

THERMAL TRANSFORMATIONS OF LEAD OXIDES

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Differential scanning calorimetry, differential thermogravimetry, X-ray analysis and electronic microscopic studies of thermal transformations of PbO_2 were carried out. Formation of fine dispersed (less than 100 nm) particles of α - PbO was observed at PbO_2 thermal decomposition at heating to 580°C. Reverse reaction of Pb_3O_4 formation from PbO was found at cooling and annealing at 400°C in air. At heating of α - PbO to 650°C the particle growth to 1 μm with formation of β - PbO took place. Thermal decomposition with formation of β - PbO particles with size from 0.3 to 1 μm at PbO_2 heating to 650°C was observed. Transition from PbO to Pb_3O_4 at cooling of sample heated to 650°C was not detected. Interpretation of observed phenomena from the point of view of particle size influences on the shift of α - $\text{PbO} \leftrightarrow \beta$ - PbO phase transition temperature and on the chemical activity of phases are presented.

Keywords: lead oxide, nanoparticles, phase transition, thermal properties

Introduction

Earlier, the oscillation reactions of carbon monoxide, hydrocarbons and nitrogen oxides conversion in the presence of lead compounds in automotive fuel was found at the study of catalytic properties of binary Pt–Rh catalyst (Fig. 1). Oscillation reactions were described earlier mainly in liquid media [1]. At the study of the plausible processes responsible for the oscillation reactions, never described in the literature earlier, we proposed that the association of oscillation gas-phase reactions with phase state and dispersity of lead oxides particles formed on the surface of Al_2O_3 – ZrO_2 – CeO_2 ceramics takes place [2]. In this connection, we studied processes going on in formation and decomposition of lead oxide particles at heating and cooling in air and in inert media.

It is common knowledge that lead–oxygen phase diagram includes a set of oxide compositions. In accordance with different references they have the following compositions: PbO , Pb_3O_4 , $\text{Pb}_{12}\text{O}_{17}$, Pb_2O_3 , Pb_7O_{11} , $\text{Pb}_{12}\text{O}_{19}$, Pb_5O_8 , PbO_2 [3–8]. In the study of lead dioxide decomposition at heating it has been found that the process occurs in temperature range 330–570°C in stages with the successive decrease of oxygen content $\text{PbO}_2 \rightarrow \text{PbO}_{1.56} \rightarrow \text{PbO}_{1.44} \rightarrow \text{PbO}_{1.33} \rightarrow \text{PbO}$ [3] (Fig. 2). It is known that lead monoxide has two polymorphous modifications: low temperature α - PbO (litharge), with tetragonal lattice ($a=3.9729 \text{ \AA}$, $c=5.0192 \text{ \AA}$), stable at heating up to 490–540°C [10, 11], and high temperature orthorhombic β - PbO (massicot) ($a=5.489 \text{ \AA}$, $b=4.755 \text{ \AA}$, $c=5.891 \text{ \AA}$ [12]).

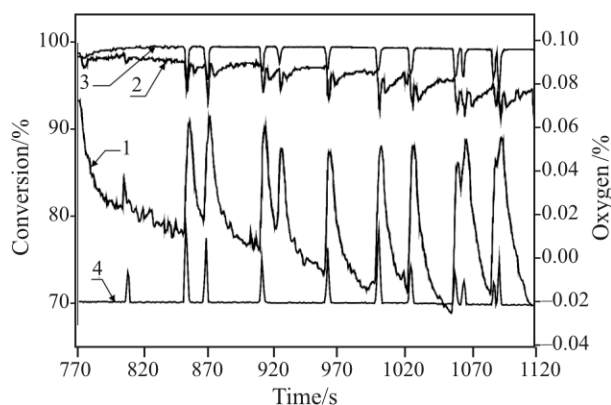


Fig. 1 Results of catalyst B08 after 80000 km (sample 4648C1) test (fuel with content of lead compound). 1 – HC, 2 – CO, 3 – NO_x, 4 – oxygen concentration

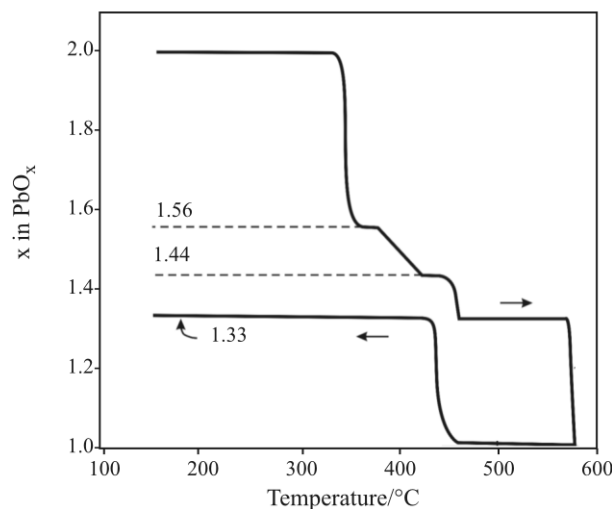


Fig. 2 Thermal decomposition of PbO_2 from [3]

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Endothermic phase transition $\alpha \rightarrow \beta$ is accompanied with small thermal effect $0.418 \text{ kJ mol}^{-1}$ [11]. At room temperature the rate of reverse $\beta \rightarrow \alpha$ transition is very low, that is why the β -phase can be stored in metastable state over prolonged period. The interesting observation was made in [4], where was reported the reverse reaction from PbO to Pb_3O_4 at slow cooling from 600°C in air. The formation of distorted ‘active’ α -PbO after thermal decomposition of lead carbonate and hydroxide and its oxidation to Pb_3O_4 at temperatures below 400°C was found in work [8].

The goal of this work is to study the oxidation–reduction processes in lead oxides at temperature variation.

Experimental

Samples

The samples of PbO (‘pure for analysis’ qualification, ‘REAKHIM’) with total impurities content less than 0.5 mass% (basic metal impurities in mass%: Cu (<0.001), Fe (<0.001), Ag (<0.0002); chlorides <0.2 mass%, mass loss at firing less than 0.2 mass%) and PbO_2 (‘pure for analysis’ qualification, ‘WEB LABORCHEMIE APOLDA’) with total impurities content less than 0.25 mass% (basic metal impurities in mass%: Fe (0.01), Ca (0.05), Pb (<0.005), Mn (0.0002); total content of chlorides, sulfates, nitrates and carbonates <0.031 mass%).

Experimental setups

Mass change at samples heating and cooling was studied using the derivatograph 1500D Paulik–Paulik–Erdey (MOM, Hungary). Sensitivity of thermobalance and accuracy of temperature measurement were 2 mg and 2°C , relatively.

Thermal effects at transformations were measured in differential scanning calorimeter DSC 2000K Setaram. Fired in air powder of α - Al_2O_3 was used as the reference substance. Reference and measured samples were placed in the alumina $100 \mu\text{L}$ crucibles. Weighing of specimens before and after study was made using ‘Analytical microbalance γ -21N4’ (accuracy 0.1 mg). DSC measurements were carried out in dried argon flow and in air.

X-ray study was conducted by HUBER powder diffractometer (CuK_{α_1} -radiation, $\lambda=1.5406 \text{ \AA}$, germanium monochromator, transmission geometry).

Electronic microscope Supra 50VP (‘LEO’) was used to study the particle size change at thermal transformations.

Results and discussion

Study of phase transition from α - to β -phase of PbO was carried out at heating rate $10^\circ\text{C min}^{-1}$ (Fig. 3). The weak endothermic peak in the temperature range $516\text{--}540^\circ\text{C}$ ($t_{\text{max}}=528^\circ\text{C}$) was observed on heating curve. The result of transition enthalpy calculation depended sufficiently on the baseline shape in the transition range as well as the change of baseline was observed. The average value of transition heat $0.46 \pm 0.10 \text{ kJ mol}^{-1}$ calculated for different shapes of baseline curves agrees satisfactorily with literature data ($0.418 \text{ kJ mol}^{-1}$ [11]). The peak of reverse $\beta \rightarrow \alpha$ PbO transition was not found on DSC curve at sample cooling.

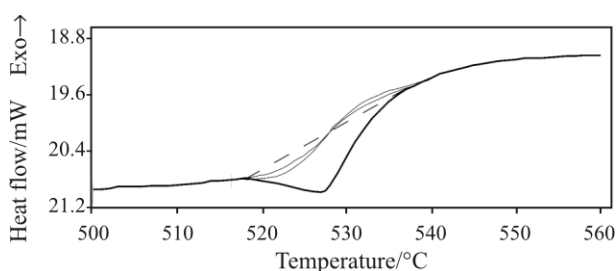


Fig. 3 DSC curve of α -PbO heating with different baselines in the transition region

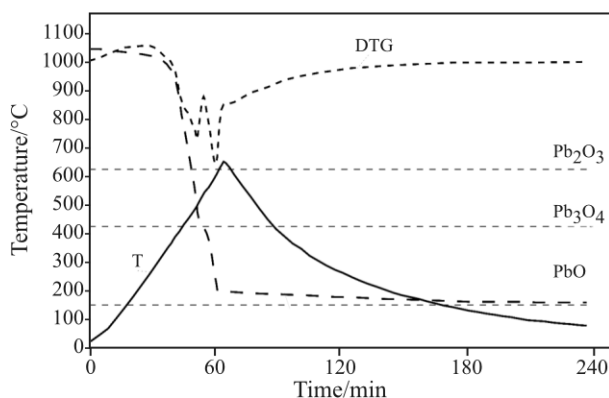


Fig. 4 DTG of PbO_2 specimen heated to 650°C

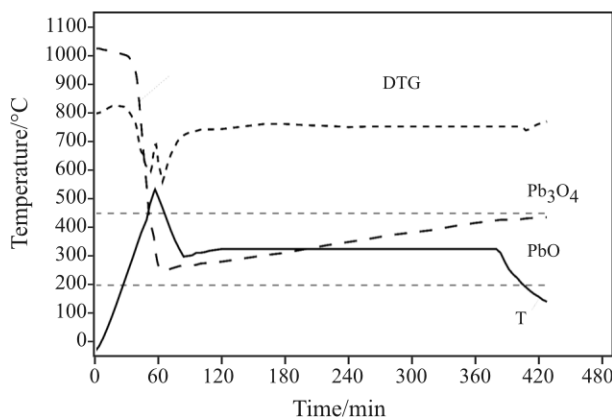


Fig. 5 DTG of PbO_2 specimen heated to 580°C

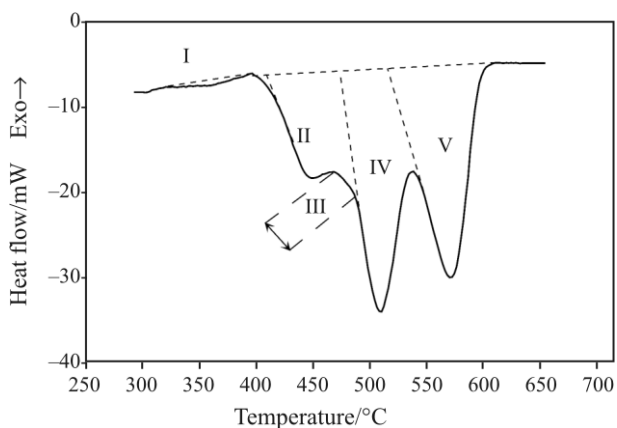
Table 1 Parameters of effects on DTG curves

Effect No.	1	2	3	4	5
Run 1					
Temperature range/°C	272–395	395–452	452–478	478–535	535–650
$T_{\max}/^{\circ}\text{C}$	332	419	459	498	597
Change of oxygen index x	$\text{PbO}_2 \rightarrow \text{PbO}_{1.89}$	$\text{PbO}_{1.89} \rightarrow \text{PbO}_{1.59}$	$\text{PbO}_{1.59} \rightarrow \text{PbO}_{1.43}$	$\text{PbO}_{1.43} \rightarrow \text{PbO}_{1.29}$	$\text{PbO}_{1.29} \rightarrow \text{PbO}$
Run 2					
Temperature range/°C	267–374	374–459	459–499	499–576	576– not complete
$T_{\max}/^{\circ}\text{C}$	337	427	458	488	(597)
Change of oxygen index x	$\text{PbO}_2 \rightarrow \text{PbO}_{1.83}$	$\text{PbO}_{1.83} \rightarrow \text{PbO}_{1.58}$	$\text{PbO}_{1.58} \rightarrow \text{PbO}_{1.45}$	$\text{PbO}_{1.45} \rightarrow \text{PbO}_{1.3}$	$\text{PbO}_{1.3} \rightarrow \text{PbO}_{1.45}$

Study of thermal behavior of PbO_2 at heating and cooling in air was carried out by TG/DTG in two different temperature ranges 50–650 and 50–580°C at the rate $10^{\circ}\text{C min}^{-1}$. In the first study sample was slowly cooled from 650°C to room temperatures during 4 h (Fig. 4). In the second measurement the sample was cooled from 580 to 400°C and annealed at this temperature in 5 h, following which it was cooled to room temperature (Fig. 5). In both studies five mass loss effects were found in the DTG curves. Temperatures of effects are given in Table 1. It should be noted that the superimposition of effects on the mass loss curve takes place and temperature ranges in Table 1 were calculated with accuracy $\pm 7^{\circ}\text{C}$. Accuracy of temperature of peak maximum was $\pm 5^{\circ}\text{C}$. Oxygen indexes x in PbO_x composition, listed in Table 1, were calculated based on the mass loss curve.

Change of sample mass at cooling was not detected in the first run, while in the second run the increase of sample mass, relates to the reaction $\text{PbO}_{1.15} \rightarrow \text{PbO}_{1.45}$, at annealing at 400°C was found (Fig. 5).

Study of thermal decomposition was carried out by the differential scanning calorimetry at heating rates 2, 5 and $10^{\circ}\text{C min}^{-1}$. It was shown that decomposition of PbO_2 to PbO consists of few stages. On the heating curves, studied at various rates, five endother-


Fig. 6 DSC curve of PbO_2 at heating rate $5^{\circ}\text{C min}^{-1}$

mic effects were revealed (Fig. 6). Superimposition of endothermic effects takes place inasmuch as the set of consecutive transformations proceeds at heating of PbO_2 . To separate these peaks the program of nonlinear approximation and data analysis ‘Fityk’ was used. Gauss functions

$$HF = a_0 \exp \left[-\ln 2 \left(\frac{T - a_1}{a_2} \right)^2 \right]$$

where HF – heat flow, T – temperature, a_0 , a_1 , a_2 – equation parameters correspond to height, maximum and width of peak were used in peaks separation. At the description of non-central peak V the sum of different Gaussians. The separation of peaks by the above mentioned method is presented in Fig. 7.

Parameters of peaks (maximum temperatures, temperature ranges, heats) calculated by the analysis are given in Table 2.

For us it was interesting to determine the influence of heating rate on the maximum temperature of peaks

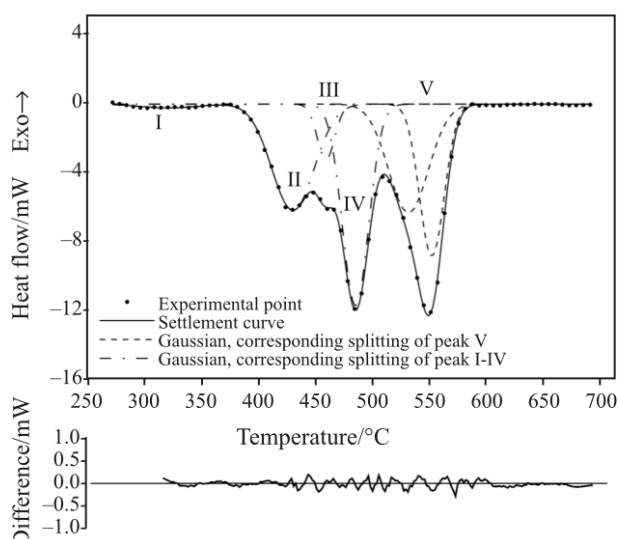
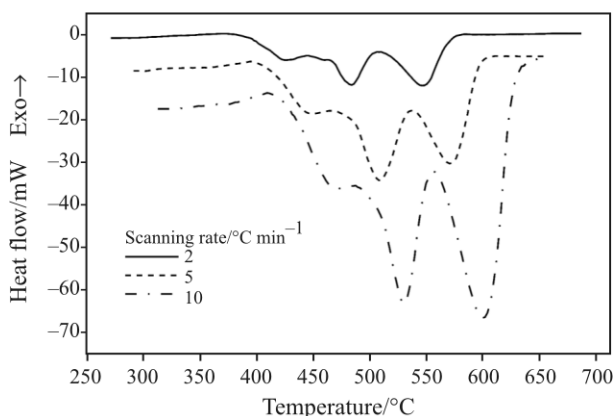

Fig. 7 Separation of peaks on DSC curve (heating rate $2^{\circ}\text{C min}^{-1}$)

Table 2 Generalized DSC data of PbO₂ decomposition

Effect No.	Decomposition stage	$T_g/^\circ\text{C}$	$T_p/^\circ\text{C}$	$-\Delta H/$	
				mJ	J g ⁻¹ of initial PbO _x
Scanning rate 2°C min ⁻¹ ; starting charge 208.3 mg					
I*	PbO ₂ →PbO _{1.89}	–	–	30	0.144
II	PbO _{1.89} →PbO _{1.59}	398.0	427.2	8360	40.426
III	PbO _{1.59} →PbO _{1.43}	405.0	460.0	1800	8.885
IV	PbO _{1.43} →PbO _{1.29}	455.3	482.9	9810	47.974
V	PbO _{1.29} →PbO	504.3	546.3	14970	70.454
Σ (I–V)	PbO ₂ →PbO	–	–	34970	167.883
Scanning rate 5°C min ⁻¹ ; starting charge 201.7 mg					
I	PbO ₂ →PbO _{1.89}	360.2	366.1	120	0.595
II	PbO _{1.89} →PbO _{1.59}	411.7	450.7	7470	37.313
III	PbO _{1.59} →PbO _{1.43}	412.9	–	1150	5.861
IV	PbO _{1.43} →PbO _{1.29}	471.4	509.4	13220	65.124
V	PbO _{1.29} →PbO	518.0	571.3	12150	60.220
Σ (I–V)	PbO ₂ →PbO	–	–	34110	169.113
Scanning rate 10°C min ⁻¹ ; starting charge 250.6 mg					
I	PbO ₂ →PbO _{1.89}	373.5	384.0	210	0.838
II	PbO _{1.89} →PbO _{1.59}	426.1	474.8	7940	31.926
III	PbO _{1.59} →PbO _{1.43}	–	–	3360	13.787
IV	PbO _{1.43} →PbO _{1.29}	489.0	530.8	8170	31.192
V	PbO _{1.29} →PbO	541.0	600.4	17640	71.180
Σ (I–V)	PbO ₂ →PbO	–	–	37320	148.923

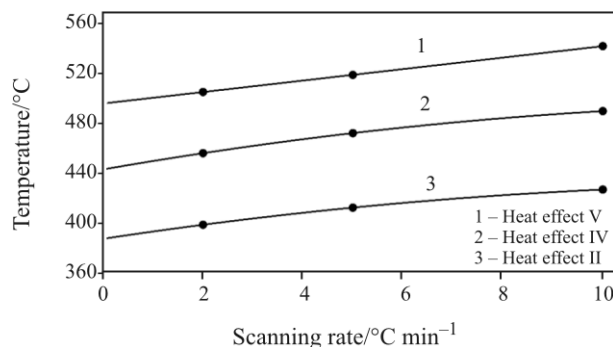
for different stages of lead dioxide decomposition. Earlier we found that transition kinetics effects on the measured peak temperature. Results of this PbO₂ study at different heating rates are presented in Fig. 8. It is evident that the shift of maximum temperature of peaks may be few tens of degrees in the process of thermal decomposition of lead dioxide (Fig. 9).

X-ray study of samples obtained after lead dioxide heating to 650°C and succeeding fast cooling (Table 1, Run 1), and after heating to 580°C and following annealing in air at 400°C (Run 2) showed that in

**Fig. 8** Shape of DSC curves for different heating rates

the first case the main final product of decomposition was lead monoxide (97.3 mass% of α -phase and 2.7 mass% of β -phase) (Fig. 10), while in the second one – the mixture of lead monoxide α -PbO (15.3 mass%) with Pb₃O₄ (84.7 mass%) (Fig. 11).

Electronic microscopy was carried out at the same magnification on four samples: (1) initial lead dioxide, (2) specimen heated to 650°C, (3) specimen heated to 580°C and (4) sample 3 kept at 580°C during 4 h. Initial PbO₂ sample consisted of particles with size near 10 μm (Fig. 12), which collapsed at smaller-size crystals during the thermal decomposi-

**Fig. 9** Variation of temperatures of peak maximum depending on the heating rate

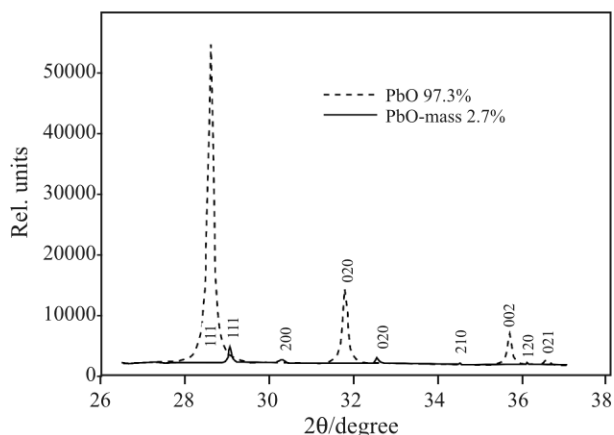


Fig. 10 X-ray pattern of sample heated to 580°C

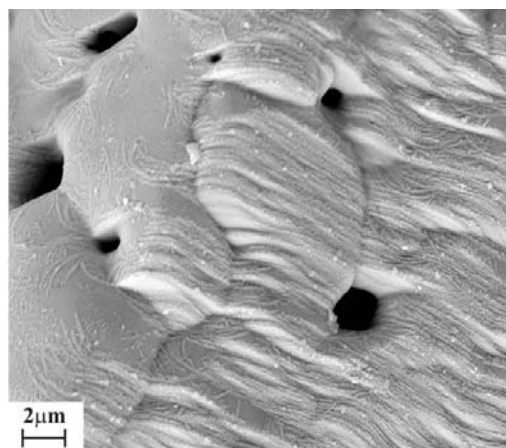


Fig. 12 Electronic microphotograph of starting PbO_2

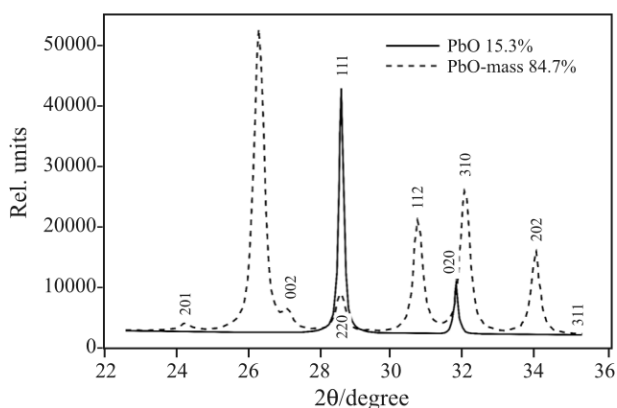


Fig. 11 X-ray pattern of sample heated to 580°C and annealed at 400°C

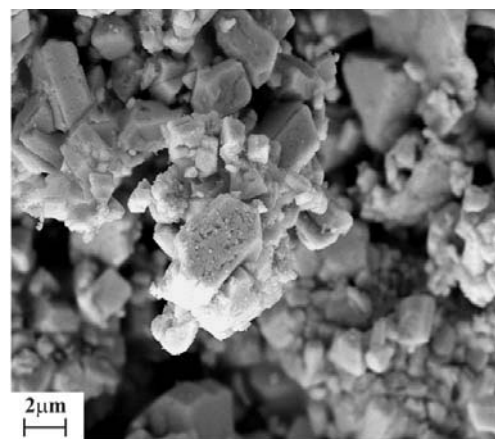


Fig. 13 Electronic microphotograph of sample heated to 650°C and cooled to room temperature

tion. At heating to 650°C particles with size from 0.5 to 4 μm (Fig. 13) were formed, whereas at heating to 580°C were formed lesser particles-size down to 50–100 nm (Fig. 14). Electronic microscopy showed that after keeping the formed powder at temperature 580°C during few hours, the enlargement and flattening of particles took place (Fig. 15).

Some inconsistencies and contradictions on heat behavior of lead oxides, described in literature, may, in our opinion, be explained by the fact that authors did not take into account the size of lead oxide particles. Whereas at present time is established that size of particles may have a pronounced effect on physical and chemical properties of matter.

In part, the difference in values of temperature and enthalpy of $\text{PbO } \alpha \rightarrow \beta$ transition, given in handbooks [11, 13, 14] may be considered as the result of variation in granulometric composition of samples, as well as at going to nano-scales the shift of phase equilibrium boundaries [15] and sufficient change of formation enthalpy takes place owing to the high surface energy [16]. In the case of lead monoxide, the structural transition enthalpy is small and the relative influence of surface energy may be significant.

The possible explanation of phenomenon observed in [4] (reverse reaction of oxidation of PbO to Pb_3O_4 at temperatures below 450°C at very slow cooling after the thermal decomposition of lead dioxide (maximum temperature 570°C), [8] (relatively weak oxidation of 'active' α - PbO to Pb_3O_4 at 400°C), as well as found in this work formation of α - or β -phase depending on the heating temperature (580 and 650°C, respectively) lies in the fact that in the process of decomposition nano-size α - PbO forms initially, characterized by the high chemical activity. At further heating it transforms to β -phase owing to particles aggregation and temperature change, as actuates the principle of maximum gap closing [17] and crystal units come within shortest distance. Atoms location in the crystal units of red (α , litharge) and yellow (β , massicot) is different. In part, the distance from central Pb atom to oxygen is near 3.69 Å, whereas for β -phase this distance is less than 2.48 Å [18]. Moreover, chemical activity of α - PbO may be connected not only with structural factor, but also with the local-

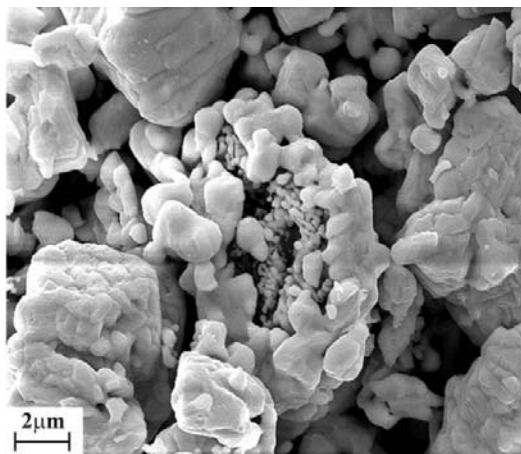


Fig. 14 Electronic microphotograph of sample heated to 580°C and cooled to room temperature

ized electronic pairs inherent for this modification. Formation of α -PbO at heating to 580°C was confirmed in this work by X-ray analysis. In [8] authors obtained α -PbO by the decomposition of hydrate of lead oxide (composition $2\text{PbO}\cdot\text{H}_2\text{O}$ and $3\text{PbO}\cdot\text{H}_2\text{O}$) and lead carbonate at various temperatures. They marked that at decomposition of lead carbonate at temperatures below 300°C formation of low temperature modification of PbO takes place. Based on the broadening of reflexes on X-ray patterns, authors described the phase as ‘distorted’ α -PbO. In our opinion, the revealed by authors [8] phenomenon can be described not as the α -PbO structure distortion but as formation of nano-size particles which also characterize the reflex broadening. Formation of PbO particles with size less than 100 nm after decomposition of lead dioxide was observed in our study (Fig. 14). Formation of α -modification of lead oxide after heating of PbO_2 to 580°C rather than β -phase, as it can be expected from reference data and our study (Fig. 3), also can be connected with the significant shift of phase equilibrium boundary to higher temperatures.

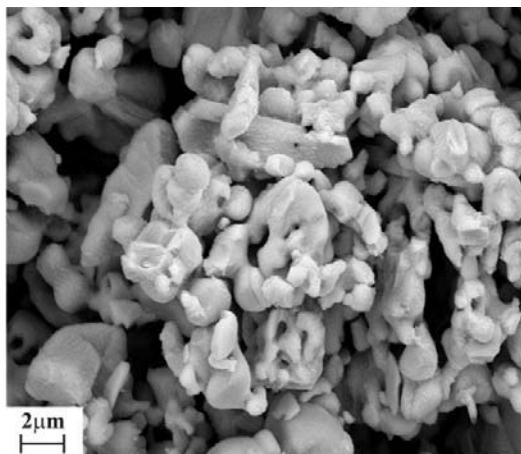


Fig. 15 Electronic microphotograph of sample heated to 580°C, annealed at 400°C and heated to 650°C

It is necessary to note, that studied in this work reaction in which the air oxygen was used for the oxidation of lead oxide to Pb_3O_4 differs from process taking place in the actual threeway catalyst (TWC) of car engines, inasmuch at the work of TWC the possible sources of oxygen may be as well as decomposition of NO_x as the oxide ceramics $\text{Al}_2\text{O}_3\text{--ZrO}_2\text{--CeO}_2$.

Based on the combination of above mentioned results we proposed the reversibility of reaction $\text{PbO}_x \leftrightarrow \text{PbO} + (x/2 - 1/2)\text{O}_2$, which direction is determined by the combination of temperature and size factors.

Conclusions

Temperature and enthalpy of structural phase transition $\alpha \rightarrow \beta$ -PbO were refined in the work. Study of thermal decomposition of lead dioxide allows determination of process stages and heat effects. Reasonable assumptions as to the possibility of reversible reaction $\text{PbO}_x \leftrightarrow \text{PbO} + (x/2 - 1/2)\text{O}_2$ were suggested based on the experimental studies and analysis of literature data from the point of view of influence of particle size on the heat and temperature of phase transition. The oxygen release in the reaction leads to the oscillation conversion of CO, NO_x and hydrocarbons on the Pt–Rh catalyst in the presence of lead oxides.

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