

Investigations on the Chemisorption of Benzene on Nickel and Platinum

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The chemisorption of ^{14}C -labeled benzene on nickel, platinum, and copper catalysts at atmospheric pressure in the temperature range of 100–300°C was investigated. The amounts of benzene chemisorbed were determined by radioactivity. In the case of different nickel catalysts the coverage with chemisorbed benzene was 0.2–0.6, in case of platinum 0.03. Chemisorption was not observed in the case of copper.

The chemisorbed benzene could be fully removed only with hydrogen, benzene removed one part of it. It was found by special measurements that a small part of the compound desorbed with hydrogen was in the form of benzene, and the other part in the form of cyclohexane. New evidence of the dissociative adsorption of benzene was given by the obtained data.

It was shown that there is no cause for metallic catalysts to be poisoned by chemisorbed benzene in the conditions of hydrogenation–dehydrogenation of six-membered rings.

1. INTRODUCTION

The chemisorption of hydrocarbons on metals is a rather important problem from the point of view of the theory of catalysis. The study of this phenomenon becomes difficult under the conditions (temperature, pressure, etc.) given for a catalytic process. Isotopic dilution, in spite of conventional methods, allows the investigation of chemisorption for a wide range of experimental conditions, different compounds, and catalysts.

There is special interest in studying the chemisorption of benzene, because of the important role of this process in the catalytic hydrogenation–dehydrogenation of six-membered hydrocarbon rings. Some authors have put forward the idea that the desorption of aromatic product is the controlling step in the dehydrogenation of hydroaromatic compounds (1). According to others (2) the inactivity of some metals in this reaction is caused by their ability to chemisorb benzene, poisoning the dehydro-

genation process. It was established, however, in our earlier experiments (3, 4, 5) that on many metal catalysts the dehydrogenation rates of cyclohexene, and, especially, cyclohexadiene are much higher than that of cyclohexane. This means that the desorption of benzene cannot be a rate-determining step for the cyclohexane dehydrogenation. It is becoming, therefore, important to obtain some data about the chemisorption occurring under the circumstances of catalytic conversion. On the other hand, it would be interesting to compare these data to the results obtained by other authors for the chemisorption of benzene (6, 7).

In the experiments reported here the chemisorption of benzene was studied on different nickel catalysts. Also some preliminary investigations were made with platinum and copper. ^{14}C -Labeled benzene was adsorbed, and the chemisorbed quantity was determined by the specific radioactivity of the solution obtained after the radio-

active compound was eluted and condensed in "light" benzene. The chemisorption experiments were carried out in a dynamic system, which was normally used for kinetic investigations.

2. EXPERIMENTAL

Catalysts

The investigations were carried out on platinum, copper, and four different types of nickel catalysts prepared in various ways. The specific surface of the examined catalysts was determined (8) with the BET method by nitrogen, and in the case of Ni No. 3, by krypton adsorption at -196°C . The surface areas used for calculation were 16.2 \AA^2 and 19.5 \AA^2 , respectively. The preparation procedures for the catalysts were as follows.

Nickel No. 1. Nickel hydroxide was precipitated at 60°C from a 10% solution of nickel nitrate with a 12.5% solution of ammonium hydroxide. The precipitate was decomposed in a stream of air at 400°C and reduced in a stream of hydrogen at $350\text{--}400^{\circ}$. The completion of the reduction process was indicated by the end of water formation. Specific surface: $7.0 \text{ m}^2/\text{g}$.

Nickel No. 2. An aqueous solution of Raney nickel ("Chinoin" made) was placed in the reactor tube and treated for several hours in a hydrogen stream at 400°C . Specific surface: $39.3 \text{ m}^2/\text{g}$.

Nickel No. 3. Schuchardt catalyst was prepared from nickel carbonyl. Specific surface: $1.3 \text{ m}^2/\text{g}$.

Nickel No. 4. Nickel formate was decomposed and reduced to metallic nickel in a hydrogen stream at 400°C . Specific surface: $3.6 \text{ m}^2/\text{g}$.

Platinum. A solution of hydrogen hexachloroplatinate obtained from potassium hexachloroplatinate (by Dowex ion exchanger) was subjected to reduction by formaldehyde, the platinum precipitate obtained was washed with distilled water, dried in a desiccator, and heated in a hydrogen stream at 150°C . Specific surface: $3.1 \text{ m}^2/\text{g}$.

Copper. Copper hydroxide was precipitated from a 10% solution of copper nitrate

with ammonium hydroxide (12.5% solution). The precipitate was decomposed in air stream at 400°C and reduced with hydrogen at $250\text{--}300^{\circ}\text{C}$. The completion of the reduction process was indicated by the end of water formation. Specific surface: $2.9 \text{ m}^2/\text{g}$.

Procedure and Analysis

The chemisorption experiments were carried out in a flow system reactor described earlier (9).

A few grams of the catalyst to be investigated was placed into the quartz reactor tube. The temperature was measured by a thermocouple placed into the center of the adsorbent. In other details the apparatus was the same as described earlier (9).

Prior to the adsorption measurements the system was evacuated and saturated with purified argon. After that, ^{14}C -labeled benzene (specific activity = $20 \mu\text{curie/ml}$) was allowed to pass through the system. It was fed with the aid of a glass syringe connected to a synchronous motor at uniform speed. Upon termination of the benzene flow, argon was again passing through for 40 min. The radioactive benzene remaining on the surface was removed by hydrogen flowing over the catalyst for 1 hr at $300\text{--}350^{\circ}\text{C}$, and it was collected in a trap containing a known amount of inactive benzene. It is important to note that hydrogen was used only for removing the chemisorbed benzene. There was no hydrogen present in the system during the adsorption of benzene. There were also some experiments performed for special reasons, in which the radioactive benzene was removed with benzene instead of hydrogen and the temperature of the desorption was different from that used in the case of hydrogen.

The radioactivity of the solution containing the desorbed benzene was measured by a Tricarb B-type liquid scintillation spectrometer. The amount of chemisorbed benzene was evaluated by comparing the counts of the solution to that of benzene present before the adsorption. The values calculated on the basis of the counting ratios were in good agreement with those calcu-

lated directly from the specific activity values of the solutions determined by an inner standard.

The chemisorption studies were carried out at atmospheric pressure at a temperature range of 100–300°C.

Proof of the Experimental Conditions

First of all it was ascertained that when using the above-mentioned method, the whole quantity of benzene chemisorbed could be removed from the surface of the adsorbents.

For this purpose, a catalyst sample, after the desorption procedure, was oxidized in a stream of air and the radioactivity of the gas formed was measured in a proportional counter. It was found that the quantity of the radioactive compound remaining on the surface of the catalyst after one measurement had been performed amounted to not more than to 2–3% of that initially chemisorbed. The results were checked with the aid of a wet method (10), by oxidation of the quantity remaining with iodates. The results were found to be in good agreement with the data obtained in the case of oxidation with air. Since the radioactivity in the oxidized species is small, it can be concluded that the above-described method for removing the chemisorbed benzene is acceptable. From the fact that the quantity remaining on the surface increased uniformly after each of the measurements, the conclusion can be drawn that—in spite of the 1-hr regeneration occurring in between the measurements—the surface of the adsorbent was covered by carbon as a result of the benzene destruction.

In all experiments the same quantity of labeled benzene, 2.88 ± 0.01 ml, was used; it was passed through the system at a constant flow rate of 0.115 ml/min for 25 min. It was ascertained by special experiments that in all cases when the amount of benzene passed was greater than 1.2 ml, the chemisorbed quantity did not depend on the total amount of benzene passed.

It has been mentioned that all the adsorption experiments were carried out at atmospheric pressure. Special experiments were carried out on the chemisorption of

benzene in presence of argon, i.e., at lower partial pressure of benzene. It was established by special measurements that the chemisorbed quantity of benzene does not depend on its partial pressure in the range of 0.2–1 atm. It means that the data obtained at 1 atm pressure can represent the chemisorption at the partial pressure of benzene existing under the conditions of catalytic hydro-dehydrogenation of six-membered hydrocarbon rings.

The adsorption experiments were carried out at different temperatures with the same sample. The sequence of the measurements did not follow the increase of the temperature. Consequently, the character of the temperature dependence of the chemisorbed amounts could not contribute to any irreversible processes occurring due to the heating in the bulk of the metal. This was ascertained also by providing two adsorption experiments at the same reference temperature.

On the basis of the data listed here one can make the conclusion that the experimental conditions applied can be used for the adsorption studies.

3. RESULTS

Chemisorption of Benzene

The results of the measurements show (Table 1) that for the different catalysts investigated the amount of the chemisorbed benzene varies in the range of 10^{-3} to 10^{-5} g/g nickel. The chemisorbed quantity depends on the temperature of adsorption to a considerable extent. It is apparent that in the case of nickel catalysts, except for the Raney nickel, the chemisorbed quantity has a definite maximum in the region of 140–160°C. The dependence of the extent of chemisorption on temperature is significant also in the case of Raney nickel, but the maximum is not to be seen; possibly it appears below 100°C. The dependence of the chemisorbed amounts of benzene on the temperature is illustrated in the case of Ni No. 1 in Fig. 1.

A comparison of the maximum quantities chemisorbed on the catalyst surface is rendered possible by Table 2, in which the

TABLE 1
THE QUANTITY OF BENZENE CHEMISORBED ON DIFFERENT CATALYSTS

Ni No. 1		Ni No. 2		Ni No. 3		Ni No. 4		Pt	
t (°C)	$\frac{10^{-4} \text{ g}}{\text{g Ni}}$	t (°C)	$\frac{10^{-4} \text{ g}}{\text{g Ni}}$	t (°C)	$\frac{10^{-4} \text{ g}}{\text{g Ni}}$	t (°C)	$\frac{10^{-4} \text{ g}}{\text{g Ni}}$	t (°C)	$\frac{10^{-4} \text{ g}}{\text{g Pt}}$
115°	1.37	110°	7.74	110°	5.00	110°	1.30	110°	2.26
130°	2.70	130°	6.00	130°	7.85	120°	2.20	120°	2.11
135°	2.90	140°	4.34	135°	8.60	130°	1.80	130°	1.77
150°	3.90	150°	3.86	160°	9.70	150°	4.50	140°	1.62
160°	5.00	150°	3.60	170°	8.76	155°	4.30	150°	1.34
160°	5.10	160°	3.70	180°	8.16	170°	3.90	170°	1.20
160°	5.70	170°	2.40	200°	6.80	180°	3.90	180°	0.80
170°	5.20	170°	2.28	210°	6.80	180°	3.60	200°	0.67
180°	2.20	180°	1.86	220°	4.90	190°	2.97	210°	0.54
190°	1.40	190°	2.19	225°	4.20	190°	3.40	220°	0.65
200°	0.95	200°	1.46	240°	4.60	200°	2.55	230°	0.58
240°	0.90	210°	1.52	260°	4.00	210°	2.50	250°	0.56
250°	0.90	230°	2.09			220°	1.90	270°	0.59
300°	0.70	240°	1.00			240°	1.30		
300°	0.70	250°	2.87			240°	1.20		
						250°	1.05		
						260°	0.50		

Error %:
 $\pm 4.1-10.0$ $\pm 1.5-3.1$ $\pm 4.5-7.0$ $\pm 1.5-7.0$ $\pm 4.0-8.0$

maximum volume of hydrogen adsorbed is also shown. These values were calculated from the Langmuir and Freundlich isotherms of H_2 adsorption obtained by the

volumetric method at 260–300°C (11). On the basis of the area of one benzene molecule [41 \AA^2 (12)], the coverage of the surface with chemisorbed benzene can be cal-

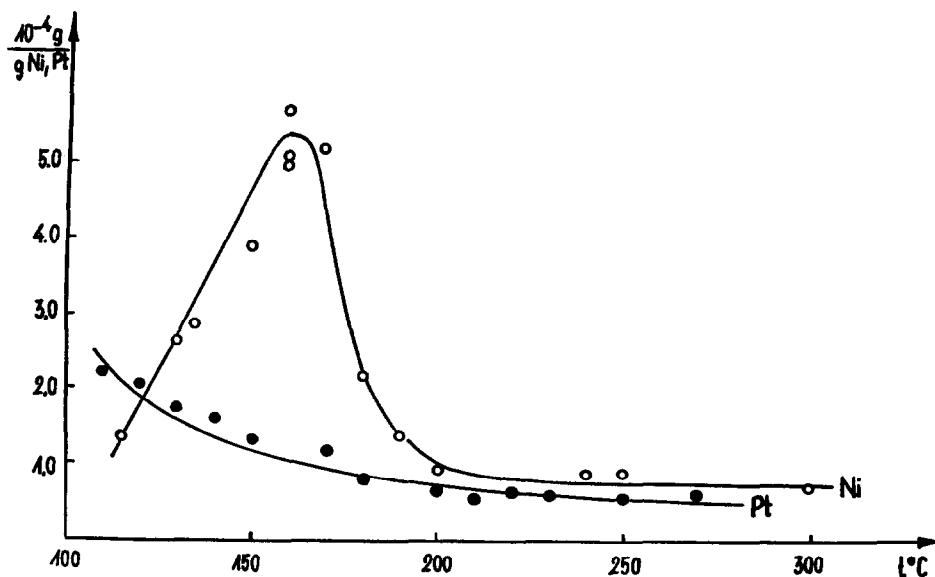


Fig. 1. The dependence of the chemisorbed quantity on temperature in the case of Ni No. 1 catalyst and Pt catalyst.

TABLE 2
THE MAXIMUM VOLUME (NTP) OF HYDROGEN AND BENZENE ADSORBED (CHEMISORBED)

Catalyst	H ₂ adsorption			Benzene chemisorption		
	V_m (ml/g)	V_m (ml/m ²)	θ_H	V_m (ml/g)	V_m (ml/m ²)	θ_B
Ni 1	1.55	0.223	0.74	0.164	0.023	0.25
2	4.92	0.125	0.42	2.220	0.056	0.63
3	0.17	0.131	0.44	0.028	0.021	0.23
4	2.28	0.634	2.10	0.129	0.036	0.40
Pt	0.71	0.078	0.26	0.064	0.007	0.08

culated, which (in the case of a maximum) turns out to be 8–60%, depending on the adsorbent. In the range of 250–300°C, at the temperature of cyclohexane dehydrogenation, the coverage with chemisorbed benzene is only 2–10%.

Some preliminary investigations were carried out also with platinum and copper. It has been stated that in the case of platinum the chemisorbed quantity of benzene is at the same order of magnitude as that of nickel. However, in this case, as well as on Raney nickel, we could not observe a maximum on the curve representing the temperature dependence of the chemisorbed quantity (Fig. 1). In the case of copper the chemisorption of benzene was not observed in the experimental conditions existing in these experiments.

We have tried also to investigate the chemisorption of cyclohexane on nickel. It has been found that catalyst No. 1 does not chemisorb cyclohexane up to 200°C. A rather small chemisorption was observed at 210°C. Since dehydrogenation can also take place at this temperature (in traces) it is more likely to say that the chemisorption observed is due to the benzene having formed under these circumstances.

Desorption of Chemisorbed Benzene

There were special experiments carried out for the removal of the chemisorbed benzene with different substances, first of all with benzene.

In these experiments after the active benzene had passed, the apparatus was filled with argon. The argon passed through for 40 min, and after that a given quantity of inactive benzene was fed. By measuring the radioactivity of the obtained solution the quantity of benzene desorbed was determined. The benzene remaining on the surface we then desorbed by hydrogen and collected in inactive benzene, as previously described. The data obtained are listed in Table 3.

From these results it is clear that only a part of the chemisorbed benzene can be removed by benzene and the remaining part only by hydrogen. It is interesting also to note that the whole quantity could be removed only at a higher temperature, over 300°C. On the basis of these data it can be suggested that the role of hydrogen in the removal is not restricted to hydrogenation of chemisorbed benzene, as the desorption cannot be accomplished at the optimum

TABLE 3
THE DESORPTION OF BENZENE CHEMISORBED—CATALYST NO. 1

Adsorption at t (°C)	Amount of benzene (in ratio of total) removed with					
	Benzene	t (°C)	Hydrogen	t (°C)	Hydrogen	t (°C)
150°	0.31	150°	—	—	0.69	380°
150°	—	—	0.81	150°	0.19	380°
150°	0.20	150°	0.74	150°	0.06	380°
160°	—	—	—	—	1.0	330°
160°	—	—	—	—	1.0	330°

temperature of hydrogenation, i.e., at 180–200°C.

To clarify this problem other experiments were provided, too. After the removal the chemisorbed benzene was dissolved in a mixture containing benzene and cyclohexane in a ratio of 1:1. These two components were then separated chromatographically by the method of the Institute of Petroleum (13). It was ascertained by special experiments that the cyclohexane and benzene were separated quantitatively. From the specific activity of these two compounds one can make some conclusions

by hydrogen the desorbed compound was mainly in the form of cyclohexane, a definite part (20%), however, in all experiments (except the above-mentioned case of Expt. 5) was desorbed in the form of cyclohexane. This is not caused by the dehydrogenation of cyclohexane as at 150°C cyclohexane cannot be dehydrogenated.

4. DISCUSSION

On the basis of the data presented here it was established that the nickel and platinum catalysts investigated do chemisorb benzene. In the case of copper the chemi-

TABLE 4
DISTRIBUTION OF THE DESORBED (LABELED) SPECIES IN AN INACTIVE
BENZENE-CYCLOHEXANE MIXTURE (1:1)^a

Expt. No.	Chemisorbed		Removed		Activity	
	<i>t</i> (°C)	Compound	<i>t</i> (°C)	Removing agent	Cyclohexane (cpm)	Benzene (cpm)
1	150°	¹⁴ C-benzene	150°	Benzene	540	3774
			380°	Hydrogen	8936	325
2	150°	¹⁴ C-benzene	150°	Hydrogen	5580	1350
			380°	Hydrogen	1470	115
3	150°	¹⁴ C-benzene	150°	Benzene	—	400
			150°	Hydrogen	2100	80
4	150°	¹⁴ C-benzene	380°	Hydrogen	1100	160
			150°	Benzene	—	880
			150°	Hydrogen	2460	730
5	150°	¹⁴ C-benzene	380°	Hydrogen	200	40
			150°	Benzene	260	4350
			150°	Hydrogen	2240	320
			380°	Hydrogen	120	—

^a Background, 6–8 cpm. Catalyst No. 1. The catalyst was treated before the adsorption experiments in vacuum at 200°C (Expts. 1, 2, 5) and at 350–380°C (Expts. 3, 4).

on behalf of the mechanism of the benzene desorption. The obtained data are listed in Table 4. It can be seen from these data that the hydrocarbon was desorbed in the form of cyclohexane and benzene, with the exception of Expts. 3 and 4, when the compound removed by benzene was not checked in the case of removal by H₂ at 380°C, probably because of the small quantity of benzene remaining on the catalyst.

The cyclohexane–benzene correlation depends on the previous treatment of the catalyst: There was no cyclohexane in the condensate if the catalyst was treated before the adsorption experiment at high temperature (Expts. 3, 4). By removing it

sorption was not observed. This is in accordance with the experience that copper is commonly a weaker catalyst in the hydrodehydrogenation processes of hydrocarbons than nickel and platinum. Copper is not able to form carbides; this fact witnesses also to the weak interaction between copper and carbon atoms. The chemisorption of benzene on copper has been observed (2) at lower temperature (0°C) and in a small quantity, so that this fact is not in contradiction to the absence of benzene chemisorption over 100°C.

The absence of cyclohexane chemisorption on the metals investigated is in accordance with the results of catalytic investiga-

tions. As has already been mentioned, cyclohexane can be dehydrogenated much more slowly than cyclohexene and cyclohexadiene (3-5). This fact, and the high values of energy of activation obtained for cyclohexane adsorption (14) were a basis for the conclusion that the dissociative adsorption of cyclohexane is one of the slowest, rate-controlling steps of the cyclohexane dehydrogenation.

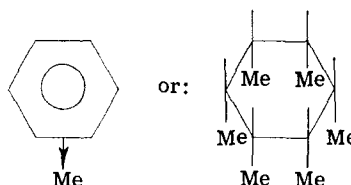
The quantity of chemisorbed benzene was smaller in all cases than the maximum adsorbed hydrogen. The θ_B were 2-5 times smaller than the θ_H values. In the case of Ni 2 the coverage with chemisorbed benzene was by 50% higher than with adsorbed hydrogen. It is impossible to make a real comparison in case of Ni 4 because of the unacceptable value of θ_H (this is probably a consequence of the hydrogen occlusion into the bulk). No direct correlation was observed between the hydrogen adsorption and benzene chemisorption. This is likely to be due to a difference in the H-Me and C-Me interaction observed also by the comparison of the activation energy values of cyclohexane and isopropanol dehydrogenation and the heat of hydrogen adsorption (15, 16).

The temperature dependence of chemisorption seems to be in agreement with other data. Selwood has found (6) that in the case of benzene adsorption the bonds formed between nickel and the substrate increase at 120-200°C and attain a terminal value at this region. The maximum values for chemisorption of benzene were observed by us at 140-160°C. The high activity of Raney nickel might be an explanation why the maximum chemisorption can take place in the case of this catalyst at a lower temperature.

It can be explained in the light of the obtained data that nickel and platinum were not poisoned with benzene in the reaction occurring in the presence of this substance (as a product or as an initial substance). Hydrogen taking part in these reactions also does remove the chemisorbed benzene. At the temperature of cyclohexane dehydrogenation the chemisorbed quantity of benzene is small enough to be desorbed

with the aid of hydrogen which is formed in the reaction. This is the explanation of the observed phenomenon, that the desorption of benzene does not become a rate-controlling step in this process even in the case of its chemisorption.

The role of hydrogen as removing agent is also easily explainable on the basis of the data shown in Tables 3 and 4. It seems to us quite reasonable to propose that benzene is chemisorbed partly due to C-Me interaction (17)



The other part can be chemisorbed due to dissociative adsorption, through dissociation of C-H bonds



The existence of the dissociative adsorption of benzene is proved, e.g., by the fact that hydrogen-deuterium and hydrogen-tritium exchange in benzene occurs on metallic catalysts very easily (18, 19). The benzene adsorbed through C-H disruption can be desorbed only with the aid of hydrogen. This circumstance can play a definite role in the removing action of hydrogen.

The latter supposition can be proved by the data shown in Table 4. It can be seen that a part of the hydrocarbon removed by hydrogen was in the form of benzene. It was explained there that the benzene content of the desorbed solution cannot be caused by the dehydrogenation of cyclohexane, resulting from the hydrogenation of chemisorbed benzene.

The presence of benzene in the hydrocarbon mixture removed by hydrogen proves the supposition that the role of hydrogen was the "hydrogenation" of C-Me bonds formed due to the disruption of C-H bond in the chemisorption process. The benzene chemisorbed in such a way cannot be fully desorbed by other benzene molecules because of the lack of hydrogen

needed for desorption. The most active sites of the surface are covered with chemisorbed molecules. As the chemisorption due to the C-H dissociation takes place probably on these sites, the hydrogen atoms required by desorption can be only very slowly replaced by those resulting from the dissociation of newly adsorbed benzene molecules. It is quite possible that the hydrogen atoms formed recombine partly with each other before the interaction with adsorbed hydrocarbon radicals. It is also understandable that in the presence of hydrogen the majority of the chemisorbed species are desorbed as cyclohexane because of the multiple hydrogenation.

The described conclusions are in good agreement with the results obtained by Selwood (20). According to those data the number of C-Ni bonds formed up to 120°C is six. It increases rapidly, reaching about 18 bonds at 200°C. This indicates an extensive fragmentation at this temperature. It is quite reasonable to accept the conclusion that the removing role of hydrogen is new evidence of the dissociative chemisorption of benzene. The observed maximum at 140-180°C concerning the temperature dependence of the chemisorption also proves the reality of this conclusion.

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