Oxidation Catalyst for Gas Oxygen Sensors

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Abstract

The metal (stainless steel) porous "metal-rubber" monolith-supported Pt, Pd, Pt–Rh and Pd–Rh catalysts are tested in the process of complete oxidation of hydrocarbons. At stoichiometric and higher oxygen content practically complete conversion of model hydrocarbon occurred at 380 °C on all catalysts. At these temperatures the catalysts work in outward diffusive area. At the oxidant to fuel ratio lower than stoichiometric the maximal conversion of hydrocarbon is reached at lower temperatures (250 °C). In complete hydrocarbon oxidation steady work of platinum catalyst is possible, if the content of sulphur in hydrocarbon does not exceed 0.3 % mass. These catalysts may be used for preparing a gas sample in oxygen sensors.

INTRODUCTION

In recent years, solid electrochemical systems have attracted attention of many researchers. These systems are used in oxygen gas sensors as well. Oxygen sensors are used in the combustion process control systems to keep the exact oxidant to fuel ratio (power plant, chemical thermal treatment, motor vehicles, *etc.*), or to control quality of technological protective gaseous medium (hydrogen, nitrogen, endogas, *etc.*) [1, 2]. The oxygen sensor signal is formed in a solid electrolyte electrochemical cell. EMF of the electrochemical cell depends on partial pressures of oxygen in complex gas mixtures. An extra catalytic block is used in sensor designs for reliable operation of the electrochemical cell. The functions of the block consist in the after-oxidation of the components of the gas sample (CH, CO, H_2, *etc.*) and conversion of the system into equilibrium in the cases of substantially nonequilibrium gas streams, blending of gas mixtures with different oxygen potentials. As a result the sensor signal does not depend on the rates of gas flows. The catalytic block protects the sensor from force majeur situations, in particular, those caused by moisture that can be condensed due to cooling. To perform these functions the catalyst must have sufficient catalytic activity in complete oxidation processes, good heat conductivity and thermostability, resistance to aggressive components of the gas mixture under analysis, in particular, sulphur containing components. The system "platinum group metal – metallic support" meets the above requirements.

A monolithic catalyst has been developed [3] in which metal (stainless steel, nickel and chrome steel) is used as a support material. The support material is a porous block of the predetermined shape and size made by cold pressing. It is a stretched wire spiral of a predetermined weight, the so-called "metal-rubber" (MR) [4]. The MR block has high porosity and a geometric surface to volume ratio that ensures a lower backpressure. The feature of this material is a steady volume and damping properties and relatively easiness of production. A method of autoclave thermolysis of complex compounds of platinum metals [5] has been used to obtain highly dispersed catalysis-effi-

cient phases (Pt, Pd, Rh, Ir) on the surface of the metal support. The content of platinum metals in the catalyst does not exceed 0.1 % mass. The catalyst showed good results [6–8] during laboratory tests in conditions simulating the oxidation process of discharge gases with hydrocarbon in industry and at power plants; as well as the neutralisation of exhaust gases of internal combustion engines.

The purpose of this paper was to determine conditions (temperature, the oxidant to fuel ratio, presence of sulphur containing compounds in the reaction mixture) for efficient operation of the block catalytic material for preparing a gas sample in oxygen sensors.

EXPERIMENTAL

Catalysts

Samples of catalysts containing platinum, platinum and rhodium, palladium, palladium and rhodium were prepared for the research.

Catalysts metallic support (MR) was made from wire of stainless steel type Kh18N10T 0.2 mm in diameter as blocks of cylindrical shape 10 mm in diameter and 20 mm high. The shape and size of the blocks are adapted to the design of the oxygen sensor. Porosity of the block (empty space in the bulk of the block) was chosen to be 0.74. The block with such parameters has low pressure-drop (pressure difference at the ends of the block at a linear velocity of 40 cm s^{-1} is 600 Pa) and rather high geometric surface to volume ratio (5200 m^{-1}).

Platinum metals from the aqueous alkaline solutions of ammonium chlorine complexes were supported onto the thermally preoxidized surface of the metal support in autoclave conditions [9, 10]. The metallic phase is formed as a result of an irreversible reduction of a complex ion by intersphere ammonia according to the equation:

$$[M(NH_3)_iCl_j] + OH^- \rightarrow M^0 + N_2 + NH_3 + Cl^- + H_2O \quad (1)$$

where M – Pt, Pd or Rh.

Bimetallic catalysts (Pt–Rh, Pd–Rh) were obtained by joint reduction of the corresponding compounds. For obtaining the samples the process of autoclave supporting of platinum metals was performed twice. Each time the necessary amount of complex salts was calculated in percent of the mass of the support, and if calculated by the metal this amount was Pt and Pd – 0.1; Rh – 0.01. In the thermolysis process part of the metal is reduced in the solution and on the autoclave walls, so, as the earlier research has shown [6, 10], the real amounts of platinum metal in the catalyst is 2–8 times lower than the calculated amount.

Catalytic research

The experiments were carried out in the flow laboratory set-up with an isothermal reactor in conditions close to the displacement mode. *n*-Hexane has been used as a model hydrocarbon. The mixture of hexane vapours with the oxidant (air) was obtained by flowing gas through a diffusion cell in which a test tube with the hydrocarbon was placed. The concentration of *n*-hexane in the mixture was 4–8 g m^{-3}. In experiments on the determination of catalyst resistance to poisoning by sulphur compounds, thiophene was added to hexane (0.1, 0.2 or 0.3 % by the mass of sulphur). When *n*-hexane and the air were mixed together the excess of oxygen was 10–20 times higher than the stoichiometric amount required for complete oxidation of hydrocarbons (the oxidant to fuel ratio (α) >> 1). The oxidant to fuel ratio close to stoichiometric ($\alpha = 1$) or lower ($\alpha < 1$) was adjusted by diluting the air with nitrogen in certain proportions. The necessary rate of air flow (V_{air}) was calculated with the help of the formula

$$V_{air} = \frac{\alpha M_{air} L_0 G_f}{\rho_{air}}$$

where M_{air} – molar mass of air, g/mol; L_0 – theoretical amount of air for complete combustion of 1 g *n*-hexane (0.471 mol/g); G_f – flow rate of *n*-hexane, g/min; ρ_{air} – density of air, g/l.

The gas mixture was supplied onto the catalyst at a rate of 15 l h^{-1} (contact time 0.36 s) which corresponds to operating condition of the catalytic block of the oxygen sensor. The temperature of the reactor was varied in the range 250–400 °C.

The degree of hexane conversion was determined using gas chromatographic analysis of reaction mixture at the inlet and outlet of the reactor: chromatograph (LKhM model 80) with FID, a 1m long column of stainless steel (inner diameter 3 mm), sorbent – zeolite CaA, temperature of the column 70 °C, gas-carrier – nitrogen.

RESULTS AND DISCUSSION

Activity of Pt metal catalysts of different composition were measured as *n*-hexane conversion in condition of a large excess of oxygen in temperature range 200–400 °C. The obtained dependencies allow to rank the used metals according to their catalytic activity in complete oxidation: Pt > Pt–Rh > Pd–Rh > Pd. Adding of a small amount of rhodium (the ratio Rh : M = 1 : 10, M Pt or Pd) results in a lower activity of the platinum catalysts and, on the contrary, causes an increase in the catalytic activity of the palladium sample. We did not study the pure rhodium catalysts in complete oxidation; however, it is known [11] that the activity of the supported rhodium in conversion of hydrocarbons is lower than that of platinum or palladium. In a previous paper [6] we showed that in supported dispersed bimetallic particles there is no interaction between platinum and rhodium; the decrease of the platinum-rhodium catalyst activity is caused by rhodium screening of the part of active platinum surface. It may be supposed that a higher activity of palladium-rhodium catalyst is caused by a change in the structure of active centres due to interaction between palladium and rhodium in bimetallic particles formed during autoclave reduction of the two metals. The study of this interaction is beyond the purposes of this paper.

On MR monolith-supported Pt and Pt–Rh catalysts kinetics of complete *n*-hexane oxidation have been studied earlier [7] in condition of a large excess of oxygen. Hexane oxidation reaction is first order with respect to the hydrocarbon concentration. Assuming that the oxidation reaction is also first order with respect to *n*-hexane concentration for Pd and Pd–Rh catalysts on the same monolith, the reaction rate constant was estimated through reagent conversion (x) using the following equation:

$$k = -\ln(1-x)\cdot\frac{v}{V_{Ct}}$$

where V_{Ct} is volume of the catalysts (1.57 cm^3); v is flow-rate (0.23 $cm^3\,s^{-1}$).

Arrhenius plots for *n*-hexane oxidation are presented in Fig. 1 for different supported platinum metal catalysts. Obtained straight lines confirm our suggestion that independently of the supported platinum metal nature the hexane oxidation reaction is first order with respect to the hydrocarbon concentration. At certain temperature the straight lines change the slope with an abscissa, pointing to a change of activation energy values. We concluded from this observation that at least two distinct (three for Pd–Rh catalyst) regions of reaction mechanism exist over corresponding temperature ranges.

At temperature below 300 °C activation energies take on values: for Pt – 58 kJ mol^{-1}, for Pt–Rh – 55 kJ mol^{-1}, for Pd–Rh – 59 kJ mol^{-1} and for Pd – 36 kJ mol^{-1}. It may be supposed that the obtained values correspond to activation energies of the heterogeneous catalytic reaction. Thus the oxidation reaction goes in kinetic region [12] at temperature below 300 °C for all tested catalysts.

On Pd–Rh catalyst the conversion of hexane increases from 25 up to 97 % with the

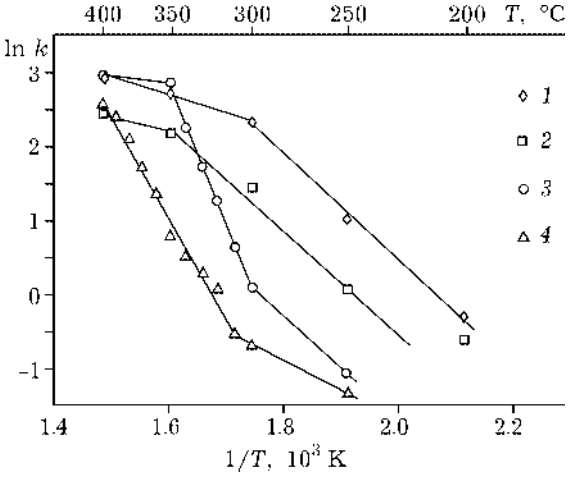

Fig. 1. Rate of hexane oxidation on platinum group metals supported on MR block as function of temperature ($\alpha >> 1$).

increase of temperature from 280 up to 340 °C. For this temperature range activation energy is 166 kJ mol^{-1}. The same abrupt increase of hydrocarbon conversion in a narrow temperature range (320–380 °C) is observed on the pure palladium catalyst, activation energy being equal to 114 kJ mol^{-1}. The increase of activation energy more than twice may be explained by a change of reaction mechanism from heterogeneous to heterogeneous-homogeneous. Just the homogeneous step of the reaction yields such considerable contribution to the value of observable activation energy. It is known [13] that the homogeneous extension of a reaction is possible when free reaction space is present. Probably, the structure of a MR monolith, where a diameter of a wire is comparable with space between catalytic surfaces, favours process intensification of the not too active Pd, Pd–Rh catalysts. As a result, reaction passes from surface to volume.

The reaction rate-temperature Arrhenius plot again changes the slope at temperatures above 340 °C in the case of Pd–Rh catalyst. The calculated activation energy is 9 kJ mol^{-1}. It corresponds to the characteristic activation energy of diffusion processes. Thus, the reaction goes in outward diffusive area [12]. Approximately the same activation energies are observed in the case of Pt and Pt–Rh sample at temperature above 300 and 320 °C, respectively.

Thus, when temperature rises the oxidation reaction on the tested catalysts gradually passes from kinetic mode of heterogeneous reaction to the heterogeneous-homogeneous one (on Pd and Pd–Rh catalysts) and then to outward diffusive area. Over low active under low temperatures Pd and Pd–Rh catalysts the oxidation process is intensified due to homogeneous step. As a result at temperatures above 380 °C the complete oxidation of hydrocarbons is almost reached on all tested catalysts. So, all these catalysts can be used in the catalytic block in oxygen sensors.

The temperature dependence of hexane conversion was measured at various oxidant to fuel ratios for the platinum catalyst which is most active in complete oxidation. These results are summarised in Table 1. Throughout the temperature range at a large excess of the oxidant ($\alpha >>$) and at its stoichiometric amount ($\alpha = 1$) the conversion values coincide. Practically complete conversion of hexane occurs at 350 °C and higher temperatures. With the lack of oxidant ($\alpha < 1$) the conversion of hexane reaches 80 % already at 250 °C and with subsequent temperature rise practically does not change, that is at a given quantity of oxygen the maximal conversion of hexane is reached. So, the temperature of reaching the highest possible conversion at $\alpha < 1$ is lower by 100° than at $\alpha \geq 1$. The effect of increasing platinum catalyst activity with decreasing the amount of the oxidant below stoichiometric is marked in literature [14]. The authors explain this effect by change of platinum state in the reducing atmosphere, since the activity of reduced platinum surface is higher than the activity of oxidised platinum surface.

The effect of the content of sulphur compounds (thiophene) in hydrocarbon (*n*-hexane) on the platinum catalyst activity in complete oxidation has been studied. The experiments were conducted during 3 h at temperature 350 °C and the oxidant to fuel ratio close to stoichiometric. The results of the experiments are presented in Fig. 2.

Irrespective of the content of thiophene in hydrocarbon fuel, a dramatic decrease of catalyst activity during the first 30 min of operation (Fig. 2) occurs. If the hydrocarbon fuel contains 0.1–0.2 % of sulphur, the activity of

TABLE 1

n-Hexane conversion on MR-supported platinum catalyst at various oxidant to fuel ratios (α)

α	Conversion, %, at *T*, °C				
	200	250	300	350	400
>>1	24	43	75	97	–
1	25	58	79	96	–
<1	–	80	77	78	79

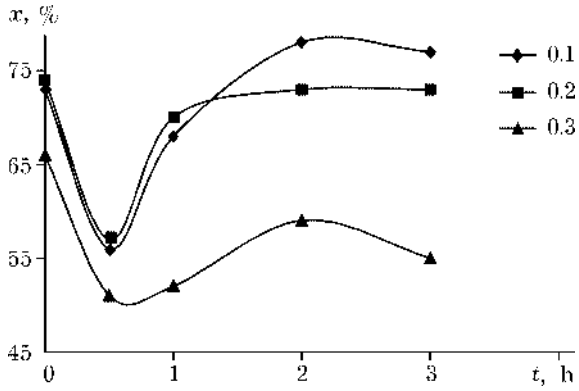

Fig. 2. Supported platinum catalyst activity as function of test period for oxidation of hexane with different thiophene content (α = 1, T = 350 °C, content of thiophene is given in % mass in of sulphur).

catalyst returns to initial value in 60 min and then remains steady. If the content of sulphur is increased to 0.3 %, the conversion of hexane insignificantly increases, but remains at a lower level with respect to initial activity. It is interesting to follow the change of the activity of the catalyst in oxidation of a mixture containing 0.3 % of sulphur during longer time (5.5 h) and at lower temperatures (280 °C). It is established that periods of the decreasing of hexane conversion and periods of the increasing of hydrocarbon conversion up to the initial level alternate.

The temperature dependence of the sulphur-free hexane conversion was determined

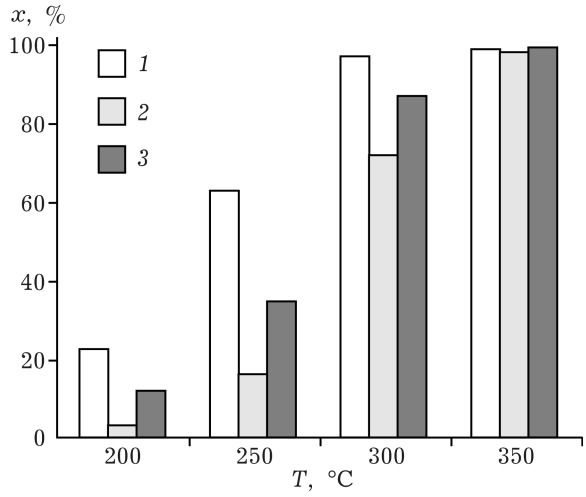

Fig. 3. Hexane conversion as function of temperature for supported platinum catalyst: *1* – starting; *2* – after 5.5 h working in oxidation of hexane doped with 0.3 % sulfur at 280 °C; *3* – after 5.5 h working in oxidation of hexane doped with 0.3 % sulphur at 280 °C and 1 h in oxidation of pure hydrocarbon at 400 °C.

after the catalyst had worked 5.5 h in oxidation of mixture of n-hexane with 0.3 % of sulphur (Fig. 3, series 2). A considerable decrease of the activity of the catalyst occurred at a low temperature (200–300 °C). Then sulphur-free hydrocarbon was oxidized on the same catalyst during 1 h at 400 °C, and again the conversion of hexane at various temperatures was found (see Fig. 3, series 3). The catalyst activity in the range of 200–300 °C increased by 4–1.5 times, respectively.

It is possible to explain the alternation of the catalyst activity in oxidation of hydrocarbon fuel with sulphur compounds as follows. Owing to a strong adsorption of thiophene, part of active centers of the catalyst appears to be occupied, and the oxidation rate of hydrocarbon is reduced. In the following step the adsorbed molecules of thiophene get oxidized to sulphur oxide (VI), which desorbes from the surface of the catalyst, clearing active centres for the molecules of hexane. Hence, the degree of hydrocarbon conversion increases.

At a low sulphur content in the hydrocarbons (0.1–0.2 %) during some time the steady state of the catalyst is reached. The adsorption rate of thiophene becomes equal to its oxidation rate. The number of active centers does not change, and the conversion of hexane remains steady for a long time. Because of slow oxidation of sulphur (II) compounds the increase of their content beyond a critical level results in permanent oxidation of active centers. The conversion of hexane decreases. If sulphur compounds are removed from the reaction mixture, the adsorbed sulphur (II) will get oxidized, which results in noticeable increase of hydrocarbon conversion.

CONCLUSION

The experiments have shown that Pt, Pd, Pt–Rh and Pd–Rh catalysts supported on a metal (stainless steel) porous MR monolith are effective in the process of complete oxidation of hydrocarbons. At stoichiometric and higher oxygen content practically complete conversion of model hydrocarbon occurred at 380 °C on all tested catalysts. At these temperatures the catalysts work in the outward diffusive area. At the oxidant to fuel ratio lower

than stoichiometric the maximal conversion of hydrocarbon is reached at lower temperatures. For the platinum catalyst it is 250 °C.

During complete oxidation of the platinum catalyst steady work is possible, if the content of sulphur in hydrocarbon does not exceed 0.3 % mass.

The catalysts have been tested successfully in gas oxygen sensors in automated fuel/oxidant control systems, in endogas and hydrogen generators, in carburizing processes and in off-gas treatment for environmental protection under industrial conditions.

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