation are observed over Ru/SiO_2, while branched C_4's are generated by CO hydrogenation over RuHY. A strong acid site is needed for structural isomerization as well as for oligomerization-cracking of linear hydrocarbons to form branched products. As the acid strength increases, the percentage of structural isomerization and oligomerization-cracking products increases, too. Barthomeuf and Beaumont (*26*), based on isooctane cracking, proposed that the first 30% of the extracted Al is associated with weak acid sites while dealumination past 33% (Si/Al = 4.5) results in the removal of strong acid sites. Thus, one would expect that the activity for acid-catalyzed reactions such as the secondary isomerization of primary products of CO hydrogenation should exhibit a maximum as Si/Al ratio was increased. This was not the case here since the percentage of branched products seemed to level off above a Si/Al ratio of 4. In this range of Si/Al ratios, the conversion to the C_4-branched products was probably close to equilibrium.

The results (Fig. 5) indicate that the secondary hydrogenation of olefins is enhanced with increasing acidity of the supports. This is evidenced by the olefin/paraffin ratio (represented by $C_4^=/C_4$ ratio). Figure 5 shows that both linear-$C_4^=$/linear-C_4 and iso-$C_4^=$/iso-C_4 ratios decreased with increasing Si/Al ratio, but leveled off when the Si/Al ratio was greater than 4. In fact, this increase in paraffinic products followed the same trend as that of the branched products, suggesting again the participation of the acid sites in olefin hydrogenation. As shown previously

(*2*, *3*), the primary olefinic products may be hydrogenated on strong acid sites via an intermolecular hydrogen transfer mechanism.

V. CONCLUSION

The dealumination of Y zeolite was carried out in an aqueous fluorosilicate solution. XRD and NMR showed that dealumination was achieved without any collapse of or creation of obvious defects in the zeolite structure. The catalytic properties of the Ru/dealuminated Y-zeolite catalysts were characterized by CO hydrogenation. An increase in TOFs for CO hydrogenation was found in the dealuminated Ru catalysts. The TOF showed a volcano shape vs. Si/Al ratio, with the maximum TOF occurring at a Si/Al ratio of 4.5. It is suggested that the activity for CO hydrogenation was probably enhanced through an increase in the secondary reactions of the primary F–T products. The overall product distribution and the chain growth probability, α, for CO hydrogenation was unaffected by variations in Si/Al ratio of the zeolite, suggesting an absence of electronic and electrostatic field effects on reactions occurring on the metal particles. The increase in secondary reaction products was due to reaction on acid sites of the zeolite where acidity was a function of Si/Al ratio. An increase in the selectivity of branched hydrocarbons with increasing Si/Al ratio was observed, caused by the increase in acid strength with dealumination.

ACKNOWLEDGMENT

Partial funding for this work was provided by the Materials Research Center of the University of Pittsburgh funded by the Department of Defense.

REFERENCES

1. Oukaci, R., Sayari, A., and Goodwin, J. G., Jr., *J. Catal.* **102,** 126 (1986).

2. Oukaci, R., Wu, J. C. S., and Goodwin, J. G., Jr., *J. Catal.* **107,** 471 (1987).

3. Oukaci, R., Wu, J. C. S., and Goodwin, J. G., Jr., *J. Catal.* **110,** 47 (1988).

4. Iwamoto, M., Tajima, M., and Kagawa, S., *J. Chem. Soc. Chem. Commun.*, 598 (1986).

5. Barthomeuf, D., *in* "Catalysis 1987 Proceedings of the 10th N. American Meeting of Catalysis Society, San Diego, CA, May 17–22, 1987," p. 127. (J. W. Ward, Ed.) Elsevier, 1988.

6. Kerr, G. T., *J. Phys. Chem.* **72,** 2594 (1968).

7. DeCanio, S. J., Sohn, J. R., Fritz, P. O., and Lunsford, J. H., *J. Catal.* **101,** 132 (1986).

8. Beyer, H. K., Belenykaja, I. M., Hange, F., Tielen, M., Grobet, P. J., and Jacobs, P. A., *J. Chem. Soc. Faraday Trans. 1* **81,** 2889 (1985).

9. Kubelková, L. Seidl, V., Nováková, J., Bednárová, and Jírû, P., *J. Chem. Soc. Faraday Trans. 1* **80,** 1367 (1984).

10. Skeels, G. W., and Breck, D. W., *in* "Proceedings of the Sixth International Zeolite Conference, Reno, Nevada, 1983," p. 87. (D. Olson and A. Bisio, Eds.), Butterworths, 1984.

11. Klinowski, J., Ramdas, S., Thomas, J. M., Fyfe, C. A., and Hartman, J. S., *J. Chem. Soc. Faraday Trans. 2* **78,** 1025 (1982).

12. Haag, W. O., Lago, R. M., and Weisz, P. B., *Nature* **309,** 589 (1984).

13. Zi, G., and Yi, T., *Zeolites* **8,** 232 (1988).

14. Garralón, G., Fornés, V., and Corma, A., *Zeolites* **8,** 268 (1988).

15. Thomas, J. M., and Klinowski, J., *Adv. Catal.* **33,** 251 (1985).

16. Gustfson, B. L., and Lunsford, J. H., *J. Catal.* **74,** 393 (1982).

17. Goodwin, J. G., Jr., *J. Catal.* **68,** 227 (1981).

18. Wang, H. T., Chen, Y. W., and Goodwin, J. G., Jr., *Zeolites* **4,** 56 (1984).

19. Fajula, F., Anthony, R. G., and Lunsford, J. H., *J. Catal.* **73,** 237 (1982).

20. Arai, H., *Chem. Abstr.* **96,** 125964f, 197 (1982).

21. Vannice, M. A., *J. Catal.* **40,** 129 (1975).

22. Leith, I. R., *J. Catal.* **91,** 283 (1985).

23. Blackmond, D. G., and Goodwin, J. G., Jr., *J. Chem. Soc. Chem. Commun.*, 125 (1981).

24. Okuhara, T., Kimura, T., Kobayashi, K., Misono, M., and Yoneda, Y., *Bull. Chem. Soc. Jpn.* **57,** 938 (1984).

25. Mirodatos, C., Bioul, A., and Barthomeuf, D., *J. Chem. Soc. Chem. Commun.*, 149 (1987).

26. Barthomeuf, D., and Beaumont, R., *J. Catal.* **30,** 288 (1973).