A STUDY OF VAPOR PHASE OXIDATION OF ORGANIC COMPOUNDS, USING RARE EARTH OXIDES AS CATALYSTS. I. METHYL AND ETHYL ALCOHOLS

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A large number of metallic oxides act as oxidation catalysts. In general this property can be explained by the fact that they are readily reduced to the metals or to lower oxides by the substances to be oxidized and are then re-oxidized by oxygen. This explanation seems to be adequate for certain oxides, such as the oxides of copper, nickel, cobalt, manganese, molybdenum, vanadium, etc. For certain other oxides, however, the mechanism is not quite so apparent, because, as far as is known, they are not readily reduced to lower oxides. For example, La_2O_3 and Y_2O_3 are active oxidation catalysts, but are not readily reduced.

A great many oxides have been used and with success in certain cases. A review of the literature indicated that even with the more commonly used catalysts there is still much work to be done, especially with regard to finer control and better methods for analyzing the products formed. In many cases the percentage of unoxidized material recovered is given, with no information concerning the method of recovery. In work of this nature where so many factors can influence the results, it is most important to choose analytical methods very carefully and only after thorough trial.

The oxidizing properties of cerium compounds have been known for a long time. In general for vapor phase oxidation at elevated temperatures they have been found to be too active, and the extent of the oxidation could not be easily controlled. The other elements of the rare earth group have not been studied. Apparently no work has been done with mixed catalysts, containing rare earth elements, for vapor phase oxidation.

The purpose of this investigation was two-fold: (1) to obtain quantitative data on the rare earth oxides as catalysts for vapor phase oxidation as compared with some less active catalyst such as copper oxide, and (2) to measure the effect produced by the addition of small amounts of rare earth oxides to some less active catalyst such as copper oxide.

After numerous preliminary experiments, samarium oxide was chosen because of its greater porosity. All of the members of the cerium group were tried and appeared to be equally active. Of the yttrium group only two, yttrium and lanthanum, were used in the preliminary work. They appeared to be less active oxidation catalysts and were much more apt to produce charring.

The preliminary work included oxidation of methyl alcohol, ethyl alcohol, ethylene, benzene and toluene. Some of the products qualitatively deter-

mined were not only interesting, but hold much promise for future work. Benzene, for example, yielded small amounts of phenol. Among the oxidation products of toluene, dibenzyl, benzaldehyde and benzoic acid were detected. Due to the greater ease of oxidation of methyl and ethyl alcohols, the rate of reaction, the temperature, etc., are more difficult to control. It was decided, therefore, to investigate carefully the oxidation of these alcohols first, with the hope that the data obtained would be useful in later experiments on the oxidation of substances not so readily oxidized.
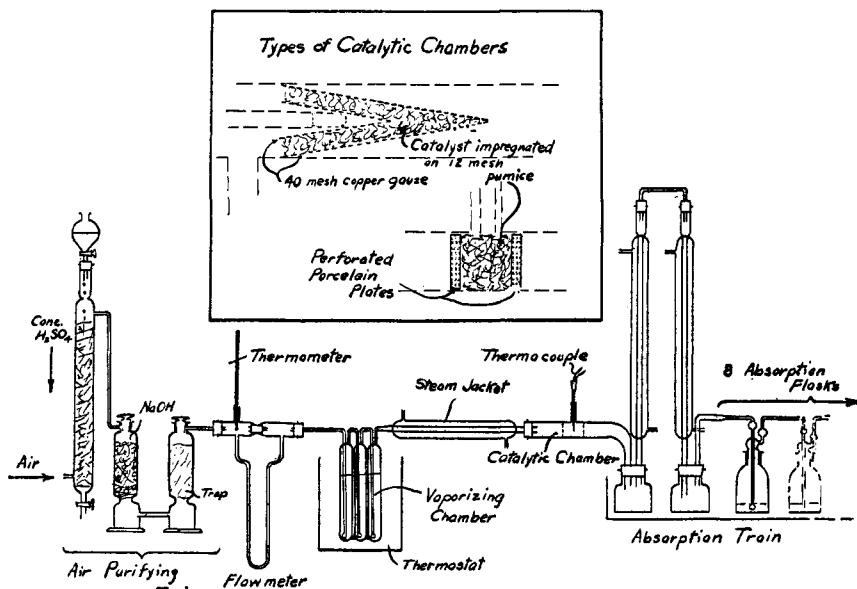

Fig. 1.—Apparatus.

The apparatus used is shown in Fig. 1. The arrangement of the apparatus was similar to that used by Le Blanc and Plaschke.[1] Dry air in definite amounts (as measured by a flowmeter) was passed through the alcohol contained in the vaporizing chamber. The outlet tube leading from the vaporizing chamber to the catalytic chamber was heated by means of a steam jacket to prevent condensation. The alcohol–air mixture was then passed over the catalyst in the pyrex catalytic chamber. The catalyst was supported (in the case of impregnated pumice) at each end by tightly fitting, finely perforated porcelain plates. The catalyst was 15 mm. in length and 17 mm. in diameter. In the cone type of catalyst two concentric cones of fine copper gauze were employed, the space between the cones being filled with catalyst impregnated upon pumice. The height of the outer cone was 60 mm., the diameter 20 mm. The diameter of the inner cone was 10 mm. The thickness of the pumice layer was 5 mm. Before the air–alcohol mixture was admitted to the catalytic chamber, the catalyst was heated to about 350° by means of a small burner. In all cases the heat of the reaction was sufficient to keep the catalyst at a red heat after the reaction had once started. The reaction temperatures were carefully measured by inserting a quartz thermometer or a

¹ Le Blanc and Plaschke., Z. Elektrochem., 17, 45 (1911).

thermocouple in the side arm of the catalytic chamber. The thermocouple arm was protected by a quartz jacket. The end of the thermometer or thermocouple jacket was well buried at what appeared to be the hottest point. It is probable that the actual temperatures were somewhat higher than those recorded, since perfect contact with the catalyst was difficult to attain. The products of the reaction were collected in the cooling system and in the several absorption flasks. The receivers were then carefully emptied and rinsed, and the resulting solution diluted to a definite volume. Aliquots were taken for analysis, check analyses being made in all cases.

In most cases about 0.5 mole of alcohol was passed over the catalyst. In order to determine whether or not the yields varied with the amount of alcohol passed over, longer runs were made in which about 1.5 moles of alcohol was passed over. The yields of aldehyde in all cases checked very well with the yields obtained from the shorter runs. The amount of alcohol used for each run was simply determined by weighing the vaporizing chamber before and after each run.

The alcohols which were used were not perfectly anhydrous. As a result the vapors carried over by the air could not be considered to be purely alcohol vapors. This is a point which has been neglected by many previous investigators. It was found that the percentage of alcohol in the vapors passing over could easily be determined by making blank runs and determining the alcohol in the condensate by means of an immersion refractometer. That is, instead of passing the vapors over a heated catalyst, they were simply passed through an empty tube, condensed and the alcohol content determined as above.

Experimental

Oxidation of Methyl Alcohol

Constant boiling (65°) methyl alcohol free from acetone was used. Three different catalysts were used: (1) pure Sm_2O_3 (prepared by heating samarium nitrate in a stream of oxygen at 450–500°); (2) pure CuO impregnated on 12-mesh pumice (prepared by dissolving 3 g. of CuO in nitric acid, to which solution was added 9 cc. of 12-mesh pumice and the mixture carefully evaporated to dryness with stirring; the dry pumice was then heated in oxygen as above); and (3) samarium and copper oxide mixtures on 12-mesh pumice (prepared similarly to the above).

The amounts of catalysts used have been given in the introduction. These figures represent the optimum amounts as carefully determined in the preliminary work.

The optimum bath or thermostat temperature was determined in preliminary experiments. Space does not permit recording all of the results of these experiments. Figure 2 shows that a bath temperature of 40° offers the best conditions (alcohol–air ratios) for obtaining the highest yields of formaldehyde.

Determination of Formaldehyde.—The aldehyde in the condensate was determined by the hydrogen peroxide–sodium hydroxide method.[2] This method gave excellent check results.

Determination of Unchanged Methyl Alcohol.—This was accomplished with satisfactory results by adding an excess of ammonium hydroxide to an aliquot of the condensate and distilling the solution. The distillate was just acidified with dilute sulfuric acid and then redistilled. The methyl alcohol content in this distillate was then determined by means of an immersion refractometer.

Use of Samarium Oxide as Catalyst.—Three to six cc. of 12-mesh oxide was used. The process yields of formaldehyde (1–5%) clearly indicated that this oxide was too active a catalyst. The catalyst temperature was always very high, never falling below 600°, even when a very low air rate was used. Even when the air supply was much less

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[2] Haywood and Smith, THIS JOURNAL, **27**, 1188 (1905).

than the amount theoretically necessary for the oxidation to formaldehyde, the yields were almost as small as before. This fact might be explained in either of two ways: (1) the oxidation does not stop with formaldehyde, but proceeds as far as carbon dioxide and water; or (2) formaldehyde is formed, but at the high temperature of the catalyst is immediately decomposed into hydrogen and carbon monoxide. That either explanation may be correct, depending upon the amount of oxygen used, was easily proved. A definite amount of absolute methyl alcohol was passed over the heated catalyst with almost the exact amount of oxygen (from air) necessary to oxidize the alcohol to formaldehyde. Of 26.97 g. of alcohol passed over, 6.4 g. was recovered. The difference between the two weights (20.57 g.) was oxidized. This amount of alcohol on oxidation to formaldehyde should yield 11.57 g. of water; actually 11.12 g. was formed. Further, it was found that fairly large amounts of hydrogen and carbon monoxide were formed but only traces of carbon dioxide. These facts seem to confirm the second explanation given above.
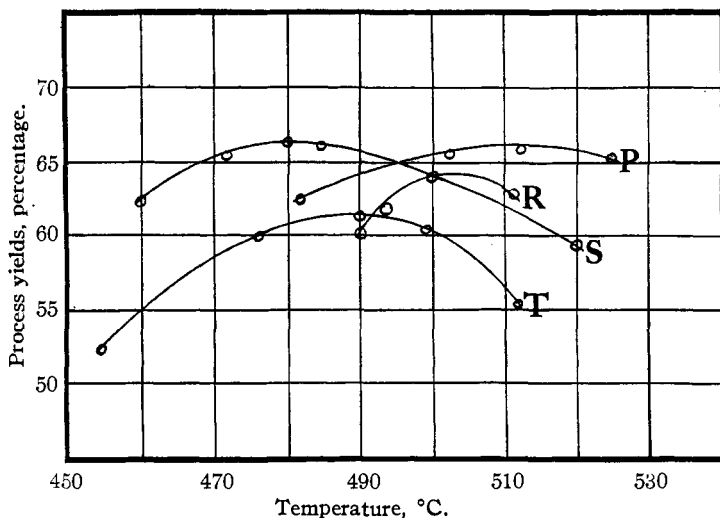
P, Bath at 37°; R, bath at 42°; S, bath at 40°; T, bath at 45°.

Fig. 2.—NOTE.—Due to the fact that a thermostat temperature of 40° permitted working at lower catalyst temperatures than a thermostat temperature of 37°, the former seemed to offer the more ideal conditions.

When an excess of oxygen is used, oxidation proceeds much further with the formation of larger and larger amounts of carbon dioxide and water.

It may be concluded, therefore, that the low yields of formaldehyde obtained even when insufficient oxygen was used were due to the catalytic decomposition of the aldehyde; and when an excess of oxygen was used the low yields were due primarily to a more complete combustion to carbon dioxide and water.

The results recorded in Table I represent mean results. The process yields were calculated on the basis of moles of methyl alcohol changed to moles of formaldehyde.

TABLE I

MEAN RESULTS (THERMOSTAT, 40°)

Catalyst	Air rate liters/min.	Oxygen ratio g. MeOH/l. O₂	Catalyst temp., °C.	Process yield, %
A. 3 g. CuO on 9 cc. pumice	1.08	1/0.296	484	63.5
	1.21	1/0.308	505	66.3
	1.30	1/0.310	515	66.5
	1.37	1/0.308	530	65.3
B. Sm₂O₃ (0.5%), CuO (99.5%), on pumice	1.08	1/0.308	494	63.4
	1.21	1/0.303	502	64.0
	1.30	1/0.308	515	64.5
	1.37	1/0.306	530	63.8
C. Sm₂O₃ (1%), CuO (99%), on pumice	1.08	1/0.309	485	58.5
	1.21	1/0.307	500	61.3
	1.30	1/0.299	513	63.7
	1.37	1/0.309	525	63.5
D. Sm₂O₃ (2%), CuO (98%), on pumice	1.08	1/0.300	473	53.5
	1.21	1/0.305	494	58.9
	1.30	1/0.309	505	59.3
	1.37	1/0.302	517	60.3
	1.58	1/0.309	532	61.1
	1.68	1/0.302	555	59.1
E. Sm₂O₃ (5%), CuO (95%), on pumice	1.21	1/0.307	506	37.6
	1.30	1/0.310	512	38.7
	1.50	1/0.306	532	40.8
	1.70	1/0.300	560	36.3

Discussion of Results

Preliminary experiments indicated that the best yields of formaldehyde were obtained at a thermostat temperature of 40° and when the alcohol-oxygen ratio was 1 g./0.3–0.31 liter of oxygen. The latter figures are somewhat below the theoretical values, as 0.35 liter of oxygen would be necessary to oxidize 1 g. of methanol completely to formaldehyde. The use of smaller or larger amounts of oxygen was accompanied by lower process yields of the aldehyde. The actual yields (based upon the actual amount of alcohol oxidized) varied inversely with the amount of oxygen used. It was possible to approach 100% actual yields when the amount of oxygen used was small. There was, of course, a corresponding decrease in the process yields, as more alcohol passed through unchanged, due to the lack of oxygen.

The alcohol–oxygen ratios recorded show the efficiency of the type of vaporizing chamber used. The constancy of these ratios certainly indicates that the air passing over the catalyst was saturated with respect to the alcohol regardless of the air rate used. This is a factor which, apparently, has been neglected in much of the previously published work.

Hofmann[3] first accomplished the formation of formaldehyde by passing

[3] Hofmann. *Ann.*, **145**, 357 (1868); *Ber.*, **2**, 152 (1869); **11**, 1686 (1878).

air laden with methyl alcohol over a heated platinum wire. Tollens[4] and Loew[5] improved the process by using copper gauze in place of platinum as a catalyst. Orloff[6] made the first careful investigation of the use of copper gauze. He reported about 50% as the highest process yield. Le Blanc and Plaschke[1] reported that silver gauze was a better catalyst than copper gauze, which fact has been confirmed by others. Fokin,[7] using asbestos impregnated with copper, reported a yield of 47%. Thomas,[8] using copper gauze as a catalyst, reported a maximum process yield of 63.6%. Bobrov[9] used copper gauze in the form of disks and reported an actual yield of 71.5%. From the published records Thomas has obtained the highest process yields.

The process yields given in Table I under A are somewhat higher than Thomas obtained when he used copper gauze. There is even a greater difference in the actual yields. Thomas reported an actual yield of 72% for the same run which gave a 63.6% process yield, whereas the actual yields using CuO on pumice in this investigation never dropped below 85%. This probably can be explained by the fact that his catalyst (copper gauze) was 74 mm. in length, while the catalyst layer (copper oxide on pumice) used in this investigation was only 15 mm. in length. Consequently, the products of the reaction escaped from the heated catalyst more quickly in the latter case with the result that a smaller percentage of aldehyde was decomposed.

All of the previous workers who used copper gauze as the catalyst have used a high air rate, generally two liters of air per minute. The best results obtained in this investigation were obtained at a much lower air rate, about 1.3 liters per minute. This rather curious difference must be due to the difference in the form of the catalyst. A comparison of copper gauze and pumice impregnated with copper oxide was made in the preparation of acetaldehyde (see Oxidation of Ethyl Alcohol).

It will be noted from the results recorded in Table I (B–E) that the introduction of small amounts of samarium oxide decreased the process yields, the decrease being very noticeable when the samarium oxide content reached 5%. The presence of the rare earth oxide had practically no effect on the catalyst temperatures. As the amount of samarium oxide increased, the yields became less and less, due to the decomposing action of this oxide on formaldehyde.

The actual yields also decreased with the introduction of Sm_2O_3, as shown by the following: A, 85–90%; B, 83–90%; C, 80–86%; D, 77–84% and E, 70–76%.

[4] Tollens, *Ber.*, **15**, 1629 (1882); **16**, 917 (1883); **19**, 2134 (1886).

[5] Loew, *J. prakt. Chem.*, [2] **33**, 324 (1886).

[6] Orloff, *J. Russ. Phys.-Chem. Soc.*, **39**, 1023 (1907).

[7] Fokin, *ibid.*, **45**, 286 (1913).

[8] Thomas, THIS JOURNAL, **42**, 867 (1920).

[9] Bobrov, *J. soc. chim. russe, Industrie chimique*, **11**, 455 (1924).

The yields in Table I if plotted against catalyst temperatures would give curves showing a gradual rise in yields and then a gradual drop. Due to the ease of decomposition of formaldehyde, temperature control is undoubtedly the most important factor in its catalytic preparation. A second factor is the length of the catalyst. The preliminary work showed very definitely that the minimum amount of catalyst should be used. When more than this amount was taken, there was a very pronounced decrease in the process yields obtained.

Oxidation of Ethyl Alcohol

Pure ethyl alcohol (97%) free from aldehydes was used for the experiments. Three different catalysts were used: (1) pure samarium oxide; (2) (a) copper gauze in the shape of a cone—two cones were used as previously described, the space between was filled with 12-mesh pumice impregnated with copper oxide (Fig. 1)—(b) pure copper oxide impregnated on 12-mesh pumice and (3) (a) copper gauze cones as above—in this case the pumice layer between the cones was impregnated with samarium and copper oxide mixtures—(b) samarium and copper oxide mixtures impregnated upon 12-mesh pumice. The catalysts were prepared in the manner described under the oxidation of methyl alcohol.

The acidity of the various condensates was so slight that it could scarcely be explained on the basis of the presence of acetic acid. In greater part it was probably due to the presence of carbon dioxide. Ester formation was not noticed at any time during the course of the experiments.

Determination of Acetaldehyde.—The acetaldehyde in the condensate was determined by Ripper's method.[10]   Check analyses were made and the results obtained usually agreed within 0.3–0.5%.

Determination of Unchanged Ethyl Alcohol.—The unchanged ethyl alcohol which was present in the condensate was much more difficult to determine. Several methods were investigated and finally the following was adopted. A suitable aliquot was taken, an excess of ammoniacal silver nitrate was added, and the resulting mixture was heated on a steam-bath under an efficient condenser for two to three hours, depending upon the amount of aldehyde present. The time may be shortened somewhat if the mixture is heated under a slight pressure. This effected the complete oxidation of the acetaldehyde in practically every case. The slightly ammoniacal mixture was distilled without filtration. The distillate was then just acidified with sulfuric acid and again distilled until about two-thirds of the solution passed over. The amount of alcohol in the distillate was determined by means of an immersion refractometer. This method proved quite satisfactory.

Use of Samarium Oxide as Catalyst.—Pumice (12-mesh) impregnated with samarium oxide was used as the catalyst. The results obtained were somewhat better than with methyl alcohol. The process yields varied from 6 to 15%. The oxide showed a great tendency to cause charring, and consequently the reactions were difficult to control. Charring was easily prevented by using an excess amount of air, but under those conditions combustion was practically complete.

10 Ripper, *Monatsh.*, **21**, 1079 (1900); Feinberg, *Am. Chem. J.*, **49**, 87 (1913).

Table II gives the average yields of acetaldehyde obtained using the various catalysts.

TABLE II

YIELDS OF ACETALDEHYDE (THERMOSTAT, 45°)

Catalyst	Air rate, l./min.	Oxygen ratio, g. EtOH/l. O₂	Catalyst temp., °C.	Process, yield, %
A. Copper cones, pumice layer impregnated with CuO	0.83	1/0.409	460	63.5
	.99	1/0.411	470	66.2
	1.08	1/0.421	481	68.4
	1.17	1/0.405	490	69.0
	1.22	1/0.418	500	68.7
	1.37	1/0.409	540	64.0
B. 3 g. CuO on 9 cc. pumice	0.59	1/0.430	429	65.4
	.71	1/0.417	482	70.5
	.83	1/0.422	501	68.8
	.88	1/0.417	512	66.2
	.99	1/0.417	532	64.4
	1.08	1/0.422	547	60.1
C. Copper cones, pumice layer impregnated with Sm₂O₃ (0.5%) and CuO (99.5%)	0.71	1/0.409	446	62.8
	.88	1/0.405	478	69.5
	.99	1/0.412	485	68.3
	1.03	1/0.409	490	68.0
	1.08	1/0.420	493	67.3
	1.22	1/0.414	540	65.6
D. Sm₂O₃ (0.5%) and CuO (99.5%) on pumice	0.45	1/0.420	397	65.1
	.59	1/9.410	460	69.8
	.65	1/0.410	472	66.9
	.71	1/0.427	488	62.3
	.83	1/0.422	496	61.1
E. Copper cones, pumice layer impregnated with Sm₂O₃ (1%) and CuO (99%)	0.83	1/0.405	455	66.5
	.99	1/0.423	485	69.6
	1.03	1/0.417	505	68.5
	1.08	1/0.407	510	67.5
	1.22	1/0.405	525	63.5
F. Sm₂O₃ (1%) and CuO (99%) on pumice	0.45	1/0.427	400	65.6
	.59	1/0.418	465·	67.4
	.71	1/0.425	495	63.5
	.83	1/0.420	525	58.8
	.99	1/0.410	555	55.4
G. Copper cones, pumice layer impregnated with Sm₂O₃ (2%) and CuO (98%)	0.83	1/0.410	430	65.6
	.94	1/0.422	500	66.2
	.99	1/0.404	505	68.0
	1.08	1/0.400	530	67.6
	1.22	1/0.420	550	63.2
H. Sm₂O₃ (2%) and CuO (98%) on pumice	0.45	1/0.420	395	67.5
	.59	1/0.410	435	65.8
	.71	1/0.412	485	60.3
	.83	1/0.417	512	57.5

TABLE II   (*Concluded*)

Catalyst	Air rate, l./min.	Oxygen ratio, g. EtOH/l. O₂	Catalyst temp., °C.	Process, yield, %
I. Copper cones, pumice layer impregnated with Sm_2O_3 (5%) and CuO (95%)	0.71	1/0.401	410	57.0
	.83	1/0.422	435	58.9
	.99	1/0.400	460	63.4
	1.08	1/0.409	475	62.0
J. Sm_2O_3 (5%) and CuO (95%) on pumice	0.45	1/0.428	370	56.8
	.59	1/0.425	412	53.7
	.71	1/0.405	445	52.5

The catalyst could not be made to continue glowing at an air rate lower than 0.45 liter of air per minute.

Discussion of Results

Preliminary runs proved conclusively that the best results were obtained with a thermostat temperature of 45°. The results of these preliminary runs, when plotted against catalyst temperatures, gave curves similar to those under formaldehyde (see Fig. 2) with the curve for a thermostat temperature of 45° showing the best yields. Consequently, only the results obtained at the latter temperature are recorded here. The preliminary results plainly indicated that the optimum alcohol–oxygen ratio was 1 g. EtOH/0.40–0.43 liter of oxygen. The theoretical ratio is 1 g. EtOH/0.2434 liter of oxygen. The use of smaller or larger amounts of oxygen was always accompanied by a decreased process yield of acetaldehyde. However, as expected, the actual yields varied inversely with the amount of oxygen used. It was possible to approach 100% actual yields when a small enough quantity of oxygen was used; at the same time there was a corresponding decrease in the process yields. The ratios recorded under acetaldehyde again indicate the efficiency of the type of vaporizing chamber used.

As with methyl alcohol, pure samarium oxide is too active a catalyst to be used for the oxidation of ethyl alcohol. It is not only apt to carry the oxidation too far, but it also probably catalyzes the decomposition of acetaldehyde similarly to formaldehyde.

Orloff[11] was the first to make a careful investigation of copper gauze as a catalyst for the oxidation of ethyl alcohol. He reported 66% as his best process yield.

Simington and Adkins[12] studied the catalytic oxidation of ethyl, isopropyl and n-butyl alcohols, using various catalysts. Using copper gauze they obtained only 37.4% process yield of acetaldehyde; using silver gauze they obtained 43.7%, and using a catalyst composed of 90% Cu and 10% Ag, they obtained 76% yields.

The results recorded in Table II (A and B) correspond more closely (for

[11] Orloff, *J. Russ. Phys.-Chem. Soc.*, **40**, 203 (1908).

[12] Simington and Adkins, THIS JOURNAL, **50**, 1449 (1928).

copper gauze catalyst) to the results obtained by Orloff, although they are somewhat higher than his. Apparently the form of the catalyst has little effect on the yields, for the results under A and B are practically the same. One notable difference between them is evident from a comparison of the catalyst temperatures for the same air rates. For example, using an air rate of 0.83 l./minute, the catalyst temperature in A was 460°; in B, however, the temperature was 501°. This probably was due to the fact that the impregnated pumice offered a larger surface than the gauze. This would explain the fact that the best yields in B were obtained at lower air rates than those in A.

It will be noted from the results in Table II (C–J) that the introduction of small amounts of samarium oxide to the catalyst decreases the process yields, the decrease being especially noticeable when the samarium oxide content reached 5%. It will also be noted (B, D, F, H, J) that with the introduction of samarium oxide the optimum temperatures were materially lowered, i. e., the best results were obtained from CuO on pumice at about 482°, with the catalyst containing 0.5% samarium oxide at 460°, with the catalyst containing 1% samarium oxide at 465°, with the catalyst containing 2% samarium oxide at 395° and with the catalyst containing 5% samarium oxide at 370°. This probably can be explained by the fact that with increasing amounts of samarium oxide the rate of decomposition of acetaldehyde, as well as the extent of oxidation, is increased and consequently best results are obtained at lower temperatures. Something not so easily explained, at present, is the fact that the temperatures measured for the 5% samarium oxide type of catalyst (for the same air rates) were lower than with pure CuO as catalyst, while with the catalysts containing 0.5% and 1% samarium oxide there was a noticeable temperature increase for the same air rates.

The introduction of samarium oxide also decreased the actual yields, as shown by the following: A and B, 76 to 89%; C and D, 76 to 86%; E and F, 75 to 85%; G and H, 75 to 81%; and I and J, 74 to 78%.

The points noted above were not so evident with the use of the double cone type of catalyst. Apparently the impregnated pumice layer was not so active, due to the fact that the copper gauze was effecting the greater part of the oxidation.

The results recorded in Table II, if plotted against catalyst temperatures, would give curves showing a gradual rise to the optimum temperature and then a fairly rapid drop. Certain workers have placed much stress upon the length of time the reacting gases were permitted to remain in contact with the catalyst (which, of course, depends upon the air rate and the length of catalyst layer). This is unquestionably an important factor, but in the case of methyl and ethyl alcohols it would seem that the catalyst temperature is the most important one as far as the yields are concerned.

Another important factor is the amount of catalyst used. In the case of copper gauze the length of the catalyst did not affect the results appreciably, but when impregnated pumice was used, the effect on the yields was quite evident. The use of too much catalyst produced a marked decrease in the yields of acetaldehyde.

Conclusions

The results obtained in this investigation indicated that the presence of rare earth oxides with copper oxide promoted oxidation. With such easily oxidizable substances as methyl and ethyl alcohols this fact was of no apparent advantage, since the oxidation tends to go too far. This enhanced activity should prove to be very advantageous in the oxidation of less readily oxidizable substances. Work has been started along these lines.

It is believed that the presence of rare earth oxides, in small amounts, helps to prevent catalyst poisoning and prolong the life of the catalyst indefinitely. Actual proof has not yet been obtained. Work is being started with rare earth oxides and silver oxide mixtures and it is hoped that this latter point can thus be easily proved.

Summary

1. Data have been obtained on the use of rare earth oxides for the vapor phase oxidation of methyl alcohol and ethyl alcohol, as compared with the results obtained when copper oxide was used for the same purpose.

2. Better yields of formaldehyde and acetaldehyde have been obtained, using pumice impregnated with copper oxide, than have been reported previously by investigators who used some form of copper as the oxidation catalyst.

3. Data have been obtained showing the effect produced on the catalytic activity of copper oxide by the addition of small amounts of rare earth oxides to the copper oxide.

PHILADELPHIA, PENNSYLVANIA