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DEPENDENCE OF ACTIVITY FOR BENZENE HYDROGENATION OF NICKEL ON CRYSTALLITE SIZE

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ABSTRACT: The effect of crystallite size on activity per unit area in benzene hydrogenation was investigated for a range of silica supported nickel catalysts. From 50 Å down to 12 Å specific activity increases with decreasing crystallite size, while for still smaller crystal size activity appears to go down.

From a kinetic study in the liquid phase a dual site stepwise hydrogenation mechanism was derived with the second hydrogen atom addition rate determining. Activity differences between catalysts appear to be reduced by internal compensation effects.

Hydrogen kinetic isotope effects for H/D-mixtures show a parallel trend to specific activity. The information derived from the isotope effect is consistent with the kinetic considerations, showing that the entropy of adsorbed hydrogen plays an important role.

1. INTRODUCTION

Since H.S. Taylor in 1925 highlighted the importance of surface heterogeneity for catalytic activity of solids (1, 2) the reality of geometric and energetic heterogeneity of solid surfaces has become well established, but the effect of this heterogeneity on catalytic activity remains controversial.

Heterogeneity of metal surfaces may arise from different crystallographic planes in the surface and from intersection lines and points of these planes. The effect of various types of lattice defects may be superimposed. For supported metals the interaction of metal and support may stabilise an abnormal state of the metal. The contact line between metal crystallite and support where metal ions are bonded to foreign atoms will provide further abnormal surface sites.

With decreasing crystallite size the extent of homogeneous crystal planes must decrease and the proportion of surface atoms of low coordination will increase. The probability of lattice defects will be less in small crystals and they will anneal out with greater ease. The lattice in small crystallites may be compressed by surface tension effects (3), interaction with the support may induce lattice extension (4). It has been argued that for small metal crystallites (< 50 Å) the proportion of high energy B5 surface sites may be expected to increase (5, 6).

There are thus abundant reasons for surface heterogeneity and for differences therein for different preparations of the same metal. It is then the more surprising that for many reactions differences in specific activity appear to be slight. Although some authors find indications that certain types of lattice disorder increase catalytic activity (7, 8) other sources (9, 10) do not confirm these findings. Different crystal faces have been shown to have different catalytic activity (9, 11, 12). Differences are generally not very large. We may expect surface heterogeneity to change with crystallite size. Nonetheless the effect of crystallite size on specific activity appears to be small for many reactions. In hydrogenolysis of C_2H_6 Yates (13) found no influence of crystallite size, Taylor (14) found large differences, whilst Carter (15) found smaller crystals to be more active. In cyclopropane hydrogenation Boudart (16) likewise found small crystals to be somewhat more active than

larger ones. In hydrogenation of benzene Aben (17), Dixon (18), Nikolajenko (19) and Taylor (20) found no influence of crystallite size on specific activity, Hill (21) and Krivanek (22) found small crystals to be less active than larger ones, whereas Selwood (23) concluded the reverse. Poltorak (24, 25, 26) found for a number of reactions specific activities which did not vary by more than a factor of 2 with crystal size. In all of the cited investigations variation of activity with crystal size remained within a factor of 3. There are some exceptional reactions known where the influence of the surface geometry on the specific activity is much stronger.

This surprising situation led Boudart (27) to divide catalytic reactions into two groups, facile and demanding reactions, the latter being those which are sensitive to surface structure. The majority of catalytic reactions appears to be facile under this definition, an unexpected result, which poses a number of problems:

1. What is the exact shape of the slight dependence of specific activity on crystallite size.
2. It appears likely that the virtual absence of a crystallite size dependence is the result of compensation effects: although the specific rates for different crystallite sizes are almost the same it is improbable that the detailed kinetics are identical. A kinetic study on a range of crystallite sizes is therefore desirable.
3. Can the data obtained under 2 be correlated with data on adsorptive behaviour, derived from independent measurements on the same catalysts.

To study these problems we chose the hydrogenation of benzene on silica supported nickel catalysts.

Benzene hydrogenation, though a 'facile' reaction under Boudart's definition, is a slow hydrogenation, which facilitates avoiding mass transport limitation. To safeguard further that our conclusions will refer to true chemical kinetics we did rate studies both in liquid and in gas phase. Since with acidic supports like alumina hydrogenation activity may not be strictly confined to the metal surface, due to 'spillover' effects (28-31) we chose a silica support. To obtain a range of crystallite sizes we preferred varying nickel content over thermal sintering, so that all catalysts could receive the same heat treatment.

To study the effect of crystallite size on specific activity reaction rates at standard conditions of temperature and pressure were measured in gas and liquid phase on catalysts with a range of nickel contents, having crystallite sizes between 5 and 50 Å.

A more detailed kinetic study was done in the liquid phase on four catalysts with rate measurements at 16 T-p-combinations.

To obtain information on surface structure isotope effects for simultaneous equilibrium adsorption of hydrogen and deuterium on the same four catalysts were measured.

2. EXPERIMENTAL

2.1. Ingredients: Pure thiophene-free benzene ex Merck was further purified by 3 hrs refluxing over NaPb-alloy and subsequent distillation into a receptacle, directly connected to the hydrogenation apparatus. Cylinder hydrogen was purified by passage over a deoxo catalyst and a molecular sieve drier and finally brought to high purity by diffusion through a PdAg-thimble. A series of silica supported nickel catalysts was prepared by precipitation from p.a. nickel nitrate solution onto 'Aerosil' silica. Precipitates were filtered, washed, dried at 120°C, ground and stored in a desiccator. Samples as needed for surface area determination, hydrogenation or deuterium exchange were re-

duced in a glass vessel with sintered glass disk at 450°C for 4 hrs with 60 ℓ/h.g. cat. hydrogen flowing through the catalyst bed.

2.2. Apparatus and measurements

a. Catalyst characterisation: Total nickel contents were determined, to refer all data to unit weight of nickel. Nickel surface areas were determined by chemisorption of hydrogen in a mercury free volumetric apparatus. After reduction the sample was evacuated during 2 hrs at 450°C and equilibrated with 1 atm hydrogen at 25°C during 16 hrs. The degree of reduction of the sample was obtained by measuring hydrogen evolution on dissolving the reduced catalysts in acid in hydrogen atmosphere and correcting for adsorbed hydrogen.

b. Liquid phase hydrogenation was performed in a constant pressure stirred tank apparatus. The double walled glass reactor was equipped with baffles and a turbine stirrer driven by means of a magnetic coupling. Thermostat liquid circulated through the jacket. All connections in contact with benzene were greaseless with teflon sleeves and viton O-ring seals. The glass reactor gas space was connected via a reflux condenser to a series of jacketed hydrogen burettes and to an oil manometer. The other leg of the manometer was connected to a thermostated gas space in which a selected reference pressure between 0.1 and 1.5 ata could be adjusted, making working pressures independent of barometric changes. A photoelectric sensor on one of the manometer legs controlled via a relay system the fluid supply to the burettes, thus maintaining a chosen pressure setting within ± 0.1 torr. Burette readings at timed intervals, corrected for temperature and pressure were used to compute rates in micromoles hydrogen per minute. Hydrogen pressures were derived from the set reference pressure, corrected for oil manometer differential and vapor pressure. Reaction temperature was read from a thermometer immersed in the liquid. On all catalysts standard rates were measured at 25°C and 600 Torr hydrogen pressure. On four catalysts rates were measured at 16 T-p-combinations (25, 45, 65, 85°C; 75, 150, 300, 600 Torr).

c. Gas phase hydrogenation was performed in a differential flow reactor. The reaction system, consisting of series connected benzene saturator, condensor, fixed bed differential reactor, GLC sampling valve and cold trap, was enclosed between two precision needle valves. The entry valve was connected to a constant pressure high purity hydrogen source, the exit valve to a vacuum line. Using the same reference pressure control system as under b, constant flow and constant reactor pressure were maintained. Incoming hydrogen flow was measured with a ball float and with a soap film flow meter. Saturator and condensor were thermostated, the latter at 10-15 degrees lower temperature than the former, ensuring saturation vapour pressure for benzene. The reactor, equipped with a preheater spiral was also thermostated. Reaction temperature was measured with an uncovered thermocouple in the catalyst bed. Degree of conversion was obtained from GLC analysis (Carbowax column, catharometer detection) of reactor effluent. Standard rates were measured at 25°C and 600 Torr hydrogen pressure.

d. Hydrogen isotope effect: Isotope effects in simultaneous adsorption of hydrogen and deuterium were measured on the four catalysts used in the kinetic study in a thermostated mercury free system consisting of a sample vessel and a number of calibrated volumes connected to H_2, D_2 and vacuum lines, Bourdon and membrane pressure gauges and an AEI MS 10 mass spectrometer. A total coverage with hydrogen isotopes could be selected and values of Θ_H, Θ_D, p_{H_2}, p_{D_2} and p_{HD} were determined.

3. RESULTS

3.1. Crystallite size and specific activity: From V_m values (ml S.T.P.) for hydrogen adsorption nickel surface areas (m^2) were obtained, assuming one H-atom

and an average area of 6.33 Å^2 per surface nickel atom: $S_{Ni} = 3.41\ V_m$. Nickel areas were used to standardise rate data on unit area. Areas per gram nickel metal were also used to obtain a measure of crystallite size D from $D = 4310/S_{Ni}$, based on hemispherical crystallites, attached with the aequatorial plane to the support. Excellent correlation with X-ray line broadening crystallite sizes was obtained earlier on 22 Ni/SiO_2 catalysts (4), with crystallite sizes between 30 and 250 Å. Below 30 Å the model used gradually loses meaning and crystallite size should be regarded as a parameter to indicate nickel dispersion. A more direct experimental parameter N_H/N_{Ni} giving number of H-atoms adsorbed per nickel metal atom is also given.

Data on the investigated catalysts is given in table 1. The crystallite sizes cover the range from below 50 Å, by several authors (5, 6, 25) said to be most interesting from the surface structure point of view.

Table 1 - Analytical and standard activity data

Cat.	% Ni	S_{Ni} m^2/g cat	Reduction degree %	S_{Ni} $m^2/g\ Ni_{met}$	Cryst. size Å	N_H/N_{Ni}	Standard activity	
							L	G
NZ 1	0.82	4.53	68.2	810	5.3	1.25	1.27	
NZ 2	2.03	6.71	84.8	390	11.0	0.60	4.60	
NZ 4	4.26	12.86	84.0	359	12.0	0.55	6.14	6.2
NZ 5	4.88	14.4	83.8	352	12.2	0.34	4.68	
NZ 10	10.20	26.2	89.9	286	15.1	0.44	3.41	4.2
NZ 29	28.9	56.6	87.6	224	19.2	0.34	2.80	3.6
NZ 54	52.5	43.1	96.3	85	50.6	0.13	2.67	3.8

In the same table standard activities A_s in liquid and gas phase are given in $\mu mol\ H_2.m^{-2}.min^{-1}$. It is noted that the gas phase activities are somewhat higher than those obtained in liquid phase. They show, however, the same trend, as shown in fig. 1.

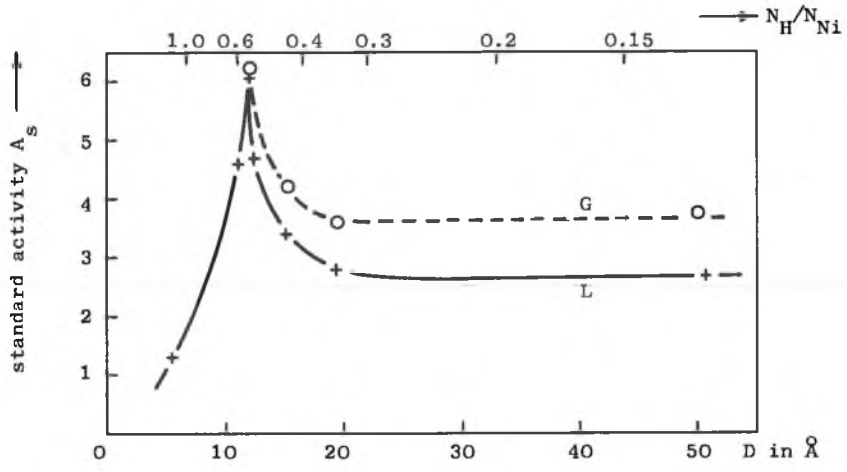

Fig. 1 - Relation between activity per unit nickel area and crystallite size

3.2. Kinetics of liquid phase hydrogenation for four catalysts: In gas phase hardly any activity decline with time was observed. In liquid phase apparent activity declined slowly with time. Therefore kinetic measurements were interspersed with runs at standard (25°C, 600 Torr) conditions, which were used to correct data for activity fall off.

Rates in liquid phase were proportional to the amount of catalyst added. The reaction order in benzene was found to be strictly zero at least down to 10% benzene. For a given catalyst at any one temperature the rate per gram catalyst or per unit nickel surface area is thus solely a function of hydrogen pressure: $R_T = k_o f(p)$. Although a slight curvature was evident in logarithmic plots of the exponential rate expression $R_T = k.p^n$, reaction orders n in hydrogen were obtained as given in table 2.

Table 2 - Reaction orders n in hydrogen and apparent activation energy E_a

Cat.	Reaction order n				Apparent activation energy E_a			
	25°C	45°C	65°C	85°C	75	150	300	600 Torr
NZ 4	0.52	0.67	--	0.81	9.5	10.0	10.7	11.6
NZ 10	0.55	0.65	0.80	0.80	9.3	10.4	10.8	11.5
NZ 29	0.56	0.60	0.68	0.78	10.5	10.8	11.2	11.7
NZ 54	0.61	0.67	0.78	0.73	11.1	11.5	11.8	11.8

The temperature dependence of the rates at a particular hydrogen pressure was analysed in Arrhenius plots, which yielded reasonably straight lines. The resultant apparent activation energies E_a are also shown in the table.

Differences between catalysts for these two empirical kinetic constants n and E_a are small and give little evidence for the expected differences in kinetic behaviour. For all catalysts there is a trend that n increases with temperature and that E_a increases with hydrogen pressure. Both trends as well as the fractional order in hydrogen are suggestive of a Langmuir type of behaviour. Therefore the rate data for the catalysts were fitted to three Langmuir type rate equations, which for the moment should be regarded purely as empirical correlation functions:

a. $R = k_o \left[\frac{(Kp)^{\frac{1}{2}}}{1 + (Kp)^{\frac{1}{2}}} \right]$ b. $R = k_o \frac{Kp}{1 + Kp}$ c. $R = k_o \frac{Kp}{[(1 + (Kp)^{\frac{1}{2}}]^2}$

with linear plots:

R^{-1} versus $p^{-\frac{1}{2}}$ R^{-1} versus p^{-1} $R^{-\frac{1}{2}}$ versus $p^{-\frac{1}{2}}$

Function b was successfully used by Aben et al (17) at higher p and T in gas phase. We obtained sixteen good fits (4 catalysts, 4 temperatures) with positive intercept only with function c, and this gave also in all cases the best fit, which was generally excellent. The logarithms of the resulting k_o and K values were then plotted against reciprocal temperature, yielding per catalyst four empirical parameters, A_o, E_o, ΔS^o and ΔH^o, which correlate the 16 rates. These are shown in table 3.

From the four parameters for each of the catalysts the standard rates at 25°C and 600 Torr were recalculated (A_s calc) to be compared with the directly observed data (A_s exp). Their agreement demonstrates both the reliability of individual rate measurements and the quality of the correlation.

3.3. Isotope effects: From the data for four catalysts an isotope effect parameter K_I was calculated as $K_I = (\Theta_D/\Theta_H)^2.(p_{H_2}/p_{D_2})$, given in table 3.

Table 3 - Kinetic parameters for liquid phase hydrogenation

Cat.	D_{cryst}	A_s exp	ln A_o	E_o	ΔS^o	ΔH^o	A_s calc	K_I
NZ 4	12.0	6.14	31.23	16.77	-29.61	-9.45	6.38	3.05
NZ 10	15.2	3.41	30.18	16.53	-27.92	-8.94	3.34	1.55
NZ 29	19.2	2.80	29.92	16.64	-26.85	-8.90	2.53	1.14
NZ 54	50.6	2.67	26.82	14.61	-14.24	-4.54	2.35	0.91
Units:	Å	μmol.min^{-1} m^{-2}		kcal/mol	e.u. (1 atm)	kcal/mol	μmol.min^{-1}.m^{-2}	

4. DISCUSSION

Reproducibility of measurement of rates and nickel areas was generally better than ± 4%. We therefore believe the differences in specific activity to be significant.

Before we attach undue significance to our data we should enquire whether mass transport effects may play a role. The fact that the rates in liquid phase hydrogenation are strictly proportional to catalyst amount definitely precludes an influence of gas/liquid transport of hydrogen. With respect to intraparticle transport reasonable values for particle size (2×10^{-4} cm), pore radius (20 Å), diffusion coefficient (7×10^{-5} cm^2 sec^{-1}) and solubility of hydrogen (2.5 μmol.cm^{-3}) yield for the fastest standard hydrogenation (NZ 4) a Thiele modulus h = 0.15, equivalent to 99.3% effectiveness. For the higher rate at 85°C h = 0.375 corresponding to 95.5% effectiveness. For t gas phase hydrogenations the situation is even more favourable. We may thus conclude that in the rate data in this paper mass transport limitation is insignificant.

As a further check on reliability a comparison with literature data is indicated. The ratio of average specific rate observed by other workers to the specific rate observed by us is 0.33 (17), 0.4 (18), 1.6 (32), 0.3 (22), 0.2 (34), 0.7 (33) and 0.4 (35). These ratios are very close to unity, considering that in most comparisons an extrapolation was involved, all workers use slightly different definitions for nickel surface area and also the ranges of nickel crystallite size differ. We may thus conclude that with present day techniques specific rates can be compared between laboratories.

The parallel behaviour of gas phase and liquid phase data is a further indication that the trend of activity with crystallite size must be real. Why then are they not identical? Three effects may explain the differences:

i. Selfpoisoning may be more serious in liquid phase, where the catalyst may be subjected to low hydrogen supply over lengthy periods. Also mechanical catalyst loss through spattering may operate. These effects may make liquid phase data too low.

ii. The reaction is strongly exothermic. It is imaginable that the temperature measured in the gas phase catalyst bed is still lower than the actual temperature of the catalysing nickel surface. This effect may be less in the liquid phase where the individual catalyst particles are immersed in the liquid in which the temperature is measured. A temperature error of 3°C would explain the average deviation. This effect would make the gas phase data slightly too high.

iii. From gravimetric measurements we know that under the conditions of gas phase hydrogenation at 45°C the catalyst is covered with about 0.7 statistical layers of physisorbed benzene, at 25°C about 1.5 layers. This situation is still not identical with immersion in liquid benzene. Also the kinetic behaviour is different in detail: in gas phase the apparent activation energy is somewhat higher than in liquid phase, the reaction order in hydrogen is slightly higher in liquid phase than in gas phase, the more so the higher the temperature; also the order in benzene differs: zero in liquid phase, 0.1-0.2 in gas phase. All these differences may be expected to disappear at a lower temperature, where the catalyst pore system gets entirely filled with liquid benzene by capillary condensation, making the situations identical.

Returning now to the dependence of specific activity on crystallite size we may conclude that the differences in activity may certainly be considered significant. The upward trend in activity, going from 50 to 12 Å crystallite size, we consider as established. The fall in activity below 12 Å, if real, is of great interest. Ideas that a minimum crystallite size is required appear to find confirmation.

Whether the effect shown is purely due to differences in crystallite size, resulting in differences in surface character, is less certain. Going from right to left in Fig. 1 not only crystallite size but also nickel content goes down. This means that unit nickel surface area is accompanied by an increasing silica area. This silica surface may help by scavenging catalyst poisons or possibly by a spill-over effect. Of course the silica surface could never explain a maximum. We should also note that the average crystallite size may be an inadequate parameter to describe the nickel surface characteristics, especially with crystallite sizes as close as 11.0, 12.0 and 12.2 Å. Differences in crystallite size distribution or crystal habit may well contribute to the curious shape of the curve, which may thus not be universal.

We have seen that the liquid phase kinetic data is well described by

$$R = k_o\left[\frac{(Kp)^{\frac{1}{2}}}{1 + (Kp)^{\frac{1}{2}}}\right]^2 \quad (i); \qquad K = e^{\Delta S^o/R}\, e^{-\Delta H^o/RT} \quad (ii); \qquad k_o = A_o\, e^{-E_o/RT} \quad (iii)$$

We introduced k_o, K; A_o, E_o; ΔH^o, ΔS^o as empirical parameters. To give them mechanistic meaning we will postulate a stepwise hydrogenation mechanism:

$B + xS_1 \overset{1}{\rightleftharpoons} B_a$	where B denotes benzene
$H_2 + 2S_2 \overset{2}{\rightleftharpoons} 2H_a$	index a indicates adsorbed state
$B_a + H_a \overset{3}{\rightleftharpoons} BH_a$	BH_n denotes C_6H_{6+n}
$BH_a + H_a \overset{4}{\rightleftharpoons} BH_{2a}$	S_1, S_2 are two types of surface site
etc	

We will assume that elimination of hydrogen from the surface by desorption is much faster than by benzene hydrogenation, which will be verified later. Then equilibrium 2 will be undisturbed.

It is then attractive to rewrite eqn. i as $R = k_o \vartheta_H^2$ (iv), which gives ΔH^o and ΔS^o the usual meaning of adsorption enthalphy and entropy for hydrogen. The observed zero order in benzene precludes a Rideal mechanism with reaction of H_a with benzene from the liquid. Chemisorption of benzene has been established by magnetic measurements (36). Further assuming that the degree of occupation with organic entities attains a fractional coverage Θ_o, independent of hydrogen pressure, this leaves $1-\Theta_o$ free for hydrogen adsorption. ϑ_H in iv is then the fraction of the remaining surface covered with adsorbed H.

To refer Θ_H to the entire surface k_o must then contain the factor $(1-\Theta_o)^2$. The proportionality to ϑ_H^2 strongly suggests addition of the second H to adsorbed benzene to be rate determining. We found experimentally that cyclohexene hydrogenation is 3500 x faster than benzene hydrogenation at 25°C in agreement with ref. (37), cyclohexadiene may be expected to be even more reactive, making our choice of reaction 4 for the slow step reasonable.

If equilibrium 3 is established $\Theta_{BH} = K_3\Theta_B\Theta_H$ and $\Theta_B = \Theta_o/(1 + K_3\Theta_H)$. The resonance stability of benzene may be partly conserved in the adsorbed state causing equil. 3 to lie to the left at moderate hydrogen pressure, so that $K_3\Theta_H << 1$. We note that $\Theta_o(1 - \Theta_o)^2$ varies by only $\pm$ 9% around its mean value of 0.136 for $0.19 < \Theta_o < 0.51$. From magnetic measurements we found that benzene adsorption at the considered temperatures tends to stop at $\Theta = 0.2 - 0.3$. The rate equation then becomes

$$R = k_4\Theta_{BH}\Theta_H = k_4K_3\Theta_B\Theta_H^2 = k_4K_3\Theta_o(1-\Theta_o)^2\vartheta_H^2/(1+K_3\Theta_H) = 0.136\ k_4K_3\vartheta_H^2 = k_o\vartheta_H^2 \quad (v)$$

which is of the experimentally observed form. By assuming equilibrium established for reactions 2 and 3 the kinetics become identical with concerted addition of two H_a to B_a rate determining.

Returning to the data A_o, E_o, ΔS^o and ΔH^o of table 3 we note that they show a qualitatively consistent trend: From NZ 4 to NZ 54 the heat of adsorption goes down and the weaker adsorption shows a smaller entropy loss. We also find that the less tightly bound hydrogen requires a smaller activation energy E_o to combine with adsorbed benzene, as is to be expected. We further recall that ln A_o must contain an activation entropy term for the surface reaction. A larger entropy of the adsorbed hydrogen clearly works unfavourably in the formation of the activated complex and we find A_o accordingly smaller.

We may make this reasoning more quantitative by using transition state theory

$$R = \frac{kT}{h} e^{\Delta S^{\ddagger}/R}\ e^{-\Delta H^{\ddagger}/RT}\ n_s\Theta_B\Theta_H^2 = \frac{ekT}{h} e^{\Delta S^{\ddagger}/R}\ e^{-E_o/RT}\ n_s\Theta_B\Theta_H^2 \quad (vi)$$

which on introduction of the experimental ϑ_H transforms to

$$R = 0.136\ \frac{ekT}{h}\ n_s\ e^{\Delta S^{\ddagger}/R}\ e^{-E_o/RT}\ \vartheta_H^2, \text{ so that } A_o = 0.136\ \frac{ekT}{h}\ \frac{A}{\sigma}\ e^{\Delta S^{\ddagger}/R} \quad (vii)$$

where A is the nickel surface area on which the reaction is taking place, $1\ m^2 = 10^{20}\ \text{Å}^2$ and σ the area taken up by one activated complex. For the latter we will choose a value of 45 Å^2, which is the cross-sectional area for benzene in adsorption on metals (38, 39). We thus find ln $A_o = 70.8 + \Delta S^{\ddagger}/R$ for a mean temperature of 328°K, so that we can calculate the activation entropy for the surface reaction $\Delta S^{\ddagger} = S^{\ddagger} - S_{B_a} - 2S_{H_a}$ from the experimental A_o values, after converting them to molecules benzene per m^2.sec. Probably $S^{\ddagger} \approx S_{B_a}$; $\Delta S^{\ddagger} \approx -2_{H_a}$.

Table 4 - Entropy per g at. adsorbed hydrogen during hydrogenation

Catalyst	ln A_o	$\Delta S^{\ddagger}/R$	$\Delta S^{\ddagger}$	S_H from A_o	S_H from $\Delta S^o = S_{H_2} - 2S_H$
NZ 4	67.0	- 3.8	- 7.5	3.75	1.2
NZ 10	65.9	- 4.9	- 9.7	4.85	2.0
NZ 29	65.6	- 5.2	-10.3	5.15	2.6
NZ 54	62.6	- 8.2	-16.3	8.15	8.9

There is a gratifying parallelism in the two sets of entropy data and for catalyst NZ 54 there is even quantitative agreement. For the other three catalysts there is a difference of about 2.5 entropy units. We should of course realise that in this confrontation all experimental errors, imperfections in empirical correlations as well as effects introduced by the theoetical assumptions come together so that possibly the agreement is as good as we may expect. The discrepancy is equivalent to a combined error in E_o and ΔH^o of a little over 1 kcal, which is not excessive. In sofar as the observed discrepancy is not trivial one may note that the observed A_o values are too low. One might imagine that on the catalysts with the smaller crystallite sizes part of the surface is so active that it becomes blocked with carbonaceous residues, by which it is poisoned irreversibly. This effect might then also help to explain the drop in activity below 12 Å. It is then difficult to explain why this does not occur at all on NZ 54.

Also for the activation energies there is the possibility of an internal consistency check, although less fundamental in nature. One may easily derive by logarithmic differentiation of eqn. (i) that the Arrhenius activation energy $E_a = RT^2$ (d lnR/dT) also equals $E_a = E_o + (1 - \vartheta_H)\Delta H^o$ (viii). The values for ϑ_H for 600 Torr and 328°K, calculated from the ΔS^o and ΔH^o values of table 3, together with the E_a values from eqn. (viii) and the directly obtained E_a values of table 2, are shown in table 5.

Table 5 - Comparison of directly observed and calculated activation energies

Catalyst	NZ 4	NZ 10	NZ 29	NZ 54
ϑ_H	0.415	0.427	0.490	0.444
E_a from viii	11.2	11.4	12.1	12.1
E_a direct	11.6	11.5	11.7	11.8

The agreement is in all cases within 0.5 kcal/mol, again showing the quality of the empirical correlation functions and the consistency of the data.

The assumption of equilibrium (3) being undisturbed is fundamental to the present kinetic description. With absolute rate theory one may estimate the rate of desorption of hydrogen and compare it with the rate of hydrogenation at the low temperatures considered. We found the assumption amply justified.

Considering now the isotope effect data (table 3) we note first of all the striking parallelism with standard activity figures. The fact that the K_I values, which were measured in a clean system where the catalysts were only exposed to hydrogen isotopes, correlate with catalytic activity in benzene hydrogenation indicates that the differences in activity really stem from differences in surface properties.

The detailed interpretation of the isotope effect on a heterogeneous surface is quite as complicated as the adsorptive behaviour of these surfaces. However, the fact that in isotope effects at least part of imperfect description tends to cancel out led us originally to choose this technique to obtain information on surface properties. For a homogeneous surface the K_I as defined here is equal to the ratio of Langmuir constants for deuterium and hydrogen for fixed site adsorption and to the ratio of Volmer constants for two dimensional gas adsorption. It can further be shown that K_I may be expected to decrease with increased mobility or entropy of the adsorbed hydrogen. This is in agreement with the entropy values obtained from the kinetic data (compare tables 3 and 4). More detailed discussion of the isotope effect will be published elsewhere (40)

The problems posed in the introduction under points 2 and 3 have now been partially answered. Differences in detailed kinetic behaviour do show compensation: NZ 54 and 29 show significant differences in A_o, E_o, ΔS^o and ΔH^o but they cancel out almost entirely. The large difference between NZ 4 and NZ 10 is entirely due to a different preexponential factor A_o, due to different mobility of adsorbed hydrogen. For the catalysts with very sma crystallites a faint indication was obtained that increased selfpoisoning may diminish activity.

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DISCUSSION

N. B. BHATTACHARYYA

1) We have done some work on crystallite size and activity in connection with nickel reforming catalysts and found that catalytic activity decreases with increasing crystallite size. The crystallite size involved in our study ranges from 180 Å to 960 Å.

2) In your paper you have made a correlation between specific activity and crystallite size. While variation was made in crystallite size (Table 1), nickel concentration also varied simultaneously. It is well known that activity of a catalyst depends not only on its physical and structural parameters, it also depends greatly on concentration of the active component. Don't you think that inferences drawn on the basis of crystallite size above may be misleading when concentration of nickel is also changing? Curves similar to Figure 1 could be obtained also when activity is plotted against nickel concentration. In my opinion the correlation of crystallite size with activity could be more significant and meaningful if the concentration of nickel in all the samples were kept fixed. This could be done through progressive sintering of the parent preparation.

3) Secondly, degrees of reduction are different for different samples. Don't you think with incomplete reduction the measured activity may be different from its real activity?

J. W. E. COENEN

1) It is difficult to comment on your statement without knowing further details. I would not expect significant differences in specific activity per unit area in crystals as large as 180 Å and 960 Å respectively. Is it quite certain that no extraneous effects such as mass transport limitation can play a role?

2) The fact that with crystallite size other parameters vary in the series of crystals, notably the nickel content is explicitly stated in the paper. To achieve a variation in crystallite size some variation in composition or history will have to be varied. We chose to keep the heat treatment constant and chose to vary nickel content. This is very much a matter of arbitrary choice and the choice of different heat treatments would be no less arbitrary and if it were chosen it could be the basis of a discussion remark, very similar to the one you made.

3) Indeed, the degrees of reduction vary a little. To attain complete reduction much more severe heat treatments would have to be chosen, which would have made the smallest crystallite sizes inaccessable. We feel that in that way the loss would be greater than the gain. It is not quite clear what is meant by "real activity." If reduction were complete the support would be exclusively silica, instead of a combination of silica and nickel silicate in our catalysts.

J. J. F. SCHOLTEN

1) In your thesis (Delft University) you introduced the concept of the

Ni crystallites being bound to the carrier via a small layer of Ni-silicate.

The extent and strength of this "chemisorption" of Ni on silica may influence the crystallographic plane distribution of the free nickel as it influences the total surface energy, and hence it influences the catalytic behavior. This effect (though resulting from the binding of Ni) may be a function of crystallite diameter (your thesis). It may be that the relation found in Figure 1 of your paper can be explained in this way.

J. W. E. COENEN

As further explained in reference (4) of the paper we may indeed assume that the nickel crystallites have a preferred orientation with (111) parallel to the silica surface. In our earlier work on Ni/SiO_2-catalysts, we found evidence for a f.c.c. nickel lattice with slightly enlarged lattice parameter, the effect being more pronounced for the smallest crystallite sizes. It is indeed an interesting suggestion to bring this observation to bear on the present activity dependence. Qualitatively the maximum in the activity/crystallite size correlation would thus be transformed into a maximum in an activity/lattice constant relation and this would be less difficult to rationalize.

G. C. BOND

I should like to ask Professor Coenen about the rather unusual dependence of crystallite size upon nickel content shown in Table 1. It does not conform to any of the expected or usually observed relations. The smallest particle size seen (5.3 Å) deserves comment: five nickel atoms in a trigonal bipyramid would be of about this size.

J. W. E. COENEN

That lower nickel contents produce smaller average crystallite sizes in this series is certainly not unexpected behavior. I am not sure in how far the more detailed behavior is unexpected. For five out of seven catalysts it is a linear relation, though not through the origin. This behavior is certainly no cause for surprise. Remains consideration of the two extremes. To understand the large crystallite size for the 52% Ni we should recall the function of the support: provided the intermediate nickel compound is closely associated with the support and evenly distributed the support restricts sintering of the metal formed in reduction. It becomes progressively more difficult to achieve homogeneous distribution and close association between intermediate nickel hydroxide and support as the ratio of the two increases. Remains the very small crystallite size for the other end. Here we should point out that due to excessive nickel silicate formation reduction is more difficult and incomplete sintering inhibition is exceptionally effective. Here moreover crystallite size losses meaning end is more an arbitrary yardstick. For our definition of crystallite size see the reference quoted for question 2.

T. KWAN

You showed a striking parallelism between the benzene-hydrogenation activity of nickel catalysts of different crystallite size and the hydrogen isotope effect in the chemisorption of H_2 or D_2 on these catalysts at equilibrium.

I cannot see immediately how these two quantities are correlated. Could you explain more about the chemisorptive character of your nickels for hydrogen?

J.W. E. COENEN

So far we have no detailed explanation for the parallelism between benzene hydrogenation activity and hydrogen isotope effect. We can only say the following:

With rather drastic simplifying assumption one can calculate K_J by statistical thermodynamics. For catalyst NZ 54 the calculated value can be made to equal the measured K_J by suitable choice of vibration frequencies. Then we find that also the temperature dependence of K_J is the same as calculated between -80 and +100°C. At higher temperatures the experimental K_J becomes much too high. This we interpret by assuming that exchange of adsorbed D with protons on silica occurs, which simulates high K_J. The high value of K_J on catalyst NZ 4 at room temperature cannot be understood by statistical thermodynamics: here we assume that already at room temperature some exchange occurs with the large SiO_2-surface.

Why then parallelism with benzene activity? Here we then have to call in a similar effect: spill-over to the large support area. This explanation is still very qualitative and unsatisfactory. We are working on a more quantitative picture.