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Gas Phase Benzene Hydrogenation on a Nickel–Silica Catalyst

III. Low-Field Magnetization Measurements on Hydrogen, Benzene, Cyclohexene and Cyclohexane Adsorption, and Benzene Hydrogenation

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Magnetization–volume isotherms of benzene, cyclohexene and cyclohexane show that chemisorption of these hydrocarbons on the nickel surface of a Ni/SiO_2 catalyst stops at partial coverage. The approximate number of bonds between the hydrocarbons and nickel can be assigned. By evacuation down to 10^{-4} Torr physically adsorbed benzene and cyclohexane are desorbed, and chemisorbed species remain on the surface.

Magnetization measurements during the hydrogenation of benzene show that only a small fraction of the nickel surface plays a part in the reaction and that a weakly bound form of dissociatively adsorbed hydrogen is active in the reaction.

INTRODUCTION

In a preceding paper (*1*) we have given a phenomenological description of the hydrogenation of benzene on a nickel–silica catalyst (NZ 10) over a wide range of conditions. In a second paper dealing with gravimetric adsorption experiments (*2*), we showed to what extent benzene and cyclohexane adsorbed and were reactive with hydrogen on this same nickel–silica catalyst. In the present paper we mainly devote attention to the mode of adsorption and the reactivity of the adsorbed hydrogen. Besides measurements of the magnetization of nickel as a function of the surface coverage by hydrogen, benzene, cyclohexene, and cyclohexane, we measured the magnetization during benzene hydrogenation as a function of the hydrogen pressure, to obtain information about the surface coverage of the reactants during the hydrogenation process. In the fourth paper (*3*) these data will be used to find an appropriate rate equation.

In high-field experiments Selwood (*4*) showed that on hydrogen adsorption the decrease in magnetic moment of a surface nickel atom ϵ equals 0.71 Bohr magneton independent of temperature, surface coverage and crystallite size. On the contrary Martin *et al.* (*6*) concluded from high-field magnetization data a temperature dependence of ϵ,

$$\epsilon(T) = \frac{I_{sp}(T\,°K)}{I_{sp}(0\,°K)}\alpha,$$

where I_{sp} is the spontaneous magnetization and α a constant equal to 0.7 Bohr magneton, independent of surface coverage and crystallite size.

In low-field magnetization measurements, assuming formation of two bonds on adsorption of a hydrogen molecule on nickel, Selwood (*4*) found a temperature dependent number of bonds for benzene from the ratio of the slopes of the magnetization–volume isotherm of hydrogen and benzene, from about 5 bonds at 25°C up to 18 bonds at 200°C. For cyclohexane the number of bonds at 150°C was about 8. In saturation magnetization measurements Martin and Imelik (*5*, *18*) found that benzene formed 8 bonds at 25°C, 25 at 150°C and still higher values at higher temperatures. For cyclohexane the number of bonds found was 10 at 25°C and 30 at 220°C.

From the comparison of high- and low-field magnetization experiments Martin *et al.* (*6*) concluded that hydrogen was distributed homogeneously over the nickel crystallites, but that benzene was not. Benzene prefers the smaller crystallites. This explains the difference in number of bonds found by Selwood and by Martin and Imelik.

Selwood (*4*) found that chemisorbed benzene could occupy only part of the metal surface, as was also found by Shopov *et al.* (*11*) in gravimetric measurements and epr spectroscopy, and by van Meerten *et al.* (*2*) in gravimetric experiments.

For the theoretical description of the magnetization we use the relation derived by Geus and Nobel (*8*) from the Langevin function for uniform small (<30 Å) superparamagnetic particles in a weak magnetic field (<400 Oe) at 300°K:

$$M_0 = \mu_0 N n^2 \beta(T)^2 \mu_B{}^2 \frac{H}{3kT}, \qquad (1)$$

with

$$\beta(T) = \beta(0°\mathrm{K}) \frac{I_{\mathrm{sp}}(T)}{I_{\mathrm{sp}}(0°\mathrm{K})}, \qquad (2)$$

M_0	magnetization at zero coverage (A m^{-1})
N	number of metal particles per unit volume catalyst (m^{-3})
n	number of metal atoms per particle
β	number of Bohr magnetons per metal atom
μ_B	magnetic moment of 1 Bohr magneton (J m^2 Wb^{-1})
H	external magnetic field strength (A m^{-1})
k	Boltzmann constant (J $°\mathrm{K}^{-1}$)
T	absolute temperature (°K)
I_{sp}	spontaneous magnetization, values taken from Ref. (*15*) (A m^{-1})
μ_0	$4\pi \times 10^{-7}$ (Wb A^{-1} m^{-1})

With the assumption that per atom adsorbed the moment of one nickel atom is decoupled, Geus and Nobel derived the following summation for adsorption on a particle size distribution

$$\frac{\Delta M}{M_0} = -1.052 \times 10^{-2} x \frac{\sum_i n_i}{\sum_i s_i} \frac{\sum_i n_i s_i}{\sum_i n_i{}^2} + 0.0028 \times 10^{-2} x^2 \left(\frac{\sum_i n_i}{\sum_i s_i}\right)^2 \frac{\sum_i s_i{}^2}{\sum_i n_i{}^2}, \qquad (3)$$

with s_i the number of gas atoms adsorbed by the i-th particle, which contains n_i nickel atoms, and x the number of milliliters of gas adsorbed (STP) per gram of metal.

For our purpose we will modify Eq. (3). In the first place our adsorption experiments concerned hydrogen; therefore, for the decrease in moment per adsorbed hydrogen atom at 0°K we use the value measured by Martin *et al.* (*6*), namely, 0.7 Bohr magneton. For the oxygen adsorption Geus and Nobel used a value of 0.606 Bohr magneton. In (*16*) Coenen *et al.* described a nickel crystallite as a hemisphere, which they assumed to be the most favorable shape energetically. With a volume of a nickel atom of 11 Å^3, an average area per surface nickel atom of 6.33 Å^2, and θ_i the degree of coverage of particle i, the number of adsorbed atoms on the surface s_i is

$$s_i = 3.0 n_i{}^{2/3} \theta_i.$$

Substitution of s_i and multiplication of x with 0.7/0.606 in Eq. (3) then gives an expression for the magnetization–volume

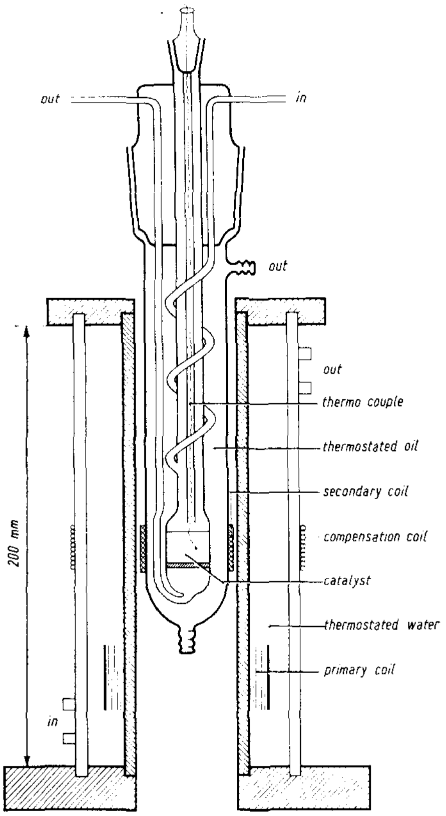

FIG. 1. AC-permeameter with glass system for flow experiments. Only one half of the coil system is shown.

isotherm for hydrogen adsorption on nickel,

$$\frac{\Delta M}{M_0} = -1.215\times10^{-2}x\,\frac{\sum_i n_i}{\sum_i n_i^2}\,\frac{\sum_i n_i^{5/3}\theta_i}{\sum_i n_i^{\frac{2}{3}}\theta_i} + 0.369\times10^{-4}x^2\left(\frac{\sum_i n_i}{\sum_i n_i^{\frac{2}{3}}\theta_i}\right)^2\frac{\sum_i n_i^{\frac{4}{3}}\theta_i^2}{\sum_i n_i^2}. \tag{4}$$

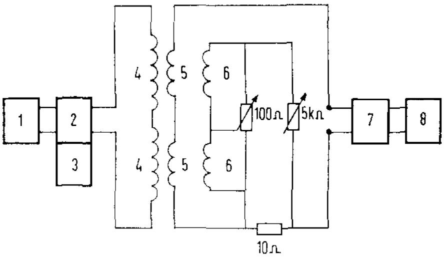

FIG. 2. Schematic diagram of the AC-permeameter. (1) Oscillator; (2 and 3) power amplifiers; (4) primary coil; (5) secondary coil; (6) compensation coil; (7) detector; (8) recorder.

EXPERIMENTAL METHODS

For the measurement of the magnetization of catalyst NZ 10 we used an AC-permeameter largely analogous to the instrument used by Selwood (*4*). However, our system consisted of *two* primary coils, each containing a secondary coil, Figs. 1 and 2. In Table 1 the data of the AC-permeameter are shown. The secondary coils were connected in opposition. Without inserted sample compensation was further improved by means of an auxiliary circuit (Fig. 2). The primary coils were fed at 270 Hz by an oscillator (1), Hewlett-Packard 299CD and two power amplifiers (2, 3), Hewlett-Packard 6824A. The detection part was formed by a lock-in amplifier (7), P.A.R. HR-8 and a recorder (8), Linseis L660/20. In the secondary coil a Dewar vessel or a flow reactor could be inserted. The Dewar vessel was used when static adsorption–desorption measurements were made with the catalyst in a glass cell, and a

TABLE 1

Data of the AC-Permeameter

Coil	Turns	Copper wire diameter (mm)	Current rms (amp)	Frequency (Hz)	Field strength (Oe)	Length (mm)	Diameter (mm)
Primary	845	1	1	270	56	190	54
Secondary	360	0.2				20	38
Compensation	12	1				12	100

flow reactor was used when magnetization changes of the catalyst were measured during the reaction. Changes of 1% of full coverage could be detected with this system. Samples of 500 mg NZ 10 were used both in adsorption and reaction experiments. Calibration with Mohr's salt showed the output voltage to be proportional to sample quantity and to the current in the primary coils. In absolute measurements of the magnetization, corrections were made for the diamagnetism of the all glass adsorption cells or glass reactor.

The volumetric adsorption system consisted of a glass system with known volume connected with a precision pressure gauge, Texas Instr. 145-01. For the adsorption of benzene and the other hydrocarbons, greaseless stopcocks were used and glass connections with Viton O-ring seals. Between successive gas doses 2 hr were allowed, after which equilibration was virtually complete. The flow reactor is shown in Fig. 1.

The catalyst was reduced at 450°C during 4 hr in a hydrogen flow of 60 liter (STP) hr^{-1}. Hydrogen was pumped off at 450°C during 2 hr at a pressure of 10^{-4} Torr. The signal generated by the catalyst in the reactor was compensated, so that changes in the magnetization were measured sensitively.

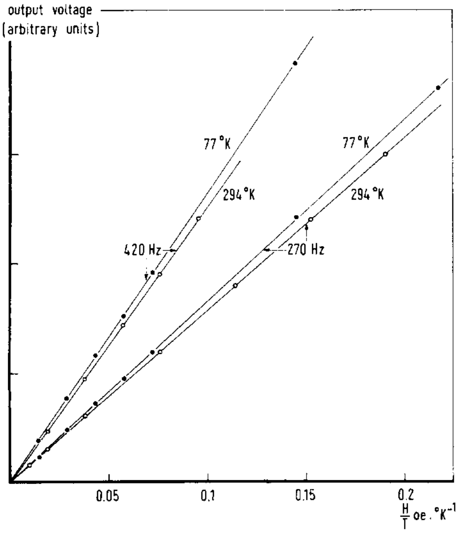

Fig. 3. Output voltage (proportional to the magnetization) as a function of H/T (field strength/absolute temperature) for nickel–silica catalyst NZ 10 at two frequencies of the magnetic field and two temperatures of the catalyst.

RESULTS

Test of Superparamagnetic Behavior

The magnetization was measured at the temperatures 294 and 77°K and the frequencies 270 and 420 Hz. The results, corrected for the temperature dependence of the spontaneous magnetization of bulk nickel derived from Ref. (*15*), are shown in Fig. 3. The signal is proportional to frequency. However, lines for 77 and 294°K do not coincide, which we have taken to indicate that the dependence of I_{sp} on temperature differs from that for bulk nickel. Choosing the Curie temperature at 551°K instead of 631°K and thereby adjusting the temperature dependence curve, the lines for 77 and 294°K are brought to coincidence. The same correction was applied to the data in Fig. 4 for a range of temperatures at fixed field strength. A straight line through the origin is obtained, demonstrating that the catalyst is superparamagnetic over the entire temperature range and that the low-field approximation of Eq. (1) applies. The Curie temperature thus found is close to the value of 561°K given by Selwood (*4*).

Theoretical Magnetization–Volume Isotherm

In order to compare experimental M–V (magnetization–volume) isotherms with a theoretical isotherm for the catalyst, an expression for the nickel crystallite size distribution has to be found.

From the hydrogen chemisorption we found an average crystallite diameter of 15.1 Å (*1*, *16*). According to Wösten *et al.* (*9*), we calculated from the volume susceptibility 0.030 erg Oe^{-2} cm^{-3} an average diameter of 25.5 Å. A measure for the

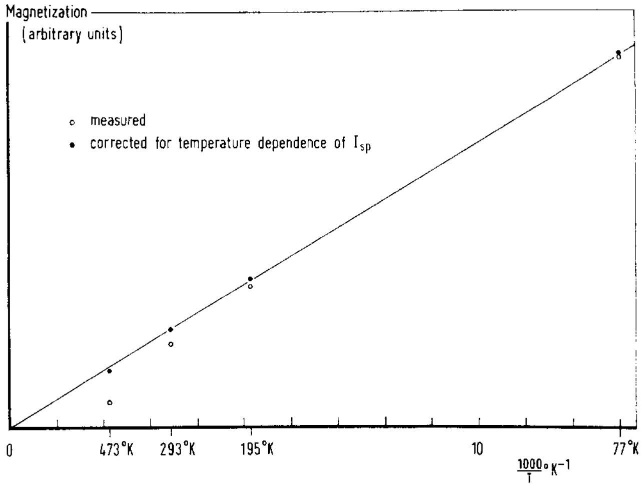

FIG. 4. Magnetization as a function of $1/T$ (1/absolute temperature) for nickel–silica catalyst NZ 10.

distribution over three arbitrarily chosen sizes 10, 20, and 30 Å can be derived from (a) the total number of nickel atoms per gram of Ni, (b) the hydrogen adsorption, and (c) the fractional change of magnetization at full coverage. The result of the three equations is the following partition:

$$N_1(10\ \text{Å}):N_2(20\ \text{Å}):N_3(30\ \text{Å}) = 27.9:2.83:1$$

Assuming homogeneous distribution of adsorbed hydrogen over all crystallites we then obtain as isotherm equation:

$$\frac{\Delta M}{M_0} = -0.762\times10^{-2}x+0.16\times10^{-4}x^2. \quad (5)$$

Magnetization–Volume Isotherm for Hydrogen Adsorption

On a sample of nickel catalyst NZ 10 reduced and evacuated at 450°C, hydrogen was admitted at 20°C in small increments. With each new hydrogen admission the magnetization strongly decreased initially, then recovered slightly due to the dissipation of the heat of adsorption. Within 30 min this temperature effect vanished, but in the first half of the isotherm a slower recovery persisted for a much longer time. The resulting magnetization–volume isotherm is shown in Fig. 5. The fractional change of magnetization amounted to 48.5% after adsorption of 76 ml H_2 (STP) g^{-1} Ni. The broken lines in Fig. 5 indicate that, instead of 2 hr, a whole night passed between gas admissions. The irregular course of the isotherm is rather striking; especially after the first night a step can be seen in the isotherm. This effect was reproducible with other samples.

To verify whether the slow process is activated, in one run the sample was placed

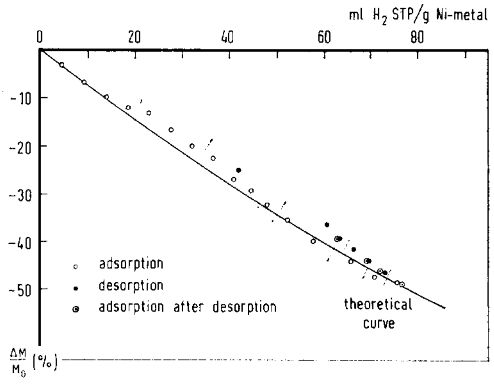

FIG. 5. Magnetization–volume isotherm for hydrogen adsorption and desorption on nickel–silica catalyst NZ 10 at 20°C. (– –) Time lapse of 16 hr.

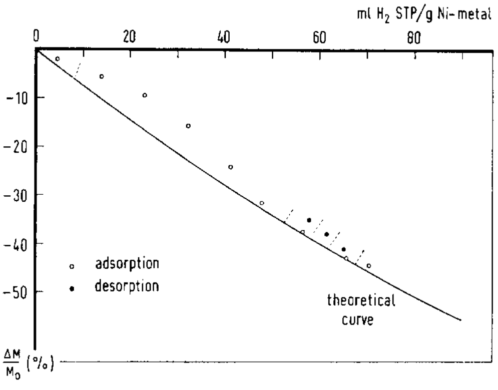

FIG. 6. Magnetization–volume isotherm for hydrogen adsorption and desorption on nickel–silica catalyst NZ 10 at 20°C. After each adsorption and desorption the catalyst sample was held at 200°C for 15 min. (– –) Time lapse of 16 hr.

during 15 min in an oven at 200°C after each gas admission. As Fig. 6 shows, a more pronounced deviation from the theoretical isotherm results. The theoretical and experimental M–V isotherms meet for hydrogen pressures above 1 Torr, where a surface coverage of about 0.7 was reached. The maximum quantity of hydrogen taken up as apparent from the data in Fig. 6 is somewhat smaller than in Fig. 5. The sample of Fig. 6 was three times evacuated at 450°C, which resulted in a slight sintering of the crystallites and a smaller total metal surface area.

In Figs. 5 and 6 the desorption branch does not coincide with the adsorption branch of the isotherm. The isotherm for renewed adsorption after desorption coincides with the desorption isotherm. Once the catalyst has been covered by hydrogen at 1 atm, the desorption isotherm may then be used to derive changes in hydrogen coverage from magnetization changes.

Apart from the normal form of hydrogen adsorption, decreasing the magnetization, a slow adsorption occurred in our experiments. This form was most clearly observable if, in one addition, hydrogen was admitted to the catalyst up to almost full coverage. After one night some more hydrogen was adsorbed and the magnetization was also somewhat decreased. This slow adsorption was measured for Ni–SiO_2 catalysts with different nickel content. It was found that after an adsorption isotherm had been measured in 8 hr, the following slow adsorption during one night was proportional to amount of unreduced nickel. The results are shown graphically in Fig. 7.

Magnetization–Volume Isotherm for Benzene Adsorption

Small doses of benzene vapor were admitted to a freshly reduced hydrogen-free catalyst NZ 10 at 20°C. As physical adsorption may occur, we kept the initial doses so small that the benzene pressure after adsorption remained below 10^{-3} Torr. A typical isotherm is shown in Fig. 8. The maximum fractional change in magnetization is only −10%. At larger amounts of benzene added, physical adsorption occurs and the isotherm shows no further decrease of the magnetization.

Upon subsequent evacuation at 20°C down to 10^{-4} Torr no increase of the magnetization could be detected.

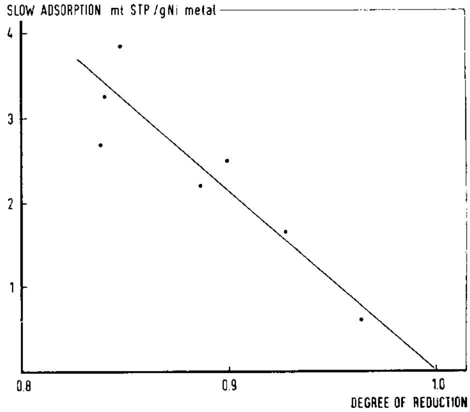

FIG. 7. Slow adsorption of hydrogen during one night after measurement of an adsorption isotherm for hydrogen in 8 hr, as a function of the degree of reduction of a series of nickel–silica catalysts.

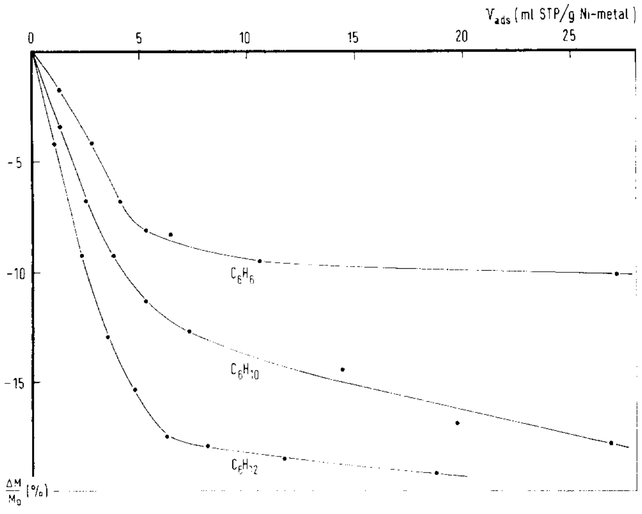

FIG. 8. Magnetization–volume isotherm for benzene, cyclohexene and cyclohexane on nickel–silica catalyst NZ 10 at 20°C.

Magnetization–Volume for Cyclohexane and Cyclohexene Adsorption

In Fig. 8 also M–V isotherms for cyclohexane and cyclohexene adsorption at 20°C are shown. The maximum fractional change in magnetization on cyclohexane adsorption is about -20%, on cyclohexene adsorption slightly less, viz, about -18%.

When physically adsorbed cyclohexane was removed by evacuation, no change of the magnetization occurred.

Hydrogenation and Disproportionation of Cyclohexene

Passing cyclohexene with nitrogen over the catalyst at 20°C, no benzene or cyclohexane was detected by glc in the effluent. At 130°C disproportionation became detectable and with increasing temperature more benzene and less cyclohexane was formed. With hydrogen (instead of nitrogen), cyclohexane was the only product up to 200°C, except at small contact times, where some benzene could be detected in the products. More benzene was formed at higher temperatures.

Adsorption of Hydrogen on a Catalyst Precovered with Benzene

After the measurement of a benzene M–V isotherm at 20°C and evacuation down to 10^{-4} Torr during 90 min at 20°C, hydrogen was added to the catalyst precovered with benzene. The resulting M–V isotherm is shown in Fig. 9. The total quantity of hydrogen added is 110 ml H_2 (STP) g^{-1} Ni.

Magnetization Measurements during the Hydrogenation of Benzene

Changes in the magnetization of the nickel catalyst could be measured during

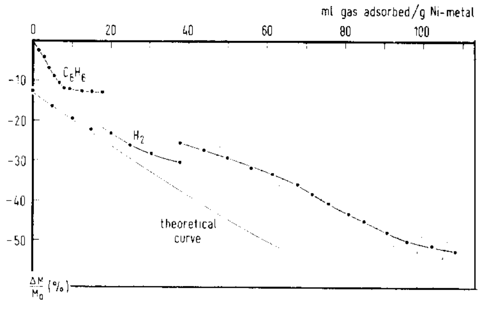

FIG. 9. Magnetization–volume isotherm for benzene and for hydrogen over preadsorbed benzene on nickel–silica catalyst NZ 10 at 20°C. (- -) Time lapse of 16 hr.

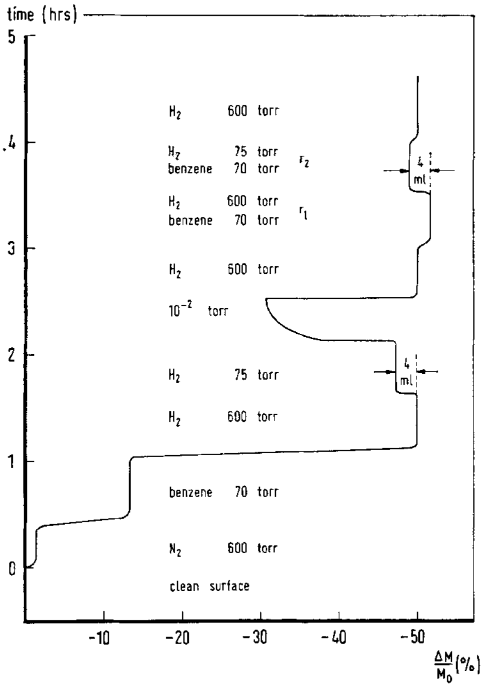

FIG. 10. Magnetization changes as a result of the adsorption of nitrogen, benzene over preadsorbed nitrogen, hydrogen over preadsorbed nitrogen and benzene, and reaction of hydrogen with benzene at different pressures on nickel–silica catalyst NZ 10 at 28°C.

the flow of different gases over the catalyst. In Fig. 10 the successive treatments are shown schematically.

Over a clean catalyst successively nitrogen, nitrogen with benzene, hydrogen, and hydrogen with benzene were passed at 28°C. Nitrogen brought about a small decrease in the magnetization, −2%, benzene with nitrogen gave −12% change. A hydrogen flow at 600 Torr then gave a fractional change of the magnetization of −50%.

A decrease of the hydrogen pressure from 600 to 75 Torr caused an increase of the magnetization. Using the desorption branch of the M–V isotherm of Fig. 5 as reference, a desorption of about 4 ml (STP) of hydrogen g^{-1} Ni was calculated. By a pressure decrease down to 10^{-2} Torr the magnetization increased further, as shown in Fig. 10. Next a flow of hydrogen at 600 Torr was reestablished. A subsequent flow of hydrogen with benzene (600 and 70 Torr, respectively) caused a further small decrease of the magnetization. The reaction rate at 29°C r_1 was 5.2 μmol H_2 m^{-2} min^{-1}. If we decreased the hydrogen pressure to 75 Torr, at constant benzene pressure of 70 Torr, the magnetization increased corresponding to a desorption of 4 ml (STP) of hydrogen g^{-1} Ni. The rate of reaction r_2 was 1.7 μmol H_2 m^{-2} min^{-1}.

After the benzene hydrogenation at a hydrogen pressure of 75 Torr, a flow of pure hydrogen at 600 Torr was passed over the catalyst for 1 hr. Next the cell containing the catalyst was evacuated. From the increase in magnetization the amount of hydrogen desorbed was calculated, viz, 27.5 ml (STP) g^{-1} Ni. Next hydrogen was admitted. After 16 hr the volumetrically measured amount of hydrogen taken up by the catalyst was 44.5 ml.

Adsorption of Benzene on a Catalyst Precovered with Hydrogen

The cell containing a hydrogen covered catalyst was evacuated at 28°C down to 10^{-3} Torr. From the increase in magnetization we could derive that 26 ml (STP) of hydrogen g^{-1} Ni was desorbed, leaving about 50 ml adsorbed. Next a flow of nitrogen (600 Torr) together with benzene (70 Torr) was passed over the catalyst. No change in the magnetization occurred. Subsequently the cell was evacuated and hydrogen was admitted. Volumetrically we determined that after 1 hr 73.5 ml (STP) of hydrogen g^{-1} Ni were taken up, which quantity increased to 85.5 ml after 16 hr.

DISCUSSION

Magnetization–Volume Isotherm for Hydrogen Adsorption

We demonstrated that the catalyst is superparamagnetic over the entire range of applied conditions. A theoretical equation for the magnetization–volume isotherm for hydrogen adsorption [Eq. (5)] was derived. In the derivation it was assumed that hydrogen is distributed homogeneously over the crystallite size distribution.

The experimental M–V isotherms for hydrogen adsorption (Figs. 5 and 6) show some deviations from the theoretical isotherm. The most plausible explanation for the increase in magnetization after 16 hr or after heat treatment at 200°C is the transition of hydrogen from large to smaller crystallites. It is assumed then that the heat of adsorption is larger on the smaller crystallites. Possibly spillover is important in migration of hydrogen atoms from one nickel crystallite to another, but transition via the gas phase appears more likely. At higher temperature the redistribution of adsorbed hydrogen proceeds at a higher rate, as shown in Fig. 6, but this would be expected for either of the two mechanisms.

That the desorption branch of the M–V isotherm for hydrogen adsorption does not coincide with the adsorption branch may be ascribed to a form of slow adsorption which takes place on our nickel catalysts. The correlation between slow adsorption after 16 hr and degree of reduction of the catalysts, shown in Fig. 7, suggests that the slow adsorption is an activated adsorption on unreduced nickel. The slow adsorption hardly contributes to the magnetization decrease. This also points in the direction of adsorption on nonmetallic nickel, e.g., nickel silicate.

Magnetization–Volume Isotherm for Benzene Adsorption

A typical isotherm is shown in Fig. 8. The maximum fractional change in magnetization is only -10%, which, in comparison with hydrogen, is rather small. Clearly benzene cannot occupy the whole surface, as was already demonstrated by Selwood (*4*) and in our own experiments (*2*). The horizontal part of the M–V isotherm indicates that this adsorption has a physical nature. Although the pressure after the last benzene addition was about 10^{-1} Torr, evacuation of the sample to 10^{-4} Torr during 15 min at 20°C did not change the magnetization. Apparently only physically adsorbed benzene is removed.

From the ratio of the slopes of the M–V isotherms of hydrogen and benzene a number of bonds per adsorbed molecule may be formally derived. Since hydrogen adsorbs inhomogeneously, we ought to compare the slopes of those parts of M–V isotherms which represent adsorption on the same crystallites, which is, however, impracticable. If we compare the initial slope of the M–V isotherm of benzene with the one for a homogeneous distribution of hydrogen, then the number of bonds is 5.3, whereas this number is 10 if we compare the benzene isotherm with a preferential hydrogen adsorption on the small crystallites. In saturation magnetization measurements Martin and Imelik (*5*, *18*) found that benzene formed 8 bonds with nickel at 25°C. If benzene is somewhat more homogeneously distributed over larger and smaller crystallites than hydrogen, the number of bonds may be close to 8.

Magnetization–Volume Isotherm for Cyclohexane Adsorption

In Fig. 8 the M–V isotherm for cyclohexane adsorption at 20°C is shown. The maximum fractional change in magnetization is about 20%, twice as much as for benzene at the same amount adsorbed. Cyclohexane physically adsorbed was removable by evacuation without a change of magnetization. Apparently, all chemisorbed species remained on the surface during this process. Depending on the reference M–V isotherm for hydrogen adsorption, cyclohexane forms between 11 and 20 bonds. If cyclohexane is adsorbed as benzene and six hydrogen atoms, as Shopov *et al.* (*11*) concluded from ir spectroscopy measurements, and as is indicated by the maximum decrease in the magnetization, the number of bonds should be between $5.3 + 6 = 11.3$ and $10 + 6 = 16$. These values are consistent with the range derived from the ratio of the slopes.

Magnetization–Volume Isotherm for Cyclohexene Adsorption

In Fig. 8 also the $M-V$ isotherm for cyclohexene adsorption is shown. In this case the maximum fractional change in magnetization is slightly less than for cyclohexane, viz, about -18%. The number of bonds derived from the ratio of the slopes is between 7.3 and 13.7, dependent on the reference isotherm for hydrogen adsorption. Possibly also cyclohexene adsorbs as benzene and hydrogen atoms. The number of bonds in this case would be between $5.3 + 4 = 9.3$ and $10 + 4 = 14$. Also the hydrogenation/disproportionation experiments suggest that at higher temperatures cyclohexene adsorbs in the form of benzene and hydrogen. The dissociated hydrogen apparently can migrate to other benzene/cyclohexene molecules and hydrogenate them to cyclohexane. At a low temperature this migration is perhaps too slow and desorption of benzene more difficult. If enough hydrogen is on the surface, immediately hydrogenation to cyclohexane, which desorbs from the surface, occurs.

Chemisorbed Quantities

The magnetization of a sample covered with benzene or cyclohexane remains constant upon evacuation to 10^{-4} Torr. From Fig. 8 the quantity of hydrocarbon (benzene, cyclohexene and cyclohexane) chemisorbed on the surface is estimated to be about 10 ml (STP) g^{-1} Ni. For benzene, cyclohexene and cyclohexane this quantity corresponds to 708, 744 and 762 μg/200 mg catalyst, respectively. The values found in the gravimetric measurements (*2*) were 500–700, 760, and 450 μg/200 mg catalyst, respectively, on a catalyst partially occupied with hydrogen. The gravimetric experiments showed that the hydrogen coverage did not influence the amount of chemisorbed benzene, while the amount of chemisorbed cyclohexane was strongly dependent on hydrogen pressure. Therefore the difference in adsorbed quantities for cyclohexane may be ascribed to the influence of hydrogen coverage.

The amount of benzene chemisorbed could also be determined volumetrically. Initially a $M-V$ isotherm for benzene adsorption was measured, shown in Fig. 9. The maximum fractional change in the magnetization on benzene adsorption (-12.5%) is slightly larger than the -10% shown in Fig. 8. The cell was evacuated and hydrogen was admitted to the catalyst precovered with benzene. Initially hydrogen is adsorbed without reaction. But after a few more additions, especially after one night, the steps in the isotherm indicate that reaction took place. These observations differ from those of Selwood (*4*), who reported that hydrogen had to be added to an almost complete coverage before hydrogen reacted with preadsorbed benzene. The total amount of hydrogen taken up is 110 ml (STP) g^{-1} Ni. From gravimetric measurements (*2*) we obtained evidence that all adsorbed benzene reacts to cyclohexane within 16 hr. According to Shopov *et al.* (*11*) the formed cyclohexane remains physically adsorbed, so it does not contribute to the pressure. To cover the nickel surface completely we would have to add 79 ml of hydrogen. Augmented with about 30 ml hydrogen required for reaction with about 10 ml benzene, the summation is in agreement with the volumetrically determined quantity of 110 ml. This result supports our earlier findings (*2*) and those of Shopov *et al.* (*11*).

Magnetization Measurements during the Hydrogenation of Benzene in a Flow Experiment

Admission of nitrogen to a clean catalyst brought about a small decrease in the magnetization. The magnetization recovers upon evacuation of the cell containing the catalyst, which shows that the nitrogen is weakly bonded to the nickel. B_5 sites on nickel may be responsible for the chemisorption of nitrogen with a rather low heat of adsorption (*20*).

The fractional change in the magnetization on benzene adsorption (-12%) is slightly larger than the -10% shown in Fig. 8. Although here nitrogen is also adsorbed and decreases the magnetization as well, in other measurements of benzene adsorption (Fig. 9) a maximum change of -12.5% is obtained.

Subsequent exposure to hydrogen changes the fractional magnetization to -50%, the same value as obtained upon hydrogen adsorption on a clean catalyst. Apparently benzene molecules adsorbed in a nonreactive form (*2*) will cover sites otherwise occupied by hydrogen at 600 Torr. If adsorbed benzene should mask some nickel atoms for hydrogen adsorption without affecting their magnetic moment, as suggested by Shopov *et al.* (*11*), the maximum fractional change in the magnetization would be less than for hydrogen adsorption on a clean surface. Clearly, in our experiments benzene adsorption produces the same change in magnetization as the amount of hydrogen adsorption which it replaces.

Upon decrease of the hydrogen pressure from 600 to 75 Torr the magnetization increased. Via the desorption branch of the M–V isotherm represented in Fig. 5, we derive that 4 ml (STP) hydrogen g^{-1} Ni was desorbed.

Evacuation of the cell down to 10^{-2} Torr caused an additional increase of the fractional change of magnetization from -50 to -30%, which corresponds to a further desorption of about 30 ml (STP) hydrogen g^{-1} Ni. Next a hydrogen flow at 600 Torr decreased the magnetization again to the same level as the preceding flow of hydrogen at 600 Torr. Addition of benzene to the hydrogen flow caused reaction on the catalyst. A further small decrease in the magnetization was observed. Physical adsorption of benzene occurs to a considerable extent. At 28°C about 0.13 g benzene $(g\ cat)^{-1}$ adsorbs (*2*). Its diamagnetism also causes a slight decrease of the magnetization. Correcting the magnetization change for this effect, we may conclude that there is a temperature rise of 3°C. By means of a thermocouple only 1°C increase was measured, but the local cooling effect of the thermocouple and inadequate heat transfer to the junction will explain this discrepancy.

As the cell for magnetization measurements was connected to the all glass flow system described in (*1*), we could measure reaction rates accurately. Reaction rate r_1 was measured at the specified conditions. A decrease of the hydrogen pressure to 75 Torr caused a desorption of 4 ml (STP) hydrogen g^{-1} Ni, as was derived from the magnetization, and a threefold reduction of the reaction rate. As the benzene coverage is independent of hydrogen coverage in the two reaction rate measurements (*2*), the reduction of reaction rate must be ascribed to the change in hydrogen coverage. If the rate determining step in the benzene hydrogenation is proportional to the first power of θ_H, then the amount of hydrogen active in the hydrogenation is 6 and 2 ml (STP) g^{-1} Ni at 600 and 75 Torr, respectively. This hydrogen is only weakly bound, because it is desorbable at 28°C by reduction of the pressure from 600 to 75 Torr. The finding is in agreement with the measurements of Aben *et al.* (*19*), who found a correlation between the capacity for weak hydrogen adsorption and specific activity for benzene hydrogenation on supported platinum, and also with as yet unreported similar findings in our laboratory on silica-supported nickel. The active hydrogen is dissociatively adsorbed, since it obeys the theoretical M–V isotherm for hydrogen, derived for dissociative adsorption (Fig. 5).

After the reaction rate measurements, pure hydrogen was passed over the catalyst. Within 1 hr a part of the adsorbed benzene was hydrogenated to cyclohexane, which left the surface (*2*). Next the cell was evacuated and hydrogen was admitted.

After 16 hr 44.5 ml (STP) hydrogen g^{-1} Ni were taken up by the sample, of which 27.5 ml are to compensate for the desorbed hydrogen. The remaining 17 ml were consumed by reaction with "nonreactive" benzene and by the benzene sites fallen vacant. If it is assumed that adsorbed benzene is replaced by 7 hydrogen atoms, that reaction to cyclohexane is complete after 16 hr, that cyclohexane remains physically adsorbed and does not contribute to the pressure in the cell, the "nonreactive" quantity of benzene amounts to 2.6 ml (STP) g^{-1} Ni. This is equivalent to 185 μg/200 mg cat, which supports our gravimetric measurement (*2*), where we found about 200 μg of the adsorbed benzene nonreactive within 0.5 hr. Also from these magnetic measurements we thus find that at 28°C only part of the chemisorbed benzene is active in the hydrogenation reaction.

Adsorption of Benzene on a Catalyst Precovered with Hydrogen

For the elucidation of the mechanism of benzene hydrogenation, it is also important to know whether benzene and hydrogen compete for the same surface sites. A flow of benzene and nitrogen over a catalyst two-thirds precovered with hydrogen did not change the magnetization. However, after contact of the surface with benzene, about 9 ml (STP) of benzene g^{-1} Ni appeared chemisorbed. This was determined volumetrically by subsequent hydrogen adsorption. In gravimetric experiments (*2*) we already found that benzene was chemisorbed on a nickel surface precovered with hydrogen. Now, we may even say that benzene was adsorbed on sites precovered by hydrogen, which was not desorbed upon evacuation. We may thus conclude that benzene is adsorbed on sites which are strongly bonding for hydrogen. Earlier we have shown that the hydrogen which is active in hydrogenation of benzene is located on weakly bonding sites. We may thus formulate the conclusion that hydrogen which is active in benzene hydrogenation at 28°C does not compete with benzene on the nickel surface of the catalyst.

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