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Studies of the Thermal Decomposition and Catalytic Properties of Some Platinum and Palladium Ammine Zeolites

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The stoichiometry, temperature dependence, and the effect of atmosphere for the thermal decomposition of Pt and Pd ammine complexes exchanged into zeolite Y were investigated by thermogravimetry. It was found that (a) the maximum rate of reduction of Pt and Pd ammine Y occurred at 300 and 250°C, respectively; (b) decomposition of Pt ammine Y in air leads to formation of Pt metal—air is essentially an inert medium, although the oxidation of evolved NH_3 is catalyzed by Pt; Pd is only partially reduced to metal when Pd ammine Y is decomposed in air; (c) decomposition in H_2 effects reduction at much lower temperatures; (d) acid sites in the zeolite are always generated stoichiometrically by the decomposition of Pt and Pd ammines, whether in hydrogen, helium, or air. The maximum rate of reduction of Pt ammine Y at 300°C correlates with reported maxima in dehydrogenation activity and Pt dispersion. In this study, the 300°C calcined catalysts showed maximum *n*-hexane dehydrocyclization activity and selectivity as well as cyclohexane dehydrogenation.

INTRODUCTION

There has been a significant number of fundamental catalytic studies of metal zeolites as examples of finely dispersed metal catalysts. Rabo *et al.* (*1, 2*) obtained improved hydroisomerization catalysts by exchange of Pt and Pd ammine cations into zeolite Y. This ion exchange procedure gave PtY catalysts with a highly dispersed metal phase with high resistance to sulfur poisoning and superior properties to catalysts prepared by impregnation with chloroplatinic acid.

Several recent reports have shown that variations in catalyst preparations, calcination, and pretreatment have a major effect on the activity and selectivity of these PtY catalysts: Kubo and co-workers (*3*) found that for PtNaY catalysts an air calcination at 300°C led to maximum Pt dispersion, H_2 chemisorption, cyclohexane dehydrogenation activity, and toluene hydrodemethylation activity. Dalla Betta and Boudart (*4*) have shown that decomposition of $Pt(NH_3)_4^{2+}$ exchanged into Y zeolite at 350°C in oxygen led, upon hydrogen reduction, to Pt metal clusters which contained less than six Pt atoms. These clusters had anomalously high activities for hydrogenation, isomerization, and hydrogenolysis. The improved dispersion of platinum in Y zeolites due to a preliminary thermal treatment in air at 350°C was confirmed by Czaran (*5*). Gallezot and co-workers (*6–8*) also found that high platinum dispersion and enhanced catalytic activity were favored by specific calcination procedures.

The present study was undertaken to examine two aspects of the relationship of calcination conditions to catalyst activity: (i) a detailed study of the stoichiometry, temperature dependence, and the effect of atmosphere (whether reactive or inert) on the thermal breakdown of the simple metal ammine salts and their metal complex zeolite forms and (ii) to examine the effects of calcination conditions upon the dehydrogenation and dehydrocyclization behavior of some selected catalyst samples. This

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latter reaction is of considerable industrial importance and has received little attention in the literature for these types of noble metal zeolite catalysts.

EXPERIMENTAL

The study of the thermal decomposition of the metal ammine complexes was carried out with a DuPont 951 thermogravimetric analyzer. The procedures for the evolved gas and ammonium chloride analyses have been described earlier (*10, 11*). Unless noted otherwise, the programmed temperature rise was 20°C/min.

All catalysts were prepared by ion exchange with commercial Linde NaY, which had been washed and air dried. The samples of metal ammine Y materials for TG studies were extensively exchanged to aid in the precision of the evolved gas analyses. Chemical analyses indicated the following number of metal ammine cations per unit cell: $Pt(NH_3)_6^{4+}$:8; $Pt(NH_3)_4^{2+}$:18; $Pd(NH_3)_4^{2+}$:17. For the catalytic studies, two PtNaY catalysts containing 0.48 and 1.3 wt% Pt were prepared by exchanging NaY with $[Pt(NH_3)_6]Cl_4$ stock solution (0.002 g Pt/ml) overnight at room temperature. The air calcinations were then performed with 3 g samples loosely packed in a small open crucible placed in a muffle furnace, preheated to temperature (200–500°C) for 3 hr. The calcined samples, PtNaY(T), (where T = temperature, °C), were then pelleted and sized between 14 and 30 mesh. In each run, 0.5 g catalyst (dry basis) was placed in a 1/2″ 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 4 hr. The charge stocks were Phillips pure grade cyclohexane and *n*-hexane. The standard testing conditions are listed below:

Feed	Cyclohexane	*n*-Hexane
T (°C)	300 ± 5	475 ± 5
WHSV	3.0	2.0
H_2/HC	12.0	9.2

After pretreatment, dehydrogenation activity was determined after passing CyC_6 over the catalyst for 10 min. The temperature was then raised (with the catalyst flushed with H_2) and nC_6 was passed over the catalyst for 2 hr, with appropriate sampling.

In addition to calculating actual weight percent yields of all reaction products, each sample was broken down in two other ways, based on (a) *n*-hexane conversion and (b) charge conversion defined as:

$$n\text{-hexane conversion} = C\ (nC_6) = 100 - \%\ nC_6\ \text{remaining};$$

$$\text{charge conversion} = C = \%\ Ar + \%\ (C_1 - C_5)\ \text{formed}.$$

The following selectivities were then determined:

$$Q(C_1\text{–}C_5) = 100 \times \%\ (C_1\text{–}C_5)/C(nC_6)$$
$$Q(C_1) = 100 \times \%\ C_1/C(nC_6)$$
$$Q(iC_6) = 100 \times \%\ iC_6/C(nC_6)$$
$$Q(C_6^{2-}) = 100 \times \%\ C_6^{=}/C(nC_6)$$
$$Q(Ar) = 100 \times \%\ Ar/C(nC_6)$$
$$S(Ar) = 100 \times \%\ Ar/C$$

The product stream was injected directly into a 10′ × 1/8″ Durapak *n*-octane/Porocil C (100–200 mesh) column installed in a Hewlett-Packard 5750 Research Chromatograph via a heated gas sample valve; a flame ionization detector was used.

RESULTS

A. Thermal Decomposition of Platinum (IV) Hexammine Chloride

The studies of the thermal decomposition of the more common platinum and palladium tetrammine chlorides have been reported (*12*). Since the hexammineplatinum(IV) cation was used in the preparation of some of the metal zeolite catalysts, the thermal properties of simple hexammine-platinum(IV) chloride were first investigated.

Under hydrogen, the following decomposition scheme for $[Pt(NH_3)_6]Cl_4$ was observed:

TABLE 1

Evolved Decomposition Products of Hexammineplatinum (IV) Chloride

	NH_3/Pt		HCl/Pt		NH_4Cl/Pt	
	Found	Calc.[a]	Found	Calc.[a]	Found	Calc.[a]
$[Pt(NH_3)_6Cl_4$	2.07	2.00	1.45	1.33	2.46	2.67
	1.96		1.31		2.33	
	2.11					
	1.93					

[a] Based on Eq. (2) $[Pt(NH_3)_6]Cl_4 \rightarrow Pt + 2NH_3 + 0.67N_2 + 2.67NH_4Cl + 1.33HCl$.

$$[Pt(NH_3)_6]Cl_4 + 2\ H_2 \rightarrow Pt^\circ + 2\ NH_3 + 4\ NH_4Cl \quad (1)$$

Ammonia is first detected at about 150°C. The main reaction (reduction of platinum by hydrogen) occurred between 200 and 260°C without the formation of any stable intermediates.

The observed stoichiometry for the decomposition of $[Pt(NH_3)_6]Cl_4$ in a helium atmosphere is shown in Table 1. The evolution of the two NH_3 ligands per platinum was observed before the main decomposition reaction at 300–325°C. This step does not represent the formation of an intermediate such as $[Pt(NH_3)_4Cl_2]Cl_2$ since ammonium chloride is detected simultaneously with ammonia evolution. The stoichiometry of Eq. (2) was indicated by the quantitative analyses of evolved NH_4Cl and HCl (see Table 1).

$$[Pt(NH_3)_6]Cl_4 \rightarrow Pt^\circ + 32\ NH_3 + 0.67\ N_2 + 2.67\ NH_4Cl + 1.33\ HCl \quad (2)$$

The somewhat lower values for NH_4Cl and higher HCl/Pt ratios suggest that some ammonia cracking could occur over Pt. The reduction of Pt(IV) to Pt(O) occurs via electron transfer from ammine ligands:

$$Pt(IV) + 1\text{-}1/3\ NH_3 \rightarrow Pt^\circ + 4H^+ + 2/3\ N_2 \quad (3)$$

B. Thermal Decomposition of the Platinum and Palladium Ammine Zeolites

$Pt(NH_3)_6NaY$. Under hydrogen,

TABLE 2

Evolved Decomposition Products of Metal Ammine Zeolites

Compound	Total NH_3/metal		Hydrogen atmosphere				Helium atmosphere			
			NH_3 evolved/metal		Chem H_2O/metal		NH_3 evolved/metal		Chem H_2O/metal	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$Pt(NH_3)_6{}^{4+}Y$	6.4	6.0	6.46	6.0[a]	2.3	2.0[a]	5.02	4.67[b]	2.27	2.0[b]
$Pt(NH_3)_4{}^{2+}Y$	3.64	4.0	3.76	4.0[c]	1.01	1.0[c]	2.97	3.3[d]	1.0	1.0[d]
$Pd(NH_3)_4{}^{2+}Y$	3.90	4.0					3.72	3.3[d]	0.99	1.0[d]

[a] Based on Eqs. (4a)–(4c) (see text).

[b] Based on Eq. (5) (see text).

[c] Based on Eqs. (8a)–(8c) (see text).

[d] Based on Eqs. (7a)–(7c) (see text).

$Pt(NH_3)_6NaY$ was found to decompose according to the following scheme:

$$Pt(NH_3)_6NaY + 2\ H_2 \xrightarrow{175°C} Pt° + 2\ NH_3 + 4\ NH_4Y \quad (4a)$$

$$4\ NH_4Y \xrightarrow{200-400°C} 4\ NH_3 + 4\ HY \quad (4b)$$

$$4\ HY \xrightarrow{700°C} 2\ H_2O + 4\ Y \quad (4c)$$

The observed values of evolved ammonia and chemical water are in reasonable agreement with this scheme (see Table 2). A low platinum analysis is probably responsible for the consistently high experimental results. Figure 1 presents differential weight loss, ammonia, and nonammonia gas evolution curves as a function of temperature. The sharp peak in the derivative of the ammonia evolution curve at 180°C corresponds to step (4a). The broad hump (between 200 and 400°C) in the same curve would then represent the decomposition of NH_4Y (step 4b). These conclusions are supported by the fact that the ammonia evolved before 200°C represents about 1/3 of the total ammonia detected. The temperature of the platinum reduction by hydrogen in the $Pt(NH_3)_6Y$ is slightly lower than in the simple chloride salt but the essential features of the decomposition are unchanged.

The overall stoichiometry of the decomposition of $Pt(NH_3)_6Y$ in a helium atmosphere can be written as follows:

$$Pt(NH_3)_6Y \rightarrow Pt° + 4\ HY + 2/3\ N_2 + 4\text{-}2/3\ NH_3 \quad (5)$$

In this case, the platinum is reduced by the ammonia ligands as in (3).

Once again the experimental values (Table 2) for the evolved ammonia and chemical water are consistent with Eq. (2). However, the differential plots (Fig. 2) of this helium experiment indicates that a multistep decomposition is quite likely. In Fig. 2, the sharp peak at 320°C in the derivative of the nonammonia evolution curve corresponds to the nitrogen released from the ammonia reduction of platinum. However, a substantial amount of ammonia is evolved before this temperature ($1.54NH_3/Pt$ before 300°C). The rate of evolution of this ammonia (Fig. 2) suggests the decomposition of NH_4Y rather than straight ammonia evolution. One possible explanation for the formation of NH_4Y before the obvious reduction step at 325°C is the formation of a platinum(II) intermediate:

$$Pt(NH_3)_6Y \xrightarrow{<300°C} Pt(NH_3)_{4-n}{}^{2+}(Z)_nY + 1\text{-}1/3NH_4Y + 1/3N_2 + 2/3HY \quad (6)$$

$$(Z = \text{lattice oxygen site})$$

The final step (300–330°C) would involve the decomposition of the proposed platinum(II) intermediate with release of ammonia (sharp peak at 310°C) and nitrogen (peak at 325°C).

Additional evidence for a platinum(II) intermediate involves the measurement of acid (2 N HCl) leached samples of $Pt(NH_3)_6{}^{4+}Y$, $Pt(NH_3)_4{}^{2+}Y$, and a sample of $Pt(NH_3)_6{}^{4+}Y$ heated to 275°C. The uv spectrum of a solution of the 275°C product showed a characteristic pattern similar to $Pt(NH_3)_4{}^{2+}Y$ and distinct from that of $Pt(NH_3)_6{}^{4+}Y$. Finally, there was no indication of an unusual dehydroxylation behavior of the zeolite, since the calculated and observed values of evolved chemical water are in close agreement.

$Pt(NH_3)_4Y$. The results of the thermal decomposition studies in helium and hydrogen are presented in Table 2. Once again, the reasonable agreement between calculated and experimental results is good evidence for a normal decomposition scheme. In helium:

$$Pt(NH_3)_4Y \xrightarrow{He} Pt° + 2\ NH_4Y + 1/3\ N_2 + 1\text{-}1/3\ NH_3 \quad (7a)$$

$$2\ NH_4Y \rightarrow 2\ NH_3 + 2\ HY \quad (7b)$$

$$2\ HY \rightarrow H_2O + 2Y \quad (7c)$$

It should be noted that Reactions (7a) and (7b) occurred almost simultaneously about 300°C. Under hydrogen the following scheme was observed:

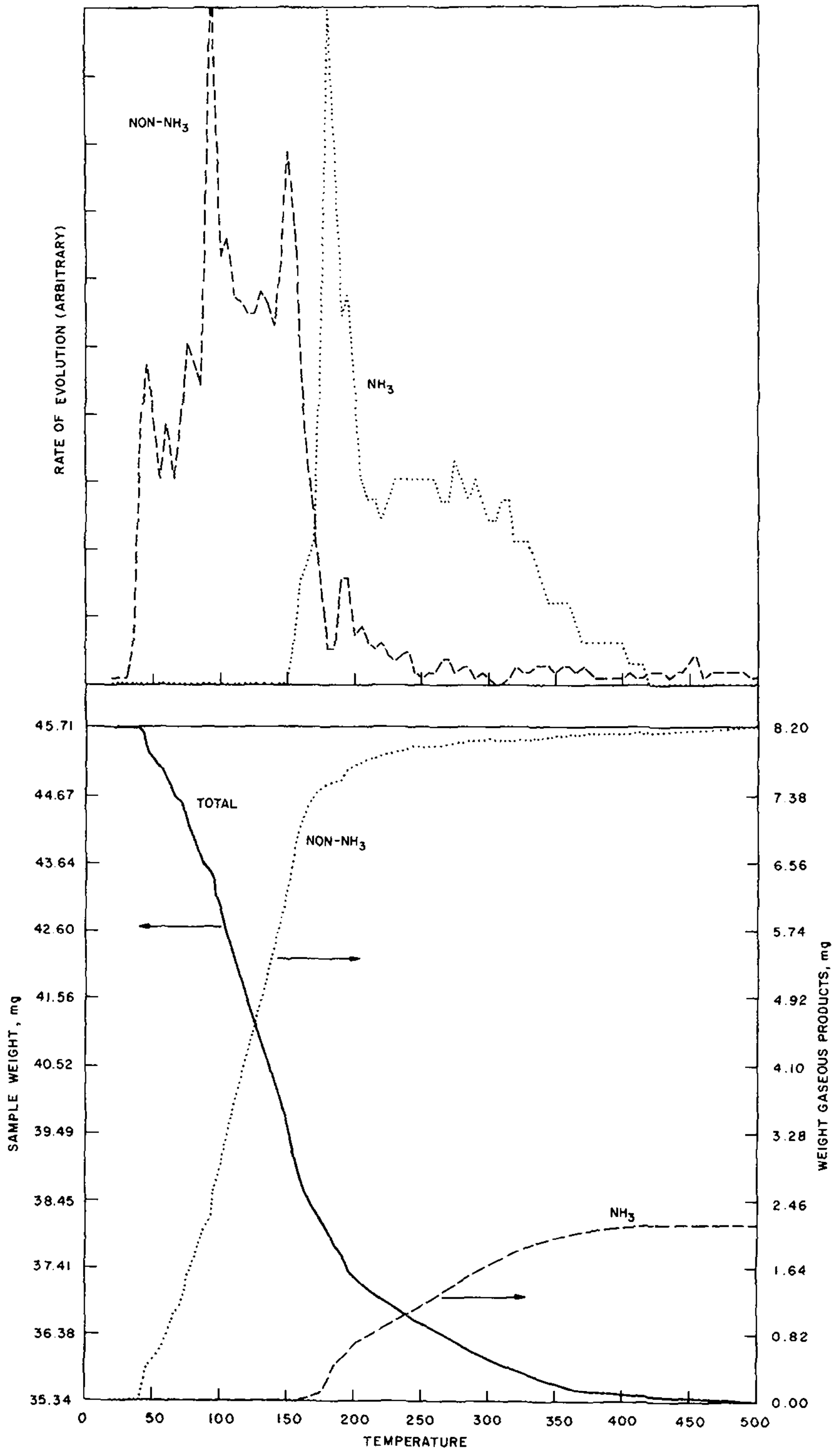

FIG. 1. Computer plots of the thermal decomposition of Pt$(NH_3)_6{}^{4+}$Y (hydrogen atmosphere). (Top) First derivative of gaseous decomposition products; nonammonia (dashed); ammonia (dotted). (Bottom) TGA curve (solid line), nonammonia gas evolved (dotted), and ammonia evolved (dashed).

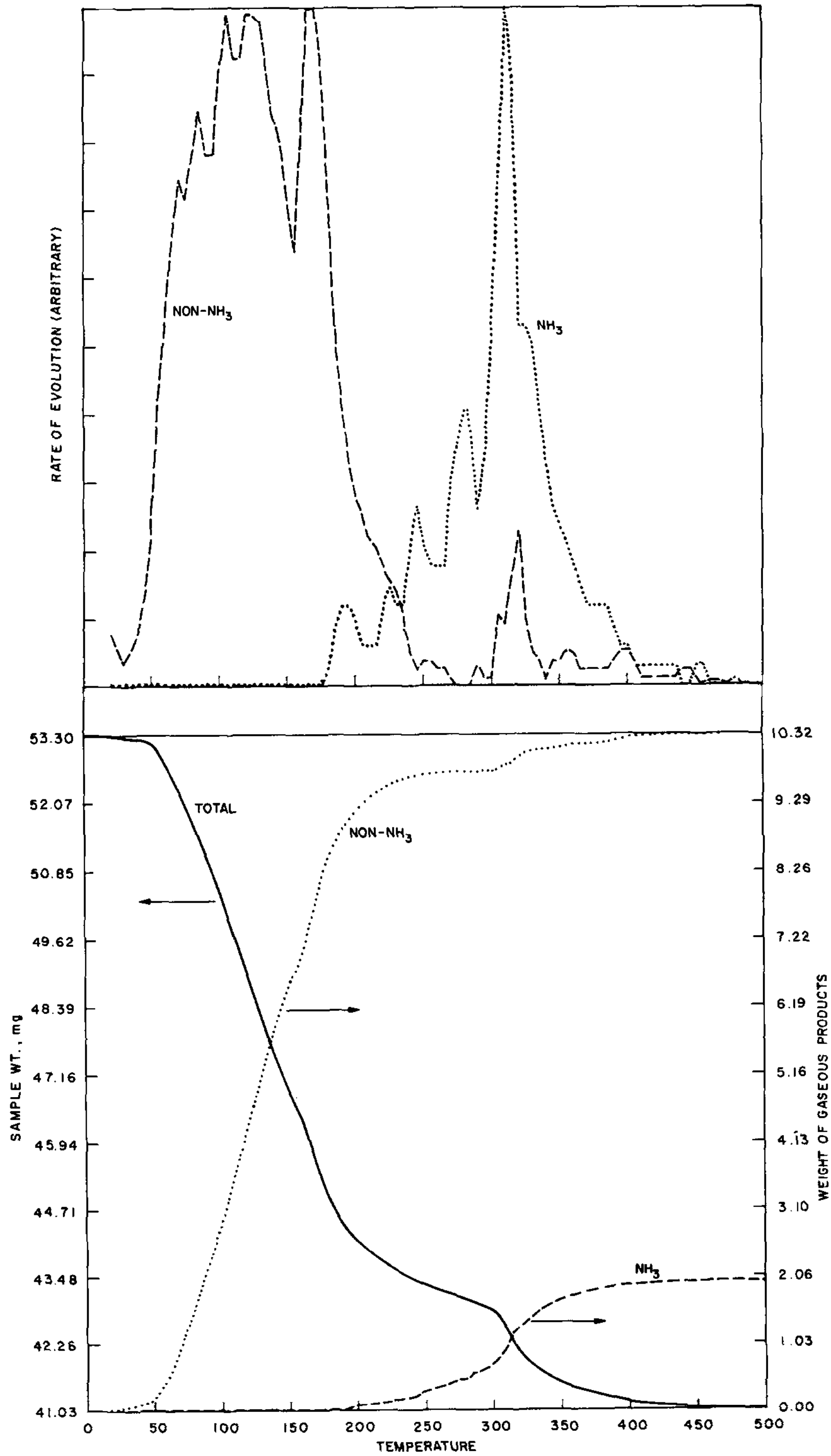

FIG. 2. Computer plots of the thermal decomposition of $Pt(NH_3)_6^{4+}Y$ (helium atmosphere). (Top) First derivative of gaseous decomposition products; nonammonia (dashed), ammonia (dotted). (Bottom) TGA curve (solid line), nonammonia gas evolved (dotted), and ammonia evolved (dashed).

$$\mathrm{Pt(NH_3)_4Y + H_2 \rightarrow Pt^0 + 2\,NH_3 + 2\,NH_4Y} \tag{8a}$$

$$\mathrm{2\,NH_4Y \rightarrow 2\,NH_3 + 2\,HY} \tag{8b}$$

$$\mathrm{2\,HY \rightarrow H_2O + 2\,Y} \tag{8c}$$

The hydrogen reduction (Eq. (8a)) took place at the relatively low temperature of 145-150°C.

$Pd(NH_3)_4Y$. The results for tetramminepalladium(II) zeolite are presented in Table 2. Only minor differences were noted between the palladium and platinum tetrammine zeolites. The lower stability of palladium complexes is reflected in the temperatures at which reactions corresponding to (7a) (~250°C) and (8a) (~125°C) take place.

Thermal decomposition in air. The possibility exists that, in air, the simplest medium for use in catalyst calcination, Pt and Pd would not be reduced to metal due to the oxidizing atmosphere. A complete investigation of $Pt(NH_3)_4$ and $Pt(NH_3)_6Y$ in air is made more difficult by the expectation that evolved NH_3 oxidation would be catalyzed by Pt metal. This is in fact observed experimentally by (a) a marked decrease in the evolved NH_3/Pt ratio and (b) observation of an exothermic reaction at ~275°C. The question of Pt reduction is easily settled; if air is acting as an "*inert*" atmosphere, then Eqs. (7) and (5) would apply to the decompositions of tetrammine and hexammine, respectively, so that the ratio chem H_2O/Pt should be 1.0 and 2.0, respectively. Experimentally, we observe chem H_2O/Pt ratios of 1.1 and 2.1 for $Pt(NH_3)_4$– and $Pt(NH_3)_6$–NaY, respectively, verifying that even in air, the platinum ammines reduce to Pt metal *via* ammonia reduction.

Investigation of $Pd(NH_3)_4NaY$, however, yields a chem H_2O/Pd ratio of *0.3*, where the calculated value for complete reduction to Pd metal is 1.0. Thus, $Pd(NH_3)_4^{2+}$ in Y is only partially reduced to metal in air, unlike the Pt ammines. For preparation of Pd metal/Y catalysts, air calcination must be followed by hydrogen reduction, whereas for Pt the hydrogen reduction is not necessary (except to remove chemisorbed O_2).

C. *Catalytic Properties of PtY Catalysts Derived from Platinum Ammine Y Zeolites*

The results of a typical run with *n*-hexane over 0.48% PtNaY(300) are presented in

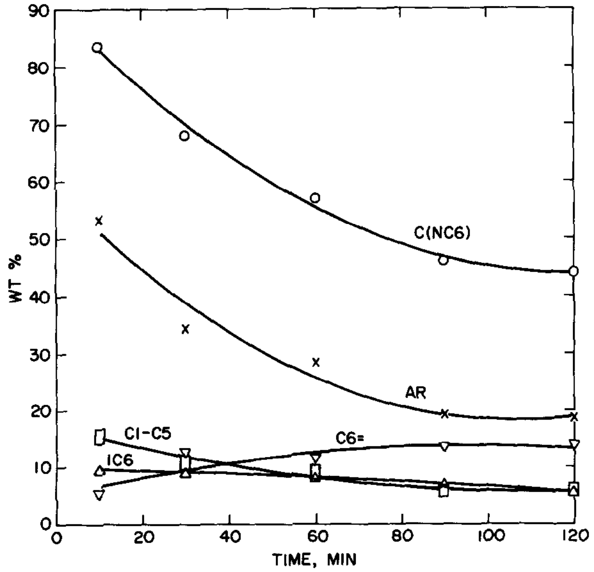

FIG. 3. Composition vs time plots for the reaction of *n*-hexane over 0.48% PtNaY (300).

TABLE 3

Catalytic Activity of PtNaY Catalysts with Cyclohexane and *n*-Hexane (0.48% Pt)[a]

Run	Catalyst	Air calc T (°C)	$C(CyC_6)$	C	$S(Ar)$	$C(nC_6)$	$Q(Ar)$	$Q(C_6^=)$	$Q(iC_6)$	$Q(C_1–C_5)$
87	0.48% PtNaY	200	60.6	4.9	53	21.6	11.9	50.9	7.9	10.7
94		250	79.9	14.6	72	34.9	30.1	45.2	13.0	11.7
85		300	89.1	24.6	76	44.1	42.5	31.3	12.9	13.3
93		350	83.5	17.8	75	38.4	34.5	40.1	13.8	11.6
88		400	85.8	13.2	71	34.2	27.4	52.5	8.9	11.2
89		500	55.0	5.3	64	26.8	12.8	73.5	6.5	7.2

[a] Cyclohexane test conditions: 300°C, 3.0 WHSV, 12.0H_2/CyC_6, atmospheric pressure; *n*-hexane test conditions: 475°C, 2.0 WHSV, 9.2 H_2/nC_6, atmospheric pressure data at 2 hr on-stream.

Fig. 3 as product composition vs time curves. It is readily seen that for the first 60–90 min on stream, rapid aging occurs, in terms of both $C(nC_6)$ and C. From 90 to 120 min, however, little change occurs. This is typical of all PtY catalysts tested; in fact, the PtNaY(300) catalyst ages *less* rapidly than any of the others. For comparison purposes then, catalysts are considered to be in an "aged" or "equilibrium" stage after *2 hr* on stream and catalyst parameters are compared at that time.

Tables 3 and 4 show the data derived for the 0.48 and 1.3% PtNaY(T) catalysts at 2 hr time on stream. Some of these data are presented graphically in Figs. 4 and 5 for the 0.48% PtNaY(T) catalysts. The dehydrogenation activity [Fig. 4, $C(CyC_6)$] is clearly dependent on calcination temperature with a maximum at 300°C, confirming the observations of Kubo *et al.* (*6*). Interestingly, the activity with *n*-hexane (Fig. 4, $C(nC_6)$ and C) show the same maximum at 300°C. In addition to activity peaking at 300°C, the aromatic selectivity parameters (Fig. 5, $Q(Ar)$ and $S(Ar)$) show the same maximum, while the olefin selectivity is at a minimum ($Q(C_6^{2-})$).

Similar plots can be derived if data for shorter time-on-stream is considered, so that the 300°C maximum is independent of time when comparable time periods are considered. The selectivities must, however, be viewed with caution, since $Q(Ar)$ and $Q(C_6^=)$ are actually functions of conversion. These parameters are better compared at constant conversion, as is done in Fig. 6 where the data are obtained for each catalyst where $C(nC_6) \simeq 40\%$ but at different times. The same maximum for $Q(Ar)$

TABLE 4

Catalytic Activity of PtNaY Catalyst with Cyclohexane and *n*-Hexane (1.3% Pt)[a]

Run	Catalyst	Air calc T (°C)	$C(CyC_6)$	C	$S(Ar)$	$C(nC_6)$	$Q(Ar)$	$Q(C_6^=)$	$Q(iC_6)$	$Q(C_1–C_5)$
79	1.3% PtNaY	200	78.0	7.3	53	21.5	18.1	56.3	9.8	15.8
81		300	85.3	49.2	67	65.4	50.7	12.4	12.4	24.5
82		400	80.2	23.2	61	43.0	33.0	33.5	12.6	21.0
83		500	76.7	4.7	45	19.2	10.9	71.9	3.8	13.4

[a] Cyclohexane test conditions: 300°C, 3.0 WHSV, 12.0H_2/CyC_6, atmospheric pressure; *n*-hexane test conditions: 475°C, 2.0 WHSV, 9.2 H_2/nC_6, atmospheric pressure data at 2 hr on-stream.

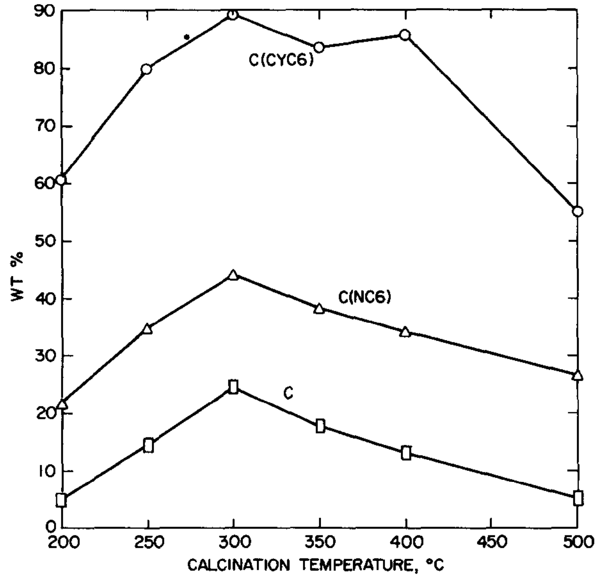

FIG. 4. Dependence of cyclohexane, *n*-hexane, and charge conversion for 0.48% PtNaY(T) as a function of *T*, the air calcination temperature.

(and corresponding minimum for $Q(C_6^{2-})$) is observed at 300°C.

The selectivity parameter S(Ar) should not be a function of conversion, since this parameter is based on the assumption that all intermediates (hexenes, isohexanes) convert either to aromatics or light gases. This is in fact observed for the catalysts PtNaY (300–350), as is evident in Table 3, for example. However, the less optimum catalysts did show a decrease in S(Ar) with time on stream.

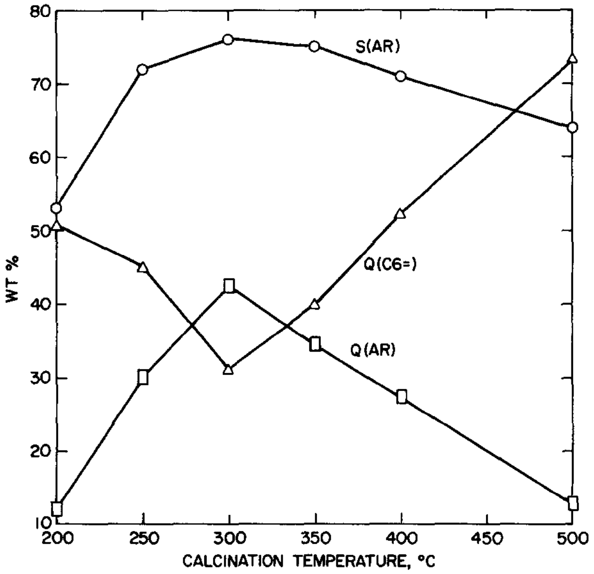

FIG. 5. Dependence of aromatic and olefin selectivities for 0.48% PtNaY(T) as a function of *T*.

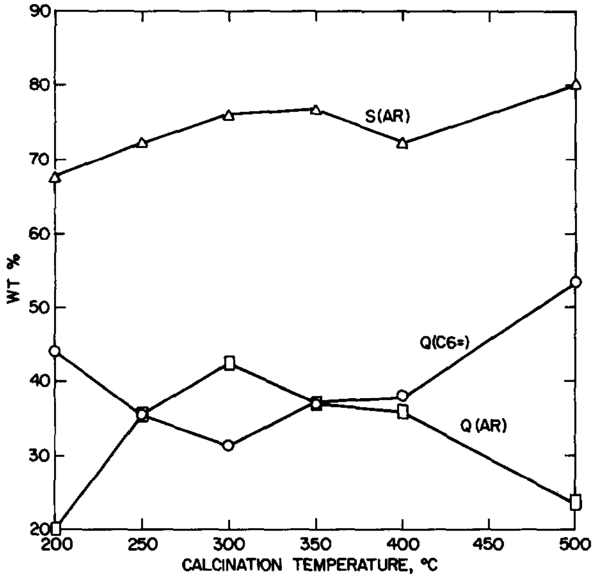

FIG. 6. Aromatics and olefin selectivities as a function of T for 0.48% PtNaY(T) at constant n-hexane conversion ($C(nC_6) \simeq 40\%$).

The results of the catalytic tests of the various 1.3 wt% PtNaY samples are presented in Table 4. The same conclusions with respect to the air calcination temperature derived from the 0.48 wt% samples are also evident from these data. A comparison of the two catalyst samples at the optimum calcination temperature (300°C) indicates that the catalyst with the higher platinum content has somewhat higher activity, due mainly to cracking (high $Q(C_1–C_5)$) with comparable aromatics selectivities.

DISCUSSION

The thermal decomposition studies clearly delineate the stoichiometries to be expected for calcination of Pt and Pd ammines in zeolite Y in hydrogen, helium (or other inert gases) and air. It is especially important to note that, whenever a Pt ammine complex is decomposed within a zeolite lattice, acid sites are generated, whether the reduction is by hydrogen or by coordinated ammonia in an inert medium. This information indicates that platinum metal is always the product of the thermal decomposition (at 300°C or higher) of Pt ammines in zeolite Y, even in air. Thus, previous literature information on calcined PtY materials which mention platinum ions (as in Gallezot *et al.* (*9*)) should be interpreted cautiously.

The results also show that decomposition in H_2 results in Pt or Pd reduction at significantly lower temperatures than does autoreduction in an inert atmosphere (He or air); apparently the complex ions are directly attacked by H_2.

Further, the maximum rate of autoreduction of the Pt ammines occurs at ~300°C (see Figs. 2 and 3), the same temperature that Kubo *et al.* (*3*) finds to be the optimum calcination temperature for $Pt(NH_3)_4Y$ in terms of maximum activity and Pt dispersion.

The results of the catalytic tests demonstrate quite clearly that a PtNaY catalyst prepared by air calcination at 300°C is optimized with respect to dehydrogenation and dehydrocyclization activity and dehydrocyclization selectivity, at least at atmospheric pressure. This optimum calcination temperature coincides with the temperature of maximum rate of decomposition of the hexammineplatinum(IV) cation in zeolite Y. Although the metal dispersions of this series of PtNaY catalysts were not measured, it is quite likely that the optimum catalysts would exhibit the greatest metal dispersions. These findings are in agreement with other studies (*3*) on the effects of calcination conditions of PtY catalysts upon platinum metal dispersion and catalytic activity. The information presented here that *n*-hexane dehydrocyclization activity and selectivity are also optimized by calcination procedures has not appeared in previous studies of PtY catalysts.

There appear to be two factors determining the optimum calcination temperature. The reduction rate for Pt ammines in Y is at a maximum at about 300°C in a dynamic, e.g., programmed system. This temperature may be regarded as a "threshold" in that at temperatures significantly below 300°C the decomposition will occur too slowly to be complete in the time used for calcination (3 hr). Thus, only a portion of the ammine is decomposed, the remainder being reduced by H_2 subsequently giving a poorer, i.e., more agglomerated, catalyst. This "threshold" or stability effect does not explain why poorer catalysts are obtained at higher temperatures, where the decomposition rate will be much more rapid.

The second factor, then, must involve an unstable, labile intermediate which would diffuse more rapidly at higher temperatures, allowing greater degrees of Pt agglomeration. Dalla Betta and Boudart (*4*) have observed infrared spectra during the decomposition of $Pt(NH_3)_4^{2+}$ in Y in hydrogen that they have attributed to a neutral unstable species, $Pt(NH_3)_2H_2$, which leads to agglomeration. This hydride was not observed in O_2 by them, but such a species could in fact be formed in air or O_2, if only at a low concentration, since sufficient NH_3 in the vicinity of already reduced Pt could crack to N_2 and H_2. Thus, at high temperatures (400–500°C) decomposition of the ammine would be almost instantaneous, providing momentarily high NH_3 concentrations around partially reduced Pt, allowing the formation of $Pt(NH_3)_2H_2$ or some similar species and leading to Pt agglomeration. The experimental verification of the existence of such a labile intermediate was not possible in the present study. Evidence for this effect of NH_3 can be found in the data presented by Kubo *et al.* (*3*) who showed that the dispersion obtained for $PtNH_4Y$ did not show a maximum of 300°C (as for Na and CaY) and that the maximum dispersion obtained at (600°C) for $PtNH_4Y$ was much lower than that for PtNaY calcined at 400°C. Clearly, the ammonia being evolved from NH_4Y from 300 to 600°C allows formation of species leading to Pt agglomeration.

The optimum temperature for calcination of Pt amine zeolites is believed to be the minimum temperature necessary to attain complete decomposition of the complex in a reasonable time. In the case of Pt, this temperature is 300°C for a 3 hr calcination. Similarly, since the removal of NH_3 from the vicinity of Pt is also an important parameter, the use of air or O_2 purges might produce better catalysts than a static system.

Further studies of the PtY catalyst system, including the effects of other metal cations and some aspects of the *n*-hexane dehydrocyclization mechanism will be published separately.

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