57. *Heterogeneous Catalysis. Part II. Hydrogenation by Binary Alloys.*[*]

By Peter W. Reynolds.

The simple geometrical theory of catalytic activity is inadequate to explain the large difference in activity for hydrogenation between the metals of group 8 and those of group 1b. The alternative correlation of the catalytic activity with the electronic properties of the metal, discussed in Part I of this paper, associates the high activity of the group 8 metals with the holes in their 3*d*-, 4*d*-, and 5*d*-bands which are filled up in the metals of group 1b. By the examination of three series of nickel–copper catalysts it has been shown that the activity of the nickel declines in parallel with the filling of the holes in its 3*d*-band by the valency electrons of the copper, and that this occurs while the crystal lattice is expanding slightly in the direction of increased activity on the simple geometric view.

It seems reasonable to believe that the interatomic spacings in the surface planes of solid catalysts must be closely related to the parameters of molecules which react upon them (see review by Griffith, " Advances in Catalysis," 1948, vol. I, p. 91). Beeck and his co-workers (Beeck, Smith, and Wheeler, *Proc. Roy. Soc.*, *A*, 1940, **177**, 62) added considerable weight to this evidence by their work on the hydrogenation of ethylene over evaporated films of Group 8 metals. Random films of nickel, evaporated *in vacuo*, had only one-fifth of the specific activity of oriented films evaporated in a low pressure of an inert gas. The catalytically active surface

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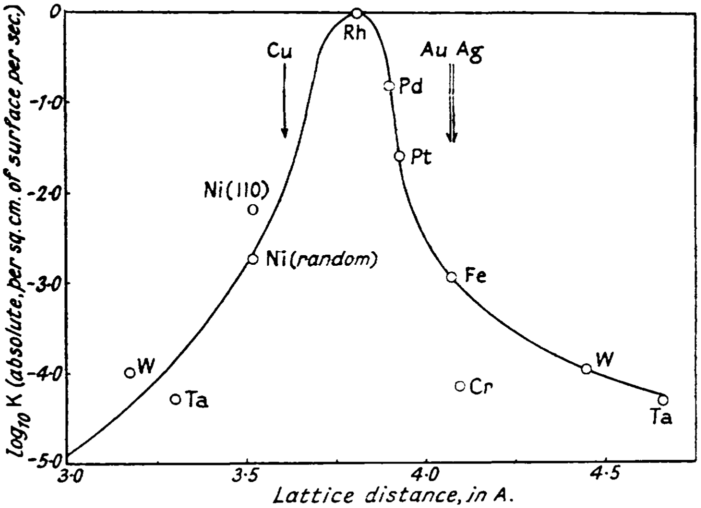
was composed of spire-like prominences (Beeck and Rust, U.S.P. 2,223,777), so that the films were porous and the total surface and activity practically proportional to the weight of the deposit. In the oriented deposits the 110 planes of the nickel were parallel to the backing. In the absence of further evidence it does not seem necessary to conclude with these authors that the 110 planes were therefore preferentially exposed, but unless the presence of the inert gas had profoundly modified the structure of the metallic deposit the activity of the nickel must have been affected by its crystallographic orientation.

Following this indication Beeck (*Review Mod. Physics*, 1945, **17**, 61) has related the activity of metal catalysts in the hydrogenation of ethylene to their crystal parameters. His conclusions are reproduced in Fig. 1 where the logarithm of the reaction-velocity constant is plotted against the parameter of the metal. It is not always clear on what grounds this parameter has been selected from the alternatives available, but in the case of the face-centred cubic metals of Group 8 (nickel, rhodium, palladium, and platinum) it corresponds with the cell dimension.

FIG. 1.

Activity of metals in hydrogenation of ethylene v. *crystal parameter* (*Beeck*).



It seems probable that such spatial factors must play their part, but even if the suggested geometrical relations are necessary for high activity, they are certainly not sufficient. Thus copper, silver, and gold crystallise with a face-centred cubic lattice, and their parameters (Fig. 1) suggest high activities where in fact there is relatively little (copper) or practically none (silver and gold). Moreover it is always possible that these geometric correspondences are only incidental, and the prevalent tendency to hunt among the Miller indices for a plane with a promising spacing is viewed with suspicion.

In Part I of this paper an attempt was made to find alternative, more fundamental correlations between the catalytic activity and the physical structure of solids. In the simplest example of hydrogenation over metallic catalysts, the activity of Group 8 metals is attributed to the unfilled electron levels in their 3*d*-, 4*d*-, and 5*d*-bands. The relative inactivity of copper, silver, and gold is thus accounted for, because in these metals those bands are filled. Moreover, it is to be expected that any factor which tends to fill up the *d*-bands in Group 8 metals will result in a corresponding decrease in their activity.

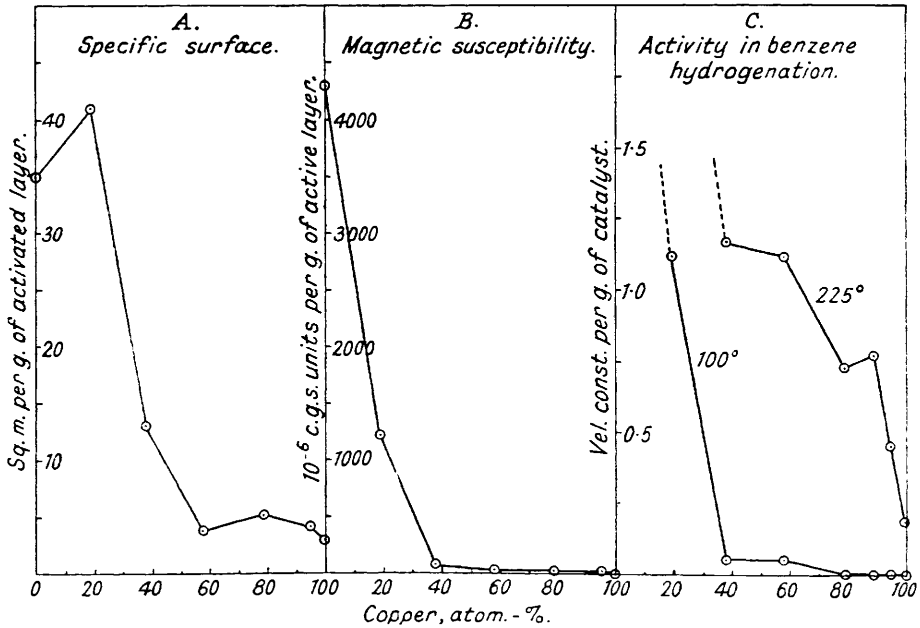
It is therefore of particular interest to study the physical and catalytic properties of the binary alloys of Group 8 metals with one another and with the metals of Group 1b (copper, silver, and gold). Work on these systems is in progress in these laboratories. The principal effort is being directed to the study of spectroscopically-pure metallic foils, but results already obtained on industrial catalysts in the nickel–copper system support the theoretical picture given in Part I and are discussed below.

Nickel and copper both crystallise with a face-centred cubic lattice; the lattice constants are 3·517 and 3·608 A. respectively. There is a complete range of homogeneous solid solution in their binary alloys within which the crystal parameter varies almost linearly with the atomic composition (Owen and Pickup, *Z. Krist.*, 1934, **88**, 116). Beeck's correlation suggests an increase in the specific activity of nickel by the inclusion of copper which expands the lattice. The electronic picture, on the other hand, suggests a marked fall in the activity of the nickel as the valency electrons of the added copper fill the holes in its 3*d*-band. In pure alloys at equilibrium these holes are just filled by the addition of about 60 atom-% of copper. The ferromagnetism, as measured by the large magnetic susceptibility at a fixed field strength, diminishes very rapidly at about the same composition (Kaufmann and Starr, *Phys. Review*, 1943, **63**, 445).

Data in the literature on the properties of nickel–copper catalysts are inadequate. Dupont and Piganiol (*Bull. Soc. chim.*, 1939, [v], **6**, 322) studied the influence of contamination of Raney nickel by copper on its activity for the hydrogenation of *allo*ocimene; the activity per unit weight of nickel decreased approximately linearly with increasing copper content to a low value at 50% of copper. Rienäcker (see Himmler, F.I.A.T. Review of German Science, Physical Chemistry, 1939—46, p. 97) examined nickel–copper foils for the hydrogenation of ethylene and the dehydrogenation of formic acid, and reduced nickel–copper oxide for hydrogenation of cinnamic acid. In each case the activity–composition curve exhibited a sharp step down to the low activity of copper, but the positions of these steps in the two cases were widely different. The specific surfaces of the catalysts were not measured.

FIG. 2.

Properties of alloy-skeletal powder nickel–copper catalysts.

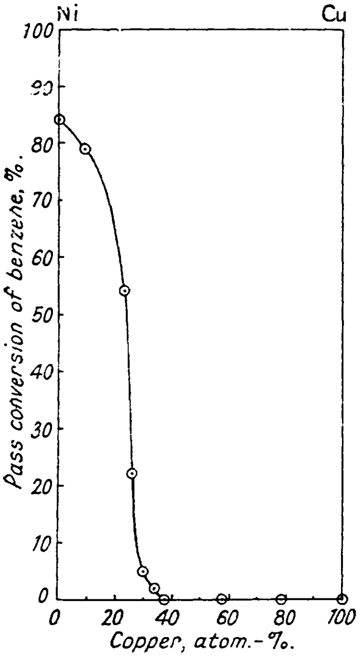


In the present work, two types of alloy-skeletal nickel–copper catalysts have been examined for hydrogenation of benzene, and reduced nickel–copper oxide on kieselguhr catalysts for hydrogenation of styrene. The specific surfaces and the magnetic susceptibilities of the catalysts were determined.

Powdered nickel–copper catalysts of the Raney type were prepared by exhaustive extraction of nickel–copper–aluminium alloy powders with aqueous sodium hydroxide. The results of specific surface and magnetic susceptibility measurements in arbitrary units are summarised in Fig. 2*A* and 2*B*, and their activities in the liquid-phase hydrogenation of sulphur-free benzene at 250 atmospheres are shown in Fig. 2*C*. The highly exothermal nature of the reaction made it impossible to determine the very high activity values for the pure nickel catalysts in the apparatus employed. This series of catalysts exhibited a marked fall in specific surface with increasing copper content until at 40% of copper the specific surface had fallen to 11% of the value for pure nickel. The activity at 100°, measured per unit weight of catalyst,

FIG. 3.

Activity of foraminate nickel–copper catalysts in benzene hydrogenation at 1 atm. and 100°.



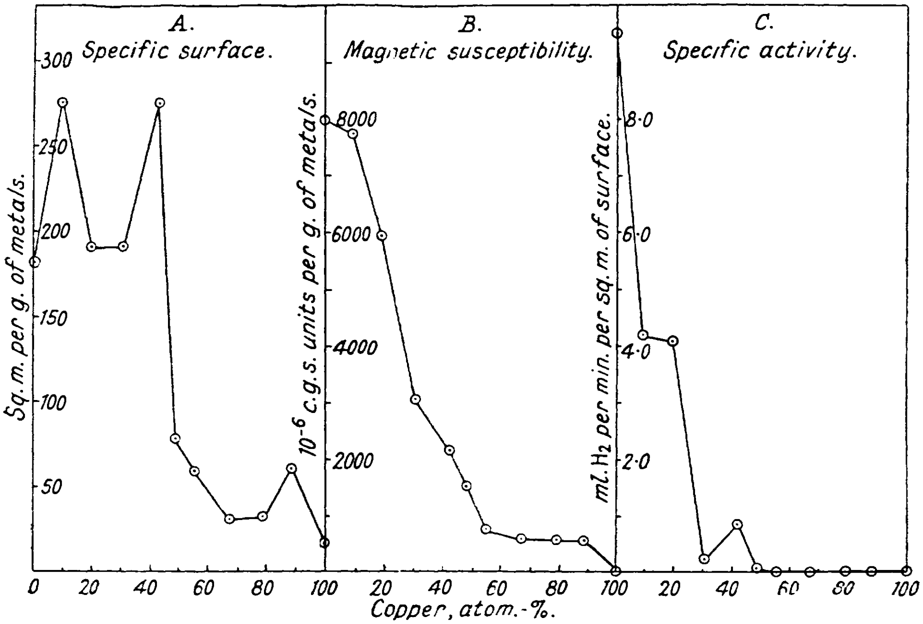
fell at a greater rate to a negligible value at the same composition. The fall in activity is thus greater than can be accounted for by the simultaneous drop in the specific surface, and it is noteworthy that it was at this composition also that the magnetic susceptibility at a fixed field strength fell to an insignificant value. Activity measurements at 225° followed the same trend, but these showed also a small decreasing residual activity at the higher copper contents, which presumably reflects the slight incompleteness of filling of the *d*-band indicated, even in alloys at equilibrium, by residual ferromagnetism at copper contents higher than the 60 atom-% where the *d*-band is ideally filled (Kaufmann and Starr, *loc. cit.*). A 100% copper catalyst prepared from spectroscopically pure metals had only one-fifth of the activity of that described above; this result suggests that an ideally pure copper catalyst would be inactive for hydrogenation of benzene. This conclusion is in line with the work of Ipatieff, Corson, and Kurbatov (*J. Physical Chem.*, 1939, **43**, 589) and of Morris and Selwood (*J. Amer. Chem. Soc.*, 1943, **65**, 2245).

Granular alloy-skeletal nickel–copper catalysts, prepared by surface activation of similar alloys, were tested in vapour-phase benzene hydrogenation at 100° at atmospheric pressure. The results are summarised in Fig. 3. Activity fell off rapidly as the copper content of the active nickel–copper layer increased from 20 to 30 atom-%; catalysts with 40 atom-% or more of copper were inactive. If it may be assumed that the specific surface and magnetic properties of the activated layer on the outside of these granules followed the same trends as in the powdered catalysts, then in this case also the specific activities disappeared with the large ferro-magnetism.

Reduced nickel–copper oxide on kieselguhr was examined in the liquid-phase hydrogenation

FIG. 4.

Properties of reduced-oxide nickel–copper catalysts.



of methanolic styrene at 30° and atmospheric pressure. The specific surface and magnetic susceptibility measurements at a fixed field strength are summarised in Fig. 4*A* and 4*B*, and the catalytic activities per unit area of active surface in Fig. 4*C*.

There is thus in all these catalysts a parallel decline in specific activity and magnetic susceptibility at a fixed field strength as the content of copper is increased. The values of both become very small or zero at 30—40 atom-% of copper in the alloy-skeletal catalysts and at 50—60 atom-% in the reduced oxide catalysts. The occurrence of the critical composition at values below the 60 atom-% which would have been expected from the properties of the pure alloys at equilibrium is undoubtedly caused by the complexity of these actual catalysts. Yet the results do show that the catalytic activity of nickel falls away in parallel with the filling of its *d*-band holes by the valency electrons of the copper, and that this occurs while the lattice is expanding in the direction of increased activity on the simple geometric view.

EXPERIMENTAL.

Alloy-skeletal Catalysts.—Alloy melts were prepared in graphite crucibles from Mond nickel pellets, electrolytic copper of greater than 99·99% purity, and virgin aluminium of greater than 99·5% purity. All the alloys were made to contain 50% by weight of aluminium, except those for the pure nickel and pure copper catalysts which contained 58 and 45% by weight of aluminium respectively. The homogeneous melts were chill-cast on to copper moulds, and the cooled slabs crushed and screened. Granules of approx. 1/8″ diameter were selected for the foraminate catalysts, and the remaining material was ground to pass a 200 B.S. sieve mesh. (Alloy-skeletal catalysts in robust granular form, prepared by surface extraction of alloy granules, are termed " foraminates " in contradistinction to the Raney-type catalysts which are in powder form. Aluminium extraction in the latter is nearly complete.) These alloys were prepared by Messrs. Murex Ltd., Rainham, Essex.

For the Raney-type catalysts, amounts of powder containing 5 g. of active metals were added during 5 minutes to 100 ml. of a mechanically stirred boiling 30% aqueous solution of sodium hydroxide. The mixture was digested for 30 minutes, the catalyst then allowed to cool and settle, and the clear liquid decanted from the sludge. The catalyst was then re-treated by boiling for 30 minutes with a further 100 ml. of 30% alkali. This liquor also was removed by decantation, and the catalyst washed by decantation with ten 500-ml. portions of distilled water at 40°, three 150-ml. portions of " refined dry " methanol, and finally with three 100-ml. portions of sulphur-free benzene. Care was taken at every stage to prevent loss of catalyst in the decantations. The activated powders were kept under benzene and used as soon as possible.

Foraminate catalysts were prepared from the same alloys by extracting the 1/8″ granules with 2% aqueous sodium hydroxide passed over them at 25 ml. per ml. of catalyst per hour at 100° until 20% of the original aluminium was removed. The progress of the extraction was followed by measuring the hydrogen evolved. The activated granules were then washed for 6 hours with cold distilled water at the same space velocity, stored under water, and used as rapidly as possible. These foraminates consisted of an activated alloy-skeletal surface layer on an unaltered alloy core.

Even the finely divided activated powders retained unextractable aluminium in their interior. The total residual aluminium in the activated 42 : 58 nickel–aluminium powder was only 2·4% and in the activated 55 : 45 copper–aluminium 6·3%. In the 20 : 30 : 50 nickel–copper–aluminium alloy, however, it was as high as 37·8%, and further extraction in molten sodium hydroxide did not greatly reduce these figures. Catalysts in the middle of the series must therefore be regarded rather as finely divided foraminates than as Raney powders, each little particle consisting of an activated surface on an unaltered alloy core. The extent of extraction was, however, more than sufficient to develop the maximum activity of the catalyst.

Reduced-oxide Catalysts.—The reduced-oxide nickel–copper on kieselguhr catalysts were prepared by precipitation from the mixed metallic nitrates. The materials taken in each case corresponded to 20% by weight of the mixed oxides on 80% of Johns Manville's " Celite 519-A." In each preparation 80 g. of iron-freed kieselguhr were suspended in 400 ml. of solution containing the requisite nickel and copper nitrates, and the metals salts were precipitated at room temperature by the stirred addition of a slight excess of solid ammonium hydrogen carbonate. The products were heated for 1 hour at 100° with stirring and then dried at 120° without filtration. The ammonium nitrate was decomposed and the basic carbonates of the metals converted into the oxides by cautious ignition in open dishes, followed by calcination for 4 hours at 400°. The powders were reduced for 4 hours at 500° in purified electrolytic hydrogen immediately before use.

Specific Surface.—The total specific surface areas of the powdered alloy-skeletal and reduced-oxide catalysts were measured by argon adsorption at the temperature of boiling liquid oxygen using the method of Brunauer, Emmett, and Teller. The results are given in Tables I and II. The areas of the powdered alloy-skeletal catalysts have been recalculated to refer to the active layer on the assumption that the whole of the residual aluminium is present in the unaltered alloy core, and these recalculated values are plotted in Fig. 2*A*.

Specific-surface measurements were not attempted on the foraminate catalysts, but it is probably safe to assume that the specific surface of the activated layer on the 1/8″ granules varied with composition in the same manner as that on the particles passing a 200 B.S. mesh.

The extent of coverage of the kieselguhr in the reduced-oxide catalysts is unknown. The small contribution of the kieselguhr to the total surface has therefore been neglected in calculating the specific surface of the active metals. The area of the " Celite 519-A " used was 3·4 m.^{2} per g., so that its maximum contribution would correspond to 17 m.^{2} per g. of active metals. The incompleteness of reduction of the oxides has also been neglected in the calculations. The values are plotted in Fig. 4*A*.

TABLE I.

Alloy-skeletal powder catalysts.

Alloy composition, % by wt.			Residual aluminium, %.	Atom-% of copper in activated layer.	Specific area.	
Ni.	Cu.	Al.			Sq. m. per g. of powder.	Sq. m. per g. of activated layer.
42	0	58	2·4	0	34	35
40	10	50	24·2	19	28	41
30	20	50	33·6	38	6·6	13
20	30	50	37·8	58	1·5	3·8
10	40	50	29·1	79	3·0	5·1
2·5	47·5	50	11·0	95	3·6	4·1
0	55	45	6·3	100	2·8	3·0

TABLE II.

Reduced-oxide-on-kieselguhr catalysts.

Analysis of material ignited at 400°.		Atom-% of Cu in reduced metals.	Specific area of reduced catalyst:	
Ni, % by wt.	Cu, % by wt.		$m.^2$/g. of catalyst.*	$m.^2$/g. of metals.
15·9	0·0	0·0	29	182
14·1	1·6	9·5	44	278
12·4	3·3	19·7	30	191
10·3	5·0	30·9	29	192
8·6	6·8	42·2	43	278
7·6	7·7	48·4	12	78
6·8	9·2	55·5	9·4	59
4·8	10·8	67·5	4·9	31
3·0	12·3	79·1	4·9	32
1·7	13·9	88·3	9·5	61
0·0	15·4	100·0	2·6	17

* Weighed before reduction.

TABLE III.

Magnetic susceptibilities (at 4000 Oersted) of alloy-skeletal powder catalysts.

	Magnetic susceptibility in 10^{-6} c.g.s. units:			Magnetic susceptibility in 10^{-6} c.g.s. units:	
Cu, atom-%.	per g. of catalyst.	per g. of active layer.	Cu, atom-%.	per g. of catalyst.	per g. of active layer.
0	4200	4300	79	23	39
19	830	1220	95	10	11
38	42	85	100	4	4
58	17	43			

TABLE IV.

Magnetic susceptibility (at 4000 Oersted) of reduced-oxide catalysts.

	Magnetic susceptibility in 10^{-6} c.g.s. units:			Magnetic susceptibility in 10^{-6} c.g.s. units:	
Cu, atom-%.	per g. of reduced catalyst.	per g. of active metals.	Cu, atom-%.	per g. of reduced catalyst.	per g. of active metals.
0·0	1280	8000	55·5	118	740
9·5	1140	7750	67·5	94	590
19·7	950	5950	79·1	90	560
30·9	490	3060	88·3	87	545
42·2	345	2160	100·0	0	0
48·4	244	1530			

Magnetic Susceptibility.—Magnetic susceptibilities were measured by a Sucksmith balance at a fixed field strength of 4000 Oersted. The susceptibilities of the unactivated nickel–copper–aluminium alloys were all very small, and they have been neglected in calculating the values given in Table III of the mass susceptibility per g. of active layer. The values for the reduced-oxide catalysts are given in Table IV. No measurements were made on the foraminate catalysts.

Alloy-skeletal Powder Catalysts in Liquid-phase Hydrogenation of Benzene.—Liquid-phase hydrogenation of benzene was carried out in a 250 ml. stainless steel Lindsay–Baskerville autoclave, which had been modified to prevent catalysts from being splashed into the upper parts of the stirrer mechanism and lagged to give reasonable uniformity of temperature in the reaction vessel. An internal thermocouple was also fitted.

Alloy-skeletal powders prepared, as already described, from 5-g. portions of alloy were charged with 75 ml. of an equimolar mixture of sulphur-free benzene and sulphur-free *cyclo*hexane. The apparatus was assembled, pressure-tested under nitrogen, and heated to the reaction temperature under

5 atm. of nitrogen (measured at 20°). The temperature was levelled out with the stirrer in operation, and the pressure made up to 250 atm. with electrolytic hydrogen. The rate of reaction was followed by the decreasing hydrogen pressure, and the activities of the catalysts are expressed in terms of the true rate constants (Fuzek and Smith, *J. Amer. Chem. Soc.*, 1948, **70**, 3743):

$$(2{\cdot}303\ V/mt)\ \log_{10} P_0/P \text{ (ml. per g. of catalyst per min.)}$$

where V = volume (ml.) of gas-filled space in reactor, m = weight (g.) of catalyst, P_0 = initial hydrogen pressure (atm.), and P = hydrogen pressure (atm.) after time t (min.).

With pure nickel, and the 19 atom-% copper catalyst at the higher temperature, the rate of reaction was so high that the temperature became uncontrollable; runs with reduced amounts of catalyst were unreliable. Results for the remaining catalysts at 100° and 225° are given in Table V. These results have been plotted in Fig. 2*C*. A catalyst prepared from copper and aluminium which were both of spectroscopic purity was also tested; the figures are included in the table.

TABLE V.

Liquid-phase hydrogenation of benzene over alloy-skeletal powders.

Copper in activated layer, atom-%.	Reaction velocity constants at 100°.	Reaction velocity constants at 225°.	Copper in activated layer, atom-%.	Reaction velocity constants at 100°.	Reaction velocity constants at 225°.
0	—	—	89	0·00	0·77
19	1·12	—	95	0·00	0·45
38	0·05	1·17	100	0·00	0·19
58	0·05	1·12			
79	0·00	0·73	100 (Spect. pure)	0·00	0·04

Foraminate Catalysts in Vapour-phase Hydrogenation of Benzene.—Vapour-phase hydrogenation of benzene was effected with an equimolar mixture of sulphur-free benzene and sulphur-free *cyclo*hexane fed at a total liquid space velocity of 10 hr.$^{-1}$ over 10 ml. of the foraminate catalyst maintained at 100°. The hydrogen rate was 60 l. per hour. Activities were estimated in terms of the mean pass conversion of the benzene calculated over 2-hour runs. The results are given in Table VI and plotted in Fig. 3.

TABLE VI.

Vapour-phase hydrogenation of benzene over foraminate catalysts.

Copper in active layer, atom-% ...	0	9	23	26	30	34	38	58	79	100
Pass conversion of benzene, % ...	84	79	54	22	5	2	0	0	0	0

Reduced-oxide Catalysts in Liquid-phase Hydrogenation of Styrene.—A 10% solution of redistilled styrene in "refined dry" methanol was hydrogenated at atmospheric pressure in a 100-ml. glass shaker tube immersed in a thermostat at 25°. Electrolytic hydrogen was further purified by passage through active charcoal cooled in liquid oxygen; its rate of absorption in the reactor was measured by a soap-film flowmeter. The rate of reaction was found to be independent of the styrene concentration and approximately proportional to the weight of the catalyst.

The reaction vessel was equipped with a ground-glass joint at the top and with an alternative head carrying inlet and outlet gas leads for catalyst reduction. In each experiment 0·1 g. of supported oxide was charged to the reaction vessel on its side, spread over the wall, and reduced for 4 hours at 500°. The catalyst was cooled under hydrogen, immersed in acceptor solution, and transferred in the reactor to the test apparatus. The charge was there quickly frozen by cooling it in liquid oxygen, the apparatus evacuated, and hydrogen admitted. The reaction mixture was then allowed to warm to 25° in a thermostat, and vigorously agitated by a Microid shaker.

The results are given in Table VII. The activities are recorded first as ml. of hydrogen (at 20°/760 mm.) absorbed per minute per g. of active metals, and then in terms of unit area of active metal surface by the use of the figures of Table II. The latter results are plotted in Fig. 4*C*.

TABLE VII.

Liquid-phase hydrogenation of styrene over reduced-oxide catalysts.

	Catalytic activity in ml. of H_2 absorbed per min.			Catalytic activity in ml. of H_2 absorbed per min.	
Copper in reduced metals, atom-%.	per g. of active metals.	per sq. m. of active surface.	Copper in reduced metals, atom-%.	per g. of active metals.	per sq. m. of active surface.
0·0	1730	9·5	42·2	235	0·84
9·5	1170	4·2	48·4	0·5	0·006
19·7	790	4·1	55·5, 67·5, 79·1, 88·3, 100·0	0·0	0·000
30·9	46	0·24			

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