[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

Heteropoly-acids as Catalysts for the Vapor Phase Partial Oxidation of Naphthalene

BY MILTON M. MARISIC[*]

The vapor phase catalytic oxidation of naphthalene results in the formation of naphthoquinone, phthalic anhydride, maleic anhydride, benzoic acid, water and carbon dioxide. Naphthoquinone and benzoic acid occur in very small amounts under the conditions at which phthalic anhydride is the major product. The vapor phase oxidation of naphthalene, employing vanadium pentoxide on asbestos as a catalyst, was first mentioned by J. Walter,[1] in 1895. However, Walter's work was overlooked and the discovery of the catalytic vapor phase partial oxidation of naphthalene was attributed to Gibbs.[2] Conover and Gibbs[3] found that the oxides of the metals of the fifth and sixth groups of the periodic system were especially effective as catalysts for this reaction. The best were vanadium pentoxide and molybdenum oxide, giving, respectively, yields of 82 and 58% of the theoretical amount of phthalic anhydride, the yields being based on the amount of naphthalene attacked.

A large number of materials have been used as catalysts for the partial oxidation of naphthalene.[4] The heteropoly-acids, however, have never been proposed as catalysts for the partial oxidation of organic compounds.

A consideration of the structure[5] of the heteropoly-acids suggests the desirability of testing them as oxidation catalysts for a number of reasons. First, the oxides vanadium pentoxide, molybdenum trioxide, and tungsten trioxide, which make up the heteropoly-acids, are known to be oxidation catalysts, their efficiency as catalysts for the partial oxidation of naphthalene decreasing in the order in which they were named. Second, the X-ray crystal structure analyses of the 12-heteropoly-acids disclose extremely porous structures. Hence, the decomposed heteropoly compound should have a large internal surface, which may result in a highly active catalyst. Third, the central ion in the complex may function as a promoter, as a poison, or simply as a support to the catalyst. No prediction can be made as to which one of these three latter possibilities will occur as is evident from the work of F. E. T. Kingman,[6] who studied the hydrogenation of phenol to benzene using heteropoly-acids containing molybdenum as catalysts.

In view of the suggestions presented above it seemed worth while to test the heteropoly-acids as catalysts for the partial oxidation of naphthalene. The ultimate purpose of this investigation was to ascertain what effect the central atom of the heteropoly-acid would have on the catalytic activity of the groups surrounding it. Hence, it was essential to establish the catalytic activity of the groups surrounding the central atom.

The catalytic activity of vanadium pentoxide for the oxidation of naphthalene has been established by numerous workers.[4] A repetition of the determination of the catalytic activity of vanadium pentoxide for the oxidation of naphthalene served as a check on the technique employed throughout this investigation. The catalytic activity of molybdenum trioxide for this reaction was determined by Conover and Gibbs,[3] but these workers did not vary their experimental conditions sufficiently to establish definitely the catalytic activity of molybdenum trioxide.[7] It was necessary, therefore, to determine the catalytic activity of this catalyst.

Catalysts from Heteropoly-compounds.—Catalysts were prepared from the heteropoly-acids or their ammonium salts by heating at 400° in a current of air for one hour. Eight to fourteen mesh size crystals of the heteropoly-acids were used; when the crystals were larger they were broken up into this size, and when they were smaller they were either pressed into pellets or deposited on asbestos fibers.

(1) **Phosphomolybdic Acid, $H_3[PO_4(MoO_3)_{12}]\cdot xH_2O$.**—Phosphomolybdic acid was prepared according to a procedure which is general for the preparation of a number of

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[*] Present address Socony-Vacuum Oil Co., Paulsboro, N. J.

(1) J. Walter, *J. prakt. Chem.*, **51**, 107 (1895).

(2) Gibbs, *Ind. Eng. Chem.*, **11**, 1031 (1919).

(3) Conover and Gibbs, *ibid.*, **14**, 120 (1922).

(4) Marek and Hahn, "Catalytic Oxidation of Organic Compounds in the Vapor Phase," Chapter XIII, A. C. S. Monograph 61, Chemical Catalog Co., New York, N. Y., 1932.

(5) For a discussion of the various types of heteropoly-acids and their structures see Emeléus and Anderson, "Modern Aspects of Inorganic Chemistry," D. Van Nostrand Co., New York, N. Y., 1939, chapter V.

(6) Kingman, *Trans. Faraday Soc.*, **33**, 784 (1937).

(7) The 58% yield of phthalic anhydride reported by these workers actually amounted to a 20% conversion of naphthalene passed over the catalyst.

heteropoly-acids and is known as the method of Drechsel.[8]

(2) **Ammonium Phosphomolybdate, $(NH_4)_3[PO_4(MoO_3)_{12}]$.**—Ammonium phosphomolybdate was prepared according to a method used for the quantitative determination of phosphorus.[9] The ammonium phosphomolybdate was made into a paste with water, pressed into pellets, and dried. The pellets were broken up into pieces of eight to fourteen mesh size.

(3) **Silicomolybdic Acid, $H_4[SiO_4(MoO_3)_{12}]\cdot xH_2O$.**—Silicomolybdic acid was prepared according to the method of Drechsel.[8,10] Three and one-half grams of silicomolybdic acid was made into a thin paste with water and thoroughly mixed with 2.0 g. of asbestos fibers. This mixture was stirred and slowly evaporated to dryness.

(4) **Arsenomolybdic Acid $H_3[AsO_4(MoO_3)_{12}]\cdot xH_2O$.**—Arsenomolybdic acid was prepared according to the method of Drechsel.[8] Asbestos fibers were impregnated with arsenomolybdic acid by making 4.0 g. of arsenomolybdic acid into a paste with water and mixing with 2.0 g. of asbestos fibers. This mixture was stirred and evaporated to dryness.

Arsenomolybdic acid was also used as a catalyst without a support. This catalyst was prepared by mixing arsenomolybdic acid with water to form a thick paste, pressing the paste into pellets and breaking up the dry pellets into pieces of 8–14 mesh size.

(5) **Ammonium Stannomolybdate, $(NH_4)_8Sn(Mo_2O_7)_6\cdot 20H_2O$.**—Ammonium stannomolybdate was prepared according to Rosenheim's[11] method.

(6) **Ammonium Ferricomolybdate, $3(NH_4)_2O\cdot Fe_2O_3\cdot 12MoO_3\cdot 19H_2O$.**—Ammonium ferricomolybdate was prepared according to a method described by Hall.[12]

(7) **Ammonium Nickel Molybdate, $5(NH_4)_2O\cdot 3NiO\cdot 16MoO_3\cdot 16H_2O$.**—Ammonium nickel molybdate was prepared according to the method of Hall.[12] Five grams of powdered ammonium nickel molybdate was moistened with water and thoroughly mixed with 3 g. of asbestos fibers. This mixture was stirred and evaporated to dryness.

(8) **Ammonium Chromicomolybdate, $3(NH_4)_2O\cdot Cr_2O_3\cdot 12MoO_3\cdot 20H_2O$.**—Ammonium chromicomolybdate was prepared according to the method of Hall.[12]

(9) **Phosphotungstic Acid, $H_3[PO_4(WO_3)_{12}]\cdot xH_2O$.**—Phosphotungstic acid was prepared according to the method of Drechsel.[8,13] The compound was converted into pellets following the procedure described above for ammonium phosphomolybdate.

(10) **Ammonium Phosphovanadate, $7(NH_4)_2O\cdot P_2O_5\cdot 12V_2O_5\cdot 26H_2O$.**—Ammonium phosphovanadate was prepared according to the method of Rosenheim and Pieck.[14]

(11) **Ammonium Phosphovanadotungstate, $13(NH_4)_2O\cdot 2P_2O_5\cdot 8V_2O_5\cdot 34WO_3\cdot 86H_2O$.**—Ammonium phosphovanadotungstate was prepared according to Rogers'[15] method.

Apparatus and Experimental Procedure.—The apparatus was of the type usually employed in such studies. It consisted of two flow meters for measuring the primary and secondary air, a manometer for determining the pressure in the system, naphthalene saturators, reaction chamber, and condensers. The primary air was passed through the naphthalene saturators, which were immersed in a constant temperature water-bath maintained at 85.5° for convenience. The air–naphthalene mixture after leaving the saturators was mixed with secondary air and then conducted into the reaction chamber, the first part of which served as a preheater and the latter part contained the catalyst. The tube leading to the reaction chamber was wound with nichrome wire and heated electrically to prevent condensation of naphthalene. The reaction chamber was heated with an electric furnace. The temperature of the furnace was regulated by means of a rheostat. The temperature of the catalyst was measured by a movable thermocouple which extended into the center of the catalyst mass. The products of the reaction were led into two condensers connected in series and immersed in Dewar flasks containing ice and water. The exit gases were scrubbed free of acidic material by bubbling them through a cylinder of water. The first condenser caught practically all of the condensate; a glass wool plug in the bottom of this condenser served to catch any sublimate which might be carried with the exit gases in the form of a dust. The first condenser was weighed to the nearest milligram before and after each run. From the weight of the condensate some idea was obtained of the amount of complete combustion occurring. The water used to scrub the exit gases was found to contain only a small quantity of acidic matter, which amounted to less than 0.5% of the total acid found.

On using a catalyst for the first time the following procedure was adopted. Air and naphthalene were passed over the catalyst for four to five hours at a temperature at which the optimum conversion was apparent. This was ascertained by varying the temperature in the catalyst. When the temperature was too low, the naphthalene passed over the catalyst unchanged. On raising the temperature oxidation commenced and a large amount of yellow material (naphthoquinone) along with naphthalene, phthalic anhydride and maleic anhydride appeared in the reaction products. On raising the temperature of the catalyst still higher, the yellow material (naphthoquinone) no longer occurred and the reaction products consisted mainly of phthalic and maleic anhydrides. After the initial four to five hours run, the length of each later run was one hour.

Method of Analysis of Reaction Products.—The reaction products were transferred from the first condenser to a one-liter wide-mouth Erlenmeyer flask. The water used to scrub the exit gases was boiled to expel dissolved carbon dioxide and then used to wash out the sublimate which adhered to the walls of the two condensers. The solution was boiled gently until the phthalic anhydride dissolved, then cooled and titrated for total acid with a standard solution of sodium hydroxide. After this titration, the solution was filtered, acidified with one to two cc. of concentrated sulfuric acid and extracted with several 40-cc. portions of carbon tetrachloride until the carbon tetrachloride extract was colorless. Generally, three extractions with carbon tetrachloride were sufficient to remove

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(8) Drechsel, *Ber.*, **20**, 1452 (1887).

(9) Scott's "Standard Methods of Chemical Analysis," Fifth edition, D. Van Nostrand Company, New York, N. Y., 1939, p. 694.

(10) Booth, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1939, p. 127.

(11) Rosenheim, *Z. anorg. allgem. Chem.*, **96**, 139 (1916).

(12) R. D. Hall, THIS JOURNAL, **29**, 692 (1907).

(13) Ref. 10, page 132.

(14) Rosenheim and Pieck, *Z. anorg. allgem. Chem.*, **98** ,223 (1916)

(15) Rogers, THIS JOURNAL, **25**, 298 (1903).

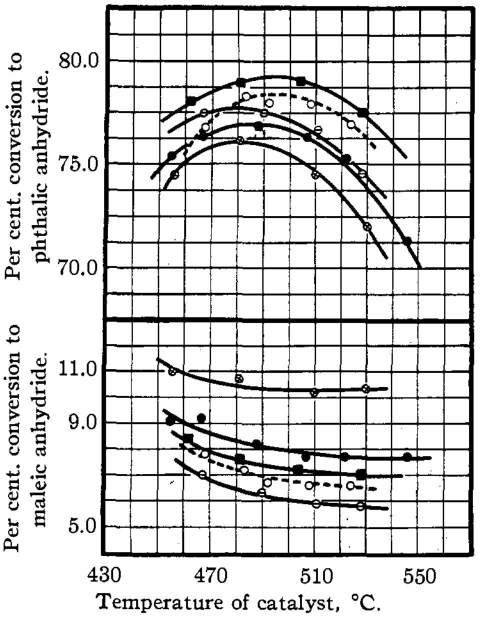


Fig. 1.—Catalyst was 5 cc. (7.43 g.) of fused V_2O_5; space velocity[a]: 2400 ⊗, 4800 ●, 7200 ■, 12,000 ○, 16,800 ⊖; molar air–naphthalene ratio: 78.5 ⊗, 157.0 ●, 235.5 ■, 392.5 ○, 549.5 ⊖.

[a] Space velocity is defined as the volume of air (at 25°) used per hour per unit volume of catalyst.

nearly all of the colored material from the solution. The carbon tetrachloride extractions were performed in order to remove naphthalene, naphthoquinone, resinous and tarry materials which would be oxidized with potassium permanganate. The aqueous solution was acidified with 25 cc. of concentrated sulfuric acid, heated to 75° and titrated with a standard solution of potassium permanganate until a pink end-point remained for thirty seconds. The potassium permanganate titration gave the amount of maleic acid in the solution.[16] The difference between the total acid and maleic acid was taken as phthalic acid. The potassium permanganate solution was standardized against maleic acid.

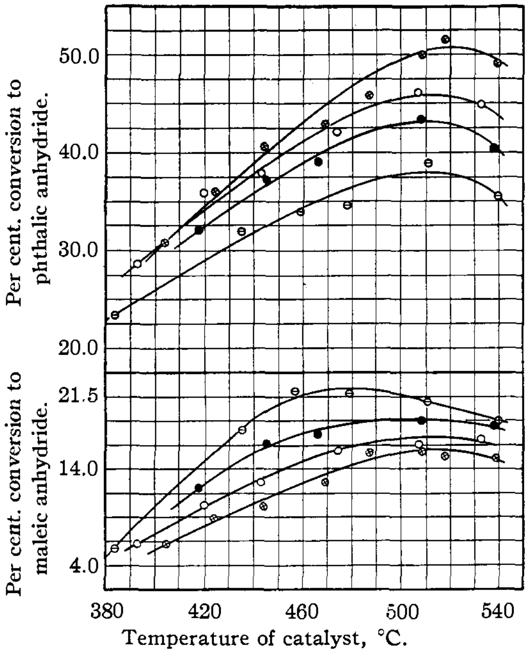


Fig. 2.—Catalyst was 5 cc. (6.87 g.) of MoO_3; space velocity: 7200 ⊖, 12,000 ●, 14.400 ⊗, 16,800 ○; molar air–naphthalene ratio: 235.5 ⊖, 392.5 ●, 471 ⊗, 549.5 ○.

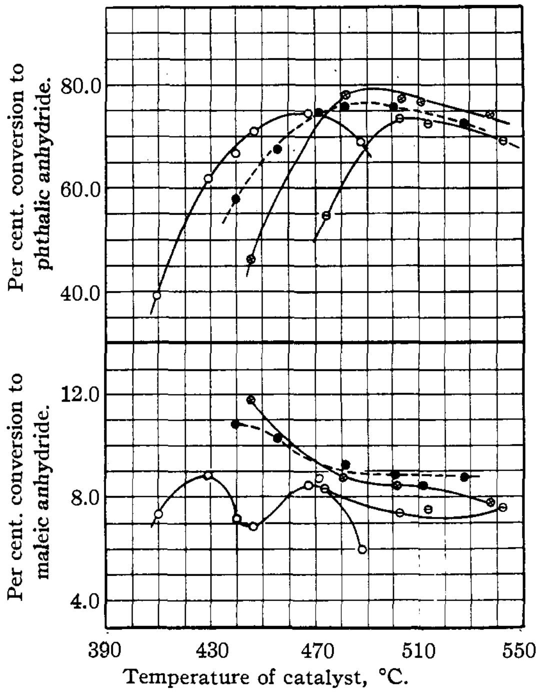
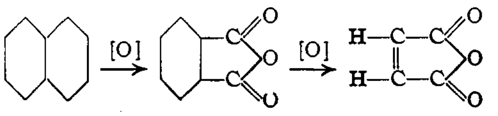


Fig. 3.—Catalyst was prepared from phosphomolybdic acid on asbestos. Volume of catalyst was 10 cc. Weight of catalyst was 6.55 g. Space velocity: 2400 ○, 3600 ●, 6000 ⊗. 8400 ⊖; molar air–naphthalene ratio: 157 ○ 235.5 ●, 392 5⊗, 549.5 ⊖.

Discussion of Results

The results of the vapor phase partial oxidation of naphthalene over heteropoly-acid catalysts, vanadium pentoxide, and molybdenum oxide are shown in Figs. 1 to 8. In each case an increase in space velocity resulted in an increase in the conversion of naphthalene to phthalic anhydride and a decrease in the conversion to maleic anhydride. This suggests that at least part of the maleic anhydride must have been formed from the oxidation of phthalic anhydride (Equation I).



(I)

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(16) Lange and Kline, THIS JOURNAL, **44**, 2709 (1922)· Sabalitschka and Tietz, *Chem. Abs.*, **22**, 43 (1928).

When the space velocity becomes too high, the proportion of unchanged naphthalene passing over the catalyst increases due to the shorter time of contact and the conversion to phthalic anhydride decreases.

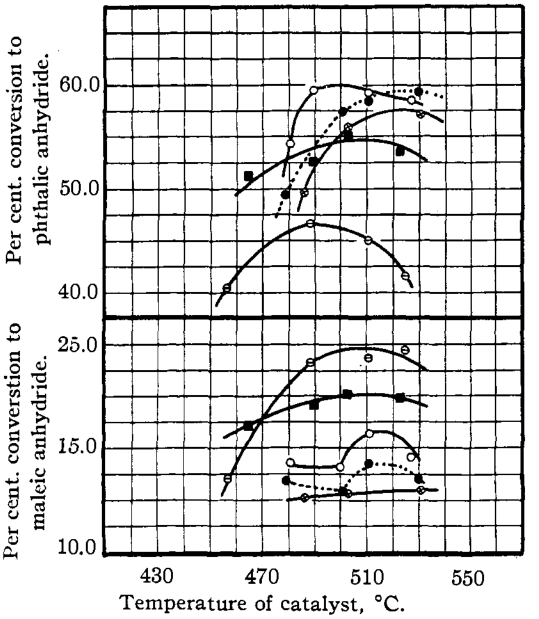

Fig. 4.—Catalyst was prepared from silicomolybdic acid on asbestos. Volume of catalyst was 5 cc. Weight of catalyst was 2.49 g. Space velocity: 2400 ⊖, 4800 ■, 7200 ○, 12,000 ●, 16,800 ⊗; molar air–naphthalene ratio: 78.5 ⊖, 157.0 ■, 235.5 ○, 392.5 ●, 549.5 ⊗.

Previous investigators, who have studied the partial oxidation of naphthalene, have not reported the amount of maleic anhydride formed along with the phthalic anhydride. It is evident from the present work that at least 5% of the naphthalene was converted to maleic anhydride at temperatures close to that at which the optimum conversion of naphthalene to phthalic anhydride was obtained.

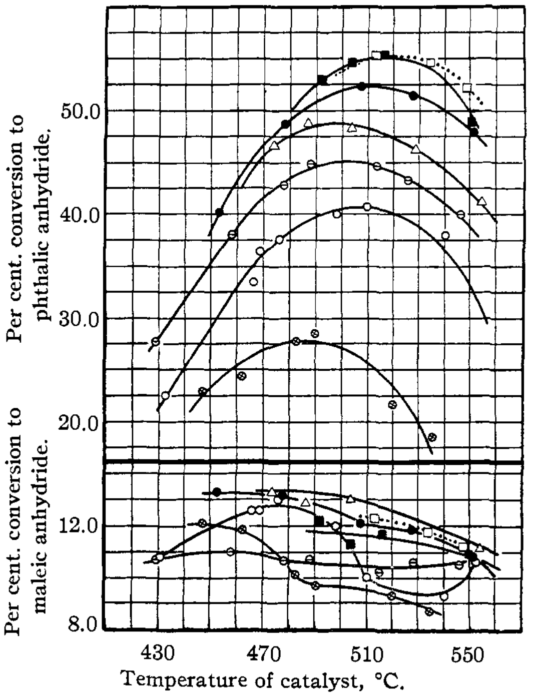

Fig. 5.—Catalyst was prepared from ammonium stannomolybdate. Volume of catalyst was 4 cc. Weight of catalyst was 7.84 g. Space velocity: 3000 ⊗, 6000 ○, 9000 ⊖, 12,000 △, 15,000 ●, 21,000 ■, 25,500 □; molar air–naphthalene ratio: 78.5 ⊗, 157.0 ○, 235.5 ⊖, 314 △, 397.5 ●, 549.5 ■, 667.3 □.

The conditions under which the maximum conversion of naphthalene to phthalic anhydride was obtained with each catalyst are summarized in

TABLE I

Temp. in catalyst, °C.	Molar air–naphthalene ratio	Space velocity	Time of contact, seconds	Surface area of catalyst in square meters	% Conversion to Phthalic anhydride	% Conversion to Maleic anhydride	Catalyst
481	236	7,200	0.198	2.12	78.9	7.6	Fused V_2O_5
518	500	14,400	.094	20.62	51.8	15.4	MoO_3
481	394	6,000	.237	12.14	78.2	8.8	$H_3[PO_4(MoO_3)_{12}]$ on asbestos
500	236	7,200	.193	7.81	59.6	13.2	$H_4[SiO_4(MoO_3)_{12}]$ on asbestos
516	552	21,000	.067	82.1	55.1	11.7	$(NH_4)_8[Sn(Mo_2O_7)_6]$
436	559	16,800	.090	59.3	33.9	24.6	$H_3[AsO_4(MoO_3)_{12}]$
492	236	10,800	.130	15.14	40.9	22.3	$H_3[AsO_4(MoO_3)_{12}]$ on asbestos
488	236	7,200	.196		39.8	10.0	$5(NH_4)_2O\cdot 3NiO\cdot 16MoO_3\cdot 16H_2O$
308	236	7,200	.256		11.3	6.4	$3(NH_4)_2O\cdot Fe_2O_3\cdot 12MoO_3\cdot 19H_2O$
510	236	7,200	.190		4.8	2.3	$3(NH_4)_2O\cdot Cr_2O_3\cdot 12MoO_3\cdot 20H_2O$
498	397	15,000	.093	57.8	17.0	11.8	$H_3[PO_4(WO_3)_{12}]$
465	553	21,000	.069	4.58	87.6	6.4	$13(NH_4)_2O\cdot 2P_2O_5\cdot 8V_2O_5\cdot 34WO_3$
418	158	3,200	.485	12.39	78.9[a]	9.6[b]	$7(NH_4)_2O\cdot P_2O_5\cdot 12V_2O_5\cdot 26H_2O$

[a] This was 72.3% after catalyst lost activity. [b] This was 8.8% after catalyst lost activity.

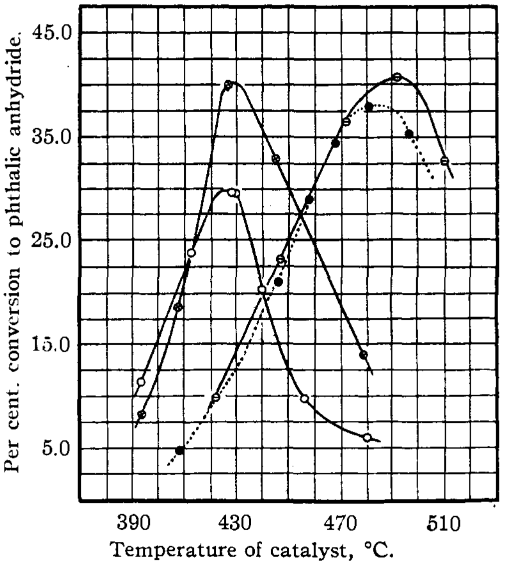

Fig. 6.—Catalyst was prepared from arsenomolybdic acid on asbestos. At space velocities 2400 and 3600 the volume of catalyst was 10 cc. (6.00 g.). At the other space velocities the weight of catalyst was 2.00 g. Space velocity: 2400 ○, 3600 ⊗. 7200 ●, 10,800 ⊖; molar air-naphthalene ratio: 157.0 ○, 235.5 ⊗, 157.0 ●, 235.5 ⊖.

Table I. Fused vanadium pentoxide catalyst[17] resulted in a 79% conversion of naphthalene to phthalic anhydride. This is in agreement with the 80% conversions reported in the literature. It is evident from Fig. 1 that conversions greater than 79% might have been attained if runs had been made at space velocities intermediate between 7200 and 12,000.

The catalytic activity of tungsten trioxide for the partial oxidation of naphthalene was not determined since the catalyst prepared from phosphotungstic acid proved to be a poor catalyst for the reaction. The maximum conversion to phthalic anhydride obtained with the latter catalyst was 17%. Over 50% of the naphthalene was oxidized to carbon dioxide and water. Probably this catalyst was no better than a tungsten trioxide catalyst, since Conover and Gibbs[3] reported that with tungsten trioxide 12% of the naphthalene was converted to phthalic anhydride, and 50% of the naphthalene was lost by complete combustion.

Phosphomolybdic acid yielded a catalyst which was considerably better than the molybdenum trioxide catalyst, and, indeed, almost as good as the vanadium pentoxide catalyst. Silicomolybdic acid and ammonium stannomolybdate produced catalysts which gave higher conversions of naphthalene to phthalic anhydride than the molybdenum oxide catalyst. It was concluded, therefore, that molybdenum trioxide was promoted by phosphorus, silicon and tin.

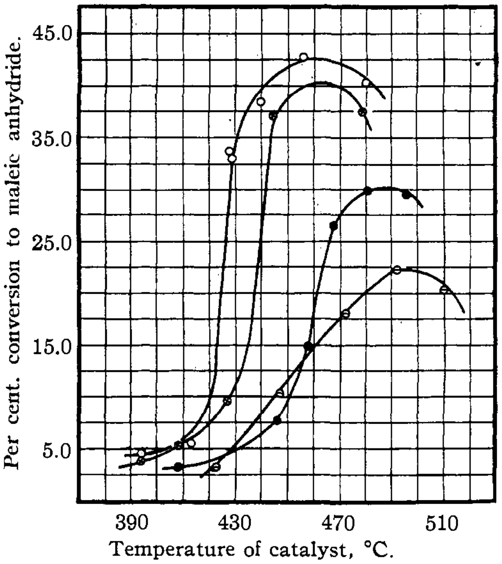

Fig. 6a.—Catalyst and notations same as in Fig. 6.

The catalysts prepared from arsenomolybdic acid, ammonium nickel molybdate, ammonium ferricomolybdate and ammonium chromicomolybdate gave lower conversions of naphthalene to phthalic anhydride than the molybdenum oxide catalyst. Hence, arsenic, nickel, chromium and iron behave as poisons to molybdenum oxide in the sense that they promote the oxidation of the primary reaction products.

Ammonium phosphovanadate yielded a catalyst which initially appeared to be as good as the vanadium pentoxide catalyst. After making fifteen runs with this catalyst, it became less active and gave more complete oxidation. Consequently, the conversions to phthalic anhydride were lower. This was the only catalyst observed to decrease in activity with use.

A comparison of Figs. 1 and 8 reveals the superiority of the catalyst obtained from ammonium phosphovanadotungstate over the vanadium pentoxide catalyst. The former catalyst, in addition to yielding higher conversions of naphthalene to phthalic anhydride, is more efficient over a wider range of space velocities. It is evident that the greater catalytic activity of the catalyst from the heteropoly compound is due to the promoted vanadium pentoxide. What is responsible

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(17) Fused vanadium pentoxide was used as a catalyst since Conover and Gibbs[3] reported that a vanadium pentoxide catalyst was better after it had been fused.

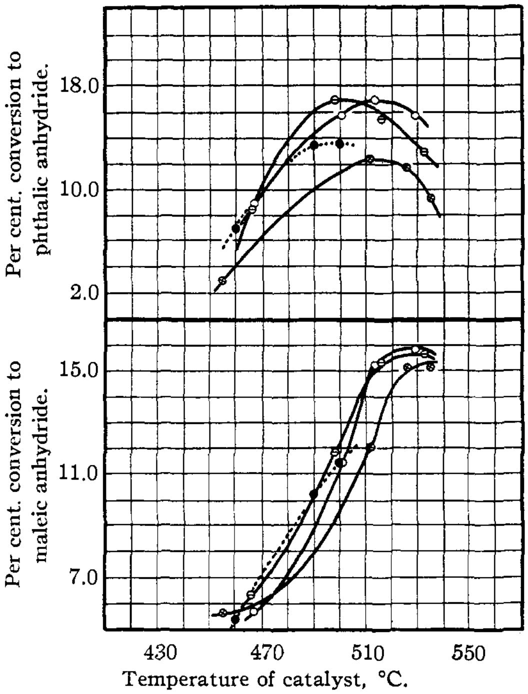

Fig. 7.—Catalyst was prepared from phosphotungstic acid. Volume of catalyst at a space velocity of 10,000 was 3 cc. (7.52 g.). At all other space velocities volume of catalyst was 4 cc. (10.03 g.). Space velocity: 9000 ⊗, 10,000 ●, 15,000 ⊖, 21,000 ○; molar air-naphthalene ratio: 235.5 ⊗, 196.3 ●, 392.5 ⊖, 549.5 ○.

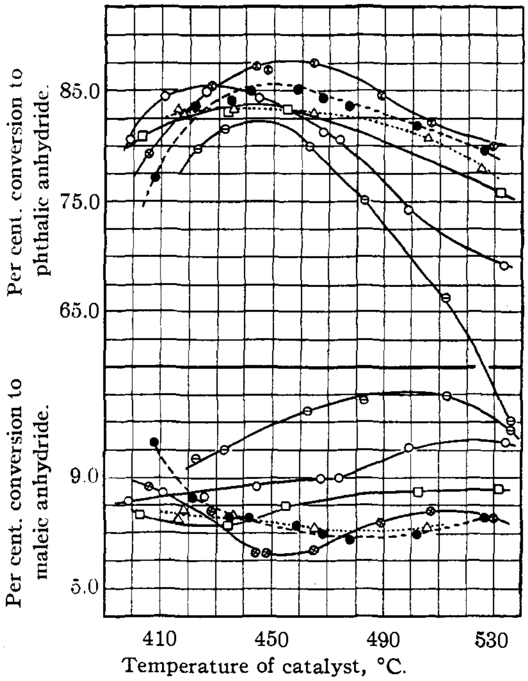

Fig. 8.—Catalyst was prepared from $13(NH_4)_2O\cdot 2P_2O_5\cdot 8V_2O_5\cdot 34WO_3\cdot 86H_2O$. Volume of catalyst was 4 cc. Weight of catalyst was 7.71 g. Space velocity: 3000 ⊖, 6000 ○, 9000 □, 15,000 △, 21,000 ⊗, 25,500 ●; molar air-naphthalene ratio: 78.5 ⊖, 157.0 ○, 235.5 □, 392.5 △, 549.5 ⊗, 667.3 ●.

for this promotion cannot be stated definitely. The lower activity of the catalyst prepared from ammonium phosphovanadate indicates that phosphorus is not a promoter for vanadium pentoxide. Phosphorus did not promote tungsten trioxide to any extent. Possibly the promoter effects on vanadium pentoxide are due to the presence of both phosphorus and tungsten oxide.

The surface areas of the catalysts were evaluated according to the method of Emmett and Brunauer[18] from the adsorption isotherms obtained by measuring the adsorption of nitrogen on the catalysts at the boiling point of liquid nitrogen. The results of these determinations are shown in Table I.

Acknowledgments.—The author wishes to express his most sincere appreciation to Professor J. C. W. Frazer for the guidance and inspiration which he has received during the course of this investigation.

The author also wishes to thank Professor P. H. Emmett of The Department of Chemical Engineering for use of his adsorption apparatus and Mr. B. L. Harris for his assistance in determining the surface areas.

Summary

1. A study of the use of heteropoly-acids as catalysts for the partial oxidation of naphthalene has been made. A catalyst prepared from ammonium phosphovanadotungstate proved to be superior to a vanadium pentoxide catalyst which is the one most commonly used for the reaction.

2. Phosphomolybdic acid yielded a catalyst whose catalytic activity was comparable to the vanadium pentoxide catalyst.

3. Phosphorus, silicon and tin were found to promote molybdenum trioxide as a catalyst for the partial oxidation of naphthalene.

4. Arsenic, nickel, chromium and iron were found to behave as poisons to molybdenum trioxide in the sense that they promoted the oxidation of the primary reaction products.

5. Phosphorus alone did not promote vanadium pentoxide nor tungsten trioxide.

6. The surface areas of the catalysts were determined.

BALTIMORE, MD. RECEIVED JUNE 19, 1940

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(18) Emmett and Brunauer, THIS JOURNAL, **59**, 310, 1553 (1937).