

The Catalytic Activity of the Reduced Vanadates of Nickel, Copper and Lead¹

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Metals and their oxides have been studied by many investigators and have been classified in the order of their activities as reducing catalysts in a number of reactions. Numerous additional investigations have been made as to the effect of various addition agents on the activity, modifications and structure of these catalysts. One of the most intimate and homogeneous alterations possible, in separating the catalyst atoms or altering their structure, should be made by the addition of a non-metallic oxide to the metallic oxide catalyst such that a salt is formed. Yet there have been few studies on these compounds, or the metals formed by the reduction of these salts, as reducing catalysts.

This paper is one of a series reporting on the activity of such reduced salts as catalysts for the vapor phase reduction of organic nitro compounds to their respective amines with hydrogen. It is hoped that the series will lead to a better understanding of the effect of these anions in modifying the activity of a catalyst and aid in predicting the behavior of an untried catalyst.

Apparatus

A vertical-type aluminum block furnace, electrically heated, thermally controlled, and containing a pyrex-glass reaction tube of 18 mm. bore was employed. Temperature was recorded by means of thermocouples extending 2 inches into each end of a 12-inch catalyst column and a third extending well into the metal block. Feed was from above, controlled by the delivery of 2.00 ml. of nitrobenzene under a variable head of mercury through a calibrated capillary tube. Hydrogen was measured in liters per hours through a calibrated flowmeter.

Catalyst

The catalysts were reduced salts as prepared by Christena (2). Fifteen grams of each salt was supported on enough asbestos fiber to give a 12 inch catalyst bed. It was then reduced under a flow of 14.5 liters of hydrogen per hour in the following manner: nickel vanadate was brought to a temperature of 300° and maintained there for one hour, copper vanadate was brought to a temperature of 340° in one hour and four minutes and maintained at that temperature for one hour, while lead vanadate was brought to a temperature of 360° in

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one hour and fifteen minutes and maintained there for two additional hours.

Reduced Nickel Vanadate Catalyst

The operating conditions for curve No. 1, Figure 1 were 2 grams per hour of nitrobenzene and 230 per cent theory of hydrogen flowing

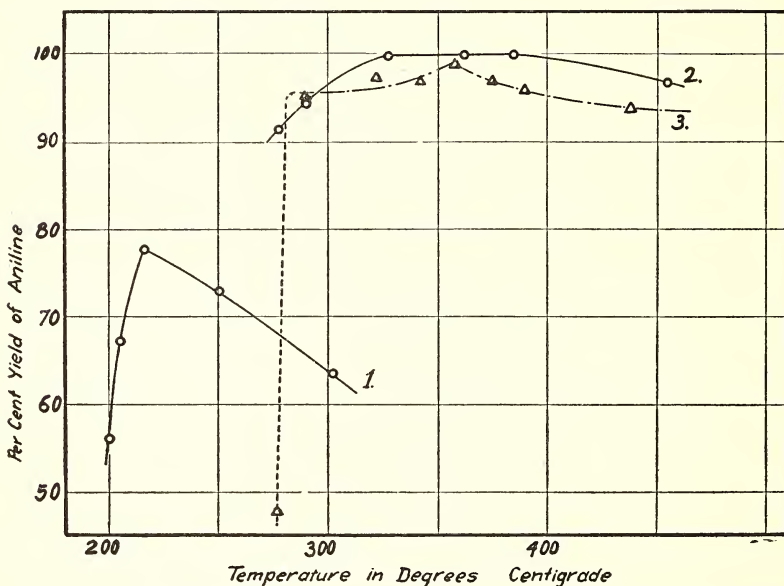


Fig. 1. The effect of operating temperature on yield of aniline. Curve 1, nickel vanadate; curve 2, copper vanadate; curve 3, lead vanadate.

over 15 grams of nickel vanadate reduced. We see the optimum furnace temperature of 216° agrees well with the 210° reported by Christena (2) for the reduction of nitronaphthalene.

A rate of 20 grams of nitrobenzene per hour gave the highest yields in percentage conversion, Table IA.

The optimum rate of flow of hydrogen, 230 per cent of theory, Table IB, is much less than the 700 to 1020 per cent of theory reported (2) for the reduction of α -nitronaphthalene.

It appears the activity of nickel vanadate is not high for the reduction of organic nitro compounds to their respective amines. This is due to its high activity as a reducing catalyst as we evidenced by the strong odor of benzene in the reduction products throughout the experiments.

X-ray powder defraction patterns revealed the reduced catalyst contained metallic nickel. There were, however, no lines corresponding to either V_2O_3 or V_2O_5 . From the results of similar studies on other reduced compound catalysts in this laboratory (3, 4) we are led to

TABLE I. Catalyst, 15 grams of Nickel Vanadate Reduced;
Furnace Temperature 235° C.

	Nitrobenzene gms/hr.	Hydrogen in per cent theory	Aniline in per cent yield
A	16	230	58.5
	20	230	75.0
	26	230	70.0
	32	230	57.5
B	20	184	50.0
	20	230	75.0
	20	294	74.0
	20	368	72.5

suspect that the remainder of the material is a salt of nickel oxide and one or more of the lower oxides of vanadium.

Reduced Copper Vanadate Catalyst

Quantitative yields of aniline may be produced over this catalyst in a range of from 325° to 385°, Figure 1 curve 2. The conditions for the construction of this curve were 9 grams of nitrobenzene and 408 per cent of hydrogen flowing over 15 grams of the nickel vanadate reduced. Here again there is good agreement with the temperature 320° to 340° reported for the maximum conversion of α -nitronaphthalene (2).

The optimum rate for the flow of nitrobenzene is seen, Table IIA, to be from 9 to 5 or less grams per hour.

Hydrogen flowing at the rate of 408 per cent of theory was found to give the maximum yield, Table IIB, however yields above 97 per cent were obtained over the entire range studied.

TABLE II. Catalyst, 15 grams of Copper Vanadate Reduced;
Furnace Temperature 325°

	Nitrobenzene gms/hr.	Hydrogen in per cent theory	Aniline in per cent theory
A	5	408	100.0
	9	408	100.0
	13	408	96.5
	18	408	93.5
B	9	257	97.5
	9	408	100.0
	9	612	98.9
	9	817	97.5
	9	1220	97.3

TABLE III. Catalyst, 15 grams of Lead Vanadate Reduced;
Furnace Temperature 358° C.

	Nitrobenzene gms/hr.	Hydrogen in per cent theory	Aniline in per cent of theory
A	1.0	367	99.0
	1.5	367	99.0
	2.0	367	99.1
	3.0	367	98.9
	3.8	367	98.4
	7.0	367	97.8
B	2	184	99.0
	2	275	98.5
	2	367	99.1
	2	550	99.0
	2	698	99.0

It is of interest to note in the study of this catalyst that excellent reductions are obtained over broad ranges for each of the variables studied.

Reduced Lead Vanadate Catalyst

The optimum temperature for the reduction of nitrobenzene over this catalyst is seen to be approximately 358°, Figure 1 curve 3. The operating conditions for establishing this curve were 4 grams of nitrobenzene and 367 per cent theory of hydrogen flowing over 15 grams of lead vanadate reduced. Christena (2) reports an optimum temperature of 390° for the reduction of α -nitronaphthalene over the same catalyst. This difference may be in part due to the fact that the temperature used to reduce the catalyst in this work was 75° lower than that used by Christena. It is also seen in this work that in the temperature range from 320° to 375° the yields are above 97 per cent. At temperatures somewhere below 280° the catalyst began to lose activity slowly due to poisoning. Large quantities of azoxybenzene were also produced at these low temperatures.

Maximum yields are obtained when the rate of flow of nitrobenzene is less than 4 grams per hour and yields are constant at least to 1 gm as shown in Table IIIA. This curve was terminated at 1 gram per hour since duplicate values and constant rates were increasingly difficult to obtain at the lower values.

It is also noted that a very wide range in the rate of flow of hydrogen gave the maximum yield of 99 per cent aniline, Table IIIB.

So far as could be determined by X-ray powder defraction patterns the reduced catalyst consisted of metallic lead and vanadium trioxide.

The highest yield previously reported (1) for aniline prepared by reduction of nitrobenzene over lead or a lead compound was 98.4 per cent obtained by Brown and Raines over lead sulfide.

Summary

1. The optimum conditions for the reduced nickel vanadate catalyst were an operating temperature of 216°, hydrogen flowing at a rate of 230% of theory and nitrobenzene flowing at a rate of 20 grams per hour, giving a yield of 75 per cent aniline.

2. Reduced nickel vanadate is too active as a reducing catalyst for the intermediate reduction to aniline.

3. The optimum conditions for the reduced copper vanadate catalyst were temperatures from 325° to 385°, hydrogen flowing at a rate of 408 per cent of theory and nitrobenzene flowing at a rate of 5 to 9 grams per hour, giving a yield of 100 per cent aniline.

4. The optimum conditions for the reduced lead vanadate catalyst were 358°, hydrogen flowing in a range of from 184 to 698 per cent of theory or possibly a greater range, and nitrobenzene flowing at a rate of one gram per hour or less up to 3 grams per hour, giving yields of 99.0%. At nitrobenzene rates as high as 7 grams per hour the yield is 97.8 per cent.

5. Reduced lead vanadate gives yields greater than any previously reported where lead or lead compounds are used as catalysts.

6. While reduced copper vanadate is the best of the three catalysts studied for the reduction under consideration, both the copper and lead vanadates gave excellent yields over a rather wide range of the variables studied.

Literature Cited

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