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The Influence of Mechanical Activation on the Adsorption Properties of Powdered Tungsten

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Abstract—Mechanical activation in a planetary ball mill activator changes the adsorption properties of powdered tungsten. The activation leads to changes in both the adsorption energy and the concentration of active adsorption sites on the surface, thus resulting in a change in the adsorption capacity. The character and degree of the change in the adsorption properties depends nonlinearly on the duration of the mechanical effect.

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INTRODUCTION

Powdered metals are widely used in technology, with the efficiency of their practical use being determined not only by the bulk properties of the material, but also the surface properties of single particles. Adsorption activity is one of the most important surface properties of powders determining their technological properties, such as flowability, internal friction, cohesion, adhesion, etc. Recently, mechanical activation, leading to changes in not only the bulk properties, but also the surface properties, of a material's particles has been increasingly used to modify the characteristics of powder materials [1, 2]. Therefore, knowledge of the character of the influence of mechanical activation on the adsorption properties of various powder materials is of not only scientific, but also practical, interest.

In addition, almost all studies performed in this field to date deal with the influence of activation on the adsorption properties of adsorbents. For example, the effect of mechanical activation on the properties of montmorillonite has been examined and, depending on the duration of the activation, an increase or a decrease in the total adsorption volume, average size of mesopores, and their surface has been found [3]. In [4], it has been shown that the mechanical activation of carbons is accompanied by a change in microporous structure, this leading, in turn, to a significant reduction of the volume of micropores and, thus, a decrease in the adsorption capacity for vapors of water and nitrogen and an increase in the concentration of active sites on the surface of carbon.

The influence of the conditions of mechanical activation on the adsorption properties of such nonporous materials as metal powders has not yet been sufficiently studied. In the present work, the influence of

the duration of the activation of powdered tungsten samples on the structural and energy characteristics of the surface of single particles was examined in a planetary mill.

EXPERIMENTAL

The powdered tungsten of PVN-1 grade with a particle size of approximately 5 μm was employed as a test material. The choice of tungsten was due to its high thermal stability, extensive use of its powder in the technology, and a good knowledge on the change in its structure after mechanical activation [5].

Mechanical activation of the tungsten powder was performed with the use of an AGO-2U activator [6], a centrifugal planetary ball mill equipped with vertical grinding rolls cooled by the running water, with the working volume of each roll being 250 mL. The following activation mode was used in the experiments: a ball load of 100 g (balls of 6-mm diameter were made of ShKh-15 steel) and a working load (weight of the processed material) of 12–15 g. To protect a metal from oxidation during the activation, up to 20 wt % of hexane was added to the powder in rolls.

The structural and energy properties of the particle surface of activated W powders were studied by the adsorption of benzene vapor with the use of a vacuum gravimetric facility designed and manufactured at the Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences. Weighted (no more than 700 mg) test powder was placed on an electronic balance located in a vacuum chamber and exposed to the vacuum regeneration at 400 K for 8 h to a residual pressure of 0.1 Pa, followed by the measurement of the equilibrium adsorption of benzene vapors at 293, 303, and 313 K. The value of the equilibrium

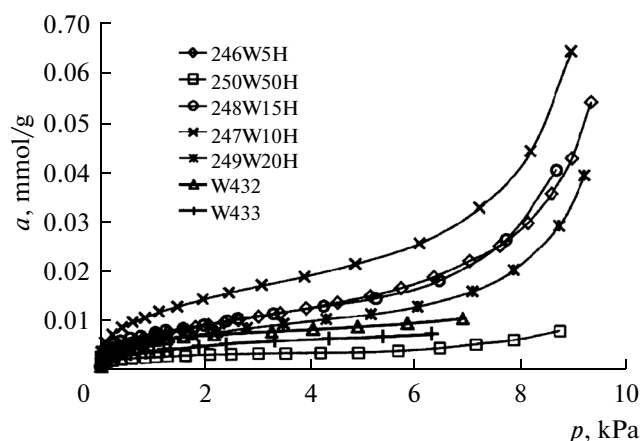


Fig. 1. Dependences of adsorption (a) of benzene on initial 432W (air dry) and 433W (prewetting with n -hexane for 24 h) tungsten samples and those exposed to mechanical activation in n -hexane medium for 5 min (246W5H), 10 min (247W10H), 15 min (248W15H), 20 min (249W20H), and 50 min (250W50H) on pressure (p) at 293 K.

adsorption was determined in terms of the change in weight of the sample recorded after the establishment of a plateau of the adsorption kinetic curve and the attainment of the equilibrium pressure with the use of a computer measuring system.

Adsorption capacity a_m of a monolayer of benzene, number N of the adsorption sites, specific surface area S_{BET} , and effective average particle size d of each powder test sample was calculated based on the adsorption isotherms obtained via the Brunauer–Emmett–Teller (BET) method [6] at 293 K. The adsorption isotherms of each sample obtained at 293, 303, and 313 K were also used to calculate the dependences of the differential molar isosteric heat of adsorption q_{st} of benzene on the adsorption value.

RESULTS AND DISCUSSION

Figure 1 shows the isotherms (at 293 K) of adsorption of benzene on the initial 432W (air dry) and 433W (previously stored in liquid n -hexane for 24 h) tungsten powders and those exposed to mechanical activation in n -hexane medium for various durations.

All individual isotherms of adsorption of benzene on the tungsten powders shown in Fig. 1 are similar. The enhancement of the pressure of benzene initially results in a rapid increase in adsorption, followed by flat curves and, again, an increase in adsorption in the region of relatively high pressures, with this increase being the most appreciable at pressures close to the saturated vapor pressure of benzene. According to Brunauer's classification, such isotherms are of type II, which is typical of the adsorption of vapors on the surface of non-porous adsorbents possibly containing micropores in their structures [7]. The steep isotherms of adsorption in the initial region are due to the formation of a monolayer of adsorption, whereas the completion of the monolayers leads to smoothing of the adsorption isotherms. The further growth of adsorption is owing to the formation of subsequent layers, and the final sharp increase in the vapor adsorption is caused by the formation of multilayers of adsorbate and the appearance of a liquid phase. The observed isotherms of benzene adsorption change in accordance with regularities typical of physical adsorption and indicate a significant increase in the capacity of monolayers and the number of adsorption sites on the surface of all mechanically activated samples in comparison to the initial 432W and 433W ones. In addition, prewetting of the tungsten powders with n -hexane (the 433W sample) results in reduction of the adsorption capacity. The obtained data are given in Table 1.

Analysis of the results of examination of the mechanical activation influence indicates the complex changes in the specific surface area. After mechanical activation for a short time (no more than 10 min), a sharp increase in the specific surface area, approximately three times in comparison to the value of the initial 433W powder, is observed. After a longer time (10–20 min) of mechanical activation, a sharp decrease (by approximately 2.5 times) in the value of the specific surface area occurs. The further increase of the time of activation up to 50 min leads to a slowdown in the decline of the specific surface area to the value approximately half that of the 433W sample.

Such a change in the specific surface area of the samples may be due to a number of factors. Thus, the decrease in the specific surface area of the 432W sam-

Table 1. The influence of mechanical activation of tungsten powders on their adsorption properties

Sample	Time of activation (t), min	Specific surface area (S_{BET}), $\text{m}^2 \text{g}^{-1}$	Number of adsorption sites, $N \times 10^{-18}$, 1/g	Effective particle size (d), μm
432W	0	1.33	3.33	2.23
433W	0	0.92	2.30	0.34
246W5H	5	1.89	4.73	0.16
247W10H	10	2.91	7.28	0.11
248W15H	15	1.82	4.55	0.17
249W20H	20	1.40	3.50	0.22
250W50H	50	0.48	1.20	0.64

ple after its contact with *n*-hexane (the 433W sample) is likely to be caused by the destruction of the microporous structure of the initial 432W porous material. This fact can be concluded from [8, 9], which report the largest deformation of expansion of microporous adsorbents attained in the atmosphere of saturated adsorptive vapor or in a liquid. It is this expansion that may result in the destruction of microporous structure of the 432W porous powder. After the transition to the 433W sample, the average particle size of the 432W tungsten powder approximately decreases by about seven times (Fig. 2, Table 1).

During mechanical activation of the tungsten powder in *n*-hexane for a short time (no more than 10 min), further dispersing takes place due to the reduction of the surface tension of tungsten particles induced by the adsorption of *n*-hexane. The particle size decreases by three times, while the specific surface area, in contrast, increases by three times (Fig. 2, Table 1). However, the dispersing limit of tungsten is attained, and, after mechanical activation for a long time ($t > 10$ min), the freshly formed surface of particles with a small surface of the interparticle contact leads to aggregation in accordance with the forging mechanism. The reduction of the specific surface area and the sixfold increase in the average particle size also confirm the above assumption (Table 1). A similar extreme dependence on the time of mechanical activation is also typical of the number of adsorption sites located on the tungsten surface (Table 1).

In order to estimate the energy characteristics of the adsorption sites, the isosteres of adsorption (curves at $a = \text{const}$) proved in the first approximation to be linear in the $\ln p - 1/T$ coordinates were constructed based on the isotherms of adsorption in the $a - \ln p$ coordinates. The differential molar isosteric heat of adsorption of benzene on the tungsten powders was calculated by Eq. (1) [10]:

$$q_{st} = -R(d \ln p / d(1/T))_a, \quad (1)$$

where $R = 8.314 \text{ J (mol K)}^{-1}$ is the universal gas constant. The results of calculations of the dependence of the isosteric heat of adsorption on the magnitude of

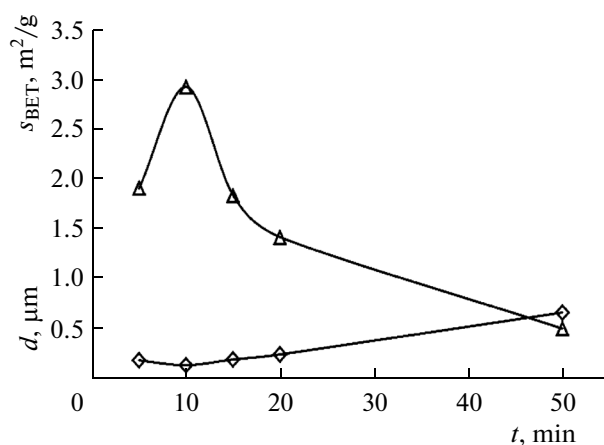


Fig. 2. Dependences of (Δ) the BET specific surface area (S_{BET}) and (t) the effective particle size d (\diamond) on the time of activation.

adsorption of benzene on the initial and mechanically activated samples are shown in Table 2 and Fig. 3.

Analysis of these data indicates strong energy heterogeneity of the surfaces of the initial 432W and 433W tungsten powders.

Figure 3 shows that an increase in adsorption leads to a sharp decrease (from 60 to 20 kJ mol^{-1} in the case of the 432W sample and from 48 to 6 kJ mol^{-1} in the case of the 433W sample) in the isosteric heat of adsorption of benzene as a monolayer of the powder surface is completed. This result may be due to endothermic processes of mechanical degradation of adsorbent during the adsorption of benzene. These effects have been previously observed in [11]. It is typical that the adsorption heat curves of the 432W and 433W samples are almost symbatically shifted from each other. The growth of the heat of adsorption after its minimum is likely to be due to the cooperative interaction between adsorbed molecules of benzene on the surface during the formation of a monolayer.

The changes in the values of the heat of adsorption of benzene on the mechanically activated tungsten powders correlate with the dependences of the specific surface area and effective particle size on the time of

Table 2. Heat of adsorption of benzene on W powders

Sample	Initial heat of adsorption of benzene (q_0), kJ mol^{-1}	Heat of adsorption of benzene in a monolayer (q_{min}), kJ mol^{-1}	Adsorption at q_{min} (beginning of the formation of a monolayer) (a_{min}), mmol g^{-1}	Adsorption at $p/p_s = 0.3$ (completion of the formation of a monolayer) ($a_{0.3}$), mmol g^{-1}
432W	62	18	0.0043	0.0070
433W	47	8	0.0038	0.0051
246W5H	33	9	0.0057	0.0101
247W10H	30	18	0.0100	0.0163
248W15H	35	9	0.0070	0.0103
249W20H	25	26	0.0060	0.0080
250W50H	41	17	0.0020	0.0027

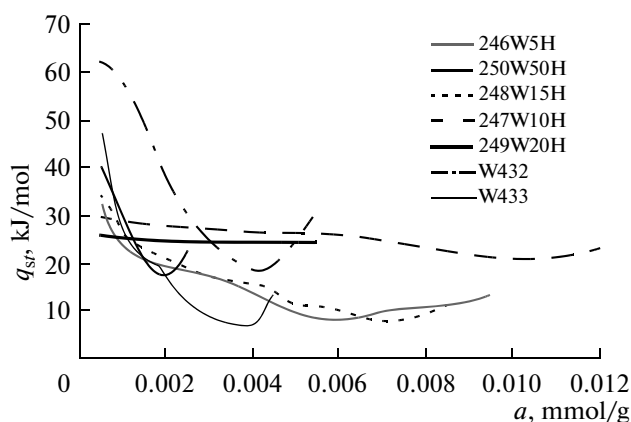


Fig. 3. Dependences of the differential molar isosteric heat of adsorption of benzene (q_{sr}) on its adsorption (a) on initial 432W (air dry) and 433W (previously stored in liquid n -hexane) tungsten samples and those exposed to mechanical activation in n -hexane medium for 5 min (246W5H), 10 min (247W10H), 15 min (248W15H), 20 min (249W20H), and 50 min (250W50H).

activation (Fig. 2). Figure 3 indicates that the increase in the time of activation initially (activation for no more than 10 min) results in an increase in the differential molar isosteric heat of adsorption of benzene up to approximately 27 kJ mol^{-1} in the region of average monolayer completion (from 0.003 to 0.004 mmol g^{-1}), followed by its decrease to approximately 18 kJ mol^{-1} at the activation for 50 min. The isosteric heat of adsorption actually independent on the magnitude of adsorption of benzene on the 247W10G powder suggests its energy homogeneity. This feature sharply distinguishes this sample from a number of other obtained powders.

The extreme reduction of the initial heat of adsorption of benzene on the 247W10G sample (Table 2) seems to indicate the degradation of the initial microporosity of the 432W sample and the energy homogenization of the tungsten powders, such as 247W10G, 248W15G, and 249W20G, after their mechanical activation for more than 10 min. In the case of mechanical activation of the 250W50G sample for a large time ($t > 10$ min), an increase in the initial heat of adsorption is likely to be due to the aggregation of the mechanically dispersed tungsten particles and the appearance of the secondary micropores in accordance with the forging mechanism.

Similar dependences consisting in the abnormal behavior of the characteristics were also qualitatively detected in the case of the heat of adsorption of benzene in a monolayer (q_{min}), that is, the adsorption at the beginning of the formation of a monolayer (a_{min}) at q_{min} , as well as the adsorption of benzene at $p/p_s = 0.3$

corresponding to the completion of the formation of a monolayer ($a_{0.3}$) (Table 2).

CONCLUSIONS

The results of the present work indicate that mechanical activation significantly changes the surface properties of metal powders. Not only the concentration of surface active sites of adsorption, but also their energy characteristics, change.

The nature and degree of the changes in the adsorption properties depends on the duration of activation. Extreme values of the changes are attained after activation of a certain duration. With a planetary mill being used, the optimal time to activate the tungsten powders is approximately 10 min.

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