the directions of Limaye and Gangal.[12] The product, 2,6-dimethoxyacetophenone, was oxidized with selenium dioxide by the procedure described for the production of 2,4-dimethyl-6-methoxyphenylglyoxal. The 2,6-dimethoxyphenylglyoxal, boiling at 115–117° (5 mm.), was converted to the corresponding quinoxaline by the usual procedure. The product separated from aqueous ethanol as yellow needles; m. p. 95.5–96.5°.

Anal. Calcd. for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30. Found: C, 72.03; H, 5.46.

2,6-Dimethoxymandelic Acid.—Confirmation of the structure of the 2,6-dimethoxyphenylglyoxal was obtained by conversion to the corresponding mandelic acid. A mixture of 0.8 g. of 2,6-dimethoxyphenylglyoxal and 12 cc. of 30% sodium hydroxide solution was shaken for thirty minutes at room temperature. It was allowed to stand in the icebox for one hour and acidified with dilute hydrochloric acid. The 2,6-dimethoxymandelic acid was extracted with ether and recrystallized from chloroform; m. p. 146–147°.

Anal. Calcd. for $C_{10}H_{12}O_6$: C, 56.61; H, 5.66; neut. equiv., 212. Found: C, 56.59; H, 5.84; neut. equiv., 206.

2-(3,5-Dinitromesityl)-quinoxaline.—To a solution of 70 cc. of dioxane, 4 cc. of water and 7.8 g. of selenium dioxide was added, with stirring, 17.6 g. of dinitroacetomesitylene. The mixture was heated under reflux for four hours, cooled and filtered. Benzene (50 cc.) was added to the filtrate and the benzene, dioxane and water were distilled under diminished pressure. To the residual dark oil was added a small amount of methanol. The product crystallized when allowed to stand. It was recrystallized from a mixture of benzene and low-boiling petroleum ether and finally twice from methanol; m. p. 122–125°, with softening at 116°.

A solution of 1 g. of the glyoxal and 1 g. of *o*-phenylenediamine in 25 cc. of glacial acetic acid turned red immediately. It was heated under reflux for thirty-five minutes, allowed to stand for three and one-half hours and poured on ice. The quinoxaline separated as a yellow semi-solid mass. It was decolorized by treatment with Norite in ethanol. It crystallized from methanol in almost white needles; m. p. 197.5–198°; yield, 0.7 g.

Anal. Calcd. for $C_{17}H_{14}N_4O_4$: C, 60.35; H, 4.17; N, 16.56. Found: C, 60.68, 60.65; H, 4.15, 4.19; N, 16.73.

Summary

Quinoxaline formation, which is inhibited by the mesityl radical in mesitylglyoxal, has been found to take place with 2,4-dimethyl-6-methoxyphenylglyoxal, 2,6-dimethoxyphenylglyoxal and 3,5-dinitromesitylglyoxal.

The effect of the nitro groups in diminishing the steric hindrance provided by the mesityl group has been ascribed to chelation.

URBANA, ILLINOIS RECEIVED FEBRUARY 25, 1943

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[12] Limaye and Gangal, *Rasāyanam*, **1**, 64 (1936); (*Chem. Abstr.*, **31**, 2182 (1937)).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, JOHNS HOPKINS UNIVERSITY]

The Catalytic Hydrogenation of Benzene over Metal Catalysts

BY P. H. EMMETT AND NIS SKAU[1]

Introduction

As part of his multiplet theory of catalysis, Balandin[2] in 1929 postulated that a metallic catalyst in order to be active at low reaction temperatures in the hydrogenation of benzene to cyclohexane must possess developed crystal faces with a triangular configuration and with lattice dimensions standing in a definite relation to the dimensions of the benzene ring. By plotting on rectangular coördinates atomic radii *vs.* metal to carbon distances Balandin showed that only the (111) planes of face-centered cubic metallic lattices with atomic radii between about 1.2 and 1.4 Å., and a few hexagonal lattices, fulfill the requirements. As two corollaries of his hypothesis he predicted that five- and seven-membered hydrocarbon rings should not be acted upon in the same manner as the benzene compounds, and that simultaneous addition of all six hydrogen atoms should take place with no formation of the intermediates in the hydrogenation of benzene.

The first of Balandin's corollaries is proved untrue by experiments of Kistiakowsky and his collaborators,[3] who in their determinations of the heats of hydrogenation of all the unsaturated intermediates in the five-, six- and seven-membered series used nickel–cobalt catalysts at temperatures below 150°. Apparently, for these hydrogenations any flat symmetrical adsorption of five- and seven-membered rings cannot be imagined.

Balandin's second corollary has been shown recently by Taylor[4] to be explainable on thermodynamic grounds, the intermediates cyclohexene

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[1] From the thesis of Nis Skau presented to the faculty of The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Balandin, *Z. physik. Chem.*, **B2**, 289 (1929).

[3] Kistiakowsky, THIS JOURNAL, **58**, 137, 146 (1936).

[4] Taylor, *ibid.*, **60**, 627 (1938).

and cyclohexadiene being unstable with respect to the end-products benzene and cyclohexane. Taylor rightly concludes that the two important corollaries of Balandin have thus lost their principal support. He makes clear, however, that this is not to be interpreted as suggesting that the hydrogenation of benzene need not involve flat adsorption on metal faces whose atoms are arranged in the manner postulated by Balandin's theory.

The principal experimental work to be cited in support of Balandin's hypothesis is that of Long, Frazer and Ott[5] who showed that in a series of iron, cobalt and nickel alloys all catalysts active for benzene hydrogenation below 200° had a face-centered cubic lattice structure. Furthermore, in those instances in which a mixture of two structures was present (Fe–Ni mixtures, for example), the activity stood in reasonable relationship to the amount of face-centered structure observed. The reverse postulate, however, that all face-centered structures were active was not entirely true, for face-centered copper catalysts were found to be entirely inactive.

The present work has been undertaken primarily for the purpose of superimposing surface area measurements on experiments similar to those of Long, Frazer and Ott, with a view to contributing additional evidence for or against the Balandin hypothesis. A study of the chemisorption of carbon monoxide and carbon dioxide on nickel and copper has been included in an attempt to ascertain whether the promoter action[6a,b] of nickel in copper might be due to a preferential accumulation on the surface of the copper.

Experimental

The apparatus used for the catalytic activity tests was essentially the same as that used by Long, Frazer and Ott.[5] The hydrogen gas, properly purified, was bubbled through liquid benzene maintained at 25.0° to produce a 7:1 hydrogen:benzene mixture and then over the catalyst, through the condenser, and into interchangeable receivers. Hydrogen could also be made to bypass the saturators for reducing the catalysts *in situ*.

An ice-bath was used for condensation of the products of hydrogenation. Since there are no complicating side reactions at the temperatures used, the condensable products consist of benzene and cyclohexane only. It was established that for low cyclohexane content the ratio of benzene:cyclohexane in the liquid condensate accurately reflected the gas phase ratio; with a cyclohexane content above 10% there was a slight preferential condensation of benzene at 0°. The composition of the vapor could thus be determined by a simple refractive index determination at 25° on the condensate with the help of a calibration chart of refractive indices *vs.* composition for benzene–cyclohexane solutions.

The surface areas of the catalysts were measured by the method described by Brunauer, Emmett and Teller.[7] Nitrogen gas was used for the surface area measurements by adsorption at about −194°; 1 cc. of nitrogen was considered sufficient to cover 4.38 sq. meter of surface.

The adsorption of carbon monoxide was measured by the same technique as for nitrogen. Chemisorption of carbon monoxide was estimated as described by Emmett and Brunauer[8] for iron by (1) measuring the total adsorption at −194°, (2) pumping off the physically adsorbed carbon monoxide at −78°, and (3) repeating the adsorption at −194°. The difference between the volumes of carbon monoxide adsorbed in steps (1) and (3) was considered a minimum value for the chemisorption.

The benzene was Baker C. P. grade, thiophene-free, and was not further purified. Linde hydrogen was purified over heated copper, and dried over sodium hydroxide and phosphorus pentoxide. Nitrogen was water pumped grade dried over phosphorus pentoxide. Carbon monoxide was obtained by dripping formic acid on phosphoric acid maintained at 170°.[9] The gas was collected in a storage vessel and dried over potassium hydroxide before using. Carbon dioxide from a commercial cylinder was dried over phosphorus pentoxide.

Iron, cobalt and the mixed iron-cobalt catalysts were prepared by the reduction of precipitates formed from 1 *N* nitrate solution by adding 1 *N* sodium hydroxide as described by Long, Frazer and Ott,[5] except that the precipitates were not dialyzed and the oxides were dried at 350° for the cobalt and the mixed catalysts. The chemical analyses of the latter are included in Table I. A previously prepared pure iron synthetic ammonia catalyst (No. 973)[10] was also included in this series.

The work with copper included seven different preparations. *Cu I:* Turnings of electrolytic copper (0.0006% Ni) were melted in a layer of copper oxide by the direct flame of a gas blow-torch with a high excess of oxygen. The molten oxide was poured into distilled water. The solidified droplets and fragments were crushed and screened to 20–80 mesh size. The reduction of the oxide by hydrogen was carried out at 200° for twelve hours, and at 250° for two hours, the space velocity being about 300.

Cu II was prepared from Baker C. P. copper oxide. The entire fraction coarser than 100-mesh was used. Analysis showed 0.001% Ni based on the reduced catalyst. The reduction was carried out at 150° for twenty hours until no more water was given off and then at 200° for five hours, the space velocity being about 500.

Cu III (0.0005% Ni) was prepared from Baker C. P. copper nitrate by precipitation at 25° with constant stirring from a 1 *N* solution with the calculated amount of 1 *N* sodium hydroxide. The precipitate was washed by decantation with distilled water until peptization began;

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[5] Long, Frazer and Ott, THIS JOURNAL, **56**, 1101 (1934).

[6] (a) Ipatieff, Corson and Kurbatov, *J. Phys. Chem.*, **43**, 589 (1939); (b) Corson and Ipatieff, *ibid.*, **45**, 431 (1941).

[7] Brunauer, Emmett and Teller, THIS JOURNAL, **60**, 309 (1938).

[8] Emmett and Brunauer, *ibid.*, **59**, 1553 (1937).

[9] Thompson, *Ind. Eng. Chem.*, **21**, 389 (1929).

[10] Emmett and Brunauer, THIS JOURNAL, **59**, 310 (1937).

thereafter it was filtered on a Büchner funnel. The oxide obtained in this manner was heated in air to 200° and sieved to eliminate material smaller than 200-mesh. The reduction was carried out at 150° for twenty hours and at 200° for two hours at a space velocity of about 500. After activity tests and a nitrogen adsorption test this particular catalyst was partially sintered by reducing a second time at 250°.

Cu IV and V were prepared in the same manner as Cu III except that 0.1 and 1% nickel, respectively, was added as nitrate. After the reduction at 150° and the initial testing, catalyst V was markedly sintered by reducing a second time for five hours at 350°.

Cu VI was prepared by igniting copper nitrate prepared from the same electrolytic copper used for Cu I. The oxide was sieved and the finest material discarded. Reduction was twenty hours at 150° at a space velocity of about 350.

Cu VII was prepared by precipitation with ammonium hydroxide from the same nitrate supply used for Cu VI. The nitrate crystals were dissolved to make a 0.20 *N* solution and the precipitation carried out by adding with constant stirring the calculated amount of 0.25 *N* ammonia. The washing did not have to be carried to actual peptization since the excess of ammonium nitrate was evaporated off by heating the oxide for twelve hours at 200°. The oxide was sieved to separate the fines and reduced for twenty hours at 150° at a space velocity of about 250.

Ni I was prepared by adding the theoretical amount of 0.25 *N* ammonium hydroxide slowly under constant stirring to a 0.2 *N* C. P. nickelous nitrate solution. The precipitate was washed a few times by decantation, filtered on a Büchner filter, dried by heating for twelve hours at 350° and reduced at 350° at a space velocity of about 2000 for four hours.

Ni II was prepared by adding 0.5 *N* sodium hydroxide slowly with constant stirring to 0.5 *N* nickelous nitrate at 80°. The precipitate was washed repeatedly with distilled water until peptization began, filtered on a Büchner, heated to 350°, and sieved to eliminate particles finer than 100-mesh. The reduction was carried out at 360° at a space velocity of about 2000 for four hours.

Palladium and Silver Catalysts.—A palladium catalyst was prepared by decomposing the nitrate at as low a temperature as possible until cessation of brown fumes. The mixed silver-palladium catalysts were obtained in the same manner by grinding the nitrates together and decomposing them by heat. The resulting oxides were reduced in hydrogen at 100° for about twenty hours at a space velocity of 500. Thereafter the temperature was raised for a short time to 150°. A silver catalyst was made from C. P. silver oxide using the same reduction schedule.

Results

Activity Tests.—In Table I the results of catalytic activity tests on the various catalysts are

TABLE I

SUMMARY OF CATALYTIC ACTIVITY TESTS

Catalyst	Wt. after reduction, g.	Vol., cc.	Reduction temp., °C.	Surface, sq. m./g.	Space velocity during tests	Temp., °C., required for producing cyclohexane 10%	50%	90%	Structure
			Precipitated Fe-Co catalysts						
Co	4.04	2.5	360	6.64	3290	37	43	50	f.c.c.
Fe-Co I (25.4 Fe-74.6 Co)	4.34	2.4	360	6.73	3430	43	55	66	f.c.c. some b.c.c.
Fe-Co II (59.9 Fe-40.1 Co)	4.05	2.4	400	7.69	3430	74	90	93	f.c.c. and b.c.c.
Fe-Co III (78.4 Fe-21.6 Co)	3.98	2.4	400	6.34	3430	190	219	...	b.c.c. some f.c.c.
Fe	3.88	2.4	400	6.99	3430	Not active			b.c.c.
			Iron synthetic ammonia catalyst						
"973"	4.34	1.8	480	1.54	950	Not active			b.c.c.
			Various copper catalysts						
Cu I (0.0006% Ni)	56.47	26.0	200	0.95	66	Not active			f.c.c.
Cu II (0.001% Ni)	25.67	14.6	150	.66	117	6.5% at 190			f.c.c.
Cu III (0.0005% Ni)	20.85	15.5	150	3.83	111	Not active			f.c.c.
Cu IV (0.1% Ni)	12.72	20.1	150	5.74	93	2.1% at 200			f.c.c.
Cu V (1.0% Ni)	9.52	15.7	150	7.33	121	112	142	158	f.c.c.
Cu V (1.0% Ni)	9.52	15.7	350	3.92	128	155	186	...	f.c.c.
Cu VI (0.0006% Ni)	21.89	22.7	150	0.72	136	1.0% at 220			f.c.c.
Cu VII (0.0006% Ni)	29.03	32.8	150	.58	55	1.6% at 225			f.c.c.
			Nickel catalysts						
Ni I	8.39	3.2	360	0.64	2600	117	131	140	f.c.c.
Ni II	5.30	2.2	360	1.52	3740	113	128	134	f.c.c.
			Ag, Pd and their mixtures						
Pd	8.33	2.7	100	0.35	3020	82	101	111	f.c.c.
Ag-Pd I (20 Ag-80 Pd)	9.35	3.6	100	.82	1850	110	138	...	f.c.c.
Ag-Pd II (55 Ag-45 Pd)	9.94	3.6	100	.86	1850	120	...	...	f.c.c.
Ag	21.30	30.0	100	.45	58	Not active			f.c.c.

TABLE II

CARBON MONOXIDE ADSORPTION COMPARED TO NITROGEN ADSORPTION ON CU AND NI CATALYSTS

	Sample, g.	N_2 monolayer, cc. at S. T. P.	CO Monolayer of "physically" adsorbed gas, cc. at S. T. P.	CO, total cc. at S. T. P.	Ratio[b] CO "Phys. Ads." / N_2 in monolayer	Ratio[a] CO (chemisorp.) / N_2 monolayer
Cu I	56.47	12.20	12.61	38.50	1.03	2.15
Cu II	25.67	2.86	4.60	6.47	1.61	1.26
Cu III (red. 250°)	20.85	15.22	19.95	23.60	1.31	0.55
Cu IV	12.72	15.67	20.30	24.50	1.30	.57
Cu V (red. 150°)	9.52	15.88	17.44	26.15	1.10	.65
Cu VI	21.89	3.61	3.69	5.30	1.02	.47
Cu VII	29.03	3.86	4.45	7.00	1.15	.81
Ni I	8.39	5.17	4.63	9.90	0.90	.92
Ni II	5.30	5.38	5.40	14.95	1.01	1.78

[a] Since part of the chemisorbed carbon monoxide appears to have pumped off at −78° the volume of chemisorbed carbon monoxide used in calculating this column was obtained in each case as column 5 minus column 3. [b] The values in column 4 were obtained by first determining the total adsorption of carbon monoxide at −195° (column 5), then evacuating the sample at −78°, and finally running carbon monoxide isotherms again at −195°. Since some of the chemisorbed carbon monoxide appears to have pumped off at −78°, column 4 represents the total physical adsorption of carbon monoxide plus such portions of the chemisorption as pumped off at −78°. Values in column 6 are those in column 4 divided by those in column 3.

summarized. Weight, volume, analysis and surface area values are given for each catalyst. The figures in the three columns headed "Per cent. cyclohexane" are read from the "ascending" branches of the activity curves, samples of which are shown in Figs. 1 and 2. If the activity was small, a single point near the temperature of maximum activity is given.

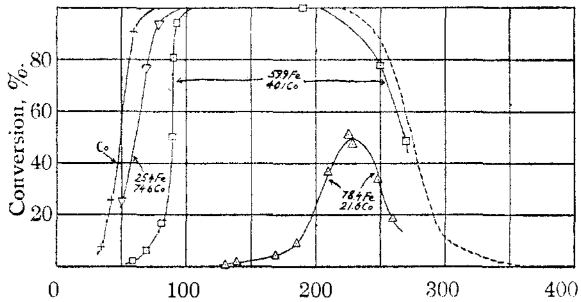

Fig. 1.—The catalytic activity of cobalt, iron and iron-cobalt catalysts toward the hydrogenation of benzene to cyclohexane in a 7:1 H_2:C_6H_6 mixture at a space velocity of about 3400.

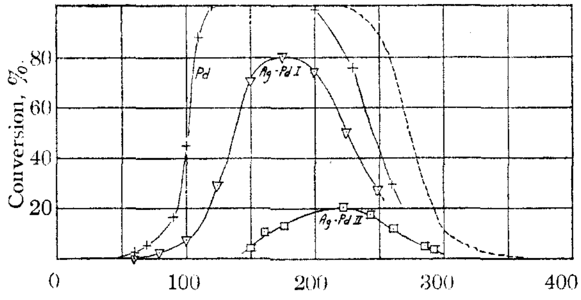

Fig. 2.—The catalytic activity of palladium, silver and palladium-silver alloys toward the hydrogenation of benzene to cyclohexane from a 7:1 hydrogen : benzene mixture.

The experimental points on the activity curves were as a rule obtained by going from lower to higher temperatures. The thermodynamic equilibrium curve is shown as a broken line on the graphs and is calculated for an initial 1:7 benzene–hydrogen mixture from the equation of Zharkova and Frost.[11] The falling away of the "descending" branches of the activity curves from equilibrium is evidently simply a reaction rate phenomenon already noted by Pease and Purdum[12] and by Juliard and Herbo.[13] When the space velocity becomes very small the thermodynamic equilibrium is gradually approached.

The sensitivity of the refractometer was such that the presence of 0.2 to 0.3% of cyclohexane in benzene could be detected. Separate experiments showed that cyclohexane equivalent to 0,5% conversion easily could be detected.

Carbon Monoxide Chemisorptions.—Chemisorption measurements for carbon monoxide on the nickel and copper catalysts are shown in Table II. Some of the adsorption isotherms are reproduced in Figs. 3, 4 and 5. It appears that some of the chemisorbed CO on copper II, III, IV, V and VII pumped off at −78° so that the second isotherms which are supposed to represent the physically adsorbed gas lie slightly higher than would otherwise be expected. Carbon monoxide has about the same area per molecule and boiling

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[11] Zharkova and Frost, *J. Chim. Gen., U. S. S. R.*, **64**, 534 (1932).

[12] Pease and Purdum, THIS JOURNAL, **47**, 1435 (1925).

[13] Juliard and Herbo, *Bull. soc. chim. Belg.*, **47**, 717 (1939).

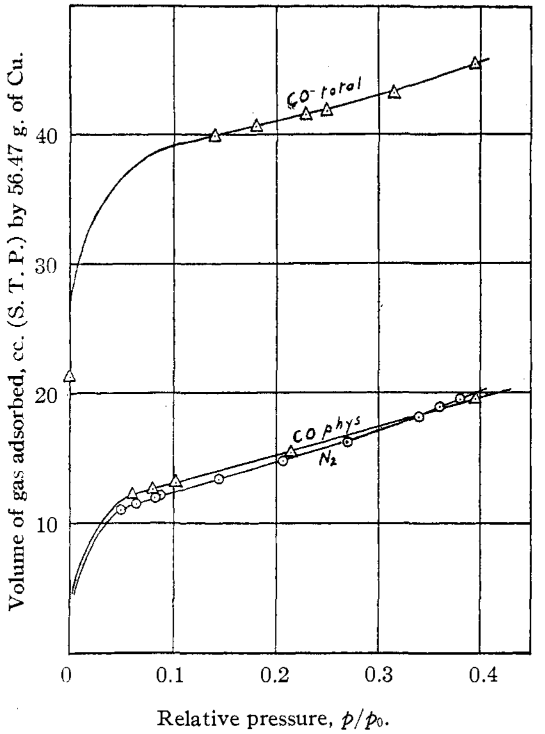

Fig. 3.—Adsorption of carbon monoxide and nitrogen on 56.47 g. of a pure copper catalyst (Cu I) at −195°.

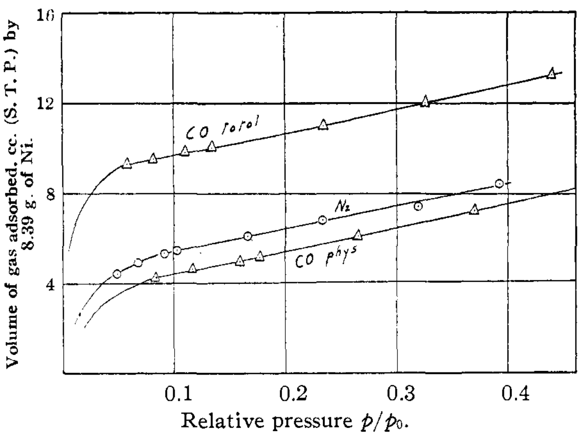

Fig. 4.—Adsorption of carbon monoxide and nitrogen on 8.39 g. of nickel catalyst (Ni I) at −195°.

point as nitrogen so that if physical adsorption alone is involved, the two isotherms should be nearly identical. Accordingly, in Table II the nitrogen isotherms and the total carbon monoxide adsorptions have been taken as a basis for estimating the chemisorbed carbon monoxide in column 6.

Carbon Dioxide Adsorption.—Carbon dioxide has been found to be strongly chemisorbed at −78° by iron catalysts containing alkali promoters but not by pure iron catalysts. It was anticipated that carbon dioxide might behave similarly on copper and nickel.

On copper catalysts there was no indication of chemisorption of carbon dioxide at −78°; all of the carbon dioxide that was adsorbed at −78° was removable by evacuation at 0°. On Ni II, however, as shown in Fig. 5 a large amount of carbon dioxide was chemisorbed.

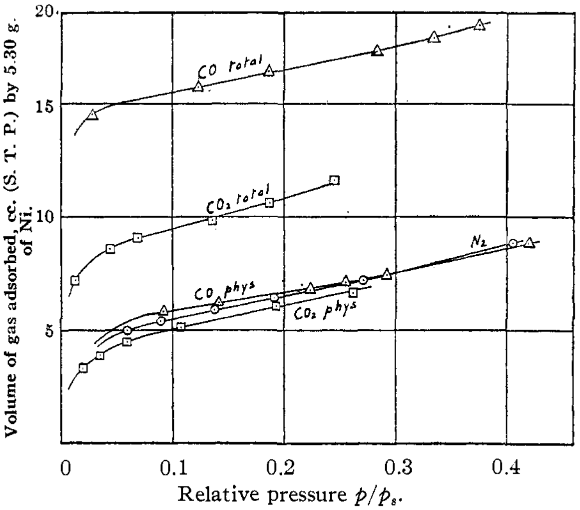

Fig. 5.—Adsorption of nitrogen and carbon monoxide at −195° and of carbon dioxide at −78° on 5.30 g. of nickel catalyst (Ni II).

Discussion

The results of Long, Frazer and Ott[5] on precipitated mixed iron–cobalt catalysts are essentially confirmed by the present work. Iron is inactive at 200° both when prepared in the same manner as the cobalt catalysts with a correspondingly large surface area, and when prepared as a fused synthetic ammonia catalyst. The activity of the mixed catalysts decreased with increased iron content. In the present work the mixed catalysts were found to have a greater activity than in the earlier work. The lesser purity of the present catalysts (due to omission of dialysis) probably accounts for this. X-Ray pictures revealed the presence of both body-centered and face-centered structures in all the mixed catalysts. The hydroxides of the metals were precipitated from rather concentrated solutions and the traces of alkali that remained after washing have presumably acted as promoters in the sense that they prevented complete alloying of the metals. The catalysts of Long, Frazer and Ott[5] were freed from alkali by electrodialysis. Their catalyst with 50% Fe and 50% Co showed only a slight irregular activity whereas the one with 75% Fe and 25% Co showed no activity; neither showed any face-centered structure by X-ray analysis. The irreproducibility or erratic behavior of the 50-50 Fe–Co catalyst was not confirmed in the present work though it was noted that both Fe–Co II and Fe–Co III required about two hours to attain a steady reaction rate after each temperature increase, compared to a few minutes required by all the other catalysts. The phenomenon may possibly be related to the "stabilization" effect referred to by Juliard and Herbo.[13]

Copper appears to be practically inactive unless nickel or some other promoter is present. This agrees with the comprehensive measurements of Ipatieff and his co-workers.[6a,b] The relatively high activity of the catalyst prepared by Pease and Purdum[12] which they reported to be free of nickel still stands as an exceptional case; possibly, as suggested by Corson and Ipatieff,[6b] small concentrations of promoters other than nickel were present. The activity of Cu II in the present work is probably also partly due to other impurities[14] than the 0.001% nickel, though as indicated by activity tests on Cu IV and Cu V containing 0.1 and 1.0% nickel, respectively, nickel undoubtedly acts as a promoter in copper catalysts for the hydrogenation of benzene to cyclohexane. This has been clearly shown by the work of Corson and Ipatieff.[6b]

For copper catalysts prepared by precipitation with sodium hydroxide, the adsorption experiments show an increase in surface area with nickel content though this increased area does not appear sufficient to account for the enhanced activity of the catalyst with 1% Ni compared to the one with 0.1%.

The mechanism by which nickel promotes copper is not clear. It may alter the crystal habit of copper by changing, for instance, the usual cubic habit with exposed (100) planes to an octahedral habit with exposed (111) planes. On the other hand, the nickel may be collecting preferentially on the surface, producing thereby a surface concentration sufficiently high to effect the catalytic conversion.

Palladium and silver both have face-centered cubic structures and form a complete series of solid solutions. Palladium with a radius of 1.372 Å. is inside the limits of Balandin's square of activity, whereas silver with a radius of 1.441 Å. is outside. For this reason it was thought that by preparing a series of alloys of these two metals in different proportions it should be possible to find an alloy with an intermediate critical parameter above which the alloy would be inactive and below which it would be active. However, the attempt to prepare a completely inactive alloy by igniting the mixed nitrates was unsuccessful. Nevertheless, the activity decreased markedly with decreasing palladium content. It is impossible to state with certainty whether the co-ignited oxides were homogeneous or contained a small amount of free palladium that might have been responsible for all activity. X-Ray pictures indicated the presence of only alloys, although a small percentage of free palladium probably could not have been detected by X-ray analysis. It may be noted from Fig. 2 that the activity of alloy I is about 12 times as great at 150° per unit palladium content as that of alloy II. Accordingly the present experiments may be said to confirm the activity of Pd, the inactivity of a large surface of silver and the relatively low activity of silver–palladium II whose spacing should place it outside Balandin's "square of activity."

After being tested, the silver–palladium mixtures were fused in vacuum in small magnesia crucibles to form buttons of metallic alloys. The fused metals, however were so soft that subdivision by filing did not give sufficiently large surface areas to cause them to be active. Even pure palladium prepared in this manner was inactive under the conditions of the test.

The chemisorption of carbon monoxide and carbon dioxide on iron catalysts[10] proved to be a valuable tool for ascertaining the surface concentration of promoters. In the present work analogous information relative to the copper catalysts could not be obtained because carbon dioxide was not chemisorbed on copper at −78°. The chemisorption of carbon dioxide on nickel II is large, as indicated in Fig. 5. By reasoning similar to that employed on the data for iron catalysts one might be tempted to conclude that about 70% of the surface is covered with alkali. However, Figure 5 shows also a chemisorption of carbon monoxide which one would expect to be occurring on the metal atoms but which is far too large to be accommodated on a surface equivalent to only 30% of that given by the nitrogen isotherm. Accordingly, quantitative interpretation of the carbon

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(14) 0.001% CaO and 0.001% Al_2O_3 were present according to the analysis on the bottles of c. p. CuO.

monoxide–carbon dioxide chemisorption data on nickel must await additional experimental work.

The carbon monoxide chemisorptions are of interest in another connection. On the catalyst made from fused copper oxide, Cu I, the chemisorbed carbon monoxide was found to be about 2.15 times the amount required for a monolayer of physically adsorbed gas. Considering the values listed in Table III for surface area available per metal atom, it is evident that the (110) plane of copper would not be able to accommodate the large amount of carbon monoxide actually chemisorbed, though either (100) planes or (111) planes could do so. It follows that at least some of the copper surface must consist of planes other than (110), provided the surface area measured by low temperature nitrogen adsorption is correct.

TABLE III

AREA PER METAL ATOM FOR VARIOUS FACES OF CU AND NI

Developed face	Cu, sq. Å.	Ni, sq. Å.
(100)	6.502	6.190
(110)	9.194	8.753
(111)	5.629	5.357

The largest carbon monoxide chemisorption value on nickel is not too large to be accounted for satisfactorily by any of the three nickel faces (110), (111), or (100). Hence no information as to the developed faces of nickel is forthcoming from the carbon monoxide adsorption measurements.

The data for the chemisorption of carbon monoxide reported in the present paper cannot be used to differentiate between the nickel surface and the copper surface, nor can they be used to prove with certainty the existence of (111) faces on the copper catalysts. We cannot, therefore, be sure that any (111) faces are developed on copper. Incidentally, several attempts to convert developed faces to the (111) variety by two methods suggested by Gwathney and Benton[15] and by Benton[16] failed to make the copper catalyst active for benzene hydrogenation.

Until some other explanation is found for the complete inactivity toward benzene hydrogenation of body-centered iron catalysts that are very active for hydrogenating olefins, some credence must be given to Balandin's multiplet hypothesis. A fair statement of it in view of the present and previous work would appear to be that a necessary but not a sufficient requirement for a low temperature metal catalyst for hydrogenating benzene is that it falls within the square of activity originally delineated by Balandin[2] for metals having face-centered cubic or hexagonal lattices.

Summary

1. Previously reported measurements on the inactivity of body-centered iron catalysts for the hydrogenation of benzene below 200° have been confirmed by experiments in which the surface area of the inactive iron catalysts have been shown to be as large as that of very active cobalt or iron–cobalt alloys.

2. Copper catalysts substantially free of nickel are inactive at 200° though their surface areas are several fold those of active cobalt catalysts. Copper containing small nickel additions is slightly active at 200°.

3. Palladium is active; silver is inactive; two palladium: silver alloys have activities per unit palladium content that decrease markedly with a decrease in the percentage of palladium.

4. Carbon monoxide is chemisorbed on both reduced copper and reduced nickel catalysts instantly at $-195°$. Carbon dioxide is chemisorbed at $-78°$ on nickel catalysts prepared by reduction of oxide formed by alkali precipitation but is not chemisorbed on copper.

5. Having dimensions and surface configuration within the "square of activity" of the Balandin hypothesis seems to be a necessary but not a sufficient prerequisite to a metal being catalytically active for benzene hydrogenation below 200°.

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(15) Gwathney and Benton, *Trans. Electrochem. Soc.*, **77**, 211 (1940).

(16) Private communication.