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Soviet-era science, translated into English

# PHYSICAL CHEMISTRY

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Sciences of the USSR

1960

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Fig. 1. Schematic of the apparatus

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**Abstract****Full Text****PHYSICAL CHEMISTRY****M. A. Avdeenko, Corresponding Member of the Academy of Sciences of the USSR****G. K. Boreskov and K. N. Zhavoronkova****SPECIFIC CATALYTIC ACTIVITY OF IRON FILMS IN THE ISOTOPIC EXCHANGE REACTION IN MOLECULAR HYDROGEN**

In establishing the relationship between the specific catalytic activity of metals and their electronic structure, the question always arises of the possible limits and causes of variation in the specific activity of one and the same metal. These differences may be connected both with structural factors (for example, the size and orientation of crystals) and with possible differences in chemical composition. It has been noted repeatedly in the literature that films, in their catalytic and adsorption properties, differ substantially from massive metals (<sup>1,2</sup>). It may be assumed that the high activity of films obtained by condensation of metal vapors in vacuum, as compared with massive metals, is associated with peculiarities of their structure. Thus, according to a number of authors (<sup>3-5</sup>), films differ from massive metals in some of their properties (lattice parameter, work function, electrical conductivity). The purpose of the present work is to clarify the influence of the conditions of deposition and sintering of iron films on their catalytic activity in the isotopic exchange reaction in molecular hydrogen.

**Fig. 1. Schematic of the apparatus**

**Experimental procedure.** Measurement of the catalytic activity of iron films was carried out by the static method. Most of the experiments were performed at a pressure of 0.5 mm Hg. At this pressure, external diffusion had no substantial effect on the rate of the reaction up to an absolute rate of the order of  $10^{-7}$  g-mole/sec. When measuring the reaction order, the pressure was varied within the range  $0.05 \div 5$  mm Hg. The basic scheme of the apparatus is shown in Fig. 1. The reaction volume ( $300-400 \text{ cm}^3$ ) included a glass vessel (1), on the inner surface of which the film was deposited, a trap (2), cooled with liquid nitrogen throughout the entire experiment, and a lamp (3) for continuous measurement of the concentration of HD molecules by the thermal-conductivity method. A

Figure 2

Figure 2: Figure 2

flask (5) of 4.5 liters capacity, containing the unreacted mixture  $H_2 + D_2$ , could periodically be connected to the reaction volume; this made it possible, without pumping the gas out of the reaction volume, to carry out repeated measurement of the reaction rate. Between the reac-

...between the reaction vessel and the trap there was a gallium seal (6), by means of which the film could be separated from the rest of the apparatus. Before deposition, the reaction volume was rigorously conditioned at  $500^\circ$  to a residual pressure below  $10^{-7}$  mm Hg. The film was obtained by heating an iron strip (2-3 mm wide and 0.2-0.3 mm thick) with direct current and condensing the vapor on the inner surface of the reaction vessel. The surface area of the films was measured by hydrogen adsorption (in the interval  $10^{-2}$ - $10^{-1}$  mm Hg) and by krypton using the volumetric method. In experiments measuring the exchange rate, an equimolar mixture  $H_2 + D_2$  was used. To obtain the films, spectrally pure Hilger iron was used. By vacuum melting in a high-frequency furnace, the initial iron was analyzed for its gas content. It was found to be  $0.12 \text{ cm}^3/\text{g}$  (mainly hydrogen, nitrogen, and oxygen), which is substantially lower than the gas content in iron samples of other grades. The oxygen content is 0.0015 wt. %. The reaction-rate constant was calculated from the first-order equation<sup>6</sup>.

**Fig. 2.** Dependence between the surface area and the weight of the films. Condensation temperature: 1  $-196^\circ$ , 2  $-20^\circ$ , 3  $-300^\circ$ .

The maximum error in measuring the specific activity is 20% if the film surface area exceeds  $1000 \text{ cm}^2$ . If the films have a surface area of the order of  $100 \text{ cm}^2$ , then the maximum error in measuring the specific activity will be considerably larger (up to 50%), mainly because of the difficulty of measuring very small surface areas.

**Characteristics of the iron films.** In our experiments, condensation of iron vapor was carried out at  $-196^\circ$ ,  $20^\circ$ , and  $300^\circ$ . This made it possible to vary the size of the primary crystals over wide limits. The average crystal size can be estimated from the weight of the film and its surface area. It was found that, when the condensation temperature is varied over a wide range (from  $-196$  to  $300^\circ$ ), a linear relation is observed between the weight of the films and their surface area (Fig. 2). Consequently, growth of the film occurs through an increase in the number of crystals without a change in their size. The crystal size depends only on the condensation temperature. The same regularities have also been observed for other transition metals<sup>7</sup>. Table 1 gives the sizes of the primary iron crystals and the specific surface area of films deposited at different temperatures.

**Table 1**

Film condensation temperature, °C	$a$ , Å	$S_{sp}$ , m <sup>2</sup> /g
−196	60	125
20	300	25
300	4800	1.6

**Adsorption of hydrogen** was measured mainly at  $-196^\circ$ . Figure 3 presents typical adsorption isotherms on three different iron films (hydrogen adsorption is referred to 1 cm<sup>2</sup> of surface, measured by krypton adsorption). As can be seen, the points lie well on a single curve. In all cases, hydrogen adsorption at  $-196^\circ$  proceeds at a high rate, and a significant part of the hydrogen (up to 95%) is adsorbed at very low equilibrium pressures. In the pressure interval  $10^{-3}$ - $10^{-1}$  mm Hg, a small additional uptake of hydrogen is observed. In this pressure interval, hydrogen adsorption is apparently reversible already at  $-196^\circ$  and proceeds at a lower rate. The slow adsorption amounts to approximately 15% of the fast adsorption. The data we obtained on hydrogen adsorption agree well with those known in the literature<sup>8-10</sup>.

Table 2

Film condensation temperature, °C	$K$ , g-mol/(cm <sup>2</sup> · s)	$a$ , Å
20	$2.3 \cdot 10^{-12}$	300
20	$3.3 \cdot 10^{-12}$	300
20	$2.8 \cdot 10^{-12}$	300
300	$2.7 \cdot 10^{-12}$	4800
300	$2.9 \cdot 10^{-12}$	4800
300	$2.1 \cdot 10^{-12}$	4800
300	$3.5 \cdot 10^{-12}$	4800

Table 3

Film condensation temperature, °C	$K$ , g-mol/(cm <sup>2</sup> · s)	$a$ , Å
20	$8 \cdot 10^{-12}$	300
20	$13.7 \cdot 10^{-12}$	300
300	$14.5 \cdot 10^{-12}$	4800
−196	$23 \cdot 10^{-12}$	60

### Effect of the conditions of film deposition on their specific catalytic activity

Table 2 gives the results of the first experiments on measuring the specific activity of iron films at a temperature of  $-196^\circ$  and  $P = 0.5$  mm.

Figure 3: Hydrogen adsorption at  $-196^\circ$

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Figure 4: Dependence of reaction rate on temperature

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Despite the fact that the size of the primary iron crystals changes by a factor of 16, the specific activity of the films remains almost constant. In the first experiments the iron samples from which the films were deposited were, apparently,

Fig. 3. Adsorption of hydrogen at  $-196^\circ$ :

*a*—deposition at  $-196^\circ$ , weight 2.1 mg, surface  $250\text{ cm}^2$ ;

*b*—deposition at  $20^\circ$ , weight 6.3 mg, surface  $1800\text{ cm}^2$ ;

*c*—deposition at  $-196^\circ$ , sintering at  $300^\circ$ , weight 53 mg, surface  $830\text{ cm}^2$

Fig. 4. Dependence of the reaction rate on temperature at a pressure of 0.5 mm:

*a*—deposition at  $20^\circ$ ,  $E = 800 \div 900\text{ cal/g-mol}$ ;

*b*—deposition at  $300^\circ$ ;

*c*—sintering at  $300^\circ$ ,  $E = 3300\text{ cal/g-mol}$ ;

*d*—sintering at  $300^\circ$ ,  $E = 5200\text{ cal/g-mol}$ ;

*e*—sintering at  $550^\circ$ ,  $E = 7600\text{ cal/g-mol}$

insufficiently well preconditioned, and therefore the films had reduced activity. In the subsequent experiments (Table 3), a single iron sample was used, from which several films had first been deposited to waste over a long period of time. As can be seen, the specific activity thereby increased several-fold; nevertheless, the films deposited at different temperatures differed very little in their activity.

Films deposited at  $-196^\circ$  are of particular interest. Owing to the low mobility of metal atoms at low temperatures, one might have expected the formation of some nonequilibrium structures. In the opinion of some authors, films deposited at low temperatures strongly

“disordered”<sup>1</sup>. However, as our experiments have shown, their activity is close to the activity of films deposited at high temperatures. Whereas the size of the primary crystals changes by a factor of 80, the specific activity changes by at most a factor of 2. The observed difference may in part be connected with a different orientation of the crystal faces. The reaction order was measured at  $-196^\circ$  in the range  $0.05 \div 5\text{ mm Hg}$  and was found to be  $0.6 \div 0.7$ . The activation energy of the reaction in the interval  $-196^\circ \div 0^\circ$  is  $800 \div 900\text{ cal/g-mole}$  (Fig. 4).

**Effect of sintering on the specific activity of iron films.** When films are sintered, their surface area decreases sharply and, in their properties, they

<sup>1</sup>R. Suhrman, Zs. Elektrochem., **60**, No. 8, 804 (1956).

approach massive metals. It was of interest to trace how their specific activity changes in this process. The first experiments, carried out on films obtained from insufficiently trained iron specimens, showed that upon sintering the specific activity decreases sharply, while the activation energy increases (Fig. 4), which is in contradiction with the fact we established of the approximate constancy of the specific activity of films deposited at different temperatures. Thus, the decrease in activity observed by us in the first experiments could not be explained by structural changes. Another possible reason for the decrease in activity upon sintering is contamination of the film surface. As a result of the strong decrease in surface area, the concentration of impurities may increase sharply. It is therefore necessary that the film subjected to sintering be as free as possible from contamination. For this purpose we used an iron specimen that had first been subjected to vacuum melting in order to remove impurities as completely as possible. Before use, several blank films were deposited from it. The results of these experiments are given in Table 4. In all cases the films were deposited at  $-196^{\circ}$ .

**Table 4**

Sintering temperature, $^{\circ}\text{C}$	$K$ , g-mole/cm $^2$ · sec
-196	$35 \cdot 10^{-12}$
300	$45 \cdot 10^{-12}$
300	$39 \cdot 10^{-12}$
300	$48 \cdot 10^{-12}$
550	$20 \cdot 10^{-12}$

As can be seen, when sufficiently stringent conditions are observed, the specific activity of the films changes hardly at all upon sintering, whereas the surface area decreases sharply (by a factor of  $50 \div 100$  at  $300^{\circ}$ , and by almost a factor of 400 at  $550^{\circ}$ ).

On the basis of the results obtained by us, it may be concluded that the specific activity of iron films remains almost constant over a wide variation of deposition and sintering conditions. The decrease in catalytic activity upon sintering is mainly associated with contamination of the surface.

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Received  
11 V 1960

## REFERENCES

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