

CATALYTIC ACTIVITY OF COPPER

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Introduction

In a previous paper¹ we have given the results of some studies on the catalytic reduction of nitrobenzene to aniline by hydrogen in the presence of nickel and copper catalysts. The catalysts were prepared by ignition of the nitrate and reduction of the oxide by hydrogen. Sabatier states² that a copper catalyst prepared from an ignited nitrate is only moderately active. He also states that a catalyst prepared by precipitating the oxide from the nitrate by sodium hydroxide and reducing in hydrogen is an excellent catalyst. The latter he describes as being violet and the former red. In this paper we shall give the results of some studies with copper catalysts prepared by reduction of the precipitated oxide.

Experimental Details

The apparatus used, method of work and analysis was the same as that described in a previous paper. In all the experiments a glass combustion tube was used instead of the iron pipe.

Purification of Copper

Some preliminary experiments indicated that the purity of the copper nitrate had a very large influence upon the activity of a copper catalyst prepared from the ignited oxide. Small amounts of iron seemed to have a beneficial effect, by preventing the copper catalyst from losing its activity. In order to get a pure copper, c. p. copper sulphate was dissolved in water, some sulphuric acid added, and the solution electrolyzed using graphite anodes and thin sheets of copper for cathodes. This electrolytically precipitated copper was used as anode in a nitric acid electrolyte, the cathode being a sheet

¹ Brown and Henke: Jour. Phys. Chem., **26**, 160 (1922).

² Sabatier: "La Catalyse," 106 (1913).

of copper covered with a thin film of vaseline. After the electrolysis the precipitated copper was broken off the original sheet of copper (the cleavage being possible because of the film of vaseline). The pure pieces of copper (140 grams) were then dissolved in nitric acid and the solution diluted to 500 cc. All the copper catalysts used in the experiments for this paper were prepared from this stock solution of pure copper nitrate.

Experimental Results

A 45-cc portion of this nitric acid solution of copper nitrate, containing 12.6 grams of copper, was diluted to 500 cc, heated to boiling and precipitated with a boiling hot solution of sodium hydroxide. To get a pure sodium hydroxide, metallic sodium was dissolved in water and the solution boiled and filtered. The hydroxide contained considerable carbonate. The precipitated copper hydroxide was filtered, washed and dried. Thirteen grams of the dry oxide was used as catalyst and placed in the same place in the catalyst tube as in our previous work. This was reduced at 260° by passing hydrogen over the catalyst at the rate of 10 liters per hour for $1\frac{3}{4}$ hours. The zone in which reduction was taking place became heated to a higher temperature due to the fact that the reduction is an exothermic reaction. When the zone of reduction reached the thermocouple (after a reduction of about a half hour) the temperature as indicated by the millivoltmeter rose in a few

TABLE I

Temperature of catalyst— 260° C.

Rate of flow of nitrobenzene—3.9 grams per hour.

Hydrogen in liters per hour	Excess of hydrogen in % of theory	Material yield of aniline in % of theory
3.5	64	97.0
7	230	97.0
14	560	97.4
25	1070	92.6
35	1540	92.6
52	2340	86.3

minutes from 260° to 312° and after a short time dropped back again to 260° . This catalyst immediately gave constant results when used. The average deviation from the mean of the first five experiments was 0.4%. The results showing the effect of rate of flow of hydrogen with this catalyst are given in Table I.

The results of Table I are shown graphically in Curve Cu-A of Fig. 1. The results show that the slower the rate of flow of hydrogen the higher the aniline yield until very slow rates are reached. For purposes of comparison

Curve Cu-B is redrawn from a previous paper in which the catalyst was prepared from an ignited nitrate. In the experiments represented by Curve Cu-B the rate of flow of nitrobenzene was the

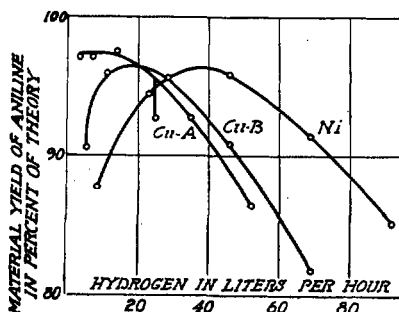


Fig. 1

same as in Cu-A. The curve for Ni is also redrawn from the same paper. The rates of flow of hydrogen as shown by curves Cu-B and Ni are probably a little too high since no glass-wool tube was used to remove the particles of sulphuric acid which were mechanically carried out of the sulphuric acid bottle. Above 20 liters of hydrogen per hour the two curves Cu-A and Cu-B are very similar but below this value they are different. Thus Cu-B gives a yield of only 90.5% at 5.7 liters per hour while Cu-A gives 97% material yields of aniline at 15 liters hydrogen per hour and does not drop even when the hydrogen flow is decreased to 3.5 liters per hour. The experiments of Curve Cu-B were carried out in the iron tube while those of Cu-A were carried out in a glass tube. However, experiments performed with a catalyst from an ignited nitrate in a glass tube show a similar decrease in yield with low rates of hydrogen flow as will be shown in Table II. This indicates that the best ratio of hydrogen to nitrobenzene for one copper catalyst

may not be the best for another copper catalyst prepared in a different way.

The decrease in yield with low hydrogen rates, with nickel as catalyst, is not due to incomplete reduction as in the case of the copper catalyst. At the lower hydrogen rates with the nickel as catalyst the product was colorless, a part of the nitrobenzene probably being reduced farther than the aniline stage, resulting in a low yield of aniline. It was impracticable with the apparatus employed to use lower hydrogen rates than 3.5 liters per hour. Even at this rate the nitrobenzene was not all carried into the furnace as soon as it was forced through the capillary into the catalyst tube, but it would drop onto the tube and then due to capillary action would tend to creep back between the capillary and the wall of the combustion tube toward the inlet end of the furnace. Pushing the capillary farther into the furnace overcomes this difficulty but then the nitrobenzene soon chars in the hot capillary and clogs it.

In our previous study of the catalytic activity of copper catalysts prepared from the ignited nitrate, ordinary c. p. copper nitrate was used, traces of iron, sulphates and chlorides being present. Also the catalysts were used in an iron tube instead of a glass tube. In Table II are given the results with two catalysts prepared from an ignited nitrate (produced from the double refined copper) and used in a glass tube. The nitrate (for both catalyst A22 and A25) was ignited in an electrically heated muffle, the temperature being allowed to rise to 420° C. About 26 grams of the ignited oxide were used for each catalyst and this was reduced with the rate of flow of hydrogen at about 4 liters per hour. In the first column are given the results with the catalyst from the pure nitrate (catalyst A22). The temperature during reduction of this catalyst rose to 295° C. In the second column are given the results with catalyst A25, which was prepared from the pure nitrate to which had been added an amount of ferric nitrate equivalent to 0.015% Fe in $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. This would make the iron content of the reduced copper catalyst equal to

0.069% Fe. The results with each catalyst are given in the order in which they were carried out.

TABLE II

Temperature of catalyst—260° C.

Rate of flow of nitrobenzene—4 grams per hour.

Rate of flow of hydrogen—14 liters per hour.

Excess of hydrogen—540%.

Catalyst No. A22 (Pure)		Catalyst No. A25 (0.069% Fe)	
Material yield of aniline in % of theory		Material yield of aniline in % of theory	
94.3	60.8 ¹	95.3	93.2
93.6	37.8 ²	93.6	92.9
87.3		94.3	64.9 ²
		90.6	

¹ Rate of flow of hydrogen in this experiment was 9.3 liters per hour.

² Rate of flow of hydrogen in these two experiments was 4.6 liters per hour.

The results of Table II indicate that a catalyst prepared from the ignited oxide of a pure copper nitrate and used in a glass tube is not as good a catalyst for the reduction of nitrobenzene to aniline as a copper catalyst prepared from the precipitated hydroxide. Thus the highest yield with catalyst A22 was 94.3%, which decreased rapidly with use to 87.3% in the third experiment while the copper catalyst of Table I (which was prepared from the precipitated hydroxide) gave 97% yields of aniline when used under practically the same conditions. The addition of a small amount of iron seems to be very beneficial. Thus catalyst A25 (from nitrate containing 0.015% Fe) for the first six experiments averaged 93.3% aniline yields while catalyst A22 (from the pure nitrate) decreased to but 87.3% in the third experiment. Catalysts A22 and A25 both gave good yields in the first experiments. It will also be noted that with each of the catalysts from the ignited nitrate when the rate of flow of hydrogen was decreased to 4.6 liters per hour the yield of aniline decreased tremendously the yield with catalyst A25 decreasing from an average of 93.3% with the hydrogen flow at 14 liters per hour to 64.9%

with the hydrogen flow at 4.6 liters per hour. With catalyst A22 when the rate of flow of hydrogen was only decreased to 9.3 liters per hour the aniline yield dropped to 60.8%. This is similar to the results with the copper catalysts from ignited nitrates when used in iron tubes as was pointed out in the discussion under Fig. 1. However, the catalyst from the precipitated oxide gave 97.5% yields of aniline even when the hydrogen flow was decreased to as low as 3.5 liters per hour.

TABLE III
Temperature of catalyst—260° C.
Rate of flow of hydrogen—14 liters per hour.

Nitrobenzene in grams per hour	Excess of hydrogen in %	Material yield of aniline in % of theory
3.9	560	97.4
6.3	300	96.5
9.3	170	92.6
17.4	50	80.2

The effect of rate of flow of nitrobenzene with a copper catalyst from a precipitated oxide was studied with the same catalyst that was used for the experiments of Table I. The results of several experiments at different rates of flow of nitrobenzene are given in Table III.

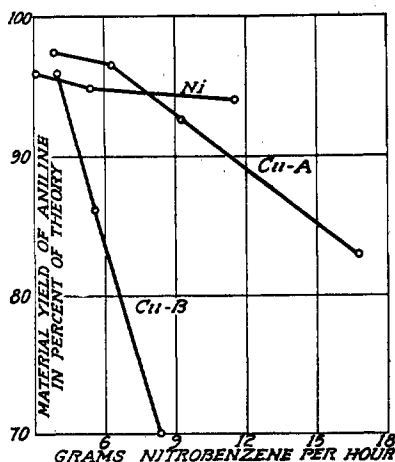


Fig. 2

The results of Table III are plotted in curve Cu-A of Fig. 2. For purposes of comparison, curve Cu-B is redrawn from a previous paper in which the catalyst was prepared from an ignited nitrate. The rate of flow of hydrogen for the experiments of curve Cu-B was 11.4 liters per hour which was the best rate for that catalyst. The curve for Ni is also redrawn from the same paper the hydrogen rate in this case being

17 liters per hour. The graph shows that the copper catalyst from the precipitated oxide is capable of carrying on the reduction of the nitrobenzene at a much greater rate than the copper catalyst from the ignited oxide. Up to 7.5 grams nitrobenzene per hour the catalyst from the precipitated copper oxide gives higher yields than the nickel catalyst.

The high rate at which the catalyst from the precipitated oxide is capable of carrying on the reduction and the high yields obtainable would make it superior to the catalyst from the ignited nitrate for commercial purposes. The higher yields obtainable would probably make it superior to the nickel catalyst up to about 8 grams nitrobenzene per hour, while with higher rates of nitrobenzene the nickel would be superior.

The copper catalyst from the precipitated oxide gave constant yields immediately when used as was noted above. After the first few experiments with this catalyst the aniline produced seemed to be perfectly colorless as not a trace of color could be detected. However, upon titration the yield was only 97 to 98%. After a few days' use of this catalyst the product became slightly colored, but upon titration the yield was found to still be practically the same.

After about three weeks' use during which time this catalyst was used at temperatures as high as 300° C it showed a slight decrease in activity, the yields of aniline being about 3% lower than at first. When this catalyst was taken out of the furnace it had a bluish black color while the catalyst from the ignited oxide was red and more compact. Upon examining this catalyst (from the precipitated oxide) it was found to contain bright pieces of hard massive copper. Upon examining these catalysts under the microscope (with a magnification of 100 diameters) the red copper catalyst looked as though it had been subjected to incipient fusion, the mass being made up of myriads of little spheres of copper. The catalyst from the precipitated oxide did not show this sintering to as great an extent as the red copper catalyst. When some of the hard

massive particles of copper (from the catalyst from the precipitated oxide) were broken up and examined under the microscope they showed a needle-like crystalline structure. From this and also from the slightly lower yields obtained after three weeks' use it appears that the catalyst slowly loses its activity probably due to a slow agglomeration or sintering of the small particles.

The catalyst from the precipitated oxide was also used in a rather extensive study of the effect of temperature upon the reduction. For this study a rather high rate of nitrobenzene, 9.7 grams per hour, was chosen. The results of experiments under different conditions are given in Table IV.

TABLE IV
Rate of flow of nitrobenzene—9.7 grams per hour.

Temperature, degrees C	Hydrogen in liters per hour	Excess of hydrogen in %	Material yield of aniline in % of theory
260	3.5	-35 ¹	73.9
260	7.0	30	90.3
260	14	160	92.6
260	25	360	92.3
260	35	550	86.6
260	52	860	78.9
279	7	30	95.9
279	14	160	91.2
279	25	360	84.9
279	35	550	82.9
298	3.5	-35 ¹	81.2
298	7	30	93.6
298	14	160	91.2
298	25	360	86.9
298	35	550	80.2

¹ In these two experiments the rate of flow of hydrogen was 35% below the theoretical amount needed.

The percentage excess of hydrogen is calculated from the rates of flow of hydrogen and nitrobenzene. However, the furnace is full of hydrogen at the beginning of an experiment and hydrogen is passed for 20 minutes or more after all the nitrobenzene has been forced into the furnace in order to wash all the material out of the furnace into the condenser.

The results of Table IV are shown graphically in Fig. 3. From the curves it is seen that 260° C is the best temperature through the greater part of the range of variation of hydrogen flow. At the lower rates of hydrogen flow, however, a temperature of 279 is better. After using the catalyst at these higher temperatures it did not give as high yields of aniline at 260 as it did before being used at the higher temperatures. This indicates that for continuous use 260 is the best temperature.

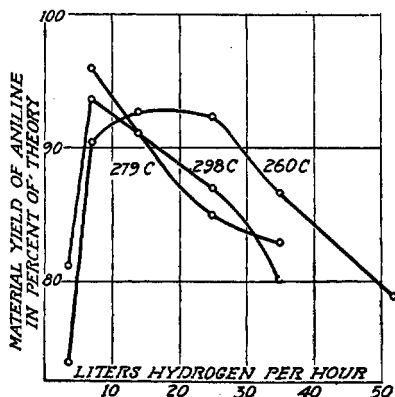


Fig. 3

An attempt was made to increase the rate at which the nitrobenzene could be reduced by precipitating the copper on a support. For this purpose some asbestos was thoroughly cleaned by boiling in HNO_3 , washing and drying. This was soaked in 15 cc of the nitric acid solution of the pure copper nitrate containing 4.2 grams of copper. This was then dropped into 50 cc of boiling NaOH solution. The asbestos copper oxide was filtered, washed and dried. In this manner 4.6 grams CuO was added to 3 grams of asbestos. Five grams of this, containing 3 grams of copper oxide, was used as catalyst. Another catalyst was prepared with pumice as support. The pumice was broken up to pass a 10 mesh sieve and remain on a 20 mesh sieve. This was boiled in HNO_3 , washed and dried. Ten grams of this pumice was soaked in 15 cc of the nitric acid solution of pure copper nitrate containing 4.2 grams copper. This was then dropped into 50 cc of a boiling NaOH solution. The pumice copper oxide was washed, filtered and dried. In this way 2 grams CuO was added to the pumice. Nine grams of this, containing 1.5 grams of CuO , was used as catalyst. The results with the copperized asbestos and pumice as catalyst are given in Table V.

TABLE V
Temperature of catalyst—260° C.

Nitrobenzene in grams per hour	Hydrogen in li- ters per hour	Excess of hy- drogen in %	Material yield of aniline in % of theory (copper on asbestos)	Material yield of aniline in % of theory (copper on pumice)
3.9	9.5	350	97.0	—
3.9	14	560	98.3	99.0
3.9	25	1070	—	98.6
3.9	35	1540	95.9	—
3.9	52	2340	93.9	92.3
9.7	5	— ¹	70.9	—
9.7	9.5	80	97.0	—
9.7	14	160	97.9	—
9.7	35	560	92.6	—
20 ²	25	120	96.3	—

¹ In this experiment the rate of flow of hydrogen was 6% below the theoretical amount needed.

² This was the fourth experiment with a new copper-asbestos catalyst.

The results of Table V (except the experiment in which the rate of nitrobenzene was 20 grams per hour) are shown graphically in Fig. 4. Curves Cu-3.9 and Cu-9.7 are redrawn from Figs. 1 and 3, respectively. The figures 3.9 and 9.7 refer to the rate of flow of nitrobenzene in grams per hour. Curves Cu-A-3.9 and Cu-A-9.7 refer to the copper on asbestos catalyst while Cu-P-3.9 refers to the copper on pumice. The experiments represented by the three curves, Cu-P-3.9, Cu-A-3.9 and Cu-3.9, were all carried out under the same conditions. The copper on pumice shows the highest yields with the copper on asbestos a close second while the curve for copper alone falls below both of these. Upon increasing the nitrobenzene flow to 9.7 the results with the copper catalyst are considerably below those for the copper on asbestos catalyst as is shown by the curves. From these curves it would appear that copper on pumice is the best catalyst with copper on asbestos a close second. However, this is not necessarily true because the copper in pumice catalyst quickly lost its activity. Thus after one day's use an experiment with 3.9 grams nitrobenzene

per hour and 52 liters hydrogen per hour gave only a 75.2% yield of aniline instead of a 92.3% yield on the first day. This bad feature places the copper on asbestos catalyst as superior to the copper on pumice when the volumes of the two are approximately the same. However, there were 3 grams CuO on the asbestos and only 1.5 grams on the pumice. When

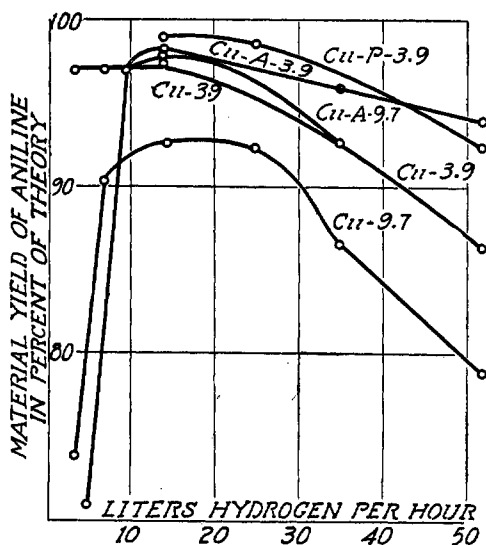


Fig. 4

copper was used without a support 13 grams of the precipitated CuO was used while 27 grams of the ignited CuO are required to fill the same approximate volume. The same volume of catalyst was used each time.

The copper asbestos catalyst may be used with a very high rate of nitrobenzene as is shown by the experiment with 20 grams nitrobenzene per hour in which the yield of aniline was 96.3% of the theoretical yield. However, at these rapid rates of nitrobenzene the catalyst quickly loses its activity. This loss in activity is probably due to a heating effect. Thus in one experiment with 17 grams nitrobenzene per hour the temperature as indicated by the thermocouple rose 20° C in

about 8 minutes. It would be reasonable to suppose that the temperature became much higher at the surface of the catalyst where the reaction took place than that indicated by the thermocouple, and that this heating causes the diminution in activity.

The yield obtained with the rate of nitrobenzene at 20 grams per hour is much higher than that obtained with nickel, which indicates that this copper with an asbestos support has an even greater speed of reduction than nickel without a support.

The higher yield with the copper on asbestos catalyst does not necessarily mean that copper on asbestos is "more active" than copper alone. Probably a greater surface of copper is exposed to the gaseous mixture when the copper is precipitated on the asbestos fibers than when it lies in the tube in the form of a powder. When it is remembered that only 3 grams CuO were used on the asbestos catalyst while 13 grams of the copper oxide were used for the copper catalyst, it is seen that the difference in rates per gram of copper is very great.

Summary

1. Sabatier's statement that a copper catalyst prepared from a precipitated oxide is a better catalyst than one prepared from an ignited nitrate has been confirmed.

2. Much lower rates of hydrogen may be used without loss in yield of aniline with a copper catalyst from a precipitated oxide than with one from an ignited nitrate.

3. The copper catalyst from the precipitated oxide is capable of carrying out the reduction of the nitrobenzene at a much greater rate than the one from the ignited nitrate.

4. The difference in physical appearance of the catalysts from the precipitated oxide and ignited nitrate has been pointed out.

5. The best temperature for carrying out the reduction was found to be near 260° C—about the same as in our previous work with catalysts from the ignited nitrate.

6. Copper on asbestos was found to be capable of reducing the nitrobenzene at a much greater rate per gram of copper than copper alone.

7. When the copper on asbestos catalyst is used at high rates of nitrobenzene it quickly loses its activity.

8. Copper on asbestos is a better catalyst than an equal volume of copper on pumice, although the latter only contained half as much copper as the copper on asbestos catalyst.

9. A small amount of iron in a copper catalyst prepared from an ignited oxide prevents the rapid decrease in the activity of the catalyst.

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