

Vapor-Phase Catalytic Oxidation of Organic Compounds

TOLUENE

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The catalytic activity of various mixtures and compounds was investigated in the vapor-phase oxidation of toluene to produce benzaldehyde and benzoic acid. Results on sixteen catalysts which showed an appreciable effect are reported. The temperature, concentration of vapor, and time of contact were varied over a wide range with each catalyst. The best results were obtained with a mixture of uranyl molybdate and boron carbide at a temperature of 575° C., space velocity (primary air) 420, space velocity (secondary air) 1010, air-hydrocarbon ratio 1.38 by weight, and volume of catalyst 19.3 cc.; the yield of benzaldehyde on the basis of toluene vaporized was 20 per cent per pass. The space velocities are expressed in terms of inlet air.

A brief discussion of this problem is given in the light of the results obtained from this investigation. A possible commercial application is suggested which greatly simplifies the apparatus and method of operation over that which has been previously suggested.

THE oxidation of aromatic compounds for the production of partially oxygenated derivatives has become of great industrial importance. Various substances which were formerly prohibitive in cost because of the complicated methods of production are now relatively cheap and abundant. An outstanding example is the manufacture of phthalic anhydride from the vapor-phase oxidation of naphthalene.

Several methods are employed in the production of benzaldehyde from toluene involving such processes as liquid-phase oxidation, hydrolysis of chlorinated toluene derivatives, and the partial combustion of toluene in the vapor phase. Notwithstanding the diversity in the methods of production, the cost of benzaldehyde (free from chlorine) is extremely high.

The purpose of this investigation was to determine the action of various catalysts in controlling the partial oxidation of toluene in the vapor phase. It was believed that the proper mixture of certain metallic oxides would result in a favorable yield of benzaldehyde. After a thorough search of the literature, the metallic oxides of the fifth and sixth groups were found to be the most effective in controlling this reaction. These substances, both singularly and in mixtures, were investigated for their catalytic properties. Various catalyst supports and promoters were also tried, and the change in partial oxidation with temperature, concentration, and time of contact was recorded.

The recognition of the fact that toluene may be partially oxidized in the vapor phase is relatively old. Coquillon (6) passed a mixture of benzene and toluene vapor with air through a tube containing incandescent platinum wire and found that benzaldehyde and benzoic acid were formed. He later reported that palladium was a better catalyst for the reaction than platinum. The vapor-phase oxidation of toluene was further investigated by Walter (24), the result of which was the important discovery of the catalytic properties of vanadium pentoxide. A comprehensive treatment of the partial oxidation of hydrocarbons was published by Orloff (22) in which he reported a 4 per cent yield of benzaldehyde on passing a mixture of toluene vapor and air over copper.

The influence of various metallic oxides such as those of nickel, manganese, and iron was investigated by Woog (25). Ferric oxide gave the best yield when the tube was heated to 280° C. and the toluene to 90° C. Coke gave excellent results in the oxidation of toluene to benzoic acid. The other substances were reported as giving mostly total oxidation products.

The field of vapor-phase oxidation of aromatic compounds became quite active following the work of Gibbs (10) on the oxidation of toluene. Later Gibbs and Conover (11) announced the production of phthalic anhydride by the vapor-phase oxidation of naphthalene, and the manufacture of maleic anhydride from benzene was announced by Weiss and Downs (9). Both processes were covered by patents. A great deal of information is to be found in the patent literature since 1917 concerning the most effective catalyst and the construction of apparatus for this purpose (19).

Kuznetzov and Stepanenko (17) investigated the catalytic activity of basic zinc manganate, vanadium pentoxide on asbestos and on pumice stone, molybdenum trioxide on asbestos, and bismuth vanadate on pumice stone. Molybdenum trioxide gave 11.1 per cent benzaldehyde when the temperature of the catalyst was 425° C., length of contact layer 24 cm., volume of air per hour 100 liters, and the temperature of vaporizing bath 63° to 65° C.

Chowdhury and Choudhury (5) reported an 18 per cent yield of benzaldehyde using reduced nickel oxide as a catalyst. Tin vanadate in the form of porous pills gave 14.1 per cent aldehyde at 450° C. The use of silica gel as a carrier improved the yield.

Numerous investigators (4) have published the results of their investigations on the vapor-phase oxidation of toluene and its derivatives in which one may find a comprehensive treatment of the catalytic activity of a number of metallic oxides and the different factors which influence this reaction.

Experimental Procedure

The oxidizing agent could be either air or pure oxygen. Air was used in this work for it was deemed advisable to adhere to industrial conditions as closely as possible. Also the presence of nitrogen acted as an excellent diluent.

TABLE I. RESULTS WITH VARIOUS CATALYSTS

Catalyst ^a	Primary Space Velocity ^b	Secondary Space Velocity ^b	Air-Hydrocarbon Ratio ^c	Vol. of Catalyst Cc.	Temp. of Reactor ° C.	O ₂ Consumed in: Total oxidation %	Partial oxidation %
1. PbCr ₂ O ₇ ^d	301	793	1.26	19.4	390	11.9	2.4
					400	16.7	7.1
					415	33.3	11.9
					435	74	21.4
					445	76.3	16.7
2. PbWO ₄ ^d	294	788	1.25	19.4	350	4.8	2.9
					385	11.4	3.3
					420	73.3	21.9
					445	75.2	23.8
					495	76.2	21.9
3. Pb(VO ₃) ₂ ^d	257	688	1.27	22.5	360	16.7	5.7
					400	68	21.9
					440	77	22.8
					465	75.3	23.8
					495	76.8	21.9
4. PbMoO ₄ ^d	258	814	1.29	19.3	345	1.9	1.9
					445	7.1	4.8
					495	32.4	14.3
					545	64.3	27.6
					585	69	29.5
5. UO ₂ WO ₄ ^d	395	1060	1.39	14.5	425	7.6	0
					445	7.8	4.8
					480	23.8	14.3
					505	39	21.4
					545	50.5	26.2
6. (UO ₂)WO ₄ ^d + Al ₂ O ₃	395	1060	1.39	14.5	405	30.9	21.4
					445	40	21.4
					500	59	25.7
					545	62.8	28.8
					575	62.8	28.8
7. UO ₂ MoO ₄ + B ₄ C ^d	228	611	1.29	25.8	375	48	0
					400	23.8	11.9
					425	41.9	21.9
					445	61.8	36
					475	58	39.1
8. UO ₂ MoO ₄ + B ₄ C ^d	420	1010	1.38	19.3	445	16.7	16.7
					495	46.6	38.1
					575	53.3	45
					455	16.7	16.7
					495	46.6	38.1
9. UO ₂ MoO ₄ + B ₄ C ^d	420	1000	1.42	19.3	560	53.3	45
					585	53.3	45
					350	0	0
					406	6.7	8.6
					430	15.2	12.4
10. UO ₂ MoO ₄ (no carrier)	414	..	1.6	65	524	74.3	23.8
					350	0	2.4
					365	0	2.4
					410	4.8	4.8
					455	28.8	12.4
11. U-Mo-B ₄ C (4-1-1) ^e	302	805	1.28	19.3	495	54.8	23.8
					540	64.3	31.4
					575	60	35.3
					350	2.4	5.7
					415	2.4	5.7
12. U-Mo-B ₄ C (4-1-1) ^e	302	1392	1.95	19.3	465	14.3	11.9
					495	28.8	17.2
					540	47.6	29.5
					575	53.3	31
					365	1.9	4.8
13. U-Mo-B ₄ C (3-2-1) ^e	302	805	1.28	19.3	410	4.8	9.5
					460	60	25.7
					535	65	35.2
					575	59	40
					425	7.1	7.1
14. U-Mo-B ₄ C (3-2-1) ^e	302	1392	1.95	19.3	470	35.7	23.8
					517	50	37.1
					575	54.3	42.9
					385	7.1	7.1
					400	16.7	10.5
15. U(MoO ₄) ₂ ^d	500	..	3.58	65	415	27.6	16.2
					450	68.6	29.5
					510	73.3	24.7
					553	77.2	21.9
					600	86.6	12.4
16. U(MoO ₄) ₂ ^d	492	..	6.33	65	650	69	29.5
					658	65.7	33.3
					390	15.2	8.6
					420	36.1	12.4
					470	75.3	16.2
					500	69	29.5
					535	72.5	26.7
					600	81	17.1

^a Unless otherwise specified, the catalysts were supported on granular aluminum.

^b Space velocity = liters of gas at S. T. P. in hours per liter of catalyst space.

^c (Grams of air at S. T. P. per hour)/(grams toluene vaporized per hour).

^d Made by precipitation from aqueous solution.

^e Weighed as UO₂(NO₃)₂·6H₂O, (NH₄)₂Mo₇O₂₄·4H₂O, and B₄C in the stated ratios.

The composition of the air-hydrocarbon mixture was controlled by changing the temperature of the vaporizing bath and thereby increasing or decreasing the toluene vapor content in the air current. It was found that under the conditions employed in this experiment Berthelot's equation for vapor

pressure was not applicable. A blank for the quantity of toluene vaporized had to be run for each primary air flow. This was done by running the apparatus under the conditions to be employed but with no catalyst in the reaction tube. At the exit of the reaction tube the toluene was condensed out and measured. The volume of air passed was measured by calibrated flowmeters.

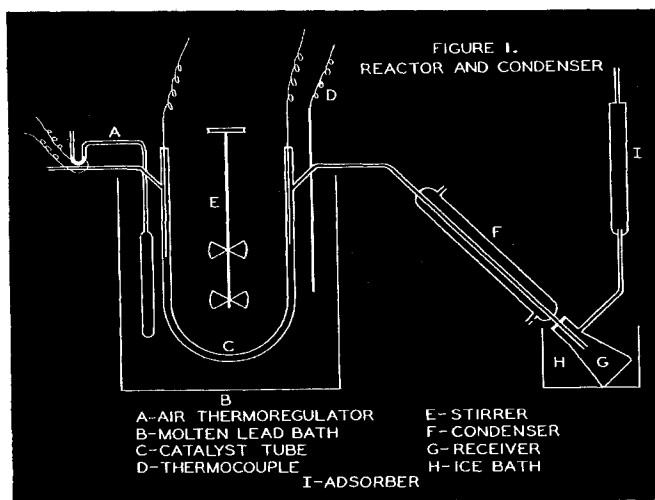
The reaction to form benzaldehyde and benzoic acid is highly exothermic (Equations 3 and 4); and since the heat of reaction (16) is greater than that necessary to heat the incoming mixture to the temperature of the catalyst chamber, good heat transfer is important.

The reaction chamber (7) was constructed by welding fourteen-gage steel to form a U (Figure 1) with a thin cross section 2 × 0.25 inches (5 × 0.635 cm.) inside diameter, the length from the side arm to the bottom of the U being 11 inches (27.9 cm.). Good heat conduction and a relatively large radiating surface per unit volume are the advantages of this unit.

Various substances were used as catalysts in this reaction. They were first tested in a smaller apparatus constructed especially for this purpose (Figure 2). If a mixture or compound was found favorably active, it was loaded in the large apparatus. Compounds of vanadium, molybdenum, uranium, tungsten, lead, chromium, silver, tantalum, and columbium were tried. Boron carbide and boron arsenate were also used.

The catalysts were prepared by standard methods as described in Mellor (20). Different substances were used as supports such as granular aluminum (8), pumice, asbestos, and alumina. The time of contact was controlled as far as possible by the temperature of the catalyst and the rate of flow of the gases.

The primary air supply was washed and dried in a standard gas train (Figure 3). It was then metered, preheated in glass coils, and bubbled successively through three vaporizing tubes containing toluene. The preheating coils and saturators were kept at a constant temperature by an automatically regulated oil bath. The mixture of air and vapor thus obtained was passed into the steel U-tube where the catalyst was suspended on granular aluminum. If an excess of air was required, a secondary air supply, purified in the same manner as the primary air and preheated to the temperature of the vaporizing bath, was admitted to the air-vapor mixture just before it entered the catalyst tube. The reaction tube was submerged in an electrically heated lead bath automatically controlled by an air thermoregulator (15). All temperatures were measured by calibrated thermocouples. A thermocouple extended into the catalyst mass to a depth of approximately 1.5 inches (3.8 cm.), and the temperature registered by this thermocouple is recorded in Table I as the temperature of the reactor. The exit gases



were condensed by a water-cooled coiled condenser connected to an ice bath and finally a charcoal scrubber to remove uncondensed toluene vapor. The length of a run varied from 2 to 4 hours, usually until 100 cc. of drip were collected.

The gaseous products of the reaction were analyzed by means of an Orsat apparatus. The liquid drip was analyzed as follows:

The water layer was determined by the physical boundary in a graduated cylindrical flask. Twenty cubic centimeters of the oil layer in the drip were shaken with saturated sodium disulfite solution, and the precipitate was dried and weighed. Another 20 cc. were treated with dilute sodium carbonate solution, then with sulfuric acid, and finally extracted with ether. The ether was allowed to evaporate at room temperature, and the benzoic acid crystals were weighed. These analyses were not carried out in all cases so that analytical data on benzaldehyde and benzoic acid are not reported. The reaction with the different catalysts was followed by gas analysis and, when the results appeared promising, the chemical analysis was carried out. Therefore, the results of the gas analysis are reported, and only the maximum yield of benzaldehyde and benzoic acid is given. No products other than the benzaldehyde and benzoic acid were determined, although the formation of anthraquinone, a yellow oil, and a brown gummy material was noted with some catalysts. The pure benzoic acid was removed from the drip by water extraction and then crystallization. After the water extraction the disulfite reaction was used to remove the benzaldehyde. The remaining liquid was distilled to recover unreacted toluene for recirculation.

Effect of Various Catalysts

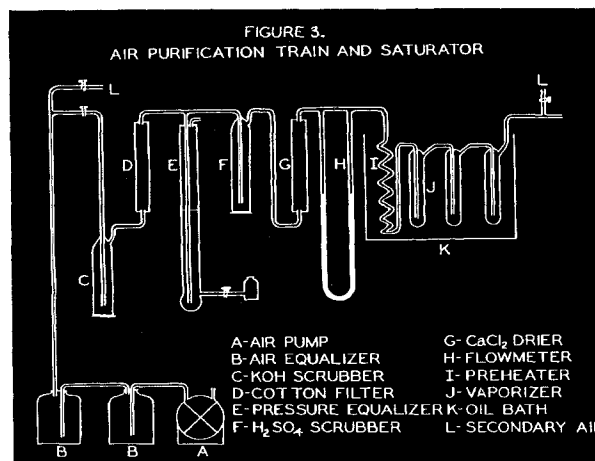
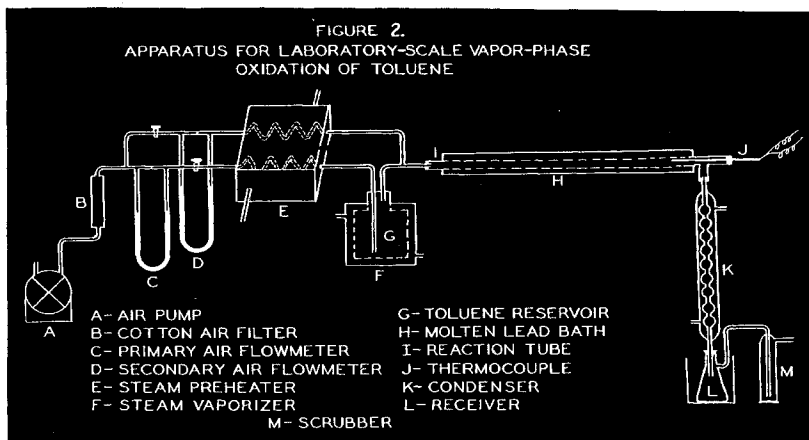
The results obtained with the various catalysts are given in Table I, and representative examples have been plotted from these data. No change for primary or secondary space velocities are reported for the various temperatures for the same catalyst. It is realized that, as the gases undergoing reaction increase in temperature, their volume increases and the time of contact is reduced, and therefore the space velocities might better be based on the temperature and pressure prevailing while the gases are passing through the voids in

the catalyst mass. However, in these results the pressure is not important; the laborious temperature calculations have been avoided and the data are reported in the customary manner. Other catalysts employed were $\text{Cr}_2\text{O}_3\text{-WO}_3$, B_4C , NH_4MoO_4 , HMoO_3 , $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, U-Mo-Ag- B_4C , Ta-Cb-U, and $\text{Co}(\text{NH}_3)_6(\text{VO}_3)_3$. No data are reported for these catalysts because the Ta-Cb-U mixture was very poor while the others were only fair and may be classified with respect to partial oxidation at optimum conditions as similar to catalyst 5 in Table I. In connection with catalyst 15 it is interesting to note that the entire mass fused and had to be drilled out. Often at lower temperatures the aluminum would pulverize or the edges would melt, undoubtedly because of the formation of hot spots.

It was thought that the lead derivatives of the metals of the fifth and sixth groups of the periodic system would favor partial oxidation of the side chain since tetraethyllead slows down the rate of oxidation of gasoline. Lead dichromate, tungstate, vanadate, and molybdate were used (Figure 4); the highest partial oxidation with these lead catalysts was 29.5 per cent of the available oxygen at 585°C . with lead molybdate. These curves show that the quantity of oxygen

consumed in total oxidation is usually in excess of that in partial oxidation and that they tend toward an inverse curve. Although we would expect total oxidation at high temperatures (600°C .), this reaction did not take place with any of the substances employed. A catalyst favorable to partial oxidation remains so at almost any reasonable temperature and concentration of the vapor.

The effect of increasing the oxygen supply and decreasing the time of contact simultaneously is shown in Figure 5. The change resulted in a lower carbon dioxide content and an increase in the yield of partially oxidized compounds. This mixture of uranyl molybdate and boron carbide supported on granular aluminum gave, besides benzaldehyde and benzoic acid, anthraquinone, a light yellow oil of pungent odor,



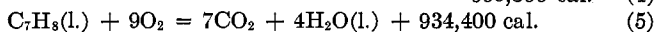
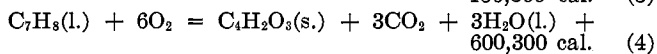
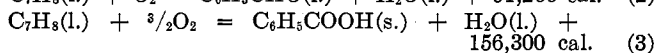
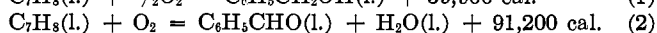
and a dark brown gummy material (18). At high temperatures small quantities of anthraquinone were formed with all catalysts. The presence of uranium and molybdenum increased this formation. With a primary space velocity of 420, a secondary space velocity of 1010, air-hydrocarbon ratio of 1.38 by weight, volume of catalyst 19.3 cc., and a temperature of 575° C., a yield of 20 per cent by weight of benzaldehyde and 1.5 per cent benzoic acid per pass was obtained. This catalyst proved to be the best of all that were investigated.

Aluminum, pumice stone, asbestos, and aluminum oxide were used as supports; since the granular aluminum was the best heat conductor, it decreased the formation of hot spots and thereby lowered the total oxidation and increased the partial oxidation (Figure 6).

A series of runs was made with uranium molybdate as a catalyst in which all the independent variables were kept constant except the temperature of the vaporizing bath. The effect caused by the change in concentration of the toluene vapor was not as might be expected. The total oxidation per weight of toluene vapor remained fairly constant and appeared to be a specific property of the catalyst employed.

Oxidation Products

There are five products of oxidation which may be expected from this reaction:



Benzyl alcohol has not as yet been isolated as one of the products of partial oxidation at atmospheric pressure, although Bone (1) reports the formation of alcohol to the extent of 16 per cent of the toluene partially oxidized under a pressure of 50 atmospheres.

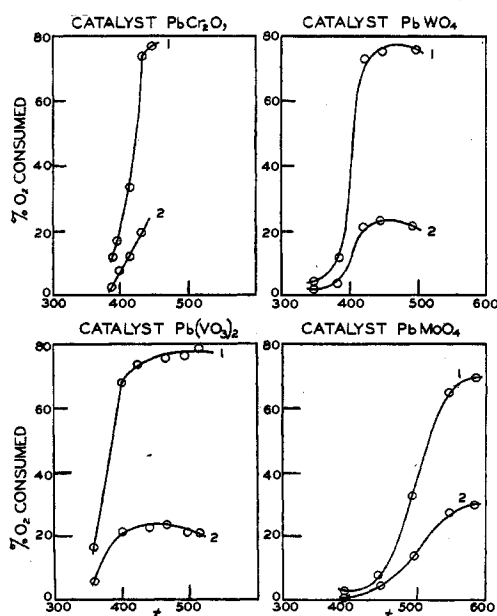


FIGURE 4. EFFECT OF LEAD CATALYSTS

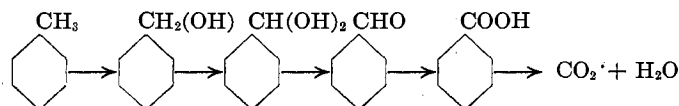
1. Total oxidation 2. Partial oxidation

The oxidation of toluene to maleic anhydride is highly exothermic. At high temperatures the added heat of combustion (151,900 calories) due to the attached methyl group on the benzene ring is enough to cause the destruction of the entire molecule if not removed as liberated. This is difficult to accomplish and is proved by the fact that no appreciable yield has been reported.

The stability of toluene (23) decreases with increase in temperature such that above 850° K. it is thermodynamically unstable with respect to the elements. Consequently in these experiments no temperature approaching this value was employed. In the presence of oxygen an even lower temperature of decomposition might be expected. The theoretical air required for the oxidation of a mole of toluene to benzaldehyde is 120 liters at 20° C. This toluene-air mixture lies on the rich side of the explosive limit as reported by Briand, Dumanois, and Laffitte (2) and is therefore relatively safe to employ. It is interesting to note from their data that the higher limit of inflammability is not a straight line at temperatures above 200° C., but the percentage of toluene decreases rather than increases as would be expected. This allows even one-half the theoretical amount of air to be used for exceptionally lean mixtures if very mild conditions are required. Although the side chain of toluene is aliphatic, it is much more stable toward oxidation than the paraffin hydrocarbon. Once the maximum partial oxidation has been reached, variations in temperature as high as 50° C. do not materially affect the yield. It is easily seen that a low concentration of oxygen and relatively high temperatures should favor the formation of benzaldehyde, whereas excess oxygen and low temperatures should favor the production of benzoic acid. This is true of catalysts that are capable of forming both and has been reported to be the case by Chowdhury and Choudhury (5).

The increased activity of mixtures of metallic oxides may be due to structural changes in the crystal lattice (12). As most of these mixed oxides were made by precipitation from aqueous solutions, the lattice structure of the pure substance may be altered by the presence of the foreign substance. These internal changes should produce a change in reactivity compared with that of the fully uniform crystal. Several investigations of such cases have proved the correctness of this hypothesis (13). Huttig (14) was able to use this theory in explaining the change in catalytic activity observed during the aging period of the catalyst.

The theory of hydroxylation which proposes that the oxidation takes place through the successive formation of hydroxylated compounds explains the mechanism of the reaction with the most satisfaction. For this reaction to take place it is necessary to have atomic oxygen. The substances which have been found favorable toward partial oxidation are members of the "gap elements" and are capable of having various valences. The colors of a catalyst when removed from the reaction chamber show these various stages of oxidation. This behavior leads us to the conclusion that these compounds are alternately oxidized by the air and reduced by the toluene, atomic oxygen being liberated each time. The temperature at which these catalysts become active is usually that point at which this oscillating effect takes place. The reaction is believed to be as follows:



The possibility of the reaction through activated molecular oxygen,

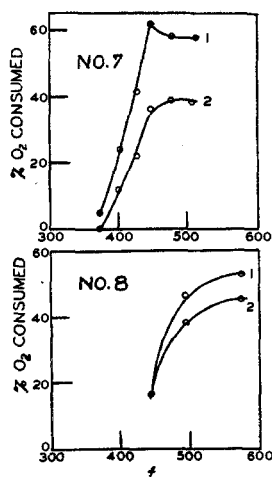


FIGURE 5. EFFECT OF INCREASING OXYGEN SUPPLY AND DECREASING CONTACT TIME

1. Total oxidation
2. Partial oxidation

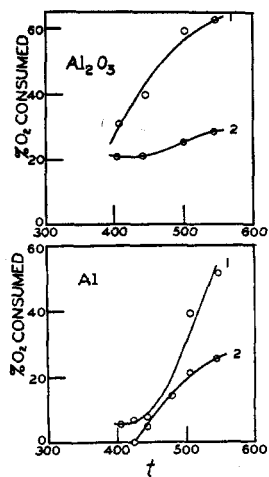
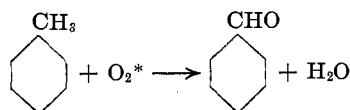


FIGURE 6. EFFECT OF CATALYST SUPPORT ON OXIDATION WITH URANYL TUNGSTATE

1. Total oxidation
2. Partial oxidation



is doubtful, for the energy of activation is extremely high and it is hard to see from whence this sum is available; the heat of adsorption or condensation is hardly enough to foster this reaction.

Newitt and Szego (21) report the formation of hydroxylated compounds using a temperature of 210° C. and a pressure of 50 atmospheres. About 60 per cent of the toluene burned appeared as hydroxy derivatives, which consisted of benzyl alcohol, a small quantity of benzaldehyde, 2, 4-dihydroxytoluene, and benzoic acid. The formation of benzyl alcohol and 2, 4-dihydroxytoluene shows that the aromatic nucleus and the aliphatic side chain may be simultaneously oxidized.

Commercial Possibilities

The data recorded in this paper show that the catalysts employed reached a point of maximum activity, both in respect to partial and total oxidation, at a definite temperature and remained almost constant over a range of 50° to 75° C. If approximately one-half the theoretical amount of air required to oxidized toluene to benzaldehyde was used, the maximum partially oxidized compounds would be about 20 per cent per pass and about 30 per cent sacrificed to carbon dioxide and water. This yield would make the concentration of the aldehyde in the drip workable for the commercial production of benzaldehyde, and the expensive and complicated converters for precise temperature control would be avoided provided such a catalyst as uranyl molybdate plus boron carbide was used.

The authors believe that this reaction could be carried out

commercially with an apparatus of moderate cost. The compressed air could be purified and preheated, and then passed through a steam jacketed toluene vaporizer, or the liquid toluene may be injected before the air enters the catalyst chamber. The mixture of air and toluene vapor then enters a metal coil where it is heated to the temperature of reaction (500° C.). The gases are then passed into the catalyst chamber which consists of a steel cylinder 1 foot (0.3 meter) in diameter and about 3 feet (0.9 meter) in height containing two layers of catalyst supported on granular aluminum. The heat generated by total oxidation would not be enough to raise the temperature of the incoming gases 50° C., but to be on the safe side a cooling device may be installed between the catalyst layers. A somewhat similar arrangement has been suggested for the production of phthalic anhydride from naphthalene (3). The high-boiling fraction could be condensed by water-cooled coils and the remaining toluene mixture scrubbed with bisulfite solution. This arrangement would simplify the apparatus as now suggested by most authors.

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