Properties of Polyamide-based Catalysts. Part I. Hydrodehalogenation of Chlorobenzene

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The activities and selectivities of platinum–, rhodium–, and palladium–poly-*p*-phenyleneterephthalamide catalysts were compared for the hydrodehalogenation of chlorobenzene, and differences in reactivity with respect to conventional Al_2O_3-based catalysts were disclosed. Conversions of PhCl decrease in the order Pd > Rh > Pt. A reaction mechanism is proposed to interpret the results.

ORGANIC polymers have recently found increasing application as supports in heterogeneous catalysis.[1,2] Catalysts based on Pt-polyamides appear particularly interesting, following observations of Harrison,[3] Dini,[4] and Rasadkina *et al.*[5] on the hydrogenation of benzene. The unique characteristic of this class of catalysts is the high selectivity, *e.g.* to cyclohexene, in contrast with conventional platinum catalysts which lead to cyclohexane.[3,4] Similar results have been obtained by Bernard [6] on the hydrogenation of styrene and cyclopentadiene, leading with high selectivity to ethylbenzene and cyclopentene, as opposed to the small amounts of ethylcyclohexane and cyclopentane over conventional platinum catalysts. The unusual selectivities of polyamide-based catalysts have been attributed to the occurrence of a particular geometrical arrangement of platinum atoms on the surface of the support [3] or to formation of a bivalent platinum complex with the central atom being co-ordinated to two chlorine atoms and two amide groups of the polymeric chain.[4]

To gain further insight into the unusual properties of these catalysts, we have now undertaken exploratory studies on their activity and selectivity in a variety of reactions which allow alternative pathways: the present paper reports on the results of the hydrogenation–hydrogenolysis of chlorobenzene. A comparative study on hydrodealkylation of toluene will be discussed in a forthcoming paper.[7]

To overcome the low thermal stability of aliphatic polyamides (nylons) used previously,[4] we have turned to aromatic polyamides, known to retain useful properties even at 300—400°. To our knowledge, such materials have not yet been explored for catalytic studies. A poly-*p*-phenyleneterephthalamide (PFT) support was chosen amongst others due to its greater thermal stability. Catalysts investigated contained Pt, Pd, and Rh at different metal percentages; Pt–Al_2O_3 was used as reference.

This work is limited to the results of catalytic activity together with some considerations on the reaction mechanism. As comprehensive evaluation strongly depends on the nature of the metal complexes present on the catalysts, a full discussion of the reaction mechanism will be postponed to a forthcoming paper.[7]

EXPERIMENTAL

Reagents.—*p*-Phenylenediamine (B.D.H.) was redistilled under nitrogen. Terephthaloyl chloride was prepared from terephthalic acid by reaction with thionyl chloride and recrystallized from n-hexane, m.p. 78°. Chlorobenzene

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[5] E. N. Rasadkina, A. T. Teleshev, I. D. Rozhdestvenskaya, and I. V. Kalechits, *Kinetika i Kataliz*, 1973, **14**, 1214.

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(C. Erba) was dried over $CaCl_2$ and redistilled. $H_2PtCl_6,6H_2O$ (C. Erba) and $PdCl_2,2H_2O$ and $RhCl_3,3H_2O$ (Schuchardt) were commercial samples. Hydrogen (Sapio) was purified by passing through a Deoxo unit and a silica gel dryer.

Carriers.—Poly-*p*-phenyleneterephthalamide was obtained by interfacial polycondensation at 5—10° of *p*-phenylenediamine and terephthaloyl chloride in NaOH–water–cyclohexanone, following the method described by Mark *et al.*[8] The product was then extracted with acetone for 32 h, and dried at 80° under reduced pressure. Thermogravimetric analysis, performed on a Du Pont 950 thermobalance under nitrogen, shows appreciable degradation above *ca.* 400°. The i.r. spectrum (KBr) obtained on a Beckman DK-2 spectrometer was consistent with that in the literature.[8] The surface area, determined by the flow method using nitrogen as the adsorbate, was 116 $m^2 g^{-1}$. γ-Alumina (Alcoa F110) had surface area 195 $m^2 g^{-1}$.

TABLE 1

Preparation of catalysts

Catalyst	Preparation	Metal content (wt %)	Surface area ($m^2 g^{-1}$)
0.6 wt % Pt–PFT	PFT powder (15 g) treated with $H_2PtCl_6,6H_2O$ (0.2 g) in water (200 ml) at r.t. for 4 h	0.6	95
4.6 wt % Pt–PFT	PFT powder (15 g) treated with $H_2PtCl_6,6H_2O$ (2.0 g) in EtOH (200 ml) at r.t. for 4 h	4.6	92
Pd–PFT	PFT powder (15 g) treated with $PdCl_2,2H_2O$ (0.13 g) in water (200 ml) at r.t. for 4 h	0.4	93
Rh–PFT	PFT powder (7 g) treated with $RhCl_3,3H_2O$ (1.0 g) in water (200 ml) at r.t. for 18 h	1.1	
$Pt–Al_2O_3$	γ-Alumina impregnated with aqueous H_2PtCl_6	0.5	
$Pd–Al_2O_3$	γ-Alumina impregnated with aqueous $PdCl_2,2H_2O$	0.2	

r.t. = Room temperature.

Catalysts.—*Preparation and analysis.* The experimental conditions for preparation of the catalysts are reported in Table 1. All polymer-based catalysts were prepared by a common procedure, comprising (a) stirring the polymer powder in an aqueous solution of the metal compound, (b) washing with water until disappearance of the metallic cation and (c) drying in an oven at 110° under reduced pressure. $Pt-Al_2O_3$ catalysts were prepared by impregnation of the support with an aqueous solution of H_2PtCl_6 and drying at 110° under reduced pressure. The metal content of the catalysts was determined by atomic absorption (Perkin-Elmer 303 spectrophotometer). The chlorine content was determined by argentometry or colorimetry after combustion of the samples in oxygen.

Experimental Procedure.—The hydrodechlorination reaction was carried out in an apparatus similar to that described in ref. 4. The catalyst (14—18 mesh; 3 ml), held in a Pyrex tubular reactor, was activated ***in situ*** for 2 h in hydrogen (4 l h^{-1}) at 140°; chlorobenzene was fed by a micropump (6 ml h^{-1}) and mixed with hydrogen in an evaporator (H_2 : PhCl 4 : 1). The catalytic activity was investigated from 140 to 250°. Each run lasted 30 min. Contact time, calculated on the basis of the volume of the catalyst, was *ca.* 1 s. No temperature gradient was observed on the catalyst mass during the experiments. Product analysis was carried out by g.l.c. (F and M 500; 2 m Carbowax 1500; 80°; H_2 carrier gas).

RESULTS

The results of the catalytic activity of various polyamide-based catalysts are given in Table 2 in terms of end-point conversions and selectivities, following a 30 min run, at each temperature level and under our experimental conditions. Results obtained on some Al_2O_3-based catalysts are also given. The comparison clearly shows the outstanding characteristics of the polyamide-based catalysts since benzene is the only product formed over the whole temperature range. On the other hand, Al_2O_3-based catalysts display lower selectivities to benzene, the difference being accounted for by the presence of cyclohexane. This also holds for the vapour-phase hydrogenation of chlorobenzene on 0.5 wt % $Rh-Al_2O_3$ catalyst,[9] where C_6H_6 selectivity never reaches 100%, not even at the highest experimental temperatures (150°). A comparison between 0.6 wt % Pt-PFT and 0.5 wt % $Pt-Al_2O_3$ selectivities to benzene at different temperatures, is reported in Figure 1. The total absence of chlorocyclohexane among the products clearly indicates that cyclohexane, whenever it occurs, is a product of benzene hydrogenation rather than a product of dehalogenation of chlorocyclohexane (Scheme 1).

TABLE 2

Hydrodechlorination of chlorobenzene [a]

Catalyst	Reaction temperature (°C)	Conversion PhCl (%)	Selectivity C_6H_{12} (%)	Selectivity C_6H_6 (%)
Pd–PFT	140	99.2	0.1	99.7
Pd–PFT	190	99.9	0.1	99.8
Pd–PFT	230	99.5	0.05	99.9
Pd–PFT	250	99.8	0.05	99.9
4.6 wt % Pt–PFT	140	0	0	0
4.6 wt % Pt–PFT	190	97.1	0.9	99.1
4.6 wt % Pt–PFT	230	99.5	0.6	99.4
4.6 wt % Pt–PFT	250	99.9	0.3	99.9
0.6 wt % Pt–PFT	140	0.2	0.0	100.0
0.6 wt % Pt–PFT	190	0.4	0.0	100.0
0.6 wt % Pt–PFT	230	27.5	0.0	100.0
0.6 wt % Pt–PFT	250	32.8	0.0	100.0
Rh–PFT	140	7.3	0.0	100.0
Rh–PFT	190	58.3	0.0	100.0
Rh–PFT	230	66.8	0.0	100.0
Rh–PFT	250	59.1	0.0	100.0
$Pt–Al_2O_3$	140	89.1	56.8	43.0
$Pt–Al_2O_3$	190	99.1	72.4	27.6
$Pt–Al_2O_3$	230	100.0	92.3	7.7
$Pd–Al_2O_3$	140	100.0	8.4	92.6
$Pd–Al_2O_3$	190	100.0	9.6	90.0

[a] H_2 : PhCl ratio 4 : 1; contact time 1 s.

The reactions thus appear to involve the hydrodechlorination of chlorobenzene as a common step, followed by the hydrogenation of the aromatic nucleus in the case of the Al_2O_3-based catalysts. Results reported in Table 2 provide for considerations on the intrinsic activity of various transition metals. Notwithstanding some differences in the metal

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content of the catalysts, the comparison shows, in the case of the polyamide-based systems, the following sequence in order of decreasing activity. Pd > Rh > Pt.

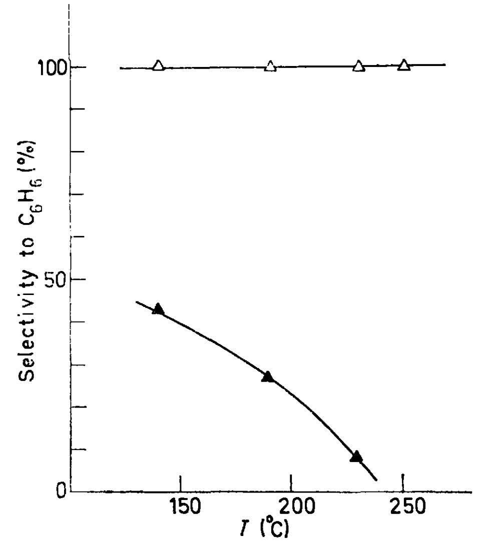
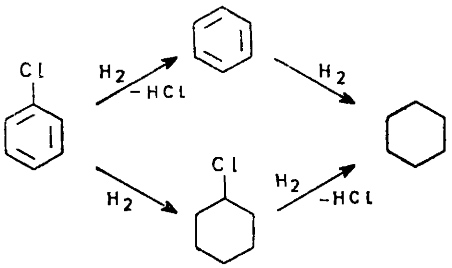


FIGURE 1 Temperature dependence of selectivities to benzene in hydrodehalogenation of chlorobenzene over 0.6 wt % Pt-PFT (△) and 0.5 wt % $Pt-Al_2O_3$ (▲) catalysts



SCHEME 1

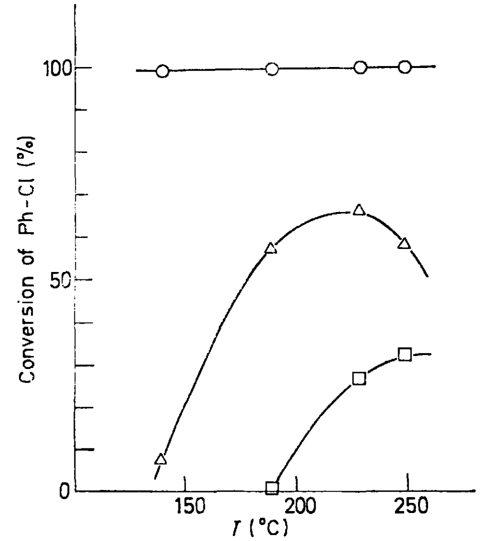


FIGURE 2 Temperature dependence of conversions of chlorobenzene in hydrodehalogenation over 0.4 wt % Pd-PFT (○), 1.1 wt % Rh-PFT (△), and 0.6 wt % Pt-PFT (□) catalysts

The differences are made more evident from plots of Figure 2 showing conversions of chlorobenzene as a function of the temperature, for few selected samples containing 0.4 Pd, 1.1 Rh, and 0.6% Pt respectively. Pd catalysts are the most active as shown by the highest conversion (100%), starting at temperatures as low as 140°; Rh and Pt catalysts, which display lower activities, show maxima at 220 and 250° respectively.

DISCUSSION

The system under investigation provides a typical example of a reaction characterized by alternative pathways, *i.e.* hydrogenolysis of the C–Cl bond (dehalogenation) and hydrogenation of the aromatic nucleus. The preferred course of the reaction is dictated by the nature of the catalyst, which is usually employed in solution;[10–12] moreover, rate and product distribution can be altered by the presence of acids or bases. Dehalogenation is promoted by bases which act by altering the catalyst and/or the substrate. Under certain conditions, dehalogenation may follow an unusual course with formation of biphenyl.[12]

On the other hand, rather scanty information is available on the gas-phase reaction. According to Nakano *et al.*[9] the reaction over $Rh-Al_2O_3$ is of the Langmuir–Hinshelwood type, involving atomically adsorbed H_2: selectivity to benzene ranges from 80 to 95% depending on the temperature and the partial pressure of H_2. Also related to the present study is the work of Kraus *et al.*[13] using a Pd–C catalyst. Although not explicitly stated, the reaction appears to be selective to benzene without products of hydrogenation of the nucleus. This finding and the parallel between the observed effects of substituents on rate in catalytic hydrogenolysis and in reduction by a complex sodium–aluminium hydride led the authors to suggest a mechanism of hydrogenolysis over Pd–C which comprises attack of H^- on chlorobenzene balanced with H^+ which reacts with the leaving Cl^-.

Our results for catalysis over transition metals on polyamides may be interpreted similarly: however, comparison with the Al_2O_3-based systems indicates profound differences in the reaction mechanisms in the two classes of catalysts, which are to be ascribed to the influence of the support and/or to a different oxidation state of the transition metal. This is supported by independent evidence, showing the absence of any metal phase on polyamide catalysts.[4] The active sites on these catalysts thus appear to be surface complexes with the transition metal in the +2 valence state. Significantly, no hydrogen is adsorbed by these samples over a wide range of experimental conditions.[4] On the contrary, Al_2O_3-based catalysts give, under comparative conditions, H : Pt ratios close to unity, in agreement with other observations.[14] Consequently, it is tempting to

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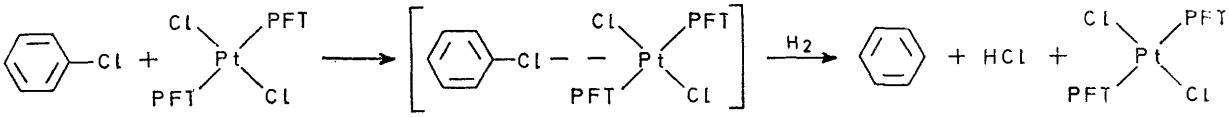
assign the observed differences in reactivity to differences in H_2 chemisorption capacities of the catalysts, thus explaining the occurrence of the various reaction paths.

On the basis of these considerations, unlike a proposed scheme for the hydrogenation of benzene over metal–nylon catalysts,[5] where activation of molecular hydrogen is invoked, we must admit adsorption and consequently activation of chlorobenzene only. In this way the Cl–C bond could be weakened by the electron-withdrawing effect of the metal so that the reaction with molecular hydrogen would become possible. Thus, the hydrogenolysis reaction could lead to benzene as shown in Scheme 2. Scheme 2, in accord with views expressed by Ballard,[15] explains the lack of hydrogenation of the aromatic ring, in agreement with the observed product distribution.



Scheme 2

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