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Abstract

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KINETICS OF THE CATALYTIC EXCHANGE OF DEUTERIUM BETWEEN WATER VAPOR AND HYDROGEN ON VARIOUS SURFACES

(Presented by Academician N. M. Zhavoronkov, 7 VIII 1962)

The kinetics of the reaction

$$HDO + H_2 = HD + H_2O \tag{1}$$

was studied by us in a flow system ([1]). Since the investigation of reaction kinetics under gradientless conditions has a number of advantages ([2]), measurements were made of the rate of reaction (1) on the surface of various catalysts in a flow-circulation system. The results of these measurements and their comparison with the kinetic equation proposed earlier ([1]) are presented below:

$$\omega = k_1 p_{HDO} \left(\frac{p_{H2}}{p_{H2O}}\right)^m - k_2 p_{HD} \left(\frac{p_{H2O}}{p_{H2}}\right)^{1-m}. \tag{2}$$

Here ω is the rate of reaction (1), p_{HDO}, p_{H2}, p_{H2O} are the partial pressures of HDO, etc., k_1 and k_2 are the rate constants of the reaction in the forward and reverse directions, m is a constant, $0 \leq m \leq 1$.

Equation (2) corresponds to a two-stage mechanism ([3]); reaction (1) consists of the stages:

$$HDO + (\ ) \rightleftharpoons HD + (O), \tag{3}$$

$$H_2 + (O) \rightleftharpoons H_2O + (\ ). \tag{4}$$

Here ( ) denotes a vacant site on the catalyst surface, and (O) a chemisorbed oxygen atom (or a surface oxygen atom of the oxide). Similar mechanisms were established on the basis of kinetic data for the water-gas reaction ([4]) and isotope exchange between CO and CO_2 ([5–7]). In all the reactions mentioned, chemisorbed oxygen atoms play the role of an intermediate. Reaction (4) and its reverse, practically coinciding with reaction (3), have been observed directly ([8–13]); in doing so it was found that, under conditions of establishment of equilibrium (4), the chemisorption of hydrogen is small and may be neglected.

The mechanism under discussion is similar to that proposed by Farkas ([14]), who, however, assumed the intermediate formation and decomposition of an exchange oxide (or oxide hydrate); in contrast, equations (3) and (4) do not include phase transformations. According to Farkas, the rate of reduction of the oxide limits the reaction rate; since stage (4) almost coincides with stage (3) in the reverse direction, at intermediate surface coverages by oxygen neither stage can be considered rate-limiting.

Instead of direct interaction of (O) with H_2 from the gas phase, one could suppose intermediate chemisorption of hydrogen. If the adsorption equilibrium of H_2 is established rapidly, as may be assumed on the basis of the available data ([15–17]), such a modification of the mechanism does not affect the reaction kinetics. Therefore, for the derivation of the kinetic equation, the simpler scheme represented by equations (3) and (4) is sufficient. It leads to equation (2) if the deuterium content is small ([1]).

The experiments were carried out in a flow-circulation system at atmo-

at atmospheric pressure. The purified hydrogen was saturated at various temperatures with water vapor containing 4.2 or 4.5 at.% D, and entered a cycle consisting of a reaction vessel with the catalyst and a glass electromagnetic pump with a valve box, placed in an air thermostat at a temperature of 125°. The water after the reaction vessel was analyzed for D content by the drop method ([18]). The hydrogen was converted into water and also analyzed. The possible error in determining D did not exceed ±0.02 at.%, which in most experiments corresponded to no more than 5% of the measured value. The kinetics was studied on the same samples of Co, Pd, Cu, Ag, and Fe_2O_4 as previously in the flow system ([1]). In addition, two new Ni samples were prepared, on one of which measurements were carried out both in the flow-circulation and in the flow systems. Porous catalyst grains were prepared by reduction of the corresponding oxides or carbonates obtained by precipitation. Their specific surface area was determined from low-temperature adsorption of nitrogen or krypton*. Massive samples consisted of cut metal foil, whose surface was taken to be equal to 1.5 times the geometric surface. The characteristics of the catalysts are given in Table 1.

Fig. 1. Kinetics of deuterium exchange between water vapor and hydrogen on various catalysts.
a —porous nickel, sample I; —porous nickel, sample II; —massive nickel; —

Fig. 1

Figure 1: Fig. 1

porous cobalt; —massive palladium; —porous copper; —porous iron oxide; — porous silver.

To judge the possible influence of diffusion on the reaction rate, let us estimate the value of the dimensionless criterion τ/t, where τ is the contact time, and t is the diffusion time. To calculate t we use Einstein' s equation $a^2 = 2Dt$, where a is the radius of the catalyst grains, and D is the effective diffusion coefficient. D may be taken equal to the coefficient of molecular

* Measurements with krypton were performed at the Institute of the Nitrogen Industry by T. A. Semenova and Yu. G. Budkina, and those with nitrogen in our laboratory by L. I. Luk' yanova and N. V. Kul' kova. The authors express their gratitude to the persons mentioned.

Table 1

Characteristics of the catalysts and results of the experiments

Catalyst	Grain diameter or platelet size, mm	Bulk weight or density, g/cm^3	Specific surface area, m^2/g	Temperature interval of the experiments, °C	E_1, kcal/mol	m (average)	$k_1^* \cdot 10^9$, mol/atm × m^2 · s at 150°	$k_1^* \cdot 10^9$, mol/atm × m^2 · s at 300°
Porous nickel I	0,25÷0,5	2,30	0,264	200÷250	12,0	0,43	2130	85000
Porous nickel II	0,5÷1,0	2,26	0,082	250	—	0,48	2500	103000
Massive nickel	1$×2×0,1 (diam.) 0,5|2,08|0,61|250|—|0,51|450|48000||*Massivepalladium*|1×2×$0,1	8,90	0,012	425÷475	—	0,51	460	60000	*Porous copper*	38	2070	0,25÷
Porous copper	0,5÷1,0	1,53	0,169	300÷375	20,4	0,32	18	9000
Porous iron oxide	0,25÷0,5	1,47	4,3	350÷400	24,6	1,00	0,16	286
Porous silver	0,5÷2,0	1,35	0,176	425÷500	21,3	0,76	0,26	185

diffusion, if the mean pore radius r is greater than the free path of the molecules; otherwise Knudsen diffusion takes place and D is calculated from r. We find the average value of r from the equality $r = 2v/\sigma$, where v is the specific pore volume, σ is the specific surface area of the pores. We obtain $\tau/t \sim 10^2$ or more, which indicates that the reaction proceeds in the kinetic region.

Table 2

Exchange reaction of D on copper

Experiment temperature, °C	$\frac{p_{H2}}{p_{H2O}}$	τ, s	$\frac{[D]_{H2O}}{[D]_{H2}}$	$k_1 \cdot 10^8$, s^{-1}, calculated from eq. (5) at $m = 0,32$
375	3,54	2,98	3,23	47,2
375	2,09	2,04	3,10	52,2
375	1,00	1,48	2,89	50,1
375	0,567	1,12	2,85	46,5
375	0,402	0,867	2,96	43,5
375	Average			47,9
350	3,76	3,25	5,02	22,2
350	2,07	2,72	3,92	25,6
350	1,02	2,06	3,52	25,5
350	0,580	1,50	3,35	26,7
350	0,370	1,12	3,80	20,4
350	Average			24,1
325	3,73	3,40	6,96	13,7
325	2,00	2,94	6,43	11,3
325	1,01	2,29	5,16	12,6
325	0,570	1,68	4,61	13,7
325	0,385	1,33	4,70	12,7
325	Average			12,8
300	3,63	4,42	10,06	6,47
300	2,10	4,02	8,35	5,35
300	1,05	2,98	7,64	5,81
300	0,611	2,30	7,32	5,72
300	0,369	1,69	6,95	5,73
300	Average			5,82
375	3,76	2,57	3,76	44,4
375	2,01	2,24	3,25	52,9
375	0,98	1,65	2,98	40,8
375	0,615	1,20	2,94	42,3
375	0,898	0,88	2,75	49,8
375	Average			46,1

Equation (2), upon replacing ω by $\frac{p_{\mathrm{HD}}U_0}{W}$, where U_0 is the volumetric flow rate of the gas mixture reduced to 0° and 1 atm, and W is the catalyst volume, gives

$$k_1\left(\frac{p_{\mathrm{H2}}}{p_{\mathrm{H2O}}}\right)^{m-1}=\frac{1}{\tau\left(\frac{[D]_{\mathrm{H2O}}}{[D]_{\mathrm{H2}}}-K^{-1}\right)}. \tag{5}$$

Here $\frac{[D]_{\mathrm{H2O}}}{[D]_{\mathrm{H2}}}$ is the ratio of the deuterium concentrations in water and hydrogen at the exit from the reaction cycle, $K=k_1/k_2$ is the equilibrium constant of reaction (1), and $\tau=W/U_0$ is the conditional contact time.

In preliminary experiments with a Ni on Cr_2O_3 catalyst, which possessed high activity, values $K^{-1}=2,10$ at 180° and $K^{-1}=1,97$ at 211° were obtained; this agrees with the experimental data of Suess [19] and the theoretical equation of Weston [20], which was subsequently used to find K. To check the applicability of equation (2), experiments were carried out at different values of $\frac{p_{\mathrm{H2}}}{p_{\mathrm{H2O}}}$, τ, and temperature. It is easy to see that, according to equation (5), the logarithms of the right-hand side of the equation, plotted against $\lg\frac{p_{\mathrm{H2}}}{p_{\mathrm{H2O}}}$, should give points lying on a straight line, whose parameters make it possible to determine $m-1$ and k_1. The graphs in Fig. 1 po-

show that equation (2) is confirmed for all the catalysts tested; moreover, from the approximate parallelism of the straight lines for a given catalyst at different temperatures it follows that m depends little on temperature. For further verification, using the average values of m found from the plots and given in Table 1, we calculated, by equation (5), the values of k_1. They proved to be constant within the accuracy of the experiments. As an illustration, Table 2 gives the results of experiments with Cu. The sequence of the data in the table corresponds to the sequence in which the experiments were carried out, the operation of the apparatus not being interrupted. The agreement of the values of k_1 at 375° at the beginning and at the end of the series of measurements shows the constancy of the activity of the catalyst. The average values of m for the various catalysts are given in Table 1; they practically coincide with the values found earlier [1] from experiments in a flow system. The activation energies E_1, calculated from the average values of k_1, are presented in Table 1. To compare the activity of the surfaces of different catalysts, the rate constants k_1^*, corresponding to the absolute rate of the reaction, may be used. The latter is determined by the number of moles of HDO entering into reaction per unit time on a unit surface of the catalyst. It is easy to see that

$$k_1^*=\frac{1}{R273\sigma\rho}\,k_1, \tag{6}$$

where R is the gas constant, σ is the specific surface area, and ρ is the bulk weight or density of the catalyst. The last column of Table 1 contains the values of k_1^*, extrapolated to 150 and 300° with the aid of the Arrhenius equation. At

$$\frac{p_{\mathrm{H2}}}{p_{\mathrm{H_2O}}} = 1$$

the reaction rate does not depend on m, so that these values of k_1^* directly characterize the activity of the catalyst surfaces in a mixture containing equal volumes of hydrogen and water vapor.

In agreement with the previous result ([1]), the absolute rate constants for porous and massive nickel samples are close.

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Note: Figure translations are in progress. See original paper for figures.