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STUDY OF THE EFFECT OF HYDROCHLORIC ACID ON THE ACTIVITY OF PLATINUM CATALYSTS

Investigations reported in the literature show that catalytic methods involving catalysts with platinum ingredients between 0.6 and 1.5% are best suited for the oxidation of chlororganic compounds. The objective of this study was to investigate the effect of hydrochloric acid on the activity of oxidation catalysts with platinum contents reduced to 0.3–0.05%. The investigations included the resistance to poisoning and the changes in the physicochemical properties of the experimental catalysts treated with hydrochloric acid.

The experiments have revealed that catalysts with platinum contents ranging from 0.3 to 0.15% are resistant to poisoning and their activity is sufficient to oxidize chlororganic complexes to the degree desired. The catalysts containing less than 0.15% of platinum require stabilization of the noble metal prior to application.

1. INTRODUCTION

In recent years, the chemical industry has developed very rapidly all over the world and has become one of the principal contributors to the increasing pollution of the atmosphere. The pollution load entering the atmosphere is composed of different chemicals, among which organic substances, in general, and chlororganic complexes, in particular, have become a matter of serious concern. In Great Britain, the results of continuous monitoring in the years 1970–75 indicate that the average annual increase in the emission of halogens amounts to about 15%, bringing about an almost 13% increase in the total concentration of airborne halogens [12]. Both organic and chlororganic complexes emitted to the atmosphere pose serious health hazards to the population living in the vicinity of

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the source. Having these in mind, there is an urgent need to undertake such preventive measures that would enable efficient neutralization of the compounds in question.

Airborne pollution loads generated by modern industries may include a great variety of substances. In such a mixture, chlororganic complexes occur in a combination with hydrocarbons, alcohols and many other compounds [6, 7, 10, 16, 17], and catalytic oxidation is the most reasonable method of their neutralization. The usability of catalytic oxidation for the decomposition of chlororganics is primarily substantiated by the fact that, contrary to thermal combustion, no carbonyl chloride is formed in the course of the process. Catalytic oxidation usually proceeds over platinum catalysts which remain active at lower temperatures than do metal oxide catalysts. In addition, platinum catalysts are more resistant to poisoning (e.g. with chlorine compounds), have a longer life and are able to withstand short cycles of overheating.

In the literature the oxidation of chlororganic complexes over metal oxide catalysts is also reported [3-5, 15]. The results show that in the initial stage of performing their duty, catalysts of that type exhibit a quite good activity, which decreases rapidly with time. Their aging is caused by loss of the active ingredient and deterioration of some other properties of the catalyst. POPE and co-workers [13] investigated the oxidation of a number of compounds — and among them also chlororganics — both over platinum and over metal oxide (Co_3O_4) catalysts. In most instances the platinum catalyst was found to be more active. Cobaltocobaltic oxide catalysts are reported to undergo premature ageing during oxidation of trichloroethylene, whereas platinum catalysts are successfully applied to the combustion of the following waste gases: from the production of synthetic rubber (these waste gases contain not only hydrocarbons, but also chlororganics [17]), from varnish coat drying plants [1], and from film stock coating [7].

Investigations on the behaviour of catalysts subject to hydrogen chloride which is formed during oxidation of chlororganic complexes are also reported. BOND [2] found that a small part of the platinum surface area was covered by chemisorbed chlorions which were ready to settle on the active ingredients of the catalyst. FEVRIER [8] reported that the chlorplatinum complexes, which had formed in the course of the process, were partially evaporated from the catalyst surface area. NATSUKAWA [11] investigated both fresh platinum catalysts and platinum catalysts exposed to hydrochloric acid vapours during complete oxidation of various solvents (hexane, n-propyl alcohol, toluene, ethyl acetate, and methyl-ethyl ketone). He found that the catalytic activity and the active ingredient surface area distinctly decreased with the increasing amounts of hydrochloric acid.

Analysis of literature data has shown that chlororganic complexes are efficiently oxidized over catalysts with platinum content ranging within 0.6-1.5% [2, 10, 11, 17]. The objective of this study was to investigate the effect of hydrochloric acid on oxidation catalysts with platinum contents reduced to 0.3-0.05%. The resistances to poisoning and the changes in the physicochemical properties of the experimental catalysts exposed to the influence of hydrochloric acid have been determined.

2. EXPERIMENTAL

2.1. POISONING METHODS

The catalysts used in the experiments differed in the content of the active ingredient, in the method of support preparation and in grain size. Their specification is given in tab. 1. The poisoning process was carried out in a through-flow reactor (fig. 1). The experimental catalyst of the volume of 2 cm³ was placed in the reactor and subject to a mixture of xylene vapour and hydrochloric acid (in the air), which was passed through the catalyst at a rate of 60 dm³/h. The reaction mixture consisted of xylene vapours of a content concentration of 1 mg/dm³ and hydrochloric acid vapour of concentrations varying from 0.3 to 1.5 mg/dm³.

Table 1

Characterization of the experimental catalysts
Charakterystyka katalizatorów

Catalyst	Method of preparation	Type and percent of active ingredient	Type and shape of support
Pt-O	industrial	0.15% Pt	γ -Al ₂ O ₃ modified with Ba and Pd drawpieces: \varnothing - 4.3-4.7 mm, L - 10-20 mm
ZChO-80	pre-production batch	0.15% Pt	γ -Al ₂ O ₃ modified with Ba drawpieces: \varnothing - 3.0-3.5 mm, L - 10-25 mm
Pt III	laboratory	0.3% Pt	γ -Al ₂ O ₃ modified with Ba, irregular in shape, \varnothing - 2.5 mm
K-1/II	laboratory	0.05% Pt	γ -Al ₂ O ₃ modified with Ba and Pd drawpieces: \varnothing - 4.3-4.7 mm, L - 10-20 mm
PA-1	industrial	0.05% Pt	γ -Al ₂ O ₃ , spheres: \varnothing - 2.5-6.0 mm
10 b*	laboratory (made in the GDR)	0.15% Pt	γ -Al ₂ O ₃ , spheres: \varnothing - 3.0-4.0 mm
Pt-Pd	laboratory	0.04% Pt 0.032% Pd	γ -Al ₂ O ₃ modified with Ba, irregular in shape; \varnothing - 2.5 mm

* Catalyst 10 b was delivered by the German Democratic Republic within an international co-operation (Project IV. 18 MEA: "Catalytic and Thermal Combustion of Pollutants").

The poisoning cycles involved two temperatures: 523 K and 623 K. Three cycles were carried out at 523 K with hydrochloric acid at concentrations of 0.3, 0.5 and 0.7 mg/dm³. In two cycles run at 623 K the hydrochloric acid vapour concentrations were higher and amounted to 1.0 and 1.5 mg/dm³. Each poisoning cycle was conducted for 50 h over the same catalyst. The degree of xylene conversion was measured continuously, while the

concentrations of hydrochloric acid were determined before entering the reactor and after leaving it. The behaviours of the catalysts in the course of the poisoning process were referred to their activities in the test reaction of oxidizing xylene vapours in a mixture with air. The tests for both fresh and poisoned catalysts were carried out at temperatures ranging from 473 to 773 K, at a xylene vapour concentration of 1 mg/dm³ and a space velocity of 30,000 h⁻¹.

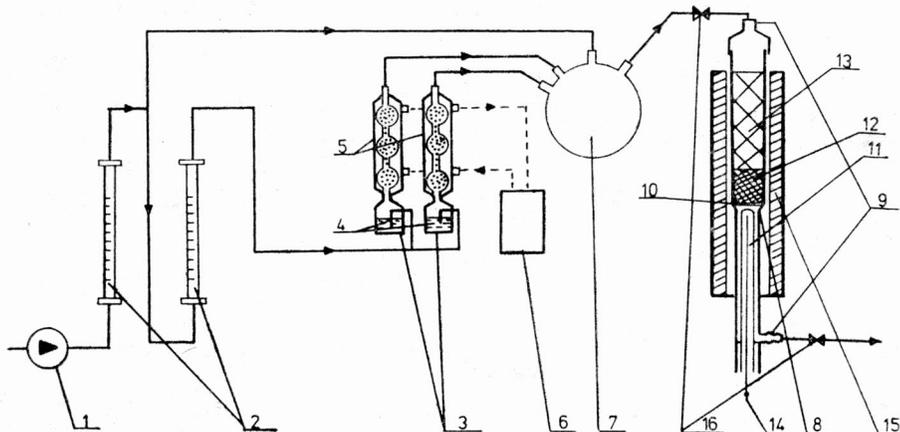


Fig. 1. Experimental apparatus

1 — pump, 2 — rotameters, 3 — vapour feeder, 4 — tanks for the compounds under test, 5 — reflux condensers, 6 — ultrathermostat, 7 — mixing vessel, 8 — catalytic reactor, 9 — pipes for gas supply and removal, 10 — glass sieve, 11 — pocket for thermocouple, 12 — catalyst bed, 13 — Rashig rings, 14 — thermocouple, 15 — electric heater, 16 — sampling point

Rys. 1. Schemat stanowiska badawczego

1 — pompa powietrzna, 2 — rotametry, 3 — dozowniki par, 4 — zbiorniki na badane związki, 5 — chłodnice zwrotne, 6 — ultratermostat, 7 — mieszalnik, 8 — reaktor katalizacyjny, 9 — króćce doprowadzające i odprowadzające badane gazy, 10 — sitko szklane, 11 — kieszeń na termoparę, 12 — warstwa katalizatora, 13 — warstwa pierścieni Rashiga, 14 — termopara, 15 — piec elektryczny, 16 — pobór prób do analizy

Xylene concentrations were measured chromatographically, using a Perkin-Elmer 3920 apparatus with a flame-ionization detector, while the concentration of hydrogen chloride was determined nephelometrically by means of a Specol colorimeter.

3. DISCUSSION OF RESULTS

The results obtained for 0.15% platinum catalysts (Pt-O, 10 b, and ZChO-80) are plotted in figs. 2-4. Corresponding curves show that neither fresh nor poisoned (in five successive cycles) Pt-O catalysts have lost their activity in the test reaction involving xylene vapours. The test reaction indicates, moreover, that poisoned catalysts yield higher degrees of xylene conversion, especially in the lower range of the experimental temperature.

A similar behaviour is reported by SADOWSKI and co-workers [15]. The values of xylene vapour conversion measured in the course of the poisoning process substantiate the following findings: the presence of hydrochloric acid has no inhibitory effect on the oxidation of xylene vapours and some slight variations in efficiency observed in the course of the poisoning cycles (both at lower and higher temperatures) are insignificant. Thus, Pt-O catalysts are found to be highly resistant to the action of hydrochloric acid.

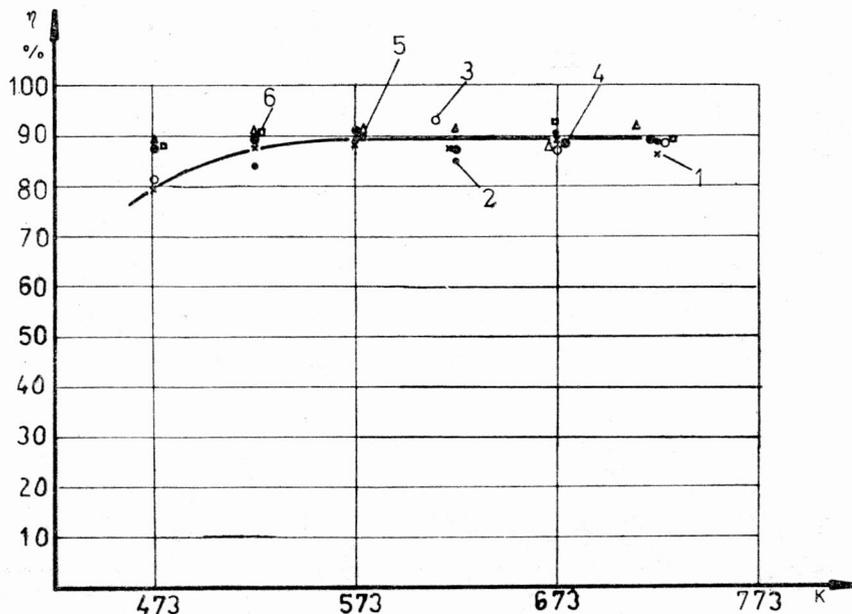


Fig. 2. Efficiency of xylene vapour oxidation over fresh and poisoned Pt-O catalysts

1 — before poisoning; after poisoning at 523 K: 2 — HCl of concentration of 0.25–0.5 mg/dm³, 3 — HCl of concentration of 0.5 mg/dm³, 4 — HCl of concentration of 0.7–0.8 mg/dm³; after poisoning at 623 K: 5 — HCl of concentration of 0.8–1.0 mg/dm³, 6 — HCl of concentration of 1.2–1.4 mg/dm³

Rys. 2. Porównanie skuteczności dopalania par ksylenu na katalizatorze Pt-O świeżym i zatrutym parami HCl

1 — przed zatrutowaniem; po zatrutowaniu w temperaturze 523 K: 2 — HCl o stężeniu 0,25–0,5 mg/dm³, 3 — HCl o stężeniu 0,5 mg/dm³, 4 — HCl o stężeniu 0,7–0,8 mg/dm³; po zatrutowaniu w temperaturze 623 K: 5 — HCl o stężeniu 0,8–1,0 mg/dm³, 6 — HCl o stężeniu 1,2–1,4 mg/dm³

Catalyst 10 b for oxidizing chlororganic complexes was prepared in the laboratories of the Dresden Technical University. The experimental results obtained for these catalysts (both fresh and poisoned) show that their resistance to hydrochloric acid poisoning is lower than that of Pt-O catalysts, particularly at temperatures between 473 and 573 K. This effect was especially pronounced at the temperature of 523 K at which the degree of xylene vapour oxidation over catalysts 10 b exhibited evident fluctuations.

Catalyst ZChO-80 follows a different behavioral pattern. In the poisoning cycles involving hydrochloric acid concentrations of 0.6 and 0.9 mg/dm³ and the temperature

of 523 K, catalytic activity not only did not decrease but even slightly increased. However, a longer time of exposure to hydrochloric acid brought about a decrease of the catalytic activity in the test reaction even at elevated temperature (623 K). This decrease was particularly pronounced at temperature below 623 K. The activity of catalysts ZChO-80 may be recovered after a short treatment with hot air at 723 K.

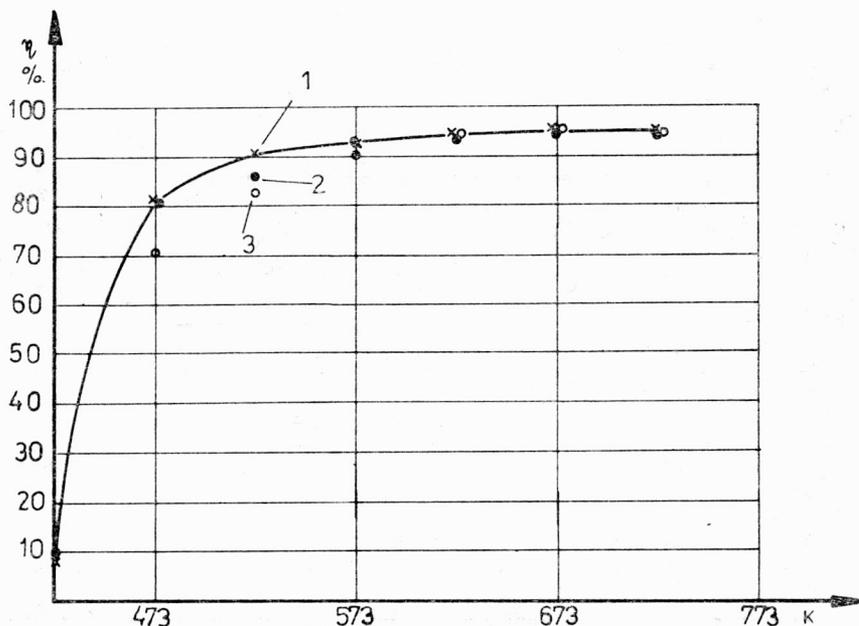


Fig. 3. Efficiency of xylene vapour oxidation over fresh and poisoned 10 b catalysts

1 — before poisoning; after poisoning at 523 K: 2 — HCl of concentration of $\sim 0.5 \text{ mg/dm}^3$; 3 — after all the poisoning cycles: HCl of concentration of $\sim 0.5 \text{ mg/dm}^3$ at 523 K, HCl of concentrations of $\sim 0.5 \text{ mg/dm}^3$ and $\sim 1.0 \text{ mg/dm}^3$ at 623 K

Rys. 3. Porównanie skuteczności dopalania par ksylenu na katalizatorze 10 b świeżym oraz zatrutym parami HCl

1 — przed zatrutowaniem; po zatrutowaniu w temperaturze 523 K: 2 — HCl o stężeniu $\sim 0,5 \text{ mg/dm}^3$; 3 — po wszystkich cyklach zatrutowania: HCl o stężeniu $\sim 0,5 \text{ mg/dm}^3$ w temperaturze 523 K, HCl o stężeniach $\sim 0,5 \text{ mg/dm}^3$ i $\sim 1,0 \text{ mg/dm}^3$ w temperaturze 623 K

The efficiency of xylene vapour oxidation over ZChO-80 catalysts shows considerable variations — from 20% for poisoning cycles at 523 K to 19% for poisoning cycles at 623 K, whereas the efficiency obtained over Pt-O catalysts approaches 10% for both temperatures. At temperatures higher than 623 K there is practically no loss in the catalytic activity of ZChO-80.

Catalysts of ZChO-80 type are found to be less resistant when exposed to hydrochloric acid at lower temperatures. In higher temperature ranges their catalytic activity becomes comparable to that of Pt-O.

The experiments with K-1/II, PA-1, and Pt-Pd catalysts aimed at determining the effect of decreased platinum content on the resistance of the contacts to hydrochloric acid. The results are plotted in figs. 6-8. As shown by these figures, the catalytic activities of K-1/II, PA-1, and Pt-Pd are comparable with those of ZChO-80 and Pt-O. So, at 573 K the degree of xylene conversion obtained over PA-1, K-1/II, and Pt-Pd was 74.5%, 85.7%, and 88.0%, respectively. After all the poisoning cycles had been completed, the activity of these catalysts decreased evidently, especially in lower temperature ranges. Hence, at 573 K the catalytic activity of PA-1, K-1/II, and Pt-Pd dropped by some 30%, 22%, and 13%, respectively.

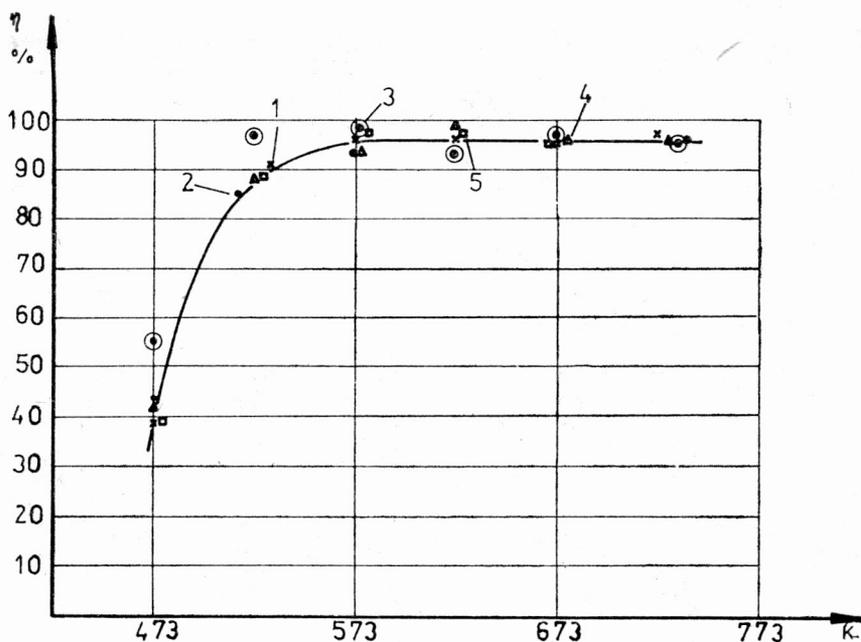


Fig 5. Efficiency of xylene vapour oxidation over fresh and poisoned Pt-III catalysts

1 - before poisoning; after poisoning at 523 K: 2 - HCl of concentration of ~ 0.5 mg/dm³, 3 - HCl of concentration of ~ 1.0 mg/dm³; after poisoning at 623 K: 4 - HCl of concentration of 1.0 mg/dm³, 5 - HCl of concentration of ~ 1.5 mg/dm³

Rys. 5. Porównanie skuteczności dopalania par ksylenu na katalizatorze Pt-III świeżym i zatrutym parami HCl

1 - przed zatrutowaniem; po zatrutowaniu w temperaturze 523 K: 2 - HCl o stężeniu $\sim 0,5$ mg/dm³, 3 - HCl o stężeniu $\sim 1,0$ mg/dm³; po zatrutowaniu w temperaturze 623 K: 4 - HCl o stężeniu $\sim 1,0$ mg/dm³, 5 - HCl o stężeniu $\sim 1,5$ mg/dm³

The efficiencies of xylene vapour oxidation over K-1/II and PA-1 measured during the poisoning process were not only markedly lower than those determined for the same catalysts in the test reaction, but also showed considerable variations. This was particularly obvious in the poisoning process carried out at 523 K, during which the oxidation reaction was even inhibited.

The poisoning effect can be eliminated by treating the catalysts with hot air at 723 K. If the catalyst PA-1 regenerated via the above route recovered its original activity, the catalyst K-1/II became even more active (90% conversion of xylene) than it was in its "fresh state" (only 85% conversion).

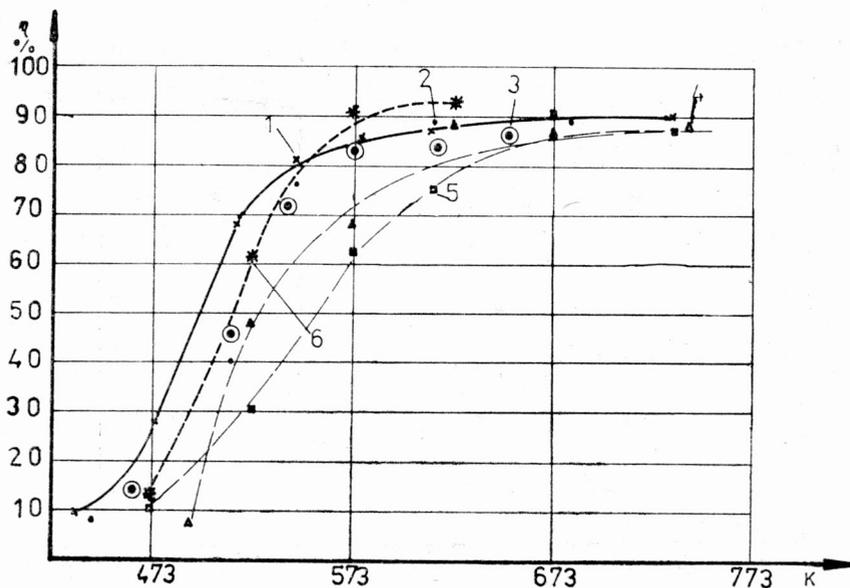


Fig. 6. Efficiency of xylene vapour oxidation over fresh and poisoned K-1/II catalysts

1 — before poisoning; after poisoning at 523 K: 2 — HCl of concentration of ~ 0.5 mg/dm³, 3 — HCl of concentration of ~ 1.1 mg/dm³; after poisoning at 623 K: 4 — HCl of concentration of 0.85–1.1 mg/dm³, 5 — HCl of concentration of 1.4–1.5 mg/dm³, 6 — after blowing

Rys. 6. Porównanie skuteczności dopalania par ksyleny na katalizatorze K-1/II świeżym i zatrutym parami HCl

1 — przed zatrutowaniem; po zatrutowaniu w temperaturze 523 K: 2 — HCl o stężeniu $\sim 0,5$ mg/dm³, 3 — HCl o stężeniu $\sim 1,1$ mg/dm³; po zatrutowaniu w temperaturze 623 K: 4 — HCl o stężeniu 0,85–1,1 mg/dm³, 5 — HCl o stężeniu 1,4–1,5 mg/dm³, 6 — po przedmuchiowaniu

The Pt-Pd catalyst prepared in the laboratory, being activated by the addition of palladium, was found to be the most resistant to the poisoning influence of hydrochloric acid (fig. 8).

It seems that the deactivation of the experimental catalyst in the presence of hydrochloric acid can be attributed to the adsorption of this compound on the catalyst surface. The surface adsorption effects are confirmed by two factors: 1) the removal of hydrochloric acid deposit under the influence of hot air makes the active component recuperate its former function, 2) in the course of the poisoning cycle hydrochloric acid concentrations measured after passage through the reactor are subject to variations. Water produced during oxidation of hydrocarbons seems to be responsible for the desorption of hydro-

chloric acid from the catalyst surface. This superficial deposit of hydrochloric acid may also unfavourably affect the efficiency of xylene vapour oxidation observed in the course of poisoning.

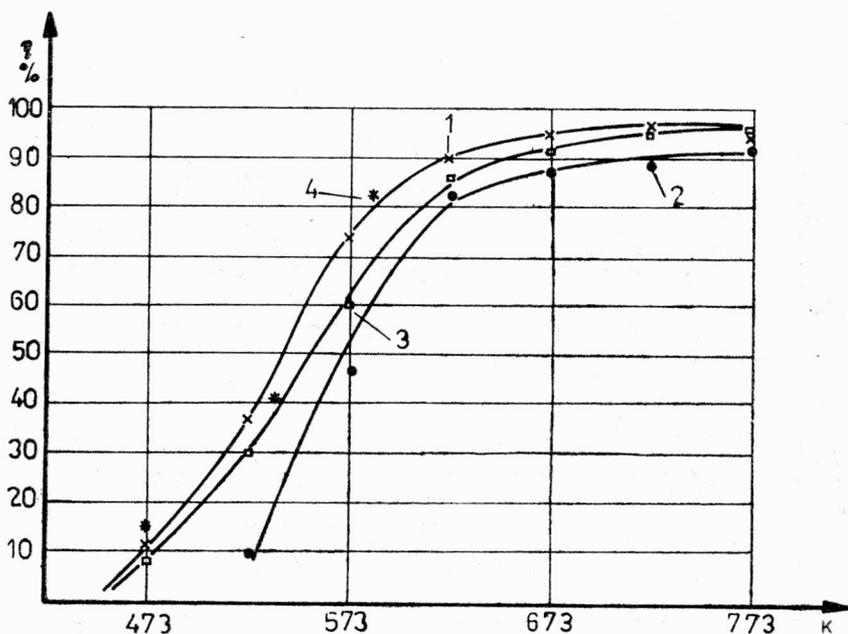


Fig. 7. Efficiency of xylene vapour oxidation over fresh and poisoned PA-1 catalysts

1 - before poisoning; after poisoning at 523 K: 2 - HCl of concentration of ~ 0.1 mg/dm³; 3 - after all the poisoning cycles: HCl of concentrations of ~ 0.1 mg/dm³, ~ 0.2 mg/dm³, and 0.5 mg/dm³ at 623 K; 4 - after regeneration

Rys. 7. Porównanie skuteczności dopalania par ksyleny na katalizatorze PA-1 świeżym i zatrutym parami HCl

1 - przed zatrutowaniem; po zatrutowaniu w temperaturze 523 K: 2 - HCl o stężeniu $\sim 0,1$ mg/dm³; 3 - po wszystkich cyklach zatrutowania: HCl o stężeniach $\sim 0,1$ mg/dm³, $\sim 0,2$ mg/dm³ i $0,5$ mg/dm³ w temperaturze 623 K; 4 - po regeneracji

The difference in catalytic activities between fresh and poisoned catalysts was also established by the differential thermal analysis and the gradientless method. The differential thermal analysis consists in comparison of differences between the temperature of initiation and the temperature of completion in the reaction in which ethanol vapours are oxidized in a mixture with air over fresh and hydrochloric acid-poisoned catalysts. Inside the experimental column there are two junctions of a differential thermocouple in which a grain of the experimental catalyst and a grain of an inert carrier are placed. The reaction mixture passing through the column was heated to 673 K and cooled down to room temperature. The temperature differences, measured both on the catalyst and on the inert support, were plotted to analyze the rapid changes of temperature occurring at the initiation of the oxidation reaction (rise in the temperature of the reaction mixture) and at the completion of the oxidation process are given in tab. 2. As shown by these data, the lowest

temperatures of initiation were obtained over Pt-III and Pt-O catalysts (at 383 K and 388 K, respectively). The initiation temperatures for K-1/II and 10 b are higher by 33° and 45°, respectively. Catalysts Pt-III and Pt-O were also found to have the highest durability at decreasing temperature of the reaction zone. The temperature at which their duty had been completed was 373 K for both catalysts. The temperature of completion for catalysts K-1/II, PA-1, and 10 b is higher by 15°, 55°, and 60°, respectively, than that for Pt-III and Pt-O. After poisoning, only catalyst PA-1 showed significant loss of activity.

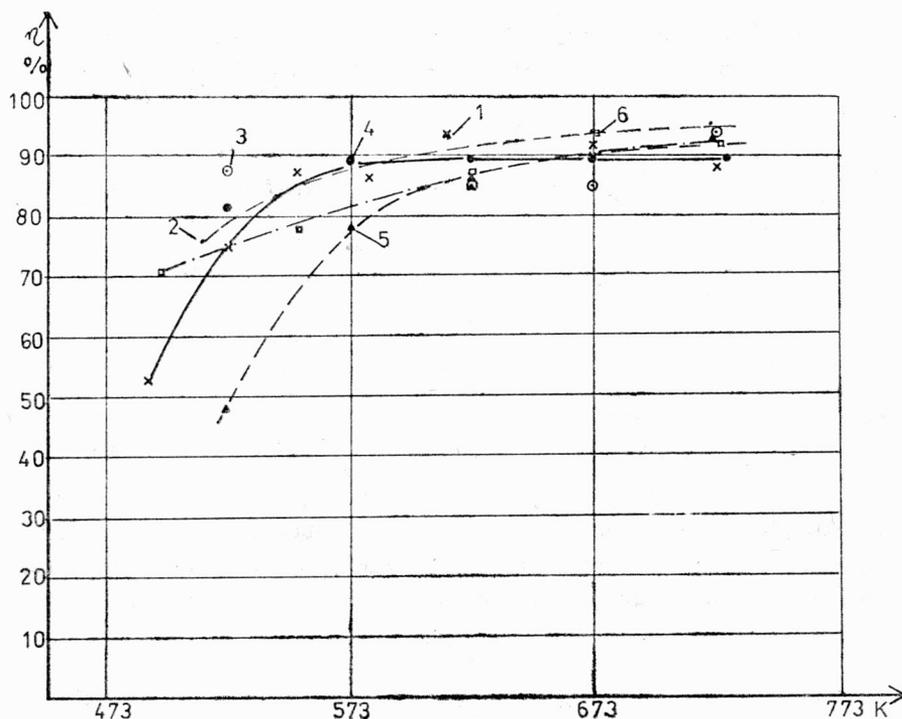


Fig. 8. Efficiency of xylene vapour oxidation over fresh and poisoned Pt-Pd catalysts

1 — before poisoning; after poisoning at 523 K: 2 — HCl of concentration of 0.13–0.24 mg/dm³, 3 — HCl of concentration of 0.45–0.5 mg/dm³, 4 — HCl of concentration of 0.7–0.75 mg/dm³; after poisoning at 623 K: 5 — HCl of concentration of ~0.75 mg/dm³, 6 — HCl of concentration of 1.1–1.45 mg/dm³

Rys. 8. Porównanie skuteczności dopalania par ksylenu na katalizatorze Pt-Pd świeżym i zatrutym parami HCl

1 — przed zatruciem; po zatruciu w temperaturze 523 K: 2 — HCl o stężeniu 0,13–0,24 mg/dm³, 3 — HCl o stężeniu 0,45–0,5 mg/dm³, 4 — HCl o stężeniu 0,7–0,75 mg/dm³; po zatruciu w temperaturze 623 K: 5 — HCl o stężeniu ~0,75 mg/dm³; po zatruciu w temperaturze 623 K: 5 — HCl o stężeniu ~0,75 mg/dm³, 6 — HCl o stężeniu 1,1–1,45 mg/dm³

The temperature of initiation for this catalyst increased by as much as 95°. For the remaining catalysts the increase in initiation temperature varied from 20° to 30°. At the decreasing temperature of the reaction zone the most durable were catalysts Pt-III and K-1/II. Their

duty had been completed at 403 K and 418 K, respectively. It is worth noting that the difference in the temperature of completion between fresh and poisoned catalyst K-1/II amounts to 30°, thus indicating that their activities after poisoning with hydrochloric acid vapours increase. Summing up, catalysts Pt-III and Pt-O show an almost identical activity in the oxidation of ethanol vapours, whereas catalyst K-1/II becomes more active after completion of the hydrochloric acid poisoning cycles.

Table 2

Temperatures of initiation and completion in the oxidation of ethanol vapours over selected catalysts

Temperatury inicjacji i wygaszania w procesie spalania par etanolu dla wybranych katalizatorów

Catalyst	Temperature of initiation [K]		Temperature of completion [K]	
	Fresh catalyst	Poisoned catalyst	Fresh catalyst	Poisoned catalyst
	Pt-O	388	418	373
10 b	433	463	433	463
K-1/II	421	441	388	418
PA-1	438	533	428	553
Pt-III	383	403	373	403

The activities of fresh and poisoned catalysts were also studied by the gradientless method, using circulation-throughflow reactor in which both the temperature and the concentration of the reagents were kept constant throughout the catalyst bed. Activation energies were calculated from the Arrhenius equation:

$$K = K_0 \exp[-E/RT]$$

where:

- K — reaction velocity constant,
- K_0 — pre-exponential factor,
- E — activation energy,
- R — gas constant,
- T — temperature.

This permitted comparison of activation energies prior to and after completion of hydrochloric acid poisoning [9].

The adopted model reaction medium consisted of a mixture of xylene vapours and air. The investigations were conducted at the following parameters: concentration of the reaction medium — 1 mg xylene/dm³ air; volume of the catalyst — 1 cm³ (0.65 g); flow rate for the reagents — 30 dm³/h; reaction temperature — 473–723 K. The rates of xylene vapour

oxidation in a mixture with air were studied as a function of temperature, assuming that the reaction over platinum catalysts is a first-order reaction. The calculated activation energies are listed in tab. 3.

Table 3

Activation energies of selected catalysts prior to
and after poisoning
Energia aktywacji wybranych katalizatorów przed
procesem i po procesie zatrucia

Catalyst	Activation energy [J/mol]	
	Fresh catalyst	Poisoned catalyst
K-1/II	40.81	20.68
Pt-O	32.40	31.72
Pt-III	21.77	21.98

As shown by these data, catalyst Pt-III (in which the platinum content is the highest) exhibits the lowest activation energy in the process of xylene vapour oxidation, and in practice the activation energy after exposure to hydrochloric acid vapours does not change. The fresh Pt-O catalyst with platinum component half that of Pt-III shows the activation energy higher (by 10.63 kJ/mol) which after poisoning decreases (by 0.68 kJ/mol). The most significant difference in activation energy between fresh and poisoned catalysts is that for K-1/II (20.13 kJ/mol). Similar results were obtained by the throughflow reactor technique and differential thermal analysis which substantiate the increased catalytic activity of K-1/II in the oxidation of hydrocarbons after exposure to hydrochloric acid.

To determine the effect of hydrochloric acid on the active ingredient of the experimental catalysts the specific surface of platinum was measured by chemisorption and platinum content (in both fresh and poisoned catalysts) by colorimetry, taking advantage of the blood-red colour characteristics of the complex formed by chlorplatinic acid and tin tetrachloride [9].

The results are given in tabs. 4 and 5. From the data listed there, it can be seen that the specific surface of platinum in all but catalyst Pt-III (which has the highest platinum content) decreased after exposure to hydrochloric acid vapours. The decrease was particularly distinct in catalyst K-1/II which had the smallest platinum content. On catalysts Pt-O and ZChO-80 which have equal percentage of platinum (0.15%), but differ in the method of support preparation (the support for Pt-O has been activated with palladium), the decrease amounts to 42% and 64%, respectively. When hydrocarbons are oxidized in the absence of hydrochloric acid, the decrease of specific surface of the platinum ingre-

dent is evidently greater. This is an indication that chlorine compounds prevent the formation of large crystallites of platinum.

Table 4

Measurements of dispersion of platinum
Pomiary dyspersji platyny

Catalyst	Fresh catalyst	Specific surface [m ² /g Pt]	
		Following oxidation of hydrocarbons	Following exposure to HCl
Pt-O	43	5	25
ZChO-80	80	18	30
K-I/II	95	no determinations were made	no chemisorption occurs
Pt-III	20	no determinations were made	24

Table 5

Platinum contents in fresh and poisoned catalysts
Zawartość platyny w katalizatorach

Catalyst	Platinum content [%]	
	Prior to exposure to HCl	Following exposure to HCl
Pt-O	0.114	0.120
PA-1	0.034	0.032

Comparison of the experimental results shows that the presence of hydrogen chloride does not account for the "escape" of platinum from the catalyst surface. The effect of hydrochloric acid on the catalytic activity depends on the quantity of the active ingredient and on the method by which the catalyst has been prepared, and decreases with the increasing content of the active component. Activation of the support material by the addition of palladium makes the catalyst much more resistant to the influence of hydrochloric acid vapours.

4. SUMMARY AND CONCLUSIONS

The review of literature has shown that the catalysts employed so far for the oxidation of chlororganic complexes had platinum ingredients greater than 0.6%. The experiments presented in this paper were conducted with catalysts in which platinum contents ranged

between 0.3 and 0.15%. The experimental catalysts were found to be resistant to poisoning, and their activity was sufficiently high to oxidize chlororganic complexes to the degree desired. Catalysts with smaller platinum contents have a poor resistance to poisoning with chlorine compounds. However, after stabilization of the noble metal, their application might be promising.

REFERENCES

- [1] ALANOVA T. G., Prom. Sanit. Ochist. Gaz., Vol. 2 (1976), pp. 12-13 (in Russian).
- [2] BOND G. C., SADEGHI N., J. Appl. Chem. Biotechnol., Vol. 25 (1975), pp. 241-248.
- [3] CHERNIUK G. P., CHELADIN L. I., Chim. Prom., Vol. 10 (1975), pp. 757-759 (in Russian).
- [4] CHERNIUK G. P., ZHUKOVSKAYA I. I., CHELADIN L. I., Kinet. i Kataliz., Vol. 5 (1976), pp. 1236-1240 (in Russian).
- [5] DOROBKINA L. M., ESHENBAKH L. F., IVANOVA G. A., Prom. Sanit. Ochist. Gaz, Vol. 1 (1977), pp. 268-270 (in Russian).
- [6] DORONINA L. M., ABRAMOVA G. B., PROKHOROV V. A., Inf. Zashch. Atm., Vol. 1 (1978), pp. 170-176 (in Russian and German).
- [7] DORONINA L. M., IVANOVA G. A., Inf. Zashch. Atm., Vol. 1 (1978), pp. 170-176 (in Russian and German).
- [8] FEVRIER D., FEVRIER G., VERNET J. L., Amer. Soc. Mech. Eng. 76-ENAS, 1976, 1-7.
- [9] MENDYKA B., *Badanie możliwości zastosowania wybranych katalizatorów do spalania związków chloroorganicznych*, Diss. of Technical University of Wrocław 1982, 1-184, PWR PRE - 2/I-15/82 (in Polish).
- [10] MENDYKA B., SYCZEWSKA K., MUSIALIK A., *Badania nad katalitycznym spalaniem mieszaniny rozpuszczalników w obecności związków chloru*, Report of the Institute of Environment Protection Engineering, Technical University of Wrocław, 1980, pp. 1-51, PWR SPR-33/I-15/80 (in Polish).
- [11] NATSUKAWA K., YASUDA K., Atm. Environ., Vol. 13 (1979), pp. 335-339.
- [12] PACK D. H., LOVELOCK J. E., COTTON G., Atm. Environ., Vol. 11 (1977), pp. 329-344.
- [13] POPE E., WALKER D. S., MOSS R. L., Atm. Environ., Vol. 12 (1978), pp. 1921-1927.
- [14] SADEGHI N., Environ. Prot. Eng., Vol. 1 (1976), pp. 67-71.
- [15] SADOWSKI G., NAUMAN H., POHL K., Inf. Zashch. Atm., Vol. 1 (1977), pp. 108-112 (in Russian and German).
- [16] SYCZEWSKA K., MUSIALIK A., MENDYKA B., *Badania procesów katalitycznego spalania mieszaniny rozpuszczalników emitowanych w procesie produkcji gamatoksu*, Report of the Institute of Environment Protection Engineering, Technical University of Wrocław, 1979, pp. 1-64, PWR SPR-28/I-15/79 (in Polish).
- [17] SHATOLOV V. P., KHROMYKH V. B., GRIGOREEV V. B., Prom. Sanit. Nauch. Tekhn. Spro., Vol. 8 (1971), pp. 7-9 (in Russian).

WPLYW KWASU SOLNEGO NA AKTYWNOŚĆ KATALIZATORÓW PLATYNOWYCH

Przegląd literatury wykazał przydatność metody katalitycznej do dopalania połączeń chloroorganicznych w obecności katalizatorów o znacznej zawartości platyny (0,6-1,5%). Celem badań było określenie wpływu kwasu solnego na aktywność katalizatorów z mniejszą (0,3-0,05%) zawartością platyny. Badano odporność na zatrucia oraz zmiany fizykochemiczne katalizatorów poddanych działaniu kwasu solnego.

Stwierdzono, że katalizatory o zawartości platyny 0,3–0,15% są odporne na zatrucie i zachowują aktywność w dopalaniu połączeń chlorowych. Katalizatory zawierające mniejszy procent platyny mogłyby być stosowane dopiero po jej stabilizacji.

DER EINFLUSS DER SALZSÄURE AUF DIE AKTIVITÄT VON PLATINKATALYSATOREN

Aus einer Literaturstudie folgt die Anwendbarkeit des katalytischen Abbrandes von chlororganischen Verbindungen in der Gegenwart von Katalysatoren mit hohem Platingehalt (0,6–1,5%). Ziel der vorliegenden Arbeit war die Untersuchung des Einflusses der Salzsäure auf die Aktivität von Platinkatalysatoren mit einem kleineren (0,3–0,5%) Platingehalt. Untersucht wurde die Gifffestigkeit sowie die physikalisch-chemische Änderungen der auf die Wirkung der Salzsäure ausgesetzten Katalysatoren. Es konnte festgestellt werden, daß Katalysatoren mit einem Platingehalt von 0,3–0,15% noch giftfest sind und ihre Aktivität beim Abbrand von Chlorverbindungen behalten. Katalysatoren die weniger Platin beinhalten, konnten erst nach einer Stabilisierung eingesetzt werden.

ВЛИЯНИЕ СОЛЯНОЙ КИСЛОТЫ НА АКТИВНОСТЬ ПЛАТИНОВЫХ КАТАЛИЗАТОРОВ

Обзор литературы показал пригодность каталитического метода для дожигания хлоросодержащих органических соединений в присутствии катализаторов со значительным содержанием платины (0,6–1,5%). Целью проведенных исследований было определение влияния соляной кислоты на активность катализаторов с меньшим (0,3–0,05%) содержанием платины. Исследовалась устойчивость к отравлениям, а также к физикохимическим изменениям, подвергнутым действию соляной кислоты. Было отмечено, что катализаторы с содержанием платины 0,3–0,15% устойчивы к отравлениям и сохраняют активность в дожигании хлоросодержащих соединений. Катализаторы, содержащие меньший процент платины, могли бы применяться только после её стабилизации.