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EFFECT OF SULFUR AND CHLORINE COMPOUNDS ON THE ACTIVITY OF PLATINUM CATALYSTS

The effects of sulfur and chlorine compounds on the activity of platinum catalysts (of contents of platinum from 0.05 to 0.15 wt. %) were investigated. The degree of poisoning was estimated by comparing the activities of fresh catalysts with those obtained after poisoning during combustion of xylene vapours and n-heptane. It has been found that, when the platinum contents in the catalysts decrease, their activities during combustion of organic air pollutants also become lower. The presence of sulfur dioxide has no significant influence on the efficiency of hydrocarbon oxidation. The presence of chlorine compounds causes deactivation of the catalysts.

1. INTRODUCTION

During the past few years we have been working on the preparation of platinum catalysts of high activity in order to provide an effective removal of gaseous organic pollutants from industrial flue gases. As a result, 0.15% platinum catalysts based on γ - Al_2O_3 drawpieces are being manufactured under the brand name ZChO-80 according to the formulae developed by our research team. Catalysts of that type have been used for many years in industrial treatment systems for flue gases coming from the oxidation of asphalt, fat splitting, and manufacture of plastics.

The mentioned investigations aim at preparing catalysts of lower, i.e., 0.1 and 0.05%, platinum contents. To obtain as much information as possible, the catalysts were tested for activity not only during combustion of a number of organic compounds differing in chemical structure, but they were exposed to sulfur and chlorine compounds which are generally regarded as catalyst poisons.

The catalysts, that are now in use for the treatment of industrial gases containing sulfur- or chloroorganic compounds, have active ingredients (predominantly platinum) varying from 0.5 to 1.5% [1]-[3]. HEGEDUS and SUMMERS [4] show that the

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catalyst resistance to poisoning depends not only on the amount of the active ingredient, but also on the method of deposition, and usually increases with the thickness of the impregnated layer. Catalysts resistant to poisoning with sulfur compounds are widely used for the post-combustion of automobile emissions. It is conventional to use either platinum or palladium contacts for this purpose. Palladium catalysts are less resistant to poisoning with sulfur compounds [5]. TAYLOR found that the presence of sulfur dioxide, even in concentration as low as 0.03%, brought about a considerable decrease in the efficiency of nitrogen oxide removal, as well as a small drop in the efficiency of carbon monoxide and hydrocarbons combustion [6]. Catalysts of AP-56 and IP-62 types manufactured in the Soviet Union are particularly resistant to poisoning with sulfur compounds. But this is to be attributed to the high platinum content which ranges between 0.5 to 0.64% [7].

Keeping all these in mind, it seemed worth-while to check whether catalysts of low platinum content would work efficiently in the presence of chlorine or sulfur compounds. The experiment involved three catalysts, ZChO-80, ZChO-85 0.1 and ZChO-85 0.05, containing 0.15%, 0.1% and 0.05% of platinum, respectively. Each of them was prepared by superficial impregnation of γ -Al₂O₃ drawpieces, which were about 4 mm in diameter and 5 to 22 mm long.

2. EFFECT OF SULFUR COMPOUNDS ON CATALYTIC ACTIVITY

2.1. SULFUR DIOXIDE

The activity of the three catalysts had been tested in an earlier study for the combustion of various organics, e.g., xylene, toluene, n-heptane or ethanol [8]. It was therefore interesting to investigate the effect of sulfur dioxide on the catalyst activity during combustion of two organic compounds differing in chemical structure, xylene and n-heptane. The choice of the two organics was additionally substantiated by the results reported by SADOWSKI [9] and LEVINE [10].

Each poisoning cycle involved a 2 cm³ portion of the catalyst tested and was carried out at 690 K for 50 h. A reaction mixture consisting of xylene or n-heptane and sulfur dioxide (each at the concentration of 1 mg/dm³) was passed through the catalyst. The activity of each contact was tested before and after the poisoning cycle by oxidizing xylene or n-heptane contained in the reaction mixture. Space velocity was constant and amounted to 30000 h⁻¹. Activity tests were conducted at temperatures ranging from 300 to 770 K. The results are plotted in figs. 1 and 2.

Fresh ZChO-80 catalyst (0.15% Pt) displayed the greatest activity, yielding 90% combustion efficiencies for xylene and n-heptane at 520 K and 598 K, respectively. Fresh ZChO-85 0.1 catalyst gave the same efficiencies at 593 K and 623 K,

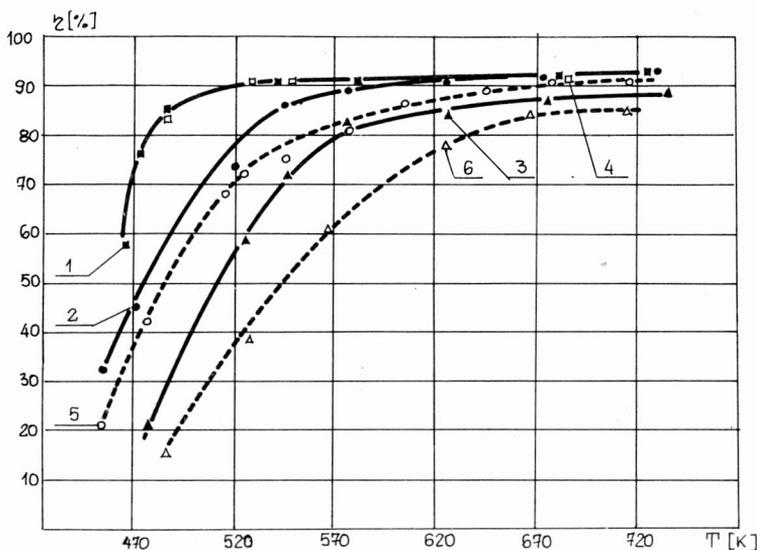


Fig. 1. Combustion efficiency η of xylene vapours over fresh catalysts and catalysts poisoned by sulfur dioxide versus reaction temperature T

	fresh catalyst	poisoned catalyst
ZChO-80	1	4
ZChO-85 0.1	2	5
ZChO-85 0.05	3	6

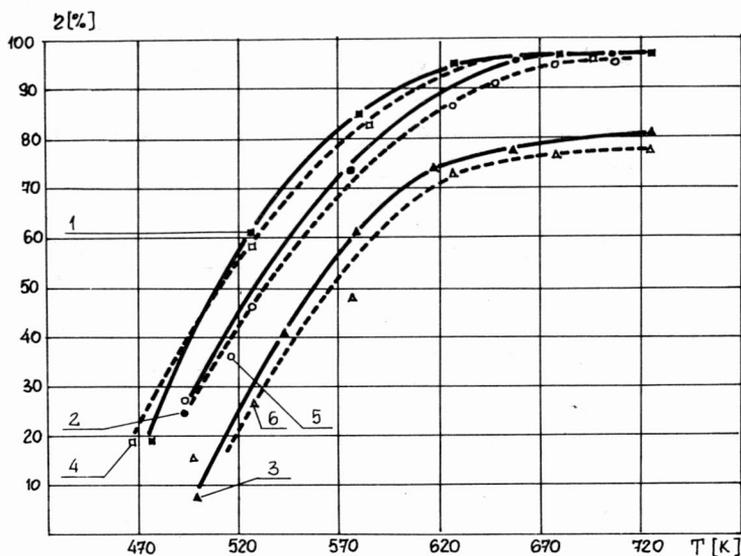


Fig. 2. Combustion efficiency η of n-heptane vapours over fresh catalysts and catalysts poisoned by sulfur dioxide versus reaction temperature T

For explanations see fig. 1

respectively. Fresh ZChO-85 0.05 catalyst failed to yield 90% efficiencies in the investigated temperature range.

ZChO-80 was found to be the most resistant to poisoning by sulfur dioxide, not only during combustion of xylene vapours, but also during oxidation of n-heptane. The results of the test reactions (combustion of the two compounds) following completion of the poisoning cycles only slightly differed from the results for fresh catalysts.

ZChO-85 0.1 and ZChO-85 0.05 displayed a slightly decreased activity during combustion of n-heptane after poisoning. The difference in the efficiency of combustion between fresh and poisoned ZChO-85 0.1 and ZChO-85 0.05 did not exceed 5% in the whole range of the investigated temperatures. The effect of sulfur dioxide on the decrease of oxidation efficiency was the greatest when xylene was combusted over ZChO-85 0.05. At lower experimental temperatures the decrease in combustion efficiency amounted to 20%. At temperatures higher than 625 K, it remained on a constant level of 5%. In the presence of ZChO-85 0.1, the drop in combustion efficiency reached as much as 10% after poisoning in the temperature range of 520 to 600 K.

The presence of sulfur dioxide in the reaction mixture was without any effect on the efficiency of xylene and n-heptane combustion. The variation of the combustion efficiency for the two hydrocarbons in the course of poisoning (for 50 h) never exceeded 5%.

2.2. SPECTRAL ANALYSIS OF POISONED CATALYSTS

To gain a better understanding of the nature of surface poisoning with sulfur compounds, the catalysts were subjected to instrumental analysis. A widespread method which makes it possible to identify the sorbed compound or the compound fixed to the catalyst surface is a spectral analysis in IR. It is worth remembering that if platinum catalysts involve γ -Al₂O₃ supports, there may occur fixation of sulfur with the support material, and the sorption of sulfur dioxide may be substantially hindered by the presence of platinum.

When oxide catalysts are used, sulfur can react both with the active ingredient and with the support to yield surface or bulk compounds which have a strong, inhibiting effect on the catalytic activity.

IR spectral analysis often reveals a surface adsorption of sulfur dioxide (identified in the 1360 cm⁻¹ band) which is desorbable almost completely under vacuum conditions in about 475 K, as well as the presence of sulfite groups (band 1040, 920 and 880 cm⁻¹) and surface or bulk sulfates (predominantly in bands 1200, 1140, 1050, 980 and below 650 cm⁻¹) [11].

The spectra of the catalysts (both fresh and poisoned with sulfur dioxide) are

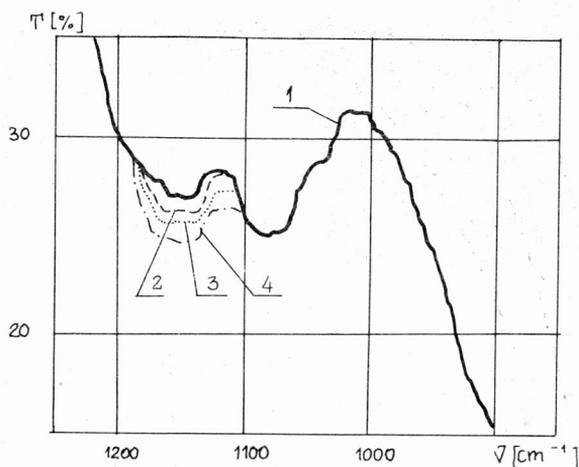


Fig. 3. IR spectral analysis for fresh catalysts (1) and catalysts poisoned by sulfur dioxide (2 — ZChO-80, 3 — ZChO-85 0.1, 4 — ZChO-85 0.05)

given in fig. 3. As shown by these data, the presence of sulfate structures is particularly distinct in band 1140 cm^{-1} . Variations are small and almost identical for all the contacts studied, irrespective of the platinum content.

3. EFFECT OF CHLORINE COMPOUNDS ON CATALYTIC ACTIVITY

Literature reports on activity loss usually refer to platinum catalysts exposed to chlorine compounds. Loss of catalytic activity occurs not only in the case of catalysts used for oxidizing a wide spectrum of solvents, but also in the case of catalysts used for automotive waste gases control, when they are exposed to halogen compounds [3].

In industrial gases chlorine appears in many different forms. It may occur as free chlorine or free hydrogen chloride, but it may also combine with organics to form chloroorganic compounds. The effect of chlorine compounds on the catalytic activity was investigated by the combustion of mixtures containing chlorobenzene or trichloroethylene (TRI) in a combination with toluene, benzene, and cyclohexane. The concentration of each component approached 1 mg/dm^3 . The chloroorganic compounds under study differ not only in chemical composition but also in the number of chlorine atoms in the molecule. It should be noted that the combustion of those compounds yields hydrogen chloride as the main chlorine-containing product. Hence, the deactivation of the catalyst may be attributed both to the presence of the chloroorganic compound and to the presence of hydrogen chloride produced during combustion. The activities of fresh and poisoned (by exposure to chlorine compounds) catalysts were tested in the reaction of xylene combustion. The portion of the

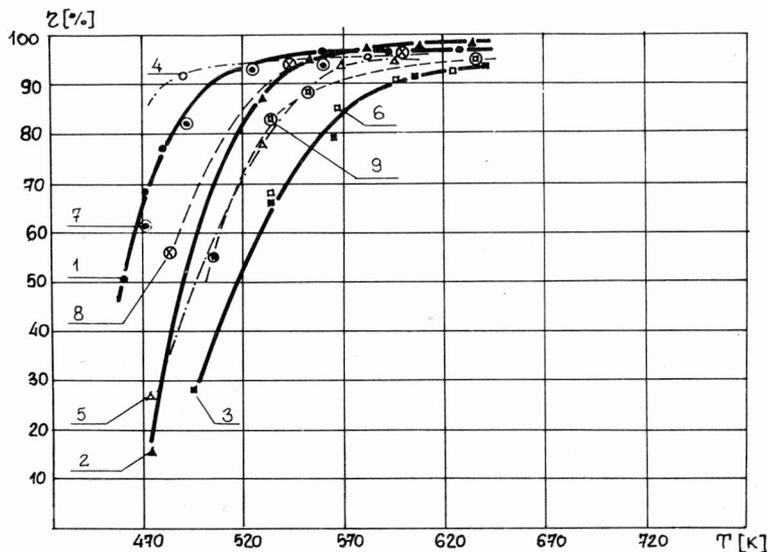


Fig. 4. Combustion efficiency η of xylene vapours over fresh catalysts and catalysts poisoned by chloroorganic compounds versus reaction temperature T

	fresh catalyst	catalyst poisoned by	
		TRI	chlorobenzene
ZChO-80	1	4	7
ZChO-85 0.1	2	5	8
ZChO-85 0.05	3	6	9

catalyst for each test reaction amounted to 20 cm^3 . The reaction was carried out at a xylene concentration of 1 mg/dm^3 , a space velocity of 10000 h^{-1} , and a temperature of 460 to 670 K. The combustion of mixtures containing chloroorganic compounds was carried out at the same space velocity and temperatures. The results of xylene oxidation test for fresh and poisoned catalysts are shown in fig. 4.

As mentioned earlier, the oxidation of xylene was conducted at a space velocity of 10000 h^{-1} . The decrease from 30000 to 10000 h^{-1} brought about a slight increase of the reaction efficiency over the most active catalyst, ZChO-80. A 90% oxidation was achieved at 513 K. The increase in the reaction efficiency was more pronounced for the two catalysts with lower platinum content. Thus, a 90% oxidation over ZChO-85 0.1 and ZChO-85 0.05 was obtained at 538 K and 600 K, respectively. The test reactions of xylene combustion, which were conducted after the combustion cycles for chloroorganics containing mixtures had been completed, revealed no significant changes in the activity of the catalysts tested.

During combustion of the investigated mixtures (containing toluene, benzene, cyclohexane and TRI or chlorobenzene vapours) the catalysts followed a different behavioural pattern (table). The results in table give support to the relationship of catalytic activity with the active ingredient. The highest efficiencies are those obtained over catalyst ZChO-80 under almost all reaction conditions. The presence

Table

Combustion efficiencies for each component of hydrocarbon mixtures and for the same mixtures with chlorobenzene or TRI added

Compound**	Catalyst*								
	ZChO-80			ZChO-85 0.1			ZChO-85 0.05		
	Combustion efficiency, %								
	573 K	673 K	723 K	573 K	673 K	723 K	573 K	673 K	723 K
cyclohexane	77	90	90	51	76	81	18	65	59
benzene	96	97	97	94	96	97	71	85	85
toluene	96	97	98	96	98	98	90	95	95
cyclohexane	12	45	66	12	20	53	0	27	31
benzene	67	94	95	49	80	91	22	59	62
toluene	88	97	97	90	96	96	77	91	93
chlorobenzene	60	91	94	30	87	93	15	65	77
cyclohexane	0	39	58	20	9	36	5	6	18
benzene	36	77	85	33	56	67	20	45	53
toluene	81	93	95	84	95	96	59	86	90
TRI	21	61	73	10	42	62	10	55	69

* Space velocity, 10000 h^{-1} .

** Concentration of each compound, 1 mg/dm^3 .

of chlorobenzene or TRI in the reaction mixture shows that the greater is the number of chlorine atoms in the organic compound, the more inhibited is the combustion of the remaining hydrocarbons. This relation is more pronounced with the decreasing platinum content. Deactivation is reversible and is likely to be attributed to the adsorption of hydrochloric acid (the product of chloroorganic combustion). This is indicated by the similar results of xylene oxidation over fresh catalysts and those exposed to chloroorganic compounds.

4. SUMMARY

The results substantiate the relationship between catalytic activity and the content of the active ingredient. The lowest efficiencies of oxidation have been achieved over the catalyst with the lowest platinum content. The same relationship is valid for catalysts exposed to sulfur and chlorine compounds.

The deactivation of catalysts exposed to chlorine compounds and sulfur dioxide runs in a different manner. The presence of sulfur dioxide has no inhibiting effect on the combustion of hydrocarbons. However, when sulfur dioxide is removed from the

reaction mixture, the catalytic activity slightly decreases, especially in the case of contacts of the low platinum content. The presence of chlorine compounds in the reaction mixture brings about a deactivation of the catalysts. This shortcoming may easily be eliminated by removing the chlorine compounds from the mixture. As soon as this is done, the catalyst activity recovers its initial value.

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REFERENCES

- [1] BOND G. C., SADEGHI N. J., Appl. Chem. Biotechnol., 25, 241 (1975).
- [2] MENDYKA B., SYCZEWSKA K., MUSIALIK A., Report Inst. Environ. Prot. Eng., TU Wrocław, PWR SPR-33/I-15/1980.
- [3] NATSUKAWA K., YASUDA K., Atmosph. Environ., 13, 335 (1979).
- [4] HEGEDUS L. L., SUMMERS J. C., J. Catal., 48, 345 (1977).
- [5] GOLDENBERG E., PRIGENT M., CAILLOD J., Rev. Inst. Fr. Pétrole, 38, 6, 793 (1983).
- [6] TAYLOR K. C., Catal. Sci. Technol., 2, 120 (1983).
- [7] MEŽIRADZKIJ Ju. A., FOKŠA G. A., Prom. Sanit. Očistka Gazov, 4, 20 (1984).
- [8] SYCZEWSKA K., MUSIALIK-PİOTROWSKA A., MENDYKA B., Report Inst. Environ. Prot. Eng., TU Wrocław, PWR SPR-52/I-15/1985.
- [9] SADOWSKI G., TREIBMANN D., Z. Chem., 19, 5, 189 (1979).
- [10] LEVINE S. P., SCHUETZLE D., STORDEUR R. T., J.A.P.C.A., 31, 1, 46, (1981).
- [11] KENT S. A., KATZER J. R., MANOGUE W. H., Ind. Eng. Chem. Fundam., 16, 4, 443 (1977).

WPLYW ZWIĄZKÓW SIARKI I CHLORU NA AKTYWNOŚĆ KATALIZATORÓW PLATYNOWYCH

Przebadano wpływ związków siarki i chloru na aktywność katalizatorów platynowych o różnej zawartości platyny (0,05, 0,1 oraz 0,15% wag. Pt) przeznaczonych do spalania zanieczyszczeń organicznych w przemysłowych gazach odlotowych. Stopień zatrucia bądź dezaktywacji katalizatorów oceniano porównując aktywność katalizatorów świeżych i po cyklach zatrucia podczas spalania par ksyłenu i n-heptanu. Stwierdzono, że aktywność katalizatorów świeżych w spalaniu par węglowodorów maleje wraz ze zmniejszającą się zawartością platyny w kontakcie. Obecność dwutlenku siarki nie ma istotnego wpływu na przebieg procesu spalania węglowodorów. Obecność natomiast połączeń chloru powoduje okresową dezaktywację kontaktów.

ВЛИЯНИЕ СОЕДИНЕНИЙ СЕРЫ И ХЛОРА НА АКТИВНОСТЬ ПЛАТИНОВЫХ КАТАЛИЗАТОРОВ

Проведён анализ влияния соединений серы и хлора на активность платиновых катализаторов разной содержимости платины (0,05, 0,1 и 0,15% веса Pt), предназначенных для сжигания органических загрязнений в промышленных отходящих газах. Степень отравления или дезактивации катализаторов оценена посредством сравнения активности свежих катализаторов и катали-

заторов после процесса отравления в сжигании паров ксилола и n-гептана. Было установлено, что активность свежих катализаторов в сжигании паров углеводородов понижается вместе с понижающейся содержанием платины в контакте. Присутствие двуокиси серы не имеет существенного влияния на ход процесса сжигания углеводородов. Зато, присутствие соединений хлора является причиной временной дезактивации контактов.