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CATALYTIC COMBUSTION OF SELECTED HYDROCARBONS

The experiments were run to determine the efficiency of three industrial catalysts when applied to the oxidation of toluene, *n*-heptane and ethanol (both separately and in a mixture) in the conditions of atmospheric air. The catalysts were prepared in the laboratory of the Institute of Environment Protection Engineering, Technical University of Wrocław, and differed in platinum content (0.15, 0.1 and 0.05%). To describe the oxidation process, a mathematical model including all of the reaction parameters was presented.

The experiments have shown that low-platinum content catalysts are efficient when the compound to be combusted is susceptible to oxidation. The presence of slow-burning aliphatic hydrocarbons in the flue gas calls for a careful choice of the catalyst to be used and for a thorough consideration of the optimum working parameters.

1. INTRODUCTION

For many years, catalytic methods have been receiving wide acceptance in air pollution control. Still, research on the activity and efficiency of catalysts is underway in many scientific and industrial centres. Some of these studies involve organic compounds (representing typical air pollutants) which are oxidized in the presence of catalysts. The objective is a better understanding of the behaviour of various catalyst types when applied to the oxidation of pollutants entering the atmosphere in a mixture with industrial gases.

Activity tests are carried out, using a wide spectrum of chemical compounds, e.g., toluene, xylene, ethanol, acetone, acetates, sulphur derivatives or chlorine derivatives. Activity tests performed in the laboratories of the Institute of Environment Protection Engineering make use of toluene, *n*-heptane and ethanol (which differ from one another in chemical structure). These studies made it possible to prepare a series of catalysts which varied in platinum content. The noble metal was spread on

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identical $\gamma\text{-Al}_2\text{O}_3$ supports which were cylindrical in shape, had a 4 mm diameter, and a length ranging from 5 to 20 mm. The experimental results reported in this paper were obtained for three industrial catalysts, ZChO-80, ZChO-85 0.1, and ZChO-85 0.05, with platinum ingredient amounting to 0.15%, 0.1% and 0.05%, respectively. The catalysts were used for the oxidation of toluene, *n*-heptane and ethanol separately and in mixture in the condition of atmospheric air.

2. EXPERIMENTAL METHODS AND PROCEDURES

The oxidation process was run in a throughflow glass reactor in the presence of the catalyst which had been placed there in 8 g portions of industrial grain size without being broken up. This is important, particularly when ethanol is used (on catalyst surfaces with no platinum ingredient, ethanol can easily undergo incomplete oxidation to aldehydes). The reaction temperature varied from 440 to 770 K. Under these conditions, the possibility to oxidize each compound was investigated at a concentration of 1 mg/dm^3 and a space velocity of $10,000 \text{ h}^{-1}$ or at concentrations of 1 and 5 mg/dm^3 and a space velocity of $20,000 \text{ h}^{-1}$. The concentration of individual compound was determined by gas chromatography. The reaction conditions were established so as to enable the identification and quantification of acetic aldehyde which may be formed as a result of incomplete oxidation.

3. RESULTS

The oxidation efficiencies obtained in the presence of the catalysts under study are presented in fig. 1. As shown by these data, toluene is oxidized most effectively over each of the three catalysts. Similar results are reported for toluene combusted over other contacts [1]. The efficiency of oxidation depends on the noble metal content, but this dependence is particularly pronounced at lower reaction temperatures and less favourable process conditions. Thus, at 520 K, at a space velocity of $10,000 \text{ h}^{-1}$ and a concentration of 1 mg/dm^3 , the degree of conversion over ZChO-80, ZChO-85 0.1 and ZChO-85 0.05 amounted to 96%, 94% and 70%, respectively. Increase of space velocity from 10,000 to $20,000 \text{ h}^{-1}$ and concentration from 1 to 5 mg/dm^3 had only a slight effect on the course of the oxidation over ZChO-80. When ZChO-85 0.1 and ZChO-85 0.05 were used, there was even an evident drop in the oxidation efficiency. Nevertheless, temperatures higher than 650 K yielded efficiencies of toluene oxidation higher than 90% over each of the three catalysts irrespective of the process parameters.

Ethanol is not so readily oxidizable. At lower reaction temperatures, the efficiency of combustion decreased with the decreasing platinum content. Hence, space velocity of $10,000 \text{ h}^{-1}$, ethanol concentration of 1 mg/dm^3 and reaction

temperature of 520 K yielded the end-product oxidation degrees amounting to 83%, 72% and only 58% for ZChO-80, ZChO-85 0.1 and ZChO-85 0.05, respectively. The concentration of acetic aldehyde, formed in the course of the process, was 0.1 mg/dm³, 0.18 mg/dm³ and 0.28 mg/dm³ for ZChO-80, ZChO-85 0.1 and ZChO-85 0.05, respectively. It is interesting to note that the highest acetic aldehyde concentrations were produced at 520 K in the presence of ZChO-85 0.1 and ZChO-85 0.05. The highest acetic aldehyde concentrations formed over ZChO-80 amounted to 0.5 mg/dm³ (viz. some 50% of oxidized ethanol) and were found to occur at temperatures ranging between 430 and 440 K.

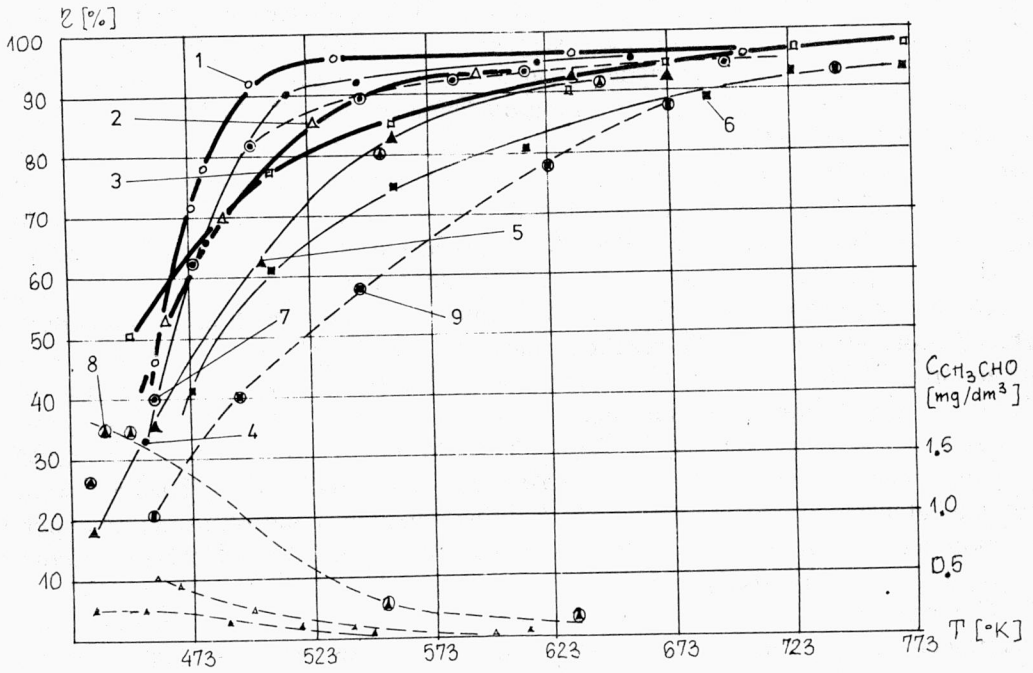
Of the three compounds studied, *n*-heptane is the most resistant to oxidation. The relationship between the reaction efficiency and the platinum content is very strong in the whole range of the temperatures tested. Only in the presence of ZChO-80 (at temperatures higher than 620 K for a space velocity of 10,000 h⁻¹, and at 680 K for a space velocity of 20,000 h⁻¹) the degree of oxidation amounted to 90%. When ZChO-85 0.1 or ZChO-85 0.05 was used, 90% efficiencies were obtained at a space velocity of 10,000 h⁻¹ at low *n*-heptane concentration and a high reaction temperature (which amounted to 698 and 723 K for ZChO-85 0.1 and ZChO-85 0.05, respectively).

The experiments have also revealed the relationship between space velocity and reaction efficiency. When the space velocity increased from 10,000 to 20,000 h⁻¹, the degree of oxidation decreased considerably, especially for *n*-heptane and ethanol. The concentration effect on the degree of oxidation varied from one compound to another. It was quite distinct for toluene, somewhat weaker for *n*-heptane, and almost insignificant for ethanol.

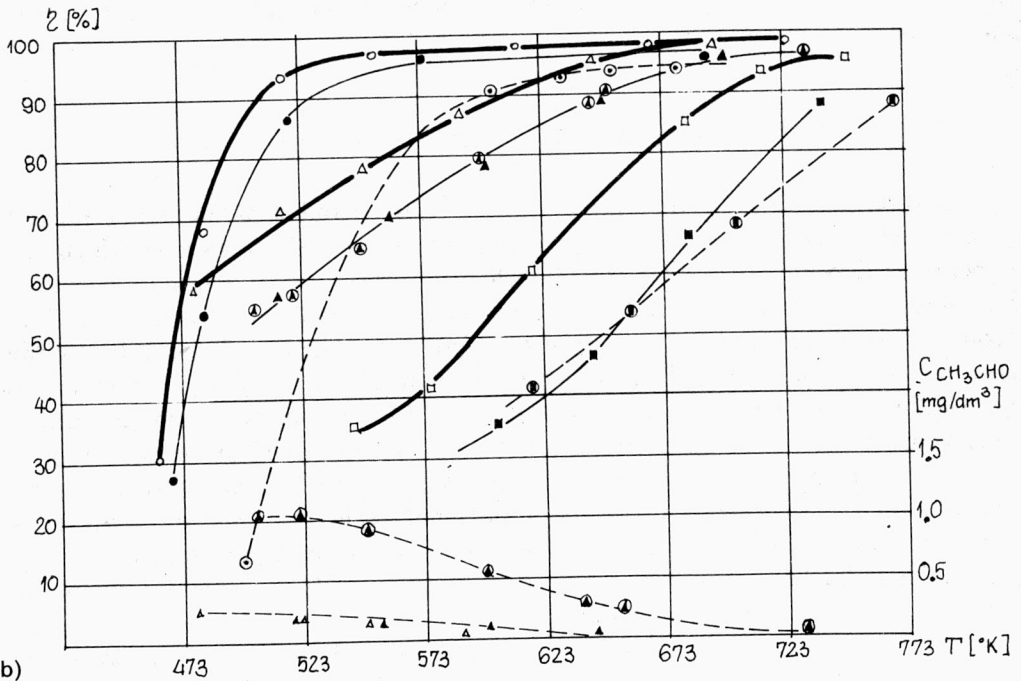
4. OXIDATION MODEL FOR AIR POLLUTANTS

Oxidation over catalysts differing in shape runs in a similar manner and is limited by the reaction rate up to a certain temperature (i.e., in the region in which the temperature dependence of the reaction efficiency shows a tendency to increase). Once this temperature value has been achieved or exceeded, the temperature effect becomes insignificant and the oxidation reaction is governed predominantly by the mass-transfer coefficient [2]. To determine the kinetic characteristics of the oxidation reaction the experimental rate constant was related to the inverse of temperature in terms of the Arrhenius equation. The plots for catalyst ZChO-80 are shown in fig. 2. The curves for the remaining two contacts are similar in shape. And this is an indication of a combined kinetic and diffusional region of reaction. Low concentrations of the reagents (equal to, or lower than, 0.1 volume percent) support this finding. A similar behaviour was reported by GIORGINI [3] who oxidized airborne carbon oxide over a platinum catalyst.

Taking into account this combined reaction region, IRVIN [4] made use of the



a)



b)

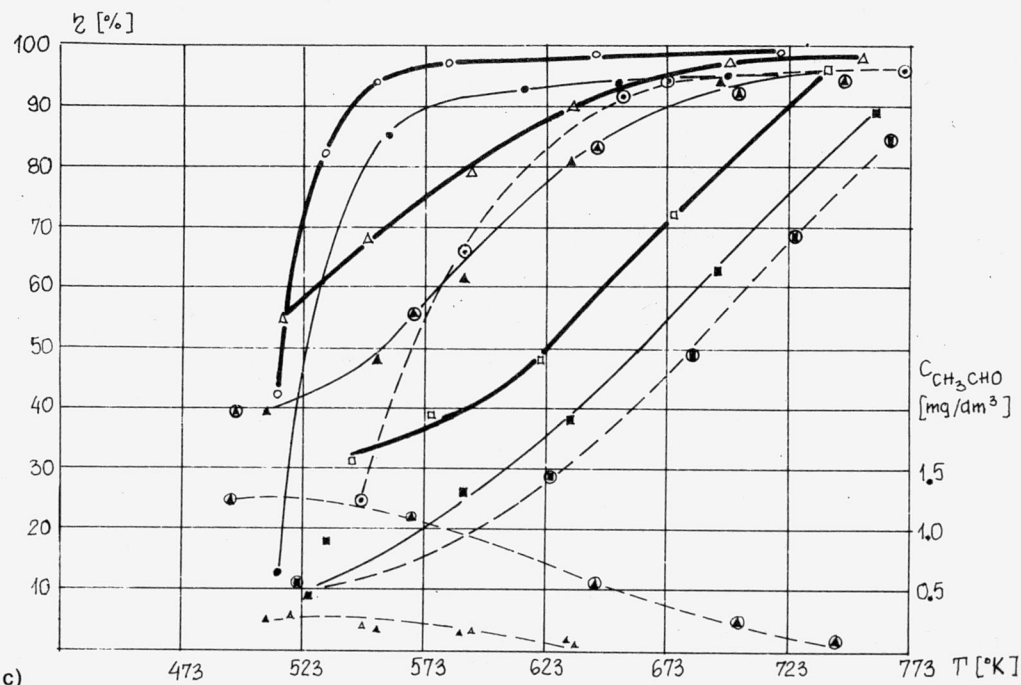


Fig. 1. Combustion efficiency for toluene, ethanol and *n*-heptane over ZChO-80 (a), ZChO-85 0.1 (b), ZChO-85 0.05 (c) catalysts

Space velocity 10,000 h⁻¹, concentration 1 mg/dm³: 1 — toluene, 2 — ethanol, 3 — *n*-heptane, space velocity 20,000 h⁻¹, concentration 1 mg/dm³: 4 — toluene, 5 — ethanol, 6 — *n*-heptane, space velocity 20,000 h⁻¹, concentration 5 mg/dm³: 7 — toluene, 8 — ethanol, 9 — *n*-heptane

following expression to calculate the overall reaction rate constant:

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

where:

k'_{chem} — effective chemical reaction rate constant,

k_{mass} — mass transfer rate constant calculated in terms of the formula:

$$k_{\text{mass}} = \frac{D_i}{L} N_{\text{Sh}}$$

where:

D_i — diffusivity of the pollutant,

L — relevant catalyst matrix dimension (effective diameter of grain),

N_{Sh} — Sherwood number depending on the catalyst shape.

An oxidation model, which comprises all of the reaction parameters, has been established for individual pollutants on the basis of experimental data. Assuming

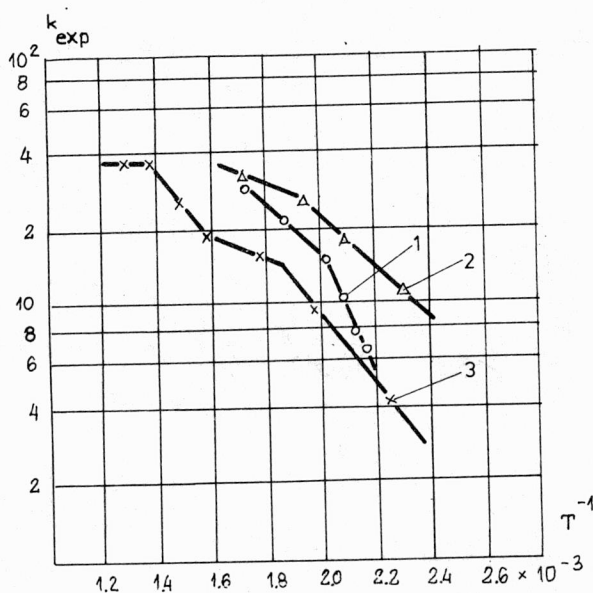


Fig. 2. Experimental reaction rate constant versus inverse of temperature for ZChO-80 catalyst
1 — toluene, 2 — ethanol, 3 — n-heptane

that the process of interest is an irreversible first-order reaction, running at atmospheric pressure in the combined kinetic and diffusion region, we can write:

$$r = G_M \frac{dy}{dz}, \quad (1)$$

$$r = k_g a(y - y_s)P, \quad (2)$$

$$r = k' a y_s P. \quad (3)$$

The solution to these equations takes the form:

$$\ln \frac{y_1}{y_2} = \frac{az}{G_M} \frac{1}{\frac{1}{k'} + \frac{1}{k_g}} \quad (4)$$

where:

- G_M — molar flow rate,
- z — catalyst bed depth,
- P — pressure,
- a — surface area of grains,
- k' — chemical reaction rate constant,
- k_g — molar transport coefficient,

y_1, y_2 — influent and effluent concentrations of reacting substances,
 y_s — concentration of reacting substances at catalyst surface.

The chemical reaction rate constant as a function of temperature was calculated in terms of the Arrhenius formula for surface reactions:

$$k = k_0 e^{-E/RT}. \quad (5)$$

The adopted mass-transport coefficient for a stationary layer is that reported by SATTERFIELD [5]:

$$k_g = 0.357 \frac{G_M}{\text{Re}^{0.359} \text{Sc}^{0.666} \varepsilon P} \quad (6)$$

where:

- k_0 — pre-exponential constant,
- E — activation energy,
- R — gas constant,
- Re, Sc — Reynolds number and Schmidt number, respectively,
- ε — void volume in the layer.

Thus, the model of catalytic oxidation can be written as:

$$\ln \frac{y_1}{y_2} = \frac{zL\varepsilon P}{d} \frac{0.357}{\text{Re}^{0.359} \text{Sc}^{0.666} \varepsilon P + \frac{0.357 G_M e^{E/RT}}{k_0}}. \quad (7)$$

The calculated values of pre-exponential constants (k_0) and activation energies (E) are listed in tab. 1.

As shown by these data, the importance of the chemical kinetics is the greatest in the case of toluene oxidation. The remaining reactions (specifically the oxidation of ethanol) occur in the combined region with a concurrent substrate adsorption and acetic aldehyde formation on the surface of the contact.

Having calculated the E and k_0 values and using equation (7), we can model the oxidation process by optimizing the catalyst bed depth or the linear rate of flow through the catalyst bed for the adopted oxidation efficiency and catalyst grain size.

Table 1

Calculated values of experimental activation energy E (kJ/mol) and pre-exponential constant k_0 (mol/m² s atm)

Catalyst	Toluene		n-heptane		Ethanol	
	E	k_0	E	k_0	E	k_0
ZChO-80	21	7.43	17	1.59	16	3.94
ZChO-85 0.1	42	649.22	37	33.67	21	4.43
ZChO-85 0.05	51	1681.90	36	21.80	24	6.44

5. OXIDATION OF THE MIXTURE OF POLLUTANTS

Industrial gases rarely contain single pollutants. Keeping this in mind, experiments with the mixture of three pollutants under study were carried out. It was interesting to find out how the presence of different pollutants influenced the efficiency of the oxidation. In this study the concentration of each component approached 1.5 mg/dm^3 , the space velocities amounted to $10,000 \text{ h}^{-1}$ and $20,000 \text{ h}^{-1}$. Examples of results are listed in tab. 2. As shown by these data, the

Table 2

Oxidation efficiencies obtained at two different temperatures and space velocities for each of the compounds combusted in the mixture

Compound	Oxidation efficiency %			
	520 K		670 K	
	$10,000 \text{ h}^{-1}$	$20,000 \text{ h}^{-1}$	$10,000 \text{ h}^{-1}$	$20,000 \text{ h}^{-1}$
	ZChO-80			
ethanol	90	78	98	97
<i>n</i> -heptane	32	20	89	80
toluene	90	86	97	95
	ZChO-85 0.1			
ethanol	78	63	98	93
<i>n</i> -heptane	8	3	77	61
toluene	94	83	98	98
	ZChO-85 0.05			
ethanol	54	43	94	87
<i>n</i> -heptane	3	2	57	42
toluene	84	69	98	96

presence of other compounds is particularly disadvantageous for the oxidation of *n*-heptane. When the oxidation reaction requires the ZChO-80 catalyst (which has the highest platinum content of the three contacts studied), the unfavourable influence of toluene and ethanol is primarily manifested at low temperatures. The oxidation of *n*-heptane in the mixture drops rapidly in the presence of ZChO-85 0.05 (with the lowest noble metal content). This holds for the whole range of the investigated temperatures (the degree of oxidation was always below 90%).

The presence of ethanol and *n*-heptane has only a slight effect on the combustion of toluene, especially at low temperatures. At temperatures up to 540 K, the catalyst ZChO-85 0.05 of low platinum content increases combustion efficiency of toluene in the mixture as compared to separate oxidation.

Only in the case of ethanol, the presence of the remaining components has a favourable influence on the oxidation. The degree of conversion increases slightly

and the formation of acetic aldehyde is not so intensive than during combustion of ethanol alone.

Increasing of the space velocity from 10,000 to 20,000 h⁻¹ brings about a decrease in the oxidation efficiency for all the components of the mixture, as it did, when the compounds were oxidized separately.

6. SUMMARY

The experiments have shown that catalysts with considerably reduced platinum content may be successfully applied to the oxidation of pollutants which can be easily combusted in catalytic processes. The presence of aliphatic hydrocarbons in industrial gases, carrying a mixture of other pollutants, requires a careful selection of the catalyst to be applied and optimization of their working parameters. The presence of hydrocarbons in the mixture is advantageous, particularly when ethanol is involved. This leads to a change in the selectivity of the contact, thus facilitating a complete combustion of ethanol and decreasing the intensity of acetic aldehyde formation which is a source of objectionable odours.

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KATALITYCZNE SPALANIE WYBRANYCH WĘGLOWODORÓW

Przebadano partie przemysłowe katalizatorów opracowanych w Instytucie Inżynierii Ochrony Środowiska Politechniki Wrocławskiej w spalaniu par toluenu, *n*-heptanu lub etanolu oraz ich mieszaniny. Zawartość platyny w badanych katalizatorach wynosiła 0,15, 0,1 lub 0,5%. Przedstawiono model matematyczny utleniania tych związków, ujmujący wszystkie parametry reakcji.

Stwierdzono przydatność katalizatora o obniżonej zawartości platyny do utleniania łatwiej spalających się połączeń. Obecność trudno spalających się węglowodorów alifatycznych w gazach odlotowych wymaga przeprowadzenia każdorazowo dokładnych badań nad doбором katalizatora i optymalnych parametrów jego pracy.

КАТАЛИТИЧЕСКОЕ СГОРАНИЕ ИЗБРАННЫХ УГЛЕВОДОРОВ.

Испытано промышленные партии катализаторов разработанных в Институте инженерии защиты окружающей среды Wrocławского политехнического института в сгорании паров толуона, *n*-гептана или этанола, а также их смеси. Содержание платины в испытываемых катализато-

рах — 0,15, 0,1 или 0,05%. Представлена математическая модель описания этих соединений, заключающая в себе все параметры реакции.

Доказано, надобность катализатора с пониженным содержанием платины для окисления легче сгорающих соединений. Присутствие тяжело сгорающих алифатических углеводов в отработанных газах требует проведения всякий раз подробных исследований подбора катализатора и оптимальных параметров его работы.