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Influence of Electronic Interactions with the Carrier and of State of Dispersion of the Metal on the Catalytic Activity of Supported Metal Catalysts

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The application of the metal-semiconductor boundary layer theory to the study of the catalytic properties of supported metal catalysts is discussed. Published work on the structure of very small metal crystals and on anomalous adsorption and catalytic centres in such crystals is discussed with particular reference to the dependence of catalytic activity on the state of dispersion of the metal deposit. 103 references.

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I. INTRODUCTION

The chemistry of catalysis has made important advances during the past 15–20 years, and a deeper understanding of the nature of the catalytic act and of catalyst structure has been acquired by applying new theoretical concepts based on recent advances in solid-state theory, as well as new physical methods of investigation.

The electronic theory of catalysis on semiconductors developed by Vol'kenshtein, Hauffe, and others, and Dowden's use of the concept of *d*-band filling to explain the catalytic properties of transition metals and their alloys, have clearly shown the importance of the collective properties of solids in the field of catalysis.

These ideas have been tested by electrical, magnetic, optical, and other methods, and as a result of this work some new and more precise concepts (involving crystal field and ligand field theories) have emerged. In addition to the collective properties of the solid, the local properties of an individual atom or ion in the lattice (determined by its electronic structure and co-ordination) began to attract attention.

These problems were considered in detail at the Fourth International Congress on Catalysis, held in Moscow, and also in the Symposium on Electronic Phenomena in Catalysis.

This review is concerned with both collective and localised interaction problems in supported metal catalysts, which include a large proportion of all modern industrial catalysts.

Relevant theoretical problems include the mechanism of the interaction between the metal and the carrier, the specific properties of small metal crystals, the relationship between the size and the catalytic activity and selectivity of such crystals, the influence of the carrier on the activity and selectivity of the catalyst, etc.

The past decade has witnessed some important advances in the study of metals on carriers [1], resulting from the development of techniques for the direct examination of disperse metal (magnetic measurements, electron microscopy, X-ray and electron microprobe analysis, CO and H_2 chemisorption). The detailed studies of supported platinum [2,3] and nickel [4–8] on various carriers will be discussed below.

No attempt will be made to review the whole of the work on supported catalysts published during the last few years. We shall deal mainly with the more complex studies of catalysts, which throw light on their structure and physical properties as well as on their precise catalytic activity.

II. ELECTRONIC ASPECTS OF METAL–CARRIER INTERACTION

The role of the carrier in mixed (metal–carrier) catalytic systems has long been thought [9] to be merely structural (protection of the dispersed metal from sintering phenomena, preservation of the large surface area and orientation of the crystals). The development of an electronic approach to catalysis, by Roginskii [10], Vol'kenshtein [11], Hauffe [12], Dowden [13], and others, has brought about a reappraisal of the role of the carrier, for which Schwab and his coworkers [14] have been mainly responsible.

Essentially, the electronic theory of catalysis states that a definite (though indirect) relationship exists between the concentration of current carriers and the Fermi level in the solid on the one hand and the catalytic activity of the solid on the other hand. A change in the semiconductor properties of the carrier, according to Schwab, should produce a corresponding change in the electronic properties of the deposited metal in contact with the semiconductor, and hence it should enhance (or inhibit) the catalytic reaction, since both the catalytic act and its precursor stages (chemisorption of reactants) involve a redistribution of the electron density between catalyst and reacting system.

Schwab's hypothesis was tested experimentally by studying a model reaction of a well characterised type (the dehydrogenation of formic acid). Assuming that the reaction involves electron transfer from the formic acid molecule to the metal, the theory predicts that if the Fermi level in the metal is raised by electronic interaction with the semiconductor the activation energy of the dehydrogenation reaction should increase, and conversely that a decrease in the Fermi level should lower the activation energy of the reaction. Experiments of this type were made by Schwab and coworkers [15] with the following catalysts: metallic nickel, cobalt, and silver, deposited on variously doped (2–5 mol.%) Al_2O_3 samples. Aluminium oxide is an *n*-type semiconductor and is inactive towards the dehydrogenation of formic acid when

heated above 900°C. Addition of oxides of lower-valency metals (NiO, BeO) lowers the electrical conductivity of Al_2O_3, whereas oxides of higher-valency metals (GeO_2 and TiO_2) increase the conductivity. The doped carriers were heated at 1050°, and coated with a thin film of nickel, cobalt, or silver by evaporation in a vacuum. As a control, the dehydrogenation of formic acid was also studied on films of these metals deposited on the corresponding massive metals.

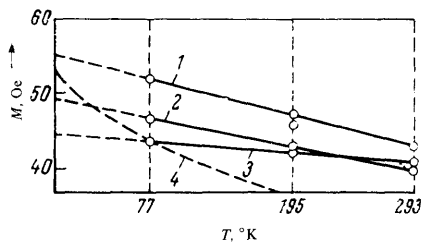


Figure 1. Thermomagnetic curves of Ni on carriers: *1*) Al_2O_3 + NiO; *2*) Al_2O_3; *3*) Al_2O_3 + TiO_2; *4*) shape of the thermomagnetic curve for small nickel particles.

As expected, the activation energy of the reaction was found to be lower than for pure Al_2O_3 on the samples doped with NiO and BeO, and higher on the samples doped with TiO_2 and GeO_2. An attempt was made to demonstrate experimentally the transfer of electrons from TiO_2-doped alumina to the metal by measuring the saturation magnetisation of the nickel and comparing the saturation magnetic moment with that of nickel on pure Al_2O_3. The metal particles were assumed to be very small and in intimate contact with the carrier. The thermomagnetic curves (Fig. 1) of three catalysts were measured: Ni on Al_2O_3, Ni on Al_2O_3 + TiO_2, and Ni on Al_2O_3 + NiO. The curves were measured in the temperature range 77 to 293°K, and extrapolated to 0°K: the magnetic moment was found to be largest on the carrier Al_2O_3 + TiO_2, and smallest on the carrier Al_2O_3 + NiO.

Schwab's next experiment was made with nickel deposited on the *n*-type semiconductor ZnO,[16] doped with Li^+ (which lowers its conductivity) or Ga^{3+} (which increases it). The catalysts were prepared by heating mixtures of the nitrates, and reducing the resulting mixture of oxides to give (according to the authors) very small crystals of nickel in a matrix of ZnO. Another donor reaction was also examined: the hydrogenation of ethylene. The rate of hydrogenation of ethylene (referred to 1 g of nickel) was found to increase when the ZnO contains fewer conduction electrons, i.e. in the presence of Li^+, and to decrease when the concentration of conduction electrons in ZnO is enhanced by adding Ga^{3+}.

Schwab also discusses the ammonia synthesis catalysts[14] from this point of view. He considers that in this case the most important additive is potassium oxide. which has the same effect on Al_2O_3 as BeO,[15] i.e. lowers the concentration of conduction electrons. Since the synthesis of ammonia is a complicated process, the simpler dehydrogenation of formic acid was studied on ammonia synthesis catalysts with and without additions of K_2O. Addition of 1% of K_2O lowers the activation energy from 18 to 13 kcal $mole^{-1}$, and 2% lowers it to 7 kcal $mole^{-1}$. Addition of an oxide of higher valency (GeO_2), which increases the conductivity of Al_2O_3, produces the opposite effect: the activation energy increases to 23 kcal $mole^{-1}$. Thus, Schwab concludes that in the dehydrogenation of formic acid the additives to the Al_2O_3 have an overriding effect both on the electrical conductivity of the alumina and on the catalytic activity of the iron.

Szabo and Solymosi[17] adopted a similar approach to the study of the decomposition of formic acid on Ni–Cr_2O_3 and Ni–TiO_2 catalysts, in which the carriers were doped with ions of different valency (Be, Al, W, Sb, Ni, Cr) in order to alter their conductivity. The pure and the doped carriers were heated at 900°, impregnated with a solution of nickel nitrate, and reduced in hydrogen. Unlike Schwab and his coworkers, these workers determined the extent of reduction of the nickel by measuring the hydrogen evolved on dissolving the catalyst in dilute perchloric acid. The activity was again measured by the activation energy of the dehydrogenation of formic acid. On a pure TiO_2 catalyst the reaction proceeds with an activation energy of 31 kcal $mole^{-1}$, and on pure Ni the activation energy is 24.6 kcal $mole^{-1}$. When the Ni is deposited on TiO_2 (in 0.2–3% amounts) the activation energy falls to 22.0 kcal $mole^{-1}$. Addition of 2% Sb_2O_3 to the carrier raises its electrical conductivity, and the activation energy correspondingly rises by 2 kcal $mole^{-1}$; addition of 1–5% BeO lowers both the conductivity and the activation energy. Doping the carrier with chromium oxide produced an anomalous result: according to Hauffe Cr_2O_3 increases the conductivity of TiO_2, but Szabo and Solymosi found that the activation energy is lowered. They explain the anomaly by pointing out that the conductivity in this system is affected by the atmosphere in which the measurements are made, and that in a reducing atmosphere the conductivity of titanium dioxide is decreased by doping with chromium oxide, i.e. the Cr^{3+} ions behave like typical lower-valency ions. With Ni–Cr_2O_3 catalysts, on the other hand, addition of titanium dioxide (0.5–5%) to the chromium oxide increases the activation energy and addition of nickel oxide (0.5–5%) lowers the activation energy, with corresponding effects on the electrical conductivity of the carrier. The authors also studied the effect of temperature (400 and 500°) and of time of reduction (1–10 h) on the activation energy of the decomposition of formic acid. In both cases the activation energy increased at 500° and on extending the duration of the reduction. Szabo and Solymosi explain this finding by suggesting that the amount of Ni/NiO in the catalysts decreases as the extent of reduction increases: as previous workers had shown[18], this couple is more active than pure nickel towards the decomposition of formic acid. In the case of Ni–Cr_2O_3 catalysts the resulting spinel is a better carrier for Ni than pure chromium oxide, and the activation energy for the reaction falls to 7 kcal $mole^{-1}$ (for a catalyst containing 5% of NiO) on raising the temperature.

Langenbeck and coworkers[19] studied the effect of *n*-type metal oxides on the catalytic properties of nickel towards the reactions of cyclohexane. They found that the *n*-type oxides ZnO, CdO, TiO_2, and ThO_2 alter the selectivity of the reaction in favour of dehydrogenation to benzene. Several series of preparations were investigated. Initially, zinc oxide was introduced as the third component in Ni–MgO and Ni–Al_2O_3 catalysts at the oxalate or hydroxide coprecipitation stage. The ternary catalysts gave a much higher yield of benzene than the binary catalysts without ZnO. It was subsequently found that a high dehydrogenation activity can be obtained with simple mechanical mixtures of ZnO and the binary catalysts, or by adding zinc powder to the binary catalysts.

Additions of CdO, ThO_2, and TiO_2 were also examined. CdO was very effective at low concentrations, but it was reduced by hydrogen to metallic cadmium at temperatures just above 300°: the cadmium was lost from the bulk of the catalyst by evaporation, and the selectivity reverted to its original value. Addition of TiO_2 and ThO_2 has an appreciable effect only on the $Ni-Al_2O_3$ catalyst, and addition of oxides which are not *n*-type semiconductors (BaO, MgO) has no effect on the properties of nickel. Langenbeck and coworkers, like Schwab, explain these effects by postulating transfer of electrons from the *n*-type oxides to the 3*d* shell of nickel, with the following results: 1) the activation of hydrogen with electron transfer to the nickel, a necessary condition for the degradative hydrogenation of cyclohexane to methane, is prevented by the filling of the 3*d* band of the nickel; 2) the possibility of electron transfer from the cyclohexane molecule to the nickel, with consequent deformation of the chemisorbed molecule and breaking of the C–C bonds, is also excluded. In practice, the observed dehydrogenation (as opposed to degradation to methane) may be due to a combination of these two factors. Another important aspect should be stressed. All promoters are oxides which are partly reduced to metals capable of forming alloys with nickel [20] under the conditions of the reaction: this effect also tends to fill the 3*d* band of the nickel. No clear-cut distinction can be drawn between the electronic effect of the *n*-type semiconductor oxide and the effect of alloying. The main conclusion from this work is that the enhanced selectivity afforded by zinc oxide is due to a change in the electronic properties of the nickel.

Nehring and Dreyer [21] extended this work by studying the reactions of cyclohexane in the presence of a $Ni-Al_2O_3$ catalyst in which the Al_2O_3 was doped with TiO_2 and ThO_2.

They tried to explain the observed dependence of the dehydrogenating activity of the catalyst on the composition of the oxide carrier in terms of the accompanying changes in the electrical conductivity of the carrier. The additions of ThO_2 and TiO_2 were made at the hydroxide coprecipitation stage. The electrical conductivity of the carriers was measured after heat treatment at 1200° (for ThO_2) and 1050° (for TiO_2) because the results obtained after heat treatment at 900° were not reproducible. Measurements of electrical conductivity were carried out in a stream of hydrogen. The conductivity of Al_2O_3 doped with ThO_2 went through a sharp maximum at 1–2% ThO_2, whereas in the $Al_2O_3-TiO_2$ system the conductivity increased continuously with TiO_2 concentration, rapidly at first (up to ~5%) and more slowly up to 100% TiO_2. The nickel was introduced by impregnating the carrier with nickel formate and reducing in a stream of hydrogen (5 wt.%). The decomposition of cyclohexane was studied at 400°: with $Al_2O_3-ThO_2$ catalysts the maximum concentration of benzene in the condensate was obtained with the catalyst containing 10% of ThO_2, and with $Al_2O_3-TiO_2$ catalysts the optimum composition was 1% of TiO_2. Neither of these compositions corresponds to an extremum in the electrical conductivity. The changes in catalytic activity were correlated also with changes in the total surface area of the catalysts. In both systems, the surface area is decreased drastically by small additions of the second oxide, but in the case of TiO_2 the decrease in area occurs in the region of composition corresponding to the maximum yield of the dehydrogenation reaction, whilst in the case of ThO_2 no correlation is found. The lack of correspondence between the maxima in conductivity and in activity is not understood. The results are discussed from the conventional standpoint of changes in the electronic properties of the carrier. It is assumed that the high dehydrogenation activity of Zelinskii and Komarevskii's [22] $Ni-Al_2O_3$ catalyst arises from a modification of the properties of nickel by the conduction electrons of the weakly *n*-type aluminium oxide. Since the addition of higher-valency oxides raises the conductivity of *n*-type semiconductor oxides, the increased selectivity of alumina produced by additions of ThO_2 and TiO_2 is ascribed entirely to this effect.

We have discussed a group of papers characterised by a common approach to the catalytic properties of metals supported on a carrier. Schwab's paper [15], in particular, played a pioneering role in this work and stimulated further research. However, the present writers believe that both the original and the subsequent work contains serious errors.

Firstly, an intimate contact between the phases (i.e. a high degree of dispersion of the deposited metal) is a necessary condition for the postulated, reversible electron transfer between the carrier and the metal. But, as Block pointed out in the discussion of Szabo's paper at the Second Congress on Catalysis [23], even if the metal particles contain as few as 10^3-10^4 atoms the influence of charge transfer on the concentration of electrons and on the position of the Fermi level in the metal is negligibly small. We may consider whether the above condition is fulfilled in the published work. In every case the carrier was heat treated at temperatures of the order of 1000° and, therefore, its surface area was not very great. Hence it is difficult to believe that under these conditions the nickel particles were small enough. Schwab and coworkers [15], assuming their nickel to be very finely divided, quote the effect of additives on the saturation magnetic moment of the nickel as their main evidence for electron transfer from the carrier to the metal. However, the thermomagnetic curves reproduced in Fig. 1 are typical of coarsely divided nickel, and the small difference in the magnetisation of the three catalysts at 77°K (the lowest measurement temperature) is probably due to small differences in the extent of reduction of the metal, which the authors assumed to be 100% without proof. Correct extrapolation to 0°K, with due allowance for the variable extent of reduction, should lead to a single value for the saturation magnetisation, and not three different values as found by the authors. Schwab and Mutzbauer [16] assume that the nickel in their catalysts is present as small particles in a ZnO matrix, but they do not substantiate their claim, which is inconsistent with a recent report [24] that nickel crystals of 360–400 Å diameter are the most stable in a ZnO matrix.

Secondly, all the work discussed attempts to correlate electrical conductivities measured at 900° with activation energies for a chemical reaction at 250–400°. There can be no doubt that the electronic properties of the carrier may be altogether different at the temperature of the catalytic reaction.

Thirdly, the activation energy is not necessarily the best measure of catalytic activity, because of the possibility of compensation which Schwab himself points out [15] without proving that the same kinetic equation applies to all the catalysts used in his experiments. Szabo and Solymosi [17] ascribe significance to changes in E_{act} of 2 kcal $mole^{-1}$, which lie within experimental error, and Langenbeck [19] estimates activity from the percentage conversion of cyclohexane into benzene. Much more reliable means of comparing catalytic activities are needed in order to characterise the more subtle physical effects [25].

Fourthly, no one has considered the direction of electron transfer, i.e. whether the electrons are donated to the conduction band of the metal (where they would have no effect on the magnetic properties), or whether they populate the narrow d_e band (where they would alter the saturation magnetic moment of the Ni atom). Although we do not know whether d electrons (which determine the magnetic properties of ferromagnetic materials) take part in electrical conduction[26], it is important to establish the direction of electron transfer when discussing catalytic activity. If the electron transfer produces a change in the magnetic moment (i.e. an effect analogous to the addition of diamagnetic metals to the nickel), Dowden's theory predicts a decrease in catalytic activity. However, if the electron enters the conduction band there should be no change in the catalytic properties of the nickel, because the resulting contribution to the total number of conduction electrons in the nickel is negligibly small.

In order to understand the physical nature of the charge transfer effect a more detailed consideration of the metal–semiconductor interface is required. We shall assume that an n-type semiconductor (work function φ_S) is in contact with a metal (work function φ_m), where $\varphi_m > \varphi_S$ (see Fig. 2).

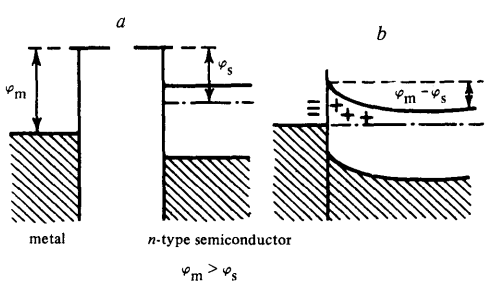


Figure 2. Energy levels at the contact between a metal and an n-type semiconductor: *a*) before contact; *b*) after contact

Since $\varphi_S < \varphi_m$, electrons will pass from the semiconductor into the metal until their chemical potentials (Fermi levels) in the two phases are equal. As a result, the layer of semiconductor immediately adjacent to the metal is depleted of current carriers and becomes positively charged, and the metal becomes negatively charged. The barrier (called a Schottky barrier) which appears at the interface is responsible for contact rectification phenomena.

It is evident from the above that the most important parameter in contact phenomena is not the concentration of current carriers in the semiconductor but the ratio of the work functions in the metal and the semiconductor. Yet, all the published work attempts to correlate catalytic activity with electrical conductivity, and work functions are completely ignored. It certainly cannot be assumed (e.g., in the case of an n-type semiconductor) that the electrical conductivity and the work function must vary in the same sense as a result of doping.

Thus, there are two prerequisites to a correct evaluation of the potential jump which appears at the boundary between the two solid phases: 1) the system must be capable of being described in terms of Schottky's theory[27]†, and 2) the ratio of the work functions in the two phases must be unaffected by interactions with the reacting system. However, even these conditions are necessary but not sufficient. The theory of surface and contact rectification, developed as a branch of semiconductor physics[28], states that the potential barrier at the interface can be modified by the presence of extraneous, poorly conducting layers between the metal and the semiconductor, such as oxide layers (which are termed chemical barrier layers), and also by chemical impurities or lattice defects at the surface (which are termed surface states). Furthermore, doping can have uncontrolled side effects on the catalytic activity by altering the structure type of the lattice, the porosity, and the grain size (i.e. the specific surface area, see Ref. 21). It is clear, therefore, that the state and the properties of the boundary layer in the metal–carrier system are controlled by many factors, and that *a priori* conclusions on the transfer of electrons from the carrier to the metal based only on measurements of the electrical conductivity of the carrier can be of little value. For this reason, attempts are being made to modify the electronic properties of semiconductor catalysts by methods other than doping, e.g. by irradiation with visible and u.v. light during the reaction[29]. Recent data are reviewed by Steinbach[30].

The carriers used by Schwab, Szabo, and Nehring were sintered oxides showing only weak semiconductivity. In the whole of their work the electronic effect of the carrier on the catalytic properties of nickel was only qualitatively assessed. Baddour and Deibert's attempt[31] to demonstrate in a quantitative way the promoting effect of electronic interactions between the carrier and the metal on the decomposition of formic acid is therefore particularly interesting. Germanium, both pure and doped with 0.01% of Zn, Sb, and As, was used as the carrier, to enable the concentration and mobility of the current carriers to be measured by the Hall effect in single crystals of the same composition. Zn-doped germanium becomes a p-type semiconductor, and germanium doped with Sb or As becomes an n-type semiconductor with a known concentration of conduction electrons. The carriers were prepared by grinding Ge single crystals in a vacuum (to avoid atmospheric oxidation). The nickel catalyst was deposited on the carriers by quantitative decomposition of nickel carbonyl. The surface area of the samples was measured (658–1143 $cm^2\ g^{-1}$), and the number of Ni monolayers was calculated (1–18.5). The potential difference at the Ni/Ge interface was calculated by Schottky's theory[27] of contact phenomena at a metal–semiconductor boundary. (A similar calculation[32] for various metals in contact with silicon had given good agreement with experiment). Using the known work functions of Ni (4.96 eV) and Ge (4.78 eV), the authors evaluated the concentration of electrons in the boundary layer of germanium at 240° (the reaction temperature) as 1.4×10^{15}, and also the extent of electron transfer from Ge to Ni for all three dopings. The results are summarised in Table 1.

The activity of pure Ni and Ni/Ge catalysts towards the dehydrogenation of formic acid was studied in a flow reactor at 240 ± 30°, and it was found to decrease with time (particularly in the case of pure nickel). The activity was therefore identified with the initial rate of reaction.

†This condition requires an intimate contact between the two phases and a large area of contact, which are achieved by preparing the metal catalyst in a highly disperse state (see above).

The kinetic order of the reaction (with respect to formic acid) is close to unity on Ni/Ge catalysts and close to zero on pure Ni. As well as the specific reaction rates (per 1 m^2 of total surface area), the authors measured the activation energies and the pre-exponential factors. As the number of Ni layers on the carrier decreases, the activation energy was found to increase sharply from 10 kcal $mole^{-1}$ (for 13–18 layers) to 18–34 kcal $mole^{-1}$ (for 6 and 4 layers respectively). However, due to the compensation effect, the specific reaction rates differed by less than an order of magnitude and increased with the number of atomic layers (for example, for Ni/Ge(Sb) catalysts, from 4×10^{-4} to 22×10^{-4} mole h^{-1} m^{-2} as the number of layers increases from 1 to 18). It is interesting to note that the specific rate of dehydrogenation of formic acid on pure Ni is 3–4 orders of magnitude higher than on supported nickel. The authors compared the specific activities of the three types of Ni/Ge catalyst (doped with Zn, Sb, and As), allowing for the number of layers of deposited nickel (i.e. for the thickness of the metal deposit). Over the thickness range 4–13 layers, the ratio of the activities remained constant (Zn : Sb : As = 1 : 3 : 4). As Table 1 shows, the extent of electron transfer increases in the same order by a factor of 100. The transfer of one electron from the carrier for every 10^5 nickel atoms is found to increase the activity of the metal towards the dehydrogenation of formic acid by a factor of 1.33–3. According to the authors, this indicates that the limiting step in the decomposition of formic acid is dissociative chemisorption, with formation of a negatively charged formate group on the surface (step *1*):

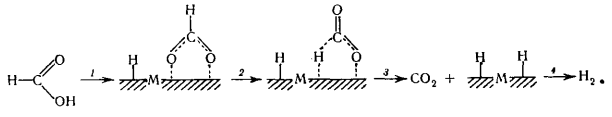


Table 1.

Carrier	Electronic properties	
	Concentration of conduction electrons at 240°, n_s, cm^{-3}	Equilibrium charge transfer at Ni–Ge interface, σ, cm^{-3}
p-type semiconductor		
Zn doped	3×10^{16}	7.3×10^{10}
n-type semiconductor		
Sb doped	3.4×10^{17}	5.3×10^{11}
As doped	2.4×10^{19}	3.7×10^{12}

An electron is transferred from the catalyst to the formic acid molecule. Of course, an increase in the concentration of electrons in the catalyst should assist this step of the reaction. Thus, according to the authors, electron transfer from the carrier to the metal is a very important factor in catalysis. Although their paper describes a well conceived and original physicochemical investigation, an analysis of their results reveals a number of weaknesses. First of all, as the authors themselves point out, effective electronic interaction at the metal–carrier interface requires a large interface area (i.e. a very small metal particle size). This condition does not appear to be fulfilled in their experimental conditions, since the germanium particles have only a moderate surface area (600 to 1100 cm^2 g^{-1}) and it is difficult to believe that the nickel can exist on these coarse particles as very fine crystals. The catalytic activity is related to 1 m^2 of total surface area rather than 1 m^2 of active surface area. The latter, apparently, decreases as the thickness of the deposited layer increases, and therefore the authors' conclusion that the activity increases with the number of layers is not convincing. Furthermore, an increase in catalytic activity by only a factor of 3 is usually interpreted as a constant activity [33,34]. It is also well known that the bulk properties of germanium can differ very substantially from the properties of its surface [35,36], which can be treated as "quasi-isolated". Therefore, Hall measurements of the electronic properties of germanium single crystals [37,38], both pure and doped, may be entirely irrelevant to the electronic properties of the surface of the germanium carrier. Furthermore, the work function of *n*- and *p*-type doped germanium is the same [39]. In any case, the characteristics of the electronic properties of the carriers had been determined before the materials were powdered and coated with nickel. It is well known that fracture can introduce various defects and dislocations in the crystal lattice, leading to the formation of large numbers of surface states which can have a profound effect on the electronic properties of the carrier surface. Lastly, the main conclusion that the transfer of one conduction electron from the carrier per 10^5 nickel atoms can have a significant effect on the catalytic activity is difficult to accept.

As regards the assessment of the catalytic activity, this work is a considerable step forward in comparison with the work of Schwab and Szabo, since the specific reaction rate (rather than the activation energy) is taken as a measure of the activity. But the observed time-dependence of the catalytic activity, and the need to extrapolate the measured rate to zero time, make the comparison of the catalytic and the physical properties of the various materials less than convincing.

Equally unconvincing is the assumption that electron transfer from the semiconducting carrier to the metal (where the concentration of intrinsic conduction electrons is higher by several orders of magnitude) can have a significant effect on the catalytic properties of the metal. Perhaps for this reason, Schwab has recently begun to develop a new approach to the problem: he has used semiconductor catalysts deposited on catalytically inert metals. Thus, the oxidation of CO has been studied on a nickel oxide catalyst deposited on silver [40], and the oxidation of SO_2 on iron oxide deposited on silver alloyed with palladium and mercury [41]. A study has also been reported [35] of the oxidation of methanol in the presence of a ZnO.Ag mixture and of separate samples of ZnO and Ag in various proportions by weight, which show a synergistic effect even when located in different parts of the reactor. In the presence of a metallic carrier the active phase (the semiconductor) is enriched or depleted of current carriers, and this effect controls its catalytic activity. Physical evidence for this hypothesis is provided by the observation, by Schwab and Kritikos [36], that the electrical conductivity of ZnO, NiO, and Cu_2O is affected by the addition of a small percentage of Ag. The latest paper in this series was published in 1969, [42] but a detailed analysis of its results lies beyond the scope of this review.

III. INFLUENCE OF STATE OF DISPERSION AND OF CARRIER ON THE CATALYTIC ACTIVITY OF SUPPORTED METAL CATALYSTS

The relationship between the catalytic activity and the degree of dispersion of the active component is one of the

basic problems of heterogeneous catalysis. In the case of metallic catalysts supported on a carrier, the following questions need to be answered first: whether the catalytic activity depends on the particle size of the deposited metal, whether the formation of a crystal lattice having the properties of the massive metal is a necessary condition for catalytic action, and lastly whether there is an optimum crystallite size giving the maximum catalytic activity. During the 1930's Dankov and Kochetkov [43] studied the hydrogenation of ethylene and the decomposition of H_2O_2 on platinum, and noted a maximum in the activity for a crystal size of 40–50 Å, followed by a rapid fall to zero activity for a diameter of 20 Å. Rubinshtein [44] found the optimum crystal size of nickel on Al_2O_3 for the dehydrogenation of alcohol in the region 60–80 Å. But only recently has a full appreciation of these problems been made possible by careful measurements of the specific catalytic activity per unit area of metal surface, combined with various physical methods of measuring the dispersenes of the metal (electron microscopy, X-ray line broadening, magnetic methods, H_2 and CO chemisorption, etc.). In spite of these advances, the problems are still controversial.

1. Platinum on Carriers

In 1953 Boreskov formulated the hypothesis [33] of constant specific catalytic activity in catalysts of constant chemical composition. He considered the specific activity to be determined mainly by factors such as the chemical composition and the chemical structure of the catalyst. The hypothesis was confirmed by the results obtained by his research team, who found that the specific activity of Pt towards the oxidation of SO_2 [45] and of hydrogen [46] varies by less than an order of magnitude as the specific surface area of the catalyst is varied by 4 orders of magnitude (Pt/SiO_2, and massive platinum in the form of sponge, wire, and foil).

However, the work of Boreskov ignores the influence of the surface structure of the platinum crystals on the catalytic activity. The problem was first formulated by Poltorak, who proposed the "mitohedric method" [47] to deal with it. The method, which is based on a crystallographic description of the co-ordination numbers of the atoms and of the fraction of the atoms in various states within the lattice, involves the following steps. Atoms of three types are considered: 1) atoms associated with microdefects on the surface of large crystals, 2) atoms on crystal edges, and 3) atoms on crystal faces. In order to distinguish their effects, we must compare the specific activities of equilibrium crystals in three regions of crystal size: 10–20 Å (average co-ordination number $\bar{x} < 6$; the atoms are equivalent to microdefects), 20–40 Å ($\bar{x} = 7$, edge elements), and 100–∞ ($\bar{x} = 9$, as on the perfect faces of an infinite crystal). Metal catalysts covering the desired range of crystal size were prepared in the form of platinised silica gels, and the Pt surface area was measured by the hydrogen chemisorption method. Somewhat later, the authors developed the "absolute adsorption isotherm" method [48] of measuring surface area. Many different hydrogenation and dehydrogenation reactions were studied: the hydrogenation of hex-1-ene, cyclohexene, and allyl alcohol [47], the dehydrogenation of cyclohexene [49] and isopropanol [50], the hydrogenolysis of pentane [50], etc. As a result, it was shown that the specific activity of faces, edges, and crystal defects in platinum is approximately constant. Anomalies in the activity were found to be associated not with surface structure, but with changes in the chemical composition of the adsorption layer (oxygen effect, varying degrees of deactivation of the catalyst as a result of secondary reactions, etc.). Poltorak's results appear to confirm Boreskov's hypothesis of constant specific activity [33], with the single exception that Poltorak's experiments dealt with the range of crystal sizes in which the effect of structure on catalytic activity should be apparent (10–50 Å), whereas Boreskov looked for this effect in a region of particle size (> 50 Å) where, according to Poltorak, the effect is normally absent.

In contrast to the results for hydrogenation and dehydrogenation catalysis, studies of the oxidation of ethanol on platinised silica gel revealed a 100-fold decrease in specific activity on changing from a particle size of ~40 Å to 11 Å particles [51]. With particles greater than 40 Å the activity remained constant, and equal to that of platinum black. Thus, crystal faces are the most active elements towards oxidation. It is interesting to note that Poltorak and coworkers did not find a single instance of enhanced activity at edges or crystal defects: this experimental fact is in direct conflict with the widely held belief that co-ordinationally unsaturated atoms in the platinum lattice have a high specific activity.

Boudart and coworkers [34] extended Boreskov's studies of the specific activity of Pt on carriers. They examined a new system—Pt on Al_2O_3, both γ and η forms—in which the platinum is very highly dispersed and the metal particle size can be accurately controlled by raising the temperature at which the catalyst is formed. They showed that the specific activity of their catalysts towards the hydrogenation of cyclopropane was independent of the amount of platinum on the catalyst, of the crystalline form of the alumina, and of the nature of the carrier (Al_2O_3 or SiO_2). By covering the range from highly disperse platinum, in which practically every atom is on the surface, to platinum foil, the specific activity varied by a factor of two whilst the specific surface area varied by 4 orders of magnitude. Thus, in this work, also, we obtain the surprising result that the catalytic activity is "insensitive" to the crystal size, the nature of the carrier, and the method of preparation.

The next paper by Boudart and coworkers [52] was devoted to a study of the catalytic activity of platinum in another reaction: the transformation of neopentane, which in the presence of Pt undergoes isomerisation to isopentane and hydrogenolysis to isobutane and methane. SiO_2, carbon, and η- and γ-Al_2O_3 were used as carriers. The disperseness of the Pt, defined as the ratio of the number of surface metal atoms to the total number of metal atoms, was varied from 3×10^{-2} (for Pt powders) to over 70 (for supported metal). The authors measured the specific activity of the catalysts for both reactions, and obtained the selectivity coefficient s, equal to the ratio of the specific activities for the isomerisation and the hydrogenolysis reaction respectively. The parameter s varied by a factor of 100 for the catalysts examined, the most selective catalysts being Pt on carbon and Pt powder. The selectivity of supported platinum increased with the forming temperature of the catalyst (from 425° to 900°). Following Anderson and Avery [53], the authors explained their results by suggesting that isomerisation occurs through a three-point adsorption of neopentane on the platinum surface, whereas hydrogenolysis involves a transition state showing two-point adsorption. The greater the number of three-atom groupings ("triplets") on the surface, the more predominant isomerisation

becomes as opposed to hydrogenolysis. A geometrical and thermodynamic treatment of the structure and stability of various crystallographic planes of the Pt lattice led the authors to conclude that the greatest number of triplets should be found on a {111} surface, which is the most stable up to 1500°, and also on face edges. Thus, the selectivity should be directly dependent on the disperseness of the platinum and on the heat treatment of the catalyst before the reaction. For example, Pt powder which has been activated in an oxygen atmosphere before being reduced in hydrogen can be expected to have a "rough" surface with a high concentration of triplets: this explains its high selectivity.

Boudart's results on the hydrogenation of cyclopropane are confirmed by the work of Dorling and Moss [3], who studied the hydrogenation of benzene in the presence of a series of Pt/SiO_2 catalysts and observed only a twofold change in the activity of catalysts covering a range of dispersion of two orders of magnitude. Zaidman and coworkers [54-56] studied the specific activity of Pt on Al_2O_3 (as a function of concentration and disperseness of the platinum) towards the dehydrogenation of cyclohexane, and they also found that the activity of the catalyst is unaffected by the disperseness of the platinum.

Other workers (e.g. Sinfelt and coworkers [57] state that the specific catalytic activity of Pt in the dehydrogenation of cyclohexane depends on the nature of the carrier and on the state of dispersion of the metal. Thus, Pt crystals of 10 Å average size (estimated by H_2 chemisorption) were obtained by depositing the metal on Al_2O_3, and 85 Å crystals on alumina–silica. The specific catalytic activity of the highly disperse platinum was the higher by a factor of 6.

Results conflicting with those of Boudart and coworkers [52] were reported also by McKee [58], who showed that the specific activity of platinum black in the propane cracking reaction decreases as the catalyst is sintered.

2. Nickel on Carriers

The effect of state of dispersion on the specific catalytic activity of nickel has been studied in detail by Sinfelt and Carter, and their coworkers: the results have been summarised by Sinfelt [59]. The assumption underlying the whole of this work is that there is no *a priori* reason to expect constant specific activity when the degree of dispersion of the metal is varied over wide limits. Since the proportion of co-ordinationally unsaturated surface atoms in very small particles is large, it is assumed that the electronic properties of small metal particles must differ from those of large crystallites and the massive metals. Furthermore, since the catalytic properties of a supported metal must be largely determined by the electronic properties of its particles, a direct relationship can be expected between the catalytic activity and the particle size of supported metals. Similar views are expressed in the magnetochemical papers of Michel [60], Selwood [61], and others, who state that the Curie temperature of a ferromagnetic metal must be a function of degree of dispersion, and that the exchange interaction parameter in small crystals must be very different from the bulk value: this explains the special electronic properties of small crystals [62]. The theory of ferromagnetism in metals and alloys cannot give an unequivocal answer to the question of the relationship between electronic properties and disperseness, and experimental data on the subject are contradictory. Thus, it is stated in a recent paper [63] that the Curie temperature and the saturation magnetisation of small Ni particles are not significantly different from the values for the massive metal. However, Carter and Sinfelt [64] have shown experimentally that Ni in Ni/SiO_2 catalysts with a low Ni content (1–7%) has a low (paramagnetic) magnetic moment as compared with the massive metal: this observation formed the physical basis of their hypothesis. Sinfelt and his coworkers made a detailed study of the catalytic activity of all the Group VIII metals on various carriers (SiO_2, Al_2O_3, Al_2O_3–SiO_2), using the hydrogenolysis of ethane as a model reaction [4-8,65-68]. Nickel was studied in greatest detail [4-8,65]. An interesting fact was discovered in one of the earliest studies [5]: varying the roasting temperature of NiO/SiO_2 catalysts containing ~10 wt.% of Ni from 100° to 760° has no effect on the specific catalytic activity, although the surface area of the reduced nickel is thereby reduced by a factor of 3. However, the activity could be varied by a factor of 50 by depositing the Ni on different carriers (the highest activity being found with SiO_2, the lowest with alumina–silica) [4], in spite of the fact that the surface of the Ni on the different catalysts varied only by a factor of 2.

A study [7] of the effect of crystal size on the catalytic activity of Ni deposited on silica–alumina showed that the specific activity of the metal is decreased 20-fold by a 3-fold increase in the size of the Ni particles (~30–90 Å).

The same team [6-8] studied also a series of catalysts containing between 1 and 5% of Ni in a highly disperse form on SiO_2 and Al_2O_3–SiO_2. The surface area of the metal was measured by the magnetic method when the hydrogen chemisorption method could not be used (at very low adsorptions) [8]. The catalytic activities and crystallite sizes of the Ni on different carriers are compared in Table 2.

Table 2.

Catalyst	Size of Ni crystals, Å	Specific activity towards hydrogenolysis of ethane
1) Ni on SiO_2		
1% Ni	12	11
10% Ni	24	500
2) Ni on Al_2O_3		
10% Ni	23	260
3) Ni on Al_2O_3—SiO_2		
1% Ni	26	>0.08
10% Ni	29	9.5

The authors stress that the differences in activity are not due to differences in the extent of reduction of the metal, and they suggest that the difference in particle size may itself be the cause of the phenomenon (see above). They put forward the view that small particles have a special activity, irrespective of their large surface area, since the comparison is between specific activities. As Table 2 shows, the enhanced activity of Ni on SiO_2 (as compared with Ni on Al_2O_3–SiO_2) can be ascribed to the higher degree of dispersion of the former catalyst. However, increasing the amount of metal on any one carrier causes both the crystal size and the catalytic activity to increase. The authors conclude that a consideration of crystal size alone is not sufficient to explain their results. The influence of the carrier on the catalytic properties of the metal is a complicated problem, which cannot be formulated exclusively in terms of state of dispersion.

An alternative explanation of Sinfelt's results (Table 2) has recently been put forward by Shephard [69], who suggests that measurements of the active surface of the metal by hydrogen chemisorption may result in misleading values of the specific activity. If the catalyst contains "blocked" pores, accessible to hydrogen but not to the reacting molecule (ethane), too high a value will be obtained for the surface area available for the reaction. But this explanation is tenable only when the specific activity decreases with increase of forming temperature, as in Ref. 7: in this case it is easy to see how the true specific activity can remain constant, or even increase, while the apparent value decreases for the reason given. However, if the specific activity increases [8] (see case 1 of Table 2), the negative correction to the surface area of the metal (to allow for the inaccessibility of narrow pores to the ethane molecule) can only lead to a still higher value of the specific activity. These views are by no means new: a method of measuring effective surface areas by the adsorption of molecules of size comparable to that of the reactant was proposed [70] in 1951.

Yates and Sinfelt [67] obtained interesting results in their study of the catalytic activity of rhodium on SiO_2 towards the hydrogenolysis of ethane as a function of degree of dispersion. The catalysts, containing 0.1–10% of Rh with 11–40 Å particle size, differed in specific activity by no more than a factor of 4, but the most highly dispersed catalysts (0.1–0.3% Rh) had the lowest activity. In contrast to Boudart's results, the activity of massive rhodium and of the samples heated to the highest temperatures (particle size greater than 120 Å) was 20–40 times lower than the activity of the dispersed catalysts. The authors conclude that the region of highest catalytic activity occurs at intermediate degrees of dispersion of the metal.

Catalysts containing nickel on SiO_2 and on alumina–silica have been studied also in the hydrogenation of cyclopropane [71] and of benzene [72]. In the former reaction, as in the hydrogenolysis of ethane, the carrier has a strong influence on the activity and selectivity of the nickel (the reaction can follow two paths: hydrogenation to propane and hydrogenolysis to ethane and methane). Thus, the specific activity of Ni on SiO_2 was 16 times higher than the activity of Ni on Al_2O_3–SiO_2 towards the hydrogenation reaction, and 44 times higher towards the hydrogenolysis reaction. In the latter system, the samples which had been used to study the hydrogenolysis of ethane were examined also for their catalytic activity towards the hydrogenation of benzene. The specific activities of catalysts containing 1 and 10% of Ni on SiO_2 had been found (see Table 2) to be approximately the same, while their particle sizes differed by a factor of 2. This work led the authors to conclude that the activity of Ni/SiO_2 catalysts is independent of the degree of dispersion of the nickel also in the hydrogenation of benzene. The behaviour of Ni/Al_2O_3–SiO_2 catalysts was entirely different. The size of the Ni crystals was practically the same in the two samples (26 and 29 Å, see Table 2), and the activity for benzene hydrogenation decreased sharply as the Ni concentration was lowered to 1%, showing (according to the authors) that the carrier can influence these catalysts. These results confirm the earlier work of Hill and Selwood [73], according to whom the specific activity of Ni/Al_2O_3 catalysts in the same reaction decreases sharply with decrease of Ni concentration in the region of ~ 8%, and preparations containing < 3% Ni are completely inactive (i.e., the finer particles are less active). Conversely, the activity of Ni–SiO_2 catalysts in the region of 1% Ni is indistinguishable, as already stated, from that of the catalysts containing 10% Ni.

We shall consider some other examples of studies of the state of dispersion and catalytic properties of Ni from the standpoint of possible effects of the carrier. Thus, Lyubarskii [74] found that the specific activity of nickel towards the hydrogenation of benzene is constant for the carriers Al_2O_3, Cr_2O_3, and MgO, and also for the catalyst prepared by decomposition of the oxalate or formate.

Nikolaenko and coworkers [75] studied the specific activity of Ni–MgO catalysts prepared by thermal decomposition of the mixed oxalates towards the hydrogenation of benzene, and found a constant activity as the particle size decreased from 3000 Å to less than 17 Å.

Aben and coworkers [76] studied the effect of metal particle size and of the nature of the carrier on the specific catalytic activity (towards the hydrogenation of benzene) of platinum, palladium, and nickel catalysts deposited on SiO_2, Al_2O_3, Al_2O_3–SiO_2, and MgO–SiO_2. The activity, referred to a single surface atom of the metal, was found to be independent of particle size and of the type of carrier.

Dixon and Singh [77] showed, for the same reaction on Ni–Al_2O_3 catalysts covering the wide range of Ni concentrations from 5 to 75%, that the specific activity calculated for 1 m^2 of nickel surface was constant and independent of degree of dispersion.

On the other hand, Swift and coworkers [78], who studied the physical and catalytic properties towards the dehydrogenation of cyclohexane of Ni and Pt deposited by impregnation on η- and γ-Al_2O_3, point out that the activity of Ni (though not of Pt) is affected by the nature of the carrier. These results can be criticised on the grounds that the percentage conversions per unit weight of catalyst and per unit area of catalyst surface were both taken as a measure of the activity. Thus, the Ni–γ-Al_2O_3 catalyst, which had almost twice the area of active phase of the Ni–η-Al_2O_3 catalyst and had a greater activity as judged by the percentage conversion, was found to be the less active when the results were recalculated for 1 m^2 of catalyst area.

Van Hardeveld and Hartog [79] studied Ni catalysts on Aerosil with different mean particle size and size distribution. By measuring the intensity of the i.r. absorption bands of adsorbed N_2, CO, and CO_2 molecules they were able to evaluate the proportion of active centres (defined below) on the nickel surface, and to compare this quantity with the activity and selectivity of the catalyst in the exchange and deuteration reactions of benzene. These workers showed that the ratio of the exchange and deuteration rates and the initial isotopic composition of the benzene are very sensitive to the type of catalyst. High activity in exchange reactions results from the presence of large crystallites, and is most probably associated with defects in such particles. This effect almost exactly balances the decrease in the number of surface atoms with decreasing crystal size, and as a result the Ni surface remains uniform towards the deuteration reaction. Thus, the size of the crystals is found to be of fundamental importance in determining the activity and selectivity of the catalysts.

As the above examples show, in most comparative studies of catalytic activity and selectivity the specific surface area of the metal is treated as a simple parameter, and the distribution of particle sizes is ignored. More latterly, as a result of the growing interest in the properties of small particles, more detailed discussions of the nature of active centres in catalysts containing very

finely divided metals on a carrier have been published [80-82]. A basic investigation by van Hardeveld and van Montfoort[80] deals with the influence of crystal size on the adsorption of molecular nitrogen on Ni, Pd, and Pt. It is shown that the stretching vibration of the nitrogen molecule is active in the infrared spectrum only when the N_2 is adsorbed at some special sites on the surface. These centres are present in significant numbers only in small crystals ($20 < d < 70$ Å), and have a co-ordination number of 5 (B_5 centres): an atom adsorbed on such a centre is in contact with 5 Ni atoms. The particle size of the Ni–SiO_2 catalysts was measured by electron microscopy. The authors examined models of particles with different numbers of atoms, in the form of perfect or incomplete cubo-octahedra. The former are bounded exclusively by {111} and {100} surface planes: B_5 centres are absent, and the co-ordination number of adsorbed atoms is 3 or 4 for the two planes respectively.

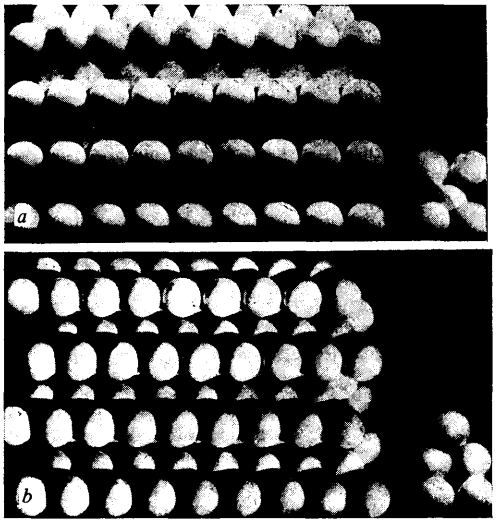


Figure 3. Models of defect planes containing B_5 centres: *a*) {110} plane; *b*) {113} plane. The configurations of the two types of B_5 centre are shown on the right.

In the second model, the less densely packed {113} and {110} planes are present as well as the {100} and {111}; these introduce two geometrically distinct types of B_5 centre (Fig. 3). The authors used a mathematical method of calculating the maximum number of B_5 (and also B_3 and B_4) centres as a function of crystal diameter, and they obtained distribution curves for the three types. B_5 centres are absent in very small particles ($d < 10$ Å), and also in particles with $d > 40$–50 Å, and their probability of occurrence is a maximum in the region 18–25 Å. The adsorption of molecular nitrogen on Ni, Pt, and Pd, first observed by Eischens and Jacknow[83], is discussed in detail in the same paper. Although the relatively high heat of adsorption (12 kcal mole^{-1}) suggests that we are dealing with chemisorption, the authors conclude from the lack of specificity of the phenomenon that adsorption on noble metals is physical. The main conclusion of the work is the following. Before making any statement as to the influence of current carriers on the catalytic and chemisorption properties of a metal, as revealed for example by changes in the spectra of adsorbed molecules (cf. the work of O'Neil and Yates[84] on nickel catalysts and of Eishens[85] on platinum), we must examine the distribution of particle size, which is determined first and foremost by the nature of the carrier. The number of B_5 centres, and hence the relative contribution of "defect" planes to the total metal surface, can be evaluated from the intensity of the absorption bands of adsorbed nitrogen. This approach was mentioned above when discussing the work of van Hardefeld and Hartog[79] on the deuteration and exchange reactions of benzene on a nickel catalyst.

Schlösser[81] extended the work of van Hardeveld and van Montfoort[80] on the number of B_5 centres in various cubo-octahedral models. He considered models of cubo-octahedra having different symmetries and defect structures, and he discussed in particular the forms obtained by cutting the corners and edges of a simple cubo-octahedron in various proportions and which can be expected to exist in real catalysts. He showed that the appearance of new low-index planes such as {311}, {210}, etc. increases the number of active B_5 centres, and he compared the number of B_5 centres and the catalytic activity for a number of systems described in the literature.

The paper presented by Bond to the Fourth International Congress on Catalysis[82-85] discusses the same problem from the standpoint of the influence of B_5 centres on the mechanism of various catalytic reactions.

When comparing the activity of a series of catalysts with their degree of disperseness it is important to note that the particle size of the metal can change in the course of the reaction, because of the increased mobility of certain atoms. For example, the size of the Pd crystals varied from 65 Å to 1300 Å, even at 40°, during the hydroisomerisation of but-1-ene on a Pd–graphite catalyst[86]. Obviously, the number of active (e.g. B_5) centres measured prior to the catalytic reaction may also be affected by the exposure of the catalyst to the reaction system. It is very important, therefore, to study the physical properties of the catalyst after, as well as before, the reaction as in the work of Rubinshtein and coworkers[24].

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In spite of the variety of apparently contradictory information on the influence of state of dispersion, and type of carrier, on the catalytic activity of metals, there is a general trend which allows us to systematise the existing knowledge and to formulate profitable objectives for future investigations. The first explicit statement of the correct approach to the problem was made by Boudart and coworkers[34], whose results are discussed on p. 865. It is proposed that all catalytic reactions be divided into two classes: "unhindered" [facile] and "hindered" [demanding]. In the former the active centres have approximately the same activity, and the specific activity is independent of particle size and of the method of preparation of the catalyst (as in Ref. 34). The second class includes reactions which require special configurations of surface atoms, produced by optimising the catalyst preparation procedure. Hindered reactions are invariably sensitive to the size of the metal particles, to heterogeneity of the catalyst surface, and to the type of carrier. Boudart's classification of catalytic reactions shows some obvious similarities with Balandin's views on

the role of the geometric factor in catalysis. As Boudart himself points out, similar ideas were put forward much earlier by Taylor [87], who stated that the catalytically active fraction of the surface is determined by the catalytic reaction in progress. Boudart stresses that the model reactions chosen for systematic studies of catalysts must not be of the hindered type. Reliable correlations between the activity and the structure of the catalyst can be expected only for reactions known to be free from structural complications. In addition to the reactions of neopentane on platinum [52], Boudart discusses other examples of reactions of both types which had been previously studied by Kemball and coworkers [88] on nickel catalysts and by Kral [89] on palladium deposited on carbon.

Table 3. Dependence of activity on state of dispersion for supported metal catalysts.

Reaction	Catalyst	Dependence on		Refs
		state of dispersion of metal	nature of carrier	
Oxidation of SO_2	Pt, Pt/SiO_2	no	no	45
Oxidation of H_2	Pt, Pt/SiO_2	no	no	46
Hydrogenation of benzene	Ni, Ni/Cr_2O_3, Ni/MgO	no	no	79
	Ni/SiO_2, Ni/Al_2O_3, Ni/C, $Ni/Al_2O_3 \cdot SiO_2$, $Ni/MgO \cdot SiO_2$			74–76, 90–92
	Co/SiO_2, Co/Al_2O_3, Co/C $Co/Al_2O_3 \cdot SO_2$	no	no	93
	Pt/SiO_2, Pt/Al_2O_3, $Pt/Al_2O_3 \cdot SiO_2$, $Pt/MgO \cdot SiO_2$	no	no	3, 76
	Pd/SiO_2, Pd/Al_2O_3, $Pd/Al_2O_3 \cdot SiO_2$, $Pd/MgO \cdot SiO_2$	no	no	76
Dehydrogenation of cyclohexane	Ni/SiO_2, Ni/Al_2O_3, $Ni/Al_2O_3 \cdot SiO_2$	no	no	78, 93
	Pt/Al_2O_3, $Pt/Al_2O_3 \cdot SiO_2$	no	no	54–57, 94, 95
Hydrogenation of phenol	Ni, Ni/Al_2O_3, Ni/ZnO, Ni/NiO	no	no	96
Hydrogenation or hydrogenolysis of cyclopropane	Ni/SiO_2, $Ni/Al_2O_3 \cdot SiO_2$	no	yes	72
	Pt/SiO_2, Pt/Al_2O_3	no	yes	34
Hydrogenolysis of ethane	Ni/SiO_2, Ni/Al_2O_3	no, or positive effect*	yes	4, 5, 7
	$Ni/Al_2O_3 \cdot SiO_2$		yes	
H–D exchange in $C_6H_6 + D_2$ mixture	Co/SO_2, Co/Al_2O_3, $Co/Al_2O_3 \cdot SiO_2$		yes	97
	Ni/SiO_2	negative effect		80
Hydrogenation of CO_2	Ni/Cr_2O_3	no		98, 99
Dehydrogenation of n-hexane	Pt/Al_2O_3	no		100
Isomerisation of n-hexane	Pt/Al_2O_3	no		
Hydro-cracking of n-heptane	Pt/Al_2O_3	transition from positive to negative effect	yes	95, 101
Dehydrocyclisation of n-heptane	Pt/Al_2O_3	no		
Isomerisation of n-heptane	Pt/Al_2O_3	negative effect		
Hydrogenation of heavy oil	Pt/Al_2O_3	no	yes	102
Hydro-cracking of heavy oil	Pt/Al_2O_3	transition from positive to negative effect		
Hydrocyclisation of methylcyclopentane	Pt/Al_2O_3	negative effect		103

*The terms "positive" or "negative" effect are used in the meaning of the classification proposed by Bond to the Fourth International Congress on Catalysis, Moscow, 1968.

For example, the deuteration of ethylene on nickel is unhindered, in contrast to the deuterium exchange of alkylbenzenes. As stated above, the hydrogenation of benzene [75–77] is an unhindered reaction (unexpectedly so, in the light of the sextet mechanism of the reaction). However, Bond has pointed out [82] that the formation of olefins by the partial hydrogenation of aromatic compounds was reported at the Third International Congress on Catalysis: this suggests the possibility of a doublet mechanism. Van Hardeveld and Hartog [79] had generally assumed that adsorbed molecules of benzene are attached to a single nickel atom, with formation of a surface compound of the π-complex type. This view is consistent with the experimental fact that the hydrogenation of benzene is unhindered. On the other hand, reactions involving linear molecules such as paraffin hydrocarbons (e.g. the hydrogenation of ethane, studied by Sinfelt and coworkers) are of the hindered type. Schlösser [81] has published a detailed analysis of the available data, summarised in Table 3, in the light of Boudart's classification. In the present state of knowledge if is not yet possible to account for all the known facts, or to predict whether the specific activity of the supported catalyst in various types of reaction should be a function of particle size or of the nature of the carrier. However, the present approach, based on the conformation of the reacting molecules and on the geometry of the assumed active centres, is much more successful than the earlier "electronic" concepts on the influence of the carrier on the properties of the metal.

Therefore, we conclude that the most important problem facing experimentalists at the moment is to compare catalytic activities (preferably, in various types of reaction) with the average particle size and also with the particle size distribution of the catalyst. Reliable information of this type must be made available before further progress can be made towards a full understanding of the nature of the catalytic action of supported metals.

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