

Hydrogen Transfer Catalysis by Platinum on Zeolites

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Platinum catalysts supported on gamma-alumina and on a variety of zeolites have been characterized and evaluated for activity in the transfer hydrogenation of propylene using butanes as the hydrogen source. Zeolite supports evaluated include both aluminosilicates and borosilicates having the ZSM-5 and beta structures. Platinum on acid zeolites shows enhanced activity for the hydrogen transfer, compared to platinum supported on alumina. However, with platinum on acidic zeolites, propylene hydrogenation is accompanied by a number of competing, acid-catalyzed reactions which lower the selectivity to propane and butenes. Of the acid zeolites studied, low aluminum, borosilicates were found to be more selective than the corresponding aluminosilicates of similar structure. Partial neutralization of the zeolitic acidity with alkali cations lowered the nonselective acid catalysis. Metal-catalyzed hydrogen transfer activity was not diminished by this partial neutralization so that hydrogen transfer selectivity increased. In the case of the borosilicate-supported catalysts, maximum activity near 90% conversion of propylene to propane and selectivity for hydrogen transfer greater than 95% were obtained when sufficient alkali was added to neutralize the acidity associated with framework aluminum while maintaining the acidity associated with boron. Feed studies with an optimized catalyst provide additional mechanistic insights. © 1998

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INTRODUCTION

Recent regulatory developments have led refiners to seek methods for reformulating motor fuels to meet increasingly stringent air quality requirements. One approach includes reducing the gasoline-range olefin (C_5^+) content while maintaining the desired octane rating. The octane rating can be maintained by the addition of high octane isoparaffins (alkylate) and other octane-enhancing additives such as oxygenates. The production of alkylate and oxygenates requires the availability of the lighter olefins (C_5^-).

The gasoline range olefin content can be reduced by saturation with molecular hydrogen but this places increased demands on typically limited refinery hydrogen supplies. Light olefins can be produced by the high severity catalytic cracking but this process also generates additional gasoline range olefins and aromatics which may have to be removed. Light olefins can also be produced by paraffin dehydrogenation and the hydrogen coproduct could be used to

saturate the gasoline range olefins. However, dehydrogenation is highly endothermic and thus equilibrium limited and costly.

Thus in very general terms, recent regulations have placed two opposing demands on the refiner. One demand is the need to remove hydrogen from hydrocarbon precursors in order to generate oxygenates and alkylates; the other is the need to add hydrogen to the unsaturates present in fuels. Conventional technologies have the limitations mentioned above.

Conceptually a hydrogen transfer process in which hydrogen is simultaneously removed from light paraffins and added to gasoline range olefins has several advantages over conventional technology. First, hydrogen transfer would permit two steps, paraffin dehydrogenation and olefin hydrogenation to be accomplished in one operation. Furthermore, the saturation of unwanted fuel range olefins could be accomplished without the need for limited refinery hydrogen. Finally, the desirable light olefins needed as alkylate and oxygenate precursors could be generated without the thermodynamic limitations associated with conventional dehydrogenation technology. The combined process is nearly thermoneutral and might be effected at significantly lower temperatures than dehydrogenation.

Several papers have been published on acid-catalyzed hydrogen transfer activity with zeolites and this area has been recently reviewed (1). Acid catalysts can exhibit significant activity for hydrogen transfer but selectivity to specific products is lowered by competing rearrangements.

There have been a number of papers in the open and patent literature describing metal catalyzed transfer hydrogenation and the area has also been reviewed extensively in two papers published in the last 20 years containing almost 400 references (2, 3). However, only a few papers describe the use of paraffins as the hydrogen source in the saturation of olefins (4-6). In these references, conversions are typically low or limited to either high temperature conditions or to very high paraffin to olefin ratios. In one study palladium was used to catalyze intermolecular hydrogen transfer in 1-hexene to form hexane and hexadiene (4). About 4 to 7% conversion was observed at 200°C in a 1-h batch reaction using 100 cc of 1-hexene and 12 g of catalyst. Interestingly

when C₁₄ or C₁₇ paraffins were added to 1-hexene feed, no hydrogen transfer was observed from the added paraffin to the hexene while the interolefin transfer continued as if the added paraffin were absent. The study concluded that strong olefin adsorption prevented the paraffin from adsorbing and undergoing cross hydrogen transfer.

There have been no detailed studies of metal-catalyzed hydrogen transfer between olefins and paraffins for metals supported on zeolites. However, zeolites have been observed to render platinum especially active for carbon-hydrogen bond activation, in comparison to platinum on nonacidic supports. The influence of faujasite on platinum and palladium's catalytic properties has been reviewed and a number of examples citing enhanced activity are provided (7). Della Betta (8) has observed high activity with platinum on calcium Y zeolite for the hydrogenolysis and isomerization of neopentane. Sachtler and co-workers (9) have proposed a platinum-proton adduct to explain enhanced metal activity in methylcyclopentane rearrangement reactions over platinum Y zeolite.

Because paraffin activation appears to be rate-limiting in paraffin to olefin transfer reactions and because zeolite-supported metals appear to possess exceptional activity for paraffin activation, a more systematic study of hydrogen transfer catalyzed by zeolite-supported metals is warranted. The present study examines the effect of catalyst properties and feed composition on paraffin to olefin hydrogen transfer catalysis for a series of platinum on zeolite catalysts. Although a goal of this study is to identify catalysts that are effective for gasoline range olefin saturation, the present work examines hydrogen transfer between propylene and butanes. This system was chosen to model the hydrogen transfer process because of its inherent simplicity and ease of product analysis. A future paper will describe the extension of this work to higher molecular weight olefins.

EXPERIMENTAL

Zeolite materials. All zeolites used in this study were obtained from commercial suppliers. Zeolite properties are summarized in Table 1. A ZSM-5 powder of silicon/aluminum ratio of 24.9 was obtained in the hydrogen form from PQ ZEOLITES, B.V., an affiliate of PQ Corporation (11 Executive Mall, P.O. Box 840, Valley Forge, PA 19482). Its soda content was analyzed to be less than 0.01%. A second ZSM-5 of silicon/aluminum ratio of 86.3 was also obtained in the hydrogen form from PQ. Its soda content was 0.024%.

The borosilicate zeolite, boron-beta, was obtained from PQ Corporation, designated VALFOR CP 711-B Type Beta-zeolite. The zeolite was obtained in its as-synthesized form containing tetraethylammonium cation. A borosilicate zeolite, boron-ZSM-5 was obtained from PQ Corporation in its as-synthesized form, designated VALFOR CP

TABLE 1
Selected Zeolite Properties

Structure	ZSM-5 (high Al)	ZSM-5 (low Al)	[B]-ZSM-5	[B]-Beta
Si/(B + Al) ratio	24.9	86.3	26.5	24.3
Al/(Al + B) ratio	1	1	0.022	0.062
% Boron (wt.)	0	0	0.5 ^a	0.61
% Aluminum (wt.)	1.69	0.51	0.028 ^a	0.10
% Silicon (wt.)	43.7	45.8	35.1 ^a	41
Crystal size	n.a.	n.a.	10 μ	2.5 μ

^a Elemental analysis on noncalcined B-ZSM-5.

711-B Type ZSM-5 zeolite. Both boron zeolites contained less than 0.01% soda. In order to remove the templates used in synthesis, both boron zeolites were calcined first at 593°C in nitrogen for 4 h, followed by two additional hours at the same temperature in dry air.

Alumina. The alumina used for comparative catalyst studies was a gamma alumina prepared from Disperal, an aluminum hydrate supplied by Vista Chemical Co. of Houston, TX. The aluminum hydrate was converted to gamma alumina prior to use as a catalyst support by calcination in air for 3 h at 873 K. Typical gamma alumina surface areas were about 200 m²/g, as determined by nitrogen adsorption.

Platinum and alkali loaded zeolite catalysts. Catalysts were prepared using the hydrogen form of the zeolite powder described above by pore filling with platinum and alkali-containing components. The procedure used in each preparation was similar. All catalysts were prepared to contain about 0.6% platinum but were prepared to contain varying amounts of alkali, either potassium or lithium. A typical preparation is as follows. A platinum and potassium loaded boron-ZSM-5 was prepared by mixing about 4.88 g of boron ZSM-5 with about 7.22 g of a stock solution containing 0.27 g of tetraamine platinum chloride, 0.83 g of potassium carbonate, and 35.57 g of deionized water. The mixture was pH adjusted to 10; the solution was slurried under reflux conditions to permit the exchange of solution cations with the zeolitic protons. Afterward, the water of impregnation was evaporated with continuous stirring under vacuum at 120°C to ensure efficient contact of the zeolite and solution components. Then it was dried overnight at 120°C under air. The dried, porefilled powder was calcined at 300°C under air for 4 h. The compositions of this and all other catalysts used in this study were determined by chemical analysis. Catalyst alkali contents are provided in Tables 3, 4, and 5 as alkali/(boron + aluminum) molar ratios.

Catalyst evaluation. Each catalyst was sieved to pass 20 mesh, U.S. Sieve Series, and 0.30 g of each were loaded

TABLE 2
Effect of Catalyst Base on Reaction Product Distribution^a

Products (mol%)	Pt on alumina	Pt on ZSM-5 (high Al)	Pt on ZSM-5 (low Al)	Pt on [B]-ZSM-5	Pt on [B]-Beta
Ethane	0.7	5.6	2.8	2.7	3.3
Ethylene	0.2	17.8	15.0	4.6	2.1
Propane	1.5	37.8	44.8	38.0	24.7
Propylene	23.3	2.5	4.0	3.7	2.3
Butanes	72.5	33.2	27.1	39.5	51.4
Butenes	1.6	1.0	4.6	9.7	15.5
C ₅ ⁺	0.2	0.2	1.9	1.8	0.8
% Propylene conversion	6.8	90.1	84.2	85.4	91.0
Molar propane/butene product ratio	0.9	38.3	9.6	3.9	1.6

^a Feed: 25 mol% propylene, 75 mol% n-butane. Results obtained at 450°C, 0.9 h⁻¹ olefin WHSV; all catalysts contain 0.6 wt% Pt.

to a tubular reactor (0.25 in. ID). The catalyst bed temperature was ramped to 550°C in hydrogen over a period of 1 h and maintained at 550°C for 1/2 h to remove volatile components and moisture, if any, and to reduce the platinum component. After this activation, the catalyst was cooled to 450°C and a mixed feed containing 25 mol% propylene and 75 mol% normal butane was passed over the catalyst (20 and 80% on a weight basis). The propylene flow rate was 2.5 cc/min while the normal butane flow rate was 7.5 cc/min. The flow rate and catalyst loading combination corresponds to a 0.95 h⁻¹ WHSV for propylene and a 3.56 h⁻¹ WHSV for normal butane to give a combined WHSV of about 4.4 h⁻¹. The reactor effluent line, connecting the reactor exit with an on-line gas chromatograph was maintained 473 K to ensure complete vapor phase transfer of all volatile reaction products. The reactor effluent

was periodically analyzed by an on-line gas chromatograph capable of separating all the products formed. Spent catalysts were occasionally analyzed for carbon content which was typically found to be less than 5%. Because of on-line analysis and the low spent-catalyst carbon contents, near complete mass balance was assumed. Product analyses are given in Tables 2 through 5. Here product compositions are given as mole percentages for each component in the reactor effluents. Propylene conversion is calculated as the mole percent change in propylene content in the feed and product mixture. Hydrogen transfer selectivity is indicated by the molar propane to butene product ratio and by the molar yields of non-C₃ and C₄ products. Reaction rates were calculated per gram of catalyst and are presented for selected reactions in Table 6 in terms of moles of product per gram of catalyst per hour.

X-ray photoelectron spectroscopy. XPS analysis was performed on a VG Instruments ESCALAB 5, Mk1 system. XPS data were collected with Mg k- α X rays at 300 W. Samples were prepared for XPS analysis by mounting on powder sample stubs as a parallel array with silver paint. The samples were oriented parallel to the X-ray beam in order to eliminate beam shadowing. Photoelectron binding energies were referenced to adventitious carbon at 284.7 eV. Relative areas for the Al 2p and the Si 2p photoelectron peaks were calculated after linear background subtraction. VG-supplied sensitivity factors were used to calculate atomic fractions.

Temperature-programmed reduction studies. The platinum on potassium [B]-ZSM-5 series of catalysts was characterized using temperature-programmed reduction (TPR). Results were obtained with calcined catalysts at atmospheric pressure in a flowing 5% hydrogen in argon stream as the reduction temperature was raised from room temperature to 700°C. Hydrogen uptake was indicated by

TABLE 3
Product Distributions^a with Platinum on Potassium-ZSM-5 Catalyst Series

Catalyst base	ZSM-5 (low Al)	ZSM-5 (low Al)	ZSM-5 (low Al)	ZSM-5 (low Al)	ZSM-5 (low Al)	ZSM-5 (low Al)
Alkali/(B + Al) (molar ratio)	0	0.47	0.83	1.21	1.45	1.81
C ₂ Yield, mol%	18.0	10.9	3.7	2.2	2.2	2.3
Propane, mol%	44.7	44.8	24.1	10.4	6.4	5.7
Propylene, mol%	3.9	3.8	5.2	15.24	17.4	17.6
Butanes, mol%	27.0	33.1	55.9	64.0	67.1	68.3
Butenes, mol%	4.6	5.4	9.1	8.1	6.7	5.9
C ₅ Yield, mol%	1.8	2.0	2.0	0.1	0.3	0.3
% Propylene conversion	84.3	84.9	79.2	39.0	30.4	29.8
Product propane/butenes (molar ratio)	9.8	8.3	2.7	1.3	1.0	1.0
Iso content of C ₄ olefin product	36.0	36.1	29.9	7.4	0.0	0.0

^a Feed: 25 mol% propylene, 75 mol% n-butane. Results obtained at 450°C, 0.9 h⁻¹ olefin WHSV; all catalysts contain 0.6 wt% Pt.

TABLE 4
Product Distribution^a Obtained with Platinum on [B]-ZSM-5 Catalyst Series

Catalyst base	[B]-ZSM-5	[B]-ZSM-5	[B]-ZSM-5	[B]-ZSM-5	[B]-ZSM-5	[B]-ZSM-5
Alkali/(B + Al) (molar ratio)	0	0.35	0.60	0.91	1.19	1.55
C ₂ yield, mol%	7.5	4.3	5.9	6.6	7.6	6.0
Propane, mol%	37.9	23.0	23.5	23.8	24.1	18.7
Propylene, mol%	3.6	3.8	4.0	4.1	4.1	5.8
Butanes, mol%	39.4	47.0	44.4	43.1	41.8	50.0
Butenes, mol%	9.7	21.6	21.7	21.9	21.9	19.0
C ₅ yield, mol%	1.8	0.3	0.5	0.6	0.5	0.5
% Propylene conversion	85.4	84.9	84.0	83.8	83.7	76.8
Product propane/butenes (molar ratio)	3.9	1.1	1.1	1.1	1.1	1.0
Iso content of C ₄ olefin product	31.0	8.8	9.2	9.5	7.8	5.1

^a Feed: 25 mol% propylene, 75 mol% n-butane. Results obtained at 450°C, 0.9 h⁻¹ olefin WHSV; all catalysts contain 0.6 wt% Pt.

TABLE 5
Product Distribution^a Obtained with Platinum on [B]-Beta Catalyst Series

Catalyst base	[B]-Beta	[B]-Beta	[B]-Beta	[B]-Beta	[B]-Beta
Alkali/(B + Al) (molar ratio)	0.0	0.48	0.92	1.34	1.88
C ₂ yield, mol%	5.6	3.2	2.2	1.9	1.5
Propane, mol%	24.7	21.7	21.7	18.8	19.2
Propylene, mol%	2.3	3.4	5.0	5.6	5.8
Butanes, mol%	51.3	49.6	50.4	54.4	53.5
Butenes, mol%	15.4	21.8	20.3	18.9	19.5
C ₅ yield, mol%	0.8	0.4	0.4	0.4	0.5
% Propylene conversion	91.0	86.5	80.2	77.4	76.7
Product propane/butenes (molar ratio)	1.6	1.0	1.1	1.0	1.0
Iso content of C ₄ olefin product	11.6	5.1	3.1	2.4	2.5

^a Feed: 25 mol% propylene, 75 mol% n-butane. Results obtained at 450°C, 0.9 h⁻¹ olefin WHSV; all catalysts contain 0.6 wt% Pt.

TABLE 6
Feed Effects on Hydrogen Transfer Rates and Deactivation over Platinum-Alkali-Zeolite Catalysts^a

Olefin feed ^b	Paraffin feed ^c	Rate: Propane production ^d	Rate: Butene production ^d	Propane/butene product ratio	Butene deactivation % Change/hour
<i>Potassium [B]-ZSM-5 base, alkali/group III = 0.91</i>					
Propylene	none	0.76	n.a.	n.a.	n.a.
Propylene	n-Butane	21.9	20.2	1.08	2
Propylene	Isobutane	4.9	4.0	1.23	71
none	n-Butane	n.a.	10.8	n.a.	0
none	Isobutane	n.a.	10.3	n.a.	1
<i>Lithium [B]-beta base, alkali/group III = 0.92</i>					
Propylene	n-Butane	18.4	18.4	1.00	8
Propylene	Isobutane	9.7	9.81	0.99	65

^a All catalysts contain 0.6 wt% platinum.

^b Olefin feed rate: 0.93 h⁻¹ WHSV.

^c Paraffin feed rate: 3.83 h⁻¹ WHSV.

^d Rates obtained at 450°C, expressed in mol/g catalyst-hour × 1000.

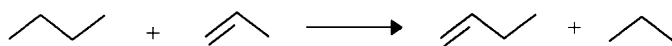
use of a thermal conductivity detector using pure argon as the reference.

RESULTS AND DISCUSSION

Catalysis over Metal Plus Acid

Several platinum catalysts, prepared on a variety of zeolite supports were evaluated for hydrogen transfer activity and selectivity in the saturation of propylene using n-butane as hydrogen source as per reaction 1. Conceivably this reaction can be catalyzed by either metal or acid function.

Reaction 1.

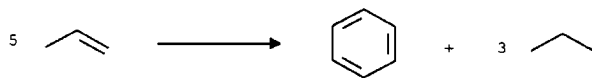


The catalytic contributions of the platinum function, as well as contributions due to the zeolite support were examined as support pore size, acid number, and acid type were varied. The supports studied included three medium pore zeolites, including two ZSM-5's and the borosilicate, [B]-ZSM-5, as well as the large pore borosilicate, [B]-beta. Platinum on gamma-alumina was also evaluated for comparison purposes. Selected properties of the zeolite supports are summarized in Table 1. The two ZSM-5 supports with Si/Al ratios of 25 and 86 provide a variation in acid number. Since boron substitution for framework aluminum has been reported to result in reduced acid strength (10), a comparison of B-ZSM-5 with the ZSM-5 of similar Si/(group III) ratio (26.5 and 24.9, respectively) provides a variation of acid strength at constant acid number. Finally, the large pore borosilicate, [B]-beta, provides a variation on pore size while maintaining acid number and strength similar to the [B]-ZSM-5 support. It should be noted that none of the borosilicates are entirely aluminum-free, but they contain from 2.2 to 6.2% of their group-III content in the form of framework aluminum. The influence of this aluminum on performance will also be explored.

All materials of Table 1, as well as gamma-alumina, were platinum loaded to contain about 0.6% platinum and were then evaluated as powders for activity in converting a 4 to 1 n-butane to propylene feed as described in the experimental section (above). The product distributions obtained after 15 min on feed are reported in Table 2. The table also provides propylene conversions and molar propane/butene product ratios for insight into the predominant paths of conversion over each of the catalysts tested.

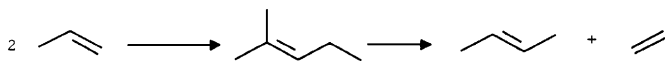
The desired reaction, hydrogen transfer between a feed olefin and paraffin, will result in a product propane/butene ratio of exactly 1. However, because both acid and metal sites are present in all zeolite-supported catalysts, a number of other reaction pathways are possible. These reactions include hydrogen transfer between olefins to form paraffins and aromatics.

Reaction 2.



Olefin scrambling is also possible over acid catalysts.

Reaction 3.



In addition acids can promote paraffin and olefin cracking to lighter products while platinum can catalyze direct paraffin dehydrogenation under the conditions of the present study. All of these competing reactions yield a propane to butene product ratio significantly different than 1.0.

From the data in Table 2, it can be seen that the platinum/alumina catalyst is not very active for model feed conversion. Propylene conversion is low at 6.8%. Only a small amount of propylene has been converted to propane with the correspondingly small production of butenes. The product propane/butene ratio near 1.0 suggests that what little conversion has occurred is via hydrogen transfer as per reaction 1 with little contribution from the acid catalyzed pathways, such as reactions 2 and 3. In addition it should be noted that the production of cracked and oligomerized product is near zero, as expected with a low acidity platinum catalyst.

By comparison, the platinum supported on the high aluminum ZSM-5 displays strikingly different behavior. Propylene conversion is nearly complete at 90%. The production of cracked products (ethane and ethylene) is high and the product propane/butene ratio is 38.3. The C₃ fraction is rich in propane but only a small amount of butenes are produced. This product distribution might be consistent with acid catalyzed hydrogen transfer as per reaction 2 but aromatic products were not observed. Alternatively, the high propane yield could result from butane cracking over strong acid sites. Again, cracking activity is indicated by the presence of C₂ and lighter products. The product distribution is not consistent with simple paraffin to olefin hydrogen transfer.

Reduction of the ZSM-5's aluminum content or partial substitution of boron for aluminum in the ZSM-5 structure results in slightly reduced propylene conversion (about 85%) and less cracking to lighter products; but both catalysts exhibit propane/butane product ratios significantly above the 1.0 expected for paraffin to olefin hydrogen transfer. It would appear that while acid activity is reduced the major pathways for conversion of these two materials is similar to the high aluminum ZSM-5 and the production of propane is largely due to nonselective acid-catalyzed reactions.

The final catalyst in this series, platinum on [B]-beta is active for propylene conversion and is most selective for the desired hydrogen transfer reaction (reaction 1) as indicated by the reduced cracking activity and a propane/butene ratio of 1.6. The reduced activity for acid catalyzed reactions suggests a weaker acidity associated with boron-beta zeolite. However, unlike platinum on low acidity alumina, the platinum on boron-beta catalyst is significantly more active for hydrogen transfer (91% vs 7% propylene conversion) producing 15.5% butenes compared to 1.6% butene production achieved with platinum on alumina. The improved activity observed using boron-beta as support compared to platinum on alumina may be due to zeolite enhancement of hydrogen transfer activity. The enhancement is consistent with previous reports of enhanced metal activity on zeolite supports (7).

The results suggest the existence of an optimal support acidity for maximum hydrogen transfer performance. The enhanced activity observed with boron-beta support compared to platinum on alumina suggests that some acidity is necessary for enhancement. The reduced selectivity observed with the more acidic supports (e.g., ZSM-5) indicates that excess acidity results in undesirable competing reactions.

Partial Acid Site Neutralization

The data in Table 2 indicate a role for acidity in promoting hydrogen transfer by reaction 1. However, a number of factors which might affect performance require further clarification. These include: the effect of acid number, the influence of acid type (e.g. borosilicate vs aluminosilicate) and the importance of zeolite pore size on hydrogen transfer performance. The role of the metal function will be considered later.

It is possible to get an insight into the role of the acid function by partial alkali neutralization of the zeolite acidity. First, addition of alkali can be used to reduce the number of free zeolitic protons. Second, since zeolite acidity associated with aluminum is stronger than that with boron (10), partial neutralization with alkali should preferentially neutralize the stronger aluminum acidity first and the boron acidity only after further alkali addition. Finally, comparison of zeolites of differing structure at comparable neutralization will provide insight into effects due to zeolite pore size.

For these reasons, the low aluminum ZSM-5 and the two borosilicates were impregnated with platinum and varying amounts of alkali cations, either potassium or lithium. The effects of alkali addition on initial product compositions using propylene/butane feed are presented in Tables 3, 4, and 5 for ZSM-5, [B]-ZSM-5, and [B]-beta, respectively. Performance indicators selected from the tables are also presented in Figs. 1 and 2. In the tables and figures the extent of neutralization is indicated by the alkali to group III ratio for each catalyst. Although all three zeolites supports have

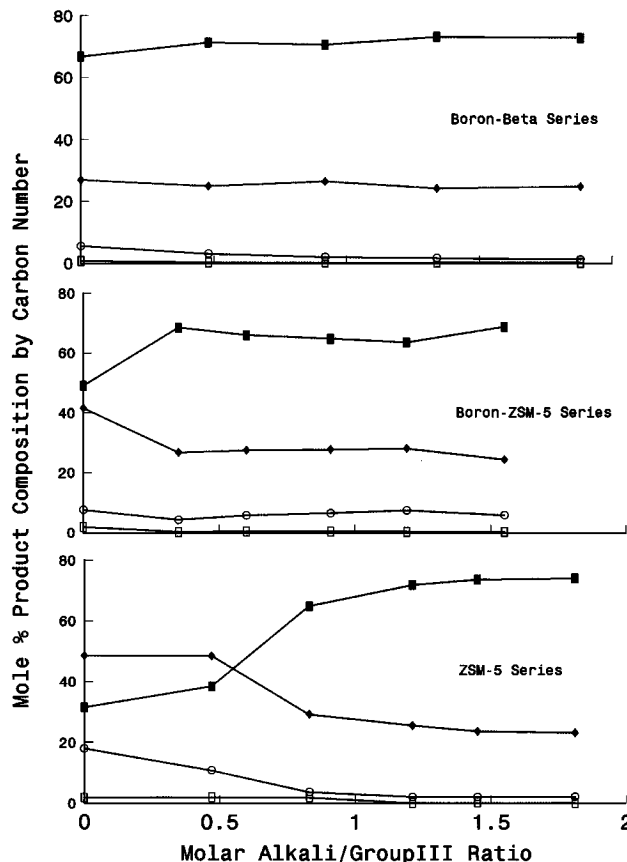


FIG. 1. Weight percent product composition by carbon number (C₂ ○, C₃ ◆, C₄ ■, C₅⁺ □) as a function of catalyst alkali content. Data presented for [Al]-ZSM-5, [B]-ZSM-5, and [B]-beta.

differing Al and B levels, it is possible to relate the extent of neutralization of one zeolite to another using the ratio of alkali to zeolitic boron plus aluminum. In this way zeolites of differing acid number can be compared.

Figure 1 presents molar product distributions according to the carbon number obtained using the Al-ZSM-5, B-ZSM-5, and B-beta supports. Data are plotted against catalyst alkali/Group III ratios. As noted earlier alkali-free platinum on Al-ZSM-5 is quite active for cracking or hydrocracking. About 58% of the feed butane is converted to C₃ and lighter products. Cracking/hydrocracking activity diminishes gradually as alkali content (potassium) is increased. Cracking activity essentially stops only after sufficient alkali has been added to neutralize all acidity associated with zeolitic aluminum (i.e., alkali/Al > 1.21).

In the alkali-free state, platinum on B-ZSM-5 is also quite active for cracking/hydrocracking. About 35% of the feed butanes are converted to C₃ and lighter products. However, unlike the Al-ZSM-5 catalyst series, cracking is almost completely repressed by partial neutralization (potassium). Thus at an alkali to aluminum plus boron ratio of 0.35, only 8% of the butane feed is cracked to lighter products. By comparison, partial neutralization of Al-ZSM-5 only

reduces the initial butane cracking from 58% in the alkali-free state to 49% at an alkali to aluminum ratio of 0.47. The aluminum in B-ZSM-5 is about 2.2% of the total group III content. Thus at an alkali/(B + Al) ratio of 0.35, sufficient alkali has been added to totally neutralize strong acidity associated with aluminum leaving weaker acidity associated with boron sites. Results suggest that the cracking activity observed with both Al-ZSM-5 and B-ZSM-5 is due to zeolitic aluminum present in these zeolites.

As noted earlier, even without alkali addition, the B-beta catalyst exhibits little activity for cracking. Partial neutralization (with lithium for this series) further represses what little cracking is observed. As with B-ZSM-5, cracking is re-

pressed before complete group III neutralization but after sufficient alkali has been added to neutralize all aluminum present. Thus acid catalyzed cracking activity appears associated with zeolitic aluminum for all catalysts studied.

Hydrogen transfer activity and selectivity are indicated in Fig. 2. Here, mole percent propane and butene yields and the molar propane to butene product ratios are plotted against catalyst alkali contents. Data are provided for all three catalyst series. Without alkali addition all three catalyst actively produce propane. In fact the propane product content of 45% for the Al-ZSM-5 and 38% for B-ZSM-5 are greater than the 25 mol% propylene present in the feed. These numbers correspond to 180 and 152% propane

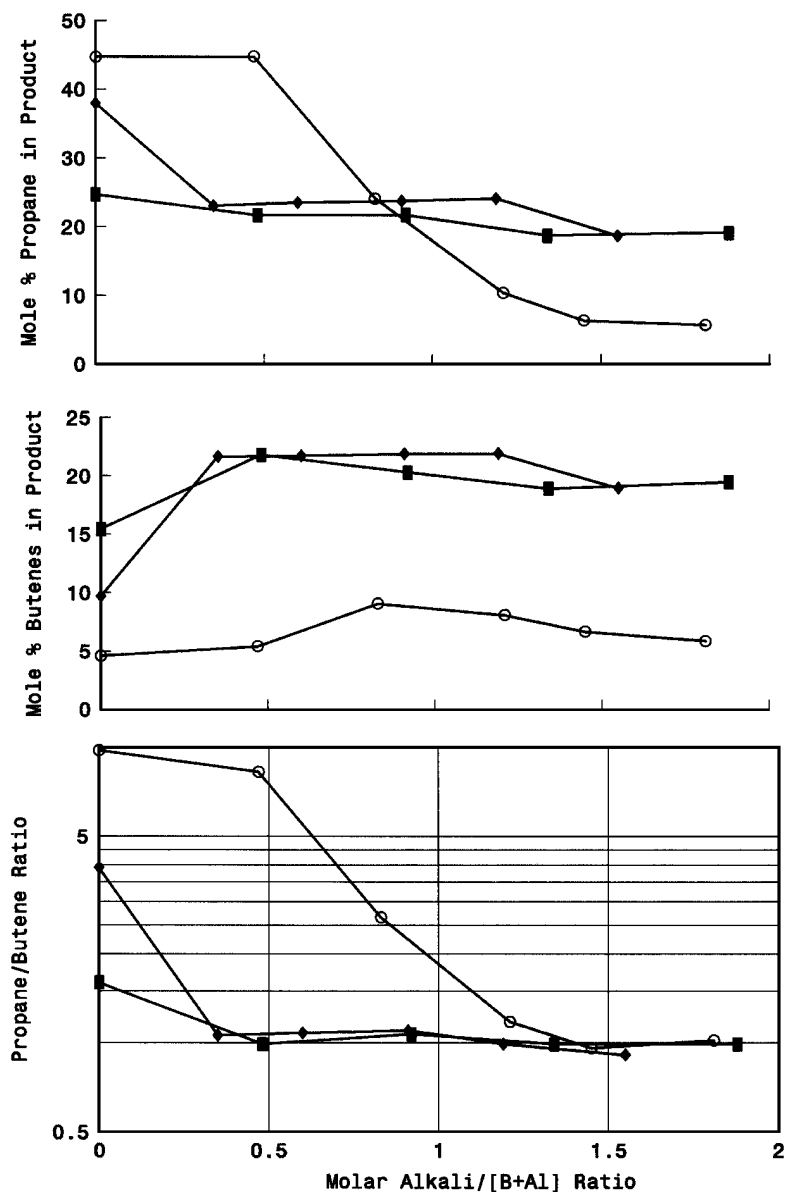


FIG. 2. Hydrogen transfer activity and selectivity as indicated by propane and butene yields (wt%) and by molar propane/butene product ratios as a function of catalyst alkali content. Data presented for [Al]-ZSM-5, ○; [B]-ZSM-5, ◆; and [B]-beta, ■.

yields, respectively, based on feed. The excess C_3 production is due to C_4 cracking/hydrocracking noted above in Fig. 1. The propane product content with B-beta at 24.7% approaches the feed C_3 content and is in keeping with the reduced cracking activity already noted for this catalyst. The contribution of nonselective acid catalyzed reaction to product distributions with the unneutralized catalysts is also indicated by the propane to butene product ratio data presented in Fig. 2. As already discussed, only the direct transfer of hydrogen from butane to propylene will yield a propane/butene ratio approaching 1.0. From the figure and as noted earlier, in their alkali-free state all three catalysts produce a ratio significantly above 1.0. The higher ratios at zero neutralization indicates that hydrocracking and other acid catalyzed reactions are contributing significantly to the observed propane production over all three catalyst systems.

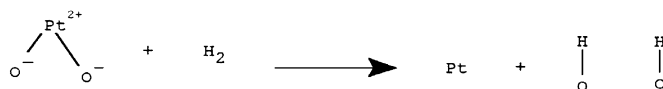
Upon partial neutralization of the borosilicates with alkali (0.35–0.48 alkali/(B + Al)), hydrocracking is curtailed (Fig. 1) and the propane product contents drop below the feed C_3 content (Fig. 2). With partial neutralization, the butene yield rises to a point where the propane to butene product ratio is almost exactly 1.0. At this point, sufficient alkali has been added to neutralize all sites associated with zeolitic aluminum and propane and butene production can be accounted for entirely by a hydrogen transfer mechanism of reaction 1. Further alkali addition has little effect upon activity and selectivity of the borosilicates up to alkali/Group III ratios as high as 1.88. It should be noted that once aluminum-related acid catalysis over the borosilicates is repressed, high propylene saturation activity is achieved at remarkably high selectivity with both borosilicate catalysts. For example, at an alkali/(B + Al) ratio of 0.35 with platinum on B-ZSM-5, propylene conversion approaches 85% with less than 5% of the feed converted to non- C_3 - C_4 products (95% selectivity.) At an alkali/(B + Al) ratio of 0.48 with the B-beta catalyst, 87% propylene conversion is achieved at 96% selectivity to C_3 and C_4 products. Because the performance of the large pore and medium pore borosilicates are remarkably similar, it appears that pore size differences between the two molecular sieves does not play a significant role in hydrogen transfer performance with propylene and n-butane feed.

The all-aluminum ZSM-5-based catalysts respond differently to neutralization. As noted earlier, hydrocracking activity is repressed only when sufficient alkali is added to neutralize all the zeolitic aluminum. From Fig. 2, complete neutralization is also required to achieve a propane to butene product ratio of 1.0. At this point, all acid contributions to propane and butene production have been repressed and hydrogen transfer activity appears to be entirely from reaction 1. At an alkali/aluminum ratio of 1.21, about 39% of the C_3 feed is converted to propane with over 97% recovery of C_3 - C_4 products.

Thus the hydrogen transfer selectivity as indicated by C_3 - C_4 recovery (95–98%) and by the product propane/butene ratios (1.0–1.3) is equivalent for all three catalyst systems after neutralization by alkali in excess of the zeolite aluminum content. The catalyst activity, as indicated by propylene conversion, appears to be less for the aluminum zeolite (39%) than for the boron containing ZSM-5 and Beta catalyst (85 and 87%, respectively). This is also indicated in Fig. 2 by the significantly lower propane and butene yields for Al-ZSM-5 when compared to the borosilicates at all alkali levels, but most significantly at the higher alkali levels where all competing reactions have been curtailed. Thus platinum on Al-ZSM-5 is significantly less active than the platinum on borosilicates. That all three catalysts are more active than platinum on alumina for hydrogen transfer, suggests a role for the zeolite and possibly acidity in promoting reaction 1. The enhanced activity observed with the borosilicates suggests that the presence of boron is especially effective in this promotional effect.

The addition of alkali, even in excess of that needed to completely neutralize all acid sites does not exclude the possible formation of acidity. Even with complete neutralization of a platinum-containing zeolite, subsequent reduction of the platinum cations added during catalyst preparation would regenerate acidity as per reaction 4.

Reaction 4.



Gallezot (7) describes several papers suggesting that the acidity generated by metal reduction in alkali zeolites is similar in strength to acidity in the corresponding hydrogen zeolite.

The presence of trace acidity in the hydrogen transfer catalysts of this study can be detected by butene isomerization activity. Isobutene is a secondary product in the hydrogen transfer between propylene and n-butane. In the presence of even mild acidity, linear butenes formed from n-butane will isomerize to form isobutene. The relative amounts of isobutene produced can be taken as an indicator of catalyst acidity following reduction and under reaction conditions.

The C_4 isobutene contents for all runs described above are plotted against catalyst molar alkali/group III ratios in Fig. 3. As expected, the highest isobutene contents are obtained using the alkali-free platinum zeolite catalysts. Isomerization activity drops significantly when zeolite alkali content is equal to or greater than the zeolitic aluminum content. With the borosilicates, isomerization approaches a minimum but nonzero value when sufficient alkali is present

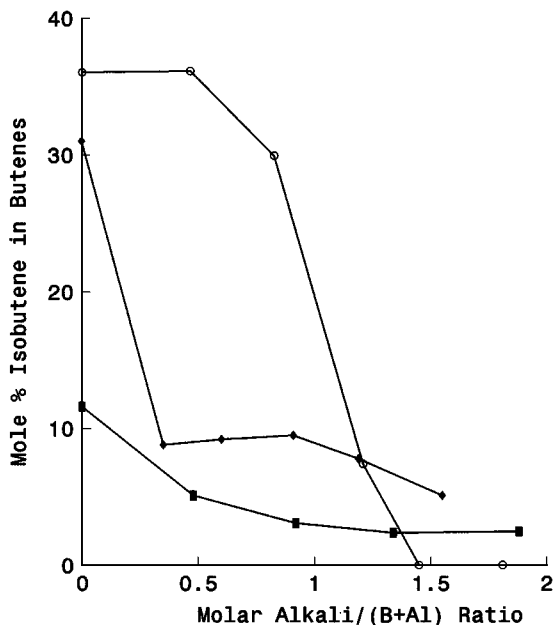


FIG. 3. Butene isomerization activity, indicated by product butene fraction's iso content as a function of catalyst alkali contents. Data presented for [Al]-ZSM-5, ○; [B]-ZSM-5, ◆; and [B]-beta, ■.

to neutralize acidity associated with aluminum. It is interesting to note that isomerization activity remains relatively constant upon further addition of alkali up to alkali/group III ratios near 2. The isomerization activity trend of the borosilicates is consistent with acidity generated by platinum reduction as per reaction 4. Since platinum content for all the catalysts is held constant (0.6 wt%), the number of acid sites generated on a neutralized zeolite by platinum reduction would also be constant. The weak isomerization activity observed with the borosilicates over a wide range of alkali levels may be attributed to acidity generated upon platinum reduction.

The response of the aluminosilicate series (ZSM-5) to alkali addition is markedly different. Isomerization activity continues to decrease as the alkali content is increased above that needed to neutralize all zeolitic aluminum so that at alkali/aluminum ratios greater than 1.21, no butene isomerization activity is observed. This difference may be attributed to the stronger acidity associated with zeolitic aluminum. The stronger acid sites generated upon reduction of platinum associated with aluminum are thermodynamically more likely to undergo solid state reaction during reduction with the excess alkali present than the weakly acidic protons generated by reduction of platinum associated with boron. If so, the presence of excess alkali in the all-aluminum zeolite would result in complete neutralization and loss of isomerization activity.

Recalling the hydrogen transfer activity differences between the borosilicates and the ZSM-5 series as in Fig. 2, the activity trends observed are consistent with the involve-

ment of weak zeolitic acidity in hydrogen transfer catalysis. Thus, upon excess alkali addition and platinum reduction, the borosilicates maintain a minimum but weak acidity (as indicated by their butene isomerization activity), whereas ZSM-5 is completely neutralized. In keeping with this acidity difference and the involvement of zeolitic protons in the transfer process, the borosilicates are about 2 to 3 times more active for transfer than ZSM-5 the higher alkali levels.

Metal Function Contributions

In order to confirm the role of platinum in the present study, the transfer activity of the platinum on potassium neutralized B-ZSM-5 (alkali/(Al + B) = 1.55) was compared with neutralized B-ZSM-5 lacking the platinum function. Catalysts were compared using the standard propylene and butane feed. The results of this comparison are presented in Fig. 4. Propane yield is used to indicate the extent of the hydrogen transfer reaction as a function of reaction temperature. From the figure, it is obvious that the zeolite lacking platinum is inactive at all temperatures studied. Thus the platinum function is involved in hydrogen transfer to saturate propane. The enhanced activity observed with the zeolite supports may indicate a zeolite support effect on platinum or bifunctional catalysis involving metal and zeolitic protons.

Catalyst Characterization

Catalyst characterization provides insight into changes occurring as [B]-ZSM-5 catalysts are prepared with

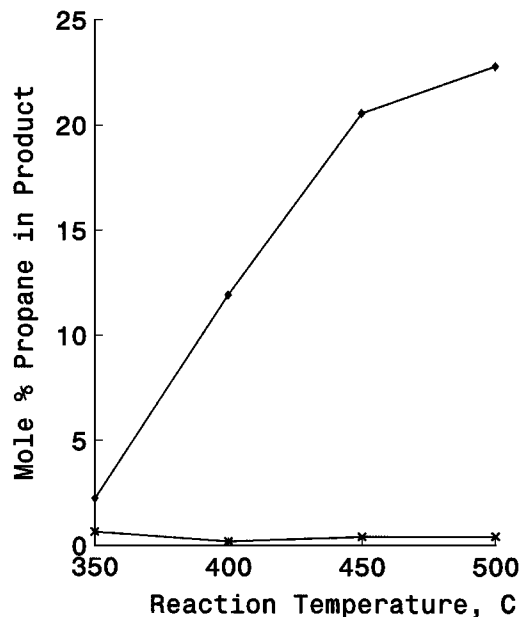


FIG. 4. Hydrogen transfer activity, indicated by propane yields as a function of reaction temperature, C. Data presented for Pt on potassium-[B]-ZSM-5, ◆; potassium-[B]-ZSM-5, ×.

increasing alkali contents. Surface compositions for the dried and calcined catalysts were determined by X-ray photoelectron spectroscopy (XPS). Results of these analyses are presented in Fig. 5 for platinum and alkali loaded B-ZSM-5. Here, near-surface platinum and alkali content is plotted as a function of the bulk alkali/(boron + aluminum) ratio. Interestingly, with low or no alkali addition, the outer zeolite crystal is greatly enriched with platinum. Although all catalysts in the series were prepared to contain 0.6 wt% platinum, XPS data reveals that at bulk alkali/(boron + aluminum) ratios less than 1.0, surface platinum contents range 10 to 20 wt%. When the alkali ratio is increased above one, surface platinum drops significantly to more closely match the bulk platinum content. XPS analysis of the surface alkali content is also presented in Fig. 5. The alkali cation, which in the B-ZSM-5 catalyst series is potassium, also shows surface enrichment relative to the bulk analysis, but the enrichment is smaller than that observed for platinum. The XPS results suggest that the bivalent platinum cation is strongly adsorbed at surface zeolite exchange sites at the lower potassium loadings. This strong adsorption leads to an enrichment of platinum close to where it first contacts the zeolite, that is, within

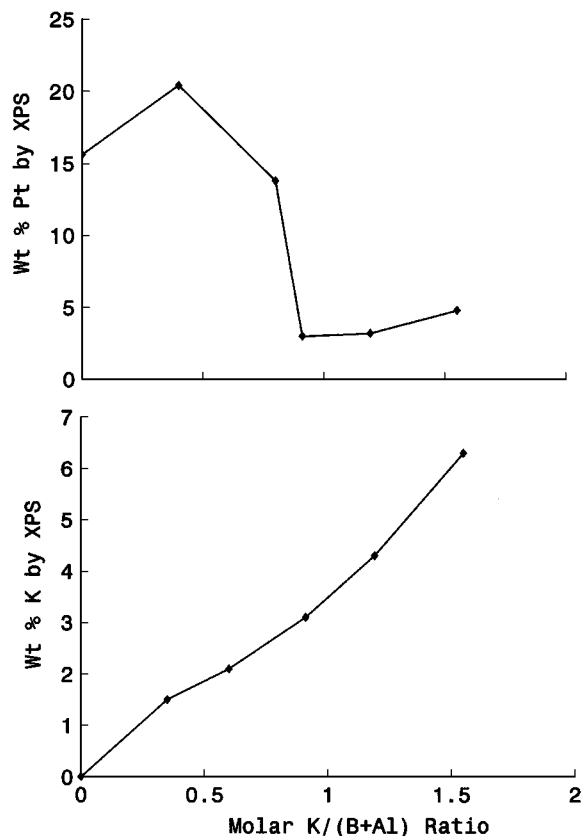


FIG. 5. Catalyst surface composition by X-ray photoelectron spectroscopy as a function of bulk catalyst alkali content (by chemical analysis) for platinum on potassium [B]-ZSM-5.

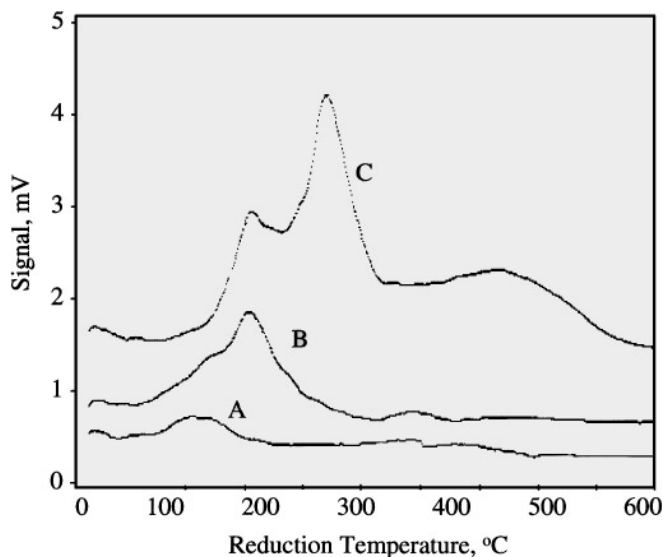


FIG. 6. Temperature-programmed reduction spectra for platinum on potassium-[B]-ZSM-5 as a function of alkali content ($K/(Al + B) = 0.0$ A, 0.8 B, 2.0 C).

the first few unit cells of the zeolite crystal. As the potassium level is increased sufficiently, potassium begins to compete more efficiently with platinum for exchange sites and platinum migrates more deeply into the zeolite crystal before it is adsorbed at an interior exchange site. The use of competitive ion exchange to enhance homogeneous bivalent cation distribution in zeolites has been documented (13).

The platinum on potassium [B]-ZSM-5 series was also characterized using temperature-programmed reduction (TPR). Selected TPR results are presented for three catalysts in this series in Fig. 6. Only three TPR traces are shown for clarity but the omitted traces support the trends observed. The results are presented for the catalysts prepared at the 0, 0.6, and 1.55 molar potassium/(boron + aluminum) ratios. Figure 6 plots the hydrogen uptake as indicated by the millivolt response of the thermal conductivity detector as a function of reduction temperature. Without potassium addition, little platinum reduction is detectable during the temperature ramp and this occurs around 130°C. As the potassium ratio is increased to 0.6, the quantity of observable reduction is increased and the temperature of reduction also increases to about 180°C. Finally, the greatest extent of reduction is observed at the 1.55 ratio and this occurs at the highest temperature, about 210°C. The results are consistent with the surface compositional changes noted above. With no potassium addition, much of the platinum is concentrated near the zeolite surface and here it behaves as bulk platinum, reducing readily before the TPR temperature ramp is initiated. As potassium content is increased, platinum penetration into the zeolite increases and so does the platinum zeolite interaction resulting in an increased

fraction of platinum reducing at higher temperatures and thus observable by TPR. Sachtler has shown that platinum on acidic supports reduces at much higher temperature than platinum on silica (14).

The XPS and TPR analyses suggest that in addition to partially neutralizing zeolitic acidity, alkali has a second function. At higher levels, it obviously promotes the even distribution of platinum throughout the zeolite and thus enhances the platinum–zeolite interaction. Although the influence of platinum dispersion has not been measured in the present study, it can be anticipated that the improved platinum distribution throughout the zeolite would be accompanied by improved platinum dispersion which in turn could contribute to the superior selectivity observed at the higher alkali loadings.

Feed Effects and Mechanistic Insights

Insight into the mechanism and catalytic sites involved in hydrogen transfer are provided by a limited feed study. Results of this feed study are summarized in Table 6. Here reaction rates for the formation of propane and butenes are presented for several feed combinations with alkali treated [B]-ZSM-5 and [B]-beta catalysts. Deactivation data are also provided as percent activity loss in the first hour of testing. The catalyst alkali contents were selected to give optimum activity and selectivity for transfer from the data presented in Figs. 1 and 2.

With the [B]-ZSM-5 catalyst and propylene feed, propane production rate in the absence of paraffin is negligible (0.756×10^{-3} moles/g-h); although not shown, acid catalyzed rates (cracking and hydrocracking) are also minimal as expected following acid site neutralization. When propylene and n-butane are cofed over the [B]-ZSM-5 catalyst, a propane production rate of 21.9×10^{-3} moles/g-h is obtained, representing a nearly 30-fold increase over propane production in the absence of normal butane. The rate of butene production with this feed (20.2×10^{-3} moles/g-h) is about equal to the rate of propane production. The increased propane saturation rate in the presence of normal butane and the nearly equivalent rates of saturation and unsaturation clearly indicate that butane is involved in the saturation of propylene, via a paraffin to olefin hydrogen transfer mechanism. However, when propylene and isobutane are co-fed, a propane production rate of only 4.9×10^{-3} moles/g-h is observed. Hydrogen transfer from isobutane is about four times slower than from normal butane.

Significant dehydrogenation activity is observed with either n-butane or isobutane in the absence of propylene. Under the conditions of this study, platinum catalyzed paraffin dehydrogenation is not unexpected. The rate of butene formation is about the same for either paraffin (10.8×10^{-3} moles/g-h for n-butane and 10.3×10^{-3} moles/g-h for isobutane). Since the rate of dehydrogenation of n-butane and isobutane are the same, steric restraints associated with

adsorption of the branched paraffin do not play a significant role in dehydrogenation over this catalyst.

The results with the [B]-ZSM-5-based catalyst are consistent with a single site mechanism involving preadsorption of propylene followed by adsorption of butane and transfer of hydrogen directly from butane to propylene at this one site. If paraffin were adsorbed prior to olefin activation or if the paraffin were adsorbed on a separate site, the rate of hydrogen transfer would not be affected by paraffin branching since branching had little effect on paraffin dehydrogenation in the absence of propylene.

A transition state where both C_3 and C_4 are within close proximity is suggested. That hydrogen transfer from isobutane is slower than from n-butane is likely due to steric interactions occurring as the larger isobutane molecule approaches the preadsorbed propylene. Isobutane has a kinetic diameter of about 4.4 Å, as compared to n-butane with a diameter of 4.0 Å. It is less likely that electronic differences between iso- and n-butane account for the observed rate differences in hydrogen transfer since the rates for dehydrogenation of iso- and n-butane are comparable. Conceivably, steric restraints could be imposed by a lack of sufficient space within the zeolite channel system to form the active complex. However, results in Table 6 obtained with the large pore beta catalyst suggest that space within the zeolite cannot be the only restricting factor. As with [B]-ZSM-5, transfer between isobutane and propylene (9.8×10^{-3} moles/g-h) occurs at a significantly slower rate than it does between propylene and n-butane (20.2×10^{-3} moles/g-h) even in this large pore zeolite. Transfer between propylene and n-butane occurs at the same rate over both catalysts. Therefore, it appears likely that steric repulsion between the preadsorbed propylene and isobutane are significant even in beta. These findings suggest that both C_3 and C_4 species are present in a single site, activated complex leading to product formation. However, since transfer is faster in beta using isobutane than in [B]-ZSM-5, the medium pore channel may also exert an additional restraining effect on transition state formation in the ZSM-5 pore structure with paraffins larger than n-butane.

One additional feed effect is worth noting. From the table we see surprisingly little deactivation within the first hour on propylene/n-butane feed. Platinum on potassium [B]-ZSM-5 loses only 2% activity in butene production; the decline in propane production is comparable. This contrasts sharply with the decline in activity observed with propylene-isobutane feed over the [B]-ZSM-5 catalyst, where 73% activity is lost in the first hour on feed. Very similar trends were observed with platinum on lithium [B]-beta. The cause of this enhanced deactivation could be related to secondary reactions of the primary isobutene product. In butene isomerization studies over acid zeolites, rapid deactivation is often observed and has been attributed to isobutene polymerization (11).

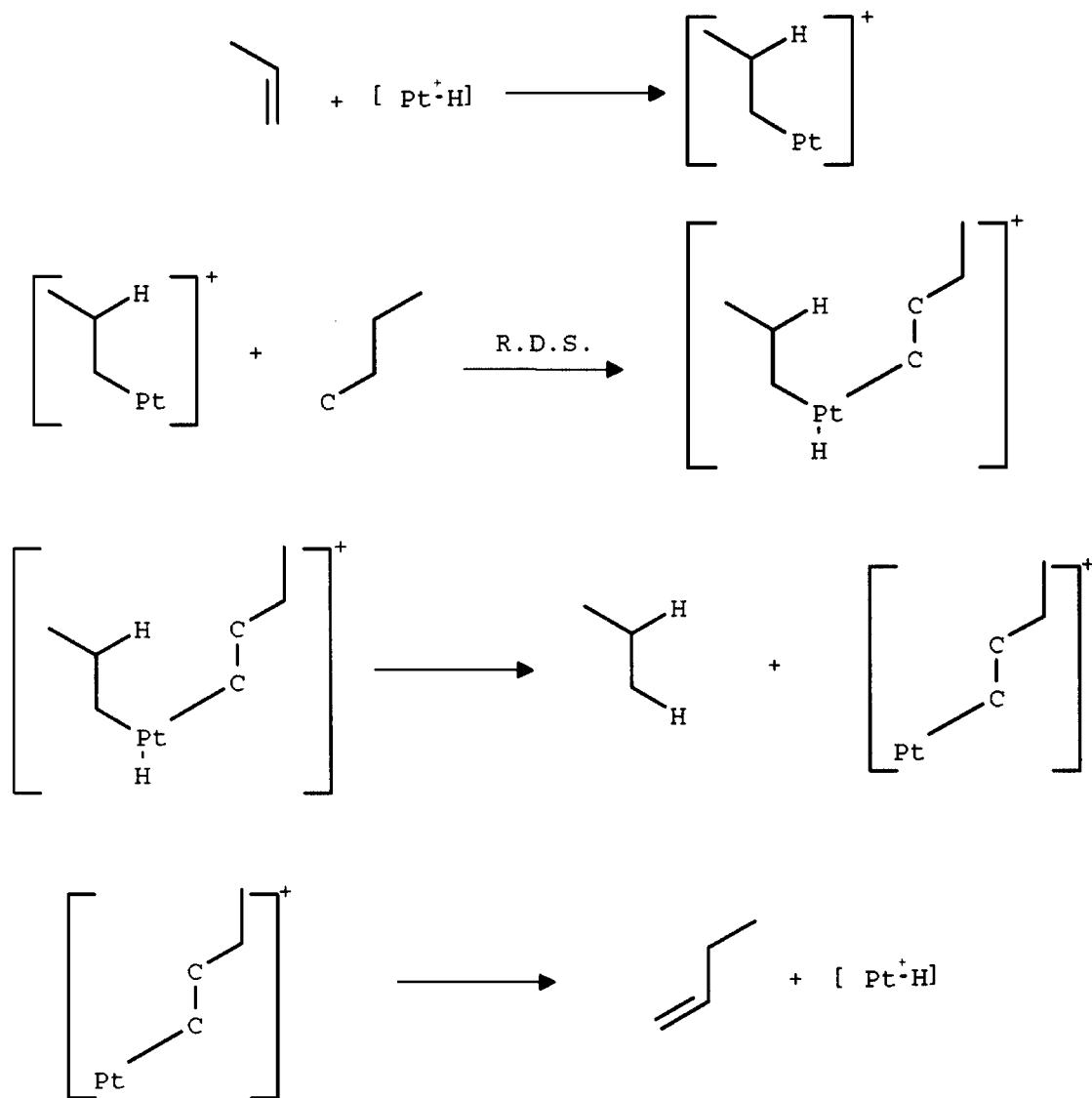


FIG. 7. A proposed mechanism for the transfer of hydrogen from normal butane to propylene over platinum on alkali zeolites.

Based on the results presented in Table 6 and preceding discussions, it is possible to propose a mechanism for hydrogen transfer over zeolite-supported platinum catalysts. A proposed mechanism is presented in Fig. 7.

The current feed studies implicate a single site for catalysis while results from partial neutralization experiments implicate both weak acidity and platinum sites in hydrogen transfer reactions over the present catalysts. Sachtler *et al.* (9) have attributed increased catalytic activity for palladium in Y zeolites to the formation of a palladium-proton adduct wherein palladium carries a formal positive charge. The activity of positively charged palladium, ruthenium, and rhodium in the gas phase dehydrogenation of n-butane has been noted by Tolbert (12). Catalysis involving a platinum-proton adduct seems a reasonable hypothesis.

In the present study, a likely initial step involves nucleophilic attack of the olefin on a platinum-proton adduct to

form a platinum-alkyl intermediate (see Fig. 7). By analogy to the mechanism proposed by Tolbert (12) for paraffin dehydrogenation over metal cations, this olefin-platinum cation next inserts into a paraffin C-H bond to form a platinum-dialkyl species. The reduced rate of transfer observed with isobutane compared to n-butane suggests that steric repulsions are involved in the formation of this dialkyl and that this is probably the rate-determining step. In the final steps, hydrogen may be transferred to the partially reduced olefin in either a concerted or stepwise fashion to release products and regenerate the platinum-proton adduct.

CONCLUSIONS

Platinum on alkali-borosilicates are remarkably active and selective for hydrogen transfer saturation of propylene

with normal butane. Propylene conversions typically exceed 85% at greater than 95% selectivity. Deactivation within the hour-long test is minimal.

More broadly, platinum zeolite catalysts are surprisingly more active for hydrogen transfer than platinum on alumina when acid catalysis is minimized by alkali neutralization of the zeolitic acidity. A minimal acidity is required in order to achieve the activity enhancements noted, whereas acidity in excess of that required for the promotional effect results in nonselective acid catalysis, leading to lower yields.

Borosilicates are especially effective catalyst supports uniquely suited to this application. Alkali neutralization of zeolites containing both aluminum and boron indicates that the weak acidity associated with zeolitic boron is sufficient to generate the promotional effect, but they are too weak to promote nonselective acid rearrangements. Enhanced hydrogen transfer activity is also observed in the aluminosilicate, ZSM-5. However, acid catalyzed rearrangements are not repressed until all zeolitic acidity has been neutralized. At this point, the promotional effect is largely diminished.

Previous studies using platinum or palladium on non-acidic supports found low activity for hydrogen transfer from paraffins to olefins. The lack of significant activity was attributed to strongly adsorbed olefin which prevented further reaction with gas phase paraffin. The surprising activity observed on zeolitic supports may be related to the formation of a platinum-proton adduct. It is likely that a positively charged platinum would react with an olefin to form a platinum-alkyl cation rather than a platinum-olefin complex, expected on zero-valent platinum. A platinum-alkyl cation may be more likely to adsorb paraffin. The tendency for palladium cations to insert in paraffinic C-H bonds has already been suggested. In the present work, kinetic differences in propylene saturation with normal and isobutane clearly indicate that both paraffin and olefin are co-adsorbed on the active site prior to transfer and that olefin repression of paraffin adsorption has been overcome.

The ability to efficiently use low value refinery paraffins as a hydrogen source should significantly increase a refiner's options in formulating future fuels and complying with mandated changes. The present study has explored factors affecting hydrogen transfer in a model reaction. A future report will expand this study to more pertinent feed molecules including gasoline range olefins. Application of this technology to the production of alkylate, trimethylpentane, will also be discussed.

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