6. The effect of temperature upon the relationship of pH to foam stability was studied for sodium caprate and laurate.
7. The effect of temperature on the foam stability of all the soaps mentioned in paragraph 2 above was ascertained for the range 27° to 82°C.
8. The effect of pH on the foam stability of mixtures of sodium laurate and palmitate was determined.
9. Good foam stability was obtained for a few solutions containing two materials neither of which, alone, is a particularly good foam stabilizer.

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THE CATALYTIC OXIDATION OF ETHYLENE TO ETHYLENE OXIDE

L. H. REYERSON AND HANS OPPENHEIMER

School of Chemistry, University of Minnesota, Minneapolis 14, Minnesota

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A number of years ago the catalytic oxidation of ethylene was studied, using a series of active metallized silica gels as catalysts (4). The results indicated that the oxidation was incomplete over the temperature range then explored. The products of the partial oxidation proved to be largely the oxides of carbon and water. However, at times when the silver–silica gel catalyst was used, a trace of a pleasant odor differing from that of ethylene was detected in the products of reaction. Attempts to identify the substance failed. Since that time less active forms of silver catalysts, giving rise to almost no oxides of carbon, have been successfully used on a commercial scale in the production of ethylene oxide. It therefore seemed desirable to study the oxidation of ethylene, using a series of silver catalysts over a wide temperature range, in an attempt to establish some of the conditions for the successful preparation of ethylene oxide from ethylene.

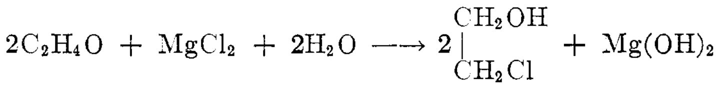
It was decided to use three different silver catalysts: (*1*) a silver–silica gel catalyst similar to the one previously used; (*2*) silver deposited on fused aluminum oxide, known to be effective in the commercial production of ethylene oxide; (*3*) finely divided silver produced by the thermal decomposition of silver oxalate. The silver–silica gel catalyst was prepared by shaking 80 g. of purified silica gel in 500 ml. of a solution of 0.5 *N* $Ag(NH_3)_2NO_3$. The solution was decanted after several hours, the gel was lightly dried, and the adsorbed silver salt was reduced in a slow stream of hydrogen at 200°C. The gel granules usually became black and lustrous. Silver gels containing 8.9, 14.7, and 22.2 per cent of silver were prepared in this way. The dark film coating was proved to be silver. In one of the preparations an interesting product was obtained. The gel was by accident treated with a silver nitrate solution that did not contain ammonium hydroxide. When this was noted the solution was decanted from the gel and ammonium hydroxide added, after which the solution was again poured onto the gel and the treatment carried out as usual. The gel was divided into two parts for reduction in hydrogen. One of them produced the regularly obtained black or gray black silver-coated gel. The other contained granules which were very shiny, and it appeared as though they were covered with silver mirrors. On crushing, the fragments looked black and treatment with strong nitric acid instantly turned the silver mirrors black. Every evidence pointed to a very thin mirror-like film that coated the granules.

The catalyst consisting of finely divided silver on fused aluminum oxide contained 5 per cent silver and had a yellow appearance. It was a sample of a catalyst used in oxidizing ethylene to ethylene oxide.

Silver oxalate was formed by mixing approximately 1 normal solution of silver nitrate and oxalic acid. The white precipitate was allowed to settle for several hours. It was then filtered, washed with distilled water, and dried at about 80°C. Thermal decomposition began at about 110°C. and became rather violent at 150°C. The residue was very voluminous, had a brownish yellow color, and possessed no structural strength.

Each of these catalysts was used in an electrically heated U-tube having a diameter of 17 mm. By using 10 ml. of the catalyst, the curved part of the U-tube was always filled to the same extent. This catalyst bed was equivalent to one 6 cm. deep. A thermometer was inserted in the tube so that its bulb was always buried in the catalyst. Variable resistances and a lamp bank in the heating circuit made it possible to work in a temperature range of 150° to 350°C. The ethylene used was a commercial product of high purity. It was taken from the tank, mixed with the required amount of air, and stored over water. In the runs without added steam the gas mixture was dried by passing it through tubes of anhydrous calcium chloride. A mixture of 2 per cent ethylene and 98 per cent air, or one of 2 per cent ethylene, 48 per cent air, and 50 per cent steam, was passed over the catalysts at a constant rate and temperature for slightly more than 1 hr. for each run. The rates of flow were measured by calibrated flowmeters and varied from 950 ml. to 3860 ml. per hour. In the earlier study (4) the concentration of ethylene was maintained at more than ten times the amount used in the present study. It has since been learned that low ethylene concentration gives better conversion to ethylene oxide.

When the catalyst tube had reached the desired temperature, the air in the system was swept out by the gas mixture before the actual run was begun. After passing over the catalyst, the gases were bubbled through three gas-washing bottles. The first two contained solutions of hydrochloric acid saturated with magnesium chloride. The third bottle contained water in order to catch any acid that might be carried over from the first two bottles. The gas was bubbled through the solutions from small orifices. Analytical determinations showed that almost all of the ethylene oxide formed in the reaction was absorbed in the first wash bottle. However, the solutions of the bottles were always analyzed to determine the total ethylene oxide absorbed. Divergent opinions still prevail as to the exact mechanism of the absorption of ethylene oxide by the acid magnesium chloride solution. W. Deckert (2) concludes that the reaction proceeds in two stages:

I 

$$\text{I}\quad 2C_2H_4O + MgCl_2 + 2H_2O \longrightarrow 2\begin{array}{l}CH_2OH\\ |\\ CH_2Cl\end{array} + Mg(OH)_2$$

$$\text{II}\quad Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O$$

On the other hand, Lubatti (3) believes that the ethylene oxide adds directly to the hydrochloric acid. The salt is required to control the activity of the acid. J. H. Brönsted and his coworkers (1) have shown that the truth probably lies somewhere between these two viewpoints. For this work, however, the mechanism is not important, since 50 mg. of ethylene oxide in a cubic meter of gas can be detected by this method. The hydrochloric acid used up by the ethylene oxide was readily determined by titration. The percentage of ethylene converted to ethylene oxide was then calculated.

The results of different runs are given in the following tables. The yield of ethylene oxide is the percentage of the ethylene which was converted to the oxide. These results show the very low efficiency of silver–silica gel catalysts in converting ethylene to ethylene oxide. The other catalysts proved effective and both showed a maximum efficiency somewhere between 260°C. and 300°C.

The results shown in table 2 indicate that changes in space velocity within reasonable limits do not appreciably affect the conversion to ethylene oxide. However, there was some evidence that the catalysts lost activity to a slight extent if used for several runs at one temperature. When the catalyst was allowed to stand overnight exposed to air, its activity appeared to be fully restored. This was especially true of the finely divided silver catalyst. Activity appeared to be definitely impaired if the catalyst was heated to 350°C. or above. Heating of the catalyst affected the color of the finely divided silver, so that the surface was undoubtedly altered. The effect of diluting the gas mixture with 50 per cent steam was studied on finely divided silver and on silver–silica gel catalysts (see table 3).

Comparison of these results with those obtained without steam showed that this catalyst lost some efficiency in the presence of steam. Silver–silica gel catalysts seemed to gain some efficiency in the presence of steam, but prolonged use of these catalysts in the presence of steam finally cut down their activity. The fact that water vapor and ethylene are strongly adsorbed by such silica gel catalysts may partially account for this effect. At any rate each of the later runs were made using fresh catalysts. The yields obtained with the silver–silica gel catalyst (14.7 per cent silver) and 50 per cent steam were about double those obtained in the absence of steam (see table 4). Since the silver–silica gel catalysts

TABLE 1

The effect of temperature on the reaction composition of the gas mixture consisting of 2 per cent ethylene and 98 per cent air

Rate of gas flow through the catalyst, 1930 ml. per hour

TEMPERATURE	YIELD OF ETHYLENE OXIDE	TEMPERATURE	YIELD OF ETHYLENE OXIDE
Catalyst: Silver on fused aluminum oxide		Catalyst: finely divided silver from silver oxalate	
°*C.*	*per cent*	°*C.*	*per cent*
208	10.6	182	6.7
228	25.1	214	14.3
246	32.6	238	34.7
254	28.9	282	45.1
268	33.5	300	42.6
291	27.2	314	39.7
307	19.3	350	29.1
Silver–silica gel catalyst, 22.3 per cent silver; rate of gas flow, 1820 ml. per hour		Second preparation of finely divided silver	
177	2.2	196	3.3
210	1.1	220	22.3
230	1 0	268	42.5
270	1.5	285	40.1
290	1.1	300	31.1
306	1.8	333	25.6

TABLE 2

The effect of changing space velocity

CATALYST	TEMPERATURE	RATE OF FLOW	YIELD
	°*C.*	*ml. per hour*	*per cent*
5 per cent silver on fused aluminum oxide	265	1080	33.2
	261	1620	32.5
	262	2070	31.4
Silver–silica gel, 14.7 per cent silver	289	1020	1.7
	292	1740	2.2
	290	1930	3.0
Finely divided silver from silver oxalate	288	980	39.1
	292	1350	39.5
	291	1820	42.8
	293	2240	38.7

were known (4) to be effective in oxidizing a portion of the ethylene to the oxides of carbon and water, it seems likely that the steam reduced this activity of the catalyst enough to increase its effectiveness in ethylene oxide formation. Finally, another silver–silica gel catalyst containing 8.9 per cent silver was prepared, and fresh samples of catalyst were used for a series of runs at varying temperatures

TABLE 3

Catalyst, finely divided silver; gas mixture, 2 per cent ethylene, 48 per cent air, 50 per cent steam

RATE OF FLOW	TEMPERATURE	YIELD
ml. per hour	°C	*per cent*
3860	263	17.7
3860	290	29.9
2180	290	30.4
1960	278	38.2

TABLE 4

Silver–silica gel catalyst, 14.7 per cent silver; gas mixture, 2 per cent ethylene, 48 per cent air, 50 per cent steam

RATE OF FLOW	TEMPERATURE	YIELD
ml. per hour	°C.	*per cent*
3860	180	4.0
3860	237	4.0
3860	272	6.3
1960	271	7.1

TABLE 5

Silver–silica gel catalyst, 8.9 per cent silver; gas mixture, 2 per cent ethylene, 48 per cent air, 50 per cent steam

TEMPERATURE	YIELD
°C.	*per cent*
153	2.3
181	3.7
235	3.8
275	4.1
293	2.7
349	1.7

and a constant rate of gas flow (see table 5). The gas mixture was diluted with 50 per cent steam. An optimum yield was obtained at 275°C., which corresponds to the optima obtained for the other two catalysts. However, the efficiency of the silver–silica gel catalysts is much lower than that of the other silver catalysts used in this investigation. The results reported in table 1 for the silver–silica gel catalyst show no such temperature optimum of activity. The presence of steam appears to make the silica gel catalysts behave more like the other silver catalysts but with a much lower efficiency.

SUMMARY

The finely divided silver and the silver on fused aluminum oxide showed an optimum activity in the conversion of ethylene to ethylene oxide in the temperature range of 260–290°C. Addition of steam lowered the activity of these catalysts slightly. Changes in space velocity of the gases did not greatly affect their efficiency. In the absence of steam the silver–silica gel catalysts showed very low activity and no such temperature optimum. The presence of 50 per cent steam about doubled the efficiency of these catalysts, and they showed an optimum of efficiency in the same temperature range as the other two catalysts. It seems likely that had steam been added to the gas mixtures in the earlier study (4) the investigators might well have found ethylene oxide in the products of the reaction.

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THE RELATION BETWEEN THE FORCE CONSTANT AND THE INTERATOMIC DISTANCE OF A DIATOMIC LINKAGE

C. K. WU and (in part) CHANG-TSING YANG
National Chekiang University, Tsunyi, China

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In recent years many empirical relations have been proposed to connect the vibration frequency, ω_e, or the force constant, K_e, with the internuclear distance, R_e, of a diatomic linkage. Among them, the Clark rule (3)

$$R_e = \frac{K_{qr} - K'_{qr}}{\omega_e\sqrt{N}}$$

the Badger rule (2)

$$R_e = (C_{ij}/K_e)^{1/3} - D_{ij}$$

and the Allen–Longair rule (1)

$$R_e = (K_{ij}/K_e)^{1/6}$$