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## Low-Temperature Hydrogen Oxidation Employing the Systems Based on Copper Oxide

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### Abstract

Results are presented concerning the studies on the activity of oxide materials obtained *via* applying copper oxide onto aluminium oxides with well-developed surface (5–26 % CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 28 % CuO/ $\theta$ -Al<sub>2</sub>O<sub>3</sub>) with respect to hydrogen absorption at the temperature of 25–90 °C and at hydrogen pressure of 40 Torr. It is demonstrated that the samples with a high content of copper oxide are characterized by satisfactory values of hydrogen oxidation specific rate and could be used as absorbers of hydrogen evolved due to radiolysis process during the transportation of mixed radioactive waste products in sealed vessels.

**Key words:** hydrogen, low-temperature oxidation, solid oxidizers, copper-containing oxide systems

### INTRODUCTION

The problem of removal/binding of hydrogen in air environments in order to gain an explosion-proof level is solved in practice employing the methods of catalytic hydrogen oxidations or using materials absorbing hydrogen (so-called getters). The absorption of hydrogen can be carried out due to reversible adsorption/absorption processes [1–3] or basing on the processes of irreversible chemical binding [4–7]. For good safety in the case of radioactive waste products transportation in the containers such as TRUPACT-II it is necessary that at the maximal possible value of hydrogen evolution rate inherent in the process of radiolysis amounting to  $1.2 \cdot 10^{-5}$  mol/s the concentration of hydrogen would not exceed 5 % [8].

In order to meet these conditions one need for the creation of compact materials to place inside containers, which materials would be capable of binding hydrogen in an irreversible fashion. Taking into account the requirements concerning the mass and time of vessels transportation imposed upon getters, the

specific capacity of absorbing materials with respect to hydrogen should be higher than  $0.3 \cdot 10^{-3}$  mol/g, whereas the specific absorption rate at the temperatures of operation should be higher than  $0.6 \cdot 10^{-10}$  mol/(s · g).

The main problem arising in the development of hydrogen absorbing materials is connected with the inconstancy of temperature inside containers, whose value can vary within the range of  $-7 \dots 125$  °C.

The analysis of the patent data demonstrates that basing on irreversibly absorbing materials mainly the compositions are under development those are capable of absorbing hydrogen due to hydrogenation processes. They include various organic polymeric materials with unsaturated bonds in combination with hydrogenation catalysts based on precious metals [4, 5]. The materials capable of reduction by hydrogen were studied to a lesser extent.

So, the authors of [6, 7] proposed oxide systems based on of transition metals with palladium additives (Pd/MeO), the greatest activity among those is exhibited by the systems based on copper and cobalt oxides. The mate-

rials are under development in order to employ in vacuum equipment and microelectronics at low partial hydrogen pressure. Owing to a high cost the use of such materials as hydrogen absorbers for safe transportation and safe storage of reservoirs with radioactive waste products is considered to be economically unacceptable.

It is well known that transition metal oxides in the systems Pd/MeO suggested belong to the most active contacts of the hydrogen oxidation catalytic process [9]. The catalytic activity is exhibited by oxide systems with the spinel structure (copper, cobalt, nickel cobaltites) and simple oxides (CuO, MnO<sub>2</sub>) those are characterized by low values of the surface oxygen binding energy and the activation energy of the process [9, 10]. At the temperature values higher than 100 °C (for Co<sub>3</sub>O<sub>4</sub> higher than 50 °C) the oxidation proceeds according to multi-stage oxidation-reduction pattern, the rate determining stage being presented by hydrogen interaction with oxide's oxygen.

The estimation of the reduction rate for the most reactive systems with the use of kinetic parameters of their reduction stage has demonstrated that these oxide systems with no precious metal addition could be reduced by hydrogen with satisfactory activity as well as at lower temperature values. The authors of [11, 12] observed a low-temperature (at a room temperature and lower) process of hydrogen reducing the surface of high-disperse oxides such as Co<sub>3</sub>O<sub>4</sub> and CuO, both with palladium additives, and with no additives (with the specific surface area of 100 m<sup>2</sup>/g).

The sample of Co<sub>3</sub>O<sub>4</sub> with the spinel structure exhibited the greatest activity the same way as in the medium-temperature reduction process. Under the conditions under investigation the authors of [12] observed the level of surface oxide reduction amounting to 8–23 % of the oxygen coverage; whereas the capacity of the samples with respect to hydrogen appeared insignificant. The total (calculated) capacity with respect to hydrogen for the materials based on the most reactive oxides meets the requirements imposed upon hydrogen getters purposed for placing within the containers filled with waste products for the period of their transportation. In this connection, of some interest was to investigate the potentiality of

employing such materials as low-temperature solid oxidizers of hydrogen.

The present work has been devoted to the investigation of low-temperature hydrogen oxidation by oxide systems those represent an active phase of copper oxide applied onto aluminium oxides with well-developed surface.

## EXPERIMENTAL

The applied samples of 5–15 % CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 28 % CuO/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> with the mass fractions of copper amounting to 5–28 % (as calculated for CuO) were obtained using the technique of impregnation with the solution of copper (II) nitrate; such carriers as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (A-1 trademark, the granules being of cylindrical shape 4–6 mm in diameter, 4–25 mm length,  $S_{sp} = 230$  m<sup>2</sup>/g) and  $\theta$ -Al<sub>2</sub>O<sub>3</sub> (ATs-2 trademark, balls, fraction of 0.4–0.6 mm,  $S_{sp} = 85$  m<sup>2</sup>/g) were employed, respectively. The samples were then dried in air at the temperature of 100 °C during 2 h and calcinated at 600 °C during 3 h. We used also an industrial catalyst for deep oxidation representing copper oxide (the mass fraction of 26 %) applied onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (A-1 trademark), the granules being of cylindrical shape 6 mm in diameter and 10–15 mm length,  $S_{sp} = m^2/g$  [13].

The specific surface area for the materials obtained was determined from thermal desorption of argon. The phase composition of the samples was determined basing on the analysis of XRD profiles registered with the help of DRON-4 X-ray diffractometer using monochromatized CuK $\alpha$  radiation. The CuO crystallite size was calculated according to formula Selyakov–Scherrer formula basing on the line of 111,  $2\theta = 35.5^\circ$ .

The reactivity of samples with respect to hydrogen absorption was investigated using a laboratory-scale static vacuum set-up 0.306 L in volume capacity (Fig. 1). To a molybdenum glass reactor about 6 ml in volume capacity was loaded 1–5 g of a sample. Before the experiment the samples were trained within a reactor in oxygen flow at 350 °C during 3 h, then the reactor was cooled down to the temperature of experiment, evacuated to gain a residual pressure  $1 \cdot 10^{-5}$  Torr and then hydrogen was fed. The absorption of hydrogen was

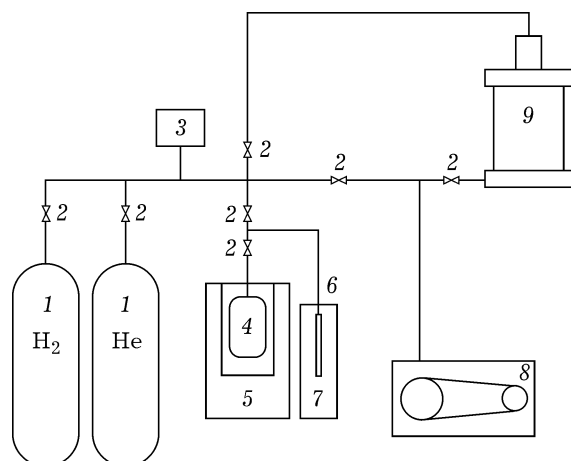


Fig. 1. Schematic diagram of the laboratory-scale static vacuum manometric set-up: 1 – gas cylinders, 2 – vacuum stopcocks, 3 – mercury manometer, 4 – reactor, 5 – thermostat, 6 – trap, 7 – Dewar vessel, 8 – forepump, 9 – high-vacuum diffusion pump.

studied at the temperature values ranging within 25–90 °C and initial pressure of ~40 Torr. During the experiment the pressure in the system was maintained within the range of 40–30 Torr (after pressure decreasing the reactor was blocked, the system was fed with hydrogen to gain the initial pressure value, and then the reactor was opened in order to continue the experiment).

The level of hydrogen absorption by the sample depending on time was registered using a KM-6 cathetometer by pressure variation with an accuracy of 0.01 Torr. The experiments were carried out without freezing water vapour out of the gas phase, except for sepa-

rate experiments where we determined the amount of water vapour formed and investigated its influence upon the activity with respect to hydrogen absorption as follows: after the reduction of a sample up to a certain extent in the system with non-cooled trap we blocked the reactor, then the trap was cooled with liquid nitrogen, then the reactor was opened and we continued the experiment with the trap under cooling.

The reduction level for a sample was calculated basing on the assumption that all the copper in the sample exists in the form of oxide CuO that is reduced to produce metal copper.

For the practical application it is appropriate to estimate the specific activity of materials as calculated for 1 g of a sample, therefore in the present work the reactivity in hydrogen absorption was calculated as a change in the amount of moles of hydrogen during one second per one gram of a sample. In the calculation of the amount of oxygen removed from the surface it was considered that there are  $1 \cdot 10^{19}$  oxygen atoms present on  $1 \text{ m}^2$  of the surface.

## RESULTS AND DISCUSSION

Table 1 demonstrates data concerning the specific surface area ( $S_{sp}$ ) and phase composition of the initial materials investigated to determine the activity with respect to hydrogen absorption. The samples applied with a high content of copper (26 % CuO/ $\gamma$ - $\text{Al}_2\text{O}_3$  and

TABLE 1

Data concerning the specific surface area, phase composition of initial oxide materials based on copper and their activity with respect to hydrogen absorption of at 60 °C

Samples	$S_{sp}$ , $\text{m}^2/\text{g}$	Phase composition	Hydrogen absorption rate ( $W$ ), $10^{-8} \text{ mol}/(\text{s} \cdot \text{g})$
5 % CuO/ $\gamma$ - $\text{Al}_2\text{O}_3$	230	Solid sol. $\text{CuAl}_2\text{O}_4$ - $\gamma$ - $\text{Al}_2\text{O}_3$ <sup>a</sup>	0.05 (3 %) <sup>b</sup>
15 % CuO/ $\gamma$ - $\text{Al}_2\text{O}_3$	198	$\text{CuO} + \gamma$ - $\text{Al}_2\text{O}_3$	0.2 (2 %) <sup>b</sup>
26 % CuO/ $\gamma$ - $\text{Al}_2\text{O}_3$	140	$\text{CuO} + \text{solid sol. } \text{CuAl}_2\text{O}_4$ - $\gamma$ - $\text{Al}_2\text{O}_3$ <sup>a</sup>	0.5 (30 %) <sup>c</sup> , 25 °C 2.3 (50 %) <sup>c</sup> 15 (35 %) <sup>c</sup> , 90 °C
28 % CuO/ $\theta$ - $\text{Al}_2\text{O}_3$	64	$\text{CuO} + \theta$ - $\text{Al}_2\text{O}_3$	0.8 (20 %) <sup>c</sup>

<sup>a</sup>According to data from [14].

<sup>b</sup>Parentetically is presented the level of CuO reduction into Cu.

<sup>c</sup>An average value for the rate during the period of sample reduction time up to gaining the reduction level presented in parentheses.

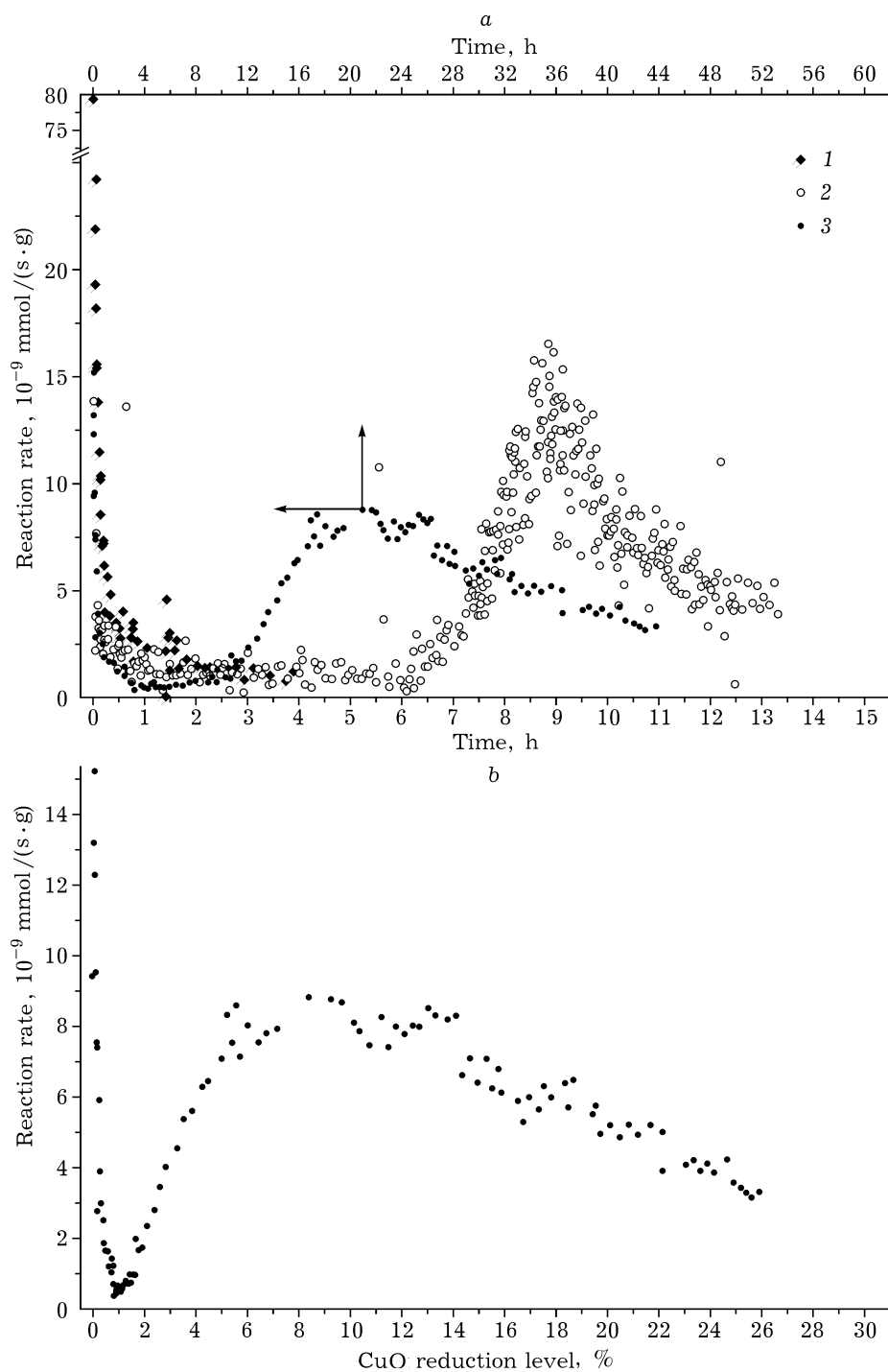


Fig. 2. Rate of hydrogen absorption by samples depending on the process time (a) and on the reduction level of copper oxide for the sample of 26 % CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at  $T = 25$  °C, initial hydrogen pressure being of 40 Torr (b): 1 - 15 % CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (60 °C,  $X = 2$  %); 2 - 28 % CuO/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> (60 °C,  $X = 18$  %); 3 - 26 % CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (25 °C,  $X = 26$  %).

28 % CuO/ $\theta$ -Al<sub>2</sub>O<sub>3</sub>) contain CuO phase with various dispersity, the average size of CuO particles for the samples of 26 % CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 28 % CuO/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> amounts to 260 and 310 Å, respectively. Much lower dispersity of CuO phase for the sample 28 % CuO/ $\theta$ -Al<sub>2</sub>O<sub>3</sub>,

to all appearance, is connected with the fact that the specific surface area for  $\theta$ -Al<sub>2</sub>O<sub>3</sub> carrier is almost twice lower than the specific surface area for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. According to data from [14], a commercial sample of 26 % CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> contains ~20 % of CuO phase; other copper is

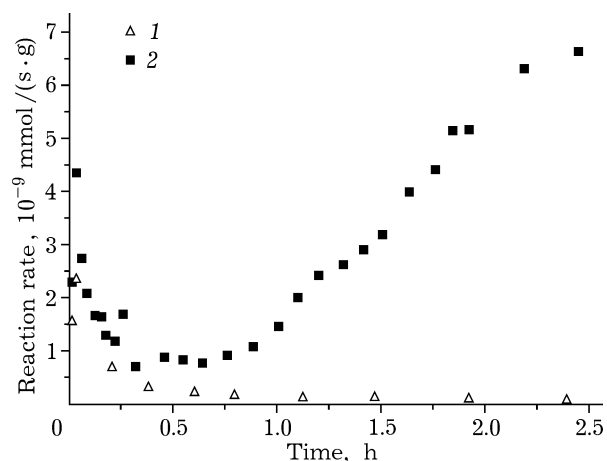


Fig. 3. Kinetic curves for hydrogen absorption by samples with various phase composition ( $T = 60^\circ\text{C}$ , initial hydrogen pressure of 40 Torr): 1 - 5 %  $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ ,  $X = 0.5\%$ ; 2 - 26 %  $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ ,  $X = 5.6\%$ .

a constituent of the solid solution based on  $\gamma\text{-Al}_2\text{O}_3$  ( $\text{CuAl}_2\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ ) with  $\text{Cu}^{2+}$  ions in octahedral positions. This fact explains the absence of  $\text{CuO}$  phase in the sample of 5 %  $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$  obtained which sample exhibits visually uniform green colouring over the surface and on the cut of granules caused by the formation of a solid solution [14]. The sample of 10 %  $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$  exhibits the appearing of  $\text{CuO}$  phase whose content grows with the further increase in the concentration of the oxide under application.

At the temperature of  $60^\circ\text{C}$  all the samples demonstrate the activity with respect to hydrogen absorption; however the kinetic curves for the rate hydrogen absorption by samples depending on time differ between each other (Figs. 2, 3). One can see that for the samples with a high content of the reactive phase (26 %  $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$  and 28 %  $\text{CuO}/\theta\text{-Al}_2\text{O}_3$ ) the rate of hydrogen absorption at first falls, then one can observe the part of the curve with almost constant rate value, further the rate starts to grow and passes through a maximum. For the sample of 26 %  $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$  such a type of time dependence is reproduced within all the temperature range under investigation ( $25\text{--}90^\circ\text{C}$ ). The point of minimum is exhibited at almost the same reduction level (1.1–1.5 %) for all the temperatures. The maximum of the rate is also corresponding to a close range of the sample reduction level (10–15 %). For the sample of 28 %  $\text{CuO}/\theta\text{-Al}_2\text{O}_3$  the position of the maximum almost coincides with the maximum

position for the sample of 26 %  $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ . Figure 2, b demonstrates a change in the specific rate of hydrogen absorption by 26 %  $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$  sample at  $25^\circ\text{C}$  depending on the value of copper oxide reduction level ( $X$ ).

For the samples  $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$  in the system with a lower content of copper oxide we observed another other type the kinetic curve with the maximal rate of hydrogen absorption during the initial moment of time; then the reaction rate decreased, further varying insignificantly.

Table 1 demonstrates data concerning the specific rate of hydrogen absorption by the samples of oxide materials based on copper with various reduction levels. One can see that the greatest activity is exhibited by the samples with a high content of copper oxide. The specific activity of 28 %  $\text{CuO}/\theta\text{-Al}_2\text{O}_3$  sample appeared much lower, which, to all appearance, could be connected with a much lower dispersity of copper oxide in this sample, as well as with the influence of various nature of surface acidic centres inherent in aluminium oxide with different phase composition [15]. Other samples exhibit only satisfactory initial specific rate of hydrogen absorption and do not meet the requirements imposed upon hydrogen absorbers for placing within the containers filled with radioactive wastes.

The observed type of kinetic dependence of the absorption rate (or of the reduction level) on time for the applied samples with a high content of reactive phase is similar to the type of kinetic dependence described for the reduction of bulky samples of copper oxide by hydrogen [16] and carbon monoxide [17]. The character of this dependence is typical for the processes of solids interacting with gases when the process switches from a homogeneous mode to the heterogeneous one when the reaction to proceed at the interface between the solid and the gas [17]. The initial descending branch of the curve observed for hydrogen absorption by applied samples is caused by the reaction of surface copper oxide reduction. It is confirmed by the fact that the point of minimum for the sample of 26 %  $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$  is exhibited at all the temperature values at almost the same reduction level. The observed activation energy value for the reaction at the point of minimum amounts to 61 kJ/mol.

The process of hydrogen-induced reduction of copper oxide applied onto aluminium oxides, as well as the reduction of a bulky sample, to all appearance, proceeds with the penetration into the bulk of oxide, since an increase in the rate after passing the minimum is observed to proceed with the removal of several oxygen monolayers. The decrease in the rate after reaching the maximum on the kinetic curve for topochemical reactions of a reducing gas with bulky oxides is connected with a decrease in the interface between phases and diffusion retardation of oxide-gas interaction due to a new phase formed. As one can see from Fig. 2, the rate of hydrogen absorption by applied samples of copper oxide with a high content of the reactive phase passes through a smooth maximum, too. Basing on the results of XRD phase analysis of 26 % CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples reduced at different temperature (Fig. 4) one could conclude that the reduction of the copper oxide phase in the applied samples under the conditions studied, as well as the reduction of bulk copper oxide samples with different values of  $S_{sp}$  at 125 °C [16], proceeds through the formation and growth of the nuclei of bulk metal copper phase.

As it was mentioned above, in the sample of 26 % CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> copper ions enter into the composition of both CuO phase and CuAl<sub>2</sub>O<sub>4</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> solid solution with the spinel structure. The authors of [18] have established that copper oxide-alumina catalysts those con-

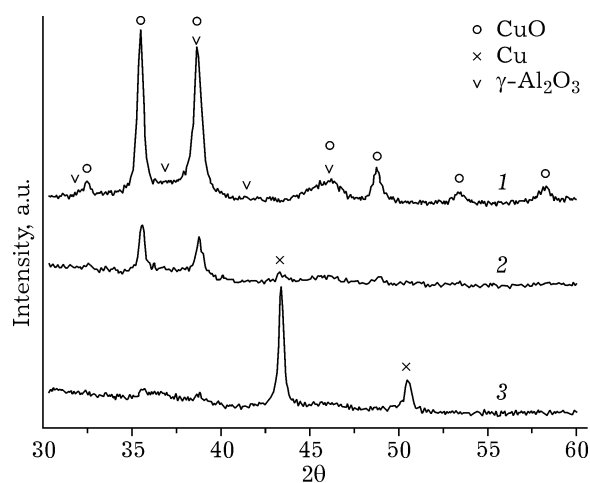


Fig. 4. X-ray diffraction profiles for 26 % CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples: 1 – initial sample; 2 – sample reduced at 25 °C, X = 30 %; 3 – outside part of the sample granules (with a high content of copper) reduced at 90 °C, X = 35 %.

tain only the phase of a solid solution and/or additionally the phase of copper oxide demonstrate a close specific reactivity with respect to hydrogen oxidation as calculated for 1 g of a sample. It is connected with the fact that the samples of a solid solution, despite of low specific reactivity calculated for 1 m<sup>2</sup>, have well-developed surface. From data presented in Fig. 3 one can see that another kind of the kinetic curve for hydrogen absorption is inherent in a solid solution sample (5 % CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), whereas its contribution to the process of low-temperature hydrogen oxidation can be exhibited only within an initial moment of time. To all appearance, under the conditions studied the only process of solid solution surface reduction can proceed.

The influence of the oxidation product (water) formed upon the reactivity was investigated in the experiments with use of a trap cooled by liquid nitrogen by the example of the most reactive sample of 26 % CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. It has been established that after the reduction of the reactive phase of the sample up to a 50 % level at 53 °C (the 1st part of the experiment) the gas phase contains <0.1 % of the total water amount which should be formed as calculated for hydrogen absorbed. Continuing the experiment (the 2nd part) with simultaneous freezing of water vapour we observed an almost five-fold increase in the rate. The results of subsequent unfreezing the trap demonstrated that the amount of frozen water was considerably higher than the amount of hydrogen absorbed during the 2nd part of the experiment. This fact indicates a partial water desorption from the catalyst, which water was formed in the 1st part of the experiment. The calculated amount of adsorbed water was equal to 2.12 g/100 g of sample at the equilibrium pressure of 15 Pa. With the increase in the reduction temperature up to 90 °C the adsorption capacity of the sample with respect to water decreases down to 1.5 g/100 g (the equilibrium vapour pressure amounting to 340 Pa). In conducting the experiments with a non-cooled trap at 90 °C (by the contrast with lower temperature values) we observed an abrupt decrease in the rate after passing the maximum, which could be connected with a masking influence of water formed, since the rate was calculated from pressure changing in the system.

Thus, the interaction between hydrogen and copper oxide in applied samples at low temperatures proceeds according to an oxidation-reduction mechanism with the formation of surface OH groups and/or water molecules those migrate from the surface of the reactive phase to the carrier surface thereby promoting the development of the volume process of the growth of reduced phase nuclei.

The studies carried out concerning hydrogen absorption by applied oxide systems based on copper have confirmed the hypothesis that weakly bound oxygen of oxides being active in the catalytic oxidation of hydrogen at moderate (100–200 °C) temperatures, could demonstrate the activity at lower temperatures, too. In this case, the low-temperature process of CuO phase reduction in applied samples with a high content of copper oxide, as well as the process of the reduction of bulky CuO samples at moderate temperature values, proceeds not only on the surface, but also in the bulk of copper oxide.

The most promising material to be employed as an absorber of hydrogen evolved in the processes of radiolysis while transportation of barrels with mixed RW in the containers such as TRUPACT-II, represents copper oxide applied onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with a high content of reactive phase (26 % CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>). The calculations performed demonstrate that the amount of this material meeting the requirement for the mass of getters placed inside containers is sufficient for binding hydrogen formed within the container during the period of transportation both concerning the volume capacity with respect to hydrogen, and concerning the rate of hydrogen absorption at the temperature higher than 0 °C. In this case, there is a possibility to place additionally an absorber of water vapour in order to extend the operation temperature range.

## CONCLUSION

Potentialities are demonstrated for obtaining the materials capable of hydrogen absorption at low temperature values, by means of applying a reactive component (copper oxide) in amounts of 26–28 % onto the carriers those can actively adsorb water ( $\gamma$ - or  $\theta$ -Al<sub>2</sub>O<sub>3</sub>). In this case, the reduction of the reactive phase up to 50 % level proceeds with reasonable rates of hydrogen absorption due to the development of a topochemical process in the bulk.

Employing such materials for irreversible hydrogen binding in the design of an absorber placed inside containers with mixed radioactive wastes allows one to provide the safety during their transportation.

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