

BOŻENA MENDYKA*, KRYSZYNA SYCZEWSKA*

OXIDATION OF A MODEL MIXTURE CONTAINING TRICHLOROETHYLENE AND XYLENE OVER A Pt-O CATALYST

The objective was to determine the usability of the catalytic method as applied to the oxidation of chlororganic compounds over a Pt-O catalyst with a 0.15% platinum ingredient. The catalyst has been used so far with success to the combustion of typical organic pollutants. The investigations reported in this paper substantiate the possibility of oxidizing chlororganic compounds in a mixture with hydrocarbons over the 0.15% Pt-O catalyst. Good results have been achieved at high space velocities and high chlororganic compound concentration.

1. INTRODUCTION

The rapid development of the chemical industry in the past few years has brought about a drastic deterioration of air quality in many countries of the world. Air pollution is a complex phenomenon. It involves gaseous as well as particulate pollutants both organic and inorganic. Among these, organic substances in general and chlororganic compounds in particular have recently become a matter of serious concern. British data recorded in 1970 to 1975 show that the annual increase of halogen emissions averages somewhat higher than 15%. This brings about an approximately 13% rise in the total concentration of atmospheric halogens [1]. On the other hand, organic and chlororganic compounds released into the ambient air account for serious threats to human health and life. It is, therefore, necessary to take such preventive measures that would enable effective degradation of the compounds under study.

Pollution loads emitted by modern industries generally include a great variety of substances. In such a mixture, chlororganic complexes occur in a combination

* Institute of Environment Protection Engineering, Technical University of Wrocław, pl. Grunwaldzki 9, 50-377 Wrocław, Poland.

with hydrocarbons, alcohols and many other compounds [2]–[5], and catalytic oxidation is the most reasonable method of degradation. The utility 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 reaction. Catalytic oxidation usually proceeds over platinum contacts which remain active at much lower temperatures than metal oxide catalysts do. Platinum contacts, furthermore, are resistant to poisoning (e.g., with chlorine compounds), have a longer life and are able to withstand short cycles of overheating.

The oxidation of chlororganic complexes over metal oxide catalysts was reported by many investigators [6]–[9]. They found that in the initial stage of performing their duty, catalysts of that type exhibit a quite good activity, which decreases rapidly with time. The aging of the contacts is caused by loss of the active ingredient and deterioration of some other properties of the catalyst.

A detailed account of relevant literature showed that catalytic methods involving catalysts with platinum ingredients between 0.6 and 1.5% were best suited for the oxidation of chlororganic compounds [2], [5], [10]–[12]. The objective of this study was to check the efficiency of a 0.15% Pt catalyst as applied to the decomposition of chlororganics. The same contact proved to be applicable to the degradation of typical organic pollutants.

There are three major factors governing the reaction of catalytic oxidation – the composition of the reaction mixture, the concentrations of particular components and the type of catalyst involved. Good catalysts have a long life with no loss of activity.

2. EXPERIMENTAL

The experiments were carried out with a Pt–O catalyst manufactured by the Chemical Plant of Oświęcim. Owing to a 0.15% platinum ingredient, the catalyst proved very efficient when applied to the combustion of various organic compounds, yielding high degrees of conversion with regard to methyl alcohol, n-butyl acetate, amyl, formaldehyde, phenol, toluene, xylene, benzene, acetone, ethyl formate, ethyl alcohol and ethyl acetate [13]–[14]. The experimental catalyst was also found to be resistant to poisoning from sulphur compounds [15].

Chlororganic compounds contained in industrial gases occur in a combination with a number of chemical substances, specifically with hydrocarbons or their derivatives. That is why the investigation of the catalyst activity in the combustion of chlororganics made use of a model mixture containing trichloroethylene (chlororganic compound) and xylene (hydrocarbon). The effect of temperature, space velocity and concentrations of the two pollutants on the activity and the working parameters of the catalyst were also studied.

The model mixture was oxidized in a through-flow reactor involving a given amount of the catalyst tested. The combustion process yielded the following products: carbon dioxide, water and hydrogen chloride. Since it was expected that chlorine might be found among the reaction products, hydrogen chloride and chlorine concentrations were also measured in the course of the process.

The experimental temperature varied from 470 to 830 K. The effect of space velocity on the catalyst activity involved four values, $10,000 \text{ h}^{-1}$, $30,000 \text{ h}^{-1}$, $60,000 \text{ h}^{-1}$, and $80,000 \text{ h}^{-1}$, and was investigated for two mixtures: I) trichloroethylene (4 mg/dm^3) and xylene (2 mg/dm^3), II) trichloroethylene (2 mg/dm^3) and xylene (4 mg/dm^3). To determine the effect of xylene concentration on the degree of combustion of trichloroethylene, an experimental series was carried out with 16 mixtures where trichloroethylene concentration was kept constant throughout the run at one of the three levels: 2, 4 or 8 mg/dm^3 , and xylene concentration was varied from 0 to 8 mg/dm^3 . The effect of trichloroethylene on the combustion of xylene was studied for mixtures with constant xylene concentration (2, 4 or 8 mg/dm^3) at different concentrations of trichloroethylene (0 to 8 mg/dm^3).

To determine the effect of water, as well as the quantity and chemical nature of the carbon included in the hydrocarbon particle, eight mixtures were tested; they contained trichloroethylene in a combination with xylene, toluene, benzene, octane, heptane, hexane, cyclohexane and water, respectively. Since it seemed worthwhile to investigate the effect of the chlorine contained in the halogen compound on the efficiency of its combustion, three more mixtures were prepared. These consisted of chlorobenzene and xylene; carbon tetrachloride and xylene, and trichloroethylene and xylene, respectively.

3. RESULTS AND DISCUSSION

The relationship between space velocity and catalytic activity is given in figs. 1 and 2. As shown by these plots, trichloroethylene (tri) displays a greater resistance to combustion than xylene, whenever the concentration of the chlororganic is higher than that of the hydrocarbon, irrespective of the space velocity value (mixture I). It is worth noting that the oxidation efficiency of interest, which amounts to 90%, is achieved at space velocities of $10,000$ and $30,000 \text{ h}^{-1}$, and drops markedly for both components of the mixture at $60,000$ and $80,000 \text{ h}^{-1}$. Mixture II, where the concentration of trichloroethylene is lower than that of xylene, shows a greater proneness to oxidation, and a similar space velocity effect. Thus, the conversion of interest, i.e., 90%, is obtained at $10,000$ and $30,000 \text{ h}^{-1}$, but at respectively lower temperatures than in the case of mixture I. At these two space velocities trichloroethylene shows a greater ease to undergo combustion than xylene. The experimental Pt-O catalyst displays a good activity at relatively high space velocities ($30,000 \text{ h}^{-1}$) when the concentration of the chlororganic com-

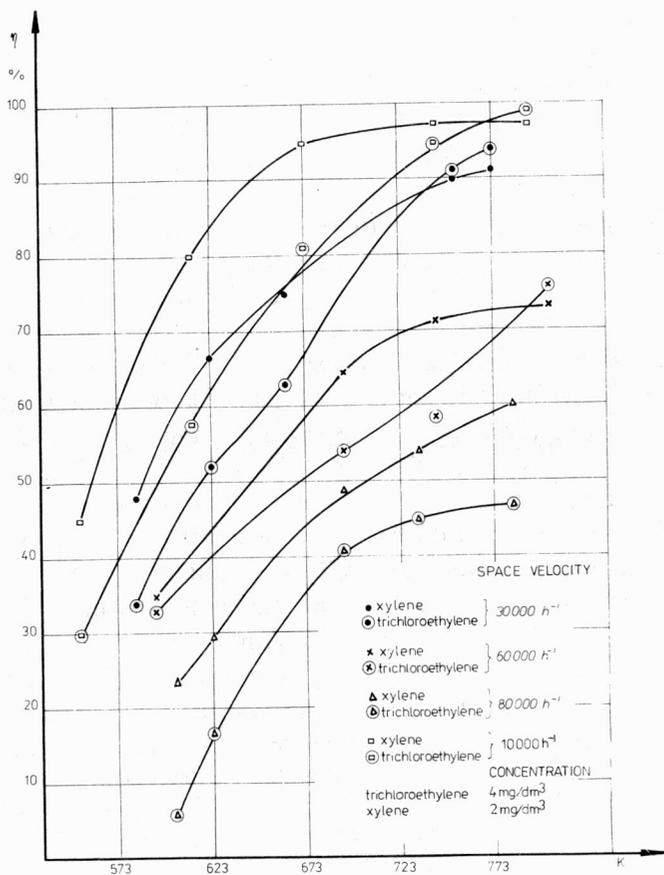


Fig. 1. Efficiency of Pt-O catalyst in oxidizing a trichloroethylene (tri) and xylene mixture in ambient air as a function of space velocity

pound in the mixture is either high or low, and that of the hydrocarbon is high.

In the absence of other compounds, trichloroethylene is resistant to oxidation (figs. 3-5). The degree of conversion never approached 90% in the temperature range applied. The resistance of trichloroethylene to oxidation increases with the concentration of this compound in the mixture. Increasing the xylene content leads to a substantial improvement of the trichloroethylene combustion. When the concentration of trichloroethylene is kept on the constant level of 2 mg/dm³, the addition of xylene at amount of 1 mg/dm³ makes the temperature required for a 50% conversion of trichloroethylene be decreased by 120 degrees. To achieve a combustion efficiency of 90%, a temperature of 743 K is necessary. Increasing the xylene content in the mixture to 8 mg/dm³ enables this temperature to be decreased by 90 degrees (fig. 3).

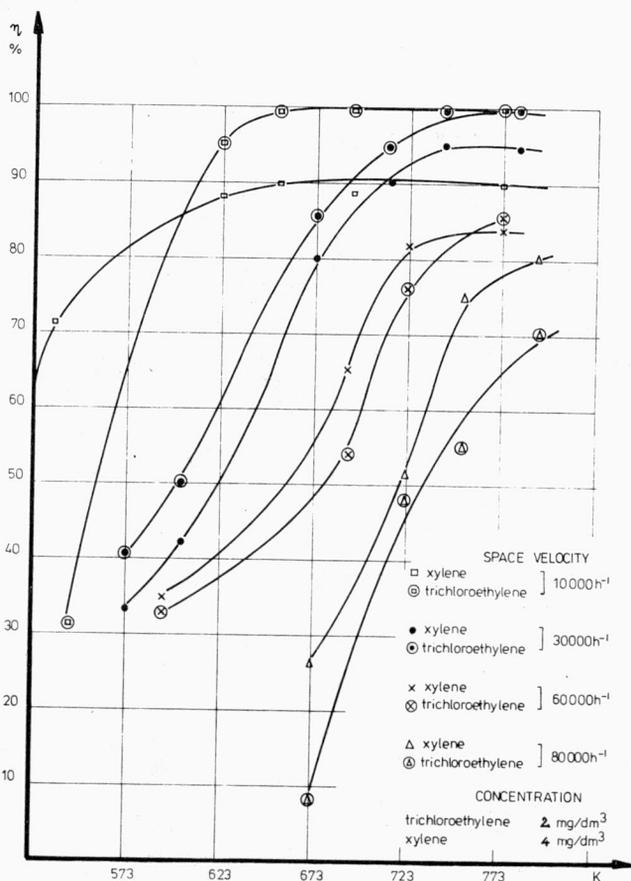


Fig. 2. Efficiency of Pt-O catalyst in oxidizing a trichloroethylene (tri) and xylene mixture in ambient air as a function of space velocity

Experimental mixtures of increased trichloroethylene content are more resistant to oxidation (figs. 4 and 5). Thus, when the trichloroethylene dose amounts to 8 mg/dm^3 and the temperature range is low, no oxidation occurs even at increased xylene concentration. Increasing the reaction temperature to 773 K (the maximum point of the investigated range) yields a degree of conversion of 83% for xylene concentration of 8 mg/dm^3 .

The plots of figs. 6-8 show that the temperature required to a 90% conversion of xylene alone (occurring in a wide range of concentrations) approaches 600 K (573 , 608 , and 613 K for 2 , 4 and 8 mg/dm^3 doses, respectively). Addition of trichloroethylene (even as low as 1 mg/dm^3) decreases the degree of xylene conversion to a level of 55 to 65% in the same temperature range. In the experimental mixture, where xylene concentration was kept at 8 mg/dm^3 , the

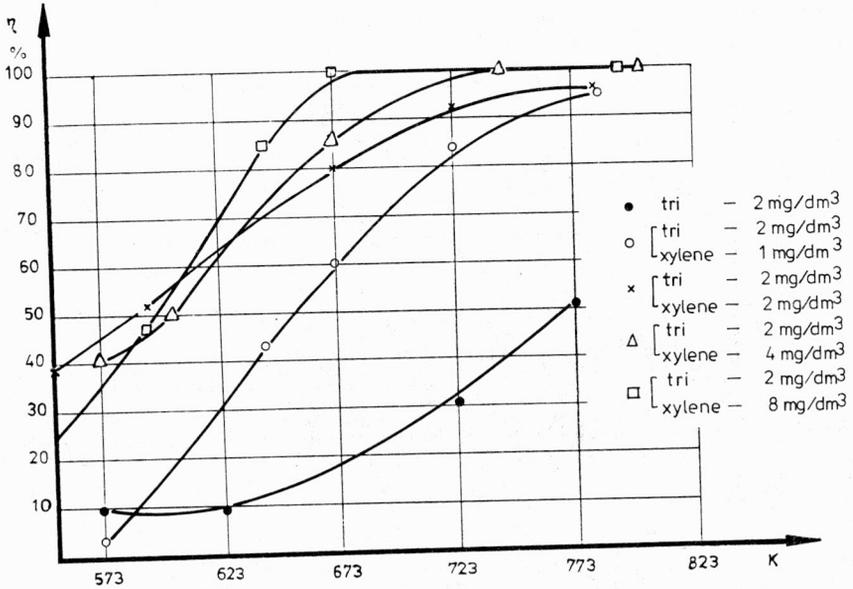


Fig. 3. Efficiency of Pt-O catalyst in oxidizing trichloroethylene (tri) of a constant concentration (2 mg/dm^3) as a function of a variable concentration of xylene in the mixture

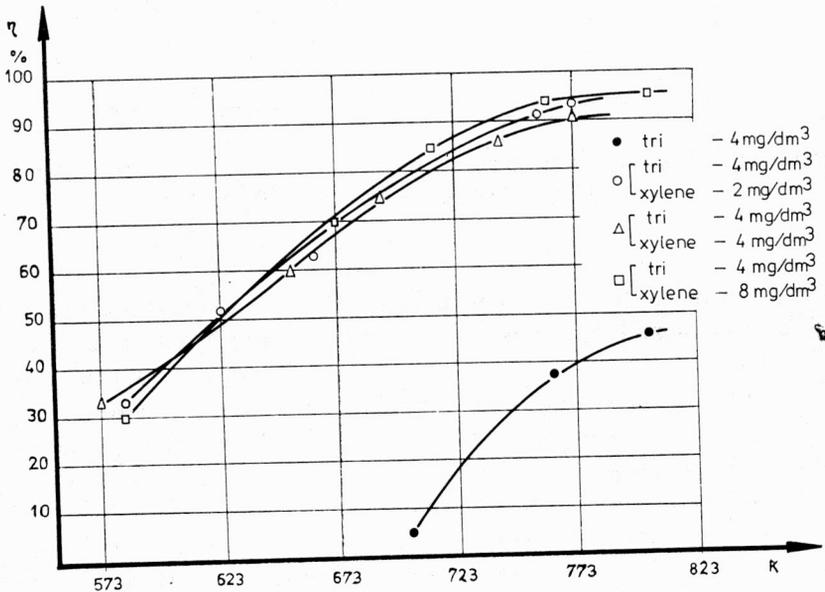


Fig. 4. Efficiency of Pt-O catalyst in oxidizing trichloroethylene (tri) of a constant concentration (4 mg/dm^3) as a function of a variable concentration of xylene in the mixture

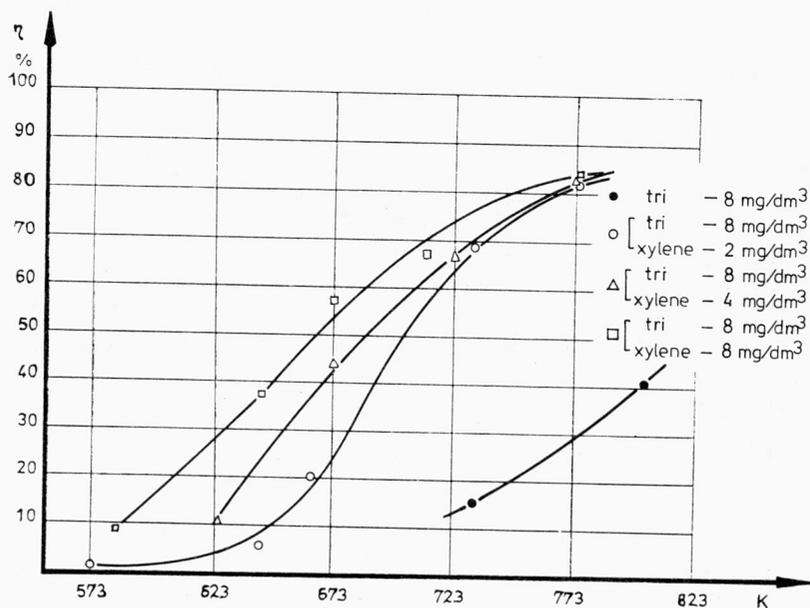


Fig. 5. Efficiency of Pt-O catalyst in oxidizing trichloroethylene (tri) of a constant concentration (8 mg/dm³) as a function of a variable concentration of xylene in the mixture

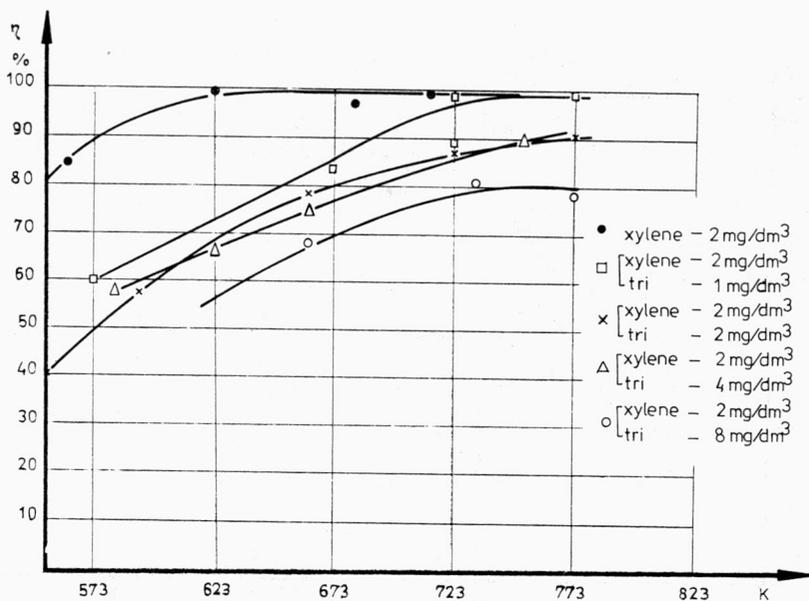


Fig. 6. Efficiency of Pt-O catalyst in oxidizing xylene of a constant concentration (2 mg/dm³) as a function of a variable concentration of trichloroethylene (tri) in the mixture

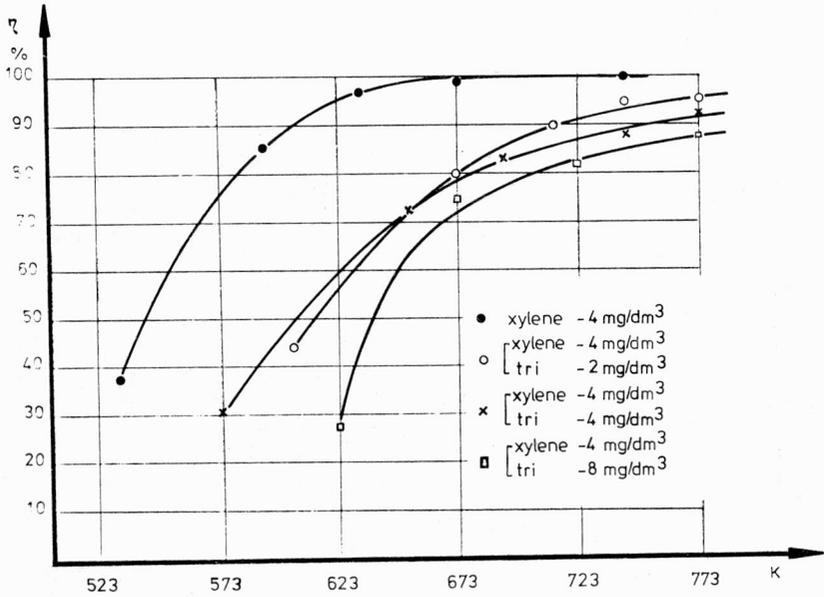


Fig. 7. Efficiency of Pt-O catalyst in oxidizing xylene of a constant concentration (4 mg/dm³) as a function of a variable concentration of trichloroethylene (tri) in the mixture

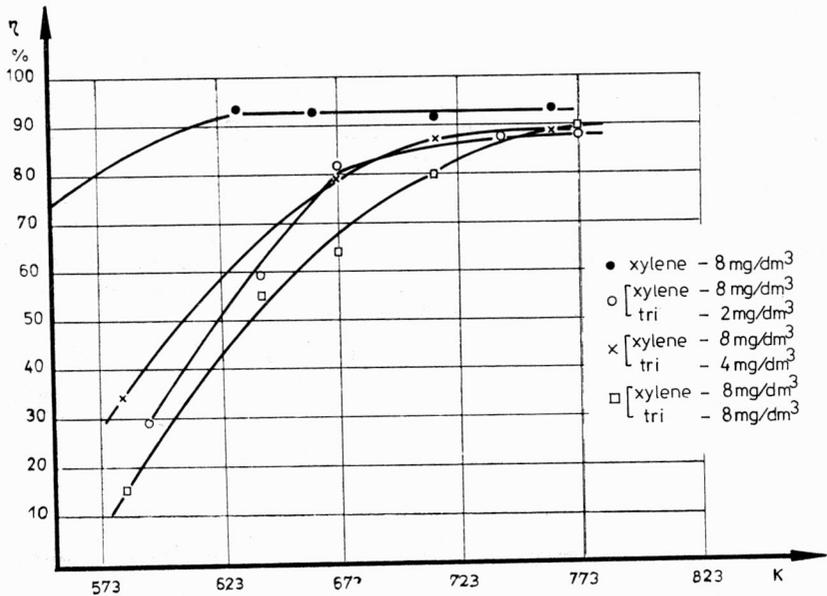


Fig. 8. Efficiency of Pt-O catalyst in oxidizing xylene of a constant concentration (8 mg/dm³) as a function of a variable concentration of trichloroethylene (tri) in the mixture

presence of trichloroethylene accounted for the drop of the oxidation efficiency to about 45%. The required 90% degree of conversion for xylene is achieved at temperatures higher by over 100 degrees even at low trichloroethylene concentrations. Trichloroethylene doses of 8 mg/dm³ fail to yield 90% conversion of xylene, especially when applied to mixtures where xylene is kept at the 2 mg/dm³ level. Increasing the xylene content to 4 mg/dm³ accounts for a considerable improvement of the degree of conversion, even if the concentration of trichloroethylene in the mixture is as high as 8 mg/dm³.

Analysis of the chlorine quantity produced during trichloroethylene and xylene combustion over a Pt-O catalyst substantiates the contribution of xylene concentration. Thus, as the xylene content in the mixture increases, the quantity of chlorine produced decreases. When xylene occurs in excess, no chlorine is formed during combustion (tab. 1).

Table 1

Chlorine produced during oxidation of the mixture wherein trichloroethylene occurred at constant concentration (2 mg/dm³), the concentration of xylene ranging from 1 to 8 mg/dm³

Xylene concentration, mg/dm ³							
1		2		4		8	
Temperature K	Chlorine concentration mg/dm ³	Temperature K	Chlorine concentration mg/dm ³	Temperature K	Chlorine concentration mg/dm ³	Temperature K	Chlorine concentration mg/dm ³
723	0.035	723	0.022	743	0.004		
773	0.042	773	0.047	783	0.018		Absent

The temperature at which chlorine is generated depends on the xylene concentration, and increases with the increasing xylene content in the mixture. In fact, chlorine appears at temperatures higher than those at which the conversion of trichloroethylene amounts to 90%. When trichloroethylene occurs at concentrations higher than those of xylene, the quantity of chlorine formed is not influenced by the trichloroethylene content in the mixture (tab. 2). Chlorine appears at temperatures lower than those required to achieve a 90% conversion of trichloroethylene. The HCl level measured after passage through the reactor is inconsistent with the calculated values. This is an indication that HCl may be adsorbed on the catalyst surface.

The experiments show that water has no significant effect on the degree of trichloroethylene combustion (tab. 3). In the presence of water vapour the degree of oxidation is almost the same as that achieved in the combination with air.

Table 2

Chlorine produced during oxidation of the mixture wherein xylene occurred at constant concentration (2 mg/dm³), the concentration of trichloroethylene varying from 1 to 8 mg/dm³

Trichloroethylene, mg/dm ³							
1		2		4		8	
Temperature K	Chlorine concentration mg/dm ³	Temperature K	Chlorine concentration mg/dm ³	Temperature K	Chlorine concentration mg/dm ³	Temperature K	Chlorine concentration mg/dm ³
723	0.005	723	0.022	753	0.021	733	0.019
773	0.025	773	0.047	773	0.042	773	0.040

Water generated during combustion of the hydrocarbon may act as a desorber of HCl from the catalyst.

The degree of combustion of the chlororganic compound is strongly influenced by the type of hydrocarbon applied (tab. 3). When the carbon content in the hydrocarbon particle increases (for the given homological series), so does the conversion of the hydrocarbon. There is also a strong relationship between the conversion of the chlororganic compounds and the chemical activity of the hydrocarbon. Thus, in the presence of inactive paraffins (which are resistant to the influence of other substances) the combustion of trichloroethylene is less efficient than in the presence of aromatic hydrocarbons.

The proneness of chlororganics contained in a mixture to oxidation increases with the decreasing number of chlorine atoms included in the particle. Of the investigated mixtures that consisting of xylene and chlorobenzene shows the greatest ease to undergo oxidation because of the advantageous ratio of chlorine atoms to carbon atoms which is 1 to 6 (tab. 4).

On the basis of the experimental results the following generalizations can be made:

1. Pt-O catalyst (with a 0.15% noble metal ingredient) may be successfully applied to the oxidation of mixtures containing high concentrations of a chlororganic compound (e.g., 8 mg/dm³) without loss of activity even at relatively high space velocities (30,000 h⁻¹).

2. During an operation of about 5000 hours, the Pt-O catalyst did not experience poisoning with HCl and Cl₂ which were formed in the course of the oxidation reaction.

3. The composition of the mixture to be treated has a substantial effect on the degree of oxidation. The combustion of the chlororganic compound itself is poor. Combined with a hydrocarbon (even with a small portion), the chlororganic substance oxidizes much easier. Although the presence of a chlorine compound

Table 3

Efficiency of trichloroethylene oxidation in a mixture with hydrocarbons and water (Pt-0 catalyst; catalyst temperature, 773 K; space velocity, 30,000 h⁻¹; trichloroethylene (tri) concentration, 2 mg/dm³; hydrocarbon concentration, 2 mg/dm³)

Aromatic hydrocarbons	Degree of conversion %	Paraffin hydrocarbons	Degree of conversion %	Cyclic hydrocarbons	Degree of conversion %
trichloroethylene	92.3	trichloroethylene	87.3	trichloroethylene	57.0
xylene	95.7	octane	89.2	cyclohexane	64.0
trichloroethylene	90.0	trichloroethylene	54.0	trichloroethylene	50.0
toluene	78.0	heptane	68.0	water	
trichloroethylene	65.0	trichloroethylene	48.5		
benzene	70.0	hexane	61.2		

Table 4

Efficiency of xylene oxidation in a mixture with chlororganic compounds as a function of chlorine content in the particle and concentration of chlororganics (2 mg/dm³) and xylene (1 mg/dm³) (Pt-O catalyst; catalyst temperature, 723 K; space velocity, 30,000 h⁻¹)

Mixture	Degree of conversion, %	
	Chlororganic compound	Xylene
chlorobenzene + xylene	91	93
trichloroethylene + xylene	81	86
carbon tetrachloride + xylene	65	69

exerts an unfavourable influence on the efficiency of xylene oxidation, the experiments show that a 90% conversion may be achieved even at very high concentrations of trichloroethylene.

4. 90% conversion may be achieved when the following requirements are fulfilled: a) at a space velocity of 30,000 h⁻¹, a trichloroethylene concentration of 2 mg/dm³ in the reaction mixture, and at 773 K, the addition of xylene should amount to at least 0.7 mg/dm³; for higher xylene concentrations, 2 mg/dm³ and 4 mg/dm³, temperature should be decreased to 723 K and 713 K, respectively; applying a space velocity of 10,000 h⁻¹ enables the process temperature to be decreased by 60 degrees; b) at trichloroethylene concentrations higher than

4 mg/dm³ and at an appropriate hydrocarbon content in the mixture, temperature should be higher than 773 K; xylene content should amount to 1.75 mg/dm³ and 8 mg/dm³ for trichloroethylene concentrations of 4 mg/dm³ and 8 mg/dm³, respectively.

5. Trichloroethylene has a relatively great number of chlorine atoms included in the particle. It may be expected that chlororganic compounds with a smaller number of chlorine atoms in their particles will oxidize easier and at significantly lower temperatures. The combustion of such compounds may also be carried out over catalysts with a lower Pt content.

4. CONCLUSION

The method of catalytic combustion may be successfully applied to the degradation of chlororganic compounds in a mixture with hydrocarbons. The 0.15% Pt-O catalyst — which is now widely used on an industrial scale for the oxidation of a variety of organic compounds — proved to be equally successful as applied to the combustion of chlororganics in a combination with hydrocarbons.

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**BADANIE DOPALANIA MODELOWEJ MIESZANINY
TRÓJCHLOROETYLEN-KSYLEN NA PLATYNOWYM KATALIZATORZE Pt-O**

Celem badań było sprawdzenie, czy metoda katalitycznego spalania związków chloroorganicznych na katalizatorze Pt-O, zawierającym 0,15% platyny i stosowanym do dopalania typowych zanieczyszczeń organicznych, może być stosowana. Stwierdzono, że katalizator platynowy może być wykorzystany do spalania mieszaniny związków chloroorganicznych z węglowodorami. Dobre rezultaty uzyskano dla dużych obciążeń katalizatora oraz dużych stężeń związku chloroorganicznego.

**ИССЛЕДОВАНИЯ ДОЖИГАНИЯ МОДЕЛЬНОЙ СМЕСИ ТРИХЛОРЭТИЛЕН-КСИЛОЛ
НА ПЛАТИНОВОМ КАТАЛИЗАТОРЕ Pt-O**

Целью исследований была проверка, может ли применяться метод каталитического сжигания хлорорганических соединений на катализаторе Pt-O, содержащим 0,15% платины и применяемым для дожигания типичных органических загрязнений. Было отмечено, что платиновый катализатор может быть использован для сжигания смеси хлорорганических соединений с углеводородами. Хорошие результаты были получены для больших нагрузок катализатора, а также высоких концентраций хлорорганического соединения.