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1961

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Abstract

Full Text

PHYSICAL CHEMISTRY

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SPECIFIC ACTIVITY OF NICKEL CATALYSTS

AND ADSORPTION OF THIOPHENE

(Presented by Academician S. S. Medvedev, April 26, 1961)

In the study of a number of complex catalysts it is necessary to be able to compare the catalytic activity of a unit surface area of the active component of the catalyst. By the BET method it is possible to determine only the total surface area of a complex catalyst, for example, the total surface area of the metal and the support.

A convenient method for determining the surface area of active metals proved to be the method, proposed by Burshtein (¹), of oxygen chemisorption at room temperatures and low pressures.

Fig. 1. Adsorption of oxygen A on catalysts: Ni on Cr_2O_3 (a) and Ni obtained from formate (b)

Characteristic curves expressing the rate of adsorption of oxygen on nickel, determined by this method, are shown in Fig. 1. A sharp decrease in the rate of adsorption is observed after a certain amount of oxygen has been absorbed. In the case of iron, the amount of adsorbed oxygen is $2 \cdot 10^{15}$ molecules/cm², and in the case of nickel the rapid adsorption of oxygen is $1.3 \cdot 10^{15}$ molecules/cm² of surface. These data are based on a comparison of the results of oxygen adsorption with data obtained by the BET method for pure metals (²).

We applied this method in comparing the specific activity (referred to 1 m² of nickel surface) of a series of supported nickel catalysts. The surface area of unsupported nickel catalysts, obtained by decomposition in hydrogen of nickel formate or oxalate, was first determined; the surface area of these samples was

determined by the usual BET method (low-temperature adsorption of nitrogen or krypton) with parallel adsorption of oxygen by method (1).

The catalytic activity of the catalysts investigated was determined from the reaction of benzene hydrogenation in the vapor phase in a flow-circulation apparatus under steady-state conditions described in (3). At the same time, the limiting adsorption of thiophene from its mixture with benzene vapors and

of hydrogen in the same flow-circulation apparatus and on the same catalysts; analysis of the residual thiophene was carried out photocolometrically, followed by analysis of the catalyst for absorbed sulfur. The results obtained are given in Table 1.

Table 1

Surface area, activity, and adsorption of thiophene on various nickel catalysts

Series	Nickel catalyst	$C_{\text{content of nickel, wt.\%}}$	Total*, m ² /g catalyst	Nickel**, m ² /g catalyst	Nickel, m ² /g	Adsorption of thiophene			
						Activity at 100°, mmol/h per 1 g Ni	Activity at 120°, mmol/g Ni	Activity, mmol/h	Adsorption of thiophene, mmol · 10 ³
I	From formate	100	4	3.8	3.8	1.74	0.028	0.46	7.4
I	From oxalate	100	7	6.5	6.5	2.85	0.050	0.44	7.7
I	On Cr ₂ O ₃	50	130	30	60	35	0.47	0.58	7.8
I	On MgO	65	200	42	65	44	0.50	0.68	7.7
I	On carbon	9.1	660	15	170	120	1.23	0.70	7.3
II	Alloyed Ni	75	90	87	87	286	0.65	3.30	7.5
II	Ni on Al ₂ O ₃	45.5	245	41	90	256	0.99	2.84	11.0

* By BET—adsorption of nitrogen.

** By adsorption of oxygen.

The data presented show that the surface area of nickel obtained from formate or oxalate (without a support) can be correctly determined both by BET and by the oxygen-adsorption method, since identical results are obtained.

Knowing the magnitude of the nickel surface area in complex catalysts and their overall activity in the benzene hydrogenation reaction, it is easy to calculate the specific activity referred to 1 m² Ni. As can be seen from the data in Table 1, the specific catalytic activity for a number of the catalysts investigated proves to be approximately constant; moreover, increasing the surface area of the support severalfold has no noticeable effect on the magnitude of the specific catalytic activity of nickel.

An analogous conclusion can also be drawn on the basis of the data obtained on the sulfur capacity of these catalysts—the limiting adsorption of thiophenic sulfur at 120° in a stream of hydrogen; the amount of thiophenic sulfur absorbed by a unit surface area of nickel remains approximately constant. The areas of nickel atoms located on different cross-sectional planes of the crystal are: for the 111 plane—5.3 Å², for 100—6.15 Å², and for 110—8.70 Å²; if the different planes on the surface of nickel crystals are considered equally probable, then the average area of a nickel atom is 6.75 Å², i.e., 1 cm² of surface contains $1.5 \cdot 10^{15}$ Ni atoms. Since the rapid adsorption of oxygen on Ni amounts to about $1.3 \cdot 10^{15}$ oxygen molecules per 1 cm² of surface, apparently, during adsorption 1 nickel atom binds with 1 oxygen molecule.

Chemisorption of thiophene at 120° in a stream of hydrogen averages about $7.5 \cdot 10^{-3}$ mmol per 1 m² of nickel. Under these conditions, hydrogenation of part of the thiophene occurs and thiophene uptake increases; at room temperature, however, in the absence of hydrogenation, the amount of thiophene absorbed from the vapor or from the liquid phase is lower and amounts to about $5 \cdot 10^{-3}$ mmol per 1 m² Ni. On the basis of these data, we can estimate the effective size of the thiophene molecule—about 33 Å². With the size of a nickel atom being 6.75 Å², we come to the conclusion that the thiophene molecule is situated on 5 Ni atoms, i.e., is adsorbed flat on the surface. Thus, measurement of the limiting adsorption of thiophene may serve as a method for determining the surface area of nickel in various catalysts.

When considering the data presented in Table 1, attention is drawn to the fact that nickel catalysts containing aluminum and alkali, obtained, for example, from an alloy of nickel with aluminum, with subsequent leaching out of most of the aluminum (Raney nickel), or by precipitating nickel with sodium aluminate, prove to be, for this reaction (benzene hydrogenation), considerably more active per unit surface of nickel than the nickel catalysts mentioned above. At the same time, in the study of other reactions (for example, isotopic exchange of H₂—D₂, hydrogenation of ethylene, etc.) no such difference in the specific activity of these catalysts is observed (⁴).

We are currently engaged in investigating the cause of the difference observed.

To determine the differential surface of nickel in supported nickel catalysts, the

method of oxygen adsorption was used. The specific catalytic activity of a unit surface of nickel in a series of catalysts in the benzene hydrogenation reaction proves to be approximately the same. The specific activity of nickel in an alloy catalyst and of Ni on aluminum oxide proved, for this reaction, to be higher than for other nickel catalysts.

Physicochemical Institute
named after L. Ya. Karpov

Received
12 IV 1961

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