

The low-temperature reduction of Pd-doped transition metal oxide surfaces with hydrogen

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Abstract

The reaction of hydrogen with a series of polyvalent metal oxides (Fe_2O_3 , WO_3 , MoO_3 , V_2O_5 , Sb_2O_3 , PbO_2 , Cr_2O_3 , NiO , CuO , Co_3O_4 , MnO_2 , PdO , Ag_2O) was investigated at low temperatures (77–320 K) and pressures (0.001–0.7 kPa). Pd-doped (0.1–0.5 wt.%) transition metal oxides can be reduced by hydrogen at 77–320 K whereas the onset of the reduction of the pure oxides occurs at temperatures higher than 500–700 K. It is shown that oxides, possessing a low stability of the metal–oxygen bond, a significant oxygen-diffusion coefficient from the oxide volume, and a large specific surface area are promising low-temperature vacuum hydrogen getters. Two temperature regions with different kinetics have been found for the most active oxides (Co_3O_4 , CuO , MnO_2): 77–210 and 220–320 K. At 77–180 K, the chemical interaction between hydrogen and the Pd-doped oxides proceeds with an apparent zero activation energy according to the equation $P = \ln \tau$. At 195–320 K, a first-order reaction is found. XPS studies of the low-temperature reduction catalysts show Pd on oxides. A possible reaction mechanism is discussed. It is supposed that proton spillover into the lattice is critical for the low-temperature oxide reduction. A electron tunnel mechanism is probable too.

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1. Introduction

Effective hydrogen absorbers, operating under vacuum and low-temperature conditions, are necessary in cryogenic technology. Mainly systems based on Ag, Pd or Pt have been suggested as such getters. The use of transition metal oxides is promising for these purposes.

It was observed [1] that the chemical reaction of hydrogen with pure and palladized Co_3O_4 occurs at very low temperatures, down to 77 K. Palladized cobalt(II, III) oxide is a promising low-temperature hydrogen absorber for vacuum systems.

It has been shown that the presence of both Pt and Co_3O_4 promotes the partial reduction of the transition metal oxide at temperatures hundreds degrees lower than in the absence of Pt. In addition, catalysts consisting of Pt and Co oxide are active in CO oxidation [2] at temperatures much lower than pure Pt or pure Co_3O_4 [3–5]. In general, multicomponent catalysts consisting of both a transition metal oxide and a noble metal show an improved activity and selectivity in heterogeneous catalytic reactions [6,7], compared

to the corresponding monometallic catalysts. The present paper describes studies concerning the effect of Pd on the reduction of a number of metal oxides by hydrogen in the temperature range of 77–320 K. Possible mechanisms for the process at 77–320 K are discussed.

2. Experiments

Oxides were prepared by decomposition of the metal salt by a procedure that provides the oxide with a highly developed energetic heterogeneous surface area. Pd was deposited by impregnating the oxide with an aqueous solution of Pd nitrate which is subsequently decomposed upon heating.

Hydrogen adsorption was studied in a static vacuum apparatus from the pressure drop in a known volume (0.300–0.900 l) with removal of the reaction product (H_2O) by freezing using a trap at 77 K. Hydrogen was purified by passing through the walls of a hot nickel capillary. During the course of the reduction the change of pressure was measured with a thermocouple gauge calibrated for hydrogen. Hydrogen consumption was determined from the measured decrease of the hydrogen pressure. Water released during the reaction was frozen in a liquid hydrogen trap.

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A series of polyvalent metal oxides were investigated in the temperature range of 77–330 K and pressures of 0.001–0.700 kPa. All the samples were first evacuated at 523 K (393 K for Ag₂O) and a pressure of 1×10^{-6} kPa for 4 h and were then kept at the same temperature in an oxygen atmosphere (13.3 kPa). The temperature of 523 K was selected in order to prevent sintering of the contact surfaces and phase transformation that occur at higher temperatures. The state of samples after such treatment was taken as our standard state and the degree of reduction of their surface was assumed equal to zero. The amount of oxygen in the surface monolayer was determined on the basis that the area, occupied by the oxygen atom, is equal to 7.83 \AA^2 .

The change in surface coverage with oxygen was calculated from the amount of unconsumed hydrogen, which was measured additionally by quantitative determination of the formed water from the increase in pressure in the system upon thawing out the trap.

Since our specimens have a high specific surface area and mild conditions for the reaction were chosen, only 0.1% of a monolayer of oxygen was removed during a single run. Therefore, the state of reduction has been determined while the surface remained almost unchanged.

3. Results and discussion

In this research project, the role of Pd was investigated with respect to the reduction of two different classes of

oxides characterized by weak and rather strong oxygen-lattice bonds, respectively. To the former class belongs Co₃O₄, studied previously [1]. Chosen as representatives of the latter class MoO₃, WO₃, Cr₂O₃, Fe₂O₃, CuO, V₂O₅, MnO₂ have been selected. Reduction of the pure oxides Fe₂O₃ and Cr₂O₃, starts at 470 K and of MoO₃, WO₃ and V₂O₅—at 700 K. As follows from Table 1, promotion by 0.3–0.5 wt.% Pd results in oxides whose initial hydrogen reduction temperature has been plummeted by hundreds degrees, and which are capable to react with hydrogen at 293 K (Table 1). Introduction of 0.5 wt.% Pd leads to a growth of the hydrogen capacity by a factor of 15–100.

A correlation has been found between the hydrogen interaction rates and the metal oxygen–oxide bond strength. The most active oxides characterized by a low energy of the surface oxygen bond, are Co₃O₄, CuO, MnO₂, NiO. Common regularities for hydrogen activation have been elicited for all the Pd-doped transition metal oxides examined.

The state of Pd on the surface of Co₃O₄ has been investigated [1] by X-ray photoelectron spectroscopy (XPS) and electron microscopy in conjunction with energy-dispersive spectroscopy. Pd on the surface of the oxides studied has been found to be uniformly distributed in the form of clusters smaller than 40 \AA in size. Using XPS it has been shown, that in its initial state Pd is present as PdO (binding energy 337.4 eV) [1,9]. Upon exposure to hydrogen the binding energy of Pd 3d_{5/2} shifts to 335.7 eV, which is higher than that for metallic Pd but lower than that for Pd⁺. Based on these data, the conclusion is drawn that the catalytically

Table 1
Hydrogen interaction with pure and Pd-doped metal oxides

Oxide	Surface area (<i>S</i> , m ² /g)	The temperature of initial reduction (<i>T</i> , K)		Capacity H ₂ (cm ³ /g(<i>P</i> _{H₂} = 0.700 kPa))
Fe ₂ O ₃	12.5	473	–	–
Pd-Fe ₂ O ₃	12	–	293	0.01
WO ₃	2.5	700	–	–
Pd-WO ₃	2.5	–	293	0.01
MoO ₃	3	700	–	–
Pd-MoO ₃	3	–	293	0.01
V ₂ O ₅	11	693	–	–
Pd-V ₂ O ₅	11	–	293	0.01
Sb ₂ O ₃	14	393	–	–
Pd-Sb ₂ O ₃	14	–	293	0.01
PbO ₂	28	493	–	–
Pd-PbO ₂	28	–	293	0.01
U ₃ O ₈	2.5	–	–	–
Pd-U ₃ O ₈	2.5	–	293	0.01
Cr ₂ O ₃	40	473	–	–
Pd-Cr ₂ O ₃	40	–	293	0.01
NiO + Ni ₂ O ₃	170	330	–	–
Pd (NiO + Ni ₂ O ₃)	170	–	293	0.10
CuO	100	300	–	3
Pd-CuO	100	–	293	50
Co ₃ O ₄	140	293	–	15
Pd-Co ₃ O ₄	135	–	293	180
MnO ₂	180	293	–	2.5
Pd-MnO ₂	180	–	293	286
PdO	–	–	293	110
Ag ₂ O	1.3	–	293	1.5

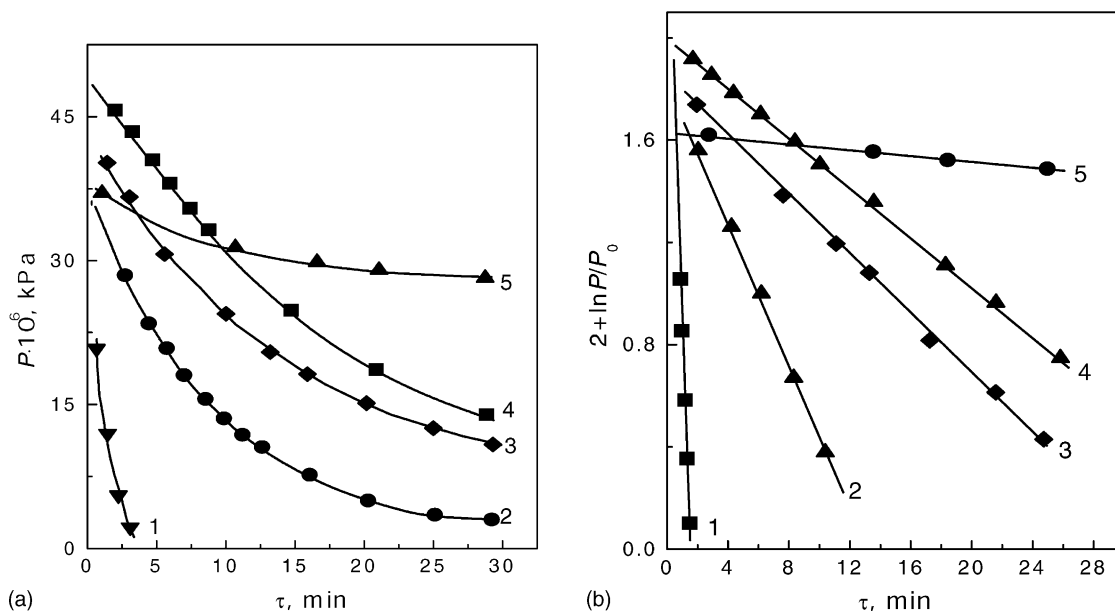


Fig. 1. The decrease of the hydrogen pressure in coordinates P – τ (a) and $\ln(P/P_0)$ – τ (b): 1, Co_3O_4 ; 2, CuO ; 3, MnO_2 ; 4, Ag_2O ; 5, NiO . $T = 293\text{ K}$, $P = 5 \times 10^{-5}\text{ kPa}$.

active form is an oxide cluster incorporating partially reduced Pd chemically bound to the oxide. During the initial interaction of Pd-doped oxides and hydrogen partial reduction of Pd occurs. It is in this form that an oxide Pd cluster makes a catalyst. Measurements of the reduction rates of oxides containing oxidized or reduced Pd clusters support this conclusion.

The typical kinetic curves, at 293 K for MeO_n represented in Fig. 1a do not show a S-shape typical of very low degree of reduction ($5 \times 10^{-6}\text{ g O}_2/1\text{ g oxide}$), in the absence of autocatalysis. Hydrogen adsorption kinetics on the oxides studied in the range of 230–330 K obeys a first-order equation in hydrogen $-dP/d\tau = KP$, which fact is supported by the rectification of a $\ln P$ – τ plot (Figs. 1b and 2). Magnitudes of rate constant of hydrogen interaction with oxides were calculated from the tangent of the angle of the straight line $\ln(P/P_0)$.

It is known that at high temperatures the bond energy of surface oxygen increases with an increase in degree of oxide reduction and the rate of its removal decreases. Our data obtained for CuO , shows that analogous regularities are also observed at low temperatures and pressures. As is seen from Fig. 3, the rate of hydrogen reaction with oxide depends significantly on the oxygen content in the surface layer: removal of 0.02% of a monolayer from the CuO surface at room temperature lowers the specific reaction rate constant by a factor of 2. The activation energy of the reaction increases from 31 kJ mol^{-1} for the oxidized sample to 47 kJ mol^{-1} upon removal of 0.08% of an oxygen monolayer. A value of E_{act} , equal to 60 kJ mol^{-1} , is obtained for a stable operating copper oxide surface and a value of 72 kJ mol^{-1} is obtained for a partially reduced surface (1% of the monolayer was

removed). This indicates a pronounced heterogeneity of the copper oxide surface: evidently the data suggest that a stable operating CuO surface has an 0.08% degree of reduction.

The adsorption capacities of pure oxides are not large even for the most active getters (Table 1). This can explain the low fraction of reactive oxygen at low temperatures. In

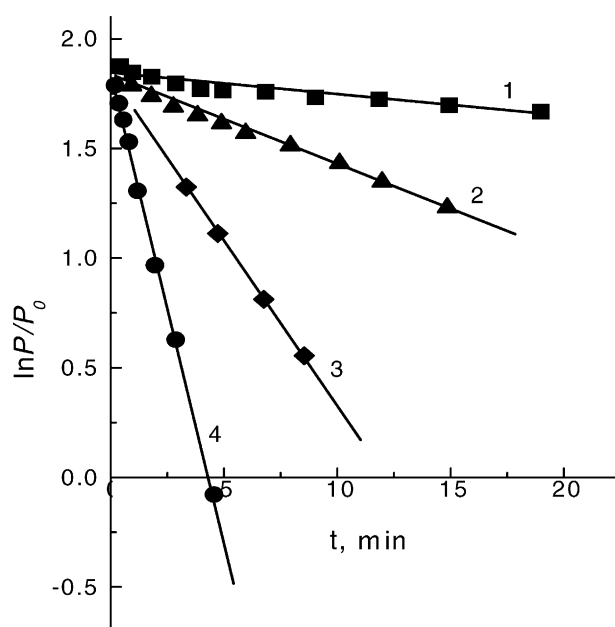


Fig. 2. The decrease of the hydrogen pressure at 293 K in coordinate $\ln(P/P_0)$ – τ for MnO_2 (1 and 2) and Pd-MnO_2 (0.5 wt.% Pd) (3 and 4) evacuated at different temperatures (1 and 3: in oxygen at 523 K, 2 and 4: after sevacuation at 523 K).

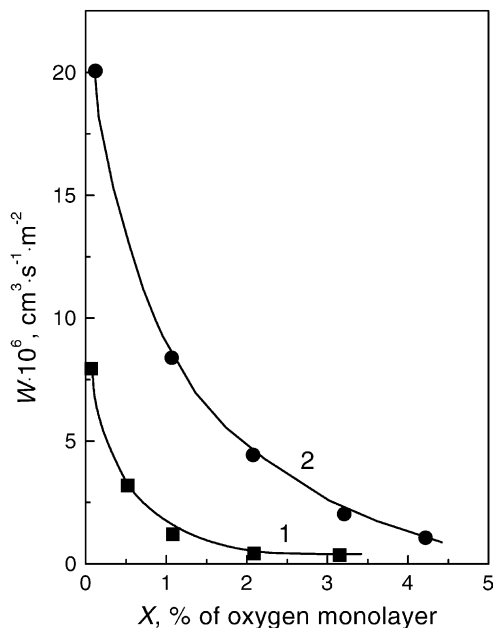


Fig. 3. Dependence of the rate (W) (1, 300 K; 2, 325 K) of the reduction on the amount of oxygen (x) removed from the surface CuO.

fact, only 8% of surface oxygen enters into reaction with hydrogen at 293 K and 26% reacts on Co_3O_4 .

The observed “relaxation” effect for certain getters should be noted: cessation of hydrogen introduction and exposure of the getter under vacuum conditions without evacuation for several hours lead to an increase in hydrogen-adsorption rate. Thus, while the rate constant falls from 5×10^{-5} to $0.5 \times 10^{-5} \text{ s}^{-1} \text{ m}^{-2}$ on copper oxide after removal of 0.1% of the oxygen monolayer, after 10 h of “relaxation” it increases

Table 2

Kinetics of the reaction of hydrogen with Co_3O_4 and $\text{Pd-Co}_3\text{O}_4$ for different initial states (reduction of the surface)

T (K)	K_s ($\times 10^4 \text{ s}^{-1} \text{ m}^{-2}$)			
	Co_3O_4		$\text{Pd-Co}_3\text{O}_4$	
	$X = 0$	$X = 10$	$X = 0$	$X = 10$
195	4.1	–	0.8	10.9
255	7.3	0.1	1.4	13.2
274	13.0	0.5	4.0	21.0
293	20.0	1.2	16.0	25.3

to a value of 2.5×10^{-5} . Evidently, this effect is associated with filling of oxygen vacancies on the surface as a result of diffusion of dissolved oxygen, the calculated diffusion coefficient of lattice oxygen for CuO at 293 K is negligibly small.

For Co_3O_4 the activation energy increases, which is due to the non-uniformity of the surface oxygen energy and the bond of the oxygen to be removed becoming increasingly stronger as the oxide is reduced. For $\text{Pd-Co}_3\text{O}_4$, when 6–8% of the oxygen monolayer is removed the reaction rate constant doubles, with the activation energy falling from 39 to 8 kJ/mol. Such reduction process of Pd-doped oxides indicates the catalytic character of the action Pd exerts in the range of 230–330 K Fig. 4 (Table 2). A similar effect was observed recently for MnO_2 and Pd-MnO_2 (Fig. 5) [8].

A sample of initial Co_2O_4 , heated at 670 K with according to [1], a more ordered surface structure with $S_{sp} = 67 \text{ m}^2/\text{g}$, was also investigated. The physical adsorption of hydrogen, which occurs at 120–125 K and lower temperatures, was considered during the determination of the rate of the chemical reaction of hydrogen with Co_3O_4 , MnO_2 , CuO. It

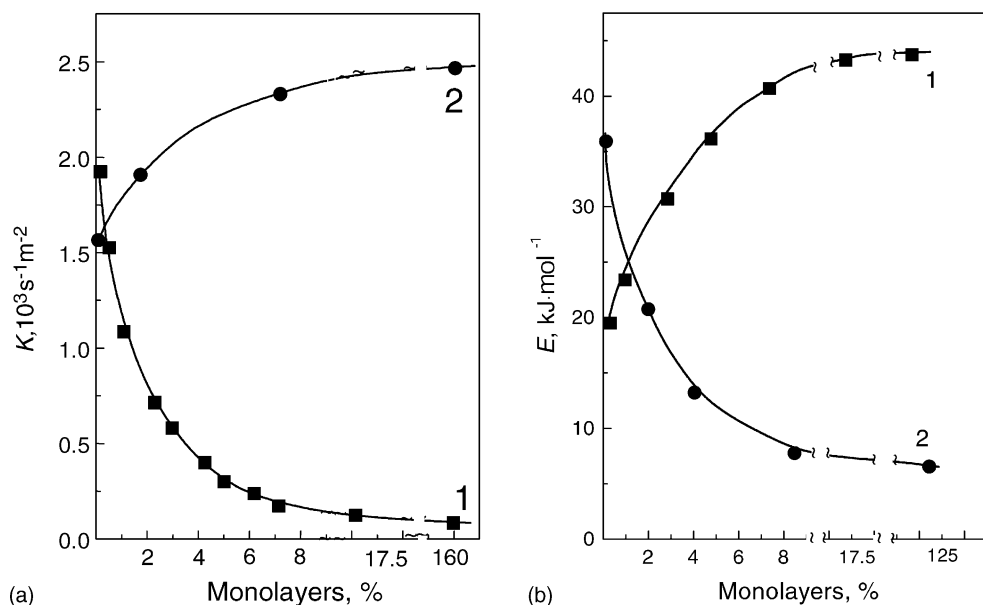


Fig. 4. Dependence of the rate constants (293 K) (a) and activation energy (b) of the reaction between hydrogen and surface oxygen on the amount of oxygen removed from the surface for Co_3O_4 (1) and $\text{Pd-Co}_3\text{O}_4$ (0.5 wt.% Pd) (2).

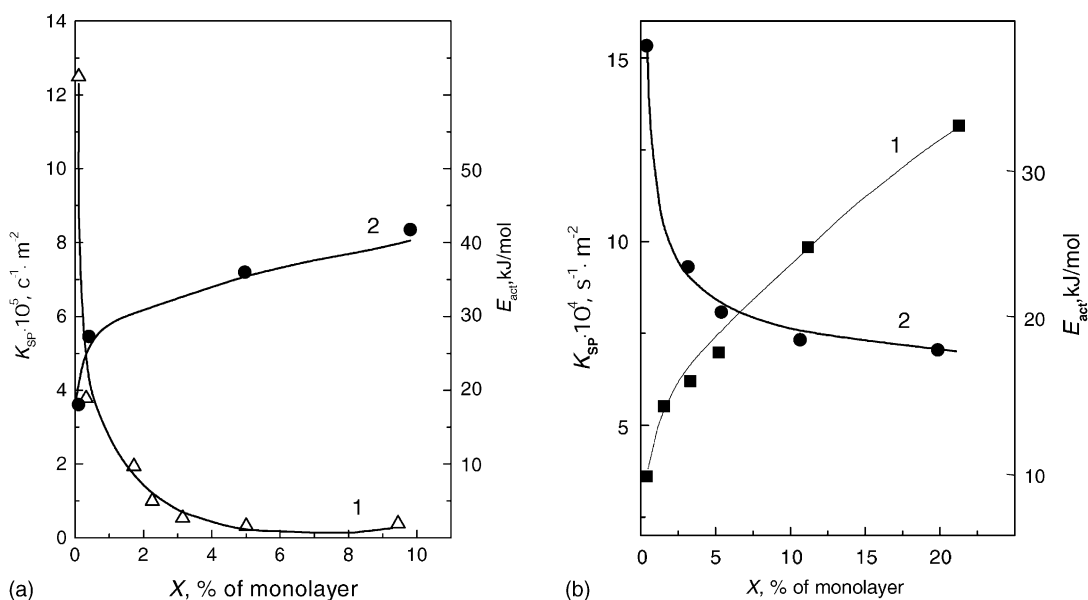


Fig. 5. Dependence of the rate constants (1) (293 K) and activation energies (2) of the amount of oxygen removed from the surface for MnO_2 (a) and Pd-MnO_2 (0.5 wt.% Pd) (b).

is believed that no reduction reaction occurs at low temperatures on commercial Co_3O_4 . The low-temperature dependence of the rate of reduction of pure and palladized cobalt monoxide-oxide with hydrogen is presented in Fig. 6a and b. Two regions are clearly traced in the studied temperature range with different dependence of the reaction rate on temperature: a normal Arrhenius dependence in the region 230–330 K and an anomalous dependence at 77–220 K. The

reaction rate does not decrease in the second region with decreasing temperature, but remains constant (Fig. 7). The character of changes in the rate of hydrogen adsorption is similar for pure and palladized Co_3O_4 . However, the rate on the palladized sample is four to five times higher than on the pure sample. It should be noted that palladized Co_3O_4 , kept in oxygen at 520 K, has a lower rate of hydrogen adsorption, practically coinciding with the rate obtained on pure

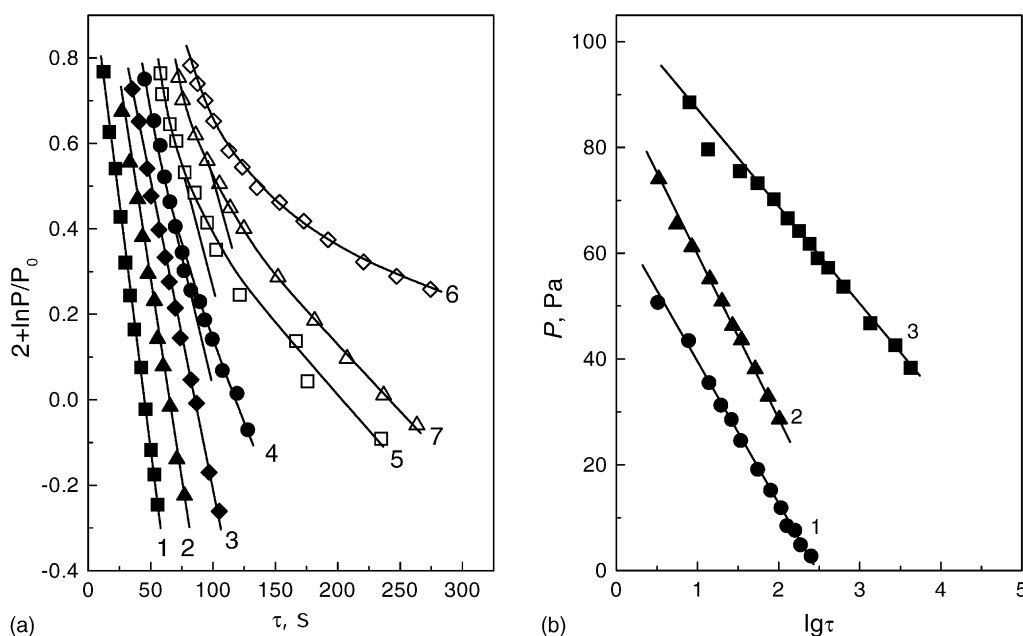


Fig. 6. (a) Dependence of the reaction between hydrogen and surface oxygen on the hydrogen pressure for $\text{Pd-Co}_3\text{O}_4$ (0.5 wt.% Pd) in co-ordinate $\ln P - \tau$: 1, 325 K; 2, 295 K; 3, 273 K; 4, 257 K; 5, 248 K; 6, 208 K; 7, 163 K. (b) Kinetics of the reaction of hydrogen with $\text{Pd-Co}_3\text{O}_4$ (0.5 wt.% Pd) at various temperatures: 1, 248 K; 2, 163 K; 3, 208 K.

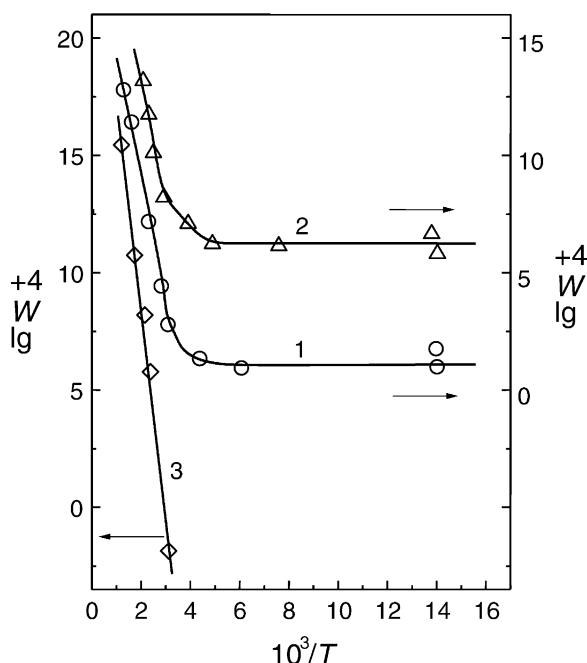


Fig. 7. Dependence of the rate of the reaction between hydrogen and surface oxygen on the temperature and method prepared: 1, Co_3O_4 (in this paper); 2, $\text{Pd-Co}_3\text{O}_4$ (0.5 wt.% Pd); 3, Co_3O_4 (were evacuated at 670 K).

Co_3O_4 . A similar effect was observed for MnO_2 and Pd-MnO_2 (Fig. 8).

The activation energy for reduction of the pure cobalt(II, III) oxide in the range of 230–330 K amounts to 12–18 kJ mol^{-1} , while it is 8–10 kJ mol^{-1} for the palladized sample; in the range of 77–230 K zero or even an apparent negative activation energy is observed on both samples, its value is in

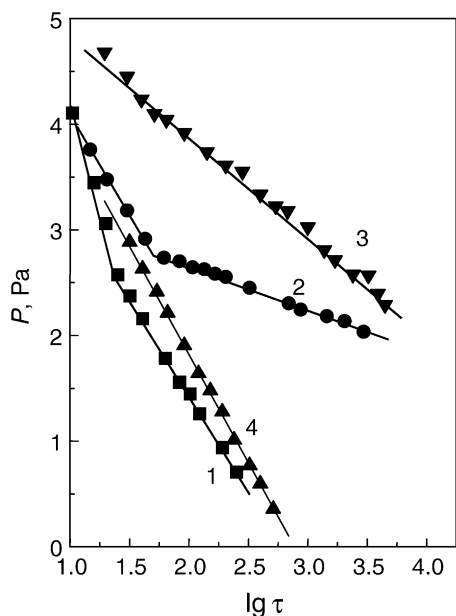


Fig. 8. The change in the hydrogen pressure in coordination $P-\ln \tau$ in the reduction of Pd-doped.

Table 3

Rate constants and activation energies of the reaction between hydrogen and surface oxygen at 295–277 K $X = 100\%$ Pd-MnO_2

T (K)	K_s ($\times 10^5 \text{ s}^{-1} \text{ m}^{-2}$)	Activation energy (E , kJ mol^{-1})
295	290	15
273	206	–
206	148	–
163	58	1–0.5
77	36	–

the limits of the experimental accuracy of this quantity. Such a dependence has also been observed on pure Co_3O_4 upon reduction to a degree $\alpha = 1.5$ mass%, while on palladized oxide it is observed up to a degree of reduction greater than 20% (almost to formation of CoO). A similar effect was also found for Pd-MnO_2 for X (reduction steps) = 100% (Table 3).

The presence of a low-temperature limit of the rate of reaction of hydrogen with pure and palladized cobalt oxide may indicate a tunnel mechanism of this reaction in the range of 77–200 K. The low-temperature limit of the rate of reduction with hydrogen has not been observed on Co_3O_4 heated at 670 K and MnO_2 —523 K (Figs. 2 and 7).

The two regions, for which different temperature dependences of the reaction rate are observed, also correspondingly differ in character of the kinetics of the reaction of hydrogen with the oxide. In the temperature range of 230–330 K, the kinetics of reaction of hydrogen with both pure and palladized Co_3O_4 and MnO_2 are described by a first-order equation with respect to hydrogen $dP/d\tau = KP$, which is confirmed by the clear linearization of the dependence of hydrogen pressure on time in $\ln(P/P_0)-\tau$ coordinates (Figs. 1 and 2). However, already at a temperature of 263–273 K and below the form of kinetics changes. At a sufficiently low temperature (77–210 K) the change in pressure with time occurs according to the law $P = A \ln \tau$. This dependence is presented in Figs. 6b and 8 in a time interval, that makes up 2 orders of magnitude of the quantity. The observed kinetics of the process in the low-temperature region is characteristic for processes, occurring by a tunnel mechanism [9–12], and confirms the above drawn conclusion. Regularities of low-temperature (430–600 K) reduction of pure and platinated transition metal oxides with hydrogen were studied. It was determined [1,8] that reduction of pure and palladized cobalt(II, III), MnO_2 oxide is achieved in the same way also in the temperature region of 250–430 K. It was established [1] that Pd oxide clusters, containing partially reduced Pd ions, significantly accelerate the process and act as catalysts of Co_3O_4 reduction.

The data obtained in this research show that a fundamentally different reduction mechanism is realized in the low-temperature region of 77–220 K. According to data [8–12], the presence of a low-temperature limit of the oxide reduction rate and kinetics, characteristic for tunnel reactions in condensed media, may indicate that the reaction

occurs via a quantum tunnel mechanism of transfer of an electron or proton or of hydrogen atoms.

The possibility of Co_3O_4 activationless reduction of cobalt(II, III) oxide, synthesized by the method described in [1], in our opinion, is due to the structure of its surface. Such Co_3O_4 surface contains a large excess of nonstoichiometric oxygen as coordinately unsaturated O^- centers and cationic vacancies in the cobalt sublattice. Using preparations, subject to a thermal treatment, results in healing of defects and loss of active oxygen and the concentration of these centres becomes insignificant. As a result low-temperature reduction of the oxide does not occur on these samples (Figs. 2 and 7).

Adsorption of hydrogen on the synthesized Co_3O_4 can occur on O^- defects, cationic vacancies, or geometrically corresponding $\text{Co}^{3+}-\text{O}^-$ centres. The presence of H_2 - D_2 exchange on Co_3O_4 at 789 K [13] makes it possible to suggest adsorption of hydrogen not only in a molecular but also an atomic form. In the case of hydrogen adsorption on O^- or cationic vacancies reduction of the oxide is determined by electron transfer from OH^- to Co^{3+} . During adsorption on the $\text{Co}^{3+}-\text{O}^-$ pair transfer of hydrogen from the Co^{3+} ion to the lattice oxygen and transfer of an electron to a metal ion are necessary. Tunneling of proton or a hydrogen atom is possible in this case.

On palladized Co_3O_4 and MnO_2 samples the reaction rate in the region of reduction by a tunneling mechanism is four to five times greater than on the pure sample as a result of facilitation of atomization of hydrogen on the partially reduced Pd ions. This agrees with the fact that the reduction rate is even slightly lower on a sample, containing oxidized Pd cluster, than for the non-promoted oxide, since atomization of hydrogen occurs on reduced Pd ions. The nature of the tunneling particles (electron, proton, and hydrogen atoms) can be determined from data on the kinetic isotope effect (KIE). In the case of tunneling of a proton or hydrogen atom substitution of hydrogen by deuterium should lead to a sharp decrease in the reduction rate and to an increase in the KIE by several orders of magnitude.

Experiments, carried out with deuterium, showed that it reduced cobalt(I, II) oxide at low temperatures at a sufficiently high rate. The KIE does not change significantly upon going from high (270–330 K) to low (77–220 K) temperature both for pure Co_3O_4 and for the Pd-containing sample: $K_D:K_H = 1.4:2.0$ (Table 4). The same value of the KIE was obtained in [13] during the study of the low-temperature chemisorption of hydrogen on Co_3O_4 . These data indicated hydrogen adsorption on O^- or a cationic vacancy with subsequent tunneling of an electron to Co^{3+} . The limiting stage of the process is evidently penetration of an electron into the surface-adjacent layer of cobalt cations through a barrier, created by a layer of oxygen ions and hydroxyl groups, increasing the surface-adjacent space change and the work function of the oxide. The hypothesis concerning tunneling of an electron also agrees with the quite broad range of the tunnel effect (77–220 K). The obtained data do not exclude

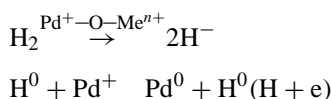
Table 4

The reduction of Pd-doped cobalt oxides by H_2 and D_2 at different temperatures

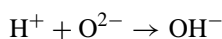
Temperature (K)	Rate of reduction ($W, \times 10^4 \text{ cm}^3 \text{ m}^{-2} \text{ s}^{-1}$)		Kinetic isotope effect
	H_2	D_2	
Pd-doped Co_3O_4			
295	13.2	8.1	1.6
273	10.4	5.9	1.8
257	8.3	3.7	2.2
163	7.6	3.2	2.4
77	8.6	4.3	2.0
Co_3O_4			
295	7.4	3.6	2.0
273	3.4	1.6	2.1
77	1.4	0.8	1.8

the possible spillover of hydrogen from Pd oxide clusters to the oxygen [14,15]. However, similar values of KIE for pure and palladized Co_3O_4 indicate that in the case of palladized oxide the reduction rate at 77–220 K is determined by tunneling of namely an electron, while cleavage of the Pd–H bond in this temperature region probably plays a secondary role [16].

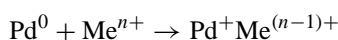
Thus, analysis of our experimental data and literature data [9,14] indicates the occurrence of a low-temperature (77–220 K) reduction of Pd- MeO_n by a tunnel mechanism of electron transfer. In our view this process can be seen as follows: hydrogen activation occurs on the oxide cluster containing partially reduced ions of Pd– $\text{Pd}^0 \dots \text{Pd}^+ - \text{O} - \text{Me}^{4+}$:



It is this process that ensures further chemical interaction of hydrogen and Pd-doped metal oxides at low temperature. Then, the proton passes via spillover to the oxide's oxygen:



Reduction of the oxide metal (Me^{n+}) occurs during electron tunneling from Pd^0 to Me^{n+} :



The existence of such stage is supported by the fact (as has been indicated by XPS) the complete reduction of an oxide cluster to PdO on the surface of transition metal oxides fails to be accomplished. Electron transfer tunnel mechanism is attested to by the experimentally observed apparent zero activation energy, logarithmic dependence of pressure on time and the invariability of KIE in a wide temperature range.

In all appearances, in the case of Pd-doped oxides, it is electron tunneling that governs the reduction rate at 77–220 K; disruption of Pd–H linkage and spillover of hydrogen to the oxygen of the oxide probably play a minor

role only in this temperature region. The systems surveyed above, Pd-doped oxides CuO, Co₃O₄, MnO₂, NiO are employed as chemical getters in cryogenic and electrochemical practices. They can find application as baseline systems.

Acknowledgements

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References

- [1] V.M. Belousov, J. Stoch, I.V. Bacherikova, E.V. Pozhkova, V.L. Lyashenko, *J. Appl. Surf. Sci.* 35 (1988/1989) 481.
- [2] Y.J. Mergler, J. Hoebink, B.E. Nieuwenhuys, *J. Catal.* 167 (1999) 305.
- [3] N.I. Il'cnenko, *Uspekhi Khimii* 41 (1972) 47.
- [4] G.C. Bond, B.P. Tripathi, *J. Chem. Soc., Faraday Trans.* 72 (1976) 933.
- [5] M. Che, B. Canosa, A.R. Gonzalez-Elipse, *J. Chem. Soc., Faraday Trans.* 78 (1982) 1043.
- [6] B.E. Nieuwenhuys, *Adv. Catal.* 44 (1999) 259.
- [7] M.W. Roberts, R.St.C. Smart, *J. Chem. Soc. Faraday. Trans.* 1 (80) (1984) 2957.
- [8] V.M. Belousov, L.V. Lyashenko, I.V. Bacherikova, I.V. Rozhkova, *Ukr. Chem. J.* 60 (1994) 33 (Translation).
- [9] Yu. Loginov, C. Spiridonov, X.K. Chokaev, U.H. Filimonov, *J. Phys. Chem.* 62 (1988) 3235.
- [10] M. Trigidis, R. Gomer, *Surf. Sci.* 155 (1985) 254.
- [11] C. Uebing, R. Gomer, *Surf. Sci.* 259 (1991) 151.
- [12] D.S. Choi, C. Uebing, R. Gomer, *Surf. Sci.* 259 (1991) 139.
- [13] N. Dowdon, N. Mackenzie, B.M. Trapnel, *Proc. R. Soc. A* 237 (1956) 245.
- [14] J. Shigehara, A. Ozaki, *J. Catal.* 21 (1971) 78.
- [15] S. Naito, Y. Tanako, High-temperature diffusion of hydrogen and deuterium in palladium, in: J.W. Hightower, N.N. Delgass, E. Iglesia, A.T. Bell (Eds.), *Proceedings of the 11th International Congress on Catalyst*, 1996, pp. 1115–1124.
- [16] W.C. Conner Jr, G.M. Pajonk, S.J. Teichner, *Adv. Catal.* 34 (1986) 1.