

DKPCAG 265(1/ 2/ 3) 493-584 (1982)

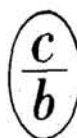
DOKLADY PHYSICAL CHEMISTRY

PROCEEDINGS of the
ACADEMY OF SCIENCES
of the USSR

Physical Chemistry Section

ДОКЛАДЫ АКАДЕМИИ НАУК СССР
(DOKLADY AKADEMII NAUK SSSR)

TRANSLATED FROM RUSSIAN



CONSULTANTS BUREAU, NEW YORK

Vol 250
22 38 / 1
982, 265 1-3
B Hannover

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PREPARATION OF GOLD HYDRIDE AT A HIGH HYDROGEN PRESSURE

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UDC 541.44

The authors of [1] (the first and the only communication on gold hydride preparation) noted formation of a bright incrustation on the surface of a gold foil when atomic hydrogen is passed over it. We succeeded in preparing gold hydride by placing the metal in an atmosphere of molecular hydrogen under high pressures. This paper describes the conditions of preparation and properties of the hydride obtained.

The samples were prepared from polycrystalline gold of 99.99% purity. The hydrogen was compressed in Toroid type chambers to pressures reaching 65 kbar by the method proposed in [2]. A hydraulic seal comprised of ПЭС-3 silicone fluid was used for sealing the hydrogen ampul. The temperature was measured by a chromel-alumel thermocouple insulated from the attack of hydrogen. The precision of pressure and temperature measurement was ± 3 kbar and $\pm 15^\circ\text{C}$, respectively.

The first gold hydride samples were obtained as follows. A gold wire 0.2 mm in diameter was held at $P_{\text{H}_2} = 50$ kbar and $T = 400^\circ\text{C}$ for 1 h, whereafter the high-pressure chamber and the sample were cooled to room temperature, the pressure was lowered to the atmospheric pressure, and the sample was taken out. On such treatment the wire became light gray with a metallic shine and very brittle; at the breaking point the hydride was found to consist of fine (up to $\sim 40 \mu\text{m}$) crystals. The wire diameter increased markedly (up to one and half times) and the surface became very uneven. An x-ray study at room temperature showed that gold hydride has a fairly complex crystalline structure. At atmospheric pressure and room temperature the hydride is kinetically unstable and breaks into gold and hydrogen in a few weeks. In the breaking process the intensity of the hydride diffraction lines diminishes monotonically and that of the fcc lines of gold increases. After complete liberation of hydrogen the sample acquires a yellow color typical for gold. In isothermal vacuum annealing for 1 h the hydride degradation occurs at $T \approx 170^\circ\text{C}$.

The boundaries of the gold hydride formation region on the T - P_{H_2} diagram were evaluated from the data on the behavior of electric resistance of the samples from a gold wire 0.2 mm in diameter (the contacts were prepared from a platinum wire of the same diameter). At $P_{\text{H}_2} \leq 25$ kbar and $T \leq 380^\circ\text{C}$ the sample resistance attained a definite value in a hydrogen atmosphere, as also in an inert medium, as soon as the temperature and pressure became constant and remained time-invariable. At $28 \leq P_{\text{H}_2} \leq 65$ kbar and $T \geq 300^\circ\text{C}$ the resistance increased with time when T and P_{H_2} are fixed. The rate of resistance drift increased rapidly with rise in temperature and diminished with fall in temperature. At $300 \leq T \leq 340^\circ\text{C}$ the drift continued for scores of hours with gradual retardation. At higher temperatures the resistance began to rise spasmodically after a few hours (sometimes even earlier) perhaps due to degradation of the sample at the point of welding of the contacts. A typical plot of the initial resistance drift rate with stepped temperature rise is shown in Fig. 1. For each sample this dependence varied little in the pressure range $28 \leq P_{\text{H}_2} \leq 65$ kbar, but for different samples the resistance drift rate at the same temperature may differ several times.

Institute of Physics of Solids, Academy of Sciences of the USSR, Chernogolovka, Moscow Province. (Presented by Academician Yu. A. Osip'yan, March 29, 1982.) Translated from *Doklady Akademii Nauk SSSR*, Vol. 266, No. 2, pp. 376-380, September, 1982. Original article submitted April 9, 1982.

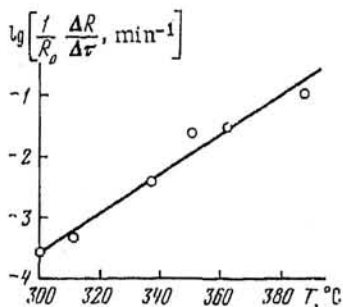


Fig. 1. Temperature dependence of drift rate of resistance R of a gold wire of 0.2 mm diameter at $P_{H_2} = 50$ kbar, plotted in the course of stepped temperature rise by holding the temperature at each point for $\Delta\tau = 15$ min, R_0 is the resistance of the sample at room temperature and atmospheric pressure. In an inert medium $R/R_0 = 1.96$ at $P = 50$ kbar and $T = 300^\circ\text{C}$.

Samples prepared from gold strips sized $3.5 \times 3.5 \times 0.1$ mm were used for determining the hydrogen content in the gold hydride. After holding for an hour at fixed T and P_{H_2} the samples and the high-pressure chamber were cooled to room temperature, whereafter the pressure was reduced and the sample taken out for further investigations. The hydrogen content in the samples was determined by two methods: from the change in their weight after annealing at $\sim 10^{-5}$ mm Hg and 300°C for 20 min and from the gas pressure after similar annealing in a closed vessel of a known volume (the pressure did not exceed 5 mm Hg). The hydrogen:metal atomic ratios n obtained by these methods for the hydride-containing samples tallied within the precision $\delta n \sim 0.04$.*

No hydride was formed when the gold was held at $P_{H_2} \leq 25$ kbar and $T \leq 500^\circ\text{C}$. When held at $28 \leq P_{H_2} \leq 65$ kbar and $T \geq 350^\circ\text{C}$ the gold surface was invariably coated with a hydride film. Diffraction pattern study showed that at room temperature and atmospheric pressure gold hydride has the same crystalline structure regardless of the conditions of preparation. It was quite difficult, however, to establish whether the entire gold in the sample reacted with hydrogen under a high pressure, especially because the hydrogenation kinetics at the same T and P_{H_2} values varied pronouncedly from sample to sample. A series of samples was prepared by holding at $T = 410^\circ\text{C}$ and $P_{H_2} = 50$ kbar. The samples with a total hydrogen content $n \approx 0.2$ were brittle, but there were gold lines in the diffraction patterns of such samples ground to a powder. The similarly obtained patterns of the samples with $n \geq 0.35$ contained no gold lines. The maximum hydrogen content in the samples was $n = 0.43 \pm 0.04$.

The experimental values of the interplanar distances d^e and the quadratic forms $Q^e = (1/d^2) \cdot 10^4$ for gold hydride at room temperature are given in Table 1. All d^e values except those with asterisks were obtained by the photomethod on a powdered sample in an RKU-114M camera using Fe K_α radiation. In addition to the line noted in Table 1, the diffraction patterns contained a notable number of very weak lines, a part of which (marked by asterisks) could be resolved by taking photographs of macrocrystalline samples. The reflections corresponding to the interplanar distances Nos. 1-4 were obtained in photographs of such samples by the photomethod on a DRON-2.0 diffractometer using Cr K_α radiation. The number of weak lines which do not submit to resolution increases rapidly with decrease of d^e and so in Table 1 we restricted ourselves only to the lines with $d^e \geq 1.160 \text{ \AA}$ even though highly intense lines are also observed for lower d^e values.

The diffraction pattern could be identified satisfactorily within the framework of the orthorhombic system. Evaluation by Lipson's semiempirical formula [3] with respect to the number of lines on the diffraction pattern up to the Bragg angle $\theta = \arcsin 0.5$ gave $Q_L \sim 150 \text{ \AA}^{-2}$ for the average value of the parameter of the rhombic cell. The frequency analysis of the differences in the Q^e values for the observed lines showed that the differences $\Delta Q^e \approx 216 \text{ N \AA}^{-2}$, where N is the number of the natural series, are encountered most frequently. It will be seen from Table 1 that the diffraction patterns also contain most of the lines with

*Note that the tally of the n values obtained by these two methods indicates that only hydrogen is liberated from the samples because in the former case the result does not depend on the molecular weight of the gas liberated.

TABLE 1

| Sl. No. | l^e | $d^e, \text{Å}$ | $Q^e, \text{Å}^{-2}$ | $Q_{hkl}^p, \text{Å}^{-2}$ | hkl |
|---------|-------|-----------------|----------------------|----------------------------|--------------------------------------|
| 1 | * | 6,62 | 228 | 217 | 100 |
| 2 | * | 5,20 | 370 | 379 | 101 |
| 3 | * | 4,71 | 451 | 433 | 020 |
| 4 | * | 4,15 | 581 | 595 | 021 |
| 5 | W | 3,92 | 651 | 650 | 002, 120 |
| 6 | * | 3,51 | 812 | 812 | 121 |
| 7 | * | 3,35 | 891 | 866 | 200, 102 |
| 8 | W | 3,14 | 1014 | 1028 | 201 |
| 9 | W | 3,04 | 1082 | 1083 | 022 |
| 10 | M | 2,77 | 1303 | 1299 | 220, 122 |
| 11 | * | 2,72 | 1352 | 1353 | 131 |
| 12 | VW | 2,625 | 1451 | 1461 | 003, 221 |
| 13 | * | 2,562 | 1523 | 1515 | 202 |
| 14 | * | 2,526 | 1567 | 1570 | 013 |
| 15 | W | 2,391 | 1749 | 1732 | 040 |
| 16 | VW | 2,355 | 1803 | 1786 | 113 |
| 17 | VW | 2,332 | 1839 | 1840 | 230, 132 |
| 18 | S | 2,262 | 1954 | 1948 | 300, 140, 222 |
| 19 | * | 2,180 | 2104 | 2111 | 301, 141, 123 |
| 20 | VW | 2,030 | 2427 | 2436 | 033, 213 |
| 21 | M | 1,958 | 2608 | 2598 | 004, 240, 302, 142 |
| 22 | VW | 1,936 | 2668 | 2652 | 133 |
| 23 | W | 1,914 | 2730 | { 2706 2760 | { 050, 312, 014 241, 223 |
| 24 | VW | 1,880 | 2829 | 2815 | 104 |
| 25 | VW | 1,817 | 3029 | 3031 | 024, 322 |
| 26 | VW | 1,790 | 3121 | 3085 | 331, 151 |
| 27 | M | 1,753 | 3254 | 3248 | 242, 124 |
| 28 | VW | 1,725 | 3361 | 3356 | 052 |
| 29 | VW | 1,697 | 3472 | 3464 | 400, 204 |
| 30 | VW | 1,653 | 3660 | { 3626 3680 | { 401 340 |
| 31 | VW | 1,636 | 3736 | 3735 | 411, 251 |
| 32 | VW | 1,610 | 3858 | 3843 | 341, 323 |
| 33 | VW | 1,598 | 3916 | 3897 | 060, 420, 224 |
| 34 | VW | 1,520 | 4328 | 4330 | 342, 044 |
| 35 | S | 1,482 | 4553 | 4547 | 062, 304, 422, 144 |
| 36 | W | 1,448 | 4769 | 4763 | 260, 162 |
| 37 | W | 1,441 | 4816 | 4817 | 354 |
| 38 | W | 1,402 | 5087 | 5088 | 432 |
| 39 | VW | 1,397 | 5124 | 5124 | 343 |
| 40 | VW | 1,388 | 5191 | 5196 | 440, 244 |
| 41 | W | 1,366 | 5359 | 5358 | 063, 441, 423, 225 |
| 42 | VW | 1,327 | 5679 | 5683 | 511, 171 |
| 43 | S | 1,309 | 5836 | 5845 | 006, 520, 360, 442 |
| 44 | M | 1,296 | 5954 | 5954 | 072, 016 |
| 45 | VW | 1,286 | 6047 | 6062 | 502, 404, 106 |
| 46 | VW | 1,274 | 6161 | 6170 | 450, 270, 512, 172, 414, 254, 116 |
| 47 | VW | 1,264 | 6259 | 6279 | 026, 344 |
| 48 | W | 1,249 | 6410 | { 6387 6441 | { 530 325 |
| 49 | M | 1,240 | 6504 | 6495 | 064, 522, 362, 424, 126 |
| 50 | M | 1,228 | 6631 | 6657 | 443, 245 |
| 51 | W | 1,218 | 6741 | { 6712 6766 | { 164, 206 073, 055 |
| 52 | VW | 1,204 | 6898 | 6874 | 503 |
| 53 | M | 1,199 | 6956 | { 6928 6982 | { 080 513, 173, 335, 155 |
| 54 | M | 1,184 | 7133 | 7144 | 180, 540, 226 |
| 55 | VW | 1,167 | 7343 | { 7307 7361 | { 541, 181, 523, 363 460, 264 |
| 56 | VW | 1,160 | 7432 | 7415 | 371 |

Note. S) Strong; M) medium; W) weak; VW) very weak; *) see text,
 $Q = (1/d^2) \cdot 10^4$. The Q_{hkl}^p values were calculated for a rhombic

cell with $Q_{100} = 216.5 \text{ Å}^{-2}$, $Q_{010}^p = (1/2)Q_{100}^p$, and $Q_{001}^p = (3/4)Q_{100}^p$.

$Q^e \approx 216 N \text{ \AA}^{-2}$ (only the lines with $N = 10, 11, 19, 23,$ and 25 are known to be absent up to $N = 34$). Extrapolation of the respective lines by $\theta = 90^\circ$ permitted precise determination of this periodicity: $\Delta Q^e \approx 216.5 N \text{ \AA}^{-2} = AN$. Such a periodicity of Q^e and ΔQ^e values as well as the fact that $A \sim Q_L$ shows that $Q_{100}, Q_{010},$ and Q_{001} are interrelated and may differ from A only by rational factors having small numbers in the numerator and denominator. The highly probable values are $Q_{100} = A, Q_{010} = A/2,$ and $Q_{001} = (3/4)A,$ which correspond to $a = 6.80 \pm 0.01 \text{ \AA}, b = 9.61 \pm 0.01 \text{ \AA}, c = 7.85 \pm 0.01 \text{ \AA}.$ The Q_{hkl}^p values calculated for these values of the parameters are cited in Table 1.

So far as systematic extinctions are concerned, the absence of the reflections $0k0$ and $00l$ with odd k and l can be affirmed with high confidence [extinctions also indicate presence of the double screw axes (010) and (001)].

It is interesting to note that calcium, strontium, barium, europium, and ytterbium have an orthorhombic lattice with the same c/a ratio and with c and a values close to those proposed for gold hydride [4].

Let us add in conclusion that the measurements by the induction method showed the absence of superconductivity in gold hydride at $T \geq 2^\circ\text{K}.$

The authors thank V. I. Rashupkin for low-temperature measurements and A. I. Amelin and V. A. Zav'yalova for their help in the preparation of the experiments.

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MECHANISM OF HYDROGEN ADSORPTION AND ACTIVATION BY TRANSITION METALS IN THE DENSITY FUNCTIONAL METHOD

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UDC 541.27+541.128:546.9

It is well known that transition metals are used as hydrogenation catalysts (see, for example, [1]). In this connection, the mechanism of hydrogen adsorption and activation by these metals is of much applied and scientific interest. The investigations into this aspect by semiempirical and nonempirical quantum-chemical methods (see, for example, [2, 3, 4]) have not disclosed the nature of the chemically activated forms of hydrogen on the surface of transition metals, the mechanism of their "strong" association with the adsorbent, and the sources of the special adsorption and catalytic properties of these metals.

The primary cause of inadequacy of the theoretical studies in the referred area consists, in our view, in the neglect of the important properties of strongly differing electron systems, viz., the correlation effects (in a wide sense of the term). The correlation effects are ignored, in principle, in the semiempirical methods, but lie outside the framework of the Hartree-Fock approximation in the traditional nonempirical methods. This cannot be achieved at present effectively even in the most powerful computers.

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