REFERENCES

(1) AUDUBERT: Compt. rend. **176,** 838 (1923).
(2) BOLAM AND COWORKERS: Trans. Faraday Soc. (a) **22,** 162 (1926); (b) **29,** 874 (1933).
(3) CANN AND MUELLER: J. Am. Chem. Soc. **27,** 2525 (1935).
(4) GUGGENHEIM AND SCHINDLER: J. Phys. Chem. **38,** 543 (1934).
(5) HASS AND JELLINEK: Z. physik. Chem. **162,** 153 (1932).
(6) HILL, A. E., AND WILLS: J. Am. Chem. Soc. **60,** 1655 (1938).
(7) KIELLAND: J. Am. Chem. Soc. **59,** 1675 (1937).
(8) KOLTHOFF AND FURMAN: *Potentiometric Titrations,* p. 248. John Wiley and Sons, Inc., New York (1926).
(9) KRUYT AND BOELMAN: Kolloid-Beihefte **35,** 183 (1932).
(10) KUNITZ: J. Gen. Physiol. **10,** 811 (1926-27).
(11) LOEB, J.: *Proteins and the Theory of Colloidal Behavior.* McGraw-Hill Book Company, New York (1924).
(12) OSTWALD, WO., AND STUART: Kolloid-Z. **79,** 49 (1937).
(13) SIMMS: J. Gen. Physiol. **11,** 613 (1927).
(14) VAN HOOK, A.: J. Phys. Chem. **44,** 751 (1940).
(15) WEISER AND MORELAND: J. Phys. Chem. **36,** 1 (1932).
(16) LANDOLT-BÖRNSTEIN: *Tabellen,* III. J. Springer, Berlin (1931).

ACTIVATION AND POISONING OF COPPER HYDROGENATION CATALYSTS

B. B. CORSON AND V. N. IPATIEFF

Research Laboratories, Universal Oil Products Company, Riverside, Illinois

Received July 3, 1940

INTRODUCTION

It has previously been shown (4,5) that copper is very susceptible to activation by traces of nickel. This paper describes a quantitative study of the promoting and poisoning effects of various metals, oxides, and salts.

Copper catalysts containing 0.002, 0.005, 0.05, 0.5, and 1 per cent of nickel hydrogenate benzene to the extent of 0, 0.5, 5.5, 42, and 79 per cent, respectively, at 225°C. and ordinary pressure in a contact time of 12 sec. The activating effect is a linear function of the nickel concentration.

An obvious objection is that this hydrogenating effect is due to nickel alone, and that the copper is merely an inert support. However, when nickel is dispersed on alumina (a typical non-reducible oxide support), it requires a 10 per cent concentration of nickel on alumina to equal a 1 per cent concentration of nickel on copper. Moreover, 5 per cent of nickel on alumina is completely inactive in the hydrogenation of benzene, even in a contact time of 100 sec., whereas 0.005 per cent of nickel on copper hydrogenates benzene to the extent of 4 per cent under the same conditions. There is something very specific in the combination of nickel on copper or, in other words, copper is an excellent carrier for nickel.

Cobalt ranks next to nickel as an activator for copper, but it is much less effective. For instance, copper containing 1 per cent of nickel hydrogenates benzene to the extent of 79 per cent in 12 sec., whereas copper containing 1 per cent of cobalt hydrogenates benzene to the extent of only 14 per cent under the same conditions. The slope of the activity curve for cobalt is steeper for the first additions of cobalt (up to 1 per cent) than for the later additions, and nickel shows the same tendency to a smaller degree.

Evidently the inferior activating power of cobalt does not justify the conclusion that cobalt, itself, is a weaker hydrogenating catalyst for benzene than nickel, since Juliard and Herbo (6) have found that cobalt and nickel possess about the same hydrogenating power. Neither does it follow that copper and iron are weaker hydrogenating catalysts than alumina, because alumina is a more effective activator of nickel than copper or iron, as shown by the same authors.

There are certain other metals—bismuth, cadmium, lead, mercury, and tin—which are poisons for the catalyst; sodium chloride and sodium sulfate also poison it. These poisons were tested both at atmospheric and at superatmospheric pressures.

For the atmospheric runs, copper was activated with 0.2 per cent of nickel at the same time that it was poisoned, in order to provide sufficient hydrogenating activity so that the poisoning effect could be evaluated, since pure copper does not hydrogenate benzene at ordinary pressure. The experiments with poisoned nickel–copper catalysts leave some doubt as to whether the poison affects only the nickel, or the copper, or both. The poisoning effect on copper alone could have been studied at ordinary pressure if a more active unsaturate, such as ethylene, had been substituted for benzene. An alternative method is to study the poisoning effect under more severe conditions of time, temperature, and pressure, choosing such conditions that pure copper shows sufficient activity to allow evaluation of the poisoning effect. This was the method employed, and the same picture was obtained at superatmospheric pressure with poisoned copper as at ordinary pressure with poisoned 99.8 per cent copper–0.2 per cent nickel.

At ordinary pressure, 0.1 to 0.2 per cent of bismuth, cadmium, or lead deactivates 99.8 per cent copper–0.2 per cent nickel almost completely. Below 0.1 per cent concentration, bismuth and cadmium have no effect, whereas lead functions as a weak promoter. This interesting behavior of lead was checked several times with different catalyst preparations, so as to make sure of the facts. Lead, therefore, is similar to certain drugs which, in small doses, stimulate the living organism, but in larger doses cause death.

A similar instance in catalysis was previously observed by Ghosh and Bakshi (2), who reported that 0.04 per cent of carbon bisulfide and 0.14 per cent of chloroform activated copper for the dehydrogenation of methyl alcohol by factors of 1.18 and 2.25, respectively, whereas 0.41 per cent of either of these poisons completely deactivated the catalyst.[1]

Sodium chloride and sodium sulfate were found to be strong poisons for nickel-promoted copper, although neither of these substances is supposed to poison the nickel hydrogenation catalyst (9, 7, 1).

Lead and bismuth showed the highest toxicity toward nickel-promoted copper, cadmium and sodium chloride being next, and sodium sulfate was the least toxic. Sodium sulfate required 0.11 mole per cent (0.24 weight per cent) to lower the hydrogenating activity by 50 per cent, and 0.17 mole per cent (0.38 weight per cent) to deactivate the catalyst completely. The corresponding requirements for lead were 0.006 and 0.03 mole per cent (0.02 and 0.09 weight per cent) to produce 50 per cent and 100 per cent deactivation, respectively.

As previously reported (5), nickel is more effective in the activation of 95 per cent copper–5 per cent chromium oxide than of pure copper, 0.2 per cent of nickel raising the activity of the former from 2 to 62 (per cent hydrogenation of benzene), and the activity of the latter from 0 to 19. On the other hand, 0.1 per cent of lead lowers the activity of the nickel-promoted 95 per cent copper–5 per cent chromium oxide from 62 to 23 (63 per cent drop) and that of nickel-promoted copper from 19 to 2 (90 per cent drop).

This preliminary survey emphasizes the extreme delicacy of catalytic processes and the necessity of careful definition of purity before drawing conclusions as to the catalytic properties of any particular element or catalyst. The sensitivity of the system benzene–hydrogen–copper competes with the spectroscope in the detection of traces of nickel, bismuth, and cadmium, and it goes beyond the range of the spectroscope in its sensitivity to traces of lead. Therefore in the case of lead, at least, spectroscopic purity is no guarantee of catalytic purity.

EXPERIMENTAL

Preparation of catalysts

Since copper preparations containing known traces of impurities cannot be obtained by simple coprecipitation, they were prepared by adding

---

[1] In similar manner, small amounts of carbon monoxide increase the adsorptive power of copper (3) and of nickel (8), whereas larger amounts decrease adsorption, but catalytic activity does not run parallel with these changes in adsorptive power.

known amounts of impurity (as nitrate solution) to freshly precipitated basic copper carbonate, followed by evaporation to dryness.

For example, 8 gram-molecules of ammonium carbonate in 5000 cc. of warm water was added to 8 gram-molecules of copper nitrate in 20,000 cc. of warm water. The amount of alkali was regulated so that the filtrate was slightly basic to litmus and only faintly blue. After standing for 1 hr., the mixture was filtered. The precipitate was stirred with 20,000 cc. of warm water and filtered again. The damp precipitate was divided into eight equal portions (1618 g. ÷ 8), which were placed in covered porcelain dishes.

According to the analysis of the filtrate, each of the eight samples should contain 61.9 g. of copper, whereas analysis of one of the actual samples showed 61.1 g. of copper, the average (61.5 g.; 96.7 per cent yield) being accepted.

TABLE 1

Hydrogenation of benzene by 99.8 per cent copper–0.2 per cent nickel

Conditions: T, 225°C.; $H_2:C_6H_6 = 7$; atmospheric pressure

CONTACT TIME	HYDROGENATION OF BENZENE, IN WEIGHT PER CENT			
	A	B	C	D
seconds				
25	38	36	38	35
50	66	64	68	62
75	85	83	89	78

An example of adding an impurity is the following preparation of copper containing 0.002 per cent of nickel. To one of the samples of copper carbonate was added 17.8 cc. of nickel nitrate solution containing 0.000069 g. of nickel per cubic centimeter, and the mixture was stirred to a thin slurry with a porcelain spatula, after which it was dried for 8 hr. at 120°C. and for 36 hr. at 180–190°C. The catalyst was pressed, granulated, decomposed, and reduced as previously described (4).

Testing of catalysts

The apparatus, procedure, and calculation were the same as previously described (4, 5).

Duplicability of results at atmospheric pressure

Considerable care was exercised to keep the variables of the preparation and testing of the catalyst constant. Table 1 presents four typical check results obtained with four individually prepared catalysts.

Duplicability of results at superatmospheric pressure

Typical check runs in the bomb gave the following per cent hydrogenation of benzene: 36, 30, 35, 39, 37, 27, 29, and 33 per cent, the average being 35 per cent. The rotating 850-cc. Ipatieff bomb used in these experiments was equipped with a glass liner. The charge was 5 g. of pure copper, 50 cc. of benzene, and 100 atm. of hydrogen; the bomb was rotated for 12 hr. at 350°C.

Activation

Activation of copper by nickel and cobalt (atmospheric hydrogenation).—Copper catalysts containing concentrations of nickel ranging from less than 0.001 per cent to 1 per cent and of cobalt from less than 0.001 per cent to 10 per cent were prepared and tested (see tables 2, 3A, and 3B). The comparisons of the activities were made at the maximum contact times at which the activity curves were still linear. Activities were not determined for catalysts containing more than 1 per cent of nickel or 10 per cent of cobalt, because the experimental technique used in testing could not handle higher activities.

TABLE 2

Activation of copper by nickel

Conditions: T, 225°C.; contact time, 12 sec.; $H_2:C_6H_6 = 7$; atmospheric pressure

NICKEL	HYDROGENATION OF BENZENE
weight per cent	*weight per cent*
<0.001	0
0.002	0
0.005	0.5
0.01	1.5
0.02	2.5
0.05	5.5
0.1	10
0.2	19
0.5	42
1.0	79

TABLE 3A

Activation of copper by cobalt

Conditions: T, 225°C.; contact time, 12 sec.; $H_2:C_6H_6 = 7$; atmospheric pressure

COBALT	HYDROGENATION OF BENZENE
weight per cent	*weight per cent*
<0.001	0
0.1	1
0.02	1
0.05	2
0.1	3.5
0.2	5
0.5	6.5
1.0	14

Poisoning

Poisoning of nickel-activated copper (and copper–chromium oxide) by bismuth, cadmium, and lead (atmospheric hydrogenation).—The poisoning of 99.8 per cent copper–0.2 per cent nickel by bismuth, cadmium, and lead is shown in table 4. The three poisons are equally effective at concentrations of 0.1 per cent to 1 per cent, but at smaller concentrations lead changes its rôle from poison to promoter, whereas bismuth and cadmium are without effect. Table 5 shows the behavior of nickel-activated copper and copper–chromium oxide when poisoned by lead.

TABLE 3B

Activation of copper by cobalt

Conditions: T, 225°C.; contact time, 5 sec.; $H_2:C_6H_6 = 7$; atmospheric pressure

COBALT	HYDROGENATION OF BENZENE
weight per cent	*weight per cent*
0.0	0
0.2	2
1.0	6
5	28
10	60

TABLE 4

Poisoning of nickel-activated copper by bismuth, cadmium, and lead

Conditions: T, 225°C.; contact time, 12 sec.; $H_2:C_6H_6 = 7$; atmospheric pressu

POISON	HYDROGENATION OF BENZENE		
	Bismuth	Cadmium	Lead
weight per cent	*weight per cent*	*weight per cent*	*weight per cent*
0.0	19	19	19
0.00001	16	20	28
0.0001	15	20	27
0.001	17	18	24
0.01	10	13	16
0.1	3	3	2
0.2	0	0	0
1.0	0	0	0

Poisoning of copper by bismuth, cadmium, lead, mercury, and tin (superatmospheric hydrogenation).—The poisoning of pure copper by bismuth, cadmium, lead, mercury, and tin, as evaluated under superatmospheric pressure, is shown in table 6. The relatively low toxicity of mercury is perhaps due to loss of mercury during the decomposition and reduction of the catalyst.

Poisoning of nickel-activated copper by sodium chloride and sodium sulfate (atmospheric hydrogenation).—The poisoning of 99.8 per cent copper–0.2 per cent nickel by sodium chloride and sodium sulfate is shown in table 7. Sodium chloride shows toxicity at lower molal concentration than sodium sulfate, but they become equal in toxicity at about 0.2 mole per cent. The poisoning effect is presumably due to the acid radicals rather than to the sodium. In fact, Juliard and Herbo (6) found that the alkali metals lithium and potassium promoted nickel for the hydrogenation of benzene. Copper containing about 0.2 mole per cent of nickel chloride or nickel sulfate is completely inactive.

TABLE 5

Poisoning of nickel-activated copper and copper–chromium oxide by lead

Conditions: T, 225°C.; contact time, 12 sec.; $H_2:C_6H_6 = 7$; atmospheric pressure

CATALYST COMPOSITION, IN WEIGHT PER CENT	HYDROGENATION OF BENZENE
	weight per cent
Copper	0
Copper + 5% chromium oxide	2
Copper + 0.2% nickel	19
Copper + 5% chromium oxide + 0.2% nickel	62
Copper + 0.2% nickel + 0.1% lead	2
Copper + 5% chromium oxide + 0.2% nickel + 0.1% lead	23

TABLE 6

Poisoning of copper by bismuth, cadmium, lead, mercury, and tin

Conditions: T, 350°C.; reaction time, 12 hr.; charge, 50 cc. of benzene, 5 g. of catalyst, 100 atm. of hydrogen; apparatus, 850-cc. Ipatieff rotating bomb with glass liner

POISON	HYDROGENATION OF BENZENE, IN WEIGHT PER CENT				
	Bismuth	Cadmium	Lead	Mercury	Tin
weight per cent					
0.000	33	33	33	33	33
0.005	21	6	5	15	15
0.05	6	1	1	11	3
0.5	2	0	0	3	0
1.0	0	0	0	0	0

Relative toxicities of bismuth, cadmium, lead, sodium chloride, and sodium sulfate (atmospheric hydrogenation).—Table 8 presents the relative toxicities of the above poisons in the order of decreasing toxicity. The comparison is based on the behavior at ordinary pressure of poisoned 99.8 per cent copper–0.2 per cent nickel catalysts. The results are calculated on the basis of both weight per cent and mole per cent. The amount of poison required for complete deactivation of the catalyst is surprisingly constant, the maximum variation being only fivefold. The variation in the poison requirement for 50 per cent deactivation is greater, being twentyfold when lead is compared with sodium sulfate on the mole per cent basis, and twelvefold when it is compared on the weight per cent basis.

TABLE 7

Poisoning of nickel-activated copper by sodium chloride and sodium sulfate

Conditions: T, 225°C.; contact time, 12 sec.; $H_2:C_6H_6 = 7$; atmospheric pressure

POISON	HYDROGENATION OF BENZENE	
	Sodium chloride	Sodium sulfate
mole per cent	*weight per cent*	*weight per cent*
0	19	19
0.025	7	19
0.05	5	18
0.1	3	7
0.2	0	1
0.24		0
0.5	0	
1.2		0

TABLE 8

Relative toxicities

Conditions: T, 225°C.; contact time, 12 sec.; $H_2:C_6H_6 = 7$; atmospheric pressure

POISON	50 PER CENT DEACTIVATION		100 PER CENT DEACTIVATION	
	Weight per cent	Mole per cent	Weight per cent	Mole per cent
Lead	0.02	0.006	0.09	0.03
Bismuth	0.02	0.006	0.16	0.05
Cadmium	0.03	0.02	0.2	0.12
Sodium chloride	0.02	0.02	0.15	0.16
Sodium sulfate	0.24	0.11	0.38	0.17

Alumina–nickel catalysts (atmospheric hydrogenation)

The catalysts listed in table 9 were prepared, some by coprecipitation followed by analysis, and others by adding a known amount of nickel nitrate to freshly precipitated alumina. They were decomposed at 400°C. in nitrogen and reduced at 225°C. in hydrogen. None of them hydrogenated benzene at 225°C. and ordinary pressure. The maximum contact times that were tried are given in table 9.

Because of the possibility that the inactivity of the alumina–nickel catalysts resulted from the non-reduction of nickel oxide at 225°C., new samples (made by adding nickel nitrate to freshly precipitated alumina) were reduced at higher temperatures. Although the nickel oxide in these catalysts was evidently reduced, the catalysts were decidedly less active than copper–nickel catalysts, and the inactivity was not caused by excessive temperature, since 400° to 500°C. is not too high for supported nickel catalysts. The conclusion is that alumina is decidedly inferior to copper as carrier for nickel.

TABLE 9

Inactive alumina–nickel catalysts

Conditions: T, 225°C.; H_2:C_6H_6 = 7; atmospheric pressure

NICKEL	CONTACT TIME
weight per cent	*seconds*
0.4	200
0.6	150
1	180
2	290
5.2	205
10	145

TABLE 10

Alumina–nickel catalysts

Conditions: T, 225°C.; H_2:C_6H_6 = 7; atmospheric pressure

NICKEL	REDUCTION TEMPERATURE	CONTACT TIME	HYDROGENATION OF BENZENE
weight per cent	*°C.*	*seconds*	*weight per cent*
1	425	95	0
2	425	170	0
2	500	180	0
2	550	175	0
5	425	90	0
5	500	100	0
10	425	7	63
10	425	23	92

Pyrophoricity of catalysts

Of all the mixed copper catalysts described in this paper, only two were pyrophoric: namely, those containing 5 per cent and 10 per cent of cobalt.

The authors express their thanks to Mr. W. J. Cerveny for much of the experimental work and to Dr. W. C. Pierce, of the University of Chicago, for spectroscopic analyses.

REFERENCES

(1) Ellis: U. S. patent 148,274 (1924).
(2) Ghosh and Bakshi: J. Indian Chem. Soc. **6**, 749 (1929).
(3) Griffin: J. Am. Chem. Soc. **57**, 1206 (1935).
(4) Ipatieff, Corson, and Kurbatov: J. Phys. Chem. **43**, 589 (1939).
(5) Ipatieff, Corson, and Kurbatov: J. Phys. Chem. **44**, 670 (1940).
(6) Juliard and Herbo: Bull. soc. chim. Belg. **47**, 717 (1938).
(7) Moore, Richter, and Van Arsdel: J. Ind. Eng. Chem. **9**, 451 (1917).
(8) White and Benton: J. Phys. Chem. **34**, 1784 (1931).
(9) Wimmer: German patent 271,985 (1914).

MIXED COPPER HYDROGENATION CATALYSTS

V. N. IPATIEFF AND B. B. CORSON

Research Laboratories, Universal Oil Products Company, Riverside, Illinois

Received July 3, 1940

INTRODUCTION

In previous papers (4, 5, 2) it was shown that pure copper is not able to hydrogenate benzene at ordinary pressure, but that the presence of small amounts of nickel, cobalt, and chromium oxide enable it to do so. It was also shown that copper is very susceptible to poisoning by bismuth, cadmium, lead, mercury, tin, chloride, and sulfate, and that lead can function either as a poison (in concentrations of 0.1 per cent and greater) or as a promoter (in concentrations of 0.01 per cent and smaller).

This paper describes the performance of fourteen series of mixed copper catalysts. These catalysts were carefully made from "reagent" chemicals, and several compositions in each series were determined by analysis, but their purities were not checked spectroscopically except in the case of the copper–chromia (5) and copper–alumina series.

Evidently there are many substances which, although catalytically inactive alone, possess the property of activating copper for the hydrogenation of benzene. The mixed catalysts described in this paper gave three distinct types of activity–composition curves (figure 1). Named in the order of decreasing effectiveness, ceria, alumina, thoria, and chromia gave maximum activity (eucoactics) when present to the extent of about 5 per cent, and the activity peak in the curve was sharply defined. The second type of curve was given by mixtures of copper with manganese oxide (and perhaps uranium oxide). The curve rose sharply on the addition of 2 to 5 per cent of oxide, and remained horizontal up to 80 per cent addition of impurity, beyond which it fell to zero activity. The third