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DEACTIVATION OF PLATINUM CATALYSTS DURING COMBUSTION OF A MULTI-COMPONENT CHLORORGANIC MIXTURE

The primary objective of the study was to select catalysts for the treatment of flue gases sent out during production of epichlorohydrin. The flue gas stream (which carried a mixture of chlororganic compounds) was treated in the presence of three catalysts differing in platinum content (0.15, 0.1 and 0.05%, respectively). Another major objective of the study was to determine the following items: the optimum operating parameters, the resistance to poisoning by chlorine compounds and the range of applications for the contacts involved. Satisfactory results were obtained during combustion in the presence of catalysts containing 0.15 and 0.1% of platinum.

1. INTRODUCTION

In terms of air pollution control, chlororganic compounds can be defined as very troublesome waste substances. They are all difficult to degrade, and some of the species have a toxic effect on the environment. Airborne chlororganics come from a variety of industrial sources. Of these, the production of poly(vinyl chloride) or chlorine-based pesticides deserves particular consideration. The flue gases from poly(vinyl chloride) production carry vinyl chloride and dichloroethane [1], whereas those from the production of the 6-chlorocyclohexane-based pesticide, Gamatox, contain chlorobenzene, 6-chlorocyclohexene, chlorine and hydrogen chloride (just to mention the major components) [2]. A considerable portion of the chlorine compounds emitted to the atmosphere comes from the production of synthetic rubber [3]. Incinerating plants are responsible for the emission of polychlorodibenzodioxines and polychlorodibenzofuranes [4], [5]. As regards the implications to health, the potential environmental impact of epichlorohydrin production gives rise to serious concern. This is so, because the chlororganics leaving the plant in the flue gas stream are notably toxic [4], [6].

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Thus, the ever increasing need for efficient and reliable treatment methods has directed the attention of environmental scientists and engineers to catalytic combustion of chlororganic compounds [7]–[10]. But exposure to chlorine or chlorine compounds may deteriorate catalyst activity by poisoning. It is therefore necessary to examine the poison-resistance of the contact when exposed to a mixture of chlororganic substances [11]–[16]. Since the combustion of chlorine compounds in the presence of oxide catalysts fails to be satisfactory [17], [18], [19], our studies will concentrate on platinum catalysts.

2. EXPERIMENTAL

2.1. CATALYSTS

Our previous investigations [6], [17] have shown that the platinum catalyst marketed under the brand name of ZChO-80 (0.15% platinum ingredient and γ -Al₂O₃ support) sustains a great activity in the oxidation of chlororganics and a strong resistance to poisoning by these species. In the presence of ZChO-80, chlorine compounds carried out by a real flue gas stream (from plastics manufacture) were subjected to combustion. In the present study we aimed at preparing platinum catalysts with reduced noble metal ingredients, as well as at examining their oxidation activity for, and poison-resistance with respect to, chlororganic compounds. Experiments were run over two industrial contacts, i.e. KP-910 (0.1% Pt) and ZChO-85 (0.05% Pt). The catalysts were prepared according to our formula by impregnation of γ -Al₂O₃ drawpieces (from 3 to 3.5 mm in diameter and from 15 to 20 mm in length). Oxidation activity and poison-resistance of KP-910 and ZChO-85 were tested in the combustion of a model mixture simulating the flue gases from the chemical plant "Organika", which carry propylene, propyl chlorides, propyl dichlorides, allyl chloride and epichlorohydrin.

The results are compared with those obtained earlier for ZChO-80.

2.2. COMBUSTION OF THE MODEL MIXTURE

The combustion process was run in a through-flow reactor over a 100 cm³ catalyst bed at space velocities of 10,000 h⁻¹ and 20,000 h⁻¹. The temperature of catalysts and concentration of the mixture components varied from 450 to 820 K and from 0 to 5 mg/dm³, respectively. The model mixture was prepared from the starting compounds and the semi-finished products in the "Organika" plant. Propylene was supplied from the cylinder to the vapour mixer via a reducer.

Chromatographic analysis was carried out so as to separate propylene, allyl chloride and epichlorohydrin and, thereafter, to quantify their concentrations. In the flue gas stream investigated, propylene and allyl chloride occurred in greater amounts than the remaining species. Since propylene is a hydrocarbon, it was interesting to see what influence it has on the oxidation of chlororganics and vice versa.

Allyl chloride was selected as a chlororganic compound. Epichlorohydrin was separated from the mixture because of its toxicity.

Under these conditions, ten chromatographic peaks were obtained, which made it possible to investigate the combustion of relevant chloroderivatives.

The efficiency of the catalytic reaction was estimated for the entire mixture, for individual component and for individual groups of components.

It is a well-established fact that the concentrations of propylene and allyl chloride may vary with change of conditions. Taking this into account, we investigated the following mixtures:

- 1) all the components were present,
- 2) propylene was absent,
- 3) propylene and allyl chloride were absent,
- 4) only allyl chloride was present,
- 5) only propylene was present.

2.3. DEACTIVATION

Deactivation of the catalysts after exposure to chlororganic compounds was assessed as follows:

in a test reaction involving combustion of xylene, toluene, benzene and ethanol vapours,

by thermal-differential analysis,

by determining the specific surface and the platinum content of the catalyst,

by kinetic characterization of the reaction.

The rest reaction was run in the temperature range from 420 to 690 K. Differential thermal analysis was used to determine the initiation and extinction temperatures for ethanol vapour combustion in the presence of a single catalyst grain located at the thermocouple junction. The specific surface of the noble metal was established by chemisorption via hydrogen reduction of the catalyst. Taking into account the hydrogen volume used for the reduction of platinum, the specific surface of the noble metal ingredient was calculated. Chemisorption stoichiometry was assumed to be $H/Pt^0 (s) = 3$. Hydrogen volume was determined chromatographically. Platinum content was determined colorimetrically, making use of the colour of the complex which is formed in the reaction of chloroplatinic acid with tin tetrachloride.

Kinetic investigations were carried out by determining the activation energy of toluene combustion for fresh and poisoned catalysts (following exposure to chlororganics). Considering the kinetic and diffusion regions, the overall reaction rate can be calculated as follows [20]:

$$\frac{1}{k} = \frac{1}{k'_{\text{chem}}} + \frac{1}{k_{\text{mass}}}$$

where k'_{chem} denotes effective chemical reaction rate, and k_{mass} is the mass transfer rate constant.

Making use of the results obtained from the calculations, a model incorporating all reaction parameters was established to determine the conversion of particular contaminants. The process was assumed to be an irreversible first-order reaction of both kinetic

and diffusional nature. The rate constant for the chemical reaction was calculated in terms of the Arrhenius equation for surface process:

$$k = k_0 e^{-E/RT}$$

and the molar transfer index for the stationary layer was adopted according to SATTERFIELD [21]:

$$k_g = 0.357 \frac{G_M}{Re^{0.359} Sc^{0.666} \epsilon P}$$

where:

- k_0 – pre-exponential factor,
- E – activation energy,
- R – gas constant,
- G_M – molar flow rate of all reagents,
- Re – Reynolds number,
- Sc – Schmidt number,
- ϵ – void volume,
- P – pressure.

3. RESULTS AND DISCUSSION

3.1. COMBUSTION OF MODEL MIXTURES

The results are plotted in figs. 1–5. As was expected, propylene (hydrocarbon) alone was the easiest to oxidize in the presence of each of the catalysts investigated. In the presence of ZChO-80, the temperature of 420 K was sufficient to yield a 90% conversion. At an almost equal temperature, viz. at 500 K, a 90% efficiency was achieved in the presence of the low platinum contact, ZChO-85. But this finding does not for the conversion of propylene in the presence of the chlororganic compounds (allyl chloride, propyl chlorides or chloropropylene). The temperature required to achieve a 90% oxidation efficiency increases with the decreasing weight percent of the platinum ingredient in the catalyst. Thus, when ZChO-85 contact is used, conversion of propylene in the presence of chlororganics will amount to 90% at a temperature by 190 degrees higher than that when the chlororganics are absent. For KP-910 and ZChO-80, this difference is not so big, amounting to 150 and 140 degrees, respectively (figs. 1, 4 and 5).

Allyl chloride (which contains chlorine in its particle) is equally prone to oxidation when combusted alone, using ZChO-80 or KP-910. In the presence of the other chlororganics, allyl chloride oxidizes less readily. But the difference in combustion between allyl chloride alone and allyl chloride in the presence of the remaining chlororganic species is less distinct than between propylene alone and propylene in the presence of chlororganics. In the presence of ZChO-85, allyl chloride (alone) is far more resistant to oxidation than in the presence of ZChO-80 or KP-910. Thus, 90% conversion was achieved at a temperature by approximately 100 degrees higher than that for the two contacts mentioned. In the

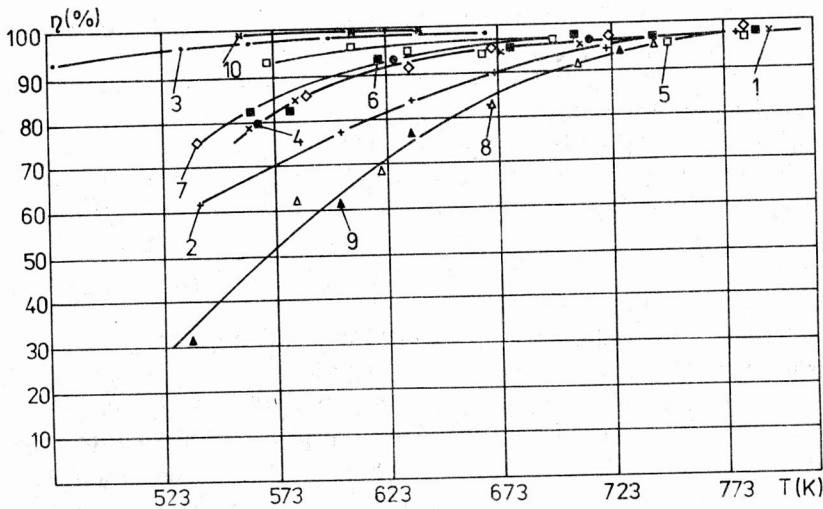


Fig. 1. Combustion of the model mixture in the presence of ZChO-80 (space velocity $10,000 \text{ h}^{-1}$). 1 - all components are present, 2 - propylene is absent, 3 - only propylene (5 mg/dm^3) is present, 4 - propylene ($2-5 \text{ mg/dm}^3$) is present in the mixture with all components, 5 - only allyl chloride ($0.2-0.6 \text{ mg/dm}^3$) is present, 6 - allyl chloride ($0.5-0.8 \text{ mg/dm}^3$) is present in the mixture with all components, 7 - allyl chloride ($0.8-1.2 \text{ mg/dm}^3$) is present, and propylene is absent, 8 - peak V (species most resistant to degradation) in the mixture of all components, 9 - peak V in the mixture with no propylene, 10 - epichlorohydrin in the mixture with all components

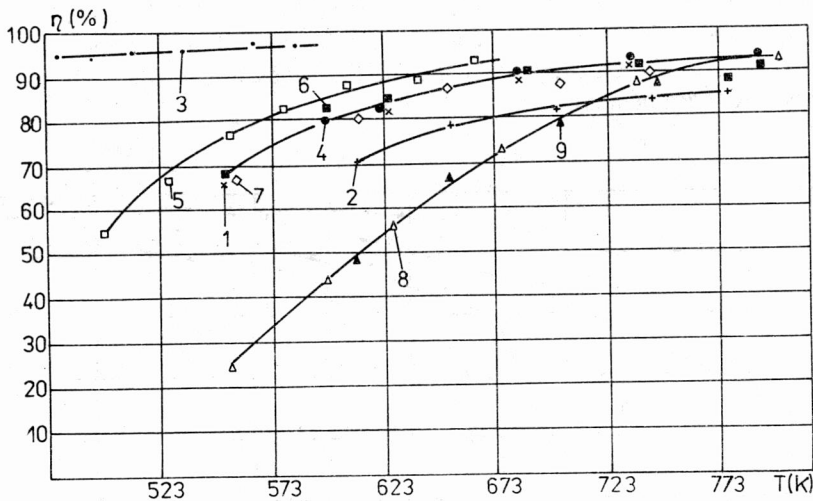


Fig. 2. Combustion of the model mixture in the presence of ZChO-80 (space velocity $20,000 \text{ h}^{-1}$). 1 - all components are present, 2 - propylene is absent, 3 - only propylene (5 mg/dm^3) is present, 4 - propylene ($2-5 \text{ mg/dm}^3$) is present in the mixture with all components, 5 - only allyl chloride ($0.2-0.6 \text{ mg/dm}^3$) is present, 6 - allyl chloride ($0.5-0.8 \text{ mg/dm}^3$) is present in the mixture with all components, 7 - allyl chloride ($0.8-1.2 \text{ mg/dm}^3$) is present, and propylene is absent, 8 - peak V (species most resistant to degradation) in the mixture of all components, 9 - peak V in the mixture with no propylene

presence of propylene and the other components of the mixture, allyl chloride oxidizes noticeably easier, especially in the lower temperature range applied.

Experiments were also run to determine the effect of propylene and allyl chloride on the overall combustion of the mixture. The results are plotted in figs. 1–5. As shown by these data, the mixture is far more resistant to oxidation when propylene is absent. For a mixture with no propylene, a 90% conversion in the presence of ZChO-80, at both space velocities $10,000 \text{ h}^{-1}$ and $20,000 \text{ h}^{-1}$, was achieved with a temperature by 60 degrees higher than that when propylene was present (figs. 1 and 2). When the same mixture was oxidized in the presence of ZChO-85, the efficiency of the reaction failed to reach 90% in the temperature range investigated (fig. 5).

Of the mixtures tested, the one with no propylene and a low concentration of allyl chloride was found to be the most resistant to oxidation (figs. 3 and 4). When the mixture to be combusted contains all the components in question, the overall efficiency of oxidation is strongly dependent on two of them, that is, propylene and allyl chloride. Epichlorohydrin (which occurs in small amounts) is very easy to oxidize, specifically when using ZChO-80 and KP-910 contacts. In the presence of ZChO-85, epichlorohydrin oxidizes slower, but a comparatively low temperature (about 620 K) is required to achieve a high degree of conversion.

Summing up, the flue gases from the chemical plant "Organika" can be combusted with 90% efficiency under the following conditions:

- in the presence of ZChO-80 at 613 K and $10,000 \text{ h}^{-1}$,
- in the presence of KP-910 at 633 K and $10,000 \text{ h}^{-1}$,
- in the presence of ZChO-85 at 703 K and $10,000 \text{ h}^{-1}$.

Combustion of flue gases with low concentration of propylene and allyl chloride should be conducted at 693 and 723 K for ZChO-80 and KP-910, respectively. In the presence of ZChO-85 (specifically when the mixture does not include a hydrocarbon), 90% conversion will not be achieved.

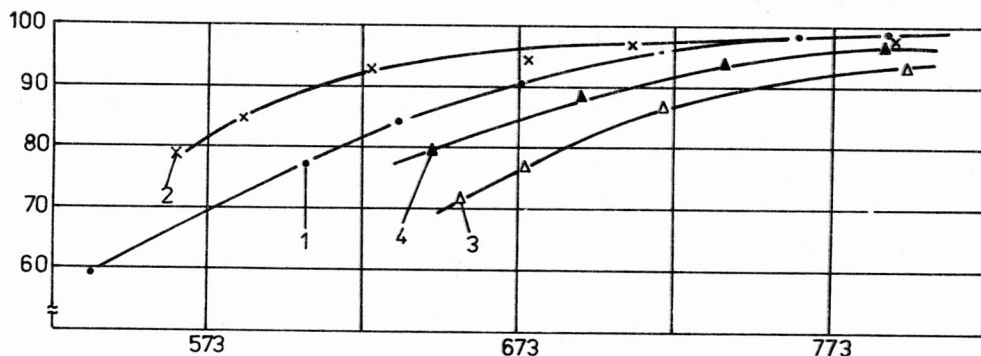


Fig. 3. Combustion of mixtures with varying allyl chloride concentrations in the presence of ZChO-80 (space velocity $10,000 \text{ h}^{-1}$). 1 - chlororganic compounds + allyl chloride (1.0 mg/dm^3), 2 - chlororganic compounds + allyl chloride + propylene ($2-4 \text{ mg/dm}^3$), 3 - chlororganic compounds + allyl chloride ($\leq 0.05 \text{ mg/dm}^3$), 4 - chlororganic compounds + allyl chloride + propylene ($2-3 \text{ mg/dm}^3$)

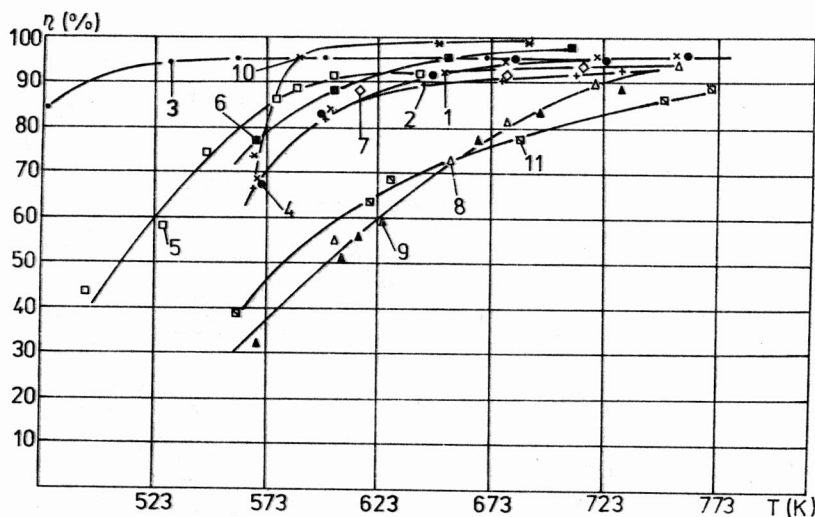


Fig. 4. Combustion of the model mixture in the presence of KP-910 (space velocity $10,000 \text{ h}^{-1}$). 1 - all components are present, 2 - propylene is absent, 3 - only propylene (2.0 mg/dm^3) is present, 4 - propylene ($2.0\text{--}2.5 \text{ mg/dm}^3$) is present in the mixture with all components, 5 - only allyl chloride ($0.4\text{--}0.5 \text{ mg/dm}^3$) is present, 6 - allyl chloride (0.7 mg/dm^3) is present in the mixture with all components, 7 - allyl chloride ($0.6\text{--}0.7 \text{ mg/dm}^3$) is present, and propylene is absent, 8 - peak V (species most resistant to degradation) in the mixture of all components, 9 - peak V in the mixture with no propylene, 10 - epichlorohydrin in the mixture with all components, 11 - the mixture with no propylene and small amount of allyl chloride

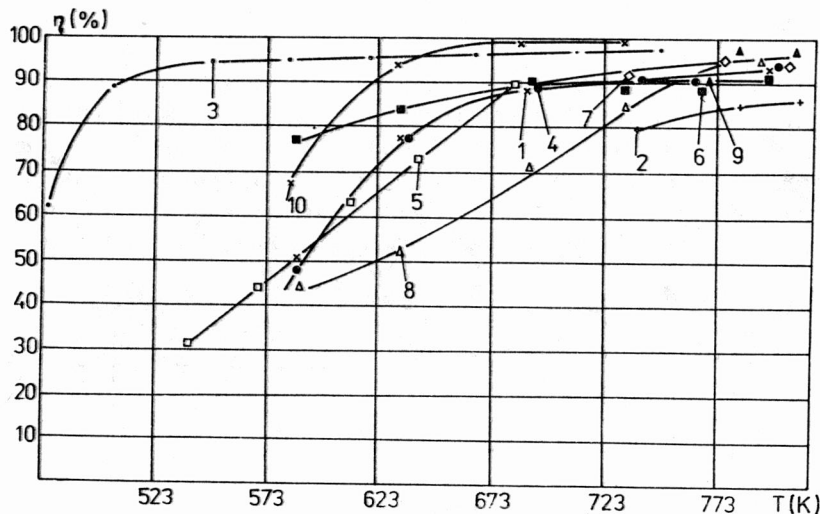


Fig. 5. Combustion of the model mixture in the presence of ZChO (space velocity $10,000 \text{ h}^{-1}$). 1 - all components are present, 2 - propylene is absent, 3 - only propylene ($2.2\text{--}2.5 \text{ mg/dm}^3$) is present, 4 - propylene ($3.5\text{--}4.5 \text{ mg/dm}^3$) is present in the mixture with all components, 5 - only allyl chloride ($1.0\text{--}2.0 \text{ mg/dm}^3$) is present, 6 - allyl chloride (0.3 mg/dm^3) is present in the mixture with all components, 7 - allyl chloride (0.3 mg/dm^3) is present, and propylene is absent, 8 - peak V (species most resistant to degradation) in the mixture of all components, 9 - peak V in the mixture with no propylene, 10 - epichlorohydrin in the mixture with all components

3.2. DEACTIVATION

Relevant results are plotted in figs. 6-9 and are listed in tables 1-4.

Table 1
Determination of platinum content

Catalyst	Platinum content (wt. %)	
	Fresh contact	Poisoned contact
ZChO-80	0.15	0.15
KP-910	0.10	0.10
ZChO-85	0.04	0.04

Table 2

Dispersion of platinum

Catalyst	Specific surface (m^2/g) of platinum	
	Fresh contact	Poisoned contact
ZChO-80	141	3
ZChO-85	113	19

As the data shows, ZChO-80 exhibits the greatest oxidation activity with respect to the model mixture, and the strongest resistance to poisoning by chlorine compounds. The test reaction of xylene combustion runs with the same efficiency, irrespective of whether the catalyst is fresh or has been exposed (for 150 h) to the chlororganic contaminants (fig. 6). There is only a slight rise in the initiation temperature for the ethanol combustion reaction, when determined by differential thermal analysis (table 4). It is a well-established fact

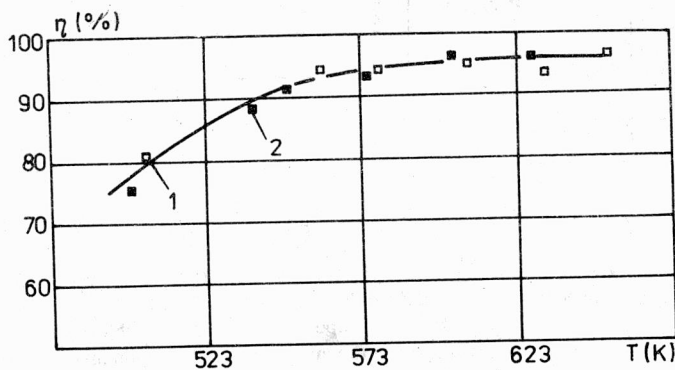


Fig. 6. Test combustion of xylene vapour in the presence of ZChO-80
1 - fresh, 2 - poisoned

that chlororganics can form volatile compounds with the active platinum ingredient and carry it away. No such phenomenon has been observed in this study (table 1). Kinetic measurements of fresh and deactivated catalysts have given evidence of the stability of ZChO-80. The value of activation energy changes only slightly, or practically does not change at all (table 3). Platinum dispersion measurements have revealed some changes in the surface area of the contact (table 2). The specific surface of the active ingredient has been reduced and larger crystallites have formed. These changes have no destructive effect on the activity of ZChO-80.

Table 3

Catalyst	Activation energies	
	E (kJ/mol)	
	Fresh catalyst	Poisoned catalyst
ZChO-80	61.9	63.6
ZChO-85	45.4	76.0

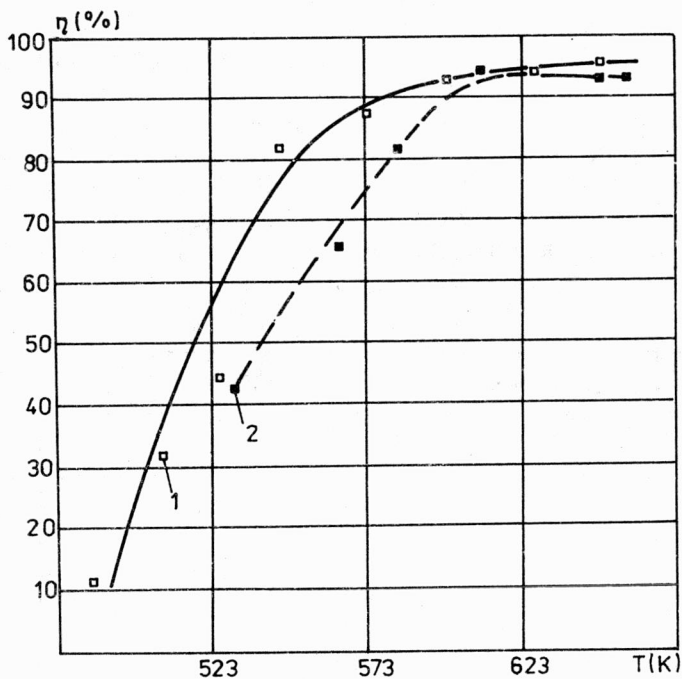


Fig. 7. Test combustion of xylene vapour in the presence of ZChO-85
1 - fresh, 2 - poisoned

Table 4

Initiation and extinction temperatures for ethanol vapour combustion

Catalyst	Initiation temperature (K)		Extinction temperature (K)	
	Fresh catalyst	Poisoned catalyst	Fresh catalyst	Poisoned catalyst
ZChO-80	387	404	387	410
ZChO-85	429	463	437	465
KP-910	438	443	-	-

The ZChO-85 contact (with an active ingredient which is one third that of ZChO-80) displays not only a reduction in the reduction in the specific surface of platinum, but also a decrease in activity during test combustion of xylene vapours below 610 K (fig. 7). In the presence of ZChO-85, there is a rise in the initiation temperature for the combustion of ethanol vapours (when measurements are carried out by differential thermal analysis) from 429 K for a fresh contact to 463 K for a poisoned contact. Exposure to chlorine compounds has a marked negative influence on the kinetic parameters of the catalyst and accounts for the rise in activation energy. Hot air drive at about 650 K enables full regeneration of the contact. No losses in the active ingredient have been recorded.

The KP-910 catalyst (with an active ingredient amounting to two thirds that of ZChO-80) does not only show an oxidation activity with respect to the chlororganic mixture, but is also resistant to the destructive influence of chlorine compounds. Such a behaviour has been clearly demonstrated in laboratory tests involving combustion of toluene, benzene and ethanol vapours (figs. 8, 9). Only a slight deterioration of catalyst in the case of toluene and benzene oxidation in the lower temperature range (with conversion below 90%) was observed. During combustion of ethanol at temperatures above 600 K there was even

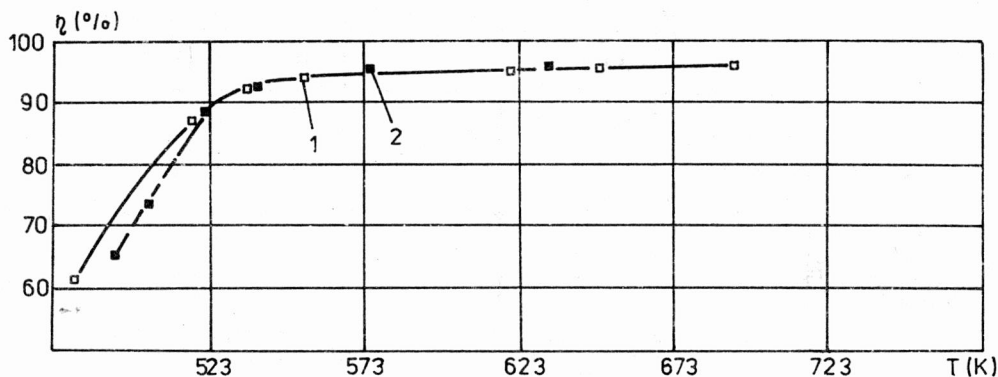


Fig. 8. Test combustion of toluene vapour in the presence of KP-910
1 - fresh, 2 - poisoned

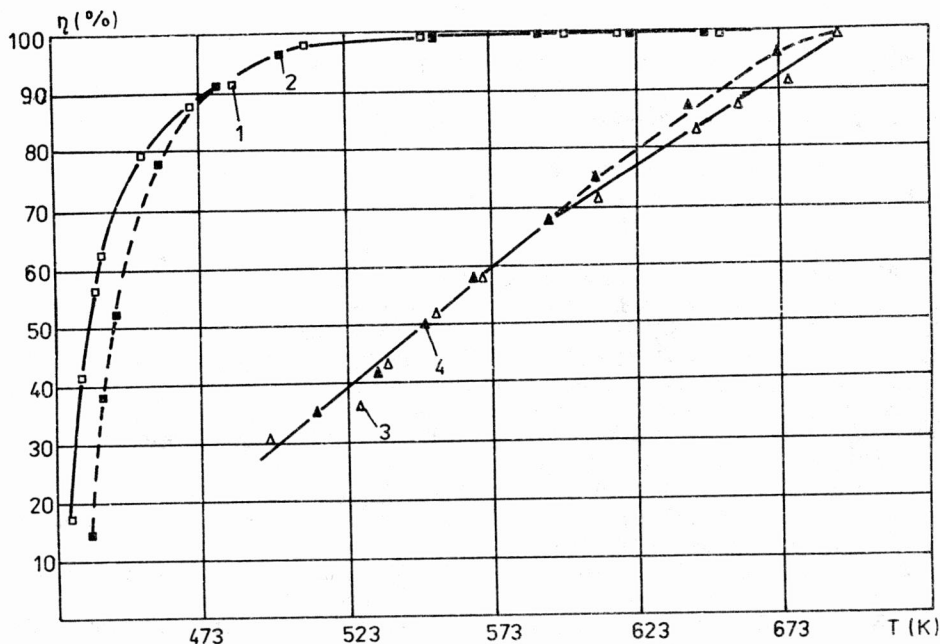


Fig. 9. Test combustion of benzene vapour in the presence of KP-910

1 - fresh, 2 - poisoned

Test combustion of ethanol vapour in the presence of KP-910

3 - fresh, 4 - poisoned

a slight increase in catalyst activity. The resistance of KP-910 to the influence of chlorine compounds has been additionally substantiated by differential thermal analysis. The initiation temperature for ethanol oxidation is practically the same whether for a fresh or deactivated KP-910.

4. SUMMARY AND CONCLUSIONS

1. Flue gases carrying chlororganic compounds can be treated by catalytic methods in the presence of platinum contacts. Apart from determining the optimum operating parameters of the contacts, it is necessary to assess the deactivation of the catalyst as a result of exposure to chlorine compounds.

2. To achieve a satisfactory conversion of the chlororganics carried by the flue gas stream, the catalyst to be applied should contain at least 0.1 wt.% of platinum.

3. Catalysts with 0.05 wt.% platinum content are effective only if the chlororganic compounds are combusted in the presence of hydrocarbon. Routine regeneration of the contact via hot air drive is also necessary.

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DEZAKTYWACJA KATALIZATORÓW PODCZAS SPALANIA WIELOSŁADNIKOWEJ MIESZANINY POŁĄCZEŃ CHLOROORGANICZNYCH

Celem pracy była selekcja katalizatorów służących do unieszkodliwienia gazów odlotowych powstających w zakładach produkujących epichlorohydrinę. Mieszaninę symulującą gazy odlotowe i zawierającą propylen oraz wiele połączeń chloroorganicznych spalano w obecności trzech katalizatorów o różnej zawartości platyny (0,15, 0,10 i 0,05% wag). Badania prowadzono w taki sposób, aby ustalić optymalne parametry pracy katalizatorów oraz określić ich odporność na zatrucia połączeniami chloru. Pozytywne rezultaty otrzymano dla katalizatorów o zawartości platyny 0,15 i 0,10% wag.

ДЕЗАКТИВАЦИЯ КАТАЛИЗАТОРОВ ВО ВРЕМЯ СГОРАНИЯ МНОГОКОМПОНЕНТНОЙ СМЕСИ ХЛОРООРГАНИЧЕСКИХ СОЕДИНЕНИЙ

Целью работы был отбор кatalизаторов, служащих обезвреживанию отходящих газов, образующихся на заводах, производящих эпихлоридрин. Смесь, имитирующую отходящие газы и содержащую пропилен, а также многие хлороорганические соединения, сжигали в присутствии трех кatalизаторов разного содержания платины (0,15, 0,10 и 0,05% веса). Исследования вели таким образом, чтобы установить оптимальные параметры действия кatalизаторов и определить их прочность к отравлению соединениями хлора. Положительные результаты были получены для кatalизаторов содержания платины 0,15 и 0,10% веса.