

n-Butane Hydroisomerization over Pd/HZSM-5 Catalysts. 1. Palladium Loaded by Impregnation

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The influence of calcination and reduction conditions, metal loading, impregnation solution pH, and dealumination treatment on the hydroisomerization of *n*-butane over bifunctional Pd/HZSM-5 catalysts was studied in order to obtain an active and highly selective catalyst. Temperature-programmed desorption of ammonia (TPDA), Fourier transform infrared (FTIR), atomic absorption spectroscopy (AA), chemisorption measurements, temperature-programmed reduction (TPR), and transmission electron microscopy (TEM) techniques were used to characterize the catalysts. Calcination and reduction conditions were found to have no significant influence on catalyst activity. When the catalyst was prepared by impregnation with palladium nitrate at pH 1.0 and then dealuminated with HCl, both conversion and isobutane selectivity were clearly enhanced. This is suggested to be due to palladium-proton adduct formation. The selected catalyst had a total conversion of 31.5 mol % and a high selectivity of 79%. Experimental conditions: weight of catalysts 5 g, reaction temperature 375 °C, total pressure 1 atm, $W/F_{n-C_4} = 1$ g/(g/h), and $H_2/n-C_4$ mole ratio 10:1.

Introduction

In the last years, the most widely studied catalysts for *n*-butane isomerization have been solid superacids, especially sulfate-treated zirconium oxide $SO_4^{2-}-ZrO_2$.^{1–10} Such catalysts have a very high acid strength and can isomerize light paraffins at low temperatures (usually 150–300 °C). This is an important goal, because the isobutane yield is limited by thermodynamic equilibrium and is favored at low reaction temperatures. Typical reaction results with these catalysts are 15–20 mol % isobutane yield and 75–90% isobutane selectivity. However, they show a fast deactivation rate under the usual experimental conditions.

Several solutions have been proposed to reduce deactivation. If the reaction is carried out in the presence of hydrogen, the addition of a metallic phase to $SO_4^{2-}-ZrO_2$, e.g., Pt or Pd, will theoretically inhibit the formation of coke precursors and, hence, catalyst deactivation. The effect of palladium addition on the activity and stability of $SO_4^{2-}-ZrO_2$ was studied by Larsen et al.⁸ They found that, in the presence of hydrogen, Pd/ $SO_4^{2-}-ZrO_2$ had a lower *n*-butane isomerization activity than $SO_4^{2-}-ZrO_2$, and Pd could not stabilize the reaction at low H_2/n -butane ratios. Garin et al.² postulated that the addition of Pt to $SO_4^{2-}-ZrO_2$ had no influence on the activity and stability of the catalyst when H_2 was used at a convenient partial pressure. Later, Yori et al.¹⁰ reconsidered the convenience of the addition of Pt to $SO_4^{2-}-ZrO_2$. They prepared a catalyst with Pt supported on Al_2O_3 and mixed mechanically with $SO_4^{2-}-ZrO_2$ and observed that the activity and selectivity were increased. Chao et al.⁶ have reported that Pt/ $SO_4^{2-}-ZrO_2$ could also be stabilized by working at high pressure. They observed that catalytic activity could be maintained at 40 wt % conversion and 80% isobutane

selectivity at 260 °C under 20.4 atm pressure for at least 10 h. However, long-term stability and the potential regeneration of modified $SO_4^{2-}-ZrO_2$ are two aspects that deserve more attention if these systems are to give back a commercially attractive catalyst for isomerization of light paraffins.

On the other hand, zeolites have also been widely used as catalysts for the isomerization of paraffins. Strongly acidic molecular sieves such as H-mordenite or H β have shown to be very promising as far as *n*-butane isomerization is concerned.^{11–14} Typical reaction results with these catalysts are 10–20 mol % isobutane yield and 40–70% isobutane selectivity, depending on reaction conditions. However, deactivation of these catalysts due to coke formation has been observed. Mordenite is usually dealuminated to avoid this problem.

Another possibility is to use a high-silica zeolite of the pentasil family, like HZSM-5, because of its acidity, shape selectivity, and temperature resistance. They can be used as catalysts to isomerize light paraffins once promoted with a metal.^{11,12} When bifunctional catalysts based on zeolites are compared with $SO_4^{2-}-ZrO_2$, a lower isobutane selectivity is always observed, as zeolites certainly need a higher reaction temperature to be active for *n*-butane isomerization. There is, however, room for significant improvement by catalyst optimization: its activity strongly depends on the preparation method, which is rarely taken into account when they are compared with superacid solids.

In this paper, the influence of the preparation method (calcination, reduction metal loading, impregnation solution pH, and dealumination treatment) of a bifunctional catalyst based on palladium and HZSM-5 zeolite on the activity and the selectivity for *n*-butane isomerization is studied.

Experimental Section

Temperature-programmed desorption of ammonia (TPDA), temperature-programmed reduction (TPR),

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Table 1. Effect of Calcination Conditions^a

catalysts	C2-400	C4-400	C16-400	C4-500
t_{cal} , h	2	4	16	4
T_{cal} , °C	400	400	400	500
D_{CO} , %	11.4	10.8	10.4	10.3
D_{H_2} , %	10.0	9.3	9.9	9.1
TPR peak maximum, °C	435	440	433	440
total acidity, mequiv/g	0.276	0.276	0.272	0.273
weak acidity, mequiv/g	0.143	0.144	0.142	0.143
$T_{\text{a}} = 290$ °C				
strong acidity, mequiv/g	0.133	0.132	0.130	0.130
$T_{\text{a}} = 390$ °C				

^a $T_{\text{red}} = 400$ °C; $t_{\text{red}} = 4$ h; $W_{\text{Pd}} = 0.55\%$.

atomic absorption spectroscopy (AA), chemisorption measurements, and transmission electron microscopy techniques have been used to characterize the catalysts, as described in a previous paper.¹⁵ For the dealuminated samples, the nature of the acid sites was determined by Fourier transform infrared (FTIR) experiments. These experiments were done on a Perkin-Elmer 16 PC spectrometer at a resolution of 4 cm^{-1} by using either KBr pellets or self-supporting wafers. Pyridine chemisorption experiments were done on self-supported wafers in an in situ IR cell. The sample was dehydrated at 500 °C for 5 h under a vacuum of 1.33×10^{-3} Pa followed by adsorption of purified pyridine vapor at room temperature for 15 min. The system was then evacuated at different temperatures, and an infrared spectrum was recorded. Typical infrared bands at 1540 and 1460 cm^{-1} , corresponding to characteristic bands of pyridine molecules chemisorbed on Brønsted and Lewis acid sites, respectively, were obtained.

The preparation of the catalysts and the experimental installation were also reported in the same paper. All catalysts were prepared by impregnation with an aqueous solution of $\text{Pd}(\text{NO}_3)_2$. Partial dealumination of some catalysts was accomplished by hydrochloric acid treatment at 75 °C for 4 h with a liquid/solid ratio of 15 mL/g, prior to the metal introduction. Next, the suspension was filtered and thoroughly washed with deionized water until chlorine ions were not detected.

The experiments were carried out in a flow-type apparatus designed for continuous operation at atmospheric pressure. This apparatus consisted of a gas feed system for each component hydrogen and *n*-butane (+99.95%, the main impurities being isobutane [max. 400 ppm] and propane [max. 100 ppm]) with individual control by mass flow meters, a fixed-bed downflow reactor and an exit gas flow meter. Experimental conditions: weight of catalysts 5 g, reaction temperature 375 °C, total pressure 1 atm, $W/F_{n-C_4} = 1$ g/(g/h), and $\text{H}_2/n\text{-C}_4$ mole ratio 10:1. It was verified that neither internal nor external diffusions were the controlling step under these experimental conditions.

Results and Discussion

1. Effect of Calcination Conditions. To study the effect of calcination conditions on the conversion, isobutane selectivity and isobutane yield, the catalysts were calcined at different temperatures and times. The notation of the catalysts and the results of their characterization are given in Table 1. Conversion, isobutane selectivity, and isobutane yield are shown in Figure 1.

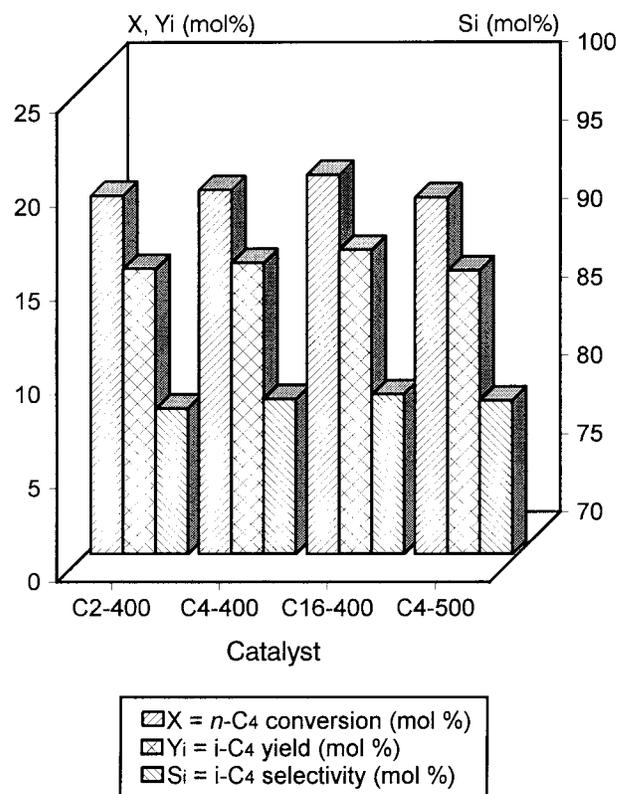


Figure 1. Influence of the calcination conditions on *n*-butane conversion, isobutane selectivity, and isobutane yield ($T_{\text{reaction}} = 375$ °C; $\text{H}_2/n\text{-C}_4 = 10$; $W/F_{n-C_4} = 1$ g/(g/h)).

It can be clearly seen that the results are very similar for all catalysts. Calcination conditions do not seem to affect the activity of the catalysts in the range investigated.

Temperature-programmed reductions were carried out in order to determine the relative differences in the reducibility of the catalysts, which is related to the location and dispersion of palladium after the calcination step. It was previously found that montmorillonite consumes some hydrogen at temperatures above 560 °C due to the reduction of the metals in its structure. This consumption is negligible at temperatures lower than 550 °C and can be accounted for without significant error by subtraction in the TPR analysis. The TPR peak maxima for these catalysts are given in Table 1.

All the catalysts exhibit very similar TPR profiles (not depicted in this paper), with a maximum around 430 – 440 °C. These results seem to indicate that the metal is similar in all catalysts, which is confirmed by the metal dispersion measurements shown in Table 1.

TPDA was carried out in order to compare the acidity of the catalysts. There is a peak at 290 °C that was assigned to both weak acid sites and nonacid sites associated to the Na^+ cation.^{16,17} The peak at 390 °C was associated with strong acid sites of the zeolite. Table 1 gives a quantitative comparison of total acidity (overall amount of ammonia desorbed) and partial acidity (area obtained by Gaussian deconvolution under each of the two peaks used to fit the desorption curve).

It can be observed that the total acidity and the partial acidity of each peak do not vary with the calcination conditions. It can be concluded that neither the metal function nor the acid function are affected by the calcination conditions in the investigated range. This fact would explain the similar results obtained in

Table 2. Effect of Reduction Conditions^a

parameters	R4-400	R4-450	R4-500
t_{red} , h	4	4	4
T_{red} , °C	400	450	500
D_{CO} , %	10.8	8.6	6.6
D_{H_2} , %	9.3	6.0	4.7
total acidity, mequiv/g	0.276	0.272	0.270
weak acidity, mequiv/g $T_{\text{d}} = 290$ °C	0.144	0.143	0.147
strong acidity, mequiv/g $T_{\text{d}} = 390$ °C	0.132	0.129	0.123

^a $T_{\text{cal}} = 400$ °C; $t_{\text{cal}} = 4$ h; $W_{\text{Pd}} = 0.55\%$.

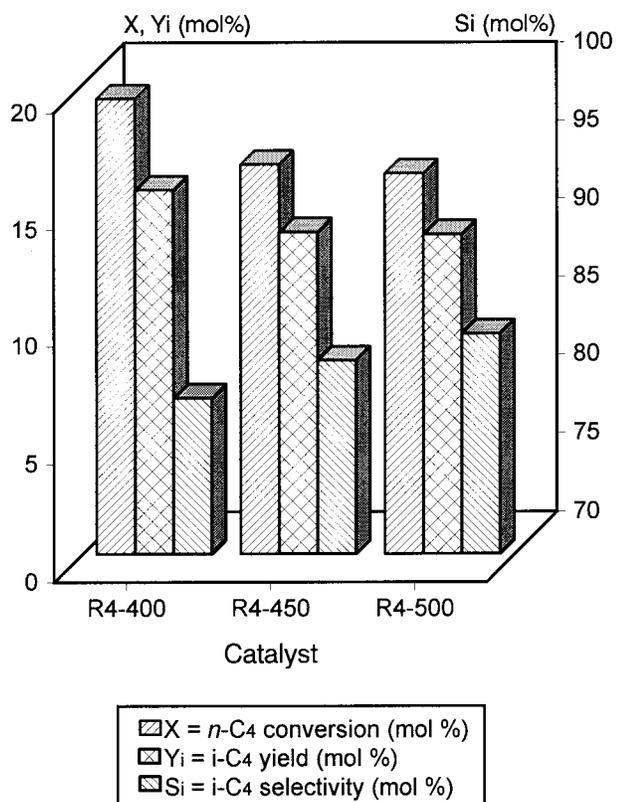


Figure 2. Influence of reduction conditions on *n*-butane conversion, isobutane selectivity, and isobutane yield ($T_{\text{reaction}} = 375$ °C; $H_2/n\text{-C}_4 = 10$; $W/F_{n\text{-C}_4} = 1$ g/(g/h)).

the reaction experiments with all the catalysts. The results are in agreement with those reported in a previous paper,¹⁵ where similar catalysts loaded with Pt instead of Pd were studied. The catalysts used in the next sections were all calcined at 400 °C for 4 h.

2. Effect of the Reduction Conditions. A set of experiments was carried out by varying the catalyst reduction temperature. The notation of the catalysts and the results of their characterization are given in Table 2. Conversion, isobutane selectivity, and isobutane yield are shown in Figure 2.

When the reduction temperature was raised from 400 to 500 °C (i.e., when the reduction severity was increased), a slight decrease in *n*-butane conversion was observed. This is due to the lower number of accessible Pd atoms when the reduction temperature is increased, as a consequence of metal sintering, as is shown by the decrease in metal dispersion (Table 2).

These results are also in agreement with those found when Pt was used.¹⁵ However, the reduction conditions for the Pd catalysts do not have as much influence on metal dispersion as those for the Pt catalysts. The latter

Table 3. Effect of Pd Loading^a

parameters	Im-0.28	Im-0.55	Im-0.94	Im-1.23
W_{Pd} , %	0.28	0.55	0.94	1.23
D_{CO} , %	10.1	8.6	5.7	5.4
D_{H_2} , %	10.0	6.0	3.9	4.0
TPR peak maximum, °C	501	440	412	376
total acidity, mequiv/g	0.272	0.272	0.273	0.273
weak acidity, mequiv/g $T_{\text{d}} = 290$ °C	0.141	0.143	0.139	0.139
strong acidity, mequiv/g $T_{\text{d}} = 390$ °C	0.131	0.129	0.134	0.134

^a $T_{\text{cal}} = 400$ °C; $t_{\text{cal}} = 4$ h; $T_{\text{red}} = 450$ °C; $t_{\text{red}} = 4$ h.

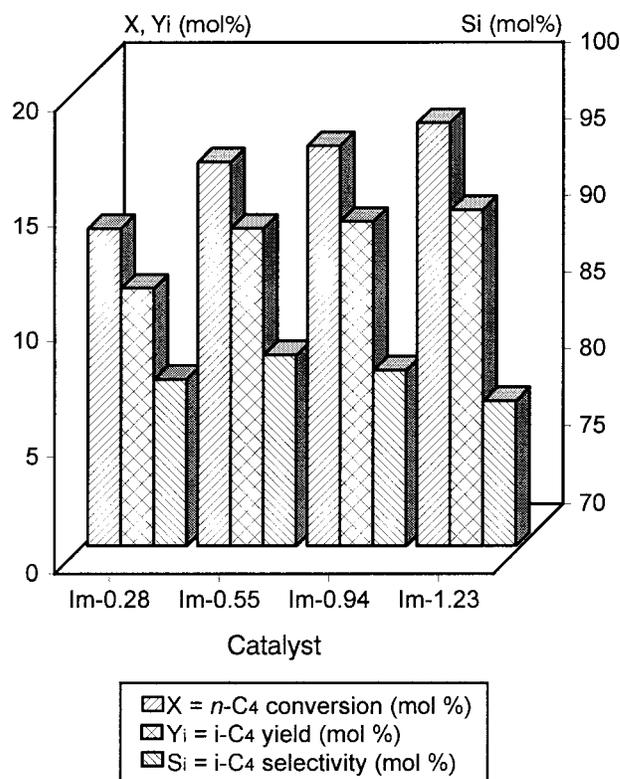


Figure 3. Influence of Pd loading on *n*-butane conversion, isobutane selectivity, and isobutane yield ($T_{\text{reaction}} = 375$ °C; $H_2/n\text{-C}_4 = 10$; $W/F_{n\text{-C}_4} = 1$ g/(g/h)).

were initially well dispersed, but there was not a strong Pt-support interaction (TPR peak maximum about 380 °C). Thus, the dispersion was strongly decreased when the reduction severity was increased. Nonetheless, the Pd catalysts were poorly dispersed, even though they were reduced at low temperatures. Therefore, the influence of the reduction conditions on dispersion decrease was much less significant.

For the subsequent experiments, the catalysts used were reduced at 450 °C for 4 h (intermediate reduction conditions).

3. Effect of the Palladium Loading. The notation of the catalysts and the results of their characterization are given in Table 3. Conversion, isobutane selectivity, and isobutane yield are shown in Figure 3. It can be observed that isobutane yield increased with palladium loading.

The TPR peak maxima for these catalysts are given in Table 3. It can be observed that when the palladium loading increases, the temperature corresponding to the maximum is shifted to lower values. It is very likely that some Pd^{2+} is ion-exchanged during the impregna-

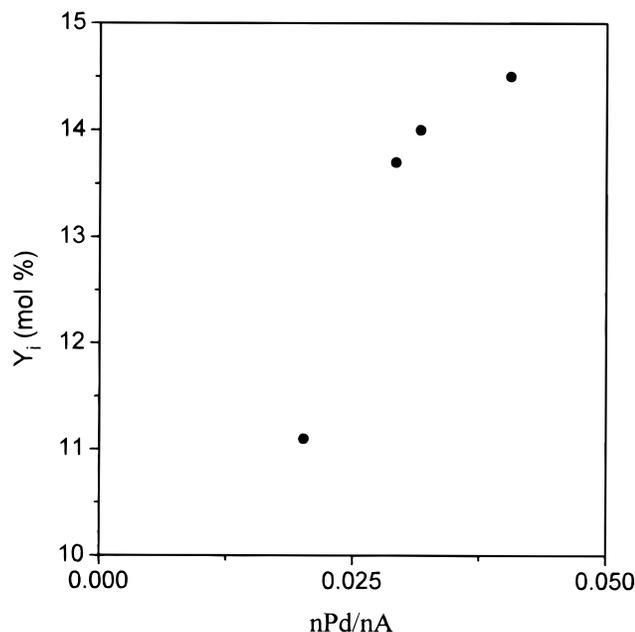
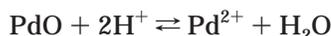


Figure 4. Isobutane yield vs nPd/nA ratio.

tion process in neutral solution. It is also possible (as suggested by a referee) that part of the PdO particles formed during the calcination of these catalysts react with the zeolite protons to form Pd²⁺ ions:



In any case, some Pd²⁺ ions are obtained. PdO particles are, obviously, reduced at a lower temperature than Pd²⁺ ions. This might explain the huge difference in TPR maxima positions: 376 °C for high Pd loading and 501 °C for low Pd loading catalysts. At low loading the Pd²⁺/PdO ratio might be higher (and, hence, more difficult to reduce) than at high loading, where PdO particles are likely to prevail. Under this assumption, the metal dispersion should decrease when the palladium loading is increased, as observed. On the other hand, TPDA measurements showed no remarkable differences in the acidity of these catalysts.

The catalytic results suggest that reaction proceeds by a typical bifunctional mechanism, the reaction on the metal sites being the rate-limiting step. To confirm this assumption, isobutane yield was plotted versus the nPd/nA ratio in Figure 4. The number of hydrogenating sites (nPd), namely the number of accessible Pd atoms was calculated from the palladium content and metal dispersion. The number of strong acid sites (nA) was drawn from the TPDA measurements.

It can be observed that isobutane yield increases with nPd/nA ratio, as expected for a bifunctional catalyst with low nPd/nA value.^{18,19} The reaction on the metal sites is the rate-limiting step, even for the Im-1.23 catalyst, since the typical plateau of this curve was not obtained. However, an ideal bifunctional catalyst requires acid function control.²⁰ So, it could be interesting to prepare a catalyst with a higher palladium content, to increase the nPd value. Nonetheless, there are some experimental problems in preparing that catalyst: (i) as the metal dispersion decreases with the Pd loading, the nPd value is hardly increased; (ii) if a high metal content is required, the impregnation solution would have a high Pd concentration. In this case hydroxylation of the metal should be taken into account.²¹

Table 4. Effect of Impregnation Solution pH^a

catalysts	pH-7.0	pH-4.0	pH-1.0	pH-0.5
solution pH	7.0	4.0	1.0	0.5
D _{CO} , %	8.6	15.1	18.2	22.2
D _{H₂} , %	6.0	14.3	16.6	20.1
W _{Na} , %	1.28	1.27	1.25	1.25
TPR peak maximum, °C	440	420	365	363
total acidity, mequiv/g	0.272	0.273	0.279	0.280
weak acidity, mequiv/g	0.143	0.141	0.139	0.139
T _d = 290 °C				
strong acidity, mequiv/g	0.129	0.132	0.140	0.141
T _d = 390 °C				

^a T_{cal} = 400 °C; t_{cal} = 4 h; T_{red} = 450 °C; t_{red} = 4 h; W_{Pd} = 0.55%.

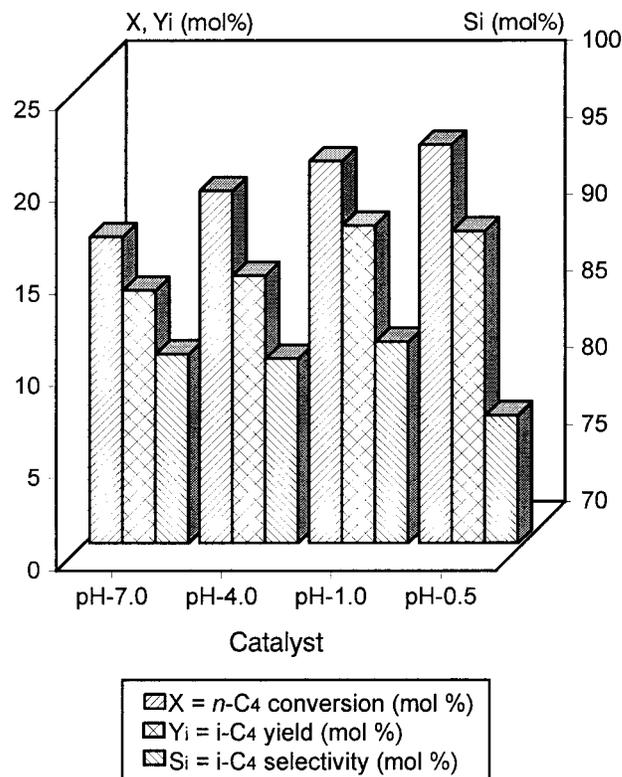


Figure 5. Influence of impregnation solution pH on n-butane conversion, isobutane selectivity, and isobutane yield (T_{reaction} = 375 °C; H₂/n-C₄ = 10; W/F_{n-C₄} = 1 g/(g/h)).

Then, catalyst improvement implies obtaining a higher metal dispersion and avoiding metal hydroxylation. This can be achieved by decreasing the impregnation solution pH. The selected Pd content was 0.55 wt %, for which the best isobutane yield/Pd loading ratio was obtained.

4. Effect of the Impregnation Solution pH. The notation of the catalysts and the results of their characterization are given in Table 4. Conversion, isobutane selectivity, and isobutane yield obtained are shown in Figure 5.

Conversion was found to be higher when the catalyst was impregnated at lower pH values. Isobutane selectivity could be considered constant in the pH range 1.0–7.0, whereas as light decrease was observed at the lowest pH.

On the other hand, both metal dispersion and strong acidity density were increased at lower pH values, whereas the temperature maximum corresponding to the TPR curves was shifted to lower values (Table 4).

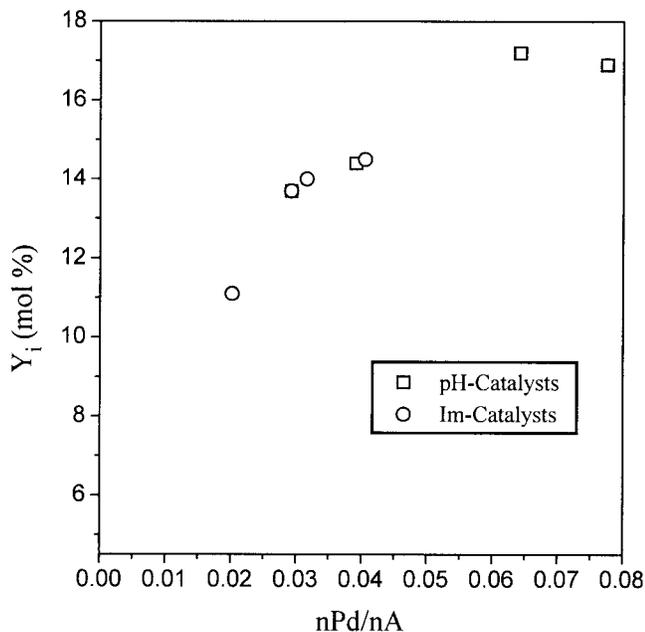


Figure 6. Isobutane yield vs nPd/nA ratio.

It is well-known that the tendency of transition metal cations to form dimeric or polymeric "polyoxo cations" increases with increasing pH. So, the accessibility to the zeolite main channel system for such large ions may be reduced at high pH values. At lower pH values, the metal ions would have a lower degree of aggregation and, hence, could enter the main channels, as has been reported for nickel ions.²² Then, the metal would be better distributed, thus obtaining a higher dispersion.

On the other hand, it was commented above that some Pd²⁺ ions are formed by ion-exchange during the impregnation process and/or by reaction between PdO particles and zeolite protons. TPR results suggest that Pd²⁺ ions are mainly formed by ion exchange. Palladium ion exchange should be very much inhibited when the impregnation is carried out at low pH, due to competition of protons. All palladium would be only impregnated and, consequently, lower TPR peak maxima should be obtained, as observed. If Pd²⁺ ions were formed by reaction with zeolite protons, then the low-pH impregnated catalysts, with a higher strong acid site density, should have a high proportion of them, opposite to the TPR results.

Higher strong acidity is obtained because some Na⁺ cations still remaining in the catalysts are now exchanged by the H⁺ of the low-pH impregnation solution (see Table 4).

Now, it is possible to add up new points to the isobutane yield vs nPd/nA curve (Figure 6). As can be clearly seen, a typical curve for bifunctional catalysts is obtained: isobutane yield increases with nPd/nA ratio until a plateau is reached. It can also be observed that the catalyst is improved when impregnation is carried out at low pH. This is a logical result, as the number of accessible Pd atoms and the strong acid site density are simultaneously increased. Finally, it can be drawn from Figure 6 that the reaction on the acid sites became the rate-limiting step for the catalysts impregnated at low pH. Now, catalytic activity will depend on acidity (number and strength).

For the subsequent experiments, the catalysts were impregnated at pH 1.0, for which the highest isobutane selectivity and yield were obtained.

Table 5. Effect of Dealumination Conditions^a

catalysts	D-0	D-2.0	D-3.5	D-5.0
HCl concn, N		2.0	3.5	5.0
Si/Al ratio	20	21.8	21.9	21.9
W _{Na} , %	1.25	0.40	0.39	0.39
D _{CO} , %	18.2			
D _{H₂} , %	16.6			
total acidity, mequiv/g	0.279	0.372	0.368	0.369
weak acidity, mequiv/g	0.139	0.047	0.046	0.046
<i>T</i> _d = 290 °C				
strong acidity, mequiv/g	0.140 ^b	0.325	0.322	0.323
<i>T</i> _d = 405 °C				

infrared data ^c	L	B	L	B	L	B	L	B
<i>T</i> _d of pyridine: 150 °C	0.79	0.96	0.79	1.54	0.78	1.53	0.78	1.53
<i>T</i> _d of pyridine: 450 °C	0.25	0.63	0.50	1.49	0.49	1.53	0.50	1.53

^a *T*_{cal} = 400 °C; *t*_{cal} = 4 h; *T*_{red} = 450 °C; *t*_{red} = 4 h; *W*_{Pd} = 0.55%. Impregnation solution pH = 1.0. Dealumination temperature = 75 °C. Dealumination time = 4 h. ^b *T*_d = 390 °C. ^c Absorbance per gram of catalyst after pyridine desorption at different temperatures for Lewis acid sites (L) and Brønsted acid sites (B).

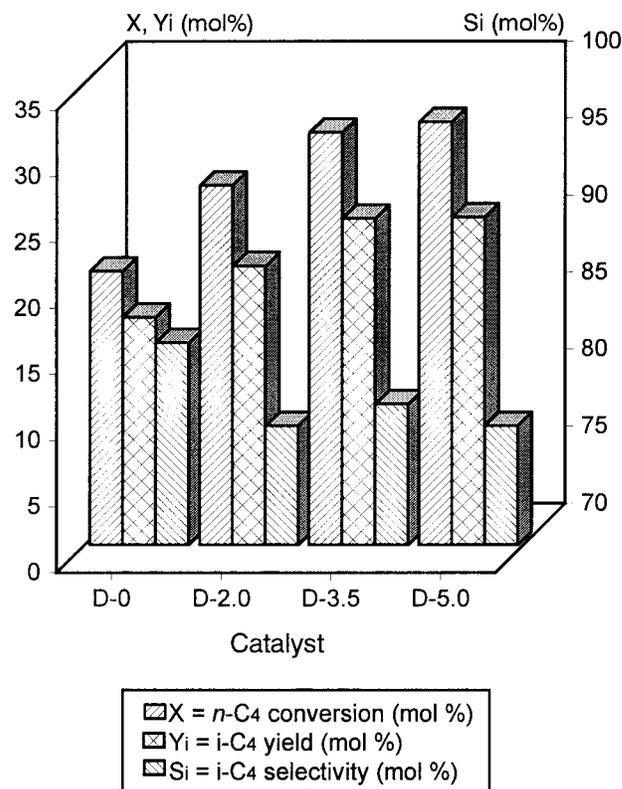


Figure 7. Influence of dealumination conditions on *n*-butane conversion, isobutane selectivity, and isobutane yield (*T*_{reaction} = 375 °C; H₂/*n*-C₄ = 10; *W*/*F*_{*n*-C₄} = 1 g/(g/h)).

5. Effect of the Dealumination Conditions. Finally, dealumination treatment with HCl was carried out in order to enhance strong acid site density. The notation of the catalysts and the results of their characterization are given in Table 5. Conversion, isobutane selectivity, and isobutane yield obtained are shown in Figure 7.

The dealumination treatment enhanced the total acid site density (Figure 8, Table 5), mainly because the strong acid site density is greatly increased. As a consequence, both conversion and isobutane yield are highly increased (Figure 7). Dealumination could increase the average pore dimensions. Thus, the increased conversion may be caused by lower diffusion

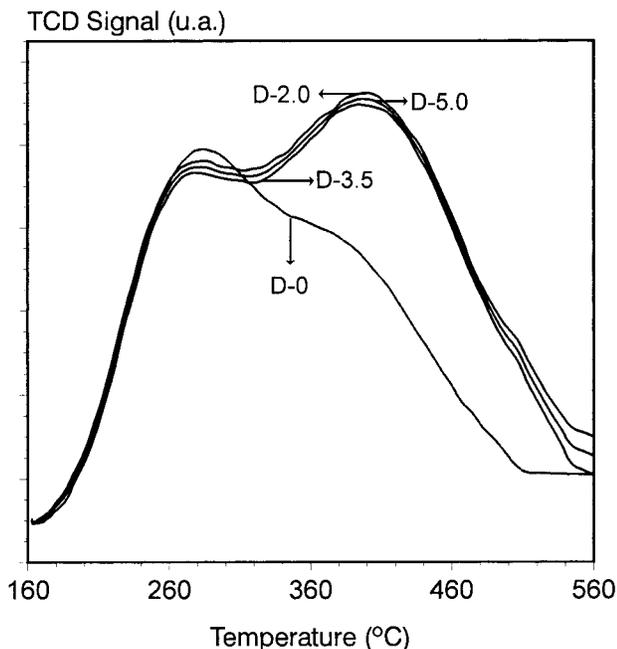


Figure 8. TPDA curves for the D-0, D-2.0, D-3.5, and D-5.0 catalysts.

limitation. Pore size distributions were determined by nitrogen adsorption and desorption data, showing no remarkable differences between the parent and the dealuminated catalysts (147 m²/g of BET surface area and 47.6 μL/g of pore volume of micropores for all parent and dealuminated catalysts). Then, this last hypothesis can be excluded.

It can be quite surprising that dealumination increases total acidity, as this result contradicts the general accepted opinion that the concentration of tetrahedral Al³⁺ ions determines the concentration of acid sites. However, higher acid density is obtained because some Na⁺ cations still remaining in the catalysts are now removed and exchanged by H⁺ during the severe treatment with HCl (Table 5). This effect, already observed for the catalysts impregnated at low pH, is now more evident. On the other hand, the Si/Al ratio increase due to dealumination treatment is not very significant, even for D-5.0 catalyst. It is known that HZSM-5 zeolite, with a low aluminum concentration, is quite resistant to attack by mineral acids.²³ Thus, the Al removal is much less important than the formation of new acid sites (Na⁺ exchanged by H⁺), and therefore, a higher acid site density is obtained. The infrared data of adsorbed pyridine confirm that the exchange of Na⁺ by H⁺ led to new strong Brönsted acid site formation. Strong acidity is mainly Brönsted acidity, as shown by infrared data of adsorbed pyridine at high temperatures (Table 5). However, strong Lewis acid site density is also increased because these centers are generated by dealumination.²³ Finally, characterization data from Table 5 show that all dealuminated catalysts have similar properties. Therefore, similar catalytic results are obtained for all of them.

Figure 9 shows isobutane selectivity vs *n*-butane conversion in order to allow comparison between the parent catalyst (D-0) and a dealuminated sample (D-3.5) at similar conversion levels. It can be seen that the latter is more selective than the former. In this way, the catalyst is also more selective when its acidity is enhanced.

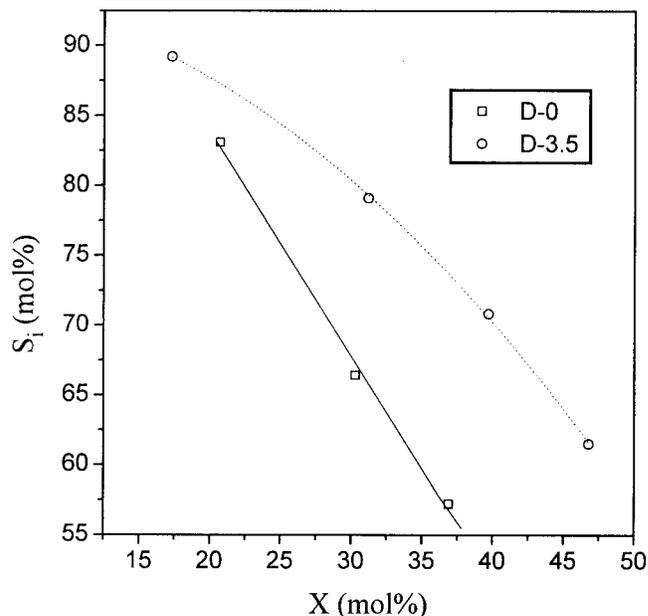
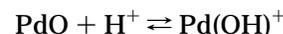


Figure 9. *i*-C₄ selectivity vs *n*-C₄ conversion for the D-0 and D-3.5 catalysts.

The metal state is also greatly influenced by dealumination. The dealuminated catalysts only give a relatively small TPR peak (Figure 10), suggesting that the metal is hard to reduce. As commented above, relatively small monomeric palladium ions exist in the impregnation solution at the low pH 1.0. These relatively small monomeric ions could enter the channel system and could preferentially occupy hidden positions (positions in five-membered units, aside the main channel system of HZSM-5), as observed for nickel ions by Hoang et al.²² Following these same workers, palladium oxide particles obtained after calcination could interact with the protons of the zeolite Brönsted sites, to form Pd(OH)⁺ cations:



Obviously, if there is a high density of strong acid centers, as observed for dealuminated catalysts, the equilibrium above will be displaced to the right. Then, there would be cation species in hidden positions, where they are difficult to reduce, as observed by Sachtler and co-workers for Y-type zeolites.^{21,24-27} Moreover, the ions are less reducible if the density and/or the strength of zeolite acidity is increased.²¹ Then, it can be expected that palladium ions would be difficult to reduce and give small TPR signals.

The negligible metal dispersion obtained from chemisorption measurements is a remarkable result. After reduction at relatively mild temperatures, the palladium ions inside hidden cages would be reduced without leaving these cages.²⁴ Moreover, the zeolite protons can inhibit migration of the Pd particles by chemically anchoring small reduced metal particles.^{21,24,28} This last assumption can be confirmed by using the TEM technique. The electron micrograph for the D-3.5 catalyst is shown in Figure 11. As can be observed, homogeneous Pd particles, the diameter being <10 Å, were obtained. As we did not observe metal particles greater than 10 Å for the dealuminated catalysts, we can assume that the zeolite protons certainly lead to stabilization of small Pd particles. Then, a high metal dispersion should be obtained from chemisorption mea-

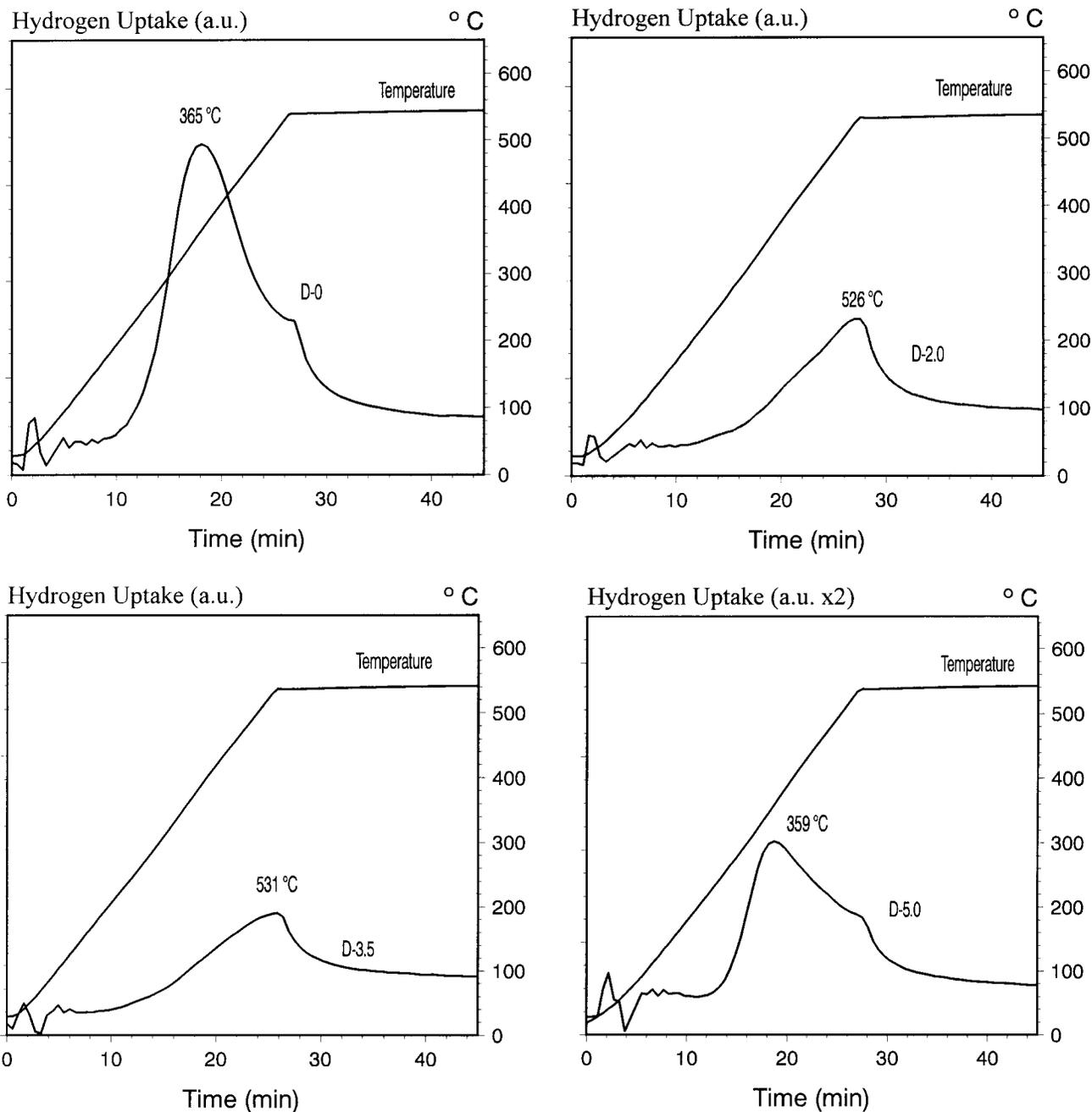


Figure 10. TPR curves for the D-0, D-2.0, D-3.5, and D-5.0 catalysts.

surements. However, this same effect (no chemisorption for highly dispersed samples) was already observed for PtHZSM-5 catalyst.¹⁵ The conclusions can be summarized as follows: the low chemisorption ability of the metal for these catalysts may be due to electron deficiency effects arising from a partial electron transfer between the palladium atoms and the acid sites on the zeolite. This electron transfer would be favored by the strong interaction between metal and zeolite, shown in TPR profiles. Other authors^{29–31} have already observed a positively charged state that could be attributed to small metal particles that exhibit an electron deficiency due to the interaction with acidic zeolite sites. Moreover, it has been reported for a similar system, Pd/Y zeolite, that the zeolite protons markedly reduce the ability of the small Pd particles to chemisorb H₂.²⁸

Finally, it can be concluded that small Pd particles in hidden positions are obtained. As suggested in a

previous work,¹⁵ these particles form, after reduction, [Pd_n-H_x]^{x+} adducts.^{21,28} Such adducts are assumed to be capable of acting as “hybrid sites” combining typical properties of metal surfaces with those of Brønsted acids. It is likely that isomerization takes place on these Pd-H adducts, as recently suggested by other workers.^{21,32} Then adduct formation contributes to higher conversion and isobutane selectivity.

Conclusions

In this work the hydroisomerization of *n*-butane was studied. Both calcination and reduction conditions have no significant influence on the catalytic results, as a poor metal dispersion is always obtained.

The catalyst can be improved by increasing the number of hydrogenating sites. However, if a high metal content is loaded by impregnation in neutral



— 50 Å
Figure 11. Electron micrograph of Pd on the D-3.5 catalyst.

solution, a very poor dispersion is obtained. Moreover, metal hydroxylation would take place.

If the impregnation is carried out at low pH, better metal dispersion is obtained since palladium can enter the zeolite main channel system more easily. A higher strong acidity is also obtained because some Na^+ cations are then exchanged by the protons of the low-pH impregnation solution.

Dealumination of the catalysts, accomplished by hydrochloric acid treatment, greatly increases the strong acid density and, hence, the isobutane yield. The metal state is also influenced by dealumination. Small Pd particles anchored by zeolite protons are obtained, thus causing an intense interaction with the zeolite. As a consequence, the catalyst is clearly improved.

Nomenclature

B = Brönsted acid site

d = particle diameter

D_{CO} = metal dispersion measured by using CO chemisorption

D_{H_2} = metal dispersion measured by using H_2 chemisorption

L = Lewis acid site

n_{A} = number of strong acid sites

n_{Pd} = number of hydrogenating sites

S_i = selectivity to isobutane

T_{cal} = calcination temperature

t_{cal} = calcination time

T_{d} = desorption temperature

T_{reaction} = reaction temperature

T_{red} = reduction temperature

t_{red} = reduction time

W_{Pd} = palladium loading

W_{Na} = sodium content

X = conversion of n -butane

Y_i = yield of isobutane

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