Chemisorbed Atoms and Molecules of Reactants As Active Sites in Heterogeneous Catalysis

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Abstract—In some heterogeneous chemical processes occurring on the solid/gas interface, reactant atoms and molecules chemisorbed during the reaction are not directly involved in chemical transformations but act as catalytic sites accelerating this reaction.

In situ investigation of the mechanisms of heterogeneous reactions at solid/gas interfaces is carried out by kinetic spectroscopic methods. In these methods, reaction rate is measured along with the rate of transformation of surface compounds resulting from the chemisorption of reactants during the reaction [1]. The chemisorption of gas molecules alters the state of the surface, changing the probabilities of chemical reactions involving adsorbed species. For example, chemisorbed molecules can participate in energy transfer and in the stabilization of highly reactive intermediates or product molecules, thereby raising the efficiency of the catalyst.

Here, we report experimental evidence for the acceleration of the heterogeneous reactions $H + H \longrightarrow H_2$ and $CO + O \longrightarrow CO_2$ by chemisorbed reactants.

Numerous studies have been devoted to the mechanism of the heterogeneous recombination of dissociated gas species and accompanying phenomena, including the luminescence of crystal phosphors and particle emission. The results of these studies have been interpreted in terms of the Eley-Rideal (ER) or Langmuir-Hinshelwood (LH) mechanism [2–5]. The following relationships are observed for the ER and LH mechanisms of the heterogeneous recombination of atoms, $R + R \longrightarrow R_2$ [6, 7]:

$$J = AnN + BN^{2}; \qquad \tau < N^{*}(J^{*})^{-1}, \qquad (1)$$

where J is the rate of the reaction (formation of product molecules), A and B are coefficients, n is the concentration of atoms in the gas medium, N is the concentration of chemisorbed atoms, and τ is the relaxation time for the occupation of the surface by chemisorbed atoms after the appearance of atoms in the gas medium. Hereafter, stars designate steady-state values. According to the author's knowledge, most of the publications dealing with the heterogeneous recombination of atoms report no direct validation of at least one of relationships (1), while reaction mechanisms deduced from indirect data are questionable.

Our kinetic studies of atomic adsorption with continuous determination of the rate of the heterogeneous recombination of adsorbed atoms have demonstrated that relationships (1) are not satisfied [6–9]. The disagreement between these relationships and similar data reported by other authors [10] was discussed earlier [7, 11]. According to [6–9], the heterogeneous recombination of hydrogen or oxygen atoms on the surface of various solids at $n \approx 10^{14}$ cm⁻³ proceeds by the mechanism $2R + 2Z \longrightarrow RZ + RZ \longrightarrow R_2 + 2Z$, where R is an atom arriving from the gas phase, Z is an adsorption site, and RZ is a physically adsorbed atom. In the case of hydrogen or oxygen atomic beam in high vacuum (n < 1 10^9 cm⁻³), the intensity of the radical-recombination luminescence (RRL) of crystal phosphors is $I \sim nN$ [4, 5], suggesting that the luminescence is excited owing to the reaction $\mathbf{R} + (\mathbf{RZ}) \longrightarrow \mathbf{R}_2 + \mathbf{Z}$ or $\mathbf{RZ} + (\mathbf{RZ}) \longrightarrow$ $R_2 + 2Z$ [7, 12], where (RZ) is a chemisorbed atom.

Thus, depending on the experimental conditions, the rate of a heterogeneous reaction can be controlled by different elementary steps. By studying the reaction in regimes differing in the rate-determining step, it is possible to derive a deeper insight into the reaction mechanism. No such studies have been devoted to the heterogeneous recombination of radicals. The purpose of our study was to use and develop the above approach. Experiments were carried out at various concentrations of active gas species ($6 \times 10^{12} \text{ cm}^{-3} \le n \le 10^{15} \text{ cm}^{-3}$) and various temperatures (293 K $\le T \le 518$ K). Furthermore, we developed a method enabling one to establish and control, in one run, different reaction regimes by modulating the flux of reacting molecules.

EXPERIMENTAL

The catalysts were ultrafine copper powder (spherical particles with an average diameter of 100 nm); fineparticle ZnS–Cu, ZnS–Tm, and CaO–Mn phosphors with a specific surface area of ~1 m²/g; and Pt/Al₂O₃ (0.6% Pt) with a specific surface area of ~10 m²/g. Hydrogen and carbon dioxide were spectroscopicgrade. Carbon dioxide was obtained by the thermal decomposition of CaCO₃ *in vacuo* and was dried using a silica gel column. Hydrogen (99.995%) was produced in a GVCh-6 hydrogen generator and was also dried in a silica gel column. The dissociation of gas molecules $(H_2 \rightarrow 2H \text{ and } CO_2 \rightarrow CO + O)$ was carried out by producing high-frequency electric discharges between electrodes placed 0.4 to 1.0 m upstream of a flow catalytic reactor. Under our experimental conditions, dissociated carbon dioxide consisted of CO₂ and nearly equal amounts of CO and O [13].

Elementary chemical processes on solid surfaces in reactive media were studied by relaxation measurements [9, 14–16]. These measurements provided information as to the participation of free, chemisorbed, and physically adsorbed species in surface reactions. Simultaneously, we recorded the time dependences of the concentration of adsorbed reacting species, N(t), of the dynamic effect of reaction (DER) [7, 17], F(t) = $[P_r(t) - P]S = GJ(t)$, and of the intensity of the RRL of crystal phosphors, $I(t) = \eta J(t)$. Here, t is time, P_r is gas pressure at the catalyst surface, P is gas pressure on the walls of the vessel, S is the surface area occupied by the catalyst, G is a quantity depending on the momentum distribution of gas species in the plane of catalyst surface, n is RRL efficiency, and J is the rate of formation of product molecules. Absolute values of J were not determined, and the J(t) dependence was studied by indirect measurements. In the case of crystal phosphors, reaction rate was evaluated by two independent methods, specifically, by measuring DER (F) and RRL intensity (I), which are proportional to J.

The flux of reactive gas species was modulated by three methods using different techniques. In the first method, gas species were allowed to flow for $\sim 10^2$ s. This time was sufficiently long for an adsorption equilibrium to be established on the catalyst's surface. After that, the flow was turned off [9]. The second method was used to study the interaction between the solid and "packets" of reactive gas species moving with the carrier gas. The transit time of these packets in the reactor was ~1 s. This time was too short for the surface to undergo any change. These periodically introduced packets were superimposed on a constant flow of reactive species, which was turned on for $\sim 10^2$ s [14]. In the third method, the surface was probed with a high-density packet of active species carried by a gas stream. To diminish the diffusion spread of the packets, the flow velocity was greatly increased. This enabled us to lower the time resolution threshold of the method by more than one order of magnitude (to 10 ms) and to study the kinetics of the heterogeneous process over time intervals of 0.1 s [15, 16].

Gas at a pressure of P = 30 Pa was continuously pumped through discharge tubes (1-3) and a glass vacuum chamber (flow reactor) as shown in Fig. 1. The walls of the chamber could be heated to 500 K. Adsorption (in relative units) was measured using a piezoelectric



Fig. 1. Schematic of the experimental setup. See text for the key.

quartz resonator with a sensitivity limit of 4.4×10^{-9} g. Both surfaces of the piezoelectric element (4) were covered with a layer (of thickness $d \approx 0.1$ mm) of an ethanolic suspension of the ultradisperse substance to be examined. The concentration of chemisorbed species, N, was judged from the decrease in the resonator frequency, f, which was measured with a ChZ-54 frequency meter: $N \sim \Delta f$; $\Delta f = f(t_1) - f$, where $f(t_1)$ is the initial oscillation frequency of the piezoelectric element. (An increase Δx in the thickness of the quartz plate of the piezoelectric element as a result of adsorption is known to change the frequency of the quartz resonator by $\Delta f = f^2 k_f^{-1} \Delta x$, where k_f is the frequency factor.) The temperature coefficient of frequency of the resonator was 1 Hz/K. The measurement error arising from the heatup of the piezoelectric sensor by the chemical reaction did not exceed 5%. The adsorption capacity of the

The dynamic effect of reaction (in newtons) was measured using an automated balance with magnetic suspension [18]. The sensitivity of this balance, which had been calibrated against a weight of 1 mg, was 2.5×10^{-6} g, and the time constant was 10^{-1} s. The signal-tonoise ratio was 10 to 10^3 . The measurement error did not exceed 10%. An ethanolic suspension of the substance to be examined was applied onto the upper surface of a substrate (5) to form a layer of thickness $d \approx 0.1$ mm. The substrate was placed near the piezoelectric element and was attached to the moving part of the balance with the use of a quartz filament. DER can be represented as $F = F_0 + F_g$ [7, 17]. Here, F_0 is the gas pres-

piezoelectric sensor surface (at d = 0) was negligible.



Fig. 2. Time dependence of (1, 2) the frequency of the piezoelectric resonator coated with Pt/Al₂O₃ catalyst and (l', 2') the dynamic effect of reaction after (1) initiation and (\downarrow) quenching of a discharge in (1, 1') carbon dioxide and (2, 2') hydrogen. T = 350 K.

sure force that acts on the catalyst surface owing to the change in the momentum distribution of the particles flying away from the surface in the course of the reaction and F_g is the pressure force due to the reaction-induced temperature step at the solid/gas interface. To reduce the cooling effect of the gas molecules on the substrate and to increase F_g , the substrate (5) was made from two 0.1-mm-thick mica plates separated by 0.2 mm. This allowed the conditions $F_0 \ll F_g$ and $F \approx F_g$ [7, 17] to be satisfied.

Gas discharges were produced using two identical high-frequency generators (G_1 and G_3 in Fig. 1). Either generator could produce either a continuous or a pulsed discharge. The duration of each pulse was 1 s, and the pulse repetition frequency was 0.02 or 0.04 s^{-1} . The pulsed discharge periodically added a value of Δn (species packets) to the constant concentration of active species, n. Either discharge was screened and was independent of the other. Discharge power could be varied between 10 and 70 W [14]. The steady-state concentration of active gas species over the sample surface in the reactor, measured by the hot probe method, was 6×10^{12} -1 $\times 10^{14}$ cm⁻³, depending on discharge power. In other experiments, a pulsed discharge with a pulse duration of 0.1 s was initiated in the gas using a highfrequency generator (G_2) with a variable power (0.1-1 kW). This discharge was confined using a capillary (6) and a magnet (7). Simultaneously, using an electronic control unit (8) and a solenoid value (9), we injected, over 0.6 s, a portion of molecular gas from an auxiliary reservoir (10) with $P = 10^4$ Pa into the discharge tube. This procedure yielded a packet of active species with a density of $\Delta n \approx 10^{15} \text{ cm}^{-3}$, whose transit time was 0.1 s [15, 16]. The vibrationally and electronically excited molecules that had formed in either discharge zone experienced at least 10^3 collisions with molecules of the gas medium while diffusing to the reactor and, thereby, lost their excess energy [19]. No charged species entered the reactor—this was ascertained experimentally. Discharge radiation was absorbed using a Wood horn. The reactor received a mixture of molecules and radicals in the ground electronic and vibrational states from the discharge tubes. The adsorption and recombination of hydrogen atoms on the walls of the discharge tube and reactor and on the sample surface did not produce any effect on the concentration of H atoms in the gas phase or on the kinetics of the processes examined [10, 16].

When pulse modulation of the flux of active species was used, the concentration of H atoms entering the reactor (in relative units) was determined from the pulsed intensity of the blue glow line of the hydrogen atom ($\lambda = 487$ nm), as described in [20]. This line was separated from the glow spectrum of H using a UM-2 monochromator. Hydrogen glow intensity in the plasma (I_g) and the intensity of RRL of crystal phosphors (*I*) during the heterogeneous reaction were measured with two FEU-85A photomultipliers. The electric current of either photomultiplier, which was proportional to I_g or *I*, was measured every 12 µs using two analog-to-digital converters. The numerical data thus acquired were entered into a PC to immediately obtain I(t) and $I_g(t)$ curves.

To remove the adsorbed surface impurities (ethanol, water, and air molecules), the samples were held in a monohydrogen-dihydrogen mixture at 350 K for 1.5 h. The sputtering of the catalyst surface by H atoms was monitored using a piezoelectric quartz resonator. Once the sputtering rate fell sharply, the treatment of the sample with monohydrogen was stopped. In the case of copper, the surface oxides were reduced by hydrogen atoms and the black powder turned red. As this took place, the dynamic effect of the H + H \longrightarrow H₂ reaction increased by one order of magnitude. The hydrogen was replaced with carbon dioxide within 2 s while maintaining the continuous gas flow regime in the reactor. After one gas had been replaced with another, the reactor was flushed with molecules and a high-frequency discharge was then initiated in the gas.

In blank runs, in which there was no catalyst on the sensor, the effects described below were not observed.

RESULTS AND DISCUSSION

After a constant flow of active gas species was established, the occupation of the surfaces of all catalysts by chemisorbed hydrogen atoms or CO and O species proceeded at a comparatively slow rate, with a characteristic relaxation time of $\tau \approx 10-100$ s. By way of example, we demonstrate, in Fig. 2, the kinetics of the adsorption of dissociated carbon dioxide and hydrogen atoms on the surface of the Pt/Al₂O₃ catalyst as the time dependence of resonator frequency (curves 1, 2). The reactions O + O \longrightarrow O₂ and CO + O \longrightarrow CO₂ occur on the solid surface in the dissociated carbon dioxide medium, the latter reaction dominating. Otherwise, since oxygen atoms leave the surface owing to the recombination reaction $O + O \longrightarrow O_2$ and the CO adsorption energy is high [21], CO molecules would accumulate on the surface during the heterogeneous reaction and the adsorption of dissociated carbon dioxide at $T \approx 300$ K would be to a significant extent irreversible. According to experimental data, this is not the case.

For the heterogeneous reaction $H + H \longrightarrow H_2$ to occur by the ER and LH mechanisms, the condition $\chi < 1$, where $\chi \equiv \tau J^* (N^*)^{-1}$, must be satisfied [6, 7]. To estimate χ , we will use the relationship $J^* = 0.25nv\gamma$, where v is the mean velocity of hydrogen atoms impinging on the surface and γ is the coefficient of the heterogeneous recombination of hydrogen atoms. Using observed τ data and γ and N^* values known from the literature, we obtained $\chi \ge 1$ for all of the catalysts. For the platinum catalyst at T = 300 K, $\gamma = 0.025$ [2] and $N^* \le 4.6 \times 10^{14} \text{ cm}^{-2}$ [21]; hence, $\chi = 10^4$. For ZnS, $\gamma =$ 3×10^{-3} [3] and $N^* \le 1 \times 10^{14}$ cm⁻² [10, 22]; hence, $\chi =$ 10³. Comparison of experimental data for the reactions $H + H \longrightarrow H_2$ and $CO + O \longrightarrow CO_2$ (see, e.g., Fig. 2) suggests that the χ values in these reactions are comparable. This violation of the condition $\chi < 1$ means that the ER and LH mechanisms are invalid for these reactions.

The shapes of the DER curve F(t) and the RRL curve I(t) depend on the concentration of active species in the gas medium and on the nature of these species. For $n \approx 10^{14} \,\mathrm{cm}^{-3}$, once a continuous discharge is initiated, F and I grow abruptly and then remain almost invariable (see, e.g., Fig. 2, curves 1' and 2'), indicating that the reaction rate is independent of the concentration of chemisorbed reactants (compare curves 1 and 1', and curves 2 and 2'). A possible explanation for this result is that the reaction involves species chemisorbed on hypothetical active sites, the concentration of these species being below the detection limit of adsorption measurements. However, the probability that the surfaces of all of the catalysts have sparse catalytic centers that are very active in both $H + H \longrightarrow H_2$ and $CO + O \longrightarrow$ CO₂ reactions is negligible. Furthermore, the cross section for the reaction taking place on these centers through the ER collision mechanism would exceed the physically plausible values. Therefore, the above results can be considered to be evidence in favor of the reaction occurring by the recombination of species that have been bound by the surface and are in a so-called precursor state [23, 24], which can be viewed as a physically adsorbed state. Similar data indicating that the rate of the 2CO + $O_2 \rightarrow 2CO_2$ reaction over platinum is independent of the dioxygen coverage of the surface $(0.4 \le \theta \le 1)$ have been explained by the participation of weakly bound (precursor) CO molecules as a twodimensional gas [25] in the reaction (CO being chemisorbed by platinum does pass through a precursor state [26]). The participation of the two CO adsorption states



Fig. 3. Time dependence of (1) $F_{\rm m}$, (2) N, and (3) F for the interaction between a periodic sequence of hydrogen atom packets and copper surface before and after a constant flux of H atoms is (\uparrow) turned on and (\downarrow) turned off. T = 293 K, $n = 1 \times 10^{13}$ cm⁻³, and $n^{-1}\Delta n = 3$. The inset shows the shape of the DER peak.

in the 2CO + $O_2 \rightarrow 2CO_2$ reaction over the Pt/Al₂O₃ catalyst is demonstrated in [27, 28].

In all systems investigated, after the discharge is quenched, the reaction rate falls abruptly at least by two orders of magnitude and gas desorption is observed (Fig. 2). The desorption curves are linearized on the t $t(\Delta f)^{-1}$ coordinates, where Δf is the time-dependent change in resonator frequency [13], indicating the recombinational desorption of chemisorbed species [22]. Therefore, the chemical reactions in the chemisorbed layer (LH mechanism) make only a negligible contribution to the rate of the heterogeneous reaction.

In the case of the H + H \longrightarrow H₂ reaction, a decrease in the concentration of H atoms in the gas medium to $n \approx 10^{13}$ cm⁻³ alters the shape of the F(t) and I(t) curves obtained after a continuous discharge is initiated: the initial portions of these curves indicate a nearly linear growth of F and I. To illustrate the effect of the concentration of active gas species on the shape of the F(t) and I(t) curves, we will consider data collected using the pulse modulation of atomic flux. The interaction between the periodic sequence of H packets and the catalyst gives rise to DER peaks and luminescence scintillation (when phosphors are used), whose amplitudes $F_{\rm m} = F(n + \Delta n)$ and $I_{\rm m} = I(n + \Delta n)$ are shown by points in Figs. 3–5. First, we will consider the recombination of H atoms on the surface of the copper catalyst. Under steady-state conditions (when the observed value does not change with time), both the concentration of chemisorbed atoms $(N^*(n))$ and DER $(F^*(n))$ increase monotonically with an increasing concentration of hydrogen atoms in the gas medium. The $F^*(N^*)$ dependence is nearly linear: $F^* \approx kN^*$, where k is a coefficient. Under unsteady-state conditions, the amplitude of the periodically emerging DER peaks (F_m) increases once a continuous discharge is initiated and then remains invari-



Fig. 4. Time dependence of (1, 2) $F_{\rm m}$ and (l', 2') F for the interaction between a periodic sequence of hydrogen atom packets and ZnS–Cu phosphor surface before and after a constant flux of H atoms is (\uparrow) turned on and (\downarrow) turned off. T = 293 K; n = (1, l') 7×10^{13} and (2, 2') 6×10^{12} cm⁻³; $n^{-1}\Delta n = (1, l')$ 0.2 and (2, 2') 6.

able (Fig. 3, curve 1). It is independent of the concentration of chemisorbed atoms (N), which increases with time (Fig. 3, curve 2). After the continuous discharge is quenched, $F_{\rm m}$ takes its initial value and recombinative desorption of H atoms is observed. The shape of the continuous F(t) curve obtained after a continuous discharge is initiated depends on the concentration of atoms in the gas medium: at $n \leq 1 \times 10^{13}$ cm⁻³, the F(t)curve has a portion where F increases together with the concentration of chemisorbed atoms (Fig. 3, curve 3). At $n \gtrsim 3 \times 10^{13}$ cm⁻³, the F(t) curve has a rectangular shape. If the concentration of atoms in a packet (Δn) is fixed and the constant component of atom concentration (n) increases (causing an increase in N), then pulseinduced increments in DER, $\Delta F = F(n + \Delta n) - F(n)$, do not increase and ΔF is independent of N. If Δn is varied at fixed values of n and N, ΔF grows with increasing Δn .

Let us see whether the symbatic time variation of N and F (Fig. 3, curves 2, 3) can be explained in terms of the heterogeneous reaction $H + H \longrightarrow H_2$ proceeding by a mechanism involving chemisorbed hydrogen atoms (ER and LH mechanisms). For this mechanism, $F = GJ = \alpha nN + \beta N^2$, where α and β are coefficients. If this were the case, changing n several times would not break down the symbasis of the F(t) and N(t) curves. Experimental data disprove this hypothesis (compare curves 1-3). Furthermore, in the case of the copper catalyst, the condition necessary for the participation of chemisorbed H atoms in chemical reactions ($\chi < 1$) is not satisfied. Reactions involving physically adsorbed or chemisorbed atoms are unlikely for the same reasons. In view of this, let us consider the following model of the reaction:

$$R + Z \xrightarrow{k_1} RZ,$$
$$R + Z \xrightarrow{k_2} (RZ),$$



Fig. 5. Time dependence of $(1, 2) I_{\rm m}$ and (l', 2') I for the interaction between a periodic sequence of hydrogen atom packets and ZnS–Cu phosphor surface before and after a constant flux of H atoms is (\uparrow) turned on and (\downarrow) turned off. T = 293 K; $n = (1, l') 3 \times 10^{13}$ and $(2, 2') 6 \times 10^{12}$ cm⁻³; $n^{-1}\Delta n = (1, l') 2$ and (2, 2') 6.

$$2RZ \xrightarrow{k_3} R_2 + 2Z,$$
$$2(RZ) \xrightarrow{k_4} R_2 + 2Z,$$

where (RZ) is a chemisorbed atom and RZ is an atom in the precursor state. The following rate equations correspond to this model:

$$\dot{N}_1 = k_1(N_0 - N) - k_1'N - 2k_3N_1^2,$$

$$\dot{N} = k_2(N_0 - N) - k_2'N - 2k_4N^2.$$

where N_1 is the concentration of precursor atoms, N_0 is the concentration of adsorption sites, and $k_1 - k_4$ are the rate constants of the reactions ($k_1 = 0.25nv\sigma$, where σ is the capture cross section of free atoms passing into the precursor state). Assuming that the precursor and chemisorbed atoms make up "rapid" and "slow" subsystems and using the adiabatic approximation, we obtain

$$J \cong k_3 N_1^2; \quad J \approx k_3 k_1^2 (N_0 - N)^2 (k_1')^{-2},$$

$$8k_1 k_3 (N_0 - N) \ll (k_1')^2; \quad 2k_3 N_1 \ll k_1'.$$

$$J \approx 0.5 k_1 (N_0 - N).$$
(2)

$$8k_1k_3(N_0 - N) \ge (k_1')^2; \quad 2k_3N_1 \ge k_1.$$
⁽³⁾

Under steady-state conditions (when $\dot{N}_1 = \dot{N} = 0$), $J^* = 0.5k_1k_2^{-1}k_2'N^* + (1 + k_1k_2^{-1})k_4(N^*)^2 - 0.5k_1'N_1^*$. At relatively small values of k_4 and k_1' (when $2k_4N^* \ll k_2'$ and $k_1' \ll 2k_3N_1^*$), we obtain the relationship $J^* \approx kN^*$ (*k* is a coefficient), which is in agreement with experimental data. In the case of $N \ll N_0$, Eq. (3) describes the $F_{\rm m}(t) = GJ_{\rm m}(t)$ and F(t) = GJ(t) dependences observed for high atom concentrations in the gas medium (Fig. 3, curve 1). Under steady-state conditions, the linear

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dependence of the reaction rate on the concentration of atoms in the gas is due to the fact that the recombination reaction $2RZ \longrightarrow R_2 + 2Z$ is controlled by the capture of H atoms passing into the precursor state RZ: $J \cong$ $0.5k_1N_0$. Expression (2) corresponds to the E(t) curves obtained at small n values (Fig. 3, curve 3). The constancy of $F_{\rm m}$ after the initiation of a continuous discharge (curve 1) indicates that the ascending portion of the F(t) curve (curve 3) is not due to any uncontrollable evolution of the state of the surface. Therefore, this increase in F can be caused only by k_3 growing with time because of the rising concentration of chemisorbed atoms. The buildup of chemisorbed atoms is likely to be due to their participation in the stabilization of resulting molecules through energy transfer in the adsorbed layer according to the scheme $2RZ + (RZ) \rightarrow$ $R_2 + 2Z + (RZ)$. There are three possible energy-transfer channels for the relaxation of the vibrational energy localized on a forming H-H bond, namely, the vibration-vibration channel, the vibration-electronic channel (which leads to an excited state of the (RZ) bond), and the vibration-translation channel (which is due to two-dimensional translations of (RZ)). Note that, as the concentration of hydrogen atoms in the gas medium increases, satisfaction of the condition $k_3 \sim N \sim n$ facilitates a crossover from the reaction regime corresponding to Eq. (2) to the regime corresponding to Eq. (3).

In the recombination of hydrogen atoms on the surface of ZnS-Cu phosphor, the parameters measured after the initiation of a discharge change with time at a lower rate than in the case of the copper catalyst, yet they show similar behavior (Figs. 4, 5). Therefore, the above reaction mechanism and Eqs. (2) and (3) are applicable to the recombination of H atoms on zinc sulfide surface. As judged from the rectangular shape of the F(t) curves, Eq. (3) is valid for the copper catalyst and ZnS–Cu phosphor at $n \approx 10^{14}$ cm⁻³; therefore, the high catalytic activity of copper as compared to zinc sulfide [2, 3] is primarily due to the higher capture cross section (σ) of H atoms passing into the precursor state. The value of σ is determined by energy removal in the stabilization of a captured hydrogen atom on the surface. The phonon relaxation of vibrationally excited states of the gas atom-surface bond is known to proceed at a comparatively low rate. For metal surfaces, the conversion of vibrational energy into the energy of electronic excitation [29] is more probable. It is due to effective vibronic energy transfer that the capture cross section of hydrogen atoms passing into the precursor state is larger for copper than for zinc sulfide.

In the case of the heterogeneous reaction CO + O \longrightarrow CO₂ occurring on the surface of the ZnS–Cu phosphor at 295 K, RRL kinetics is affected by O and CO adsorption, which is extensive and partially irreversible under the conditions examined. When both the continuous and pulsed sources of active species are turned on $(n^{-1}\Delta n = 6)$, the following conditions are satisfied: $I_{\rm m}I^{-1} > 10^2$ and $I_{\rm m}I^{-1} \gg n^{-1}\Delta n + N^{-2}(\Delta N)^2$, where $I_{\rm m} =$



Fig. 6. Time dependence of (1', 2') scintillation intensity for the ZnS–Cu phosphor interacting with a periodic sequence of CO and O packets and (1, 2) permanent glow intensity for the same phosphor before and after a constant flux of CO and O species is (\uparrow) turned on and (\downarrow) turned off. $n^{-1}\Delta n = 6$; T = (1, 1') 293 and (2, 2') 390 K.

 $I(n + \Delta n)$ is the amplitude of the RRL peaks and $\Delta N =$ $N(n + \Delta n) - N(n)$ (Fig. 6, curves 1, 1'). Raising the temperature to 390 K under the same conditions decreases the amount of chemisorbed CO and O several times, causing a reduction in $I_{\rm m}$ and a marked decrease in $I_{\rm m}/I$ (curves 2, 2'). These results cannot be explained by the participation of chemisorbed species in the heterogeneous reaction. We will consider a model in which reaction rate is determined by the recombination of CO and O in the precursor state. The equality $I_m I^{-1} \approx n^{-1}(n + \Delta n)$ is valid for curves 2 and 2', implying that $J = \eta^{-1}I \approx$ $0.5k_1N_0$. This is the highest possible reaction rate. Therefore, the fact that the reaction rate increases with decreasing temperature if the other conditions are invariable (see curves l' and 2') is explained by the increasing capture cross section for CO and O passing into the precursor state. This effect is due to surface coverage increasing as the temperature is decreased, considering that chemisorbed species participate in the removal of excess energy from precursor species, stabilizing them on the surface according to the scheme $R + Z + (RZ) \longrightarrow RZ + (RZ)$. Here, the most plausible scenario, in terms of energy, is the relaxation of the vibrational energy localized on the resulting RZ bond through the excitation of bending vibrations in chemisorbed species or through translations of (RZ) species (vibration-vibration and vibration-translation energy transfer, respectively).

Let us consider the RRL scintillation of crystal phosphors under the action of single high-density packets of hydrogen atoms. For the CaO–Mn crystal phosphor, the plot of RRL intensity versus time, I(t), has a nearly rectangular shape (Fig. 7, curve 2). The I(t)



Fig. 7. Time dependence of (1) hydrogen atom glow intensity in the discharge tube and (2) luminescence intensity for the CaO–Mn phosphor at T = 509 K under the action of a single hydrogen atom packet. $\Delta n \approx 10^{15}$ cm⁻³.

curve is shifted relative to the glow intensity curve for H atoms in the discharge plasma ($I_{g}(t)$; Fig.7, curve 1) by the time it takes for an H packet to travel from the discharge tube to the reactor (17 ms). As the power of the pulsed discharge is raised at a fixed pulse duration, the RRL scintillation amplitude I_m for the CaO-Mn phosphor shows an approximately quadratic dependence on the density of the H packet (Fig. 8). The reliability of the least-squares approximation $I_{\rm m} \sim n^2$ is $\rho^2 =$ 0.71 at T = 345 K (curve 1) and $\rho^2 = 0.83$ at T = 518 K (curve 2). Depending on the power of the pulsed discharge, the ratio of I_m to the intensity of RRL due to the constant flux of H atoms from the generator G_3 (Fig. 1), I^* , is 2 to 50. Therefore, the highest density of a hydrogen atom packet under our experimental conditions is $\Delta n \approx 10^{15} \text{ cm}^{-3}$.

According to adsorption measurements, the interaction between H packets and the surface of the CaO-Mn phosphor results in an increase in the concentration of chemisorbed species, N. (The maximum surface coverage is $N_{\text{max}} \approx 0.25 \Delta n v t_g \alpha_1 \sim 10^{14} \text{ cm}^{-2}$, where $t_g = 0.1 \text{ s}$ is the time of transit of atom packets through the reactor and $\alpha_1 \approx 10^{-5}$ [22] is the sticking coefficient of H atoms passing into the precursor state.) If chemisorbed hydrogen atoms were involved in the heterogeneous recombination responsible for RRL (through the ER and LH mechanisms), it would be expected that $I \approx Bt + Ct^2$, where $I = \eta J = anN + bN^2$ ($N \sim t$; B, C, a, and b are coefficients). The fact that this condition is not satisfied (Fig. 7) means that the heterogeneous reaction $H + H \longrightarrow H_2$ proceeds by the recombination of precursor hydrogen atoms. Since the condition $I_{\rm m} \sim n^2$ is met at 518 K (Fig. 8), the desorption rate of precursor atoms at this temperature is high as compared to the recombination rate of these atoms (see Eq. (2)).



Fig. 8. RRL scintillation amplitude for the CaO–Mn phosphor at T = (1) 345 and (2) 518 K versus the square of $I_g(t)$ averaged over the discharge pulse duration.

Similar data indicating that the heterogeneous reaction H + H \longrightarrow H₂ responsible for RRL proceeds through the recombination of precursor atoms are obtained for the interaction between high-density H packets and ZnS-Tm and ZnS-Cu phosphors. We found that the RRL efficiency η of the ZnS-Cu phosphor decreases with increasing hydrogen atom concentration in the gas medium. This effect is due to the specific features of the electronic spectrum of this phosphor [16].

When gas molecules are chemisorbed on a solid surface, they pass through a precursor state [24]. As the gas pressure is raised, the concentration of molecules in the precursor state increases and the probability of chemical reactions involving these molecules grows whenever it is possible. However, since relaxation methods for the study of surface reactions at "high" pressures of $P = (10^2 - 10^5)$ Pa are not well developed, it is still unclear whether precursor molecules are involved in heterogeneous reactions. The results of this study draw attention to heterogeneous reaction models that take into consideration the participation of precursor molecules in reaction steps. It is expected that such models will adequately describe some real chemical processes. Indeed, the approach that takes into account molecule capture resulting in a precursor state has provided a solution for the problem of getting over the pressure gap in hydrogen oxidation over platinum, $2H_2 + O_2 -$ 2H₂O. That is, it has resulted in a unified reaction model valid for both high vacuum and moderate and high pressures [30].

CONCLUSION

At 293–500 K and active gas species concentrations of $n = 10^{13}-10^{15}$ cm⁻³, the heterogeneous reactions H + H \longrightarrow H₂ and CO + O \longrightarrow CO₂ on solid (Cu, Pt, ZnS, and CaO) surfaces proceed through the recombination of physically adsorbed (precursor) species. The cross sections of heterogeneous reactions occurring by

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the Eley–Rideal collisional mechanism are negligible in this case, and the reactions in the chemisorbed layer (Langmuir–Hinshelwood adsorption mechanism) do not make any considerable contribution to the reaction rate. Depending on the concentration of active gas species, temperature, and the nature of the catalyst, the rate of these reactions is limited either by the capture of incident gas species with the formation of precursor species or by the recombination of precursor species. The participation of precursor species in the heterogeneous reaction is most obvious in the case of "high" concentrations of these species in the gas medium ($n \ge 10^{14}$ cm⁻³). These results were obtained by independent methods.

For "low" concentrations of hydrogen atoms in the gas medium ($n \leq 10^{13}$ cm⁻³), the concentration of chemisorbed hydrogen atoms and the rate of the heterogeneous reaction $H + H \longrightarrow H_2$ vary with time in the same way. This symbasis is not explained by the participation of chemisorbed H atoms in the reaction. It is due to the fact that chemisorbed monohydrogen alters the state of the surface, increasing its catalytic activity. This increase probably arises from the stabilization of resulting hydrogen molecules through energy transfer taking place during the reaction according to the scheme $HZ + HZ + (HZ) \longrightarrow H_2 + 2Z + (HZ)$. This is accompanied by a relaxation of the vibrational energy of the forming H-H bond in the H₂ molecule through the excitation of the (HZ) bond. The similar enhancing effect of CO and O chemisorption on the catalytic activity of zinc sulfide surface in the heterogeneous reaction $CO + O \longrightarrow CO_2$ is due to the increase in capture cross section for the particles reacting on the surface and passing into the precursor state according to the scheme $R + Z + (RZ) \longrightarrow RZ + (RZ)$. The most likely cause for the stabilization of surface-captured species is the conversion of vibrational energy of the forming bond RZ into the energy of bending vibrations of the (RZ) bond.

Metals (Cu and Pt) show a higher catalytic activity in the H + H \longrightarrow H₂ reaction than nonmetals (ZnS and CaO) [2, 3] (see Eq. (3)). This is primarily due to the difference in capture cross section for hydrogen atoms passing into the precursor state. According to theory [29], the larger values of σ for metals may be due to the active participation of conduction electrons in energy removal stabilizing precursor H atoms on the surface.

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