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Investigation of Benzene Adsorption on Cobalt Catalyst

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Benzene adsorption was studied on metallic cobalt at temperature intervals of 35–85 and 160–200°C by a chromatographic method. Benzene chemisorption was also investigated by an isotope-dilution method at a temperature interval of 130–200°C. Observed values proved that the data obtained with these two methods are in accordance. Under 100°C the whole surface of the catalyst became saturated with reversibly bound benzene. At higher temperatures also irreversible adsorption and chemisorption occurred. Data for the isotherm equation, benzene adsorption enthalpy, as well as for the proportion between reversible adsorption and chemisorption were obtained.

INTRODUCTION

The investigation of hydrocarbons adsorption on metals encounters various difficulties. The relatively small specific surface of metals hampers the determination of the quantitative characteristics of adsorption. Furthermore, saturated hydrocarbons are adsorbed to a smaller extent at low temperatures, while at a higher temperature chemical reactions (dehydrogenation, cracking) also take place on the surface of metals. As regards unsaturated hydrocarbons, the investigation of their adsorption is rendered difficult also in consequence of the simultaneous chemical reactions, as well as owing to the fact that the surface becomes saturated at a relatively low pressure, which prevents the registration of the initial section of the adsorption isotherm.

It is probably due to these circumstances that only a few quantitative data are available (*1–3*) concerning the adsorption of hydrocarbons by metals. Most of the authors rather tried to draw conclusions regarding the mechanism of adsorption and chemisorption on the basis of spectroscopic (*4*), isotope exchange (*5*), and magnetic (*6*) data. This is the reason why we hardly have any data concerning the adsorption isotherms of hydrocarbons, the thermodynamic characteristics of adsorption. There are no data available either for the proportion of reversible adsorption and chemisorption.

In our present work, we studied benzene adsorption on a Co catalyst with the help of the chromatographic method developed by Pitkethly (*7, 9*). The adsorption isotherms were recorded and the isosteric adsorption heat values were calculated at a relatively wide temperature interval (35–200°C). The applied method also made it possible to compare the extent of reversible and irreversible adsorption. The chemisorption of benzene was separately investigated on the catalyst with the isotope-dilution process we had formerly described (*8*), so we could compare the values obtained by both the chromatographic and isotopic methods.

EXPERIMENTAL METHODS

Adsorbent

The investigation was carried out on metallic cobalt. Cobalt hydroxide was precipitated at 60°C from a 15% solution of cobalt nitrate with a 12.5% solution of ammonium hydroxide. The precipitate was decomposed in an airstream at 350–400°C,

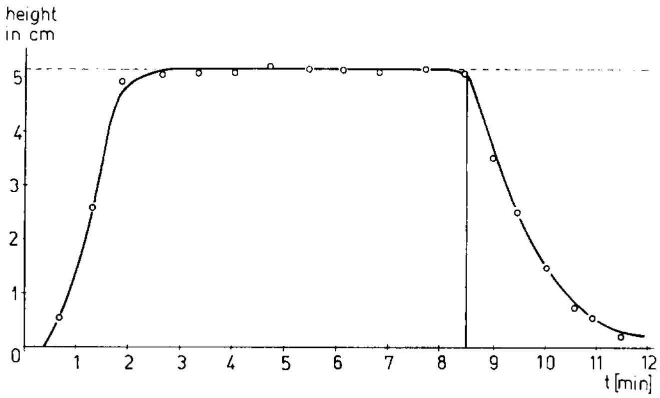

FIG. 1. The "chromatographic" curve representing the sorption of benzene at 160°C and 0.1891 Torr. partial pressure.

and the oxide was reduced in a hydrogen current at 250, 300, 350, and 400°C for 2 hr. The end of the reduction was indicated by the end of water formation. Specific surface: 7.28 m^2/g determined with the BET method by nitrogen adsorption.

Procedure

The experimental method used for the measuring of benzene adsorption is the same as that developed by Pitkethly (*7, 9, 10*). The scheme of the equipment is shown in Fig. 1 of Ref. (*7*).

Thiophene-free benzene was put into the vaporization pot from where it was vaporized in a nitrogen stream at a given temperature. With given partial pressure and flow speed of benzene, the nitrogen–benzene mixture is flowing through an empty pipe, the value shown then by the detector provides the bypass line. Following this, the mixture is transmitted through a pipe containing the adsorbent and the pressure decrease compared to the bypass line is measured. The setting in of adsorption equilibrium is ensured by the constant pressure value. After equilibrium is achieved, clean carrier gas is passed through the adsorbent and benzene desorption takes place.

Knowing the values of flow speed and partial pressure, the quantities adsorbed and desorbed can be calculated from the areas limited by the ascending branch and the bypass line, as well as by the descending branch and the base line, respectively. The difference between the adsorbed and desorbed quantities gave the quantity of irreversible adsorption.

Figure 1 shows a curve recorded during adsorption measurements on and off at 160°C. After each of the measurements the catalyst was treated for 1 hr in hydrogen stream at 360°C, and after it the hydrogen was evacuated at 380°C.

The partial pressure value of benzene was measured with a separately calibrated discharge detector, to check the results observed in this way we carried out some experiments also with benzene labeled with radiocarbon. We put labeled benzene into the vaporization pot, eluted the adsorbed substance in a hydrogen stream, and collected it in a trap containing 5 ml of inactive benzene. The quantity of trapped benzene was calculated from the activity value, that was measured in a Tricarb liquid scintillation spectrometer.

Table 1 contains the values obtained under identical conditions with the help of activity and pressure measurements. It is obvious that the values, received with the two different methods agree well, and this proves the reality of the data obtained by the methods applied.

The isotope dilution method was used also to determine the extent of chemisorption on cobalt. ^{14}C-labeled benzene was passed through the adsorbent layer at atmospheric pressure. Then the adsorbed

TABLE 1
ADSORPTION DATA, OBTAINED BY DISCHARGE DETECTOR AND RADIOACTIVITY MEASUREMENTS

		v(nml × 10^{-2})[a]	
t (°C)	P (Torr)	Discharge detector	Radio-activity
200	0.28	0.62	0.71
200	0.35	0.64	0.63
200	0.42	0.84	0.87
200	1.14	1.64	1.52

[a] nml = NTP ml.

benzene was eluted in a nitrogen and hydrogen stream at 360°C and was collected in 5 ml of inactive benzene. On the basis of the activity of this solution, we calculated the quantity of benzene being bound. The details of this method were described in our former work (*8*).

RESULTS

Benzene adsorption was measured in a temperature interval below 100°C and above 150°C. In the interval between 35 and 85°C adsorption proved to be absolutely reversible; the quantities adsorbed and desorbed were identical. The isotherms showing the pressure dependence of the adsorbed amounts are illustrated in Fig. 2. The pressure dependence of the adsorbed quantities is in accordance with Freundlich's isotherm equation, as by plotting $\log v$ vs. $\log p$, we obtain straights. The maximum amount adsorbed at 36.4 Torr, calculated from the intersection point of these straights, is: $v_m = 0.80$ nml/g = 0.11 nml/m^2.*

As the straights were intersected in one point, the obtained p_m and v_m values are common for different temperatures in this interval (35–85°C).

The benzene adsorption isosterms were recorded on the basis of adsorption isotherms. The isosteric adsorption enthalpy values are given in Table 2.

In the temperature interval above 150°C, benzene adsorption is of a different character. A part of benzene was not desorbed at this temperature from the metal surface. The surface could be entirely cleaned only by heating in a hydrogen stream to 360°C. The isotherms characterizing reversible adsorption were recorded from the quantities desorbed and they could be linearized, also in this case, according to Freundlich's equation (Fig. 3). At $p_m = 16.6$ mm, $v_m = 0.08$ nml/g = 0.01 nml/^{2}.

The adsorption enthalphy values obtained from isosteres designed on the basis of adsorption isosteres is shown in Table 2.

The irreversibly adsorbed amounts were

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* nml = NTP ml.

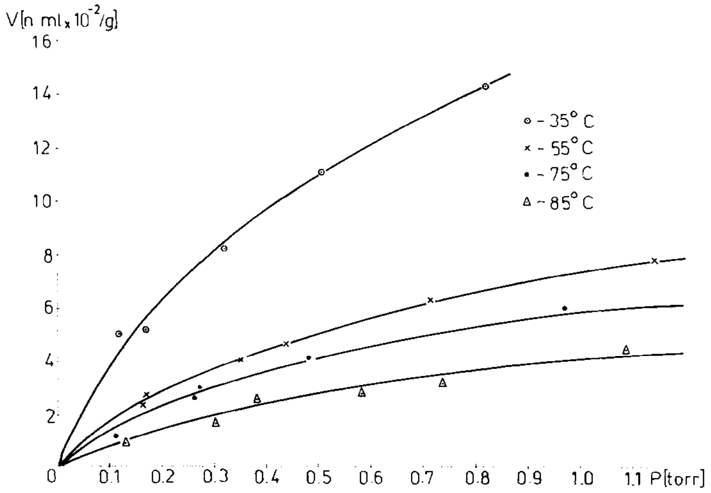

FIG. 2. Isotherms of the adsorption of benzene at 35–85°C.

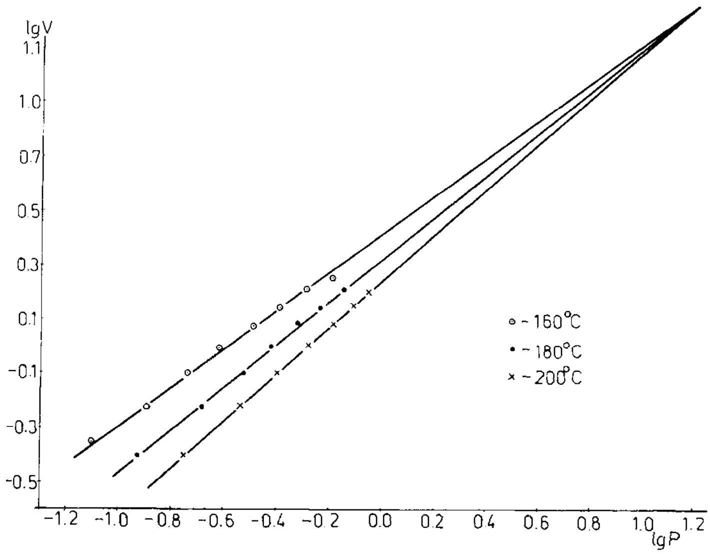

FIG. 3. Isotherms of the reversible adsorption of benzene at 160–200°C, transformed according to Freundlich.

TABLE 2
THE ISOSTERIC ADSORPTION ENTHALPY VALUES OF BENZENE

Coverage	Temp range (°C)	$-\Delta H$ (kcal/mole)
0.125	35–85	8.6
0.250	35–85	8.2
0.375	35–85	7.8
0.500	35–85	7.5
0.025	160–200	10.5
0.050	160–200	9.8
0.075	160–200	8.0
0.125	160–200	7.4
0.175	160–200	6.1
0.225	160–200	5.5

calculated as the difference of adsorbed and desorbed quantities:

$$v_i = v_a - v_d.$$

Values v_a may be regarded as the total (reversibly and irreversibly) adsorbed amounts (v_t), while v_d have to be equal to the reversibly adsorbed amounts of benzene. Figure 4 contains the values v_t and v_i obtained at 200°C. Analogical data were obtained at 160 and 180°C also. As shown, about 30–50% of the adsorbed benzene was bound irreversibly. The surface became visibly saturated quickly with regard to irreversible adsorption. Table 3 contains the maximum values of irreversible benzene adsorption for 160, 180, and 200°C.

With a view to determine whether saturation at low pressure corresponds to actual chemisorption saturation with regard to irreversible adsorption, we determined the extent of benzene chemisorption at atmospheric pressure, too. We applied the already described and proved (*8*) isotope dilution method with ^{14}C-labeled benzene. In order to make a comparison with nickel and platinum catalysts the measurement was carried out in a temperature interval between 130 and 200°C. The data obtained also are shown in Table 3.

TABLE 3
THE MAXIMUM VOLUME OF IRREVERSIBLY ADSORBED AND CHEMISORBED BENZENE
($v_{i,m}$ and v_{ch})

t (°C)	P (Torr)	$v_{i,m} \times 10^{-2}$ (nml/g)	P (Torr)	$v_{ch} \times 10^{-2}$ (nml/g)
130	—	—	760	2.9
140	—	—	760	2.1
145	—	—	760	1.6
150	—	—	760	1.0
160	1.52	[illegible]	760	1.0
170	—	—	750	0.6
180	1.38	0.7	760	0.7
200	1.05	0.6	760	0.6

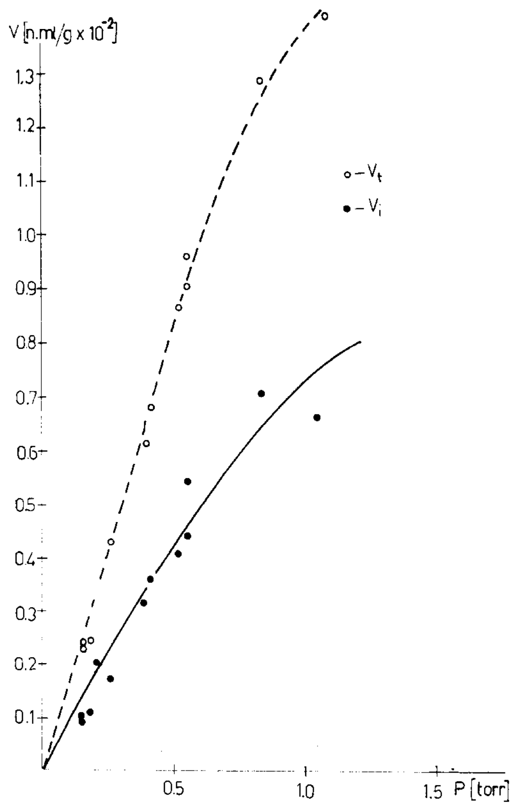

FIG. 4. The dependence of total v_t and irreversible v_i adsorption on the partial pressure at 200°C.

TABLE 4

THE VOLUME OF BENZENE CHEMISORBED (v_{ch} AT P = 760 mm)

t (°C)	$v_{ch} \times 10^2$ (nml/g)	$v_{ch}' \times 10^3$ (nml/m²)
130	2.9	3.9
140	2.1	2.9
145	1.6	2.2
150	0.95	1.3
160	0.95	1.3
170	0.58	0.8
180	0.68	0.9
200	0.61	0.8

DISCUSSION

The experimental data show that there are considerable differences between the adsorption measured in temperature intervals of 35–85 and 160–200°C. Below 100°C, benzene adsorption is absolutely reversible, while at a higher temperature a considerable quantity is irreversibly bound.

Although the reversible adsorption can be described in both temperature intervals with Freundlich's isotherm equation, the characterizing values differ considerably. In the interval below 100°C the v_m value corresponds practically to the full coverage of the surface. Accepting 41 Å² for the area of a benzene molecule (*11*), on the basis of v_m, its surface area requirement comes to 8.8 m²/g, that shows a good coincidence with the BET surface area measured by nitrogen adsorption. This proves, on the one hand, the applicability of the method, and shows, on the other hand, that the reversibly adsorbed benzene at 0.05 atm pressure fully covers the cobalt surface. On the contrary, however, the v_m value corresponds only to a 10–12% coverage when adsorption takes place at a temperature interval of 160–200°C.

A remarkable difference also occurred as regards adsorption enthalpy. Though there are not too big differences between numerical values, in the case of adsorption at the higher temperature interval the enthalpy depends considerably on the coverage.

The vaporization heat of benzene is 7–8 kcal according to the data given in literature (*12*, *13*). Adsorption enthalpy obviously ranges near these values, especially when adsorption takes place at a lower temperature.

Kemball and Rideal obtained the value of —16.4 kcal/mole for benzene adsorption on mercury (*13*). In our former investigations on nickel, the benzene adsorption enthalpy value was —12 kcal/mole (*14*). It is understandable that the values obtained for cobalt are close to those for nickel. It is also noteworthy, that the adsorption heat falls near the values obtained for silica gel and aluminosilicate (*15*, *16*).

In the interval above 100°C, simultaneously with the considerable decrease of the extent of reversible adsorption, irreversible adsorption and chemisorption occurred. This is equally proved by the values obtained both from ^{14}C-labeled benzene at atmospheric pressure (Table 3) and the chromatographic method (Table 3 and

Fig. 4). The data provided by the two different methods correspond to each other also numerically, which proves, on the one hand, the applicability of these methods, and on the other hand, that chemisorption coverage already ensues at 1–2 mm pressure.

As shown, the amount of benzene chemisorbed, decreased with temperature. This is analogous to that observed with platinum and one of the nickel catalysts (*8*). The chemisorption maximum observed (*8*) for another nickel catalyst in the case of cobalt probably lies at a temperature lower such as 130°C.

At lower pressure, benzene chemisorption comes to 30–50% of the reversible adsorption. The quantity of maximum chemisorption amounts to about 10% of the v_m value which characterizes the reversible adsorption.

A comparison of the values with those obtained for nickel and platinum catalysts (*8*) shows that the extent of chemisorption on cobalt is about 10–20% of that on various nickel and 45% of that on platinum catalysts. Hence, cobalt has a weaker chemisorption capacity than these metals.

Certain conclusions can be drawn from the values of benzene adsorption and chemisorption regarding a frequently-discussed reaction, the mechanism of cyclohexane dehydrogenization. Benzene chemisorption takes place only on a smaller surface area, while a considerable amount of benzene adsorbs reversibly. The chemisorbed layer can be removed with hydrogen. All this indicates that chemisorption cannot lead to the entire contamination of the catalyst under the conditions of the dehydrogenation process. The catalytic activities of Ni, Co, and Pt (*17*) are not in direct correlation (or in direct either in inverse proportion) with their chemisorption capacity, which is shown by the following comparison:

Catalytic activity: Pt > Ni > Co,
Chemisorption capacity: Ni > Pt > Co.

Therefore, we cannot accept the former idea (*18*) according to which the desorption of aromatic products is the rate-determining step of the dehydrogenization of hydroaromatic hydrocarbons. This supports our earlier conclusion (*17*) drawn on the basis of comparing the rate of cyclohexane, cyclohexene, and cyclohexadiene dehydrogenation.

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