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Short Note

SOME NOTES ON THE DIFFERENTIAL ISOTOPE METHOD FOR STUDYING THE SURFACE OF ADSORBENTS AND CATALYSTS

By

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Finding whether the surface of an adsorbent of a catalyst is homogeneous or heterogeneous is a question of primary importance for interpreting the mechanism of catalytic and adsorption processes. Unfortunately, there is no method to-day which could give a satisfactory answer to this question. The only method, capable (in some cases) of presenting a direct qualitative information about the type of the surface, is the one proposed by S. Z. ROGINSKY and N. P. KEIER[1,2]. It is known that this method has substantial imperfections. Most outstanding one is the following: Due to the possible interchange between the adsorbed particles, the adsorbate may become homogenized with respect to isotopes, and the various portions of gas will then have the same or almost the same isotope composition on desorption[3].

To remove this defect, a variation of the Differential Isotope Method (DIM) was recently proposed, according to which the adsorption of the isotope portions is to be carried out at different temperatures[4]. By means of lowering the temperature leapwise, an opportunity is given for gradually exposing the various adsorption levels, thus reducing—above all—the importance of migration. The perspectives of this variation of DIM were demonstrated by studying the surface of NiO and ZnO upon adsorption of CO_2. The grade of maximal coverage in the case of NiO was about 5.2%, and that of ZnO—32.7%. Four portions of CO_2, two of which with radioactive (C^{14}), were successively adsorbed at 150°C, 100°C, 50°C, and 10°C. The operations were performed rather quickly. After the desorption of each portion, the sample was evacuated for 2–3 minutes and its temperature immediately lowered. This enabled the adsorbed portion to become well fixed and in cases of "biographical" heterogenity, helped the exposure of new levels, capable of holding the new isotope portion. Upon desorption, caused by a gradual raise of temperature to about 400°C, a relationship between the activity of the desorbed gas portions and their quantity gas obtained, shown in Fig. 1.

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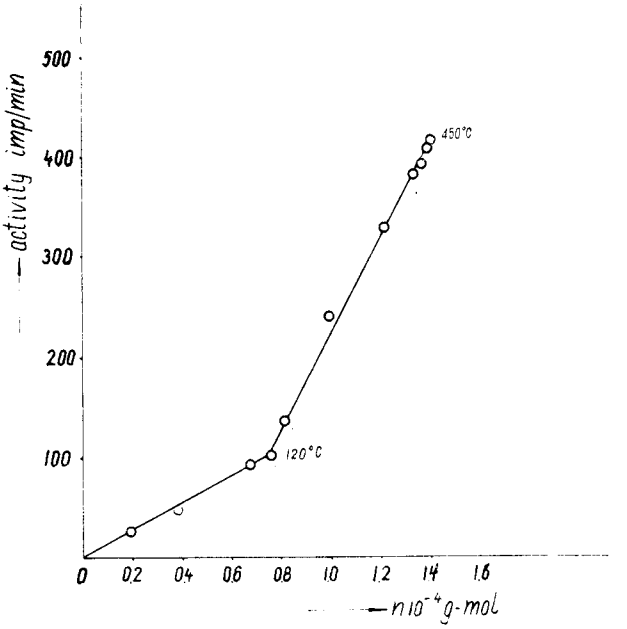

Fig. 1.

The two rectilinear sections of the curve are assigned to the two types of adsorption centres upon the surface of the adsorbent. The point of the abrupt change in the slope of the curve is characteristic of the system adsorbent–adsorptive and appears in a narrow temperature interval. In NiO it shows up at 100–120°C, and in ZnO at 220–230°C. This point is related to the variations in the adsorption properties of the surface, but it can also be explained with the alteration of the adsorption type with temperature, upon one and the same type of adsorption centres. By the shape of the curve and the size of the projections of the linear sections upon the abscissa, we can determine not only the number of sectors upon the surface, differing in their adsorption properties, but also their relative participation.

Lately, T. TOYA published a research with some new reasoning concerning the lack of conformity in DIM[5]. The author considers the state of the adsorbate and points out that with the existence of repulsion between neighbouring adsorbed particles, it is possible to create upon a surface of homogeneous origin an induced heterogeneity which could be called fluctuation heterogeneity. Fig. 2 a shows a scheme of the potential field of a homogeneous surface. In case "b" the adsorption leads up to a uniform lowering of all adsorption levels (proportional approximation). In case "c", due to repulsion between neighbouring adsorbed particles, the adsorption potential undergoes local alterations. Evidently, particles 3 of group III will be separated most easily upon desorption, followed by particles 2 of group II and the last will be particles

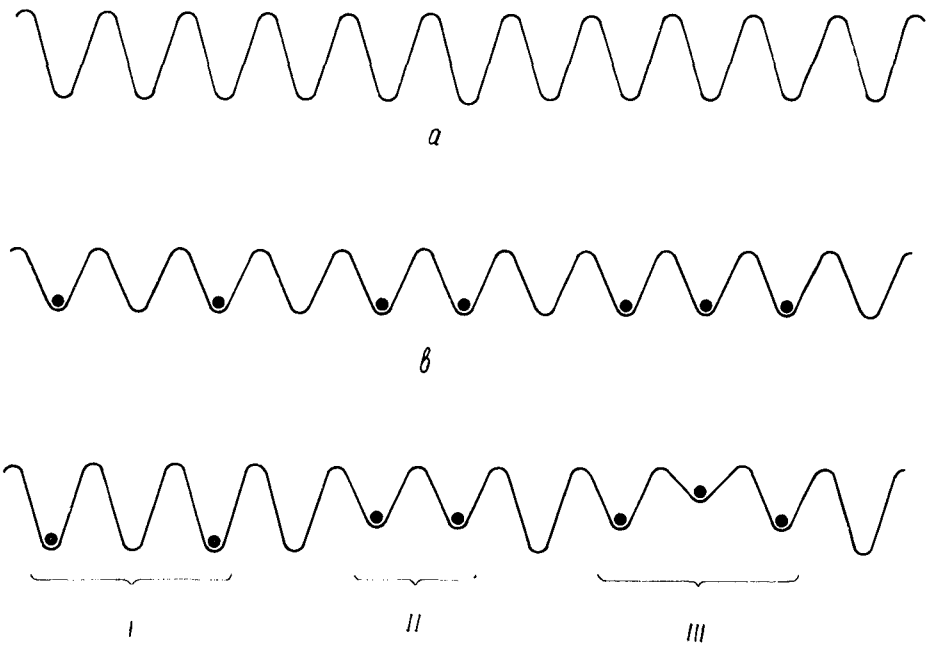

Fig. 2.

1 of group I. After the separation of particles 3 (of one particle of type 2, respectively), the rest of the particles will immediately "sink" to the level of particles 1. TOYA calculates the probability of formation of these groups, taking the adsorption of H_2 upon (110)-plane of Ni as an example. With a considerable coverage, it is possible to create cases where, upon adsorption of the first isotope portion, preferably every second adsorption centre will be occupied. This creates the opportunity for the formation of groups III, if the coverage is additionally raised to about, say 1/5–1/4 of its initial value, at the expense of adsorption of the second isotope of the same substance. The particles of this second portion are now mainly in the particular position 3 and, isotope interchange being avoided, the first desorbed portion will be enriched in the secend isotope of the substance. This results in giving a false idea of the character of the surface, which will seem biographically heterogeneous. In connection with this conclusion, the following notes can be made. If the probabilities of formation of all three types of groups were calculated as a function of coverage, for the model and method used by TOYA, we would have the picture shown in Fig. 3. In reality, the functions introduced here, are defined in the following way:

$$\beta(\omega) = \frac{n_a(\omega)}{(\sum n_a)_\theta}$$

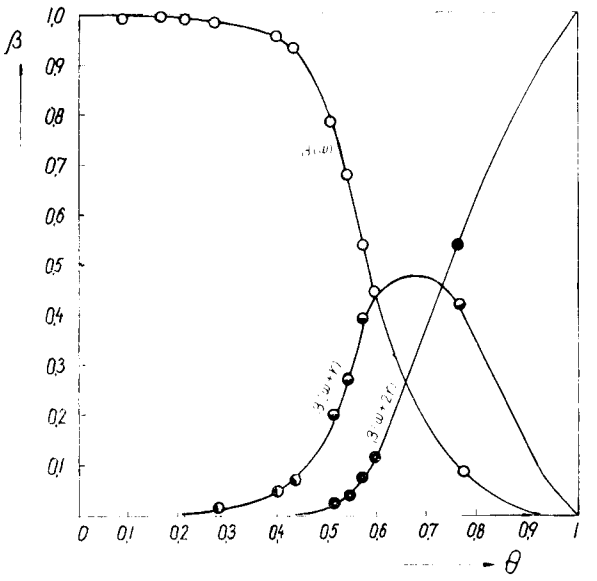

Fig. 3.

$$\beta(\omega+r_0)=\frac{n_a(\omega+r_0)}{(\sum n_a)_\theta}$$

$$\beta(\omega+2r_0)=\frac{n_a(\omega+2r_0)}{(\sum n_a)_\theta}$$

where n_a is the number of atoms of a given group upon the surface and $(\sum n_a)_\theta$ represents all atoms adsorbed at a given coverage, ω is the change of free energy in the whole system upon adsorption of an atom in position 1, and r_0 the potential of repulsion between two neighbouring particles.

From the given curves it is evident that with a coverage even of about 50–60%, the probability of formation of groups III is very little. This means that with a coverage of about 30–40%, almost all the adatoms, up to 95%, are isolated. Upon extending the coverage to approximately 50–55%, about 30% groups II are formed, consisting almost exclusively of both isotopes, found under equal conditions. Meanwhile, the single atoms are reduced to about 40%. Groups III, where one of the isotopes is in the particular position 3, are only about 5%. It is evident that upon desorption, the desorbed portions in all these cases will not differ in their isotope composition.

In the present consideration we use the equilibrium distribution of the atomic groups for different values of θ, because they are similar to those calculated by TOYA.

The analysis of the curves shows clearly that also with a very high coverage, where the surface is almost entirely saturated, an equalisation in the position of the

adsorbed atoms takes place again, the desorbed quantities being almost of the same composition. In his work TOYA shows that with the accepting of approximation in regions of low coverage, and under definite relations between the isotope adsorptions, DIM may in reality give a false idea about the surface. It is evident, however, from the analysis above that thare is a wide region where these conclusions may correspond to the actual condition of the surface.

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