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Abstract

Full Text

PHYSICAL CHEMISTRY

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THE INFLUENCE OF THE RADIOACTIVITY OF MOLYBDENUM ANHYDRIDE ON THE CHANGE IN THE VALUE OF ITS SPECIFIC SURFACE AREA

Using electron-microscopic photographs it was previously shown ⁽¹⁾ that the surface of radioactive samples of molybdenum anhydride and of certain other substances is characterized by the development of irregularities, projections, and similar defects that are absent in nonradioactive preparations. A significant change in the specific surface area of radioactive barium sulfate was noted in ⁽²⁾. However, when the specific surface area of 10 samples of tricalcium phosphate catalysts containing radioactive Ca^{45} or P^{32} was measured, a noticeable increase in surface area was found only for several of them ⁽³⁾.

We studied the specific surface area of 9 samples of molybdenum anhydride containing different amounts of the radioactive isotope Mo^{99} ($T_{1/2} = 68.3$ hours, $E(\beta)_{max} = 1.23$ MeV). All preparations were prepared under strictly identical conditions. A mixture of calculated amounts of a highly radioactive preparation and nonradioactive MoO_3 was converted by the action of NH_4OH into ammonium molybdate; its solution was evaporated, and the dry residue was calcined with the addition of a small amount of nitric acid to prevent the reduction of hexavalent molybdenum by ammonia. The resulting MoO_3 was mixed with small additions of Nb_2O_5 and ZrO_2 , and, for purification from radiochemical impurities, was sublimed at 850° in a weak stream of air. Fractions with particle sizes of 0.5-0.25 mm, obtained by sieving through the appropriate sieves, were used for surface-area measurements. Preparations of nonradioactive molybdenum anhydride were obtained in an analogous manner.

The external specific surface area, without allowance for dead-end pores, was measured by the method of Deryagin ⁽⁴⁾, based on filtration through the sample of strongly rarefied air under steady flow and measurement of the resistance offered by the porous body to its passage. The results obtained are presented in Fig. 1. Each point corresponds to the mean of 3-4 parallel measurements.

It may be concluded that in the region of small values of radioactivity there is observed a certain decrease in the surface area of the samples, which, at a specific radioactivity of 14 mCu/g, reaches approximately 5% in comparison

Fig. 1. External specific surface area of radioactive MoO₃ samples, measured by the Deryagin method

Figure 1: Fig. 1. External specific surface area of radioactive MoO₃ samples, measured by the Deryagin method

Fig. 2. Total specific surface area of radioactive MoO₃ samples, measured by the BET method

Figure 2: Fig. 2. Total specific surface area of radioactive MoO₃ samples, measured by the BET method

with the nonradioactive sample. A further increase in the specific radioactivity leads to an increase in the surface area of the samples. For example, the specific surface area of MoO₃ with an activity of 34 mCu/g is 16% greater than the surface area of the nonradioactive sample. The value of the total surface area of the MoO₃ preparations was determined by krypton adsorption according to the BET method ⁽⁵⁾. The measurements were carried out on an apparatus whose design is analogous to that described in ⁽⁶⁾. In calculating the specific surface areas by the BET equation, the value 19.5 Å² was adopted for the area occupied by a krypton molecule on the adsorbent surface ⁽⁷⁾. The results are presented in Fig. 2.

It can be seen that in this case as well, just as in the measurements by Deryagin's method, a decrease in the dimensions of the surface is observed in the region of radioactivity values of 1-10 mCu/g, and a deeper one (up to 30%).

A further increase in the specific radioactivity of the preparations leads to a considerable increase in the specific surface area. Comparing the results obtained by the two methods, it can be seen that in absolute magnitude they are fairly close. For example, the specific surface area of the nonradioactive preparation of MoO₃, measured by the Deryagin method, is 0.83 m²/g, and by the BET method 0.90 m²/g. This makes it possible to conclude that the investigated MoO₃ samples contain a small number of dead-end pores.

Fig. 1. External specific surface area of radioactive MoO₃ samples, measured by the Deryagin method

Fig. 2. Total specific surface area of radioactive MoO₃ samples, measured by the BET method

The observed regularity is apparently connected with the fact that molybdenum anhydride, at low specific radioactivity, is characterized by a reduced rate of evaporation, as was shown in work ⁽⁸⁾. An increase in the specific radioactivity above 5-10 mCu/g leads to a considerable increase in the rate of evaporation of MoO₃ preparations and to the formation of dendrites owing to the appearance of a large number of new crystallization centers as a result of the action of β-particles.

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