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Dehydrocyclization of *n*-Hexane by Highly Dispersed Platinum in Zeolite Y

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The behavior of an optimally dispersed PtNaY catalyst, prepared by air calcination of Pt-exchanged NaY at 300°C, has been investigated for *n*-hexane dehydrocyclization at atmospheric pressure. The catalyst is found to be regenerable without serious loss of activity or selectivity. Neutralization of acid sites generated during preparation reduces both activity and aromatization, indicating that zeolite acidity is necessary for isomerizing substituted cyclopentanes. The reaction appears to proceed via both 1,6- and 1,5-ring closure to form olefin intermediates. Replacement of Na^+ with Li^+ or K^+ has only minor effects, but replacement with Ca^{2+} or Mg^{2+} increases acidic cracking as expected. Addition of Cu, Zn, and Ag reduces aromatization activity and selectivity. The zeolite structure does not appear to allow the type of interactions (e.g., alloying) that can occur on other supports.

INTRODUCTION

Many recent investigations have dealt with the optimal methods for dispersing platinum metal in faujasite zeolites. Early work by Rabo (*1*) showed that ion-exchange of Pt cations with zeolite Y led to highly dispersed Pt metal and improved catalysts (*2*). Later, Kubo *et al.* (*3*) and Dalla Betta and Boudart (*4*) showed that air (or oxygen) calcination of platinum ammine exchanged Y at 300°C led to superior catalytic properties as well as maximum Pt metal dispersion. Czárán *et al.* (*5*) showed that, in addition to optimum dispersion occurring with a 350°C air calcination, Pt metal dispersion was also affected by Pt content and zeolite acidity.

Gallezot *et al.* studied reduced PtY zeolites with X-ray diffraction, small angle X-ray scattering, chemisorption (*6*), electron microscopy (*7*), and benzene hydrogenation (*8*). They concluded that an activation at 300°C led to formation of Pt^{2+} ions in the supercages which, after reduction with hydrogen at 300°C, formed 6–13 Å Pt metal agglomerates within the zeolite pore structure that were stable up to 800°C. Higher temperature air activation led to formation of Pt^{2+} in the smaller sodalite cages which remained after reduction as nonchemisorbing (and catalytically inactive) Pt atoms.

Recently, Reagan *et al.* (*9*) showed that the optimum Pt metal dispersion obtained by air calcination of Pt ammine Y at 300°C is a consequence of the decomposition kinetics of Pt ammine cations, which have a maximum rate of decomposition at 300°C. According to the stoichiometry found in that study, Pt is auto-reduced to the metallic state by the amine ligands during the calcination, in air as well as inert atmospheres; Gallezot *et al.* state that the Pt atoms in the supercage are Pt^{2+}, although they could not be explicitly located or characterized (*6*). In addition, Reagan *et al.* showed that the optimally dispersed PtY catalyst also had maximum *n*-hexane dehydrocyclization activity at atmospheric pressure (*9*); others have shown similar maximum activities for cyclohexane dehydrogenation (*3, 9*), toluene demethylation (*3*), neopentane isomerization and hydrogenolysis (*4*), benzene hydrogenation (*8*), cyclopropane hydrogenation, and ethane hydrogenolysis (*10*).

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TABLE 1

Properties of PtRY Catalysts

Catalyst	Pt (%)	Exchange by R (%)
Pt*Li*Y	0.54	60.4
Pt*K*y	0.55	84.4
Pt*Mg*Y	0.60	78.6
Pt*Ca*Y	0.58	83.2

In the current investigation, the properties of the optimally dispersed PtY(300) catalyst from the previous investigation (*9*) for *n*-hexane dehydrocyclization at atmospheric pressure are further characterized. In addition, the effects of some alkali, alkaline earth, and transition metals are described. A similar series of materials have been investigated by Merrill and Arey (*11*) for higher pressure naphtha reforming; the catalysts in that study were probably not optimally dispersed.

EXPERIMENTAL

All catalysts were prepared by ion exchange with commercial Linde NaY, which had been washed, air dried, and equilibrated. Platinum was introduced as the hexammine–platinum(IV) cation by exchange with a solution of $[Pt(NH_3)_6]Cl_4$ (a stock solution containing 0.002 g Pt/ml was used). All catalysts were air calcined at 300°C as described (*9*).

PtRY series (R = Li, K, Ca, Mg). A series of catalysts in which Na^+ is exchanged by Li^+, K^+, Mg^{2+}, and Ca^{2+} was prepared by exchanging NaY twice with hot 1 *N* metal chloride solution, followed by Pt exchange as above. The Pt content and degree of exchange of Na^+ are shown in Table 1.

PtMNaY series (M = Ni, Cu, Zn, Ag). A bimetallic series was prepared in which the second metal had approximately the same content as Pt. For M = Ni, Cu, and Zn, NaY was exchanged with the Pt stock solution and appropriate amount of metal chloride simultaneously. For M = Ag, platinum was exchanged first, followed, after filtration and drying, by Ag^+ (as $AgNO_3$); this procedure was adopted to prevent AgCl formation if $AgNO_3$ and $[Pt(NH_3)_6]Cl_4$ were used together. The metal analyses for these catalysts are shown in Table 2.

Catalyst tests and calculations. Catalysts were pelleted and sized between 14 and 30 mesh. In each run, 0.5 g catalyst (dry basis) was placed in a ½-in.-o.d. Vycor reactor tube including a thermowell. The tube was packed with Vycor chips on either side of the catalyst bed. All catalysts were pretreated on-stream with flowing hydrogen at 475°C and VHSV ≃ 2400 for 16 hr. A calibrated Sage Instruments Model 355 syringe pump fed pure *n*-hexane to the reactor at 2.0 WHSV, 9.22 H_2/nC_6, 475 ± 5°C (where noted, other conditions were used for variation of WHSV, H_2/nC_6, T). Product analyses and the standard regimen have been described (*9*).

Results were calculated as both *n*-hexane conversion ($C(nC_6) = 100 - \%nC_6$ remaining) and charge (or C_6) conversion ($C = \%Ar + \%C_1–C_5$ formed). Selectivities, in terms of *n*-hexane conversion, were calculated as $Q(i) = 100 \times \%i/C(nC_6)$; in addition, S(Ar) is the aromatic selectivity in terms of charge conversion ($S(Ar) = 100 \times \%Ar/C$).

Cyclohexane dehydrogenation activity ($C(CyC_6)$) was determined for fresh catalyst at 3.0 WHSV, 12.0 H_2/CyC_6, and 300 ± 5°C after 10 min on-stream.

RESULTS

The standard PtNaY(300) (0.48% Pt) catalyst, prepared as previously described (*9*), was investigated in some detail in the fresh

TABLE 2

Properties of PtMNaY Catalysts

Catalyst	Pt (%)	M (%)
Pt*Ni*NaY	0.51	0.48
Pt*Cu*NaY	0.52	0.46
Pt*Zn*NaY	0.50	0.46
Pt*Ag*NaY	0.51	0.70

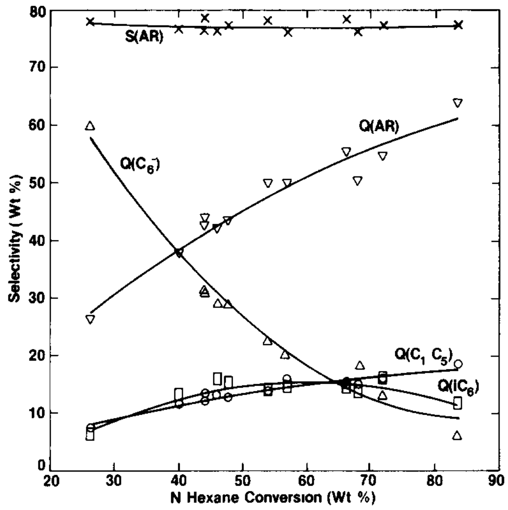


FIG 1 Selectivity parameters for *fresh* PtNaY(300) for *n*-hexane dehydrocyclization (475°C, 2 0 WHSV, 9 2 $H_2/n\text{-}C_6$)

state The effect of conversion on selectivity is shown in Fig 1, derived from three separate runs, where the various *selectivities* are plotted against *n*-hexane conversion The aromatic selectivity, $S(\mathrm{Ar})$ is constant at about 77 5% for *n*-hexane conversion levels between 25 and 85% The isomerization selectivity, $Q(iC_6)$ decreases above 60% conversion, while the cracking selectivity $Q(C_1\text{-}C_5)$ shows an increasing slope in the same region, suggesting that at high conversion, isohexane "intermediates" are being cracked rather than aromatized Figure 1 is useful in comparing similar catalysts with different preparative histories

The effect of regeneration on the catalytic parameters for the dehydrocyclization of *n*-hexane is shown in Table 3 The regeneration procedure, described in Table 3, was followed by a 4-hr hydrogen pretreatment at 500°C Regeneration led to a lower activity, but the selectivity data [$S(\mathrm{Ar})$] indicate that regeneration does not seriously affect the overall dehydrocyclization selectivity The data also show that, prior to regeneration, the severely aged catalyst did not show any significant loss of selectivity

TABLE 3

Effect of Regeneration[a] and NaOH Treat on the Catalytic Activity of PtNaY(300)[b]

	Fresh catalyst					Base treated	
						NaOH	NaOH
Time (hr)	1	2	20	R + 1	R + 2	+ 1	+ 2
Temperature (°C)	474	475	478	475	479	479	
$C(nC_6)$	54 0	44 2	25 4	40 9	33 8	35 0	30 7
Product composition (wt %)							
C_1	1 1	0 75	0 24	0 55	0 38	0 41	0 34
$C_1\text{-}C_5$	10 1	5 3	1 9	4 5	3 2	3 6	3 0
iC_6	9 6	5 7	1 6	5 4	3 6	8 4	6 1
$C_6^{2=}$	9 8	13 6	15 6	14 7	15 4	16 6	16 7
Aromatics	36 7	19 4	6 3	16 4	11 6	6 4	4 9
Selectivities (%)							
$Q(C_1)$	2 0	1 7	0 96	1 3	1 1	1 2	1 1
$Q(C_1\text{-}C_5)$	13 8	12 0	7 3	11 0	9 5	10 2	9 6
$Q(iC_6)$	14 1	12 9	6 3	13 3	10 5	24 0	19 8
$Q(C_6^{2=})$	22 4	30 8	61 4	35 8	45 4	47 3	54 5
$Q(\mathrm{Ar})$	49 6	43 9	25 0	39 9	34 5	18 3	16 1
C	46 8	25 0	8 2	20 9	14 8	10 0	7 9
$S(\mathrm{Ar})$	78 4	77 6	76 8	78 5	78 4	64 2	62 6

[a] Regeneration procedure 20% air, 2 5 hr, 50% air, 0 5 hr, 100% air 1 0 hr, 300°C, VHSV ≈ 3000

[b] 2 WHSV, 9 2 H_2/nC_6, atmospheric pressure

TABLE 4

Variation of H_2/nC_6 and Temperature for Regenerated, Aged PtNaY(300)[a]

H_2/nC_6	9.22	4.6	6.9	13.8	9.22	9.22	9.22
Temperature (°C)	478	478	478	478	479	503	527
$C(nC_6)$	43.7	42.3	39.4	40.6	35.5	49.2	59.2
Product composition (wt %)							
C_1–C_5	5.4	5.5	5.0	4.4	3.8	5.6	9.8
iC_6	6.0	5.0	4.4	5.6	3.6	2.9	2.6
$C_6^{2=}$	15.4	16.2	16.5	16.0	16.9	21.8	20.9
Aromatics	17.0	15.3	13.5	14.7	11.2	18.8	25.9
Q(Ar)	38.8	36.2	34.3	36.1	31.5	38.3	43.8
C	22.3	20.8	18.5	19.0	15.0	24.5	35.7
S(Ar)	75.8	73.5	73.1	77.1	74.6	76.9	72.6

[a] Atmospheric pressure

although its activity was considerably reduced.

In addition to regenerability, acidity is a potentially important variable. While acidity is unimportant in dehydrogenation, it can play a crucial role in the dehydroisomerization of five-membered ring naphthenes to aromatics. The decomposition of $Pt(NH_3)_6NaY$ produces acidity via the formation of protons during the reduction of Pt^{4+} by the NH_3 ligands (*9*). In the case of the PtNaY(300) catalyst, this acidity amounts to about 1–1.5 protons per unit cell.

A sample of PtNaY(300) was stirred overnight with 1 *N* NaOH in order to neutralize protonic sites (or exchange NH_4^+ cations) formed in the decomposition of the Pt ammine. The catalytic parameters for this neutralized catalyst are also shown in Table 3. A comparison of these data with the corresponding fresh catalyst data in Table 3 shows that dehydrocyclization (aromatization) *activity* and *selectivity* are reduced. From the reduction in S(Ar) by more than 10%, it would appear possible that acidity is involved in dehydrocyclization, but such a conclusion must be quite tentative. Neutralization had little effect on light gas formation [$Q(C_1$–$C_5)$], indicating that even in the unneutralized PtNaY, the cracking of charge to C_1–C_5 is primarily *metal* cracking (hydrogenolysis).

Several other variables were investigated for 0.48% PtNaY(300). Prior to these variations, the fresh catalyst was aged by treating with *n*-hexane for 2 hr (standard run), then regenerated and again aged with *n*-hexane. The regeneration procedure in this case involved treatment with undiluted air at 300°C for 0.5 hr, then at 475°C for 1.0 hr, followed by hydrogen pretreatment for 1.0 hr. The variation of H_2/nC_6, WHSV, and temperature were then investigated (in that order).

Data from the variation of H_2/nC_6 between 4.6 and 13.8, and variation of temperature from 478 to 527°C are given in Table 4 in the order performed. In the H_2/nC_6 variation, only minor changes are evident, with a somewhat higher aromatics selectivity [S(Ar)] at the higher ratios. Increase in temperature produced the expected higher activities, with a slight decrease in S(Ar) at 527°C.

The space velocity variation is presented in Fig. 2 as a plot of wt% of each component group against contact time (1/WHSV) (the H_2/nC_6 ratio was held constant at 9.22). The initial increase, followed by a decrease, in total *hexene* content indicates that the hexenes are common intermediates, reacting further to form aromatics, isohexanes, and light gases. The same data, for regenerated and aged PtNaY(300), are shown in comparison to the selectivity pa-

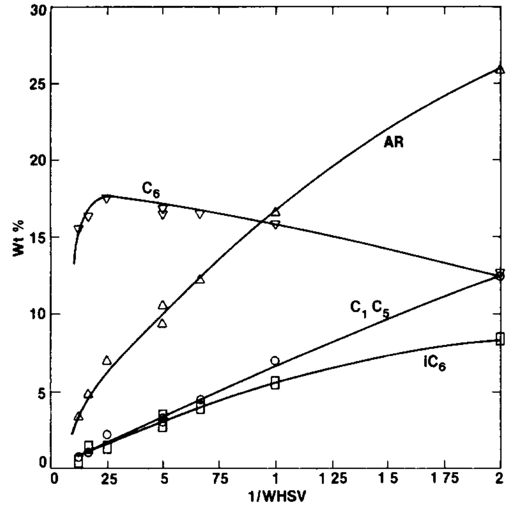


FIG 2 Effect of contact time on product composition for regenerated and aged PtNaY(300) at 475°C

rameters of fresh PtNaY(300) in Fig 3 While aromatics, olefin, and isohexane parameters are similar, the increased metal cracking at higher *n*-hexane conversions results in a loss of overall aromatization selectivity perhaps caused by some Pt crystallite growth during regeneration (which was not optimized)

Effect of Zeolitic Cation (PtRY Series (R = Li, K, Mg, Ca)

The product composition data at 2 hr onstream with *n*-hexane for PtRY (R = Na, Li, K, Mg, Ca) are given in Table 5, cyclohexane dehydrogenation activity is also given [$C(\mathrm{CyC}_6)$] The Na and K forms have very similar activities and selectivities, although the K form has the lowest dehydrogenation activity in the series Both activity and selectivity are somewhat reduced for Li, but are considerably reduced for the divalent ion forms, Ca and Mg These conclusions are in general agreement with those of Merrill and Arey (*11*), who found that the divalent cations produced a higher cracking selectivity They found the Li form to have a greater aromatization selectivity than the Na and K forms, in contrast to the results presented in Table 5, but their catalysts had not been optimized with respect to Pt activity

The distribution of light gases varies for the alkali (Na, Li, K) and alkaline earth (Mg, Ca) catalysts Thus the composition of olefins in the C_4 gases from the Mg and CaY's is 5–10 times that found in the alkali Y's (Table 5) Moreover, the alkali metal Y's produce approximately equal amounts of total C_4 and C_3 gases, while MgY and CaY produce greater amounts of C_3 than C_4 This latter result contrasts with the data of Merrill and Arey (*11*), who found that alkaline earth led to greater amounts of C_4 than C_3 Reaction pressure might be involved in this difference

Effect of a Second Transition Metal [PtMNaY Series (M = Ni, Cu, Zn and Ag)]

Sinfelt and co-workers have shown that the hydrogenolysis activity of a Group VIII (Pt group) metal is inhibited by alloying with a Group Ib metal (Cu, Ag, Au) (*12*) It was therefore of interest to introduce a second metal in PtNaY(300) and observe the effect on the standard *n*-hexane run The results are shown in Table 6

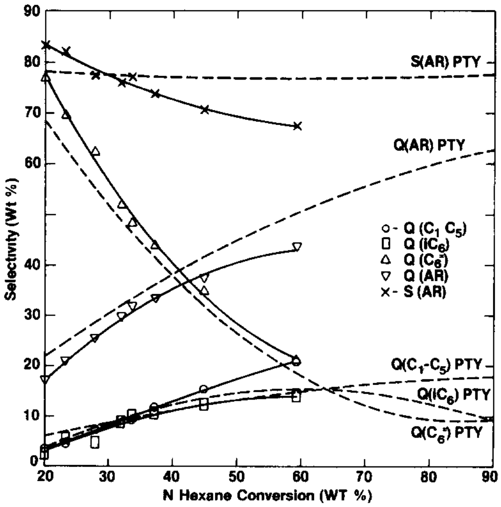


FIG 3 Comparison of selectivity for regenerated, aged PtNaY(300) (from contact time variation) with fresh PtNaY(300) (dashed curves)

TABLE 5

Hexane Dehydrocyclization Data for the PtRY Series[a]

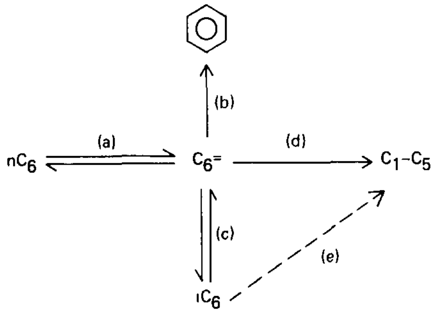
Catalyst	PtNaY	PtLiY	PtKY	PtMgY	PtCaY
$C(nC_6)$	44 1	41 0	44 7	26 1	27 4
Product composition (wt %)					
C_1–C_5	5 8	5 3	5 5	4 2	4 7
C_4/C_3	1 00	1 00	1 105	0 540	0 650
$C_4^{2=}/C_4$	0 055	0 092	0 057	0 34	0 26
iC_6	5 7	8 1	5 1	4 2	4 5
$C_6^{2=}$	13 8	17 0	15 5	15 5	15 0
Aromatics	18 7	10 7	18 6	2 3	3 2
$Q(\mathrm{Ar})$	42 5	26 1	41 6	8 6	11 6
C	24 6	16 0	24 1	6 4	7 8
$S(\mathrm{Ar})$	76 2	67 0	77 1	35 0	40 4
$C(\mathrm{CyC_6})$	89 1	87 1	76 1	81 2	86 8

[a] 475°C, 2 0 WHSV, 9 2 H_2/nC_6, atmospheric pressure Data at 2 hr on-stream

For M = Cu, Zn, and Ag, activity was considerably lower than for PtNaY(300), as was selectivity for aromatization In these cases, dehydrogenation activity was also lower, the major effect appears to be an increase in metal cracking For M = Ni, however, activity is very high, giving a product composed primarily of methane (85% purity) and benzene

DISCUSSION

The data in Figs 1 and 2 suggest that the pathways involved in *n*-hexane dehydrocyclization may be qualitatively represented as



The dehydrogenation and isomerization reactions (a) and (c) are reversible, while

TABLE 6

Hexane Dehydrocyclization Activity of Some Bimetallic Platinum Y Catalysts The PtMNaY Series[a]

Catalyst	PtNaY	PtNiNaY	PtCuNaY	PtZnNaY	PtAgNaY
$C(nC_6)$	44 1	99 99	27 1	28 2	28 4
Product composition (wt %)					
C_1	0 82	56 0	0 39	0 44	0 51
C_1–C_5	5 8	65 8	2 2	3 1	3 0
iC_6	5 7	—	3 7	4 3	4 1
$C_6^{2=}$	13 8	—	17 9	17 6	17 5
Aromatics	18 7	34 2	3 3	3 2	3 9
$Q(C_1)$	1 9	56 0	1 4	1 6	1 8
$Q(\mathrm{Ar})$	42 5	34 2	12 2	11 3	13 6
C	24 6	99 99	5 5	6 3	6 9
$S(\mathrm{Ar})$	76 2	34 2	59 8	50 9	56 3
$C(\mathrm{CyC_6})$	89 1	93 9	76 6	72 1	80 0

[a] 475°C, 2 0 WHSV, 9 2 H_2/nC_6, atmospheric pressure Data at 2 hr on-stream

TABLE 7

Effect of Contact Time on the Methane Selectivity in the Dehydrocyclization of *n*-Hexane over Regenerated, Aged PtNaY(300)

Contact time (1/WHSV)	$Q(C_1)$, %wt
0.125	0.35
0.167	0.50
0.25	0.70
0.50	0.98
0.667	1.20
1.00	1.60
2.00	2.60

the aromatization and cracking reactions (b), (d), and (e) are presumably irreversible, although small amounts of toluene and traces of xylenes were observed in almost all experiments. Reaction (e) is suggested by the high conversion data in Fig. 1 and most likely involves hydrogenolysis to methane. This is demonstrated in Table 7, where the data for $Q(C_1)$ taken from the space velocity variation with aged, regenerated PtNaY(300) (Fig. 1) show the increase in methane yield with increasing contact time. However, at high conversions, methane yields are expected to be higher due to cracking of heavier gas products.

Davis (*13*) has summarized the various mechanisms proposed for dehydrocyclization with nonzeolitic catalysts and concluded that, on nonacidic supports and at atmospheric pressure, 1,6-ring closure was preferred to 1,5-closure. A definitive judgment as to which, if any, of these mechanisms apply to the PtY catalysts cannot be made on the basis of the data made available in this study. However, some qualitative observations may lead to a reasonable, although tentative, conclusion.

In every sample a minor peak was qualitatively observed on the chromatogram that was identified, on the basis of retention time, as cyclohexene. The concentration of this component followed the behavior of the $C_6^{2=}$ group in general. Thus, dehydrogenation–cyclization mechanisms, e.g., that of Rozengart and Kazanskii (*14*), would be eliminated, since cyclohexene could not be an intermediate. In addition, the neutralized PtNaY(300) catalyst did show a reduction in dehydrocyclization activity *and* selectivity, indicating that a reduction in acidity does affect aromatization, as called for by the mechanisms of Muller and Gault (*15*) and Kogan *et al.* (*16*). Further, comparison of the data for NaOH treated PtNaY(300) in Table 3 with the selectivity data in Fig. 1 indicates that the neutralized catalyst gives much higher selectivities for isohexanes [$Q(iC_6)$] than PtNaY(300), indicating that the aromatization of methylcyclopentane has been prevented by the lack of acidity, so that isohexanes, formed via ring hydrogenolysis, are the exclusive product.

Based on these observations, it would appear that the PtNaY(300) catalyst follows the mechanism discussed by Kogan, *et al.* (*16*) involving aromatization via both 1,6-ring closure, which is not inhibited by removal of acid sites, and 1,5-ring closure to methylcyclopentanes, the aromatization of which are inhibited by a lack of acidity. Both dehydrocyclization and dehydrogenation activity of PtY catalysts are improved by decreasing the Pt particle size, although ring closure also occurs in the case of dehydrocyclization at the same sites. Following ring closure, of course, dehydrogenation would occur as in the case of cyclohexane, producing cyclohexene as an intermediate. These considerations do not necessarily eliminate the direct dehydrogenation pathway, however, since cyclohexene may also be formed via hydrogenation of benzene or cyclohexadiene particularly at higher pressures.

Effect of Other Cations and Metals

Replacement of Na^+ with other cations (Li^+, K^+, Mg^{2+}, Ca^{2+}) primarily influences cracking activity and selectivity (Table 5). Several literature reports (*17–19*) indicate that hydrogenolysis of *n*-paraffins over Pt catalysts (metal cracking) produces attack at all C–C bonds equally The product distribution in the alkali metal Y's (Li, Na, K) is typical for Pt hydrogenolysis, as is the low degree of olefin formation Replacement of these cations with alkaline earth cations (Mg^{2+}, Ca^{2+}) results in the addition of acidic cracking sites (due to Ca^{2+} hydrolysis), increasing the degree of center cracking to C_3 gases, as well as increasing olefin products The light gas distributions observed for PtMgY and PtCaY are similar to those found for CaY (*20*)

Thus, in PtLiY, PtNaY, and PtKY the cracking is due primarily to Pt hydrogenolysis In PtMgY and PtCaY, the cations produce additional acidic cracking, resulting in a higher cracking selectivity (thus a lower dehydrocyclization selectivity) The lower activities of the latter catalysts are due to more rapid aging due to acidic cracking (coking), the initial activities for all PtRY catalysts were similar (*n*-hexane conversion ≃ 70–90%)

The addition of Cu, Zn, and Ag to PtNaY had a generally negative effect, with respect to both aromatization activity and selectivity (Table 6) Apparently, the zeolite lattice does not permit the type of interactions between metals (e g , alloying) that occur on other supports (*12*)

State of Pt in Fresh Catalysts

The neutralization experiments (Table 3), performed on fresh calcined catalyst prior to pretreatment, provide indirect evidence of the state of platinum While Gallezot *et al* have maintained that air calcination leads to formation of divalent Pt ions in the zeolite structure (*6*), Reagan *et al* have shown by thermogravimetric studies that Pt(II) is reduced to Pt(0) by the ammonia ligands (*9*) The existence of catalytic acidity in the fresh catalyst indirectly confirms that Pt is reduced to the zerovalent state with the consequent formation of acidic sites

REFERENCES

1 Rabo, J A , Schomaker, V , and Pickert P E "Proc Int Congress Catalysis, 3rd, 1964" Vol 2, p 1264 North Holland, Amsterdam, 1965

2 Rabo, J A , Pickert P E , and Mays, R L , *Ind Eng Chem* **53,** 733 (1961)

3 Kubo, T , Arai H , Tominaga, H , and Kunuzi, T , *Bull Chem Soc Japan* **45,** 607, 613 (1972)

4 Dalla Betta, R A , and Boudart, M "Catalysis," Vol 1, p 1329 North Holland, Amsterdam, 1973

5 Czaran, E , Schnabel, K -H and Selenina, M *Z Anorg Allgem Chem* **410,** 225 (1974)

6 Gallezot, P Alarcon-Diaz, A , Dalmon J -A Renoprez A J and Imelik B , *J Catal* **39,** 334 (1975)

7 Gallezot, P , Mutin, I Dalmai-Imelik, G , and Imelik B , *J Microsc Spectrosc Electron* **1,** 1 (1976)

8 Gallezot, P Datka, J , Massaidier J , Premet, M , and Imelik, B "6th Int Congr Catal ,' Vol 2, p 696 Chemical Society, London, 1977

9 Reagan, W J , Chester, A W , and Kerr, G T , *J Catal* **69,** 89 (1981)

10 Naccache, C , Kaufherr, N , Dufaux, M , Bandiera, J and Imelik, B , *ACS Symp Ser* **40,** 358, 1977

11 Merrill, H E , and Arey, W F , Jr , *Preprints, Div Petroleum Chem A C S* **13,** 193 (1968)

12 Sinfelt, J S , Carter, J L , and Yates, D J C , *J Catal* **24,** 283 (1972)

13 Davis, B H , *J Catal* **46,** 348 (1977)

14 Rozengart, M I , and Kazanskii, B A , *Russ Chem Rev* **40,** 715 (1971)

15 Muller, J F , and Gault, F G , *J Catal* **24,** 361 (1972)

16 Kogan, S B , Bursian, N R , and Davydova, Z A , *Kinet Catal* **10,** 1137 (1969)

17 Myers, C G , and Munns, G W , Jr , *Ind Eng Chem* **50,** 1727 (1958)

18 Kikuchi, E , Tsurumi, M and Mouta Y , *J Catal* **22,** 226 (1971)

19 Carter, J L , Cusumano, J A , and Sinfelt, J H , *J Catal* **20,** 223 (1971)

20 Turg, S E , and McIninch, E , *J Catal* **10,** 166 (1968)