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Dinickel Phosphide as a Heterogeneous Catalyst for the Vapor Phase Reduction of Nitrobenzene with Hydrogen to Aniline and Water

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Dinickel phosphide, prepared by the reduction of nickel orthophosphate in excess hydrogen for 15.7 hours at 545°, was found to be a surprisingly active heterogeneous catalyst for the vapor phase reduction of nitrobenzene with hydrogen to aniline and water. Yields of over 95 weight % aniline were obtained under the following conditions: pressure, atmospheric; temperature, 360 to 420°; feed rate of nitrobenzene, 10 millimoles per hour per gram of $NiP_{0.584}$ catalyst; and mole ratio of hydrogen to nitrobenzene in the feed, 11 to 23.

Introduction

Reduction catalysts usually are prepared by reducing precipitated metallic hydroxides or oxides with hydrogen. This Laboratory has been concerned with a study of the effect on catalytic activity of other anions as precipitating agents.[1-5] Herein the nickel cation was precipitated with the phosphate anion to prepare nickel phosphate octahydrate which was reduced with hydrogen to obtain a reduction catalyst identified as dinickel phosphide.

Previously, none of the crystalline phosphides of nickel have been reported to be active catalysts. However, there are several references to the use of nickel phosphate as a heterogeneous catalyst under conditions which might produce dinickel phosphide. Denton and Bishop[6] have described the use of a nickel phosphate catalyst for the production of nitriles from alkenes or alkylbenzenes and ammonia at 465 to 580° and atmospheric pressure. Britton and Dietzler[7] and Heath[8] describe a mixed calcium and nickel phosphate catalyst for the dehydrogenation of butene to butadiene at 600 to 700° and atmospheric pressure. Hutter[9] reports that nickel phosphate reduced in hydrogen forms dinickel phosphide beginning at 450°, and that calcium phosphate is not reduced in hydrogen at 1000°. Therefore it is possible that the active catalyst in each of the above cases is a phosphide of nickel formed from the phosphate by the reducing action of (1) ammonia, (2) hydrocarbon or (3) by-product hydrogen. However none of these workers[6-8] claimed a nickel phosphide catalyst.

An amorphous solid solution of phosphorus in nickel has been described as a catalyst for the reduction of nickel ion by hypophosphite ion in aqueous solution. In the Kanigen[10] chemical plating process the nickel plate formed is an amorphous supercooled liquid solution of 7 to 10 weight % phosphorus in nickel[11] which acts as an efficient catalytic surface for continued deposition of a smooth, dense, non-porous plate of any desired thickness.

Apparatus and Procedure.—The apparatus consisted of an electrically heated, thermostatically controlled, vertical cylindrical metal block furnace containing a 24-mm. bore Pyrex reaction tube 30 inches long. Under a variable head of mercury the 2.00-ml. samples of nitrobenzene were introduced at a constant measured rate through a capillary at the top of the furnace into a glass wool vaporizing zone. Excess hydrogen gas flowing at a constant measured rate carried the nitrobenzene vapors through the 6-inch catalyst column (11.4 g. of $NiP_{0.584}$ catalyst mixed with 4 g. of shredded asbestos) where reaction occurred and swept all products out through a gas scrubber containing 250 ml. of 1.2 *N* HCl which removed the aniline formed. The aniline was titrated with bromide–bromate solution according to the method of Hull.[12] The catalyst efficiency was calculated as the weight % yield of aniline. The temperature reported was that of the metal block furnace.

The apparatus and procedure were checked (a) with a copper catalyst of proven activity and (b) with all the materials present except the catalyst. Part b yielded no titratable conversion of nitrobenzene to aniline.

Dinickel Phosphide Catalyst Preparation.—Using the method of Ephraim and Rossetti[13] one gram-mole of freshly precipitated nickel hydroxide was stirred into two liters of boiling distilled water containing 50 ml. of 85% phosphoric acid. The light-green, crystalline nickel phosphate octahydrate formed was filtered, washed, dried several days in air, and weighed as 0.28 gram-mole of $Ni_3(PO_4)_2 \cdot 8H_2O$ (85% yield). The calculated percentage nickel is 34.51%, that found was 34.06%. An X-ray powder pattern checked that of $Ni_3(PO_4)_2 \cdot 8H_2O$ as given by The Dow Chemical Co.[14]

Nickel phosphate octahydrate was dried at 145° for 24 hours to a yellow powder[15] containing 43.45% nickel and 15.0% phosphorus, thus having an atomic ratio of nickel to phosphorus of 1.528. Twenty grams of this powder was mixed with 4 g. of shredded asbestos and reduced for 15.7 hours at 545 ± 10° with excess hydrogen. The X-ray powder pattern of the reduced catalyst after 50 runs matched that of dinickel phosphide as reported by Biltz and Heimbrecht[16] and Nowotny and Henglein,[17] and analysis showed

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(1) O. W. Brown and E. D. Raines, *J. Phys. and Colloid Chem.*, **43**, 383 (1939).

(2) C. S. Rohrer, J. Rooley and O. W. Brown, *ibid.*, **55**, 211 (1951).

(3) C. S. Rohrer, R. C. Christena and O. W. Brown, *J. Phys. Chem.*, **56**, 662 (1952).

(4) C. S. Rohrer, P. F. King and O. W. Brown, *Proc. Indiana Acad. Sci.*, **61**, 135 (1952).

(5) J. Rooley, C. S. Rohrer and O. W. Brown, *J. Phys. Chem.*, **56**, 1082 (1952).

(6) W. I. Denton and R. B. Bishop (to Socony–Vacuum Oil Co., Inc.), U. S. Patents 2,478,464 (Aug. 9, 1949), 2,496,659 (Feb. 7, 1950), 2,561,787 (July 24, 1951).

(7) E. C. Britton and A. J. Dietzler (to Dow Chemical Co., Inc.), U. S. Patent 2,442,319 (May 25, 1948).

(8) S. B. Heath (to Dow Chemical Co., Inc.), U. S. Patent 2,542,813 (Feb. 20, 1951).

(9) J.-C. Hutter, *Ann. chim.* (*Paris*), **8**, 450 (1953).

(10) Kanigen is a trade name used by General American Transportation Corporation and its licensees to identify the nickel deposit or coating which is the product of a catalytic nickel reduction process.

(11) A. W. Goldenstein, W. Rostoker, F. Schossberger and G. Gutzeit, *J. Electrochem. Soc.*, **104**, 104 (1957).

(12) A. W. Hull, *Phys. Rev.*, **9**, 84, 564 (1917); **10**, 661 (1917).

(13) F. Ephraim and C. Rossetti, *Helv. Chim. Acta*, **12**, 1025 (1929).

(14) "X-Ray Diffraction Data Cards," American Society for Testing Materials, Philadelphia, Pa., (Original Set) June, 1945; (First Supplement) August, 1945.

(15) H. Bassett and W. L. Bedwell, *J. Chem. Soc.*, 854 (1933).

(16) W. Biltz and M. Heimbrecht, *Z. anorg. u. allgem. Chem.*, **237**, 132 (1938).

(17) H. Nowotny and E. Henglein, *Z. physik. Chem.*, **B40**, 281 (1938).

only nickel (76.48%) and phosphorus (23.58%) to be present in the atomic ratio of Ni/P of 1.711. This is in keeping with the findings of Hutter[9] who states that nickel phosphates of atomic ratios of Ni/P of (a) 1.49, ortho; (b) 1.02, pyro; and (c) 0.50, meta, are all reduced with hydrogen to dinickel phosphide with the reduction of the nickel orthophosphate starting at 450°.

Results

Table I indicates the optimum furnace temperature to be approximately 374°, where $NiP_{0.585}$ catalyzes a 96.9 weight % yield of aniline. Table II indicates that dilution of the feed stream with hydrogen beyond the mole ratio of hydrogen to nitrobenzene of 11.3 adversely affects the yield of aniline. Under the following rather broad condition $NiP_{0.584}$ catalyst effected yields in excess of 95 weight % aniline: pressure, atmospheric; furnace temperature, 350 to 420°; feed rate of nitrobenzene, 10 millimoles per hour per gram of $NiP_{0.584}$ catalyst; and mole ratio of hydrogen to nitrobenzene in the feed stream, 11 to 23.

TABLE I

EFFECT OF FURNACE TEMPERATURE ON CATALYST EFFICIENCY

Weight of $NiP_{0.584}$ catalyst, 11.4 g.; average feed rate of nitrobenzene, 10 millimoles, hr.$^{-1}$, g. $NiP_{0.584}{}^{-1}$; average mole ratio of $H_2/C_6H_5NO_2$ in the feed, 13.

Furnace block temp., ±5°C.	Catalyst efficiency (weight % aniline)
335	93.7
360	95.6
374	96.9
406	96.2
421	95.3

TABLE II

EFFECT OF MOLE RATIO OF HYDROGEN TO NITROBENZENE IN THE FEED UPON CATALYST EFFICIENCY

Weight of $NiP_{0.584}$ catalyst, 11.4 g.; average feed rate of nitrobenzene, 11 millimoles, hr.$^{-1}$ g. $NiP_{0.584}{}^{-1}$; average furnace temperature, 380°.

Mole ratio $H_2/C_6H_5NO_2$	Catalyst efficiency (weight % aniline)
11.3	96.9
23.0	95.1
25.0	94.9
31.6	92.5

Discussion

Rooley, Rohrer and Brown[5] found that both nickel molybdate and nickel chromate when reduced in hydrogen formed catalysts containing significant amounts of nickel metal, and Rohrer, King and Brown[4] discovered the same to be true for reduced nickel vanadate catalyst. However, the following evidence indicates that nickel phosphate is reduced in hydrogen according to the reaction

$$8Ni_3(PO_4)_2 + 64H_2 = 12Ni_2P + P_4 + 64H_2O$$

to form dinickel phosphide catalyst containing no metallic nickel. 1. The method of preparation of Ni_2P was that of Hutter[9] and Rose.[18] 2. The thirteen strongest lines in the X-ray powder diffraction pattern of the catalyst correspond to those for Ni_2P.[16,17] 3. The insolubility of the catalyst in hydrochloric acid, its solubility in nitric acid to give nickel and phosphate ions, and its gray-black color correspond to the properties of Ni_2P prepared and described by Biltz and Heimbrecht.[16] 4. Insufficient metallic nickel is present in the catalyst to give a test for the nickel ion in the hydrochloric acid solubility test. 5. It would be extremely difficult to account for the rate at which aniline was produced by this catalyst if the catalytic activity were due only to an immeasurably small trace of metallic nickel possibly present. 6. When metallic nickel is prepared as a catalyst for this reaction the optimum operating temperature is 192°[19] or lower,[20] depending upon the method of preparing the catalyst, whereas the optimum operating temperature for Ni_2P is 374.° 7. There is a slight excess of phosphorus over the stoichiometric Ni_2P, *i.e.*, $Ni_2P_{1.169}$.

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(18) H. Rose, *Pogg. Ann.*, **24**, 232 (1832).

(19) O. W. Brown and C. O. Henke, *J. Phys. Chem.*, **26**, 161 (1922).

(20) Unpublished data from this Laboratory.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Stability of Metal Chelates of Compounds Related to Anthranilic Acid

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The acidity constants of anthranilic acid, N-methylanthranilic acid, 2,2′-iminodibenzoic acid, 2,2′-hydrazodibenzoic acid, N,N′-methylenedianthranilic acid, N,N′-trimethylenedianthranilic acid, N-(2-aminoethyl)-anthranilic acid, α-amino-*o*-toluic acid, α-carboxy-*o*-anisic acid, N-(carboxymethyl)-anthranilic acid, and N,N-bis-(carboxymethyl), anthranilic acid were determined in 1:1 volume water–dioxane and the stabilities of the chelate compounds of cobalt, nickel, copper, zinc and cadmium with each of these acids were obtained. The variations in the constants were related to the properties of the metal ions and the structural differences in the ligand molecules.

The acidity constants of anthranilic acid and some related compounds and the apparent formation constants for chelation of these substances with the divalent cations of cobalt, nickel, copper, zinc and cadmium in 1:1 volume water–dioxane have been studied. The method that was used is similar to that previously described for substituted anthranilic acids[2] and N,N′-ethylenedianthranilic acid.[3]

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(1) Abstracted in part from the doctoral dissertation of Allen Young, March, 1957.

(2) W. F. Harris and T. R. Sweet, *J. Phys. Chem.*, **60**, 509 (1956).

(3) T. R. Sweet and W. F. Harris, *ibid.*, **61**, 694 (1957).