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Catalytic Vapor-Phase Oxidation of Xylenes

The importance of phthalic anhydride as an organic intermediate pinpoints the industrial significance of this process which utilizes readily available o-xylene for its manufacture

 $\mathbf{D}_{\text{URING}}$ the past two decades, phthalic anhydride has become one of the important intermediates of the organic chemical industry, being mainly employed for the manufacture of dyes, alkyd resins, and plasticizers. Its corresponding acid, o-phthalic acid, has two isomers of which terephthalic acid (p-isomer) is the more important—its polyesters form the fiber base for Terylene and Dacron. The m-isomer, isophthalic acid, also has industrial application in a number of processes and products.

For a long time, phthalic anhydride was manufactured by the liquid-phase oxidation of naphthalene with nitric acid or with sulfuric acid in the presence of mercury sulfate. In 1916, Wohl (29) and Gibbs and Conover (12) discovered that, in the presence of vanadium pentoxide, naphthalene is oxidized to phthalic anhydride at 350° to 550° C. This discovery formed the basis of the established process for the production of phthalic anhydride. The ever-increasing demand for phthalic anhydride has in recent years stimulated search for alternative raw materials. Among those investigated, o-xylene, which is available in large quantities from petroleum refineries, appears to be the most suitable.

As a starting material for the production of phthalic anhydride, *o*-xylene has several advantages. The theoretical amount of air required for oxidation of one mole of *o*-xylene is less than that for naphthalene, the evolution of heat during the reaction is less, the product is of a higher purity, and no carbon dioxide is formed because *o*-xylene contains the requisite number of carbon atoms, while naphthalene oxidation involves ring cleavage and formation of carbon dioxide : Furthermore, being a liquid at ordinary temperatures, o-xylene is easier to handle in plant operation.

The p- and *m*-xylenes are starting materials for the other two phthalic acids. Of these, only terephthalic acid is produced commercially by the liquid phase oxidation of p-xylene.

Petroleum refining is the main source of xylenes, and great progress has been made in separating individual isomers economically. Gradually expanding uses of terephthalic and isophthalic acids have created markets for p- and *m*-xylenes; cost of refining and separation is hence shared by all the three isomers.

In spite of the technical importance of the reactions, no published data are available on the catalytic vapor-phase oxidation of individual xylenes. Maxted (19) has mentioned the possibility of such an oxidation. The liquid-phase oxidation of p-xylene using nitric acid, chromic acid, or manganese sulfate in sulfuric acid and oxygen in the presence of oil-soluble catalysts has been described in a number of patents (3, 5, 8, 30). The oxidation of *m*-xylene has received much less attention. Only laboratory synthesis of isophthalic acid using methods similar to those for p-xylene oxidation has been described. The oxidation of mixed xylenes containing a high proportion of o-xylene has been the subject of some patents (16, 24, 25), and some of these have recommended the use of sulfur dioxide along with the reaction gases to obtain greater yields of phthalic anhydride.

Parks and Allard (20) studied the oxidation of a commercial sample of mixed xylenes over oxides of vanadium, uranium, tungsten, and cerium and



¹ Present address, Central Fuel Research Institute, Jealgora P.O., Bihar, India. reported their results on the basis of total acids formed. Maximum conversion to water-soluble acids, reported as phthalic anhydride, was 18.2% using a vanadium pentoxide-Alfrax catalyst at 530° C., with a contact time of 0.0025 second and an air to xylene ratio of 34.4. Their data do not show the extent of oxidation of each isomeric xylene nor the amount of dicarboxylic acid formed in each case. Because these isomers may require specific catalysts and different reaction conditions for maximum oxidation yields, detailed and systematic investigations were carried out in this laboratory on the catalytic vapor-phase oxidation of each xylene separately to evaluate the most satisfactory catalyst and optimum conditions for maximum yields of each corresponding dicarboxylic acid.

Though vanadium oxides have long been used as catalysts for oxidizing sulfur dioxide to sulfur trioxide and for the partial oxidation of hydrocarbons, few studies have been made of their role in these reactions. From color changes and chemical analysis of vanadium oxide catalysts, the formation of lower oxides was envisaged by earlier workers (22, 23, 27). Adadurov (1) reported that during the oxidation of sulfur dioxide, using vanadium pentoxide catalyst, the latter was not reduced when the airsulfur dioxide mixture was properly contacted and oxygen was not adsorbed by the catalyst. Measurement of adsorption rate of sulfur dioxide on vanadium pentoxide at various temperatures showed (2) that catalyst reduction could not be an intermediate step in sulfur dioxide oxidation, as adsorption rate was about $1/_{100}$ th of oxidation rate.

On the other hand, Calderbank (4) reported that chemisorption of oxygen by vanadium oxide catalyst determined the gross reaction rate for naphthalene oxidation. Mars and van Krevelen (18) observed that concentration of aromatic compound and oxygen influenced reaction rate and interpreted the reaction kinetics by assuming two successive steps; reaction between the aromatic compound and oxygen and reoxidation of the partly reduced catalyst surface.

During the present work on the oxidation of individual xylenes, a few highly active catalysts containing vanadium oxides as the main constituent (13, 14) were developed for oxidizing oxylene to phthalic anhydride; the temperature to which these catalysts were heated greatly influenced yield. To study their role in xylene oxidation, the kinetics of oxygen adsorption was determined for a few typical catalysts. Changes in catalyst composition during the reaction were elucidated by following oxygen uptake by the catalyst system at various stages. Surface areas of the important catalysts used in this work were determined by the well known B.E.T. technique.

Experimental

Apparatus. A flowsheet for the apparatus used is shown in Figure 1. A purified and metered stream of air was passed through a xylene bubbler immersed in a constant temperature glycerol bath (GB). Along with the desired amount of secondary air, the vaporized xylene entered a reactor (R)immersed in an electrically heated salt bath (SB). Salt bath and glycerol bath temperatures were controlled by means of two Sunvic energy regulators. A glass coil wound around the reactor acted as a preheater for the reactant gases. The catalyst was packed in the glass reactor around a sealed central thermocouple tube between two purified asbestos wool plugs.

The gases, preheated by passage through the glass coil, entered the reactor at the bottom. Exit gases from the side tube at the top of the reactor were passed through an air condenser (AC), two ice-cooled condensers $(C_1 \text{ and } C_2)$ and two water bubblers $(B_1 \text{ and } B_2)$. A portion of the gas was collected over saturated brine in a calibrated gas reservoir (GR), while the rest was metered through a wet-test gas meter.

The apparatus used for adsorption measurements was essentially the same as described by Ghosh, Sastri, and Kamath (11), except that there were a few modifications in the design of the catalyst tube.

Reactants. Xylene isomers of laboratory reagent grade (British Drug Houses, Ltd., London, England) were redistilled before use.

For studies on adsorption, 99.5% pure nitrogen was further purified by passing it first over hot copper gauze at 300° C. and then through anhydrous magnesium perchlorate to remove any moisture. Helium, used for measuring dead space at low temperatures, was also similarly purified. High-purity oxygen was passed through a tube containing hot copper oxide and then through anhydrous magnesium perchlorate.

Catalysts. Three types of catalysts were used: single catalysts, including vanadates; promoted vanadium pentoxide catalysts; and fused vanadium pentoxide catalysts. The composition of the catalysts used (Nos. 1 to 20) is given in Table I. Catalysts containing vanadium pentoxide were prepared either by the decomposition of vanadyl oxalate (Nos. 2, 7-13, and 17) or by the decomposition of ammonium metavanadate (Nos. 14-16 and 18-20). Vanadyl oxalate for the former series was prepared by the addition of ammonium metavanadate to oxalic acid. The kieselguhr was a purified Indian product.

Oxalates for the preparation of promoted catalysts were prepared by adding ammonium metavanadate and ammonium molybdate, or a nitrate of cobalt, uranium, or cerium, to a solution of oxalic acid. These oxalates were decomposed in a current of air at 400° to 440° C. for 4 hours. Molybdenum oxide-kieselguhr catalyst (No. 1) was prepared by the decomposition of molybdenum oxalate at the same temperature.

Tin vanadate, silver vanadate, and copper vanadate catalysts (Nos. 3–5) were precipitated from a solution of ammonium metavanadate by tin(IV) chloride, silver nitrate, and copper sulfate, respectively.

Table I. Fused Vanadium Pentoxide Was the Most Active Catalyst for Conversion of o-Xylene to Phthalic Anhydride

		a.				Convor	tion 07		Space-Time
		Space	Molar	Temp	° C	DI IL I	1011, 70	0.1. // //	Yield,
NT.	(]- t -] t	Velocity,	Air/Aylene	Dut	., <u>U</u> .	Phthalic	Maleic	Selectivity,	Grams/Hr./
IN O	o. Catalyst	Cc./Hr./Cc.	Ratio	Bath	Bed	anhydride	anhydride	%	Liter
1	MoO ₃ -kieselguhr (32.6:100)	6180	335	400	420	9.3	6.7	58.1	11.4
÷ 2	V_2O_5 -kieselguhr (31.1:100)	6180	360	360	440	42.7	11.3	79.1	51.3
		3910	230	360	480	36.9	13.3	73.4	42.0
		7110	230	360	500	40.0	14.8	72.9	78.4
		6722	171	360	520	37.0	15.2	71.0	95.7
3	$Sn(VO_3)_4$	4240	230	330	410	14.5	5.5	72.5	17.8
4	AgVO ₃	6180	360	320	380	12.4	5.3	70.1	12.1
5	$Cu(VO_5)_2$ -kieselguhr (34:100)		No acid	l formation	at any tem	perature betwe	en 240° and 3	340° C.	
6	Phosphomolybdic acid-kieselguh	r							
	(31:100)	4050	210	400	425	6.2	10.8	36.4	8.2
7	V ₂ O ₅ -silica gel (20:100)	4290	220	420	465	15.4	14.2	52.2	20.2
		6180	320	400	430	10.0	13.3	42.9	12.8
8	V_2O_3 -kieselguhr (51.8:100)	6180	360	360	420	42.4	12.5	77.2	50.4
9	V ₂ O ₅ -MoO ₃ -kieselguhr	4770	155	350	430	36.6	12.6	74.4	71.8
		7150	205	360	450	36.0	11.6	75.7	78.5
		3460	357	350	400	39.5	11.0	78.1	25.2
10	V ₂ O ₅ -Co ₂ O ₃ -kieselguhr (31.1:								
	1.4:100)	4290	210	340	440	31.8	14.1	69.3	41.8
		4290	515	360	400	25.3	9.6	72.6	13.9
		5720	280	360	440	31.0	15.1	67.3	41.6
11	V_2O_5 - UO_2 -kieselguhr (31.1:4.6:								
	100)	4290	220	360	450	30.5	16.4	65.0	38.6
		7145	367	360	430	36.8	12.5	74.7	47.3
12	V ₂ O ₅ -Cerium oxide-kieselguhr								
	(31:1:2.9:100)	4290	222	340	460	8.9	5.5	61.8	10.9
13	V ₂ O ₅ -Co ₂ O ₃ -MoO ₃ -kieselguhr								
	(19.5:1.3:7.7:100)	6190	365	380	450	39.0	14.8	72.5	42.8
		8110	206	370	520	37.8	13.7	73.5	98.5
14	Fused V_2O_5	5740	365	460	465	59.0	9.1	86.7	61.4
		5740	275	460	490	61.7	9.6	86.6	85.6
		5740	685	460	475	56.3	7.9	87.8	31.1
15	Fused V ₂ O ₅ -Co ₂ O ₃	5760	290	460	500	55.2	15.5	78.1	72.2
16	Fused $V_2O_5 - K_2SO_4$ (100:26)	5760	275	470	510	45.0	9.3	83.2	66.1
17	Fused V ₂ O ₅ -kieselguhr (31.1:100) 5760	285	450	510	39.0	10.4	78.9	53.2
18	Fused V_2O_5 -pumice (162:100)	5760	410	480	500	46.9	9.5	83.5	42.0
19	Fused V_2O_5 -pumice (243:100)	5760	383	480	510	51.8	9.3	84.8	51.4
20	Fused V_2O_5 -silica gel (229:100)	5760	290	480	500	48.4	9.4	83.8	63.5

XYLENE OXIDATION



Figure 1. Gaseous xylene and air, preheated by passage through the glass coil, entered the reactor at the bottom

AC. Air condenser, B₁, B₂. Water bubblers. C₁, C₂. Ice-cooled condensers. F₁, F₂. Flowmeters. GB. Constant temperature glycerol bath. GM. Gas meter. GR. Gas reservoir. M. Manometer. P₁, P₂. Purification towers. R. Reactor. SB. Electrically heated salt bath. TC. Thermocouple. U₁, U₂. Calcium chloride tubes. WC. Water-cooled condenser

Fused catalysts were prepared by gradually heating the catalyst mass containing ammonium metavanadate (and the requisite amounts of promoter and support, if any) in an open silica dish to the point of fusion. After cooling, the lumps were broken and the product sieved; 20 cc. of the catalyst of 6–10 mesh size were used in each experiment.

Analysis of Reaction Products. A typical reaction product obtained by the oxidation of o-xylene contained phthalic anhydride, maleic anhydride, quinone, and carbon dioxide. The product was dissolved in hot distilled water, the solution was boiled to drive off dissolved carbon dioxide, and, after cooling, was diluted to a known volume. There was no water-insoluble portion in the product. An aliquot portion was titrated against standard alkali. From the titer, the total amount of o-xylene converted to phthalic anhydride and maleic anhydride was calculated.

Maleic acid was estimated according to the method of Marisic (17), by titrating against standard potassium permanganate after carrying out repeated extractions with carbon tetrachloride to remove quinone. Quinone was determined by estimating the iodine liberated from potassium iodide in the presence of sulfuric acid (28). Carbon dioxide in the exit gas was determined by passing the gas through a series of bubblers containing potassium hydroxide and backtitrating the excess alkali.

Oxidation of p-xylene may be expected to give, apart from toluic anhydride, three acidic products: p-toluic acid, terephthalic acid, and maleic anhydride. Based on their solubility characteristics, suitable methods for separating and estimating them were evolved.

The reaction product was washed with the minimum quantity of hot distilled water, cooled to 4° C., and filtered to remove *p*-toluic acid and terephthalic acid which had low solubilities in water at this temperature. Maleic acid was estimated in the filtrate by alkali titration. The value was checked by permanganate titration or by estimation as barium maleate. Whenever necessary, correction was applied to the alkali titer for the slight solubility of *p*-toluic acid at 4° C. and for the presence of quinone.

The residue containing p-toluic acid and terephthalic acid was washed with chloroform, in which terephthalic acid was completely insoluble, to dissolve ptoluic acid. The chloroform extract was titrated to determine the acid value, while the residue from chloroform extraction was dried at 110° C. and weighed as terephthalic acid. In many experiments, the final residue was dissolved in a known amount of standard alkali and the excess alkali was back-titrated. Using this method, the product from the oxidation of p-xylene over vanadium pentoxide-kieselguhr catalyst was found to contain all three acids.

Drops of a yellow, oily liquid, which turned pink with fuchsin, were found in most runs. The oily liquid, after being separated, was treated with saturated bisulfite. The aldehyde was then liberated by means of sodium carbonate and extracted with ether. It was identified as p-tolualdehyde by its boiling point and by the melting point of its 2,4-dinitrophenylhydrazone. The reaction product also liberated iodine from potassium iodide, indicating the presence of quinone.

Quinone was estimated by determining the amount of iodine liberated from potassium iodide in the presence of sulfuric acid (28). It was experimentally determined that addition of sodium carbonate could liberate bisulfite only from its aldehyde complex and not from unsaturated acid addition product. The aldehyde was hence estimated by titrating the liberated bisulfite against standard iodine solution. This procedure for the estimation of aldehyde could be adopted only when the product did not contain any quinone. In the presence of quinone, the 2,4-dinitrophenylhydrazones of the aldehyde and the quinone were precipitated in presence of hydrochloric acid and estimated gravimetrically. From the total weight of hydrazones, the weight due to *p*-benzoquinone 2,4-dinitrophenylhydrazone, as calculated from the values for quinone (determined originally by the iodometric method), was subtracted and, from the balance, the amount of aldehyde was computed. This method was checked for accuracy by analyzing mixtures of pure compounds.

As the solubility characteristics of isophthalic acid and *m*-toluic acid are analogous to those of the respective *p*-isomers, the reaction product from *m*-xylene oxidation also was fractionated using a similar procedure.

Results and Discussion

Oxidation of o-Xylene. A preliminary study of the oxidation of o-xylene was conducted over a number of common oxidation catalysts. Table I records some results pertaining to yields of phthalic and maleic anhydrides during oxidation; results of conversion to carbon dioxide and quinone are not shown. While various vanadates as well as molybdic oxide and phosphomolybdic acid were poor catalysts, the activity of vanadium pentoxide-kieselguhr was appreciable.

With molybdenum(VI) oxide-kieselguhr catalyst (No. 1), a maximum conversion of only 9.3 % to phthalic anhydride was obtained along with a conversion of 6.7 % to maleic anhydride. Using mixed xylenes, Parks and Allard (20) reported a conversion of 1.8% to total acids with silica gel-supported molybdic oxide.

Vanadium pentoxide-kieselguhr catalyst (No. 2) was much more active and gave a maximum conversion of 42.7%to phthalic anhydride and 11.3% to maleic anhydride at 440° C. (bed temperature). Beyond this temperature, phthalic anhydride yield decreased though conversion to maleic anhydride still showed a progressive increase even above this temperature.

Vanadates of tin and silver (Nos. 3 and 4) gave about 12 to 14% conversion to phthalic anhydride. In this connection, tin vanadate was reported to be an excellent oxidation catalyst by Maxted (19) and by Huitema and Brown (15). The catalyst containing copper vanadate deposited on kieselguhr (No. 5) failed to produce any conversion to phthalic anhydride or maleic anhydride at any temperature, though from 260° C. upward a vigorous reaction producing carbon dioxide and water was observed. Fester and Berraz (10) had reported that copper vanadate was a suitable catalyst for such mild oxidations as an alcohol to an aldehyde.

Marisic (17) found that phosphomolybdic acid was as good as vanadium pentoxide for the oxidation of naphthalene to phthalic anhydride. The present observations with phosphomolybdic acid catalyst supported on kieselguhr (No. 6) showed that for o-xylene oxidation, this catalyst had little efficiency below 400° C. Above this temperature, the maleic anhydride yield increased sharply, indicating the great capacity of this catalyst for bringing about increased oxidation of ring structure.

Parks and Allard (20), who used mixed xylenes, reported a maximum conversion of 18.2% to total acids with a vanadium pentoxide-Alfrax catalyst. In the present work, 54% conversion of oxylene to total acids was obtained using a catalyst composed of vanadium pentoxide and kieselguhr. Perhaps in the low conversions reported by Parks and Allard, p- and m-xylenes were not oxidized to acids as much as o-xylene.

The activity of catalyst No. 8 shows that use of vanadium pentoxide concentrations above 31% did not increase yields over those obtained with this concentration. Silica gel as a support for the vanadium pentoxide catalyst (No. 7) did not improve results: the catalyst with this support had poor selectivity for oxidation to phthalic acid.

PROMOTED CATALYSTS. In view of the high activity of vanadium pentoxide-kieselguhr catalyst, the influence of various "promoters" on its capacity was investigated. Instead of using an arbitrarily fixed weight of each promoter compound, a concentration based on a constant ratio of promoter atoms to vanadium atoms was employed. Five atoms of promoter were used for every 100 vanadium atoms. A few selected values for the activity of these promoted catalysts (Nos. 9–13) are given in Table I.

The addition of molybdenum(VI)

oxide to vanadium pentoxide (No. 9) did not improve conversion to phthalic anhydride. The vanadium pentoxidecobalt oxide-kieselguhr catalyst was much more degradative in action than the unpromoted catalyst of the same concentration. With this catalyst (No. 10), conversion to maleic anhydride was high and was considerably enhanced by an increase in reaction temperature, The average temperature of the middle zone of the catalyst bed--"bed temperature"-was particularly high in those experiments in which increased conversions to maleic anhydride occurred. Thus, cobalt oxide increased catalyst activity to the extent of undesirable degradation.

The use of uranium oxide with vanadium pentoxide resulted in a catalyst (No. 11) which was very sensitive to heat. At 450° C. (bed temperature) this catalyst gave a conversion of 30.5% to phthalic anhydride and 16.4% to maleic anhydride. Beyond this temperature, there was a steep drop in conversion to phthalic anhydride. For the oxidation of toluene to benzoic acid-a reaction involving oxidation of side chain only-oxides of uranium have been reported (7, 21)to be suitable promoters for vanadium, molybdenum, and copper catalysts. Parks and Allard (20) found that uranium molybdate granules had poor activity for oxidation of mixed xylenes. The activity of uranium oxide-promoted vanadium pentoxide-kieselguhr catalyst, as determined in the present work, was less than that of the unpromoted catalyst.

The vanadium oxide-cerium oxidekieselguhr catalyst (No. 12) gave quite poor yields of phthalic anhydride because of the extremely degradative characteristics of this catalyst.

A doubly promoted catalyst (No. 13) containing vanadium pentoxide, molybdic oxide, cobalt oxide, and kieselguhr exhibited maximum activity at 450° C. (bed temperature) (Table I). With a higher xylene feed rate (air to xylene ratio 206), the catalyst produced almost the same conversion and exhibited the same selectivity, thus giving a space-time yield which was nearly twice the one obtained with the lower feed rate. The selectivity at low feed rates was better, but there was no improvement in phthalic anhydride yields.

These experiments showed that addi-

Table II. Percentage Conversions of o-Xylene Were Higher with the Fused Catalyst

	х - С	Space Velocity.	Molar Air/				Co	nversion, %		
No.	Catalyst	Cc./Hr./ Cc.	Xylene Ratio	$\frac{\text{Temp.}}{\text{Bath}}$, ° C. Bed	Phthalic anhydride	Maleic anhydride	Quinone	Carbon dioxide	Total
19	Fused V_2O_5 -pumice	5650 5650 4525	305 305 225	470 470 470	490 490 510	50.9 51.5 50.2	9.6 10.1 10.9	Traces Traces Traces	16.3 18.4 19.1	76.8 80.0 80.2
2	Unfused V2O5-kieselguhr	5650 5650	270 330	360 360	410 400	39.5 41.2	12.6 12.3	0.2 0.2	24.6 25.2	77.0 78.9



Figure 2. Space-time yield of phthalic anhydride increased when higher oxylene concentration was used

Fused vanadium pentoxide catalyst (No. 14). o-Xylene feed rate, 1.95 grams/hour. Bath temperature, 460° C. Bed temperature, 485° to 490° C.

tion of "promoters" resulted in a catalyst so highly active that, instead of phthalic anhydride, maleic anhydride was produced in comparatively larger amounts. The doubly promoted catalyst was more steady and gave high space-time yields.

FUSED CATALYSTS. Although heating vanadium catalysts to the point of fusion to make them more rugged and less degradative has been claimed to be beneficial (17, 26), Parks and Allard (20) found that a fused vanadium pentoxide catalyst was less active for oxidizing mixed xylenes than the Alfrax-supported vanadium pentoxide catalyst heated only to 400° C. In view of these contradictory observations, the activity of some fused vanadium pentoxide catalysts was tested for the oxidation of o-xylene. Fused catalysts, when unsupported, gave very promising results, so the work was extended to other fused catalysts prepared from various catalyst supports and promoters with vanadium pentoxide.

Below a temperature of 440° C., the fused vanadium pentoxide catalyst (No. 14) did not exhibit any activity. The reaction started at 450° C., and above 460° C. the catalyst became quite active, giving conversions as shown in Table I. A higher space-time yield was obtained at the same space velocity but at a higher o-xylene concentration corresponding to an air to xylene ratio of 275. The activity of the catalyst did not change much at higher temperatures. Using o-xylene feed rates of 0.75 and 1.95 grams per hour, experiments with this catalyst were performed at 460° C. (bath temperature; bed temperature, ranging from 475° to 490° C.) (Figures 2 and 3). Conversions to phthalic anhydride passed through maxima in both cases of 60%, corresponding to a process yield of 86

grams of phthalic anhydride per 100 grams of o-xylene per pass.

Comparison of the activities of the unfused vanadium pentoxide catalyst supported on kieselguhr (No. 2) and the fused catalyst revealed that on the basis of equal volumes the temperature for optimum conversion was about 100° C. higher, conversion to phthalic anhydride was higher by 19% with a consequent rise in space-time yield, and conversion to maleic anhydride was about 2% lower with the latter catalyst; thus, selectivity was appreciably higher.

Incorporation of cobalt oxide with vanadium pentoxide made the fused catalyst quite degradative. With the promoted catalyst (No. 15) the conversion to maleic anhydride increased to 15.5%. Fused vanadium pentoxide catalyst containing potassium sulfate also gave low conversions.

The suitability of pumice, silica gel, and kieselguhr as supports for the fused vanadium pentoxide catalyst was tested. The fused vanadium pentoxide-kieselguhr catalyst had less activity than even the unfused catalyst of the same composition. Furthermore, reaction temperature was higher by 80° to 100° C. Heating to 800° C. probably destroyed the highly porous structure of kieselguhr, as the molten vanadium pentoxide choked most of the capillaries.

The fused vanadium pentoxide-pumice catalyst (No. 18), containing 1.62 parts of vanadium pentoxide per part of pumice, had better activity than the unfused vanadium pentoxide-kieselguhr catalyst (No. 2). Conversions to phthalic and maleic anhydrides increased with a catalyst containing higher concentration of vanadium pentoxide on pumice (No. 19). The pumice-supported fused catalyst was thus quite efficient for the oxidation of o-xylene to phthalic anhydride. Using half the amount of vanadium pentoxide required for the unsupported catalyst, it retained almost all the essential properties of the latter. The silica gel-supported fused vanadium pentoxide catalyst (No. 20) had practically the same activity as the pumice-supported fused vanadium pentoxide catalyst.

The fused vanadium pentoxide catalysts, in general, improved conversions to phthalic anhydride considerably and also improved selectivity. About 55 to 60% of the *o*-xylene fed was converted per single pass to phthalic anhydride, the yield being 75 to 85 grams of phthalic anhydride per 100 grams of *o*-xylene.

A comparative study of carbon balance made on the pumice-supported fused vanadium pentoxide catalyst (No. 19) and the unfused vanadium pentoxide-kieselguhr catalyst, showed that conversion of o-xylene to carbon dioxide was 8% higher in the case of the unfused





AIR, LITER/HR.

Figure 3. Space-time yield of phthalic anhydride dropped at lower o-xylene concentration

Fused vanadium pentoxide catalyst (No. 14). Bath temperature, 460° C. Bed temperature, 475° to 485° C.

Conversion to phthalic anhydride

Conversion to maleic anhydride

Space-time yield of phthalic anhydride, gram/hour/liter

Selectivity

catalyst (Table II). With the fused catalyst at 490° C. (bed temperature), 16.3% of o-xylene feed was completely oxidized to carbon dioxide per single pass at a space velocity of 5650 cc. per hour per cc. and an air to xylene molar ratio of 305. On the other hand, under similar reaction conditions, the conversion to carbon dioxide with the unfused catalyst was 25%. With either catalyst, nearly 15 20% o-xylene remained unreto acted. Thus, though the total conversion of o-xylene was nearly the same for the fused catalyst as for the unfused one, percentage conversions to oxidation products were quite different.

OXYGEN INSTEAD OF AIR. The use of cheap tonnage oxygen for the catalytic vapor phase oxidation of organic compounds has been attracting great attention. In the present work, the oxidation of o-xylene was studied over the fused vanadium pentoxide-pumice catalyst (No. 19) using oxygen in place of air. For these experiments, a small quantity of nitrogen was used in place of primary air for feeding *o*-xylene, while oxygen was used in place of secondary air. The results showed that the use of oxygen did not in any way affect conversion to either phthalic anhydride or maleic anhydride.

A phenomenal improvement in spacetime yield, however, was attained at higher o-xylene concentration. Keeping the oxygen rate fixed at 107.0 or 80.0 liters/hour, runs were conducted



Figure 4. Using oxygen instead of air resulted in a substantial increase in space-time yield

Fused vanadium pentoxide-pumice catalyst (No. 19). Oxygen feed rate 107.0 liters/hour. Bath temperature, 470° C. Bed temperature, 490° to 540° C.

Conversion to phthalic anhydride

Conversion to maleic anhydride
 Space-time yield of phthalic anhydride,

gram/hour/liter

▲ Selectivity

at 470° C. (bath temperature; bed temperature ranging from 490° to 540° C.) with different o-xylene feed rates (Figures 4 and 5). In both cases, percentage conversion to phthalic anhydride remained practically constant throughout the xylene concentration range studied, and as a result spacetime yield increased rapidly with a progressive increase in o-xylene feed rate. Space-time yield as high as 189.3 grams per hour per liter was secured at a space velocity of 5480 and an oxygen to xylene molar ratio of 85. Oxygen concentration even at this high o-xylene feed rate was about 28 times the theoretical amount required for the oxidation of o-xylene to phthalic anhydride. However, if air had been used the oxygen to xylene molar ratio would have been only six times the theoretical requirement.

In actual practice, a considerable amount of oxygen is also needed for the oxidation to maleic anhydride and carbon dioxide. Because the reactions involved are highly exothermic, it was necessary to work at high air to xylene ratios to prevent the catalyst bed temperature from rising too high and to avoid the formation of hot spots in the fixed bed reactor.

In the studies using oxygen, the percentage of *o*-xylene completely oxidized to carbon dioxide and water was also nearly the same as in the case of oxidation with air. Hence, by using oxygen, it was possible to work at a low oxygen to xylene molar ratio (that is, high *o*xylene concentration), keeping the conversions to various reaction products practically unchanged. High yields of phthalic anhydride per hour per liter of catalyst were attained in this way.

Oxidation of p-Xylene. Experimental results from the oxidation of p-xylene over various catalysts are summarized in Table III. The products of oxidation, in this case, consisted mainly of p-tolualdehyde, maleic anhydride, carbon dioxide, and small quantities of terephthalic acid, p-toluic acid, and benzoquinone.

The vanadium pentoxide-kieselguhr catalyst (No. 2) was quite active at 340° C. The conversion of *p*-xylene at 450° C. (bed temperature) to different products is shown in Table III. At higher temperatures, yields of *p*-tolualdehyde and maleic anhydride decreased. In many runs with this catalyst, quinone was also formed to the extent of 1.0 to 1.2%.

The activity of singly and doubly promoted catalysts, vanadium pentoxidemolybdenum oxide-kieselguhr (No. 9) and vanadium pentoxide-molybdenum oxide-cobalt oxide-kieselguhr (No. 13), for oxidation of p-xylene was similar to that of the unpromoted catalyst. In both cases conversion to terephthalic acid or to p-toluic acid at low temperatures was very small. On raising the temperature, the production of maleic anhydride and p-tolualdehyde predominated.

In view of the drastic nature of these vanadium pentoxide catalysts, two mod-



Figure 5. Even with a slightly lower oxygen feed rate, space-time yield remained high

Fused vanadium pentoxide-pumice catalyst (No. 19). Oxygen feed rate, 80.0 liters/hour. Bath temperature, 470° C. Bed temperature, 500° to 520° C.

- Conversion to phthalic anhydride
- Conversion to maleic anhydride

➡ Space-time yield of phthalic anhydride, gram/hour/liter

▲ Selectivity

erate oxidation catalysts, tin vanadate (No. 3) and silver vanadate (No. 4), were also studied. Conversions to ptoluic acid and terephthalic acid were nearly the same as with vanadium pentoxide-kieselguhr catalyst, but yields of maleic anhydride and p-tolualdehyde were much lower. Moreover, the activity of tin vanadate decreased appreciably after the first few runs. Thus, although less drastic in oxidizing a compound involving ring rupture, these catalysts did not improve the oxidation of p-xylene to p-toluic acid or terephthalic acid.

The fused vanadium pentoxide catalyst (No. 14) gave higher conversions to maleic anhydride, *p*-tolualdehyde, and quinone than the unfused catalysts mentioned above (Table III), but yields of terephthalic acid and *p*-toluic acid

Table III. Oxidation of p-Aylene Froduced Only Small Amounts of Terephinalic and p-Toluic.	JIC ACIDS
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		Space	Molar Air/	Temp	., ° C.			Conversion, %		
No.	Catalyst	Velocity Cc./Hr./Cc.	Xylene Ratio	Bath	Bed	Terephthalic acid	p-Toluic acid	Maleic anhydride	<i>p</i> -Tolu- aldehyde	Quinone
2	$V_2O_{\bar{o}}$ -kieselguhr	5765 5765	270 270	360 380	450 480	0.7 0.6	1.0 1.0	22.5 21.0	7.0 5.8	1.2 1.0
9	V2O5-M0O3-kiesel- guhr	5910 5010	190 550	340 340	380	0.7	1.0	14.8	10.8	1.0
13	V2O5-M0O3-C02O3- kieselguhr	5765	240 240	360 380	480 500	0.5	1.1	13.7	8.5	1.0
<mark>ِ 3</mark>	$Sn(VO_3)_4$	7940 7940	355 320	310 330	360	0.9	1.3	5.3	3.3	Nil 0.5
4	AgVO ₈	5910 5910	250 202	310 330	410	Nil 0.6	$1.1 \\ 1.0$	3.2 3.2	3.2 8.0	Nil Nil
14	Fused V_2O_δ	5765 5765 5520 5780	225 225 445 145	440 460 460 460	540 550 510 565	1.1 0.9 1.3 0.9	2.1 1.6 1.2 1.5	32.3 32.4 28.0 31.6	10.6 10.2 13.2 9.7	$5.7 \\ 4.3 \\ 6.0 \\ 6.7$

XYLENE OXIDATION

		Space	Molar				Conversion, %				
No.	Catalyst	Velocity, Cc./Hr./Cc.	Air/Xylene Ratio	Temp. Bath	<u>, ° C.</u> Bed	Maleic anhydride	<i>m</i> -Tolu- aldehyde	Quinone	Isophthalic acid		
2	V ₂ O ₅ -kieselguhr	5680	265	360	520	15.7	0.2	Traces	0.6		
•		5680	265	380	560	21.3	0.1	0.8	1.1		
		5680	195	380	580	13.4	0.2	0.8	0.9		
13	V ₂ O ₅ -MoO ₃ -Co ₂ O ₃ -										
	kieselguhr	5685	365	380	430	22.3	0.4	1.1	1.2		
		5685	272	400	540	18.7	0.4	1.0	1.0		
		5685	177	400	550	15.1	0.4	0.5	0.9		
14	Fused V ₂ O ₅	5685	280	490	550	18.2	8.3	0.7	1.1		
		5685	280	515	560	18.4	15.2	1.3	1.2		
		5685	160	490	560	21.0	10.7	1.2	0.9		
	1	5685	525	480	550	16.3	12.9	0.6	1.0		

Table IV. No m-Toluic Acid Could Be Detected in the Oxidation Products of m-Xylene

were nearly the same. Even at higher concentrations of p-xylene, conversion to various products remained much the same. At lower xylene feed rates, conversion to maleic anhydride decreased, but the yield of p-tolualdehyde increased. Estimation of carbon dioxide in the reaction products showed that about 14.5 to 17.0% p-xylene was completely oxidized to carbon dioxide in the runs conducted at 550° C. (bed temperature) and 570° C. (bed temperature).

Although p-toluic acid and terephthalic acid were invariably formed in the vapor phase catalytic oxidation of p-xylene, their yields in the final products were quite low. Appreciable amounts of p-tolualdehyde, the first of a series of oxidation products, were obtained. Its further oxidation led mainly to an attack on ring structure, resulting in the formation of maleic anhydride and carbon dioxide, quinone being possibly formed in the intermediate stage.

Oxidation of m-Xylene. The oxidation products obtained as a result of oxidizing m-xylene consisted mainly of maleic anhydride, m-tolualdehyde, and carbon dioxide, though small quantities of quinone and isophthalic acid were also formed. No m-toluic acid could be detected in any run. Maximum conversion to isophthalic acid was about 1%, but conversion to maleic anhydride was as high as 22% of the input *m*-xylene. Only small quantities of m-toluic aldehyde were formed over the unfused catalysts, but with fused vanadium pentoxide catalyst conversion to this aldehyde was appreciable.

The results obtained with three typical oxidation catalysts are shown in Table IV. The vanadium pentoxide catalyst promoted by molybdic oxide and cobalt oxide (No. 13) gave a higher conversion to maleic anhydride, but yields of other products were of the same order as obtained with the unpromoted catalyst.

Comparatively larger yields of aldehyde were obtained with the fused vanadium pentoxide catalyst (Table IV). Analysis of gaseous products showed that nearly 14% m-xylene was completely oxidized to carbon dioxide.

Unlike o-xylene which was readily oxidized to phthalic anhydride, the catalytic vapor-phase oxidation of mxylene led mainly to the formation of maleic anhydride and m-tolualdehyde. About 20 to 22% conversion to maleic anhydride was obtained in the present work, though with a proper arrangement for effective removal of the heat of reaction, it should be possible to increase the yield of maleic anhydride even further.

Oxygen Adsorption Studies on Vanadium Oxide Catalysts

Catalysts used for surface area determination and for oxygen adsorption studies were fresh samples from the preparations used for reaction studies. First each sample was evacuated for eight hours at 300° C. in the case of nitrogen adsorption for surface area measurement and at 520° C. for oxygen adsorption studies.

For oxygen adsorption isotherms, the first reading was taken 12 hours after the introduction of the gas, and subsequent readings were made every two hours. A period of two hours' duration was sufficient for attaining equilibrium in all cases except when fused vanadium pentoxide catalyst was used at temperatures of 480° and 520° C. At these temperatures, a slow creep in oxygen adsorption continued for several hours. This was believed to be due to processes other than surface adsorption of gas;

hence, the usual schedule for oxygen isotherms was followed instead of allowing gas uptake to continue to its ultimate limit.

Results and Discussions. Surface areas of some typical catalysts used for oxidation of xylenes are recorded along with the corresponding conversion data in Table V. Comparison of surface areas with data on efficiency of o-xylene oxidation to phthalic anhydride does not show any correlation. While unfused vanadium pentoxide-kieselguhr catalyst (No. 2) had a surface area of 22.19 sq. meters per gram, fused, unsupported vanadium pentoxide catalyst (No. 14), which exhibited the highest activity, had the lowest surface area of 0.4578 square meter per gram.

Vanadium pentoxide-kieselguhr catalyst adsorbed little oxygen below 440° C. The amount adsorbed at 440° to 520° C. was only 0.94 to 1.81 cc. per 22.093 grams of catalyst. Adsorption increased with increasing pressure up to about 350 mm. but above this pressure tended to become constant. Assuming gas adsorption in a unimolecular layer and taking the area of oxygen molecule as being 14.1 sq. A. (9), catalyst No. 2 with surface area of 22.19 sq. meters per gram had only 1.4% of the total surface covered at the point of maximum adsorption.

Adsorption on fused vanadium pentoxide up to 400° C. was approximately the same as on the unfused vanadium pentoxide-kieselguhr catalyst, but at

Table V. No Correlation Could Be Found between Surface Area and Catalytic Activity of Vanadium Pentoxide Catalysts

No.	Catalyst	Surface Area, Sq. Meters/Gram	Optimum Conversion to Phthalic Anhydride, %
2	V ₂ O ₅ -kieselguhr	22,19	42.73
13	V2O5-C02O3-M0O3-		
and the second	kieselguhr	23.01	39.03
17	Fused V ₂ O ₅ -kieselguhr	7.034	39.01
14	Fused V ₂ O ₅ , unsupported	0.4578	61.73
19	Fused V ₂ O ₅ -pumice	0.6471	51.80
	Indian kieselguhr	35.83	• • •

440° C. and 288 mm. of mercury equilibrium pressure 0.087 cc. of oxygen per gram was adsorbed-more than the maximum adsorption over the same amount of vanadium pentoxide-kieselguhr catalyst even at 520° C. Maximum adsorption over the fused catalyst was nearly five times the adsorption obtained over the vanadium pentoxide-kieselguhr catalyst. Isotherms at 480° and 520° C. over the fused catalyst did not indicate saturation; slow uptake of gas continued for more than two hours after the introduction of the gas for recording the second and subsequent points on the adsorption isotherm.

It was estimated that 2.64 cc. of oxygen was required for the formation of a monomolecular layer over 22.093 grams of this catalyst. This value was attained at the second point of the 480° C. isotherm at about 80 mm. of mercury pressure. Adsorption values above this pressure for this isotherm, as well as those for the 520° C. isotherm at all pressures, were higher. Maximum adsorption recorded at 520° C. was about 3.5 times the amount required to form a monolayer. Because this high uptake occurred particularly at high temperatures and pressures, it was concluded that oxygen was not only adsorbed on the surface but also had penetrated to layers below, indicating that some vanadium pentoxide molecules might have decomposed to a lower oxide during evacuation at 520° C. Readmission of the gas at 480° C., and especially at 520° C., to the oxygen-deficient solid obviously resulted in penetration into the solid and a restoration of the original condition.

The possibility that vanadium pentoxide loses part of its oxygen on heating in vacuum was recently envisaged by Cameron and coworkers (6) who studied the exchange of oxygen-18 between vanadium pentoxide and oxygen. On baking vanadium pentoxide microspheres at 400° C. in vacuum prior to an exchange run, the orange color changed to blue because of loss of oxygen. Also the isotope content of oxygen brought into contact with freshly evacuated vanadium pentoxide dropped suddenly because of a rapid initial exchange.

In the present work, oxygen loss on heating in vacuum occurred only with fused, unsupported vanadium pentoxide catalyst; the unfused vanadium pentoxide-kieselguhr catalyst showed oxygen isotherms of the Langmuir type, indicating coverage of only a tiny fraction of the surface even at saturation. Gas diffusion inside the solid seemed, therefore, to depend on the catalyst structure.

Oxygen adsorption rate over fused vanadium pentoxide catalyst at 440° and 480° C. was quite high during the first 30 minutes but decreased later, and the amount of adsorption attained a steady value. At 520° C., adsorption rate increased after two hours. It was inferred that adsorption at 520° C. for the first two hours involved gas uptake by the surface only, while the progressive increase in oxygen uptake after this period indicated probably slow diffusion of gas inside the solid.

To ascertain changes occurring in the catalyst during the reaction, the kinetics of oxygen adsorption was also studied over spent catalyst samples. Oxidation of o-xylene was carried out on each sample for two hours under typical reaction conditions. The catalyst tube was modified so that it could be used for adsorption as well as reaction studies. After baking the catalyst sample in oxygen for eight hours at 520° C., a mixture of air and o-xylene was passed over it for two hours at the established optimum reaction conditions, the sample was flushed with nitrogen for an hour, and then quenched in nitrogen. After degassing for eight hours, oxygen adsorption was studied and the sample was again heated in oxygen at atmospheric pressure for 12 hours at 520° C. to carry out kinetic measurements after evacuation.

A significant increase in the rate and amount of oxygen adsorption was observed in the case of spent catalysts. Using a fresh sample, 0.70 cc. of oxygen was adsorbed on the unfused vanadium pentoxide-kieselguhr catalyst during the first 30 minutes. After the o-xylene oxidation, the same catalyst adsorbed as much as 5.70 cc. of oxygen in the same period. Oxygen adsorption on the fresh fused catalyst in the first 15 minutes was 1.06 cc., whereas for the same period the used sample adsorbed 8.99 cc. of oxygen.

Complete decomposition of the vanadium pentoxide in 1 gram of vanadium pentoxide-kieselguhr catalyst (No. 2) to the tetroxide should liberate 14.61 cc. of oxygen. Similarly 1 gram of fused vanadium pentoxide catalyst should liberate 61.5 cc. Actual maximum adsorptions obtained over the two catalysts, after using them for reaction studies, were 7.62 and 10.5 cc., respectively. Only 52% of the former and 17% of the latter catalyst were decomposed, assuming that the decomposition proceeded only to the tetroxide stage.

This kinetic study indicated that, during the oxidation reaction, the catalyst partly decomposed to a lower oxide; this was oxidized rapidly to the original oxide as soon as oxygen was introduced into the system at 520° C. During the reaction, when air was present along with the o-xylene vapors, reoxidation of the catalyst occurred simultaneously with its reduction, setting up an equilibrium. Presumably, this equilibrium had almost been established when the o-xylene oxidation step was discontinued and the catalyst flushed with nitrogen.

Even without passing the mixture of air and xylene, the fused vanadium pentoxide catalyst lost part of its chemicallybound oxygen on being degassed at 520° C. and was reoxidized as soon as oxygen pressure in the system was increased. This indicated the mobility of oxygen in the vanadium pentoxide lattice at this temperature. In the presence of o-xylene, oxygen exchange between the gas phase and bulk phase was greatly facilitated because of the continuous reduction of the solid by the hydrocarbon.

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