JOURNAL OF CATALYSIS 30, 1–12 (1973)

# A Study of Platinum–Polyamide Catalysts. Catalytic Behaviour in the Benzene Hydrogenation Reaction

P. DINI, D. DONES, S. MONTELATICI, AND N. GIORDANO

*Montecatini Edison S.p.A., Centro Ricerche Bollate, Via S. Pietro 50,*
*20021-Bollate (Milano), Italy*

Received May 31, 1972

The activities and selectivities of several platinum catalysts (Pt–polyamides, Pt–polyacrylonitrile, Pt–molecular sieves, Pt–ion exchange resins, Pt–alumina, etc.) were comparatively studied in the hydrogenation reaction of benzene, and a direct influence of the support on the catalytic behaviour was disclosed. The selectivity properties of the Pt–polyamide class are special, and only when a catalyst of this type is used can cyclohexene be found as a reaction product. On the basis of results obtained by different techniques, the presence on the polyamide surface of a bivalent platinum complex was proved, and the complex was identified as the agent responsible for the special selectivity characteristics of this class of catalysts.

## INTRODUCTION

Several recent studies have been concerned with catalytic activity of platinum metals supported on polymers. Most noteworthy amongst others is the work of Harrison and Rase (*1*) on the hydrogenation of benzene in the presence of Pt–nylon catalysts. Two aspects of this work are remarkable, namely the unique behaviour observed for this type of platinum catalyst and the effort to establish a link between the catalyst behaviour and the nature and structure of the materials used as supports. Unique characteristics are self-evident from the high selectivities to cyclohexene found over nylon-6, 66, and 610-based catalysts (nylon-3 is a notable exception): the results are in contrast with previously published information for conventional platinum catalysts, wherein only the completely hydrogenated product cyclohexane has been reported. According to Harrison and Rase, the unusual selectivity is connected with the occurrence on the surface of some particular polyamides of a monoatomic dispersion of platinum metal atoms in a suitable geometric arrangement.

Regarded in this way, it was at first sight surprising, when studies were attempted in our laboratory on the effect of crystallite size on activity, to find that a very low H:Pt ratio was always associated with these Pt–nylon catalysts. Moreover, we found that selectivity to cyclohexene was a general characteristic of all the polyamides, independently of the amide group spacing. It was therefore suggested that geometric effects invoked by Harrison and Rase could not be an entirely valid explanation for the observed selectivities, and that a different interpretation might apply. We therefore considered the possibility of a more direct chemical action of the amide groups of the support on the catalytic behaviour of platinum. The work along this direction has been successful insofar as a complex of bivalent platinum has been discovered on the surface of the polymeric support, and its role on catalytic activity has been adequately proved by the experiments reported below.

## EXPERIMENTAL

### *Carriers*

*Nylon-6,*

$$[-(CH_2)_5-CO-NH-]_n,$$

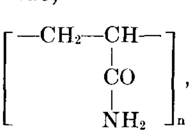
obtained by polymerization of ε-caprolactam (*2*). Nylon-6 powder was obtained by cooling, under stirring, a hot solution of the polymer in ethylene glycol. The material was washed with methanol and dried at 80°C under reduced pressure. The x-ray analysis showed a crystallinity of about 30%. The surface area was 27 $m^2/g$.

*Nylon-3,*

$$[-(CH_2)_2-CO-NH-]_n,$$

obtained by polymerization of acrylamide, using $NaNH_2$ as catalyst (*2*).

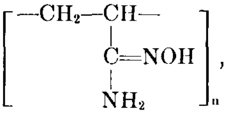
*Polyacrylamide,*



$$\left[-CH_2-\underset{\underset{NH_2}{|}}{\underset{CO}{\underset{|}{CH}}}-\right]_n,$$

obtained by polymerization of acrylamide, using $K_2S_2O_8$ as catalyst (*2*).

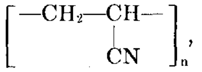
*Polyacrylamideoxime,*



$$\left[-CH_2-\underset{\underset{NH_2}{|}}{\underset{C=NOH}{\underset{|}{CH}}}-\right]_n,$$

obtained from polyacrylonitrile by reaction with $NH_2OH$ (*2*).

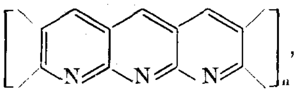
*Polyacrylonitrile,*



$$\left[-CH_2-\underset{CN}{\underset{|}{CH}}-\right]_n,$$

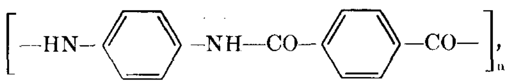
obtained by polymerization of acrylonitrile using $K_2S_2O_8$ as catalyst (*2*).

*Pyro-polyacrylonitrile,*



obtained by pyrolysis of polyacrylonitrile (*2*).

*Poly-*p*-phenylenterephthalamide,*



obtained by reaction of *p*-phenylendiamine with terephthalic acid chloride in dimethylacetamide (*3*).

*Ion-exchange resins:* Dowex 50 W (F. T. Baker Chemical Co.), Amberlite C. G. 400 (Rohm & Haas Co.).

*Molecular sieves:* NaY (Linde Co.).

*γ-Alumina:* Alcoa F-110.

*Reagents*

*$H_2PtCl_66H_2O$:* RP Carlo Erba.

*$K_2PtCl_6$, $K_2PtCl_4$, $(NH_3)_4PtCl_2$, $PtCl_2$:* prepared according to the literature (*4*).

*Benzene:* RS Carlo Erba, dried by distillation over Na.

*Hydrogen:* SAPIO product, purified by passing through a Deoxo unit and a silica gel dryer.

*ε-Caprolactam:* Montecatini Edison product, recrystallized from petroleum ether; mp = 70°C.

*(ε-Caprolactam)$_2$$PtCl_2$:* this compound, not yet reported in the literature, was obtained by reacting $PtCl_2$ with melted ε-caprolactam. The brown product was purified by repeatedly washing with dry ether. Found: C, 30.2; H, 4.5; N, 5.4; Cl, 14.1; Pt, 39.4. $(C_6H_{11}NO)_2PtCl_2$ required: C, 29.3; H, 4.5; N, 5.7; Cl, 14.4; Pt, 39.6. The ir analysis showed a shift of the CO stretching band from 1670 $cm^{-1}$ in the free ligand to 1615 $cm^{-1}$ in the complex; correspondingly, the NH stretching band frequence shifts from 3200 $cm^{-1}$ to 3280 $cm^{-1}$.

*Catalysts*

**Preparation and analysis.** The different experimental conditions for preparation of the various catalysts are reported in Tables 1 and 2. All polymer-based catalysts were prepared by a common procedure comprising stirring of the polymer powder in a solution of the platinum compound: (a) aqueous or alcoholic solutions of $H_2PtCl_6$; (b) aqueous solutions of $K_2PtCl_6$; (c) aqueous solutions of $K_2PtCl_4$. The products obtained were thoroughly washed with the solvent and air dried in an oven at reduced pressure. Notable exception was polyacrylamide due to its solubility in aqueous $H_2PtCl_6$: in this case catalysts were prepared by precipitation from the reaction solution with methanol.

Ion-exchange resins (cationic) and molecular sieves were exchanged with aqueous solutions of $(NH_3)_4PtCl_2$; ion-exchange resins (anionic) were exchanged with aqueous solutions of $H_2PtCl_6$. The catalysts were repeatedly washed with the solvent used in the preparation and then

TABLE 1
PREPARATION PROCEDURE OF POLYAMIDE-BASED CATALYSTS

| Catalyst | Preparation | Pt concn in preparative soln. (g/100 ml) | Carriers in the soln. (g/100 ml) | Pt content (wt %) |
|---|---|---|---|---|
| 0.4 Pt–Ny-6 (a) | Nylon-6 powder treated with aqueous $K_2PtCl_6$ at 60°C for 3 hr | 0.20 | 2.5 | 0.40 |
| 3.7 Pt–Ny-6 | Nylon-6 powder treated with aqueous $K_2PtCl_4$ at 20°C for 3 hr | 0.24 | 2.5 | 3.70 |
| 4.5 Pt–Ny-6 | Nylon-6 powder treated with $H_2PtCl_6$ in isoamyl alcohol at 20°C for 6 hr | 0.19 | 3.0 | 4.55 |
| 0.4 Pt–Ny-6 (b) | Nylon-6 powder treated with aqueous $H_2PtCl_6$ at 20°C for 32 hr | 0.19 | 3.0 | 0.39 |
| 3.8 Pt–Ny-6 | Nylon-6 powder treated with $H_2PtCl_6$ in ethanol at 20°C for 32 hr | 0.19 | 3.0 | 3.84 |
| 0.6 Pt–Ny-6 | Nylon-6 powder treated with aqueous $H_2PtCl_6$ at 100°C for 0.5 hr | 0.15 | 3.8 | 0.61 |
| Pt–Ny-3 | Nylon-3 powder treated with $H_2PtCl_6$ in isoamyl alcohol at 20°C for 2 hr | 0.19 | 1.5 | 0.29 |
| Pt–PAA | Polyacrylamide powder dissolved in aqueous $H_2PtCl_6$ at 80°C. After 4 hr the catalyst was precipitated with methanol | 0.12 | 3.3 | 3.61 |
| Pt–PFT | Poly-*p*-phenyleneterephthalamide powder treated with aqueous $H_2PtCl_6$ at 20°C for 24 hr | 0.05 | 7.5 | 0.62 |
| $L_2PtCl_2$–Ny-6 | Nylon-6 powder impregnated with a solution of $(C_6H_{11}NO)_2PtCl_2$ in ethanol | — | — | 0.5 |

TABLE 2
PREPARATION PROCEDURE OF OTHER PLATINUM CATALYSTS

| Catalyst | Preparation | Pt concn in preparative soln. (g/100 ml) | Treated carriers (g/100 ml) | Pt content (wt %) |
|---|---|---|---|---|
| Pt–PAAO | Polyacrylamideoxime powder treated with aqueous $H_2PtCl_6$ at 100°C for 2 hr | 0.37 | 5.0 | 2.8 |
| Pt–PAN | Polyacrylonitrile powder treated with aqueous $H_2PtCl_6$ at 100°C for 20 min | 0.42 | 4.3 | 0.6 |
| Pt–pyro PAN | Pyrolyzed polyacrylonitrile powder treated with aqueous $H_2PtCl_6$ at 60°C for 2 hr | 0.12 | 2.4 | 1.0 |
| Pt–Amb. IR | Amberlite IR-120 resin exchanged with aqueous $(NH_3)_4PtCl_2$ at 20°C for 3 hr | 0.92 | 16.6 | 6.6 |
| Pt–Dowex | Dowex 50 W resin exchanged with aqueous $(NH_3)_4PtCl_2$ at 20°C for 3 hr | 0.92 | 16.6 | 9.5 |
| Pt–Amb. CG | Amberlite CG 400 resin exchanged with aqueous $H_2PtCl_6$ at 20°C for 8 hr | 0.62 | 16.6 | 4.5 |
| Pt–NaY | NaY molecular sieve exchanged with aqueous $(NH_3)_4PtCl_2$ at 20°C for 2 hr | 1.0 | 22.5 | 0.05 |
| Pt–$Al_2O_3$ | $\gamma$-Alumina impregnated with aqueous $H_2PtCl_6$ | 0.19 | 37.5 | 0.05 |
| $L_2PtCl_2$–PAN | Polyacrylonitrile powder impregnated with a solution of $(C_6H_{11}NO)_2PtCl_2$ in ethanol | — | — | 0.5 |

dried at 60°C under reduced pressure. $Pt/Al_2O_3$ catalyst was prepared by impregnation of the support with aqueous $H_2PtCl_6$ and dried at 60°C under reduced pressure. The Pt content of the catalysts was determined by an atomic absorption spectrophotometer (Perkin-Elmer 303). The Cl content of the catalysts was determined by argentometry or colorimetry after mineralization of the samples in an oxygen atmosphere, according to Schöniger (*5*).

**Physico-chemical characterization.** The surface area of nylon-6 powder was determined by a flow method using $N_2$ as the adsorbate. Hydrogen chemisorption experiments have been carried out following the experimental procedure and the apparatus described in Ref. (*6*). The sequence of steps during each chemisorption experiment was as follows: first the catalyst sample was reduced *in situ* at some selected value of $T$ ($T_R$) in the range between 100 and 160°C, and then was eluted for several hours with purified nitrogen at $T = T_E =$ 25, 80, 160°C. After cooling to some predetermined value of $T_C$ (temperature of chemisorption) between 25 and 160°C, slugs of hydrogen were injected and the amount of hydrogen chemisorbed was recorded from the chromatograms. X-ray diffraction patterns were obtained by the use of a Philips PW 1050/1051/4082 x-ray diffractometer.

### *Experimental Procedure*

The hydrogenation reaction was carried out in the apparatus shown in Fig. 1. Benzene was fed by a micropump and mixed with hydrogen in an evaporator; the catalyst (14–18 mesh), held in a Pyrex tubular reactor (ca. 10 ml), was heated by a cylindrical oven. Before the use, the catalyst was activated *in situ* for 7 hr in a hydrogen flow (4 liters/hr) at 160°C. The catalytic hydrogenation of benzene was investigated in the range from 140 to 190°C by a stepwise procedure as follows: at the end of the activating period, the temperature was stabilized in hydrogen flow at some prefixed value. Thereafter the benzene feed was switched to the reactor and the gaseous mixture ($H_2:C_6H_6 = 3:1$) allowed to flow through the catalyst for a period of 0.5 hr, at which time a sample of the products was taken for chromatographic analysis. Afterwards the benzene feed was discontinued while maintaining the hydrogen flow until the temperature was stabilized at some new level; benzene was thereafter adjusted again to the prefixed value. Contact time, calculated on the basis of the volume of the catalyst, was made to vary from 0.2 to 22 sec. by adjusting either the total flow rate or the volume of the catalyst. No temperature gradient was observed in the catalyst mass during the hydrogenation experiments. Product analysis was carried out by gas chromatography (F & M 500; a column of polyethylene glycol on Carbowax 1500 was used at 120°C; $H_2$ was the carrier gas).

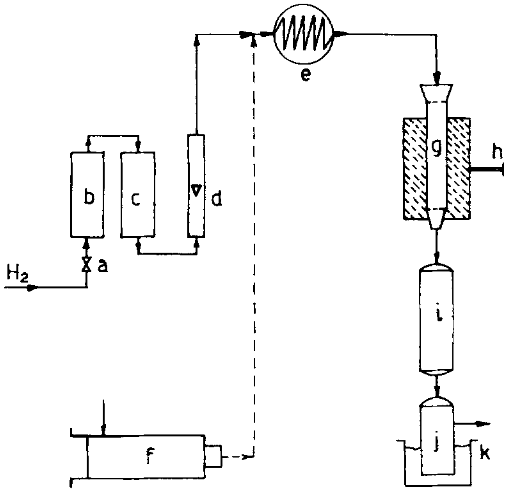


FIG. 1. Hydrogenation apparatus: (a) hydrogen flow control, (b) deoxo unit, (c) silica-gel drier, (d) hydrogen flow meter, (e) evaporator, (f) benzene injector, (g) microreactor, (h) electric heater, (i) refrigerator, (j) reaction products collector, (k) cooling bath.

## RESULTS

### *Pt–Nylon-6 Catalysts*

**Preparation.** Experimental details on the preparation of nylon-6 based catalysts are reported in Table 1; changes in the nature of the solvent resulted in different platinum contents of the final catalysts. Thus, with $H_2PtCl_6$, platinum contents of 0.4, 3.8, and 4.5% were found, respectively, when water, ethanol or isoamyl alcohol were used as solvents. Understandingly this variability can be attributed to differences in the swelling of the polymer powders depending on the solvents used in the preparative step. Platinum contents of 0.4 and 3.7% were obtained when the starting metal compounds were respectively aqueous solutions of $K_2PtCl_6$ and $K_2PtCl_4$; in this case the difference can be interpreted in terms of a higher reactivity of the planar $PtCl_4^{2-}$ anion toward the amide groups of the nylon chain.

**Physicochemical characterization.** Various techniques were used in an attempt to clarify the nature of active compounds present in the catalyst and the degree of dispersion of platinum. The results of hydrogen chemisorption measurements are reported in Table 3. Various catalyst samples, having different platinum contents, were investigated. In all cases the H:Pt atomic ratio was found to be surprisingly low, which implies that only a small fraction of platinum atoms do chemisorb hydrogen. This result was found to be uninfluenced by the temperature of reduction and chemisorption and by the platinum content of the catalyst. By comparison, chemisorption measurements carried out at 160°C, using a Pt–$\gamma$-$Al_2O_3$ catalyst reduced at 160°C, gave a H:Pt atomic ratio more than ten times higher.

TABLE 3

HYDROGEN CHEMISORPTION[a]

| Catalyst | Pt % | $T_R$ °C | $T_E$ °C | $T_C$ °C | H:Pt |
|---|---|---|---|---|---|
| 0.6 Pt–Ny-6 | 0.61 | 100 | 25 | 25 | 0.08 |
| 0.6 Pt–Ny-6 | 0.61 | 100 | 80 | 80 | 0.08 |
| 3.8 Pt–Ny-6 | 3.80 | 110 | 25 | 25 | 0.11 |
| 3.8 Pt–Ny-6 | 3.80 | 110 | 80 | 80 | 0.11 |
| 0.4 Pt–Ny-6 (b) | 0.39 | 140 | 80 | 80 | 0.11 |
| 0.6 Pt–Ny-6 | 0.61 | 140 | 80 | 80 | 0.11 |
| Pt-PFT | 0.62 | 160 | 160 | 25 | 0.15 |
| 0.4 Pt–Ny-6 (b) | 0.39 | 160 | 160 | 160 | 0.15 |
| Pt–$Al_2O_3$ | 0.05 | 160 | 160 | 25 | 1.34 |

[a] Reduction *in situ* at $T_R$; elution with purified $N_2$ at $T_E$; chemisorption with purified $H_2$ at $T_C$.

The possibility that the low chemisorption capacity could be due to a low degree of dispersion, i.e., formation of clusters of platinum atoms, had to be ruled out on the grounds of the results of x-ray measurements which failed to show any characteristic platinum diffraction patterns on all the samples investigated. The question then arises as to what the state of platinum is. In this sense it is interesting to consider the analysis results of chlorine content of the catalysts, before and after the activation step (Table 4): the value of the Cl:Pt atomic ratio is about 6 before activation, and becomes 2 after reduction in $H_2$ at 160°C. Moreover this residual chlorine content was found to be unaffected by further heating in hydrogen or nitrogen: even a 7-hr run of benzene hydrogenation did not cause the Cl:Pt ratio to vary, while both activity and selectivity remained constant.

**Benzene hydrogenation. Reaction temperature and contact time.** Platinum–nylon-6 catalysts have been studied under various conditions in the benzene hydrogenation reaction: results reported in Tables 5 and 6 show the influence of reaction temperature and contact time on the catalysts behaviour. Benzene conversion generally decreases by increasing the temperature from 140 to 190°C and by decreasing the contact time; selectivities to cyclohexene are higher at lower conversions and increase by increasing the temperature. This behaviour is exemplified in Fig. 2 where cyclohexene selectivities are shown as a function of benzene conversion for runs at 160°C: shapes of the curves for various catalysts are similar, with experimental values lying within a narrow band along a hyperbola. Inside this band a series of parallel curves can be distinguished: the lowest one relates to the catalyst with the highest platinum content, and the uppermost one to that with the lowest platinum content.

**Reaction mechanism.** The product distribution of the effluent reaction mixture is shown in Fig. 3 as a function of the contact time for the 0.4 Pt–Ny-6 (a) catalyst, run at 160°C and with a molar ratio

TABLE 4

CHLORINE CONTENT OF PLATINUM–NYLON-6 CATALYSTS

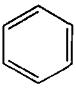
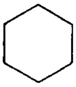
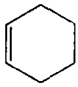
| Catalyst | Activation and reaction conditions | Non-activated catalyst |  |  | Activated catalyst |  |  |
|---|---|---|---|---|---|---|---|
|  |  | Pt wt % | Cl wt % | Cl:Pt | Pt wt % | Cl wt % | Cl:Pt |
| 0.6 Pt–Ny-6 | Activated at 160°C for 7 hr in $H_2$ atm | 0.61 | 0.61 | 5.5 | 0.61 | 0.22 | 2.0 |
| 0.6 Pt–Ny-6 | Further treated at 160°C for 7 hr in $H_2$ atm | 0.61 | 0.61 | 5.5 | 0.61 | 0.25 | 2.3 |
| 0.6 Pt–Ny-6 | Activated at 160°C for 7 hr in $N_2$ atm | 0.61 | 0.61 | 5.5 | 0.61 | 0.24 | 2.2 |
| 0.6 Pt–Ny-6 | Activated at 160°C for 7 hr in $H_2$ atm and used in a 7 hr reaction at 160°C with a contact time of 2 sec[a] | 0.61 | 0.61 | 5.5 | 0.61 | 0.22 | 2.0 |
| 0.4 Pt–Ny-6 (b) | Activated at 160°C for 7 hr in $H_2$ atm | 0.39 | 0.40 | 5.6 | 0.39 | 0.17 | 2.4 |

[a] Conversion and selectivity to cyclohexene after 2, 5, and 7 hr reaction were, respectively: 2.3, 12%; 2.05, 11.5%; 2.13, 11.0%.

$H_2$:$C_6H_6$ of 3:1. Increasing the contact time causes the cyclohexene yield to rise sharply reaching a maximum at about 2.5 sec; afterwards a continuous decrease is observed. Cyclohexane yield shows a continuous and fast rise during the first 15 sec, thereafter it levels off. This behaviour is consistent with a reaction mechanism going along a consecutive pathway, cyclohexene being the intermediate which reacts

TABLE 5

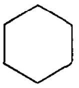
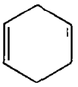
PLATINUM–NYLON-6 CATALYSTS, INFLUENCE OF REACTION TEMPERATURE[a]

| Catalyst | Reaction temperature °C | Conversion  wt % | Selectivity  % | Selectivity  % |
|---|---|---|---|---|
| 0.6 Pt–Ny-6 | 140 | 5.2 | 92.7 | 7.3 |
| 0.6 Pt–Ny-6 | 160 | 6.0 | 91.2 | 8.8 |
| 0.6 Pt–Ny-6 | 190 | 2.0 | 90.3 | 9.7 |
| 0.4 Pt–Ny-6 (a) | 140 | 0.7 | 71.2 | 28.8 |
| 0.4 Pt–Ny-6 (a) | 160 | 0.6 | 71.7 | 28.3 |
| 0.4 Pt–Ny-6 (a) | 190 | 0.8 | 72.1 | 27.9 |
| 0.4 Pt–Ny-6 (b) | 140 | 3.5 | 84.4 | 15.6 |
| 0.4 Pt–Ny-6 (b) | 160 | 2.2 | 78.5 | 21.5 |
| 0.4 Pt–Ny-6 (b) | 190 | 0.4 | 52.0 | 48.0 |
| 3.7 Pt–Ny-6 | 140 | 3.0 | 98.3 | 1.7 |
| 3.7 Pt–Ny-6 | 160 | 3.0 | 95.6 | 4.4 |
| 3.7 Pt–Ny-6 | 190 | 1.3 | 87.3 | 12.7 |
| 4.5 Pt–Ny-6 | 140 | 23.4 | 98.2 | 1.8 |
| 4.5 Pt–Ny-6 | 160 | 14.5 | 95.8 | 4.2 |
| 4.5 Pt–Ny-6 | 190 | 2.2 | 89.3 | 10.7 |

[a] $H_2$:Benzene ratio 3:1; contact time 1 sec.

TABLE 6

PLATINUM–NYLON-6 CATALYSTS, INFLUENCE OF CONTACT TIME[a]

| Catalyst | Contact time (sec) | Catalyst (g) | Conversion  % | Selectivity  % | Selectivity  % |
|---|---|---|---|---|---|
| 0.4 Pt-Ny-6 (a) | 22.5 | 0.4 | 4.1 | 98.5 | 1.5 |
| 0.4 Pt-Ny-6 (a) | 9.0 | 0.4 | 3.2 | 94.7 | 5.3 |
| 0.4 Pt-Ny-6 (a) | 4.5 | 0.4 | 1.6 | 86.3 | 13.7 |
| 0.4 Pt-Ny-6 (a) | 2.2 | 0.4 | 0.9 | 70.2 | 29.8 |
| 0.4 Pt-Ny-6 (a) | 0.9 | 0.4 | 0.4 | 55.8 | 44.2 |
| 0.4 Pt-Ny-6 (b) | 5.0 | 1.6 | 6.7 | 96.8 | 3.2 |
| 0.4 Pt-Ny-6 (b) | 2.0 | 1.6 | 2.9 | 92.0 | 8.0 |
| 0.4 Pt-Ny-6 (b) | 1.0 | 1.6 | 1.9 | 84.3 | 15.7 |
| 0.4 Pt-Ny-6 (b) | 0.5 | 1.6 | 1.0 | 71.5 | 28.5 |
| 0.4 Pt-Ny-6 (b) | 0.2 | 1.6 | 1.0 | 64.2 | 35.8 |
| 3.7 Pt-Ny-6 | 28.9 | 1.6 | 25.9 | 99.9 | 0.1 |
| 3.7 Pt-Ny-6 | 11.6 | 1.6 | 9.1 | 99.4 | 0.6 |
| 3.7 Pt-Ny-6 | 5.8 | 1.6 | 5.2 | 98.7 | 1.3 |
| 3.7 Pt-Ny-6 | 2.9 | 1.6 | 3.9 | 96.0 | 4.0 |
| 3.7 Pt-Ny-6 | 1.2 | 1.6 | 2.2 | 91.5 | 8.5 |
| 3.8 Pt-Ny-6 | 17.8 | 1.6 | 49.1 | 100.0 | 0 |
| 3.8 Pt-Ny-6 | 7.1 | 1.6 | 10.0 | 98.6 | 1.4 |
| 3.8 Pt-Ny-6 | 3.6 | 1.6 | 3.9 | 97.8 | 2.2 |
| 3.8 Pt-Ny-6 | 1.8 | 1.6 | 2.6 | 95.4 | 4.6 |
| 3.8 Pt-Ny-6 | 0.7 | 1.6 | 1.4 | 90.3 | 9.7 |
| 4.5 Pt-Ny-6 | 19.8 | 1.6 | 6.2 | 100.0 | 0 |
| 4.5 Pt-Ny-6 | 7.8 | 1.6 | 4.4 | 99.4 | 0.6 |
| 4.5 Pt-Ny-6 | 3.9 | 1.6 | 3.8 | 98.7 | 1.3 |
| 4.5 Pt-Ny-6 | 1.9 | 1.6 | 2.3 | 97.5 | 2.5 |
| 4.5 Pt-Ny-6 | 0.8 | 1.6 | 1.9 | 94.6 | 5.4 |

[a] $H_2$:Benzene ratio 3:1; reaction temperature 160°C.

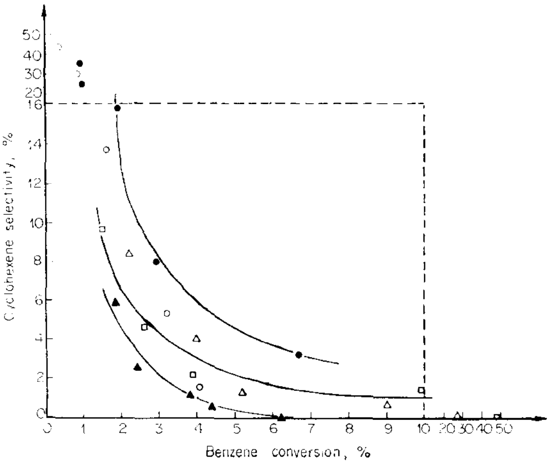


FIG. 2. Selectivity to cyclohexene vs benzene conversion. Reaction temperature 160°C; ratio $H_2$:$C_6H_6$ = 3:1; ○, cyclohexene selectivity on 0.4 Pt-Ny-6 (a); ●, cyclohexene selectivity on 0.4 Pt-Ny-6 (b); △, cyclohexene selectivity on 3.7 Pt-Ny-6; □, cyclohexene selectivity on 3.8 Pt-Ny-6; ▲, cyclohexene selectivity on 4.5 Pt-Ny-6.

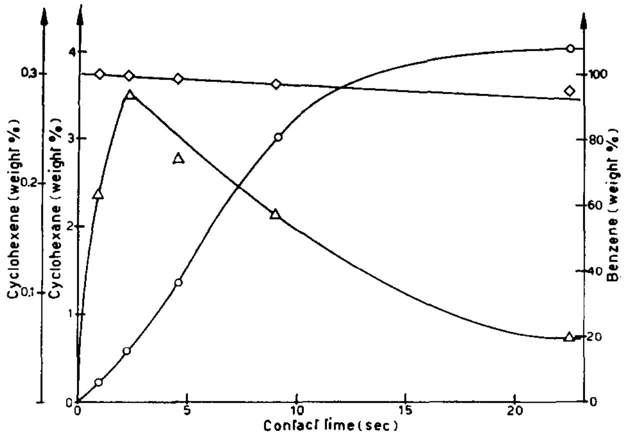
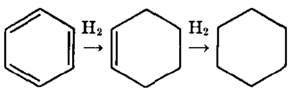


FIG. 3. Reaction mixture composition vs contact time. Reaction temperature 160°C; ratio $H_2$:$C_6H_6$ = 3:1; ◇, benzene; ○, cyclohexane; △, cyclohexene.

further giving the final product cyclohexane:



This is conclusively confirmed by the data shown in Fig. 4, where the cyclohexene and cyclohexane selectivities are plotted as a function of contact time for three different nylon-6 based platinum catalysts: 0.4 Pt-Ny-6 (a), 0.4 Pt-Ny-6 (b), and 3.8 Pt-Ny-6. Kinetic experiments, performed at 160°C over a 0.4 Pt-Ny-6 catalyst at varying $H_2$:$C_6H_6$ ratios, gave results well in agreement with previous findings (*1*): as in the case of the cited work, rate constants at various molar feed ratios of reactants were found to fit into a rate equation which was zero order with respect to hydrogen and first order with respect to benzene.

**Platinum catalysts supported on other polyamides.** Experimental conditions for the preparation of these catalysts are reported in Table 1.

Platinum catalysts based on nylon-3 and polyacrylamide were tested in order to evaluate the influence of smaller spacings between amide groups; the platinum-poly-

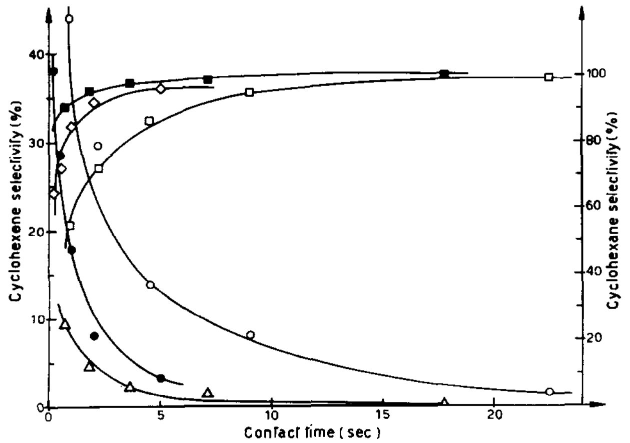
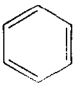
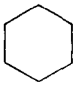
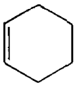


FIG. 4. Cyclohexane and cyclohexene selectivities vs contact time. Reaction temperature 160°C; ratio $H_2$:$C_6H_6$ = 3:1; □, cyclohexane selectivity on 0.4 Pt-Ny-6 (a); ○, cyclohexene selectivity on 0.4 Pt-Ny-6 (a); ◇, cyclohexane selectivity on 0.4 Pt-Ny-6 (b); ●, cyclohexene selectivity on 0.4 Pt-Ny-6 (b); ■, cyclohexane selectivity on 3.8 Pt-Ny-6; △, cyclohexene selectivity on 3.8 Pt-Ny-6.

TABLE 7
PLATINUM CATALYSTS BASED ON OTHER POLYAMIDES[a]

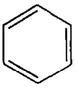
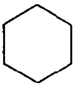
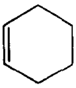
| Catalyst | Reaction temperature (°C) | Contact time (sec) | Conversion  % | Selectivity  % | Selectivity  % |
|---|---|---|---|---|---|
| Pt-Ny-3 | 160 | 1 | 0.05 | 60.0 | 40.0 |
| Pt-Ny-3 | 190 | 1 | 0.04 | 41.0 | 59.0 |
| Pt-Ny-3 | 210 | 1 | 0.02 | 33.0 | 67.0 |
| Pt-PAA | 160 | 4 | 0.60 | 90.0 | 10.0 |
| Pt-PAA | 190 | 4 | 0.20 | 84.5 | 15.5 |
| Pt-PAA | 220 | 4 | 0.10 | 33.5 | 66.5 |
| Pt-PFT | 140 | 1 | 0 | 0 | 0 |
| Pt-PFT | 160 | 1 | 0.10 | 82.0 | 18.0 |
| Pt-PFT | 190 | 1 | 0.08 | 62.5 | 37.0 |

[a] $H_2$:Benzene ratio 3:1.

*p*-phenyleneterephthalamide catalyst was designed to ascertain the effect of the aromatic nature of the polymer chain. The results of catalytic experiments, shown in Table 7, substantiate for these catalysts the general behaviour found over the platinum–nylon-6 catalysts since they, too, give cyclohexene as a reaction product. Benzene conversions are, however, considerably lower, but diminish with increasing reaction temperatures; correspondingly, selectivities to cyclohexene are remarkably high, but still in the range of those found over nylon-6 based catalysts.

**Other platinum catalysts.** Some polymers bearing complexing groups and ion exchange resins were also tested as platinum carriers in the hydrogenation of benzene:

TABLE 8
OTHER PLATINUM CATALYSTS[a]

| Catalyst | Reaction temperature (°C) | Contact time (sec) | Conversion  % | Selectivity  % | Selectivity  % |
|---|---|---|---|---|---|
| Pt-PAN | 140–190 | 2 | 0 | — | — |
| Pt-pyro-PAN | 150–250 | 2 | 0 | — | — |
| Pt-PAAO | 140 | 0.5 | 0 | — | — |
| Pt-PAAO | 160 | 0.5 | 0.1 | 100 | 0 |
| Pt-PAAO | 190 | 0.5 | 0.1 | 100 | 0 |
| Pt-Amb. IR | 140–190 | 0.4 | 0 | — | — |
| Pt-Dowex | 140–190 | 0.4 | 0 | — | — |
| Pt-Amb. CG | 140 | 0.4 | 0.1 | 100 | 0 |
| Pt-Amb. CG | 160 | 0.4 | 0.25 | 100 | 0 |
| Pt-Amb. CG | 190 | 0.4 | 0.30 | 100 | 0 |
| Pt-NaY | 160 | 0.15 | 1.20 | 100 | 0 |
| Pt-NaY | 190 | 0.15 | 1.30 | 100 | 0 |
| Pt-$Al_2O_3$[b] | 160 | 0.07 | 1.60 | 100 | 0 |
| Pt-$Al_2O_3$[b] | 190 | 0.07 | 3.30 | 100 | 0 |
| Pt-$Al_2O_3$[c] | 160 | 0.07 | 1.00 | 100 | 0 |
| Pt-$Al_2O_3$[c] | 190 | 0.07 | 3.60 | 100 | 0 |

[a] $H_2$:Benzene ratio 3:1.
[b] Activated at 400°C in $H_2$.
[c] Activated at 160°C in $H_2$.

the nature of these materials and the catalysts preparation techniques (see Experimental Section) were aimed at obtaining an ordered distribution of the platinum on the surface of the support. The results of catalytic experiments (Table 8) showed, among the studied catalysts, that only those supported on polyacrylamideoxime and Amberlite CG exhibited some hydrogenation activity, but the only reaction product was cyclohexane. A similar behaviour was also evidenced in two platinum catalysts based respectively on γ-$Al_2O_3$ and on NaY molecular sieve: choice of a very low platinum content (0.05%), and a very short contact time (0.07 sec), made it possible to obtain conversion levels comparable to that of platinum–nylon-6 catalysts, but, again, cyclohexene was absent, the only reaction product being cyclohexane.

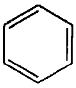
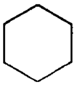
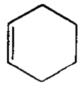
**(ε-Caprolactam)$_2$PtCl$_2$ complex as hydrogenation catalyst.** To clear up the influence, if any, of amide groups on the activity and selectivity of platinum–polyamide catalysts in the hydrogenation of benzene, a novel class of catalysts has been prepared by impregnation of nylon-6 and polyacrylonitrile polymers with solutions of $L_2PtCl_2$ (L = ε-caprolactam) in acetone (Table 9). The results, obtained over $L_2PtCl_2$–Ny-6 and $L_2PtCl_2$–PAN, were found to agree quite well with the characteristics of platinum–nylon-6 catalysts. Chlorine analysis in the effluent stream as well as on the solids, showed that the original Cl:Pt ratio in the catalyst remained unchanged after the reaction had taken place. Catalytic experiments were also performed on a catalyst based on the $L_2PtCl_2$ complex supported on γ-$Al_2O_3$, which had been previously calcined at 1100°C for 8 hr. With this catalyst (0.05 Pt), a chlorine loss was noticed during the benzene hydrogenation reaction (τ = 160°C; $H_2$:$C_6H_6$ = 3:1; contact time = 0.07 sec). The decomposition of the complex was attributed to the hydrolytic action of residual —OH groups on the alumina surface; in fact the complex $L_2PtCl_2$ was found to be very sensitive to water. Results of catalytic activity showed, in addition to cyclohexane (ca. 1% conv.), only feeble traces of cyclohexene.

## DISCUSSION

The results reported in the text make it evident that all the catalysts investigated can be divided, according to the formation of cyclohexene, into two classes: the first one includes all the catalysts based on polyamides, sharing unique selectivity characteristics independently of the type of their polymeric chain. Within this class, selectivities to cyclohexene span over a broad range, depending upon experimental conditions. Inspection of the results (Figs. 3 and 4) provides strong evidence in favour of a consecutive mechanism, in a more evident manner than ever indicated hitherto. The catalysts other than platinum–polyamides constitute the second class: herein the lack of selectivity to cyclohexene agrees with all previously published information for platinum on supports. It is noteworthy that, in our experiments, the presence of cyclohexene has been purposedly sought at conversion levels as low as those of polyamide based catalysts: failure to detect any cyclohexene

TABLE 9

$L_2PtCl_2$ SUPPORTED ON NYLON-6 AND POLYACRYLONITRILE AS CATALYSTS[a]

| Catalyst | Pt content (g %) | Reaction temperature (°C) | Contact time (sec) | Conversion  % | Selectivity  % | Selectivity  % |
|---|---|---|---|---|---|---|
| $L_2PtCl_2$–Ny-6 | 0.5 | 160 | 1 | 5.6 | 96.3 | 3.7 |
| $L_2PtCl_2$–PAN | 0.5 | 160 | 1 | 0.3 | 21.4 | 78.6 |
| $L_2PtCl_2$–$Al_2O_3$ | 0.05 | 160 | 0.07 | 1 | ~100 | ~0 |

[a] $H_2$:Benzene ratio 3:1.

should therefore remove any doubt of the existence of a true and significative difference between the two classes.

In principle there is the possibility that the different selectivity characteristics of the two classes could be simply due to differences in the pore size and pore size distribution, in case the hydrogenation reaction was diffusion controlled. The problem has already been dealt with by Harrison and Rase (*1*); moreover, a mathematical treatment applied by us to the Pt–$Al_2O_3$ and Pt–nylon-6 catalysts enabled the presence of diffusion controlling factors to be definitely ruled out. On the other hand, the explanation given by Harrison and Rase for the selectivity characteristics of Pt–nylon catalysts, which, according to their opinion are linked with a high and ordered dispersion (geometric factor) of platinum metal atoms on the surface of some polyamides having appropriate amide group spacing, does not seem consistent with our findings: the collection of results presented here in fact clearly indicates that no influence can be ascribed to the amide group distance in the polymer chain or to the aliphatic or aromatic nature of the support. Thus platinum catalyst based on polyacrylamide, having pendant carboxamide groups at a very short distance from one another, possesses selectivity properties to cyclohexene. In our experiments, also nylon-3 based catalyst is selective (Table 7), a result which contradicts previous observations (*1*); actually, since the polymeric support used in the cited work was a copolymer of 4-methyl-$\beta$-lactam and 4,4-dimethyl-$\beta$-lactam, the lack of selectivity could have been caused by steric factors (pendant methyl groups) and not by the small distance separating the amide groups. In fact, with the aim to verify the existence of such an influence, we prepared an unsubstituted nylon-3 starting from acrylamide; even in this case, the catalyst obtained by supporting platinum on nylon-3 proved to be as active and selective as Pt–nylon-6 catalysts, and no influence of the amide group spacing was noticed. A high degree of dispersion of platinum atoms, such as could be expected on Pt–NaY and Pt–$Al_2O_3$ having very low platinum content, helped to conclude that dispersion itself is not a controlling factor: in fact the catalysts were found to be not selective at all.

Summing up all the experimental results already reported, it seems that the unique properties of the Pt–polyamides catalysts can be more properly described by the postulate of a true chemical influence of the polymeric support upon the catalytic activity of platinum. During the catalyst preparation, the treatment of the polyamide powder with the solution of the platinum compound results in a reaction between the superficial amide groups and the metal compound: this seems sufficiently proved. Hydrogen chemisorption measurements on activated catalysts (Table 3) have evidenced a sharp difference between Pt–$Al_2O_3$ and Pt–polyamide systems. Compared with Pt–$Al_2O_3$ catalyst, a very low H:Pt atomic ratio is in fact observed on Pt–polyamide catalysts and a possible explanation of this unexpected result could be the existence of platinum in a valence state different from zero. Moreover, chemical analysis of activated Pt–polyamide catalysts revealed the presence of two chlorine atoms for each platinum atom. This residual chlorine content could not be removed even after a prolonged period of activation and it was found unchanged even after the hydrogenation reaction runs. We have deduced from this that the chemical bond established between the metal compound and the amide groups of the support lead, during the activation step, to the formation of a stable polyamide–platinum–chlorine compound. A decisive proof in favour of this interpretation can be found in the results obtained over nylon-6 and polyacrylonitrile impregnated with the complex ($\epsilon$-caprolactam)$_2$$PtCl_2$: both these catalysts proved to be active in the hydrogenation reaction of benzene and selective for the formation of cyclohexene. It is remarkable that the polyacrylonitrile based catalyst, prepared from hexachloroplatinic acid, was, on the contrary, completely inactive under the same experimental conditions.

Assuming the presence on the nylon surface of a bivalent platinum complex containing two chlorine atoms and two amide groups as ligands, the maximum allowable platinum content in the Pt–nylon-6 catalysts was calculated. Using the idealized two-dimensional diagram of the nylon-6 surface and the crystal parameters determined by Holmes, Bunn and Smith (7), a value of about 1% was found, which is in a sufficient agreement with the experimental findings as far as catalysts prepared with aqueous solutions of $H_2PtCl_6$ are concerned. For the catalysts prepared from alcoholic solutions of $H_2PtCl_6$ or aqueous $K_2PtCl_4$ the agreement is not so good, but in this case, as shown before, it is possible that also the amide groups beneath the polymer surface can react with the platinum compound.

We can therefore conclude that both catalytic hydrogenation activity and selectivity properties of platinum–polyamide catalysts can be reasonably attributed to the presence on the catalyst surface of a chlorine-containing platinum complex, where the metal atom is coordinatively bound to two amide groups of the polymeric chain.

## ACKNOWLEDGMENTS

The authors are grateful to Prof. I. Pasquon and Prof. R. Ugo for their helpful discussions.

## REFERENCES

1. HARRISON, D. P., AND RASE, H. F., *Ind. Eng. Chem. Fund.* **6**(2), 161 (1967).
2. SORENSON, W. R., AND CAMPBELL, T. W., "Preparative Methods of Polymer Chemistry." Interscience Inc., New York, 1961.
3. MORGAN, P. W., "Condensation Polymers." Interscience Inc., New York, 1965.
4. (a) FERNELIUS, W. C., "Inorganic Syntheses," Vol. II, pp. 247–253. McGraw-Hill, New York, 1946. (b) MOELLER, T., "Inorganic Syntheses," Vol. V, pp. 208–210. McGraw-Hill, New York, 1957.
5. SCHÖNIGER, W., *Mikrochim. Acta,* 869 (1956).
6. GIORDANO, N., AND MORETTI, E., *J. Catal.* **18**, 228 (1970).
7. HOLMES, D. R., BUNN, C. W., AND SMITH, D. J., *J. Polymer Sci.* **17**, 159 (1955).