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Uspekhi Khimii

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Specific Activity of Metallic Catalysts

V.A.Dzis'ko

This review deals with published work on the influence of chemical composition, degree of dispersion, and method of preparation on the specific activity of metallic catalysts. In most cases the specific activity is determined by the nature of the metal, and is independent of the degree of dispersion or other parameters. This behaviour is probably due to interaction between the catalyst surface and the surrounding medium, which converts the initial catalyst surface into a state which is relatively unaffected by variations introduced during the preparation of the catalyst. 131 references.

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I. INTRODUCTION

The catalytic activity of unit surface area of solid catalysts, usually termed the "specific activity"†, is the most characteristic parameter of the catalytic properties of the material, and it can be used, together with a knowledge of the accessible surface area, to predict the activity of the catalyst.

The specific activity of a catalyst can be influenced by various factors: 1) the chemical composition; 2) the degree of dispersion of the active component, i.e. its crystallite size, which determines the relative proportions of atoms on the corners, edges, and faces of the crystallite; 3) the method of preparation, and some other factors. The relative importance of chemical composition and of the structural factors listed above in determining the specific activity is one of the most important problems facing the development of an effective theory of catalyst preparation.

During the first phase of the development of catalyst theory, before the advent of effective methods of measuring surface areas, most workers believed that catalytic activity was associated with non-equilibrium structures possessing a large amount of excess free energy, and therefore that the method of preparation of the catalyst could be the predominant factor in determining the specific activity[4-13]. These *a-priori* views were put to the test when methods of measuring surface areas were developed and generally adopted. The results of specific activity studies on one-component oxide catalysts have been discussed[14] by the present writer. The general conclusion was that the specific activity of catalysts of a given composition, measured in the activation-controlled regime

† Some ambiguity exists in the concept of "specific activity": some workers refer the term to the activity of 1 g of the catalyst[1], others to the activity of 1 m^2 of total surface area[2], yet others to the activity of unit "working" surface, by which they understand the "true" surface accessible to the catalytic reaction[3]. The most rational characterisation of the catalyst is to relate the activity to unit surface area of the active component.

with the catalyst and the reacting medium under steady state conditions, is approximately constant and independent of the method of preparation and of the thermal history of the catalyst.

The present review is concerned with the influence of chemical composition, degree of dispersion, and method of preparation on the specific activity of metallic catalysts‡. In Sections II–IV we shall discuss the results of experimental studies available at the time of writing. A discussion of the results obtained by different workers and of possible explanations of the discrepancies observed will be found in the concluding Section. The selection of publications relevant to the present review was limited by the following conditions: 1) we shall consider only those papers in which the reported activities can be compared with the surface area or the degree of dispersion of the active component; 2) we shall confine our discussion to gas-phase reactions, because reactions at a liquid–solid interface or in three-phase gas–liquid–solid systems often involve diffusional limitations which could obscure the effects of interest to us; 3) although the most precise characteristic of the specific catalytic activity is the rate constant of the reaction, related to unit surface area [18,19], we shall also include (for the sake of a balanced presentation of relevant work) those papers in which the activity is characterised by the extent of reaction.

II. EFFECT OF CHEMICAL COMPOSITION ON THE SPECIFIC ACTIVITY OF METALLIC CATALYSTS

The relationship between the specific catalytic activity and the nature of the non-reducible oxide support and the concentration of metal is an important aspect of the study of metal–oxide catalysts.

Table 1. Effect of chemical composition on the activity of cyclohexane dehydrogenation catalysts (Ref. 21).

Catalyst	Carrier	Concn. of metal in catalyst, %	Surface area of metal in catalyst, $m^2\ g^{-1}$	Specific activity (% conversion $m^{-2}\ h^{-1}$)
Pt	η-Al_2O_3	0.4	0.9	97.1
Pt	η-Al_2O_3	0.78	2.3	36.1
Pt	γ-Al_2O_3	0.4	1.1	74.5
Pt	γ-Al_2O_3	0.82	2.33	35.2
Ni	η-Al_2O_3	2.57	—	—
Ni	η-Al_2O_3	6.0	1.46	18.4
Ni	η-Al_2O_3	6.48	0.58	27.6
Ni	γ-Al_2O_3	2.56	—	—
Ni	γ-Al_2O_3	6.0	1.24	20.2–21.0
Ni	Al_2O_3-SiO_2	6.0	1.11	22.3
Ni	SiO_2	6.0	1.29	10.3

Platinum and the platinum metals. Cusumano and coworkers [20] studied the effect of the nature of the carrier on the specific activity of platinum towards the dehydrogenation of cyclohexane. Aluminium oxide and alumina–silicas were used as carriers; the Pt content of the catalysts was 2%. The size of the platinum crystallites, calculated from H_2 adsorption measurements, was less than 10 Å on alumina and 85 Å on Al_2O_3–SiO_2. Measurements in a flow reactor showed that Pt is approximately 6 times more active on Al_2O_3 than on alumina–silica gel, as a result of differences in surface area. The specific activity of the platinum, referred to 1 m^2 of Pt, was found to be independent of the nature of the carrier and of the degree of dispersion of the metal.

Swift and coworkers [21], who studied the same reaction on nickel and platinum supported on γ- and η-Al_2O_3, came to a similar conclusion. Table 1, which is a compilation of their results, shows that samples prepared from γ- and η-Al_2O_3 have practically the same specific activity for equal concentrations of Pt. When the Pt concentration in the catalyst is raised from 0.4 to 0.8% the specific activity falls by a factor of 2–2.5.

Hightower and Kemball [22] have compared the activity and selectivity of platinum catalysts supported on silica gel and on γ- and α-alumina with the activity of a platinum foil towards the more complex deuteration and H exchange reaction in *p*-xylene. No significant difference was found in the specific activity and selectivity of samples deposited on the same carrier and differing only in Pt concentration. Catalysts prepared by depositing Pt on different carriers, on the other hand, differed in selectivity among themselves as well as from the platinum foil. The authors suggest that the water adsorbed on the carrier may have a poisoning effect on the catalyst.

Table 2. Effect of carrier on the activity of Ru, Pt, Tc, Pd, and Re in the hydrogenation and hydrogenolysis of benzene (Ref. 23).

Catalyst composition*		Specific activity, mol. $cm^{-2}\ s^{-1}$, $\times 10^{-12}$		Catalyst composition*		Specific activity, mol. $cm^{-2}\ s^{-1}$, $\times 10^{-12}$	
metal	carrier	hydrogenation	hydrogenolysis	metal	carrier	hydrogenation	hydrogenolysis
Ru	SiO_2	395	300	Tc	γ-Al_2O_3	20	16
Ru	γ-Al_2O_3	350	390	Pd	SiO_2	16	—
Pt	SiO_2	175	—	Pd	γ-Al_2O_3	8.4	—
Pt	γ-Al_2O_3	142	—	Re	SiO_2	1.2	3.4
Tc	SiO_2	4.6	8.9	Re	γ-Al_2O_3	0.5	1.1

*The catalysts contained 1% of metal.

Kubicka showed [23] that the nature of the carrier does not significantly influence the specific activity of ruthenium, platinum, palladium, and rhenium supported on γ-Al_2O_3 and on silica gel (see Table 2) towards the hydrogenation and the hydrogenolysis of benzene. Differences in specific activity for any one metal were less than a factor of 2, and differences in activation energy less than 1 kcal $mole^{-1}$. Only technetium was exceptional its activity towards the hydrogenation of benzene being 4 times greater on Al_2O_3 than on SiO_2. Also rhenium was 3 times more active towards both reactions on SiO_2 than on Al_2O_3.

Witekowa and Matyjewski [24] studied the effect of the nature of the carrier on the specific activity of platinum (on metallic aluminium and on Al_2O_3) and of Pt black towards the oxidation of hydrogen, and found that the total activity is slightly increased, but the specific activity is greatly decreased, by increasing the coverage of aluminium by platinum.

‡ Recent publications by Boudart [15] and Slinkin [16,17] include brief reviews of the specific activity of metallic catalysts, but comprehensive coverage is not claimed.

Nickel and cobalt. The influence of chemical composition on the specific activity of nickel towards the hydrogenation of benzene was investigated [25-29] by examining a large number of catalysts with difference non-reducible components and covering a range of nickel concentrations. Chromium oxide, alumina, magnesia, silica gel, and carbon were used as carriers. The catalysts were prepared both by impregnation and by coprecipitation. Samples of nickel black, prepared by decomposing nickel salts, were also investigated. The catalytic activity was measured by circulating-flow [25-28] and by flow [29] methods. The results of this work are summarised in Tables 3 and 4 and in Fig. 1. It is evident that, in spite of the large difference in chemical composition, the activity of all the catalysts (except the Raney-nickel) is proportional to the surface area of Ni in the catalyst; the specific activity is constant and independent of the nature of the non-reducible oxide and of the Ni content.

Table 3. Effect of carrier on the specific activity of nickel in the hydrogenation of benzene (refs. 25-27).

Carrier and method of preparation	Ni content, wt.%	Area of metallic nickel, $m^2 g^{-1}$	Crystal size, A	Specific activity at 100°, mmole $h^{-1} m^{-2}$ Ni
Nickel black (decomposition of formate)	100	4	1250	0.46
Chromic oxide	50	60	94	0.58
Magnesium oxide	65	65	86	0.65
Carbon	9.4	203	28	0.58
Raney nickel	75	87	65	3.30

Table 4. Effect of Ni content on the activity of $Ni-Al_2O_3$ catalysts in the hydrogenation of benzene (Ref. 29).

Nickel concentration	%	5.4	16.9	29.5	53.0	75.0
Ni surface area	$m^2 g^{-1}$	1.3	14.3	24.5	51.7	43.0
Apparent activation energy	kcal $mole^{-1}$	41.03	39.77	39.35	41.03	37.26
Rate at 35°	mole $h^{-1} g^{-1} \times 10^5$	3.7	48	68.1	138	123
Specific activity at 35°	mol. $s^{-1} cm^{-2} \times 10^{-11}$	4.78	5.62	4.66	4.48	4.8

Taylor and Staffin [30], who studied the effect of carrier on the specific activity of dilute nickel catalysts in the same reaction, obtained rather different results. Their measurements were made under pulsed conditions, in 5-minute experiments. It can be seen from Table 5 that the specific activity increases as the amount of nickel in the catalyst is increased, the effect being slight on SiO_2 but very marked on alumina-silica gel. The nature of the carrier is significant only at low nickel concentrations, samples containing 10% Ni show only marginal differences in activity.

The role of nickel content in nickel-magnesia catalysts has been studied [31] in the particular case of the dehydration of cyclohexane (Fig. 2). The activity was measured in a flow apparatus at 250°, and it was found that the catalytic activity and the H_2 adsorption give similar plots at low nickel concentrations. The plots begin to diverge at Ni concentrations greater than 15%: the adsorption increases monotonically, but the catalytic activity goes through a maximum at 36.5 wt.% Ni. Hence, the specific activity (expressed in relative units) varies in the range 1 ± 0.5 as the nickel content of the catalyst is varied. The authors [31] explain this observation by assuming that the catalytic activity of the nickel is determined by the "coordination of the surface atoms", which is apparently an optimum at a Ni content of 36.5%.

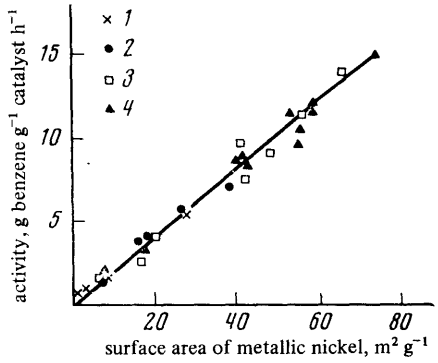


Figure 1. Surface area of nickel against activity of benzene dehydrogenation catalysts of different composition (Ref. 28): *1*) Ni black, *2*) $Ni-Cr_2O_3$, *3*) $Ni-Al_2O_3$, *4*) $Ni-Al_2O_3.Cr_2O_3$.

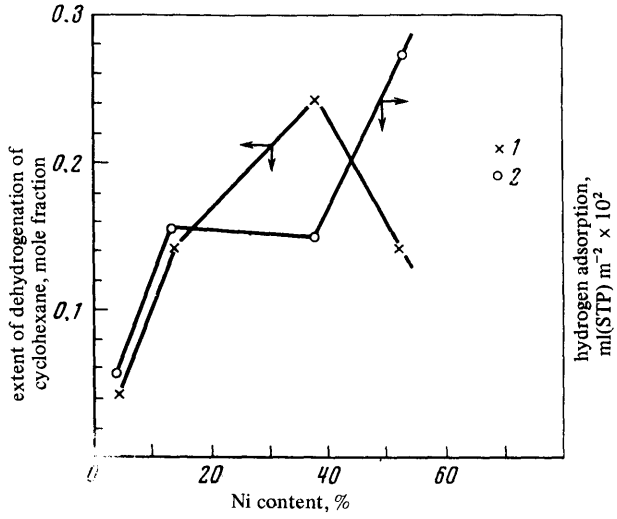


Figure 2. Effect of chemical composition on the activity of catalysts towards *1*) the dehydrogenation of cyclohexane and *2*) hydrogen adsorption (Ref. 31).

Swift and coworkers [21] also studied the effect of the nature of the carrier and of nickel content on the specific activity of nickel towards the dehydrogenation of cyclohexane. They found that samples containing ~2.5% of

nickel were catalytically inactive, and they suggested as an explanation that the nickel in these samples is chemically combined with the carrier and cannot be reduced. Samples containing 6–6.5% Ni on γ- and η-Al_2O_3 and on Al_2O_3–SiO_2 have almost identical specific activities (see Table 1), but the activity of nickel on silica gel is lower by about a factor of 2. The authors ascribe the enhanced activity of the catalysts containing Al_2O_3 to compound formation between the nickel and the aluminium oxide, the nickel being converted into an ionic form. The role of the nickel ions is to capture electrons and transfer them to the metallic nickel, thus modifying its catalytic activity.

Table 5. Effect of chemical composition of the catalyst on the specific activity of Ni in the hydrogenation of benzene (Ref. 30).

Carrier	SiO_2			$SiO_2 - Al_2O_3$		
Ni content, %	1	5	10	1	5	10
Ni crystallite size, Å	12	—	24	26	—	29
Ni surface area, $m^2 g^{-1}$	0.7	5.9	13.6	0.1	3.1	6.8
Specific activity, mole m^{-2} Ni $h^{-1} \times 10^4$	17.9	19.9	22.1	<1	3.84	17.2

Slinkin and coworkers [32] have reported an extensive investigation of the activity of Ni towards the dehydrogenation of cyclohexane as a function of the concentration of nickel in nickel–chromium catalysts. The reaction was studied in a flow reactor; it was found to follow the same kinetic law on all the samples examined. The surface area of metallic nickel was calculated from the concentration of metallic nickel and from its degree of dispersion, determined from X-ray diffraction and from magnetic measurements. The specific activity of the catalysts was found to vary by not more than a factor of 4 as the nickel content was varied from 2.4 to 34.8%: only the sample containing 70.5% Ni had an activity 46 times lower than the maximum. This behaviour is ascribed to incomplete removal of oxygen from the nickel surface.

An approximately constant specific activity was observed also in a study [33] of the influence of composition and degree of dispersion on the activity towards the hydrogenation and hydrogenolysis of cyclopropane of Ni catalysts deposited on kieselguhr, Al_2O_3, and alumina–silica gel.

It is evident from Table 6 that the hydrogenation rate constants for the various catalysts differ by not more than a factor of 2, and the hydrogenolysis rate constants by a factor of 4. According to a more recent study [34], the overall reaction rate varies only within the range ±25% (last column of Table 6).

Taylor and coworkers [35] also studied the hydrogenation and hydrogenolysis of cyclopropane on nickel catalysts, using pulsed conditions in 3-minute experiments. The nickel content of the catalysts was 10 wt.%. The nature of the carrier was found to have a marked influence, the specific activity of nickel being approximately 2 orders of magnitude higher on silica gel than on Al_2O_3–SiO_2.

The same group of workers [36–38] found that the nature of the carrier has a strong effect also on the specific activity of nickel and cobalt towards the hydrogenolysis of ethane: the specific activity of nickel on silica gel was higher than on Al_2O_3 by about a factor of 2, and almost 50 times higher than on Al_2O_3–SiO_2.

Similar results were obtained in the work on cobalt [37], samples based on silica gel and aluminium oxide having the highest activity, and samples based on Al_2O_3–SiO_2 and carbon the lowest. The specific activity of the former was about 20 times greater than the specific activity of the latter, even though the degree of dispersion of the catalysts differed only by a factor of 3.

Table 6. Specific activity of nickel in the hydrogenation and hydrogenolysis of cyclopropane at 60° (Refs. 33, 34).

Ni content, %	Carrier	Nickel surface, $m^2 g^{-1}$	Ni disperseness, (fraction of atoms on surface)	Specific activity, mole $h^{-1} m^{-2} \times 10^3$			
				hydrogenation k_1 (Ref.33)	hydrogenolysis k_2 (Ref.33)	total $k_1 + k_2$ (Ref.33)	total $k_1 + k_2$ (Ref.34)
58	Kieselguhr	63	0.163	5.8	1.28	7.0	7.9
5	$SiO_2 - Al_2O_3$	0.2	0.006	4.0	0.45	4.4	5.0
40	Al_2O_3	5.7	0.022	3.1	1.6	4.7	6.3
14	Al_2O_3	2.8	0.03	2.58	2.0	4.58	6.1

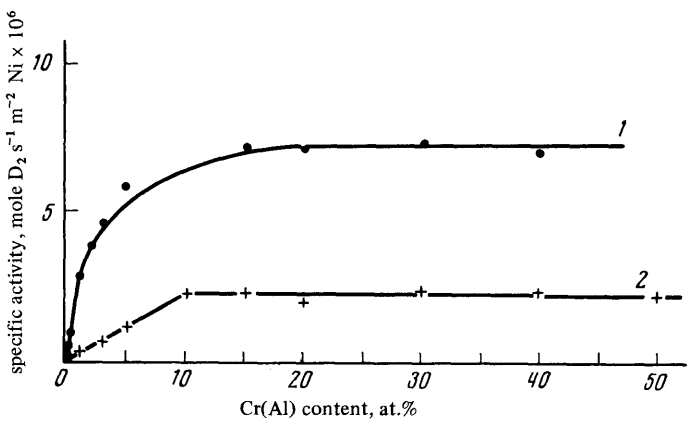


Figure 3. Effect of Cr_2O_3 and Al_2O_3 content on the specific activity of nickel catalysts in the reaction HDO + H_2 → H_2O + HD: [39–41] *1*) Ni–Cr_2O_3; *2*) Ni–Al_2O_3.

When the nickel concentration in silica gel and alumina–silica catalysts was changed from 1 to 10% it was found [38] that the specific activity of the nickel varied in the same sense as the nickel content. This observation was explained by postulating an interaction between the nickel and the carrier, which can be expected to be stronger when the nickel content is low. However, the nature of this interaction is not clear.

Margineanu and Olariu [39,40], who studied the reaction HDO + H_2 → H_2O + HD, found a relationship between the specific activity and the chemical composition of a nickel–chromium catalyst. The concentration of chromium oxide

in the binary system was varied from 0.1 to 40 mole %. With pure nickel, both the surface area and the specific activity were found to be very low. As the concentration of chromic oxide was increased to 5% the activity of the nickel increased 100-fold. However, at still higher concentration of chromium oxide the specific activity of the nickel remained approximately constant (curve *1* of Fig.3).

The authors explain these results by assuming that the "promotion" of the nickel catalyst involves an interaction with the chromium oxide, yielding a surface compound which has a very high activity towards the exchange reaction. As the concentration of chromium oxide in the catalyst is increased, the concentration of active surface centres increases at first and then reaches a constant level. As a result, the specific activity also rises to a constant level, independent of the concentration of Cr_2O_3. The decrease in specific activity with decrease in chromium oxide content could also be explained in terms of increasing crystallite size. The same authors[41] observed a similar relationship between the specific activity of nickel and the concentration of non-reducible oxide in nickel–alumina catalysts: as the concentration of Al was raised from 0 to 10 at.% the specific activity rose from 0.057 to 2.22 mole D_2 m^{-2} s^{-1}, and remained constant at still higher Al concentrations (curve *2* of Fig. 3).

Müller and coworkers[42] studied the effect of nickel content in nickel–chromium catalysts on the total and the specific activity towards the hydrogenation of CO_2 to CH_4. The activity was measured in a circulating flow apparatus in the presence of a large excess of hydrogen. As Table 7 shows, a change in nickel concentration alters the total activity by more than an order of magnitude without significantly affecting the specific activity.

Table 7. Effect of Ni : Cr_2O_3 ratio on the activity of nickel–chromia catalysts in the hydrogenation of CO_2 at 175° (Ref. 42).

Ni:Cr_2O_3	∞ (100% Ni)	21.6	9.03	4.37	1.96	0.925	0.25
Total activity, mole $CO_2^{0.5}$ litre$^{0.5}$ g^{-1} h^{-1}	0.047	0.463	0.490	0.530	0.381	0.043	0.046
Specific activity, mole $CO_2^{0.5}$ litre$^{0.5}$ m^{-2} Ni h^{-1}	0.67	0.721	0.716	0.731	0.839	0.906	—

Iron. Shcheglov and coworkers[43] studied the effect of catalyst promotion on the specific activity of the catalyst towards the dissociation of ammonia. The measurements were made in a circulating flow apparatus at atmospheric pressure.

Table 8 shows that catalyst promotion results in a 15-fold increase in the rate constant (referred to 1 g of catalyst), whereas the specific activity increases at most by 30%. The authors conclude that the role of the promoting agent is to increase and stabilise the iron surface.

Similar conclusions were reached in studies of the effect of alumina content on the activity of iron catalysts in the synthesis of ammonia[44]. There was no direct relationship between the catalytic activity and the total surface area. As the proportion of aluminium oxide in the catalyst increases, the fraction of the surface occupied by free iron decreases. However, since the total surface area is increased, the area of metallic iron goes through a maximum. The yield of ammonia goes through a similar maximum. The rate constant, calculated by the Temkin–Pyzhov equation, varies in direct proportion to the iron surface (Fig. 4), and therefore the specific activity is constant.

Table 8. Effect of catalysts composition on the activity of iron towards the decomposition of ammonia[43].

Catalyst	Rate constants x 10^2*			
	375°		400°	
	k_g	k_{sp}	k_g	k_{sp}
Armco-iron	11	9.9	65	59
Promoted Fe catalyst	171	12.9	943	69

*k_g is the rate constant per 1 g of catalyst, k_{sp} is the rate constant referred to 1 m^2 of metallic iron surface (cm^3 NH_3 m^{-2} Fe h^{-1}).

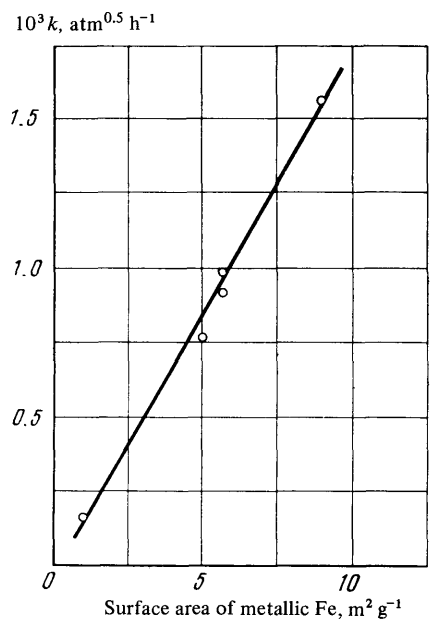


Figure 4. Metallic iron surface against rate constant calculated by the Temkin–Pyzhov equation[44].

The specific activity of iron towards the synthesis of ammonia was investigated by Lachinov and coworkers[45], who varied the composition of their catalysts over wide limits. It is clear from their experimental results, summarised in Table 9, that with the exception of sample 12a (which had a very small iron surface) the specific activity of the catalysts varies by no more than a factor of 2.7, which is probably within the limits of experimental error in this type of measurement.

In contrast to these results, the same group of workers[46] had previously found that the specific activity of iron increases from 30 to 1200 when the fractional occupancy of the surface by alkali is increased from 0.08 to 0.78. They had concluded that the active component in iron catalysts for ammonia synthesis is not elemental iron, but an iron compound formed on the catalyst surface during the reduction stage.

Table 9. Effect of Al_2O_3 content on the surface area and specific activity of Fe ammonia synthesis catalysts at 400° (Ref. 45).

Sample No.	Al_2O_3 content, wt.%	Surface area, $m^2 g^{-1}$		k_{sp}, $atm^{0.5} h^{-1} m^{-2}$ Fe
		total	metallic iron	
12a	0.0	1	1.0	0.75
8a	0.6	6	2.5	20.3
7a	1.1	8	3.4	15.5
6a	2.4	13	3.8	20.0
4a	5.4	24	7.7	11.7
3a	7.9	35	5.2	11.3
2a	13.4	91	4.1	16.3
1a	37.5	91	5.5	7.5

The effect of Al_2O_3 and K_2O additions on the specific activity in the synthesis of ammonia was investigated also with iron–cobalt catalysts containing 15% of cobalt. It was found that the additives have a significant effect on the surface area and on the total activity of the catalysts, but the rate constant (referred to 1 m^2 of metal surface) remains unchanged[47].

Table 10. Specific activity of silver catalysts for the oxidation of ethylene to ethylene oxide (Ref. 48).

Ag content of catalyst, $g l^{-1}$	17	33	43	73	10	23	53	83	50	1600 Ag pellets
Surface area of carrier, $m^2 g^{-1}$	5.0	5.0	5.0	5.0	2.8	2.8	2.8	2.8	0.5	—
Specific activity of silver, $10^5 k$, m^{-2}	2.8	5.1	4.7	2.8	5.9	5.6	4.2	3.1	3.1	2.8—4.2

Table 11. Specific activity of catalysts with different silver contents towards the oxidation of ethylene to ethylene oxide (Refs. 49, 50).

Silver content, wt.%	4.3	11.1	11.6	17.8	19.1	21.5	26.7
Specific activity, g ethylene oxide m^{-2} Ag $h^{-1} \times 10^2$	28	41	36	42	42	31	32

Silver. Soviet workers[48-50] have investigated the effect of method of preparation and of silver content on the activity of silver catalysts for the oxidation of ethylene to ethylene oxide. In the activation-controlled region the activity of the catalysts per 1 m^2 of silver surface was found to be approximately constant (Tables 10 and 11).

III. DEGREE OF DISPERSION OF METALLIC CATALYSTS AND THEIR SPECIFIC ACTIVITY

The dependence of the specific activity on the crystallite size of the active component has been actively investigated during the past 50 years. According to Taylor and others[4,7], who published their work in the 1920's, the catalytic activity resides mainly in the atoms which are weakly bound to the surface and therefore have an excess of free energy. Hence, the specific activity should increase on decreasing the size of the crystallites, thus increasing the proportion of atoms weakly bound to the surface. More recently, Bond has shown[51] from theoretical considerations that changes in crystallite size can influence the specific activity in different ways. 1) The specific activity may be independent of crystallite size. 2) Small crystals may be more active than large crystals: in this case the specific activity decreases if the crystal radius increases. Bond called this the "positive internal effect". 3) If the larger crystals are more active than the smaller crystals (negative internal effect) the specific activity increases with crystallite size. It is also possible for very small crystals to have a negative internal effect and larger crystals to have a positive internal effect: in this case the specific activity goes through a maximum. In the present section we shall discuss the results of experimental studies of the effect of degree of dispersion on the specific activity of catalyst particles. [Dispersion in this context is sometimes defined as the fraction of the total metal atoms which are the metal surface. (Ed. of Translation)].

Table 12. Specific activity of platinum towards the oxidation of sulphur dioxide and hydrogen (Refs. 53–55).

Catalyst	Surface of 1 g Pt, cm^2	Rate constants*			
		Oxidation of sulphur dioxide at 427°		Oxidation of hydrogen at 100°	
		k_g, $cm^3 s^{-1}$	k_{sp}, 10^2 cm s^{-1}	k_g, $cm^3 s^{-1}$	k_{sp}, cm s^{-1}
0.2% platinum on silica gel	$3 \cdot 10^5$	$1.1 \cdot 10^3$	0.37	$4.9 \cdot 10^3$	1400
0.5% platinum on silica gel	$7 \cdot 10^5$	$(0.7—2.8) \cdot 10^3$	0.1—0.40	—	—
Platinum sponge	$1.7 \cdot 10^3$	1.5—3.9	0.09—0.23	—	—
Wire 0.1 mm diameter	20.6	0.054	0.26	$1.1 \cdot 10^4$	535
Gauze	22.6	0.1	0.49	—	—
Foil	6.9	0.12	1.74	$6.2 \cdot 10^3$	900

*k_g is the rate constant per 1 g of catalyst, k_{sp} is the rate constant referred to 1 cm^2 of Pt surface.

Platinum, palladium, and rhodium. Boreskov and coworkers[52-56] made a comparative study of the activity of "massive" platinum samples (sponge, wire, gauze, foil) and of platinum deposited on silica gel towards the oxidation of sulphur dioxide and hydrogen, and towards the homomolecular H_2-D_2 exchange reaction. In the oxidation reactions (SO_2 and hydrogen) the activity was measured in the activation-controlled region by the circulating flow method, which ensures isothermal conditions in the catalyst bed. The surface area of metallic platinum was varied from 6.9 $cm^2 g^{-1}$ (foil) to 7×10^5

$cm^2 g^{-1}$ (platinised silica gel containing 0.5% Pt), i.e. more than 100 000-fold. In spite of this enormous difference in the degree of dispersion of the catalysts, the specific activity towards the oxidation of SO_2 was found to vary only by a factor of 4 (excepting only the foil sample). The foil had an unexpectedly high specific activity, tentatively ascribed to the presence of impurities (Table 12).

The catalytic activity of the same samples towards the oxidation of hydrogen[55], referred to 1 g of platinum, was found to vary by 4 orders of magnitude, while the specific activity varied only by a factor of 2.5. The differences in specific activity of different samples were comparable to the differences in specific activity of a given sample in different experiments: this effect probably arises from the slow establishment of a steady state over the catalyst surface.

Similar values of the specific activities of massive platinum, platinum sponge, and platinum black were observed also in a study[56] of homomolecular exchange. In this case, the platinised silica gel samples had a substantially higher specific activity, which the authors ascribed to a significant catalytic activity of the silica gel itself (in the presence of platinum) towards the H_2 exchange reaction. More recent work[57] failed to confirm the higher specific activity of Pt deposited on silica gel, although the absolute values of specific activity observed were close to those reported by Boreskov and Avdeenko[56].

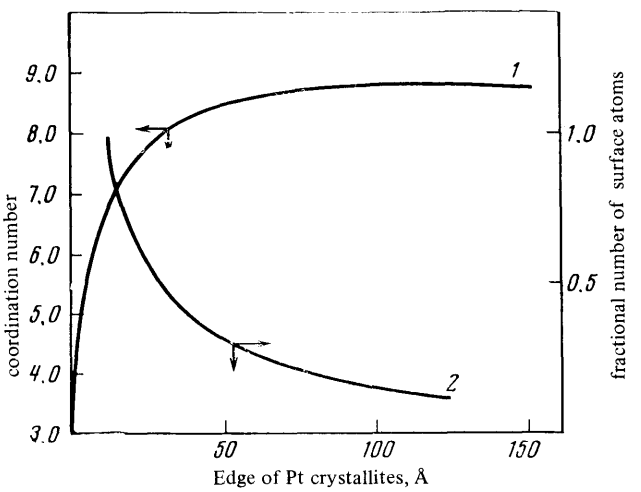


Figure 5. Coordination number (*1*) and fractional number of surface atoms (*2*) against platinum crystallite size (Ref. 58).

Poltorak and coworkers[57-62] published a series of papers on the effect of dispersion on the specific activity of platinum crystallites towards various reactions. The structural properties of the crystallites were evaluated from a theoretical treatment of the octahedral model. Plots of the coordination number (c.n.) and of the fractional number of surface atoms (γ) against the size of the platinum crystallites[58] are shown in Fig. 5. It is clear that the most important changes in structural properties occur when the edge length l is varied from 5 to 30–40 Å: further increase in crystallite size produces only minor changes in these parameters, and for crystals greater than 100 Å the changes are insignificant. These considerations lead to the conclusion that studies of the effect of dispersion on the activity of catalysts are not likely to be meaningful unless the catalyst is highly disperse. It is convenient to consider three cases: 1) crystallites containing less than 15 atoms, in which $\gamma \simeq 1$ and c.n. < 6, whose properties can be equated to those of micro-defects on crystal surfaces; 2) crystallites with $\gamma = 0.8-0.9$ ($l = 10-15$ Å), in which the properties of the atoms in the surface layer are similar to those of edge atoms in coarser crystal; 3) crystallites with $\gamma < 0.3$ and $l > 50$ Å, in which the properties of the surface atoms are no different from those of ideal crystal faces.

By applying these considerations, samples of platinised silica gel covering the appropriate range of crystallite size were prepared. The effect of platinum concentration on the catalytic activity towards the homomolecular H_2-D_2 exchange reaction was studied[57]; it was found that, in spite of the large difference in dispersion, samples in the first and second series had almost identical specific activities, and samples in the third series had a slightly lower specific activity (1.5–2-fold, almost within the limits of experimental error).

Table 13. Influence of dispersion on the specific activity of platinum (Refs. 60–62).

H/Pt	Average size of Pt crystallites, Å	Initial specific activity, mol. min^{-1} $atom^{-1}$ Pt		
		dehydrogenation of C_6H_{12}	dehydrogenation of C_3H_7OH (Ref.61)	hydrogenolysis of cyclopentane (Ref.60)
0.98	7	4.8	7.65	0.236
0.79*	—	—	—	0.28±0.026*
0.63	20	—	—	0.535
0.55	24	4.85	6.3	—
0.5	27	—		0.388
0.475	30	4.2	11.8	—
0.4	37	4.65	—	—
0.05	100	5.3	—	—

*From Ref. 62.

Mitrofanova and coworkers[60-62] studied the dehydrogenation of cyclohexane and isopropanol, and also the hydrogenolysis of cyclopentane. The catalytic activity was measured in a circulation apparatus. It is evident from the results (Table 13) that the specific activity of catalysts in the above reactions is not significantly influenced by the size of the crystallites, and hence that the ratio of surface to bulk platinum atoms does not play a major role. The authors conclude[58] that "in no single instance has the enhanced activity of crystal edges or structural defects, axiomatically assumed in theoretical discussions of heterogeneous catalysis, been experimentally confirmed for gas-phase reactions".

Constant specific activity of alumina–platinum catalysts towards the dehydrogenation of cyclohexane has been reported also by Zaidman and coworkers[63-65]. The dispersion of the catalysts was varied by varying the platinum content and the annealing temperature, and was

characterised by the H/Pt ratio. The activity was measured in a circulating flow system at low extents of reaction, for which the kinetic order is zero. It can be seen from Fig. 6 that the activity is proportional to H/Pt, and hence the specific activity of the platinum is constant within experimental error.

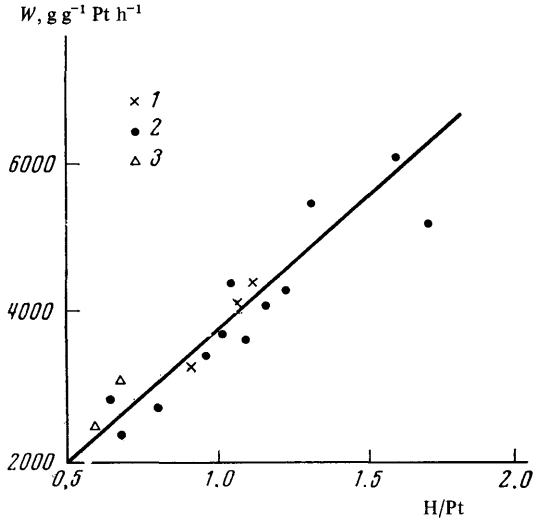


Figure 6. Activity of platinum in the dehydrogenation of cyclohexane against H/Pt (Refs. 63–65): *1*) 300°, *2*) 500°, *3*) 700°.

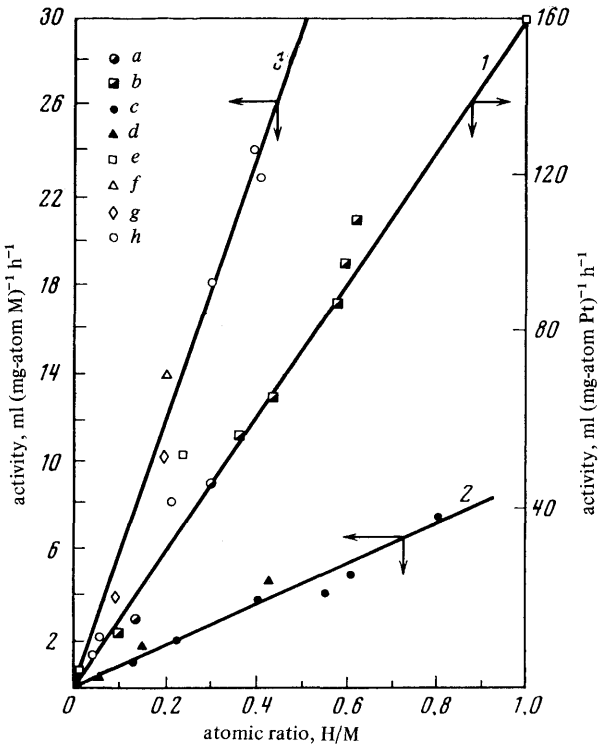


Figure 7. Benzene hydrogenation activity against fractional number of surface atoms (Refs. 66, 67): *1*) Pt, *2*) Pd, *3*) Ni; (*a*) Pt–SiO_2, (*b*) Pt–Al_2O_3, (*c*) Pd–SiO_2, (*d*) Pd–Al_2O_3, (*e*) Ni–Al_2O_3, (*f*) Ni–SiO_2.MgO, (*g*) Ni–SiO_2.Al_2O_3, (*h*) Ni–SiO_2.

Similar results were obtained in work [66,67] on the influence of the crystallite size of platinum and palladium on the specific activity of these metals towards the hydrogenation of benzene. The size of the crystallites was varied between 10 and 200 Å, and silica gel, alumina, SiO_2–MgO, and SiO_2–Al_2O_3 were used as carriers. The activity was found to be proportional to the degree of dispersion of the platinum (Fig. 7), showing that the specific activity is constant and independent of the degree of dispersion of the metal.

Dorling and Moss [68] also studied the relationship between the size of Pt crystallites deposited on silica gel, the surface area of the metal, and the activity of these catalysts towards the hydrogenation of benzene. The crystallite size was varied between 45 and 980 Å by varying the temperature of heat treatment. It can be seen from Table 14 that in spite of the large (15-fold) difference in crystallite size the specific activity of catalysts heated at 500° and below varies only by a factor of 2.

Larsen and coworkers [69] have studied the effect of dispersion on the activity of platinum towards the hydrogenation of aromatic compounds, using the extent of hydrogenation to characterise the activity. The reaction was found to proceed only to a maximum of 60% conversion, which was ascribed to achievement of equilibrium. It can be seen from Fig. 8 that for up to 30% reaction (i.e. 50% of the maximum) the relationship between percentage conversion and platinum surface area is approximately linear, but at higher extents of reaction the proportionality no longer holds.

Table 14. Influence of sintering temperature and dispersion on the specific activity of platinum towards the hydrogenation of benzene (Ref. 68).

Sintering temperature	120	250	300	400	500	600	800
Pt crystallite size, Å	45	220	210	360	640	980	890
Pt surface area, $m^2 g^{-1}$	2.0	1.32	1.52	3.0	1.53	0.2	0.04
Specific activity (molecules cm^{-2} Pt s^{-1}) × 10^{-13}	2.8	2.7	3.2	1.4	1.3	inactive	

Boudart and coworkers [70] studied the effect of crystallite size on the catalytic activity of platinum towards the hydrogenation of cyclopropane in order to account for the existence of an optimum particle size. Their measurements were made in a circulation system. The dispersion was varied by varying the platinum concentration and the temperature of heat treatment, and was characterised by the surface area as determined by H_2 adsorption, and also by the ratio of the number of surface atoms to the total number of atoms (%-age dispersion). For comparison, Pt foil 12.7 μm thick was also examined. It was found (Table 15) that the specific activity remained relatively constant (within a factor of 3) in spite of very large differences in dispersion (20 000-fold) and in the nature of the carrier.

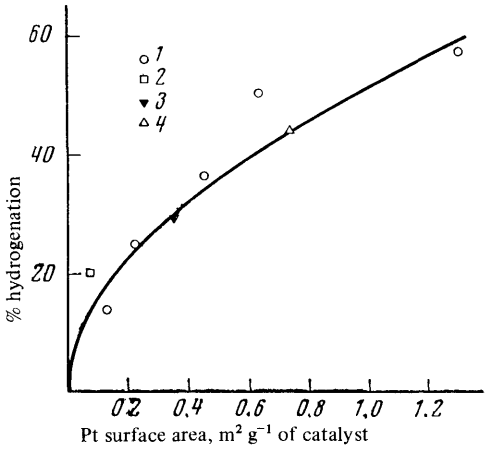


Figure 8. Influence of platinum surface area on the extent of hydrogenation of aromatic compounds in a petroleum fraction (Ref. 69): *1*) normal catalyst preparation, *2*) heated at 760°, *3*) heated in rotating furnace, *4*) impregnated 5 times.

Table 15. Effect of dispersion on the activity of platinum towards the hydrogenation of cyclopropane (Ref. 70).

Catalyst	Fraction of surface Pt atoms, %	Specific surface area of Pt, μmole H_2 g^{-1}	Activity at 0°	
			total mole C_3H_6 min^{-1} g^{-1}	specific mole C_3H_6* min^{-1} cm^{-2} Pt
0.3% Pt on η-Al_2O_3	44	10.2	82.4	8.2
0.3% Pt on γ-Al_2O_3	59	13.5	100	7.4
0.6% Pt on γ-Al_2O_3	73	33.5	186	5.4
1.96% Pt on η-Al_2O_3	64	97.0	637	6.5
ditto after sintering	7 6	11.5	44	3.8
4.3% Pt on silica gel	17	57.3	160	2.8
Foil (100% Pt)	0.0039	0.55	1.4	2.5

*Calculated from data in Table 1 of Ref. 70.

To explain these "strange" results the authors proposed the concept of "easy" and "difficult" catalytic reactions. In the former, most of the surface sites are active, and therefore the non-uniformity of the surface is immaterial. In the "difficult" reactions, on the other hand, surface non-uniformity can be expected to play an important role, and hence the reaction rate should be influenced by the dispersion of the metal, the method of preparation, and other factors. In a more recent paper by Boudart [71] a typical "difficult" reaction is discussed in detail (the isomerisation and hydrogenolysis of neopentane). The activity in this case was measured in a micro-reactor operating under pulsed conditions.

As Table 16 shows, changes in dispersion and in the method of preparation of the catalyst give rise to substantial differences in specific activity and selectivity for this system: the activity in the isomerisation reaction varied by a factor of 15 and the activity in the hydrogenolysis reaction varied by a factor of 300; the selectivity varied by a factor of 100. The large differences in activity were explained by the need for three-point adsorption of the neopentane molecule: "triplet" sites, able to adsorb the reacting molecule in the appropriate configuration, must be present on the surface. The concentration of triplets can be expected to depend on the dispersion and on the method of preparation of the catalyst.

Table 16. Specific activity and selectivity of platinum towards the isomerisation and hydrogenolysis of neopentane (Ref. 71).

Catalyst		Disperseness, %	Specific activity, (molecules Pt $atom^{-1}$ s^{-1}) × 10^3		Selectivity N_I/N_H
Pt content, wt.%	Carrier		isomerisation N_I	hydrogenolysis, N_H	
0.6	γ-Al_2O_3 [a]	73	2.6	4.7	0.55
1.96	η-Al_2O_3 [a]	64	5.3	13.0	0.41
0.60	γ-Al_2O_3 [b]	73	2.8	1.9	1.5
1.96	η-Al_2O_3 [b]	64	3.4	2.3	1.5
4.3	SiO_2	17	3.8	13	0.29
1.0	Spheron [c]	12	1.1	0.04	27
1.96	η-Al_2O_3 [d]	7.6	11	4.5	2.4
100	— [e]	0.028	0.73	0.08	9.1

Note. [a] reduced in H_2 at 425° for 10 h; [b] ditto, at 500°; [c] reduced at 500°, vacuum-baked at 900° for 16 h, stored in air, and reduced as for "b"; [d] heated in a stram of H_2 at 650° and reduced as for "b"; [e] heated in hydrogen and oxygen alternately, and finally reduced as for "b".

Boudart's hypothesis was put to the test by other workers. In one of the most interesting investigations of this topic, due to Dorling and coworkers [72], the activity of platinum towards the hydrogenation of ethylene was studied as a function of crystallite size and method of preparation. Catalysts were prepared by impregnating silica gel with a solution of H_2PtCl_6, and by adsorption of ammine. The platinum content, and the reduction conditions, were also varied. The catalytic activity was measured in a flow apparatus. Catalyst poisoning by the decomposition products of ethylene was observed in all cases (Table 17). The specific activity was found to vary by more than 2 orders of magnitude as a result of changes in Pt content and conditions of preparation. With the catalysts prepared by impregnation with H_2PtCl_6, samples containing less than 1% of Pt had the lowest activity. The highest activity was found in samples containing 1% Pt or more, and reduced at 80°. As the reduction temperature was raised, the activity fell to a limiting value of about 2×10^{12} molecules cm^{-2} Pt s^{-1}. Samples prepared from the ammine had an approximately constant specific activity of $2-3 \times 10^{12}$ molecules cm^{-2} Pt s^{-1}. From these results the authors concluded that the specific activity of platinum is constant ($2-3 \times 10^{12}$ molecules cm^{-2} Pt s^{-1}), and independent of the platinum crystallite size. The low specific activity of samples prepared by impregnation and containing less than 1% of platinum is due to poisoning effects, which can be very marked in catalysts with a low surface area. The enhanced activity of samples reduced at 80° is due to the promoting effect of traces of Cl, which are removed at higher reduction temperatures. Thus, the observed differences in specific activity are fortuitous.

Kraft and Spindler[73] studied the effect of dispersion on the activity of platinum (supported on Al_2O_3) towards the dehydrogenation of cyclohexane and the dehydrocyclisation of n-heptane. The activity was measured in a flow apparatus, and was characterised by the extent of reaction. The specific activity at low extents of reaction (23–31%) was found to be constant; at higher extents of reaction the specific activity fell by a factor of 3.5–4. This effect was ascribed to the approach to equilibrium. In the dehydrocyclisation of n-heptane no simple relationship between dispersion and specific activity was found.

Table 17. Effect of dispersion and preparative conditions on the specific activity of platinum towards the hydrogenation of ethylene (Ref. 72).

Catalyst	Average crystallite size, Å	Pt surface, $m^2 g^{-1}$	Reduction temp., °C	Specific activity at −80° (mol. cm^{-2} Pt s^{-1}) × 10^{-12}	Comments
Impregnated < 1% Pt	30—40	0.1—0.5	210	0.1—0.6	Low specific activity due to poisoning
Heated at 600°	200	0.2	80	3	
Impregnated 3.4% Pt	40	2	80	20	Specific activity decreasing due to loss of Cl_2 during reduction
			210	7	
			500	2	
Impregnated 9.8% Pt	50—75	3—5	80	15	
			210	8	
			500	2	
Impregnated 1-11.5% Pt	30—60	0.8—4.5	80	5—23	—
			210	2—8	
Ammine adsorption 2.45% Pt	13—30	3—4	300	2—3	Approximately constant specific activity

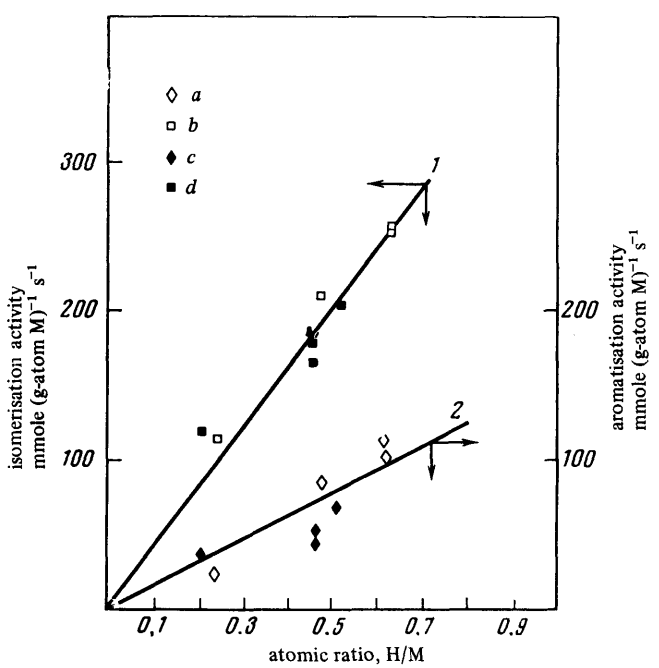


Figure 9. Effect of dispersion on the activity of platinum towards the isomerisation (*1*) and aromatisation (*2*) of hexane (Ref. 74): *a*) and *b*) 0.5% Pt; *c*) and *d*) 1.0% Pt.

Dautzenberg and Platteuw[74] studied the influence of dispersion on the activity of platinum towards the isomerisation and cyclisation of hexane. The measurements were made in the flow regime. Aluminium oxide, which is inert in isomerisation reactions, was chosen as the carrier. The platinum was deposited from $Pt(NH_3)_4(OH)_2$ solution in order to avoid the inclusion of acidic groups. It is evident from Fig. 9 that in both reactions the activity is directly proportional to the surface area of platinum. These results were confirmed by a subsequent observation[75] that the selectivity in the isomerisation of n-hexane is unaffected by changes in platinum particle size from <10 to ~80 Å.

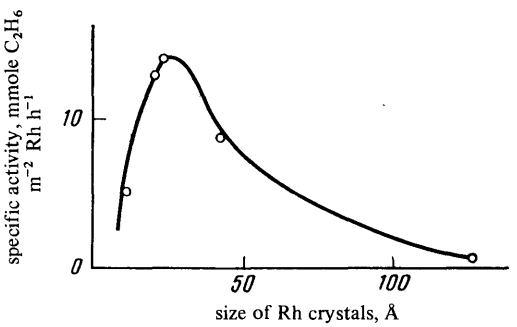


Figure 10. Length of crystallite edge against the specific activity of rhodium in the hydrogenolysis of ethane (Ref. 76).

The specific activity of rhodium towards the hydrogenolysis of ethane has been studied[76] as a function of particle size. The reaction rate was measured in a pulsed reactor. The specific activity was characterised by the number of millimoles of ethane reacting per hour on a square metre of rhodium surface at 253°. As Fig. 10 shows, samples in which the rhodium crystallites have a diameter of ~20 Å have the highest activity. When the crystallite size is decreased to 10 Å the specific activity falls by a factor of 3. The specific activity of coarsely gound samples of massive rhodium, and of samples deposited and heat treated at 800°, is 20–40 times lower than the maximum.

The effect of particle size on the activity of platinum in thin-film form towards the hydrogenolysis of n-hexane, 2- and 3-methylpentane, and methylcyclopentane has been studied[77] under static conditions. The reaction rate fell rapidly during the course of the reaction, reaching a steady value at an extent of conversion of 0.1–0.2%. This effect can be ascribed to "self-poisoning" of the catalyst. When the platinum crystallite size is increased from 15 to 58 Å both the initial and the steady-state specific activity decrease by an order of magnitude.

McKee[78] studied the effect of dispersion on the activity of platinum black towards the cracking of propane in a static apparatus with an initial propane pressure of 17.5 mmHg. The dispersion of the metal was varied by varying the sintering temperature between 150 and 220°, and it was characterised by the surface area measured by nitrogen adsorption. The particle size of the catalysts

was not stated. The activity fell during the reaction owing to the formation of a carbon deposit. The catalytic activity of the platinum (Fig. 11) decreases as the extent of sintering increases: in order to produce a measurable rate of reaction the surface area of the sample must be greater than some minimum value (depending on the reaction temperature). The dispersion also influences the activation energy of the reaction, which increases from 12 to 24 kcal mole^{-1} as the samples are more heavily sintered. These observations are explained by assuming that sintering causes a decrease not only in surface area but also in the concentration of surface defects which behave as active centres in the cracking reaction.

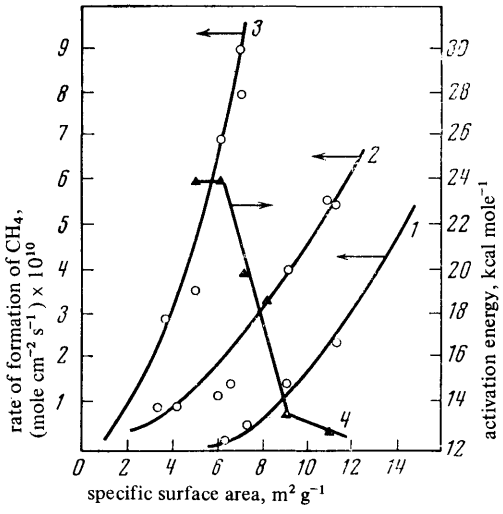


Figure 11. Effect of surface area on the activation energy and activity of platinum black towards propane cracking at different temperatures: *1*) 153°, *2*) 180°, *3*) 200°, *4*) activation energy (Ref. 78).

The specific activity of platinum samples of different degrees of dispersion towards the exchange reaction $HDO + H_2 \rightleftharpoons H_2O + HD$ has been studied[79] under flow conditions. The catalysts were prepared by three methods, and within each series the particle size was varied from 5 to 250 Å. The platinum surface area was measured by H_2 adsorption. The specific activity was characterised by the rate constant per unit surface area. By varying the sintering temperature the specific activity within each series could be varied by a factor of 3, reaching a maximum after sintering at 500°. Varying the crystallite size from 5 to 250 Å produced a change in the specific activity at 127° from 1.9×10^{-8} to 5×10^{-8} mole D_2 cm^{-2} s^{-1}.

Nickel. Rienäcker and coworkers[80] studied the activity of nickel powder and of heat-treated sheet nickel towards the decomposition of formic acid. In spite of the very large (more than an order of magnitude) difference in dispersion, the specific activity of the catalysts differed only by a factor of 1.5.

A group of Czech workers[81-83] has investigated the effect of dispersion on the activity of a nickel–magnesia catalyst towards the hydrogenation of benzene. The catalysts were prepared by thermal decomposition of the double oxalate of nickel and magnesium. Particle size was determined by X-ray diffraction and thermomagnetic methods.

Table 18. Effect of crystallite size on the specific activity of nickel in the hydrogenation of benzene at 40° (Ref. 81).

Sample No.	Prepared from	Metallic nickel content, wt %	Nickel surface m^2 g^{-1}	Crystallite size, Å	Specific activity, (mole min^{-1} m^{-2} Ni) × 10^7
7	Mixed Ni and Mg oxalates	32.3	97.0	22	4.9
11	ditto	86.6	52.0	148	4.9
3	Nickel oxalate	100	11.6	580	7.8
6	ditto	100	3.6	1870	5.25

Table 18 shows that the specific activity of nickel is constant within experimental error in spite of large differences in dispersion. The authors point out that their value of the specific activity is close to that reported[25] by Lyubarskii ($3-5\times10^{-7}$ mole min^{-1} m^{-2}).

Table 19. Effect of crystallite size on the specific activity of nickel in the dehydrogenation of benzene (Ref. 84).

Nickel content, %	4.26	10.2	28.9	52.5
Ni surface area, m^2 g^{-1}	12.86	26.2	56.6	43.1
Average crystallite size, Å	12.0	15.1	19.2	50.6
Specific activity, μmole min^{-1} m^{-2} Ni	6.2	4.2	3.6	3.8

Rijnten and coworkers[84] also failed to observe a significant effect of crystallite size on the specific activity of nickel towards the gas-phase hydrogenation of benzene (Table 19). It is evident from the Table that even in the region of large changes in the relative numbers of centres with different coordination (12–50 Å particle size) the changes in specific activity are only marginal.

In contrast to these findings, Sinfelt and coworkers[85] (who studied the effect of crystallite size of nickel deposited on $Al_2O_3-SiO_2$ on the rate of hydrogenolysis of ethane) observed a sharp decrease in the specific activity of nickel with increase of crystallite size (Fig. 12). The same workers[86] reported a 50-fold increase in the specific activity for the hydrogenolysis of ethane associated with an increase in crystal size from 12 to 24 Å, but in this case the situation was complicated by a simultaneous increase in nickel content from 1 to 10%. There is also a large difference in specific activity between nickel catalysts supported on Al_2O_3 and on $Al_2O_3-SiO_2$, in spite of the similarity in particle size (Table 20).

Van Hardeveld and Hartog [87] found that the specific activity of nickel catalysts towards the deuteriation of benzene remains approximately constant as the nickel particle size is varied from 20 to 185 Å, but the relative rates of deuteriation and exchange are significantly affected.

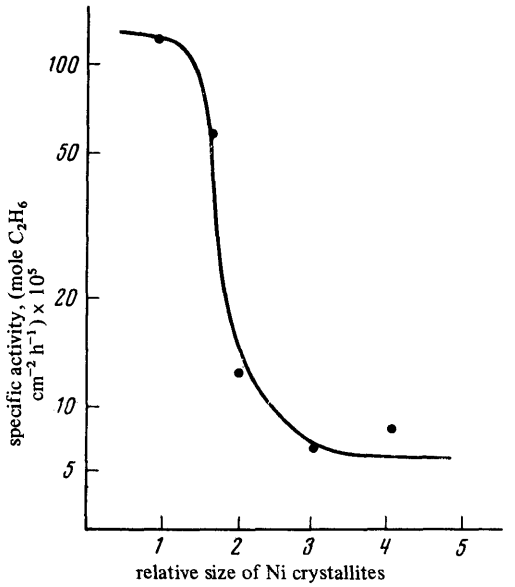


Figure 12. Specific activity of nickel in the hydrogenolysis of ethane at 267° against relative crystallite size. The size of the crystallites in the sample reduced at 370° is taken as unity (Ref. 85).

Table 20. Effect of crystallite size on the specific activity of nickel towards the hydrogenolysis of ethane (Ref. 86).

Ni content, wt.%	Carrier	Crystallite size, A	Specific activity, mole h^{-1} m^{-2} Ni
1	Silica gel	12	11
10	Silica gel	24	500
10	Al_2O_3	23	260
1	SiO_2 — Al_2O_3	26	0.08
10	SiO_2 — Al_2O_3	29	9.5

IV. DEPENDENCE OF THE SPECIFIC ACTIVITY OF CATALYSTS ON THE METHOD OF PREPARATION

Platinum and palladium. Schnabel and coworkers [88] studied the effect of the heat-treatment temperature of an activated charcoal on the specific activity of platinum (deposited on the charcoal) towards the dehydrogenation of cyclohexane, the C_5-dehydrocyclisation of iso-octane, and the hydrogenation of benzene. As the temperature was raised from 100 to 1070°, the specific activity of the platinum decreased by a factor of 2 for the first reaction and varied by not more than a factor of 4 for the second. The sample deposited on charcoal heat treated at 300° was inactive towards the hydrogenation of benzene. Samples prepared by depositing platinum on BAU charcoal heated at 1100° and treated by the Curtius method have a specific activity of 3.8×10^{-2} and 2.76×10^{-2} mole m^{-2} Pt respectively (i.e. practically identical). Another paper [89] from the same laboratory describes the changes in specific activity of platinum deposited on BAU charcoal heat treated at 300–2300° towards the C_5-dehydrocyclisation of iso-octane. It can be seen from Table 21 that the specific activity varies by less than a factor of 2.

Table 21. Specific activity of platinum on BAU activated charcoal towards the dehydrocyclisation of iso-octane (Ref. 89).

Carrier heat-treatment temperature, °C	300	1400	2000	2300	2800	1000 vacuum
Specific activity of Pt at 310° (mmole m^{-2} Pt h^{-1}) × 10^2	4.7	4.0	6.3	7.6	9.3	5.7

The specific activity of Pt and Pd catalysts prepared by different methods has been found [90,91] to be approximately constant also in respect of the hydrogenation of benzene.

Nickel. Tetenyi and coworkers [92] have studied the influence of method of preparation on the dispersion and specific activity of nickel black towards the dehydrogenation of cyclohexane and the decomposition of isopropanol and t-butanol. They were unable to establish any definite correlation between the activity and the dispersion of the nickel crystallites, the specific activity increasing more than 30-fold for relatively small changes in crystallite size. The conclusion from this work was that the specific activity depends on the method of preparation of the catalysts.

Crawford and coworkers [93], who studied the effect of sintering temperature on the specific activity of nickel black towards the hydrogenation of ethylene, disagree with this conclusion. They found that the specific activity varies only from 8.9 to 1.1 min^{-1} over a range of sintering temperatures between 25 and 400°, and they conclude that the loss of activity could be due to poisoning of the small catalyst surface by impurities evolved from the apparatus.

Catalysts prepared by reduction of NiO obtained by thermal decomposition of the hydroxide, basic carbonate, and acetate, and also by reduction of various mixtures of NiO, SiO_2, Al_2O_3, and Cr_2O_3 have been examined in the writer's laboratory [28]. Their catalytic activity towards the hydrogenation of benzene was found to be directly proportional to the surface area of metallic nickel and independent of the starting materials and of the method of preparation (Fig. 1).

Sinfelt and coworkers [94] studied the activity of nickel catalysts on silica gel towards the hydrogenolysis of ethane in a flow system. By varying the preparative conditions they were unable to vary the surface area by a factor of 3, but the specific activity varied only by a factor of 1.5.

Shephard [95] has described a detailed study of the effect of washing, and of heat treatment at 340–1160°, on the specific activity of an industrial nickel–alumina catalyst for the hydrogenolysis of propane. The catalytic activity was measured in a flow system. With the exception of one

sample, the catalytic activity before the leaching treatment was found to be proportional to the surface area of nickel. After being leached the catalysts contained a small amount of sodium, and their activity was somewhat higher. However, it is pointed out that these results could be due to insufficient precision in the measurement of surface area by hydrogen adsorption.

The specific activity of the nickel in nickel–chromia and nickel–magnesia catalysts for the hydrogenation of CO and CO_2 has been found to be independent of the temperature of heat treatment [96,97].

Vasserberg and coworkers [98] studied the effect of the preparation on the activity of nickel catalysts for the hydrogenation of CO_2. The catalysts were prepared by gas-phase deposition of carbonyl nickel on Al_2O_3 (series I) and by impregnation with a solution of $Ni(NO_3)_2$ (series II); three samples of industrial catalysts were also examined. Surface areas were measured by O_2 chemisorption. The activity was measured in a vacuum system with circulation, and characterised by the first-order rate constant of the reaction. It was found that samples of series I (containing less than 0.75% Ni) and of series II (containing 1.5% Ni or less) do not adsorb significant amounts of O_2 and have negligible catalytic activity. In samples with a higher nickel content the specific activity varies between 5.3 and 25.6×10^{-3} min^{-1} m^{-2} Ni.

Iron. Samchenko and coworkers [99,100] studied the effect of preparative conditions on the activity of doubly promoted iron catalysts in the synthesis of ammonia. The catalysts were characterised both in terms of total surface area and in terms of fractional occupancy of the surface by metallic iron, alkali, and aluminium oxide. The rate constants calculated for a unit area of alkali and Al_2O_3 were very variable, but the specific activity of the free iron surface was practically constant for all the samples, irrespectively of composition.

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The experimental work discussed in this review justifies the following statements: 1) in spite of the widely held view that the specific activity of catalysts should be a function of dispersion, method of preparation, etc., in the vast majority of cases the specific activity is found to be approximately constant; 2) contradictory results are reported by different workers: some workers find a constant specific activity whilst others, working on the same system, find large changes in specific activity under the influence of various factors. The constancy or otherwise of the specific activity is unrelated to the nature of the catalyst or to the type of reaction under study. In this Section we shall attempt to analyse the possible causes of these discrepancies, and to clarify as far as possible the validity of "Boreskov's rule" [55], which predicts an approximately constant specific activity.

The discrepancy between the results of different workers may be due to the following causes: 1) inadequacy of the experimental procedures used to determine the surface area of metal on the carrier, and also incorrect characterisation of the catalytic activity; 2) neglect of heat and matter transport processes; 3) influence of uncontrolled impurities in the catalyst and in the reaction mixture; 4) blocking of the surface by reaction products, and 5) measurements of the activity before the catalyst surface has reached a steady state in the reaction mixture.

In order to measure the specific activity correctly, the following conditions must be satisfied: a) the catalytic surface area (in this case, the area of metal on the carrier) must be measured correctly, and b) the catalytic activity must be correctly characterised. The surface area of metals on carriers is usually measured [101,102] under conditions when gas adsorption occurs only on the metal. The shortcoming of this method is the possible dependence of the adsorption capacity per unit area of the metal upon the dispersion. For example, the H/Pt or O/Pt ratio can vary from 1 to 2 when the particle size of Pt on Al_2O_3 is varied [103,104]. Similar effects have been observed on nickel. Hence, even if the true specific activity is strictly constant it is possible for the apparent specific activity to vary by a factor of 2 unless due allowance is made for changes in the gas/metal ratio.

There is still no generally accepted method of measuring the activity of catalysts. The most satisfactory method [18,19] appears to be to characterise the activity in terms of the rate constant. If the kinetic equation is not known, the activity of the catalyst can be characterised by the reaction rate at a given extent of reaction. Consistent results are obtained if the extent of reaction is small, the kinetic order of the reaction is nearly zero, and the system is not allowed to approach equilibrium. On the other hand, serious discrepancies can result if the extent of reaction is large enough to bring the system near equilibrium. The changes in specific activity reported by Larsen and coworkers [69] are probably due to this effect.

The effect of diffusion on catalytic reactions has been investigated by Boreskov [105–107], Slin'ko [108–110], and their coworkers. Diffusional limitations can have a very marked effect on the observed reaction rate. Thus, on varying the size of Al_2O_3 granules from 0.10–0.15 to 2–3 mm the specific activity of a given catalyst towards the decomposition of ethanol decreases by more than an order of magnitude as a result of diffusional control [111]. The extent of diffusional control depends on the porosity of the catalyst structure: the smaller the typical pore radius, and the larger the grain size, the lower will be the temperature at which rate limitation by the diffusion of reactants will set in [112]. If the experimental catalysts have different pore structures, and the measurements are not made under activation-limited conditions, the observed activities can be in error through differences in the amount of diffusional limitation. Furthermore, the imposition of diffusional limitation influences the selectivity of the catalyst in the direction of smaller yields of intermediates and greater yields of final products [113]. Hence, one of the most important prerequisites to ensure reliable results is the adoption of activation-limited conditions. Unfortunately, only a minority of authors specifies whether their results were obtained under activational or diffusional control. Very probably, some of the faster reactions studied on relatively large-grained catalysts were taking place in the diffusion-limited region. This effect could explain the reported dependence [92] of catalytic activity on crystallite size, since that investigation of a very active catalyst (nickel black) was carried out without the necessary precautions.

Impurities, often uncontrolled, can contaminate the catalyst both at the preparation stage and during the investigation. The reaction can be inhibited or accelerated by impurities. Thus, small amounts of alkali metals are known to lower the activity of oxides towards reactions involving an acidic mechanism [114,115], and traces of Al_2O_3 (less than 0.1%) can increase very substantially the activity of silica gel [116,117]. Similar effects have been reported [118,119] for metallic catalysts. Dorling and coworkers [72] have shown that the large changes in the

specific activity of platinum towards the hydrogenation of ethylene brought about by changes in preparative conditions are due to traces of HCl, which is sorbed by the catalyst and has a promoting effect on the reaction. Higher heat-treatment temperatures decrease the surface area of platinum and at the same time remove the HCl, thus lowering the specific activity.

Changes in catalytic activity associated with the take-up of impurities from the reaction medium are due to the formation of surface compounds between the impurity and the catalyst. The mechanism of the poisoning effect, and its reversibility, are determined by the stability of this compound under the experimental conditions. If the compound is not very stable it can be dissociated by lowering the partial pressure of the impurity or raising the temperature, and the activity of the catalyst can be restored to its initial value [120]. If, on the other hand, a very stable surface compound is formed by adsorption, the poisoning effect is irreversible [120-122].

Quite small concentrations of impurities are usually sufficient to produce significant poisoning effects. For example, Lyubarskii found [26] that a sulphur concentration of 10 parts per million (p.p.m.) in benzene is sufficient to cause appreciable poisoning of a nickel–chromia catalyst. In another investigation [123], 5 p.p.m. of water were found to deactivate small quantities of catalyst completely towards the polymerisation of ethylene: to obtain a measurable reaction rate the amount of catalyst in the reactor had to be kept above some "threshold" level. A similar effect has been reported by Poltorak and coworkers [124] for the decomposition of H_2O_2.

The poisoning effect of impurities will be stronger, of course, the higher the impurity concentration and the smaller the surface area of the active component of the catalyst. This is the most likely explanation of the large differences in specific activity obtained from studies in different laboratories of the effect of dispersion and of the temperature of heat treatment. Thus, Dorling and Moss [68] observed an approximately constant specific activity with increasing heat-treatment temperature until the surface area of Pt had fallen to 0.2 $m^2 g^{-1}$, when the catalyst suddenly became inactive. Similarly, Crawford and coworkers [93] found that the specific activity of their nickel films fell by a factor of 3 when the annealing temperature was raised from 300 to 400°. It is quite possible, also, that the deactivation of nickel catalysts containing small amounts of nickel reported by Dergachev and coworkers [98] was due to poisoning by traces of mercury (present in the vacuum system as a manometric fluid).

The opposite effect, activation of the catalyst by impurities in the reacting system, is far less commonly observed [72].

It follows from these considerations that a correct judgement of the constancy or otherwise of the specific activity can be made only in the knowledge of the impurity content of the reacting system and of the type of interaction to be expected between the impurity and the catalyst.

In addition to the impurities introduced with the reactants, any relatively involatile reaction products retained on the catalyst surface can affect the reaction rate. Catalyst poisoning by "fragments" of organic molecules has been observed in many reactions, including simple reactions (like the hydrogenation of ethylene [72,126]) as well as reactions involving the decomposition of large organic molecules [125].

Carbonisation of the catalyst can affect the selectivity as well as the rate of the reaction. Thus, Panchenkov and coworkers [127] found that the selectivity of an industrial alumina–silica catalyst for the cracking of n-decane changes very significantly with increasing reaction time (and hence extent of carbonisation of the catalyst): the yield of intermediate products (olefins) goes through a maximum, and the yield of the final products increases continuously.

We may conclude from these observations that time-variations in the activity of the catalyst may be responsible for some of the erroneous results obtained in studies of the influence of various factors on the specific activity. McKee's results [78] for the cracking of propane on platinum black were very probably vitiated by the non-stationary activity of the catalyst.

Changes in catalytic activity due to changes in catalyst composition brought about by interactions with the reacting medium are less clearly recognised, but nonetheless very common. According to Boreskov [128], these interactions can lead to: 1) deep-seated changes in chemical composition, accompanied by phase transitions of the active component; 2) changes in chemical composition without phase transitions; 3) compositional changes in the surface layer of the catalyst. All these changes are accompanied by more or less pronounced changes in specific activity. A good example of this effect is Boreskov and Matveev's observation [129] of a 500-fold increase in the specific activity of zinc oxide due to partial reduction of the catalyst during the decomposition of methanol: a phase of metallic zinc is not formed, but the stoichiometric ratio of oxygen to zinc in the oxide phase is lowered by the reducing action of the medium. A similar effect takes place during the reaction between H_2 and O_2 on platinum [130]. Boreskov also showed that the interaction between the catalyst and the reacting system can produce changes in the kinetics of the reaction as well as in the specific activity of the catalyst [131].

The steady-state composition (and hence activity) of the catalyst depends on the composition of the reacting system and on temperature: sufficient time must be allowed for the catalyst to reach a steady state.

Different workers, investigating similar (or even identical) catalysts and reactions by flow and by pulsed methods, usually find that the specific activity is constant if they are using the flow method and variable if they are using pulsed methods. It seems likely that in the pulsed regime [36-38,85,86] the surface layer cannot reach steady state, and the observed specific activity is seriously in error. We may suggest that the large differences in specific activity observed in pulsed measurements [36-38,85,86] are not due to the "difficulty" of the reaction, or to the "need" for a special surface topography [71], since other workers [33,35,70,74,75] found no evidence of this type of specificity. The most likely reason for the discrepancy is the use of a pulsed method to measure the activity, since it is difficult to believe that steady state can have been achieved in the short time (3–5 min) allowed for each experiment.

Thus, this review of the published work leads us to conclude that in most cases the specific activity is found to be constant if the correct experimental procedure has been used. Large changes in dispersion, and in the method of preparation of the catalyst, yield only a 3-fold change in specific activity. This relative constancy may be due to interaction between the catalyst surface and the reaction medium, which converts the initial surface structure into a final state independent of the previous history of the catalyst. Lastly, we cannot exclude the possibility of genuine differences in specific activity arising from the

retention of a non-steady-state structure in low-temperature reactions, but we have not found any experimental evidence of this effect in the published literature. Significant differences in specific activity are not encountered under the normal conditions of the majority of industrial catalytic processes.

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Institute of Catalysis
Siberian Section of the
USSR Academy of
Sciences, Novosibirsk