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Gas Phase Benzene Hydrogenation on a Nickel–Silica Catalyst

II. Gravimetric Experiments of Benzene, Cyclohexene, and Cyclohexane Adsorption and Benzene Hydrogenation

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Studies of benzene adsorption on a nickel–silica catalyst have suggested the existence of three forms of chemisorption, in addition to physical adsorption. The chemisorbed forms cover only a part of the surface and are, respectively: (a) a reactive form, active in normal benzene hydrogenation, and discernible up to 110°C, (b) a form of low reactivity, not contributing to normal benzene hydrogenation, and removable by several hours hydrogen flow at the temperature of adsorption, and (c) a dissociatively adsorbed form, occurring above 120°C, in the absence of hydrogen. This last form acted as a poison for the hydrogenation reaction and was only removable by hydrogen at 400°C or above.

Cyclohexane adsorbed in hydrogen atmosphere (30–200°C) proved to be easily removable by hydrogen.

INTRODUCTION

In a preceding paper (*1*) we gave rate data for the hydrogenation of benzene on a 10% nickel–silica catalyst, designated NZ 10. This work was purely phenomenological and only a few possible mechanisms were mentioned.

Before evaluating the extent to which postulated mechanisms were able to describe and explain our experimental rate data, we wished to have more information on the state of chemisorbed benzene on the nickel surface, especially under reaction conditions, i.e., in the presence of hydrogen.

Accordingly, we decided to study adsorption and reaction phenomena on our NZ 10 catalyst (a) gravimetrically and (b) magnetically. In this paper we report on the gravimetric determination of benzene and cyclohexane adsorption under various conditions. The magnetic study involves measurements of the changes in the magnetization of the superparamagnetic nickel catalyst resulting from adsorption of hydrogen, benzene, cyclohexene, and cyclohexane, and will be reported later (*2*).

Moyes and Wells (*3*) have recently reviewed benzene chemisorption on a range of metals. Our attention here will be confined to nickel. Shopov *et al.* (*4*) used ir and epr spectroscopy in combination with gravimetric measurements to study benzene and cyclohexane adsorption at room temperature. They found that about $\frac{2}{3}$ of the chemisorbed benzene and less than half of the chemisorbed cyclohexane could be removed by hydrogen. Both hydrocarbons covered only part of the surface. This led them to the conclusion that there are different active centers for the interaction of benzene and cyclohexane with nickel. (De)hydrogenation was supposed to take place on one of these sites and hydrocarbon deposition on the other. This deposition could be removed only by hydrogen treatment above 300°C.

In experiments with ^{14}C-labeled benzene, Tetenyi and Babernics (*5*) also found only a partial coverage. A maximum in the quantity of benzene adsorbed occurred between 140 and 160°C. A fraction of the chemisorbed benzene could be exchanged with gaseous benzene. Chemisorbed benzene could be fully removed only by hydrogen (for a small part in the form of benzene, the rest as cyclohexane). No poisoning of the (de)hydrogenation reaction occurred. Up to 200°C they could not detect cyclohexane adsorption.

Reversibly chemisorbed benzene may be held in a π-adsorbed form (*6*). However, Erkelens and Egginck-du Burck (*7*) could not detect π-adsorbed benzene by ir spectroscopy on nickel–silica: a broad band in the spectrum pointed to a mixture of adsorbed species with a range of C–H vibrations, apparently indicating that benzene had lost its aromatic character.

Most of the work described so far has been concerned with adsorption of benzene on a hydrogen-free surface. For the elucidation of the mechanism of nickel-catalyzed benzene hydrogenation, however, the important matters are the manner and extent of benzene and cyclohexane adsorption in a hydrogen atmosphere. The present paper deals with these problems.

EXPERIMENTAL METHODS

Purification of hydrogen and benzene was described earlier (*9*). Nitrogen, cyclohexane and cyclohexene were purified in similar ways.

The catalyst NZ 10 contained 11.3% nickel; the nickel surface area, measured by hydrogen adsorption at 20°C and 1 atm, was 26.2 m^2 $(g\ cat)^{-1}$ and the total BET (N_2) area was 222 m^2 $(g\ cat)^{-1}$. The reduction time was 4 hr at 450°C, and the evacuation took 2 hr at 450°C and 10^{-4} Torr. For further details, see Ref. (1).

The heart of the gravimetric flow system consisted of a Cahn electrobalance (2550 RH Ventron Instr. Corp.), shown in Fig. 1. It was connected with the glass flow system described earlier (*1*). Weight changes were registered with 10 μg precision on a Kipp BD 6 recorder. The reactant flow was introduced a few millimeters above the catalyst bed, which consisted of a thin layer spread over the bottom of a glass basket. The temperature of the reference and sample baskets was kept constant up to 75°C by a waterbath, and at higher temperatures by an electrical furnace. Reduction of the catalyst was performed *in situ* at 450°C. When the temperatures of reference and sample baskets were not equal, a buoyancy correction was taken into account. Weight registration *in vacuo* proved impossible because of unknown, probably electrostatic forces. The phenomenon persisted when the hang-down tubes were immersed in electrically earthed sodium chloride solution. Already at rather low gas pressures these effects were avoided: readings at 20 Torr nitrogen or hydrogen were therefore arbitrarily chosen as a gravimetric zero, after a small correction

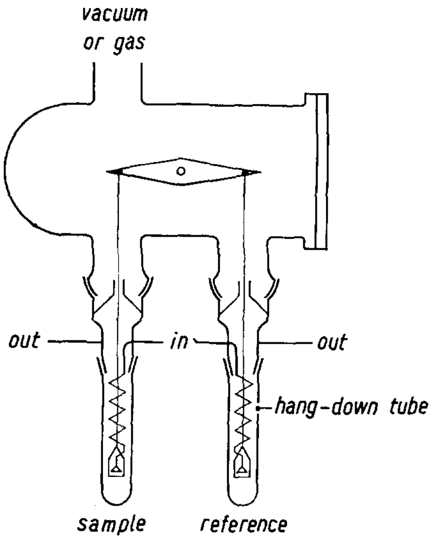

FIG. 1. Experimental setup for gravimetric measurements.

for resultant adsorption. The electrical measuring part of the balance was kept free from benzene vapor by means of a stream of nitrogen or hydrogen along the suspension wires. The temperature of the catalyst could only be measured a few millimeters above the catalyst bed. To test the balance, flow and static measurements were made without catalyst with different gases (hydrogen, nitrogen, hydrogen with benzene and nitrogen with benzene) at temperatures from 20 to 200°C and buoyancy effects were tabulated. In all experiments samples of 200 mg catalyst were used and corrections for buoyancy were made. In most experiments a benzene vapor pressure of 70 Torr, the saturation vapor pressure at 18.5°C, was used.

The sensitivity of the electrobalance was insufficient to measure changes in hydrogen adsorption above 20 Torr. Nitrogen adsorption was measured at different temperatures and these values were used for corrections in relevant hydrocarbon adsorption measurements.

Chemisorption and Physical Adsorption

The measurement of benzene chemisorption was complicated by a much larger simultaneous physical adsorption. To measure chemisorption of benzene, the physically adsorbed quantities were removed by either evacuation or nitrogen flow. By this procedure chemisorbed benzene was not removed as was ascertained by magnetic measurements (*2*).

RESULTS

Benzene Chemisorption on a Hydrogen-Free Catalyst

Successively nitrogen (670 Torr), nitrogen with benzene (600, 70 Torr, respectively for 0.5 hr) and nitrogen (670 Torr, to constant weight) were led over a hydrogen-free catalyst sample. The chemisorption of benzene, measured at five temperatures on the same sample, is presented in Table 1. The surface coverage by benzene was calculated with the assumption that one benzene molecule occupies 41 Å^2 (*4, 10*). From these data the coverage of the metal surface proved to be only partial and appeared to have a maximum at 150°C. Above 110°C the benzene adsorption was time-dependent. Reduction at 450°C between the measurements at the different temperatures removed all the adsorbed hydrocarbons. In later experiments we could not reproduce the 59°C value. Several repeated measurements at 60°C on fresh catalyst samples yielded values of 500–600 μg. Low values may be due to some sintering in repeated heat treatments.

TABLE 1

Benzene Chemisorption on Nickel–Silica Catalyst NZ 10 (200 mg) with a Hydrogen-Free Surface

Temp (°C)	Amount benzene chemisorbed (μg); exposure (hr):		Degree of occupation θ_B
	0.5	1	
28	450		0.27
59	290		0.17
60[a]	500–600		0.3–0.36
105	410		0.24
153	690		0.42
		750	0.45
196	490		0.30
		600	0.36

[a] Fresh sample.

The reactivity of benzene adsorbed on a hydrogen-free sample was measured by subsequent exposure to hydrogen of a pressure of 600 Torr. From the 590 μg benzene adsorbed at 60°C, 400 μg was removed by a hydrogen flow within 1 hr at 25°C.

Benzene Chemisorption on a Catalyst Partially Covered with Hydrogen

By hydrogen exposure and subsequent evacuation during 15 min to 5 × 10^{-4} Torr at the temperature of the following benzene adsorption, the catalyst was partially

TABLE 2

Benzene Chemisorption on Nickel–Silica Catalyst NZ 10 (200 mg) Partially Covered with Hydrogen

Temp (°C)	Amount of benzene chemisorbed (μg)			R^a (μg min^{-1})	r^b (μmol H_2 m^{-2} min^{-1})
	Exposure 0.5 hr (p_{H_2} = 0 Torr)	After an injection of hydrogen (p_{H_2} = 20 Torr)	After 0.5 hr hydrogen flow (p_{H_2} = 700 Torr)		
34	570		160	100	6.7
60	680		200	100	
104	500	400	300	100	
144	740	720	400	10	5.7
196	1000	1020	700	10	5.1
202	1250[c]	1200	750	10	3.8

[a] R is the reactivity of the chemisorbed benzene with the first hydrogen flowing over the catalyst.

[b] r is the activity after the adsorption procedure and the hydrogen flow (0.5 hr). r relates to the conditions: temp, 31°C; p_{H_2} = 600 Torr; p_B = 70 Torr. The standard activity at these conditions was 6.8 μmol H_2 m^{-2} min^{-1}.

[c] Benzene was flowed over the catalyst for 2 hr.

covered with hydrogen. The remaining coverage with hydrogen will thus be slightly lower at higher benzene adsorption temperature. On the catalyst thus pretreated benzene adsorption was measured in a nitrogen atmosphere. The results are given in Table 2. The quantity of benzene adsorbed at temperatures below 120°C was about 600 μg, at 200°C about 1000 μg. In this set of experiments it was also found that benzene adsorption at high temperature is time-dependent, e.g., at 202°C about 100 μg/hr on the amount of sample used.

Subsequent hydrogen admission immediately started the hydrogenation of adsorbed benzene, but there was a different reactivity R for benzene adsorbed at high or low temperature, viz, 100 μg min^{-1} at temperatures below 104°C, and 10 μg min^{-1} above 104°C. In all cases it appeared from glc analysis that only cyclohexane and traces of benzene were eluted. A hydrogen flow during 30 min did not remove all the adsorbed species. A catalyst activity test under standard conditions (p_{H_2} 600 Torr, p_B 70 Torr, 31°C) showed partial poisoning of the catalyst, progressively stronger at higher preadsorption temperature. The benzene adsorbed at low temperature was totally removable after 1 night in hydrogen atmosphere. The fraction of benzene adsorbed at high temperature and not removable by the normal hydrogen treatment could be removed only by hydrogen at 400°C.

Benzene Chemisorption under Normal Hydrogenation Conditions (30–110°C)

A mixture of hydrogen (600 Torr) and benzene (70 Torr) was led over the catalyst. Sudden evacuation almost stopped the reaction and removed physisorbed benzene. An attempt was then made to obtain the weight of benzene remaining adsorbed, but this proved impossible due to electrostatic effects. A hydrogen pressure of 20 Torr had to be established, but then the reaction proceeded immediately. Consequently an extrapolation to the moment of hydrogen admission had to be carried out. The results are tabulated in Table 3.

Next a hydrogen flow at a pressure of 700 Torr was led over the catalyst for 30 min. Under these conditions a faster desorption of benzene (as cyclohexane and benzene as was determined from glc analysis) occurred at higher temperatures.

About $\frac{1}{3}$ to $\frac{1}{2}$ of the adsorbed benzene remained on the surface. This very slowly reactive adsorbed quantity was of the same order if no intermediate evacuation procedure was applied, e.g., in the experiments at 25 and 31°C shown in Table 3.

At temperatures above 60°C the degree of conversion became too high, so that, due to the heat of reaction, the temperature of the sample was higher than measured directly. The amount of physical adsorption gave an indication for the real temperature inside the catalyst particle. By comparing with the data on physical adsorption of benzene in nitrogen atmosphere (Table 4) it could be derived that in the experiment at 110°C in Table 3 the temperature difference between catalyst and surrounding gas was about 40°C. Assuming then a catalyst temperature of 150°C, we found that also at this temperature 200 μg of very slowly reactive benzene remained. We recall that at low precoverage with hydrogen this amount was about 400 μg (Table 2).

Physical Adsorption of Benzene

On catalyst NZ 10 we measured the amount of physical adsorption: (a) in nitrogen atmosphere as a function of temperature, Table 4, (b) during reaction of benzene with hydrogen from 30–110°C, Table 4, (c) as a function of benzene pressure during reaction at 30°C, Table 5.

TABLE 3

Benzene Chemisorption on Nickel–Silica Catalyst NZ 10 (200 mg) under Normal Hydrogenation Conditions[a]

Temp (°C)	Amount benzene chemisorbed (μg)	
	After evacuation[b]	After 0.5 hr hydrogen flow (p_{H_2} = 670 Torr)
25		200
25	670	130
31		300
32	600	300
59	400	200
110[c]		200

[a] p_{H_2} = 600 Torr; p_B = 70 Torr.

[b] Extrapolated values, see text.

[c] Temperature of catalyst is about 40°C higher, see text.

TABLE 4

Physical Adsorption of Benzene on Nickel–Silica Catalyst NZ 10 (200 mg)[a]

Temp (°C)	Physisorbed benzene in nitrogen atmosphere (μg)	Number of monolayers	Physisorbed benzene in hydrogen atmosphere[b] (μg)
32	20,500	1.45	19,600
60	8,100	0.57	7,200
112	1,700	0.12	500
152	700	0.05	
195	0	0	

[a] p_B = 70 Torr.

[b] During reaction with hydrogen p_{H_2} = 600 Torr.

In all cases a correction was made for the chemisorbed quantity of benzene. The number of monolayers was calculated from the BET surface area of catalyst NZ 10, 222 m^2 (g cat)$^{-1}$, and a molecular cross section for benzene of 41 Å^2.

Adsorption of Cyclohexane in a Hydrogen Atmosphere

In these experiments hydrogen was led over a freshly reduced catalyst, followed by hydrogen with cyclohexane (600 and 70

TABLE 5

Physical Adsorption of Benzene on Nickel–Silica Catalyst NZ 10 (200 mg) during Benzene Hydrogenation at 30°C as a Function of Benzene Pressure[a]

p_B (Torr)	Physisorbed benzene (μg)	Number of monolayers	r (μmol H_2 m^{-2} min^{-1})
70	21,200	1.50	6.30
21	9,800	0.70	5.61
4.8	2,800	0.20	4.5
1.93	850	0.06	—

[a] p_{H_2} = 600 Torr.

TABLE 6

Cyclohexane Adsorption on Nickel–Silica Catalyst NZ 10 (200 mg) in a Hydrogen Atmosphere[a]

Temp (°C)	Physisorbed cyclohexane (μg)	Chemisorbed cyclohexane (μg)	
		After evacuation ($p_{H_2} = 20$ Torr)	After 20 min hydrogen flow
33	15,200	50	0
73	3,400	100	0
107	1,350	100	0
140	650		0
172	400	300	150
205	400		50

[a] $p_{cy} = 70$ Torr; $p_{H_2} = 600$ Torr.

Torr, respectively); next the sample was evacuated, hydrogen was admitted up to 20 Torr and finally hydrogen was flowed over at a pressure of 600 Torr for 20 min. The results are given in Table 6.

At the low temperatures no cyclohexane remained on the surface after exposure to a hydrogen flow during 20 min. At higher temperatures, however, a stronger adsorption occurred. One hundred fifty micrograms of cyclohexane that remained on the catalyst at 172°C after flowing over hydrogen during 20 min, was removed by a hydrogen flow during 2 hr at 200°C.

Adsorption of Cyclohexane on a Catalyst Partially Covered with Hydrogen

In one experiment at 35°C we evacuated a hydrogen-covered catalyst sample, flowed over the catalyst successively nitrogen (670 Torr), nitrogen with cyclohexane (600, 70 Torr) and nitrogen (670 Torr). The resulting adsorption of cyclohexane was 450 μg/200 mg cat. After a hydrogen flow for 0.5 hr at the same temperature about 150 μg still remained on the surface. This quantity was removed from the surface after 1 night under 1 atm hydrogen pressure.

Adsorption of Cyclohexene in Nitrogen Atmosphere at 34°C on a Catalyst Partially Covered with Hydrogen

In one experiment this was 760 μg/200 mg cat. The same procedure as described above for cyclohexane was used.

DISCUSSION

The experiments described above deal primarily with adsorption and reactivity of benzene on a nickel–silica catalyst. Before exposure to benzene the hydrogen coverage of the samples was zero in the experiments of Table 1, partial and depending on the temperature of evacuation in the experiments of Table 2, and almost full in the experiments of Table 3.

Adsorption of Benzene at Temperatures below 110°C

Benzene adsorbed in an amount of 500–700 μg (Tables 1, 2, 3) independent of the hydrogen coverage. Assuming a surface area for benzene of 41 Å^2 (*4*, *10*) the degree of coverage of benzene is then 0.3–0.4. This result is not unexpected for a catalyst with a mean nickel particle diameter of 15 Å, where the fit of molecules requiring 41 Å^2 will hardly be such that all nickel surface atoms are engaged. However, in the work of others (*4*, *5*, *8*) involving larger crystallites benzene adsorption was also found to be limited to a partial coverage. The fact that at temperatures below 110°C the benzene coverage appears largely independent of the hydrogen coverage on the same surface suggests a larger heat of adsorption of benzene than of hydrogen on that part of the surface. This means for the reaction mechanism of benzene hydrogenation that benzene and hydrogen each have their "own" part of the surface and that to a first approximation their adsorptions may be considered noncompetitive.

The Reactivity of Benzene Adsorbed below 110°C

We observed that about $\frac{2}{3}$ of the benzene chemisorbed below 110°C at various hydrogen coverages was reactive with hydrogen within 0.5 hr. The same quantity was found by Shopov *et al.* (*4*) on a clean surface at 25°C. The remaining part of the adsorbed benzene was much less reactive. This difference in reactivity of benzene with hydrogen points to different forms of adsorption. Possibly a π-adsorbed form exists next to a σ-bonded type, the π form being reactive via Rooney's mechanism (*12*), the σ form being slowly reactive.

Adsorption and Reactivity of Benzene Adsorbed at Temperatures above 110°C

At temperatures above 110°C benzene adsorption is time-dependent in contrast to the low temperature adsorption, and covers a larger part of the surface.

As is shown in Table 2 the reactivity of the adsorbed benzene with hydrogen under a pressure of 20 to 700 Torr appeared to be quite different for the species adsorbed at low or high temperatures. In normal benzene hydrogenation (*1*) the reaction rate at 200°C was of the order of 1000 μmol H_2 min^{-1} m^{-2}, but here at 200°C the rate at which the adsorbed benzene disappeared from the surface was 10 μg benzene/min, equivalent to 0.1 μmol H_2 min^{-1} m^{-2}. In these experiments the benzene pressure is low but there is a high benzene coverage. Less than half of this benzene could be removed by hydrogen, in contrast with the desorption experiments of Tetenyi and Babernics (*5*) at 150°C, where only a small part was not reactive. The quantity of hydrocarbons remaining on the surface after hydrogen treatment gradually increased with temperature, possibly because before benzene was adsorbed at higher temperatures less hydrogen remained on the surface after the evacuation than at lower temperatures. At 200°C an irreversible adsorption form, probably dissociated CH_2-, CH_3-species (*7*) or nickel carbides (*11*), can occupy part of the surface active in the benzene hydrogenation as follows from the decrease in activity under standard conditions. This was observed on a catalyst sample partially covered with hydrogen, but in normal benzene hydrogenation (*1*) we do not find such a decrease in activity under standard conditions. It may be concluded that with hydrogen on the catalyst such a dissociation is suppressed. This also follows from the data in Table 3, which show that during the reaction of benzene with hydrogen, the nonreactive fraction of adsorbed benzene remains confined to 200 μg/200 mg catalyst up to 150°C. This statement is further confirmed by Martin and Imelik (*11*). From measurements of the saturation magnetization of their nickel–silica catalyst they found that above 160°C on a bare surface benzene formed 24 bonds with nickel. If, on the contrary, benzene was adsorbed on a nickel surface partially precovered with hydrogen, benzene cracking was suppressed and the number of bonds was found to be much smaller.

Two important observations have to be explained: (a) the normal hydrogenation proceeds much faster than the rate of elimination of preadsorbed benzene with hydrogen at the same temperature and (b) after the adsorption/hydrogenation procedure at 196°C given in Table 2, 700 μg of unreactive material remain on the catalyst surface, corresponding to a surface coverage of 0.4, and yet the decrease of activity under standard conditions is only 25%.

If under hydrogenation conditions, with continuous hydrogen supply, benzene adsorbs in another form, as the findings of Martin and Imelik indicated (*11*), but on the same sites on which benzene adsorbed irreversibly, then the standard activity should decrease much more than 25%. Therefore it looks most probable that active benzene adsorbs on other sites, but could not be detected in our experiments because it was removed together with physisorbed benzene during the nitrogen flow. Irremovable adsorption will take place for the greater part on sites where benzene molecules are adsorbed so strongly that they hardly contribute to the rate of benzene hydrogenation under any conditions.

As a conclusion we can say that benzene adsorbs in different forms on part of the nickel surface. Three forms of chemisorption can be assigned to benzene:

a. A reactive form, being the active form in the normal benzene hydrogenation and in our experiments discernable up to 110°C.

b. A form of low reactivity not contributing to the normal benzene hydrogenation.

c. A dissociatively adsorbed form, only occurring if no hydrogen is present during the adsorption at high temperatures. It can act as a poison for the hydrogenation reaction.

Adsorption of Cyclohexane

In contrast to Tetenyi and Babernics we found chemisorption of cyclohexane if the adsorption took place without hydrogen in the gas phase. Shopov *et al.* (*4*) also found adsorption of cyclohexane at 25°C, but in a smaller quantity than benzene. Half of the adsorbed cyclohexane was not removable by hydrogen according to Shopov *et al.* In our experiment some hydrogen was still on the surface when adsorption took place and $\frac{2}{3}$ of the adsorbed cyclohexane was then removable by hydrogen.

More important for the elucidation of the mechanism of the benzene hydrogenation is the adsorption of cyclohexane in a hydrogen atmosphere. As is shown in Table 6 no chemisorption occurred up to 172°C. The nonremovable quantity at this temperature can be ascribed to the evacuation after the adsorption, so that a temporary lack of hydrogen dissociated the cyclohexane, since at 205°C on a sample which was not evacuated the nonremovable quantity was only 50 μg. From these data we conclude that in normal benzene hydrogenation cyclohexane is removed quickly and forms no inhibition for benzene adsorption. In our previous work (*1*) it was already found that the order in cyclohexane pressure was zero from 25 to 200°C. The dissociative adsorption of cyclohexane is prevented by hydrogen, as was the case with benzene in the benzene hydrogenation and in the experiments of Martin and Imelik (*11*).

In a forthcoming paper (*2*) dealing with magnetization measurements, the chemisorbed quantities of benzene, cyclohexene and cyclohexane determined by the gravimetric and magnetic methods will be compared.

Physical Adsorption of Benzene

The physisorbed quantities of benzene on silica and nickel surfaces (Tables 4 and 5) have not had much attention in the literature.

The chemisorbed quantity is small compared to the physisorbed quantity up to 110–150°C. Perhaps this physisorbed benzene acts as a store from which benzene molecules can be taken to fill vacant chemisorption sites situated especially near the metal–support boundary where only migration over a small distance is needed. This may be the reason why the order with respect to benzene pressure in the benzene hydrogenation is low (about 0.1) up to 120°C (*1*), and why above this temperature the order increases rapidly with decreasing physically adsorbed benzene to reach a value of about 0.4 at 200°C.

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