

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Studies on Nickel Effect on Kinetics of Lead Reduction from Its Oxide by Hydrogen.

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ABSTRACT

Studies were carried out on kinetics of lead reduction from its oxide by hydrogen in the presence of nickel within 450-525°C temperature range. It was demonstrated that nickel addition enhanced the rate of lead reduction from its rhombic and tetragonal form oxides and caused changes in the shape of kinetic curves. Lead reduction rate increased monotonously with the increase of nickel content. It was shown that acceleration of reaction of lead reduction from its oxide caused by nickel addition was of catalytic nature.

Keywords: lead oxide, hydrogen, impurities, nickel, kinetics, catalysis.

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INTRODUCTION

Studies on the effect of the impurities on metal oxide reduction kinetics is of great importance for two reasons. First, this effect makes it possible to identify the details of mechanism of the reaction itself, for instance, to learn whether nucleation stage is pronounced (Delmon, 1969). Second, it is important to take into account the effect of impurities on metal oxide reduction rate as applied to the development of technologies of smelting, refining and processing of metals and alloys.

It is shown in (Culver et al., 1962) that lead oxide containing impurities is reduced more quickly than chemically pure lead oxide, however, no detailed study has been carried out on the effect of any impurities on the kinetics of lead reduction from its oxide by hydrogen. Besides, effect of various factors on the process of lead reduction from its oxides is highly important for the reasons described below (Adamov et al., 2015, Goverdovsky and Rachkov, 2014, Rachkov et al., 2014).

Liquid lead is currently considered as promising coolant for commercial nuclear power plants with fast reactors. Thermal and neutronic characteristics of liquid lead facilitate development of potentially safer and more cost effective nuclear reactor design as compared to existing reactors. However, contact of lead coolant with air oxygen results in accumulation of impurities in it. This contact may occur in case of lead circuits opening for the purpose of components replacement, repair work, etc. Interaction of liquid lead with oxygen causes formation of solid lead oxides, which deteriorate thermal and hydraulic characteristics of lead circuits. Reduction of lead oxides by hydrogen is the best known method of their removal from lead coolant circuit. This method is based on lead oxides interaction with hydrogen followed by lead reduction from the oxide and its return to the coolant of the circuit. However, the real coolant always contains some impurities in it. And yet, as it was mentioned above, effect of the impurities (in particular, nickel) on kinetics of lead reduction from its oxide has not been studied till now.

Thermodynamic analysis of lead and nickel interaction with hydrogen containing gas impurities

Characteristics of the processes under study are revealed by thermodynamic analysis of chemical reactions. Let us consider interaction of these phases with hydrogen taking, as an example, the following reaction:



with equilibrium constant $K_p = P_{H_2O} / P_{H_2}$. Me – Pb and Ni metals, Me_xO_y – PbO and NiO oxides.

Value of standard variation of isobaric-isothermal potential for (1) type reactions can be determined by the following relationship (Guggenheim and Prue, 1955):

$$\Delta Z^0 = \Delta Z_{form.fin.}^0 - \Delta Z_{form.in.}^0 = Y \cdot (\Delta Z_{form.H_2O}^0) - \Delta Z_{form.Me_xO_y}^0, \quad ((2))$$

where ΔZ^0 – standard variation of isobaric-isothermal potential in reaction (1); $\Delta Z_{form.H_2O}^0$ – standard variation of isobaric-isothermal potential in the reaction of formation of one mole of water steam from gaseous hydrogen and oxygen; $\Delta Z_{form.Me_xO_y}^0$ – standard variation of isobaric-isothermal potential in the reaction of formation of one mole of the oxide from metal and gaseous oxygen.

For reaction (1), ΔZ^0 value determines equilibrium composition of gaseous hydrogen and water steam mixture in the reaction zone:

$$\Delta Z^0 = -R \cdot T \cdot \ln K_{eq.} = -R \cdot T \cdot \ln \left(\frac{P_{H_2O}}{P_{H_2}} \right)^y, \quad ((3))$$

where T – temperature, K; R – constant, $R = 8.314 \text{ J}/(\text{mol}\cdot\text{K})$; K_{eq} – equilibrium constant with $P=\text{const}$ and $T=\text{const}$; P_{H_2O} – partial pressure of water steam in gas phase; P_{H_2} – hydrogen partial pressure in gas phase.

Reduction of Me with formation of the above oxides is determined, taking into account (1), by the following reactions:



Below presented are the equations describing standard variation of isobaric-isothermal potential in the reaction of formation of the oxides, indicated in the left-hand side of equations (4) and (5), from Me and one mole of water steam (Wicks and Block, 1963, Weeks and Romano, 1969):

$$\Delta Z_{form.H_2O}^0 = -246000 + 54.84 \cdot T, \quad (6)$$

$$\Delta Z_{form.PbO}^0 = -216940 + 96.52 \cdot T, \quad (7)$$

$$\Delta Z_{form.NiO}^0 = -239810 + 92.34 \cdot T, \quad (8)$$

where ΔZ_{form}^0 – standard variation of isobaric-isothermal potential, J/mol; T – temperature, K.

As a result, standard variation of isobaric-isothermal potential for reactions (4) and (5) are as follows:

$$\Delta Z_{r.4}^0 = -29060 - 41.68 \cdot T, \quad (9)$$

$$\Delta Z_{r.5}^0 = -6190 - 37.5 \cdot T. \quad (10)$$

In Table 1, there are the results of calculation of standard variation of isobaric-isothermal potential for reactions (4) and (5), Table 2 gives calculated values of equilibrium constants, and in Table 3 presented are the results of calculation of water steam and hydrogen equilibrium concentrations for these reactions. Calculations were made for 500 - 1000 K temperature range. Data presented in Table 3 was obtained bearing in mind that relationship $K_{eq.} = P_{H_2O} / P_{H_2}$ was correct for reactions (4) and (5) and, hence:

$$K_{eq.} = \frac{P_{H_2O}}{P_{H_2}} = \frac{C_{H_2O}}{C_{H_2}}, \quad (11)$$

$$C_{H_2} + C_{H_2O} = 100, \quad (12)$$

$$C_{H_2O} = \left(\frac{K_{eq.}}{1 + K_{eq.}} \right) \cdot 100\%, \quad (13)$$

$$C_{H_2} = \left(\frac{1}{1 + K_{eq.}} \right) \cdot 100\%. \quad (14)$$

Table 1: Standard variation of isobaric-isothermal potential ΔZ^0 [J/mol H₂O] values for reactions (4) and (5)

Temperature, K	Reaction number	
	4	5
500	-49900	-24940
600	-54068	-28690
700	-58236	-32440
800	-62404	-36190
900	-66572	-39940
1000	-70740	-43690

Table 2: Equilibrium constant K_{eq} values for reactions (4) and (5)

Temperature, K	Reaction number	
	4	5
500	$1.63 \cdot 10^5$	$4.03 \cdot 10^2$
600	$5.10 \cdot 10^4$	$3.15 \cdot 10^2$
700	$2.22 \cdot 10^4$	$2.64 \cdot 10^2$
800	$1.19 \cdot 10^4$	$2.31 \cdot 10^2$
900	$7.31 \cdot 10^3$	$2.08 \cdot 10^2$
1000	$4.96 \cdot 10^3$	$1.92 \cdot 10^2$

Table 3: Equilibrium concentrations of H_2 and H_2O (vol.%) for reactions (4) and (5)

Temperature, K		500	600	700	800	900	1000	
Reaction number	4	C_{H_2}	$6.12 \cdot 10^{-4}$	$1.96 \cdot 10^{-3}$	$4.51 \cdot 10^{-3}$	$8.42 \cdot 10^{-3}$	$1.37 \cdot 10^{-2}$	
		C_{H_2O}	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
	5	C_{H_2}	0.25	0.32	0.38	0.43	0.48	0.52
		C_{H_2O}	99.75	99.68	99.62	99.57	99.52	99.48

Data from Tables 1, 2, and 3 shows that reactions (4) and (5) are carried out up to practically complete conversion of hydrogen into water. Thus, from the standpoint of thermodynamics, interaction of lead, nickel, and their oxides with hydrogen would cause reduction of the two metals from the oxides as long as hydrogen exists in the reaction zone.

However, thermodynamics only confirms the feasibility of reduction of studied metals by hydrogen. Characteristics and mechanism of reduction process can only be revealed by carrying out kinetics study (Emanuel and Knorre, 1974, Turkdogan, 1988).

Also it's important to note that lead monoxide exists in, at least, two polymorphous forms: low-temperature tetragonal form (so called "lead oxide red form") and high-temperature rhombic form (so called "lead oxide yellow form") (Izvozchikov and Timofeev, 1979). Temperature of polymorphous transition PbO_r - PbO_t is between 488 and 530°C values. In spite of the similarity of thermodynamics and crystallography of the two forms (Izvozchikov and Timofeev, 1979), they might differ from the standpoint of their reactivity with hydrogen, since chemical properties of solids were quite sensitive to the slightest changes of composition, structure, and texture of specimens (Delmon, 1969). It is shown in (Chijikov et al., 1961) that tetragonal form of lead oxide is much more easily restored by carbon monoxide than rhombic form. Thus, the comparative study of kinetics of rhombic and tetragonal form lead oxides reduction by hydrogen is relevant.

EXPERIMENTAL STUDIES

Authors studied kinetics of lead oxide reduction by hydrogen in test facility (its flow diagram - see Figure 1).

Test facility included the following main components: reaction chamber (1), gas analyzer (2), gas pipeline (3), and data collection system (4). Inside the reaction chamber with heater (5) attached on its right side, there are thermocouple, quartz boat (6) for lead oxide specimens, and piston (7) for moving boat with the sample from the cold area to the heated area of the chamber.

Lead oxide specimen was put into quartz boat located in the left (not heated) section of reaction chamber. Then hydrogen was supplied from cartridge (8) to the reaction chamber in order to arrange hydrogen flow in it at constant rate (~3 L/hour), and the right section of the chamber was heated up to the working temperature. Boat containing specimen was moved by piston (7) to the right (heated) section of the reaction chamber. Hydrogen - water steam mixture produced as a result of the reaction was delivered through the heated gas pipeline (3) to the gas analyzer (2) in order to determine its composition (Leibnitz and Struppe, 1984, Kiselyov et al., 1973).

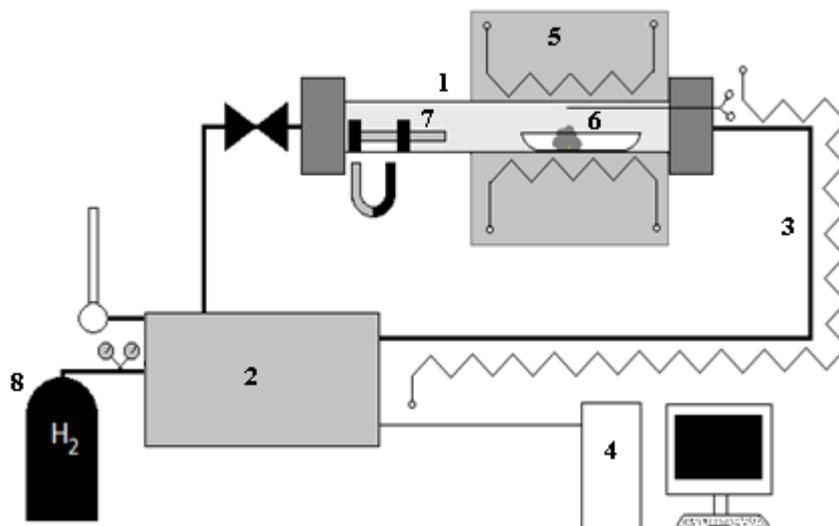


Figure 1: Flow diagram of test facility for studying kinetics of lead reduction from its oxide by hydrogen

Reaction chamber and boats for specimens were made of quartz, since quartz does not interact with either hydrogen, water steam, or lead oxide at the temperatures of experimental studies (450-525°C) (Loskutov, 1956). Temperature of not heated section of the reaction chamber was within 100°C in order to prevent premature reaction of lead oxide with hydrogen, which start at 270°C according to our experimental results. Temperature in the central area of the heated section of the reaction chamber was measured by the thermocouple within the accuracy of $\pm 1^\circ\text{C}$.

Upon putting boat with specimen to the central area of reaction chamber heated section, working temperature value restored in 1-2 minutes.

The following materials were used in the experiments: lead monoxide rhombic form PbO (used in mass exchangers with heavy liquid metal coolants (Martynov et al., 2009)) and tetragonal form PbO powders of about 50 μm size particles, Pb₃O₄ powder of about 10 μm size particles, nickel powder with particles of size ranging from 1 to 20 μm , aluminum oxide powder produced by the technology described in (Askhadullin and Osipov, 2014, Dmitriev et al., 2012, Martynov et al., 2006) in compact form, and nickel oxide powder of about 1 μm size particles. In the course of studies on the effect of the impurities on kinetics of lead reduction from its oxide by hydrogen, impurities powders were mixed with lead oxide powder in the certain mass ratio, and these mixtures were reduced.

THE RESULTS OF EXPERIMENTS

First, comparison of reactivity of lead oxide rhombic and tetragonal forms with hydrogen was made. Such comparison was made in previous work (Ivanov et al., 2015), but some results were refined to obtain more precise data. In current work samples of lead oxide with bigger mass (1 g vs. 0,34 g) and method of affine transformation (to determine activation energy of reduction not only tetragonal, but also rhombic lead oxide, see below) were used.

It was revealed that reduction degrees of these forms vs. time were similar (Figure 2). One can see from Figure 2 that kinetic curves are not sigmoid, i.e. there are no near-zero reaction rate sections in the curves in the beginning of the process. This is also the case for kinetic curves obtained at the different temperatures. The result shows the absence of pronounced stage of reaction product (lead) nucleation in the course of reduction. In order to confirm the absence of this stage, studies were carried out on lead reduction from rhombic form powder with added pure lead metal powder (10 wt.%, lead particles size 5-40 μm , and reduction temperature 500°C), since it was well known that with pronounced processes of nucleation or reacting surface extension in the early stage of heterogeneous reaction, addition of reaction product or finely powdered agent fraction would increase reaction rate (Delmon, 1969). This experiment showed that addition of lead metal powder neither decreased complete

lead reduction time, nor changed kinetic curve configuration. Neither increase of rate of lead reduction from its oxide was observed when 10 wt.% of lead oxide powder of 1-10 μm size particles was added. Thus, in the course of lead reduction from its oxide, neither nucleation, nor autocatalysis was detected.

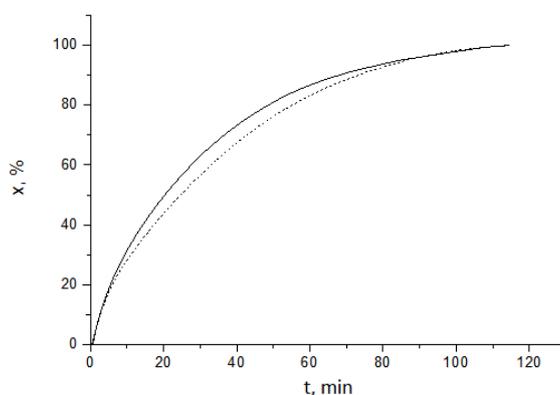


Figure 2: Degree of lead reduction from powders of tetragonal (dotted line) and rhombic (solid line) forms vs. time at 475°C.

Then, the activation energy values were determined for reduction of both lead oxide forms. For this purpose, “reduction degree - time” relationships were determined for each lead oxide form at various temperatures, and relationships obtained for each form were superposed using time compression (affine transformation) method (Barret, 1973). Upon verifying coincidence of their configurations, $\ln(k)$ vs. $1/RT$ relationships were constructed, where k – affine transformation coefficient and T – temperature, K. For rhombic form, 450-525°C temperature range was chosen, while for tetragonal form, contracted range (450-500°C) was taken because, as it has been mentioned above, temperature of tetragonal-to-rhombic form polymorphous transition was higher than 488°C. It is known that rhombic form of lead oxide, being thermodynamically stable at the temperatures exceeding polymorphous transition point, is metastable at the temperatures below transition point (Izvozchikov and Timofeev, 1979). The tetragonal form is stable at the temperatures below polymorphous transition point (Izvozchikov and Timofeev, 1979). Therefore, there are no limitations for the temperature range of rhombic form tests, while in case of tetragonal form, studies temperature below polymorphous transition point seems to be the most proper approach.

One point (500°C) is somewhat higher than polymorphous transition temperature. Taking into account that transition from tetragonal to rhombic lead oxide form is characterized by high activation energy, and the process slows down significantly when approaching polymorphous transition point (Morales et al., 1985), as well as satisfactory coincidence of kinetic curves after affine transformation, one can suppose that tetragonal form lead oxide interacted with hydrogen within the whole temperature range.

Results of activation energy evaluation are presented in Figure 3.

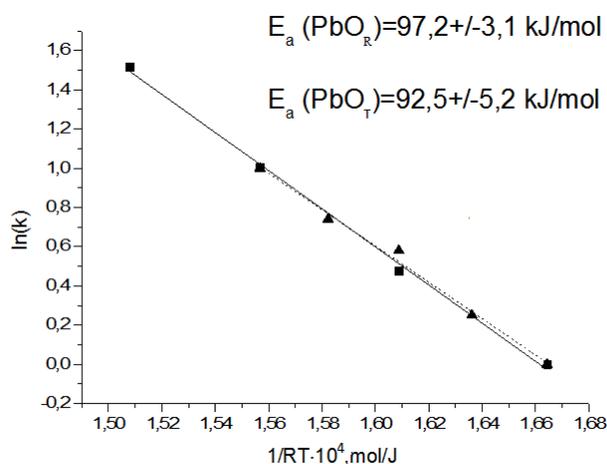


Figure 3: Relationship $\ln(k)$ vs. $1/RT$ for lead reduction by hydrogen from rhombic (solid line) and tetragonal (dash line) form of oxide powder. T – temperature, K.

Values of activation energy of lead reduction from its oxide of tetragonal and rhombic forms are equal within reasonable errors. Figure 2 shows that the reduction time values are almost equal for two lead oxide forms. Taking into account the similarity of the size (50 μm) and configuration of lead oxide crystals of both forms revealed by optical microscopy, one may also talk of the similarity of specific rates of these forms reduction. All the above considerations indicate the similarity of reactivity of different form lead oxides interacting with hydrogen within the temperature range under study.

Then studies were carried out on the effect of nickel additive on kinetics of lead oxide reduction by hydrogen. Studies showed that addition of nickel metal or nickel oxide powder (1 wt.% or higher amount) to lead oxide resulted in significant (2- or 4-fold) increase of the rate of lead reduction from its oxide. Both quantitative and qualitative changes of reduction kinetics curves caused by addition of 1 wt.% of nickel were the same for tetragonal and rhombic forms of lead oxide at the reduction temperature within 450-500°C range. Nickel metal was added to the lead oxide powder. Kinetic curve of lead reduction rate vs. time in case of nickel addition differs essentially from that for rhombic form pure lead oxide (Figure 4).

Spikes appearing in the early stage of reduction were caused by desorption of water present in the lead oxide powder. It is characteristic that in the early stage (reduction degree below 5% and samples preliminarily heated up to 500°C in order to eliminate the impact by the adsorbed water), no reaction acceleration was observed after addition of 50 wt.% of nickel and, therefore, the assumption of association of acceleration of the reaction owing to the added impurities with nucleation stage (when impurities would serve as reaction product nucleation centers (Delmon, 1969)) can be eliminated.

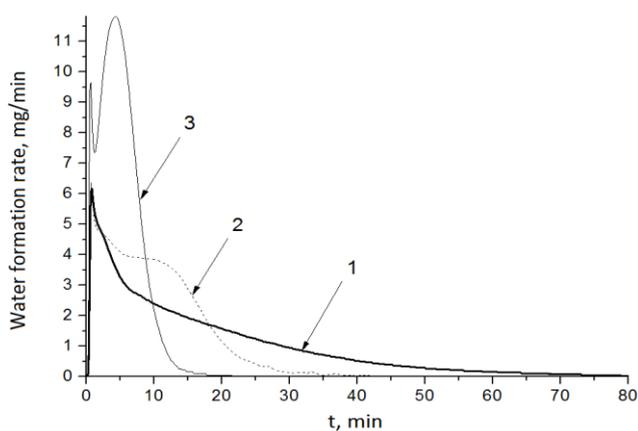


Figure 4: Rate of lead reduction from its oxide vs. time at 500°C: 1 – pure lead oxide; 2 – lead oxide containing 5 wt.% of nickel; 3 – lead oxide containing 50 wt.% of nickel

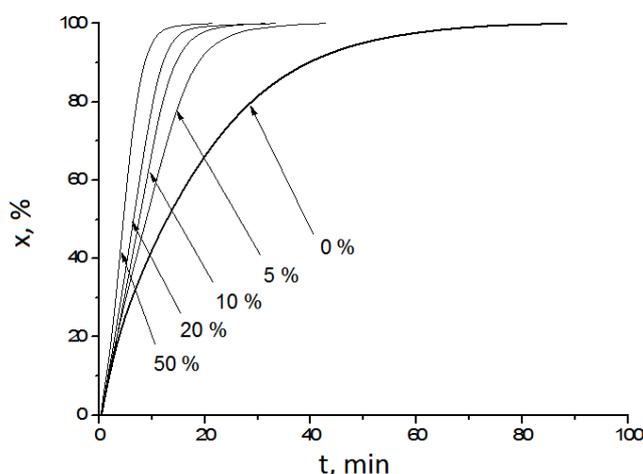


Figure 5: Degree of lead reduction from its oxide vs. time and nickel content (wt. %) at 500°C

Increase of nickel content in lead oxide powder resulted in monotonous decrease of complete lead reduction time over the whole considered range of nickel content values (5-50 wt.%, Figure 5). Moreover, the shape of kinetic curve of reaction rate vs. time also changed from monotonously decreasing line to that with pronounced maximum.

It should be noted that in case of pure lead oxide reduction (taking place at any temperature within considered interval: 450-500°C), reaction product (lead metal) is released as 1 or 2 large size (several mm in diameter) shining drops, which are tightly bound with quartz, i.e. boat material. It is also the case for Pb₃O₄ oxide reduction going several times faster at 500°C than PbO reduction, and so this phenomenon should not be associated with the reduction rate. Reduction of lead oxide with nickel additive results in many blind metal drops of rather small size (less than 1 mm in diameter), which are never bound to the boat material.

One can assume that the decrease of metal drops size is caused by formation of nickel oxide layer on the surface of lead drops being in contact with lead oxide. Quartz adherence of this layer is, perhaps, low, and also it could prevent small lead-nickel alloy drops from fusing. Because of the small size of metal drops, they do not strongly block the surface of non-reacted lead oxide, and so, the rate of lead reduction may increase. Actually, lead reduced from the pure oxide isolates to a great degree lead oxide surface, thus preventing its contact with hydrogen and decreasing reduction rate – that is why almost exponential decrease with time of lead oxide reduction rate takes place, which, in case of absence of the surface blockage by lead, would be described by contracting sphere equation (Zelikman and Nikitina, 1978):

$$1 - \sqrt[3]{1 - a} = K \cdot t, \tag{1}$$

where a – reduction degree, t – time, K – constant. Using relationship (1) reduction degree can be presented as a function of time:

$$a = 1 - (1 - K \cdot t)^3 \tag{2}$$

Time differentiation of equation (2) shows that reaction rate vs. time relationship in this case is parabolic.

Then lead reduction by hydrogen from its oxide with addition of 50 wt.% of aluminum oxide powder was carried out. Aluminum oxide particles are capable of isolating lead oxide particles from appearing lead metal drops, and therefore, according to our hypothesis, they would increase reduction rate. Indeed, examination of the reaction products by optical microscopy showed that the size of reaction product drops was ~ 50 μm, which was equal to that of the initial lead oxide particles. However, no significant increase of reduction rate was achieved in this case (the time of complete lead reduction from its oxide was reduced by about a factor of 1.5), i.e., apparently, there was no effect of reduced metal drops size on reaction rate.

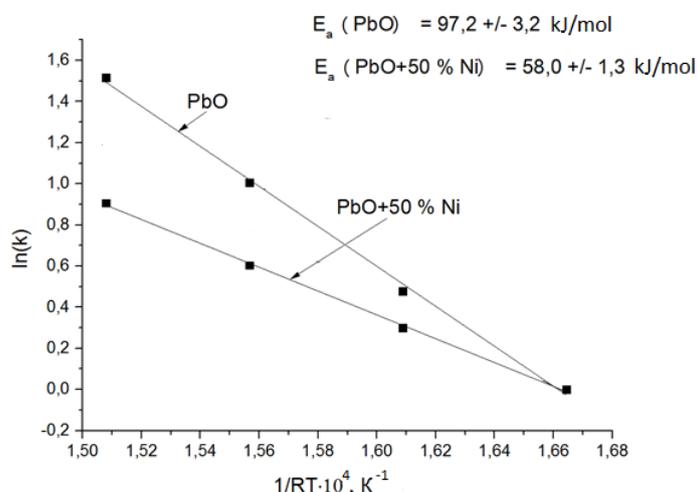


Figure 6: Relationship between ln(k) and 1/RT for lead reduction from its oxide powder by hydrogen

In order to determine whether mechanism of nickel addition effect on the kinetics of lead reduction from its oxide was catalytic, hydrogen reduction of samples of pure lead oxide and that with addition of 50 wt.% of nickel was carried out at the temperature ranging from 450 to 525°C (mass of each sample was 1 g). Activation energy was determined by the time affine transformation method (described above). Kinetic curves were adequately superposed by the time affine transformation for each sample, this allowing to assume consistency of reduction mechanism over the whole temperature range and to start determining activation energy.

In Figure 6, presented are obtained reduction rate constants logarithms vs. reciprocal temperature.

Evaluated activation energy of lead reduction from its pure oxide by hydrogen is equal to 97.2 ± 3.2 kJ/mol. Addition of 50 wt.% of nickel would cause decrease of this value down to 58.0 ± 1.3 kJ/mol, this providing strong evidence of catalytic mechanism of nickel effect on the process of lead reduction from its oxide by hydrogen.

A special experiment was conducted for the purpose of determining the possibility of direct reduction of lead by nickel metal. Nickel metal was produced by reducing nickel oxide by hydrogen at 500°C and further calcination of nickel in the argon gas flow during 0.5 hour at 500°C to assure hydrogen desorption from nickel. Then produced nickel was cooled in argon down to the ambient temperature and mixed with lead oxide powder (in the air atmosphere) in 1:1 mass ratio. This mixture was put into the reaction chamber together with pure lead oxide sample (serving as a reference) and held there in hydrogen flow at 200°C during 20 minutes. Then the samples were calcinated in the argon flow during 20 minutes at 220°C (to let hydrogen be desorbed from nickel) and during 20 minutes more at 500°C (in order to determine the possibility of lead oxide reduction by nickel). It is known (see Figure 5) that the time of complete lead reduction by hydrogen at 500°C from lead oxide mixed with nickel metal in 1:1 ratio is equal to 20 minutes. Before supplying industrial argon to the reaction chamber, its flow was arranged over the molybdenum wire at 500°C in order to remove oxygen traces. Oxygen content in argon was controlled by oxygen sensor, its functional principle being given in (Askhadullin et al., 2011). Sensor EMF as a function of oxygen partial pressure is described by Nernst equation: EMF value increases with the decrease of oxygen partial pressure. In argon gas flowing over heated molybdenum wire, sensor EMF was equal to 300-310 mV (EMF is 250 mV, if measured over the mixture of nickel and its oxide at 500°C). Thus, the possibility of nickel oxidation by oxygen traces in the purified argon was eliminated.

Examination of the reference lead oxide sample by optical microscope did not show formation of reaction products on the surface of lead oxide crystals. Neither any change was revealed in the sample of mixture of lead oxide and nickel metal; particles of the initial components were only found in it. This result is in agreement with indistinguishability of reduction rates of pure lead oxide and mixture of lead oxide with nickel powder (1:1 mass ratio) up to the achievement of 5% reduction degree, indicating the absence of strong effect of nickel on lead reduction kinetics in the early stage when the amount of reaction product (liquid lead) is not too large.

Thus, apparently, no direct lead reduction from its oxide by nickel metal occurs within the considered temperature range. One can assume that catalysis process requires formation of the layer of reaction product (lead metal) serving as dissolvent of chemical agents and materials formed as a result of catalysis (nickel, lead oxide, and, probably, nickel oxide).

CONCLUSIONS

Studies were carried out on kinetics of lead reduction from its oxide in the presence of nickel. It was demonstrated that nickel addition increased lead reduction rate, this rate increasing monotonously with the increase of added amount of nickel. Increase of reduction rate being of catalytic nature was not caused by the increase of reaction product nucleation rate. Activation energy of lead reduction from its oxide with the presence of 50 wt.% of nickel was equal to 58 ± 1.3 kJ/mol (for chemically pure lead oxide, activation energy was 97.2 ± 3.2 kJ/mol). No direct interaction was revealed between lead oxide and nickel metal within considered temperature range. Presumably, catalysis was conducted through the mediation of liquid lead (reaction product).

ACKNOWLEDGMENTS

Studies were conducted with the support of the Russian Ministry of Education and Science (Unique Identifier of applied scientific research RFMEFI57914X0065).

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