The Mechanism of the Action of Alkaline Earth Compounds as Additives to Silver Catalysts in the Direct Oxidation of Ethylene

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The mechanism of the action of SrO_2, CaO_2, $SrCO_3$, barium formate and barium oxalate used as additives to silver catalysts (2–20 mole %) in the oxidation of ethylene to ethylene oxide and $CO_2 + H_2O$ has been studied. Two methods of preparation were employed, i.e., mixing of the components (AgO + additive) in alcohol (type I) and acetone (type II), respectively, and the characteristic differences are discussed. In a stream of ethylene/air the additives in presence of silver transform into their respective carbonates of increased surface area, the actual catalyst matrix consisting of the carbonates highly doped with Ag atoms and covering with a thin layer the network structure of metallic silver. The processes occurring during the conditioning period are favored if the components are vibrated in alcohol (type I) instead of acetone (type II). The resulting catalysts have largely increased activity but lower selectivity than have properly defined standard pure silver catalysts. The two principal mechanisms, i.e., a primary effect with additives stable to decomposition ($SrCO_3$), and a secondary effect with additives that transform into their carbonates in a stream of ethylene/air at 300°C have been well established. The data of different catalyst series have been correlated by a normalization method discussed in the Appendix.

NOMENCLATURE

E ethylene
EO ethylene oxide
BaFo barium formate
BaOx barium oxalate
x fraction of E oxidized
x_1, x_2 fractions of E oxidized to EO and ($CO_2 + H_2O$), respectively
A activity, $A = 100 \cdot x$ (%)
A_0 normalized activity with respect to catalyst mass (%)
A'_0 normalized activity with respect to specific surface area (%)
C conversion, $C = 100 \cdot x_1$ (%)
C_0 normalized conversion with respect to catalyst mass (%)
S selectivity, $S = x_1/x \cdot 100$ (%)
x_E^0 fraction of E in feed gas
M mass of catalyst (g)
F volumetric flow rate (ml at NTP/ sec)

y $y = 1/x_E^0 \cdot (M/F)$ (g catalyst sec/ ml at NTP)
s_t total specific surface area of catalyst (m^2/g)
s_{Ag} specific surface area of Ag-component in catalyst (m^2/g)
s_a specific surface area of the additive in catalyst (m^2/g)
Δw change in weight of catalyst (arbitrary units)
Δw_0 change in weight of AgO in catalyst (arbitrary units)
ΔM change in weight per mole of the additive (molecular weight units)
z mole fraction of additive in catalyst
α fractional conversion (thermobalance)
$R(x)$ rate of reaction (ml E at NTP/g catalyst sec)
T temperature (°C)
e index referring to final state

INTRODUCTION

This is the second part of a series of papers dealing with the mechanism of the action of additives (2–20 mole %) to silver catalysts used in the oxidation of E to EO and $CO_2 + H_2O$, respectively. The temperature of interest ranges from 200 to 280°C and therefore a study of the chemical and physical changes of the starting materials (AgO + additive) that occur at these temperatures in a stream of E/air (conditioning period) is of utmost importance for the interpretation of the properties of the resulting catalyst matrix. It has been shown (1) that an increase in activity of silver catalysts by addition of $BaCO_3$ and BaO_2 is based upon two different mechanisms which are operative separately or simultaneously. They have been termed "primary" and "secondary" effects, and essentially influence the geometric and surface properties of the catalyst matrix, although the electronic properties of the resulting Ag/additive interface are also altered (2).

In the case of the primary effect, dispersion of the initial AgO + additive and of the resulting silver rods and particles is improved (dilution effect), thus preventing the silver from strong sintering. This effect is to be expected with inert additives, stable to decomposition/transformation under reaction conditions (i.e., at temperatures below 300°C in a stream of E/air). A secondary effect will be exerted by an additive which decomposes or transforms into a stable compound (preferably the carbonate) under these conditions. During this decomposition/transformation process the surface area of the additive should be markedly increased. This effect is well established with BaO_2. The resulting $BaCO_3$ is highly doped with Ag atoms acting as donors. The actual catalyst, in this case, is no longer silver, but is considered to be an n-type semiconductor covering the underlying silver matrix with a thin film in intimate electrical contact with it. This coating is formed during the conditioning period at 300°C in a stream of E/air due to the high mobility of the ions in the course of the transformation process. The resulting catalyst is stable to sintering and further alteration in its structure and has constant catalytic properties over long periods of operation. The morphological structure of the catalysts has been well established from scanning electron micrographs (1).

A similar situation should be met in the case of additives other than BaO_2, but which also transform into their respective carbonates. In this paper we present the results using SrO_2, CaO_2, BaFo, BaOx and $SrCO_3$ as additives. From this study it should be proved whether or not the proposed mechanisms are generally valid. Two alternative methods of mixing the components (AgO + additive) were employed. On the one hand, the starting materials were mixed by vibration in alcohol (type I); on the other hand, vibration was carried out in acetone (type II). From the discussion given in (1) some characteristic differences in the properties of the resulting catalysts are to be expected.

The processes occurring during the conditioning period were followed in a thermobalance and by X-ray methods. The catalysts were further characterized by their specific surface areas as well as by the individual surface areas of the two components. The catalytic properties (A, C, S) were classified relative to defined silver catalysts of type I or II with known characteristics over a wide range of experimental conditions (T, x_E^0, M/F). In order to correlate unambiguously the catalytic properties of different catalysts, a normalization method was worked out, allowing comparison of data obtained at varying parameters x_E^0 and M/F to any chosen standard state (Appendix).

EXPERIMENTAL METHODS

Materials

AgO was used as starting material for the Ag component. Commercial A.R. grade $SrCO_3$ was used. The peroxides were prepared from the nitrates as $CaO_2 \cdot 8H_2O$ and $SrO_2 \cdot 8H_2O$ by standard methods (3) in a glove box free of CO_2 and then dehydrated

over P_2O_5. Well shaped crystals of anhydrous BaFo were prepared according to Funk and Römer (4). $BaOx \cdot \frac{1}{2}H_2O$ crystals were obtained from a hot slurry of $Ba(OH)_2$ by slowly adding a hot solution of oxalic acid. Both the formate and the oxalate crystals were carefully powdered in an agate mortar to a particle size of a few microns.

Methods

Thermogravimetric and X-Ray Studies

The chemical changes of the catalyst components during the conditioning period were followed in a thermobalance (Linseis Prüfgerätebau KG, Western Germany). Both an E/air and, for comparison, a N_2 atmosphere were employed over the samples. The heating rates varied from 0.5 to 5°/min. X-Ray patterns have been taken from both the catalyst components and the compound catalysts at various stages of the preparation and conditioning processes using a Guinier technique.

Surface Area Measurements

The specific surface areas of the catalysts and the catalyst components have been determined using both a standard static Kr BET method, and a flow-type BET method (5, 6). The surface areas were determined after removing the catalysts from the carrier sheets.

The surface areas of the silver component in the catalysts were determined after dissolving the additive in acetic acid (1:1) as described earlier (1). From the difference $s_t - s_{Ag}$ the specific surface area s_a of the additive was obtained.

Catalytic Studies

The flow-type apparatus and experimental setup described earlier (1) was used. A, C and S were determined in an integral reactor. The components (AgO + additive) were thoroughly mixed by vibration for 2 hr in either alcohol (type I) or acetone (type II) and the resulting suspension was sprayed homogeneously as a thin film over both sides of the silver carrier sheets.

A stream of a standard mixture of E/air ($x_E^0 = 0.035$) was then passed over the raw catalyst at a constant flow rate of $F = 3.5$ ml/sec. The temperature was raised to 300°C at a rate of 2°/min and then held constant for 12–15 hr.

Several series of catalysts with 2–20 mole % of the additive were studied. The catalyst mass varied from 0.6 to 1.4 g, T from 190 to 280°C and F from 3 to 11 ml at NTP/sec. E and air were premixed in steel cylinders at a pressure of 70 atm ($x_E^0 = 0.03$–0.11, $x_{O_2}^0 = 0.18$–0.19, balance N_2). Analysis of the feed gas and of the reaction products was carried out by gas chromatography (carrier gas: He, columns: Poropak R or Q).

RESULTS

Catalyst Preparation and Conditioning

There are three stages in the process of catalyst preparation:

i. Homogenization of the components (AgO + additive) in either alcohol (type I) or acetone (type II) for 2 hr at room temperature.

ii. Spraying of the resulting suspension onto the silver carrier sheets at somewhat elevated temperature (50°C in case of type I, 30°C in case of type II) in order to evaporate the suspension agent quickly.

iii. Heating of the raw catalyst at a rate of 2°/min in E/air to 300°C and conditioning for 12–15 hr at this temperature.

Type I catalysts. Pure AgO is affected somewhat by alcohol. From X-ray analysis it was found that about 10% of the AgO was reduced to Ag_2O, 5% have been transformed into the acetate, but only small traces of metallic silver were found. In case of a mixture of AgO/SrO_2, 10–15% of metallic silver, some Ag_2O and 5–10% Sr–acetate but no $SrCO_3$ were found after vibration. A similar situation is met for AgO/BaO_2 and AgO/CaO_2. It is already at this stage that strong incorporation of the silver into the matrix of the additives occurs. However, the main portion of the components is present in their original form, i.e., AgO and the peroxide.

Type II catalysts. In this case no chem-

ical changes of the components occurred, neither during vibration nor during spraying. Acetone is a completely inert suspension agent.

Thermogravimetric Studies and X-Ray Analysis

From these investigations it was found that in N_2 atmosphere AgO decomposes in two distinct steps into Ag (1). BaO_2, SrO_2 and CaO_2 in a mixture with AgO or Ag are stable to decomposition below 600, 450 and 400°C, respectively, in N_2. In a stream of E/air, AgO completely transforms into Ag already around 150°C (depending on the heating rate). The peroxides in contact with Ag above 180°C are no longer stable but transform into their respective carbonates (increase in weight). This is shown in Fig. 1 for the three peroxides in a mixture with 80 mole % of AgO. The experiments have been carried out under the same conditions as met in the reactor during conditioning. At 300°C the transformation of the peroxides is completed in less than an hour. The pure peroxides are not affected in E/air at 300°C.

The fractional conversion α of a mixture AgO + additive is given with respect to the decrease in weight of AgO, i.e., $\alpha = \Delta w/\Delta w_0$. The final conversion α_e as expected from the composition of the mixture is given by

$$\alpha_e = \Delta w_e/\Delta w_0^- = \left(1 - \frac{\Delta M}{16} \cdot \frac{z}{(1-z)}\right) \quad (1)$$

For the peroxides ΔM is positive (increase in weight), therefore $\alpha_e < 1$ ($\alpha_e = 0.55$). For BaFo and BaOx transformation into the carbonates is accompanied by a decrease in weight (ΔM negative) and $\alpha_e > 1$. This is shown in Fig. 2, where the thermograms of AgO + 20 mole % of either BaFo or BaOx are given. Again, as expected, BaFo in E/air transforms completely into $BaCO_3$. This, however, is not true for BaOx which only partly transforms into $BaCO_3$ at 300°C. After 15 hr (usual duration of conditioning) only 10–20% of the oxalate have transformed. This was also proved from X-ray analysis, showing metallic Ag, BaOx and some $BaCO_3$. Pure BaFo and BaOx in N_2 are stable below 350°C; above this temperature they quantitatively decompose into the carbonates.

Surface Area Measurements

The specific surface areas s_t are summarized in column 2 of Table 1 for the catalysts investigated. For comparison the data for BaO_2 and $BaCO_3$ (both type I) have been included in the table [cf. (1)]. The data marked with an asterisk have been measured by the flow-type BET method. As in the case of BaO_2, the total surface area s_t increases with increasing
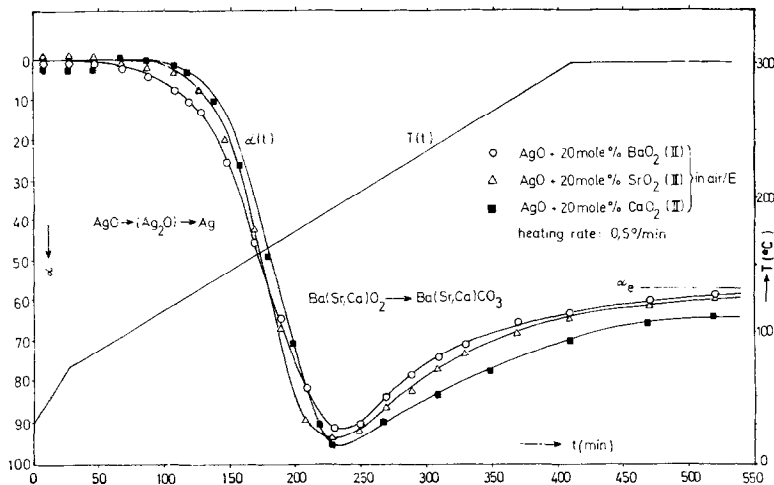

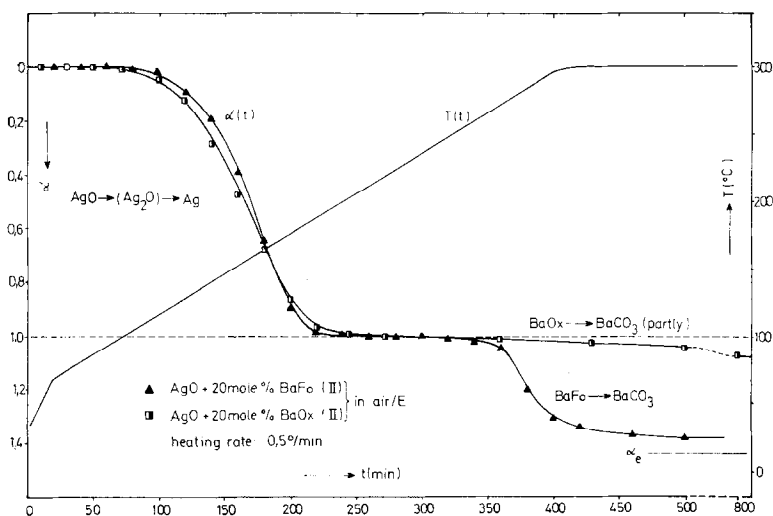FIG. 1. Thermograms of the decomposition of AgO + 20 mole % of CaO_2, SrO_2 and BaO_2 in E/air.

FIG. 2. Thermograms of the decomposition of AgO + 20 mole % of BaFo and BaOx in E/air.

amounts of the additives for SrO_2 (I, II), CaO_2 (II), BaFo (II) and BaOx (II).

Column 3 of Table 1 contains the specific surface areas of the silver component s_{Ag} as measured after dissolving the additives. This has been done with the series AgO/BaFo (II), AgO/SrO_2 (I), AgO/BaO_2 (I) and AgO/$BaCO_3$. For the other series a mean value as obtained from several runs with pure AgO was taken [i.e., 0.32 m²/g for AgO/$SrCO_3$ (II) and 0.42 m²/g for the other series]. This did not lead to any considerable error in determining the specific surface area s_a of the additives actually present in the catalysts, because s_{Ag} is small and is almost unaltered with increasing amounts of the additives. In any case, the large increase in surface area uniquely is due to the additive. This is shown in column 4 of Table 1 where the values for s_a are summarized. Column 5 contains the mean $\bar{s}_a$ as calculated from column 4. The values in parentheses give the original surface areas of the respective additives.

For the peroxides, in case of type I catalysts the increase in surface area is more pronounced than in case of type II [cf. BaO_2 (I), SrO_2 (I) and SrO_2 (II), CaO_2 (II)]. For BaFo (II), in principle, the same is true, although the increase in s_a is less, probably due to the better crystalline state

of the formate compared to the dehydrated peroxides. With BaOx there is only a slight increase in s_a. This has been expected because only part of the oxalate had transformed into $BaCO_3$. However, this portion of the carbonate again has a much increased surface area.

Additives that are stable to decomposition have an almost unaltered s_a compared to the initial state, as seen with both $BaCO_3$ (I) and $SrCO_3$ (II).

Catalytic Studies

A, C and S of the catalysts have been measured immediately after the conditioning period. For any catalyst, activity rapidly increases with increasing temperature. For conversion there is a pronounced maximum at a temperature T_m which decreases with increasing amounts of the additives. Selectivity decreases with increasing temperature and with increasing amounts of the additives. A and C increase with increasing M/F and decreasing x_E^0. In order to compare unambiguously the oxidation properties of different catalysts, A and C must be correlated to a chosen standard state $y_R = 1/x_E^0 \cdot M/F$ at some temperature. In this study a temperature of 220°C was selected, because at 220°C consecutive oxidation of EO is negligible. At this temperature S is inde-

TABLE 1
Data for the Catalyst Series Investigated

Additive (I, II) (mole %)	s_t	s_{Ag}	s_a	$\bar{s}_a$	A_0	C_0	S	A'_0
Ag (I)	0.51	0.51	—	—	18	11.5	64.5	25
Ag (II)	0.41	0.41	—	—	17	12	69.5	26
SrO₂ (I)								
2	1.10	0.50	22.1		37.5	19	50.5	35
4	2.36	0.52	34.0		46.5	23	49	29.5
6	3.09	0.57	30.7		45	21	45.5	24
8	3.79	0.47	31.3	31	45	15.5	35	21
8	3.50	0.65	31.0	(11.5)	46	13.5	30.5	22.5
12	5.49	0.57	34.3		48	15	31	17.5
12	6.80	0.52			42	14	32.5	13
20	9.35	0.55	34.6		43	11.5	26.5	10
SrO₂ (II)								
2	1.07*	0.42	24	23	34	20.4	60	33
4	1.47*	0.42	19.5	(11.5)	37	19	51	30
10	3.65*	0.42	24.5		35.5	16.5	46.5	16.5
SrCO₃ (II)								
2	0.54*	0.32	8.2		19.5	13.5	67	29
4	0.63*	0.32	5.7		20.5	18.5	65	27.5
8	0.90*	0.32	5.5	5.4	21	18	66	23
12	1.08*	0.32	4.8	(5.7)	21.5	15.5	64	21
20	1.37*	0.32	4.2		25.5	17.5	60	21
20	1.32*	0.32	4.0		29	16	54	24.5
CaO₂ (II)								
2	1.04	0.42	32.5		39	23.5	60	38
4	0.83	0.42	12.5		40.5	23.5	58	38
6	1.10	0.42	12.5	26	28	16.5	59	26.5
8	2.72	0.42	30.5	(11.8)	33	18.5	56	18.5
12	3.66	0.42	29.0		33.5	17	51	15
20	8.05	0.42	40.0		40	18.2	45.5	10
BaFo (II)								
4	1.26	0.46	11.2		36.5	20.5	56	32
8	1.64*	0.47	8.5	10.5	43	21	49	33
12	2.90*	0.43	12.3	(2.5)	40	17.5	43	20
20	3.95*	0.36	11.3		41	18	44	18
BaOx (II)								
2	0.87*	0.42	10.5		31	18	58.5	33.5
6	1.76*	0.42	11.2		33.5	18	54	22
10	2.70*	0.42	12.0	9.2	34	16.5	48.5	16
10	1.64*	0.42	6.4	(7.6)	31	16.5	53	24
20	3.46*	0.42	8.8		36	17.5	48.5	13.5
BaO₂ (I)								
1.30	1.30	0.73	23.8		40.5	23.5	58	36.5
2.55	2.00	0.79	26.6		52	26	50	38
4.20	3.30	0.73	35.9		53	25.5	48.5	30
5.60	4.05	0.88	33.1	32.4	53	24.5	46.5	25.5
7.70	5.25	0.78	34.3	(2.85)	52.5	22	42	20.5
10.35	7.59	0.79	40.1		49	20	40.5	12.5
18.35	—	—	—		39	12.5	33	—
BaCO₃ (I)								
2.70	0.60	0.54	1.68		21.5	13.5	61	31
6.45	0.70	0.57	1.68	1.68	32	18	56.5	37
22.5	0.92	0.52	1.68	(1.68)	36	18.5	51.5	38

pendent of both M/F and x_E^0. The principle of the correlation adopted in this study is outlined in the Appendix. Changes in M, F and x_E^0 that might occur are accounted for by this normalization. As pointed out in the Appendix, a catalyst has definite A and C at any $y = 1/x_E^0 \cdot M/F$, where x_E^0, M and F may vary independently. The data of this study were normalized to $y_R = 8.35$, corresponding, e.g., to $M = 1$ g, $x_E^0 = 0.04$ and $F = 3$ cm^3 at NTP/sec. A_0, C_0 and S for all catalysts are summarized in columns 6, 7 and 8 of Table 1. The last column contains the activities A'_0 as obtained if normalization is done with respect to the specific surface areas of the catalysts instead of their masses, i.e., comparison is made at $y_R = 8.35$ corresponding, e.g., to $s_t = 1$ m^2/g, $x_E^0 = 0.04$ and $F = 3$ cm^3/sec.

Addition of CaO_2, SrO_2 and BaFo results in a strong increase in activity up to a maximum, whereas selectivity steadily decreases. In case of the inert $SrCO_3$, as expected, A increases only slightly and S decreases correspondingly more slowly. An intermediate situation is met with BaOx. At 2 mole % A has increased to about 30% and stays almost constant at higher BaOx contents.

A plot of A'_0 (normalized with respect to s_t) vs mole % addition for additives that transform into their carbonates and

which are stable to decomposition, respectively is shown in Figs. 3 and 4.

In Fig. 5 A_0 is plotted vs S for all catalysts investigated. The symbols used are the same as in Figs. 3 and 4. Three regions can be clearly distinguished. Type I catalysts with additives exerting a secondary effect have high activity and rather small selectivity, whereas type II catalysts occupy a region of lower activity and somewhat higher selectivity. Type II catalysts containing inert additives ($SrCO_3$) have low activity and high selectivity. Type I catalysts containing, e.g., $BaCO_3$ fall in an intermediate region, i.e., they have activity and selectivity pointing towards some contribution from a secondary effect.

DISCUSSION

The principal aim of this study was to find out the general behavior of alkaline earth compounds (peroxides, formates, oxalates and carbonates) used as additives to silver catalysts in the direct oxidation of ethylene. Both A and S are altered substantially by these additives. The two principal mechanisms that might be exerted by these additives have been discussed in a previous paper (1) on the basis of BaO_2 and $BaCO_3$. The common feature of these additives (besides the carbonates) is the decomposition/transformation into their carbonates in a stream of E/air at 300°C.
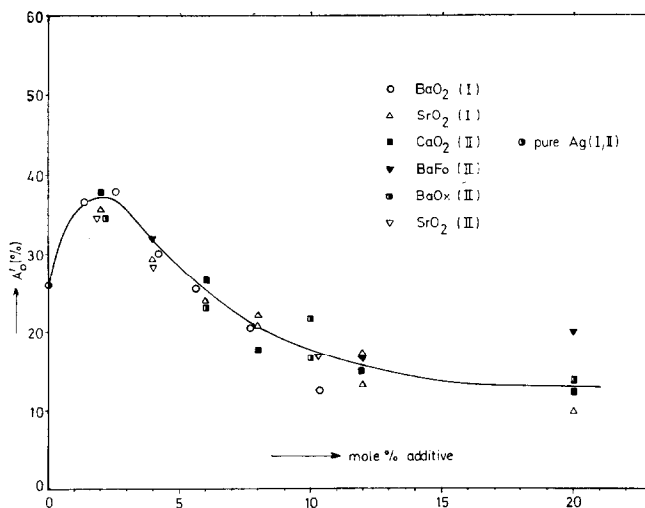

FIG. 3. Activity A'_0 vs mole % additive at $T = 220$°C.

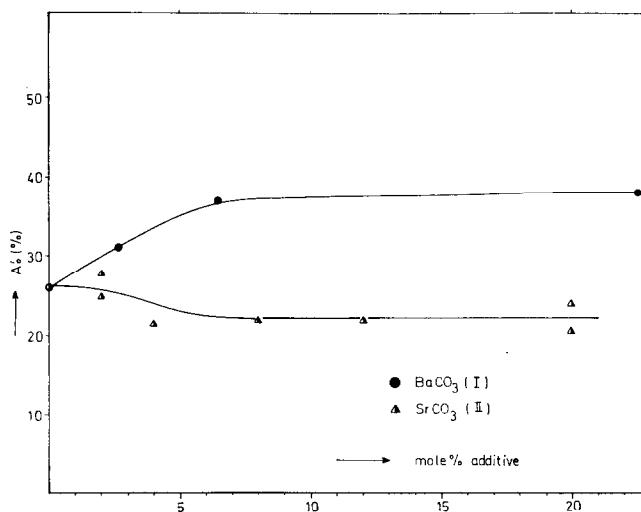FIG. 4. Activity A'_0 vs mole % additive at $T = 220°C$.

The actual catalysts thus always contain the respective carbonate (the only exception being BaOx, which transforms only partly). Nevertheless, direct addition of the carbonates has a far less pronounced effect on A and S.

Two methods of catalyst preparation were employed in this study, vibration of the components (AgO + additive) in alcohol (type I), and vibration in acetone (type II), respectively. The principal feature of the action of the additives is the same for both types of catalyst, but quantitatively they differ from each other. The total surface area s_t increases markedly with increasing amounts of the additives

and from selective surface area measurements it was shown that the increase in s_t is almost exclusively due to the additives, s_{Ag} remaining almost unaltered. Direct addition of the carbonates results in a slight increase in s_t only (Table 1).

A_0 strongly increases with type I (BaO$_2$, SrO$_2$) up to a maximum around 5–8 mole %. The same is true for type II (SrO$_2$, CaO$_2$, BaFo), although the maximum A_0 is smaller than for type I. Direct addition of the carbonates results in a slight increase in A_0 with type II (SrCO$_3$), and a more pronounced increase for type I (BaCO$_3$). Catalysts containing BaOx lie in between the two alternatives (Table 1).

S strongly decreases with type I (BaO$_2$, SrO$_2$), but decreases less with type II (CaO$_2$, SrO$_2$, BaFo, BaOx). Direct addition of the carbonates causes only a small decrease in S which is more pronounced with type I (BaCO$_3$) than with type II (SrCO$_3$) (Table 1).

As already pointed out in (1) the interpretation of these results is based upon two mechanisms that might be exerted by the additives. However, from the differences in type I and type II catalysts some supplementary arguments have to be included in the discussion. These are most clearly seen with the peroxides. The main difference in the two methods of preparation lies in the fact, that AgO and the
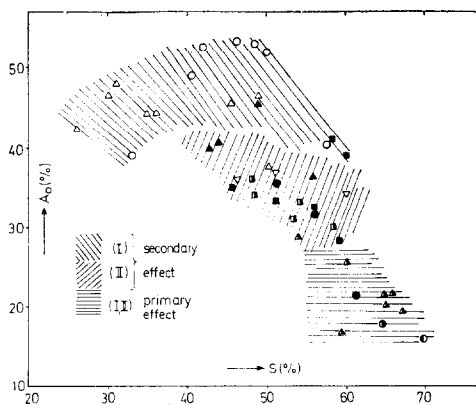

FIG. 5. Activity A_0 vs selectivity S at 220°C (the symbols are the same than those of Figs. 3 and 4).

peroxides are somewhat affected by alcohol during vibration. This has been proved from X-ray analysis where some Ag_2O, Ag and Ag–acetate were found after vibration and some of the peroxide was present as acetate, too. It is already at this stage that a thorough agglutination of the components occurs, i.e., finely divided Ag and Ag_2O (as seen from the broadened diffraction lines) are incorporated into the pores of the additive or cover its outer surface, and vice versa. In the following conditioning period a very favorable situation is established for transformation of the peroxide, a process that only takes place in the presence of metallic silver. The resulting carbonate of largely increased surface area is thoroughly doped with Ag and covers the underlying silver matrix with a thin coating, as shown earlier (1). Thus, the prerequisites for the formation of the actual catalyst, i.e., a carbonate/Ag semiconductor in intimate contact with metallic silver, are established in the early stages of the preparation process. In acetone there is no alteration of the chemical composition of the starting materials, the process of incorporation of Ag into the forming carbonate are brought about purely by diffusion. However, the resulting catalyst matrix, in principle, is the same as for type I, although the active surface is smaller and less properly doped and therefore activity is smaller than for type I catalysts.

That these arguments are valid is shown in Fig. 3 where A'_0 (normalized with respect to s_t) is plotted vs mole % additive. The points (independent of the type of preparation) approximately lie on the same curve. However, if instead of mole % the specific surface area s_t of the catalysts is plotted as abscissa, the curve splits and the points for type I catalysts (due to their larger s_t) then lie above those of type II. It follows that the specific activity A'_0 of type I catalysts is higher as compared to type II in agreement with the more favorable conditions of forming the actual catalyst matrix in the case of type I.

Thus, in principle, the same specific catalyst matrix is formed for both types of preparation and for any of the additives

not stable to decomposition. No specific influence of the cation is to be noted. It is only a question of s_t and thus of the overall preparation method and specific decomposition/transformation behavior of the respective additive, that determines A_0. Type I catalysts have higher A_0 because of (i) higher A'_0; (ii) larger s_t compared to type II.

In any case, A'_0 is markedly increased with compound catalysts as compared to pure silver. The most favorable situation with respect to A_0 is reached around 4–8 mole % of the additive. At higher amounts of the additives optimum doping of the whole carbonate with Ag is no longer developed. From this and the fact that the actual specific surface area s_{Ag} is almost unchanged for compound catalysts, it follows that metallic silver cannot be the catalytically active component in the compound catalysts. The active sites for these catalysts are imagined to be Ag-atoms or groups of Ag-atoms embedded in the carbonate, the actual catalyst being an n-type semiconductor in intimate contact with the metallic silver [cf. Fig. 3 of (1)]. Evidence for this interpretation is given elsewhere (2), where changes in the work function of the compound catalysts are reported. The decrease in A'_0 at higher concentration of the additives may be due to a decreased density of the active groups of Ag-atoms in the carbonate matrix.

Catalysts resulting from direct addition of $BaCO_3$ (I) and $SrCO_3$ (II) have a A'_0 vs mole % characteristics as illustrated in Fig. 4. For the type II catalyst A'_0 formally decreases somewhat with increasing $SrCO_3$. This means that $SrCO_3$ has no direct influence on activity with respect to a secondary effect. In case of $BaCO_3$ (I), during the process of vibration, some highly dispersed metallic silver enters the pores and covers the outer surface of $BaCO_3$, and thus initiates the formation of the $BaCO_3$/Ag matrix of a type similar to that discussed above. There is some kind of secondary effect even with $BaCO_3$ for preparation of type I, although this effect is brought about by a different mechanism. The effect is more pronounced at higher

BaCO$_3$ concentrations, the final specific A'_0 being almost the same as for AgO/BaO$_2$ catalysts. However, the total surface area of the AgO/BaCO$_3$ catalyst is considerably smaller and so is its activity A_0.

At higher temperatures and high activities, selectivity is considerably lowered by consecutive oxidation of EO. This is clearly seen from the maximum in the conversion vs temperature curves, the temperatures of maximum conversion T_m decreasing with increasing activity. It is only some 20° below T_m that the intrinsic selectivity of the catalysts is disclosed, and comparison of the catalysts was therefore made at 220°. Although S decreases with increasing amounts of the additives, A increases correspondingly faster and there is a maximum in the space–time–yield function (amount of EO formed per unit catalyst weight per unit time). This fact accounts for the commercial importance of compound catalysts.

APPENDIX

Normalization of Catalytic Data

In order to correlate in quantitative terms the properties of catalysts containing different additives, a method was worked out which allows comparison of catalytic data (A and C) at some reference temperature even if M/F and x_E^0 vary in the individual series and runs. This correlation is necessary, because A and C strongly depend upon M/F and x_E^0, and from an experimental point of view it often is preferable (or even inevitable as in case of catalyst mass) that experimental conditions (x_E^0, M/F) are changed.

The principle of this correlation (normalization) method is as follows. In an integral reactor (as used in this study) the following relationship holds between the fraction of E oxidized, x, and M/F:

$$\frac{1}{x_E^0} \cdot \left(\frac{M}{F}\right) = \int_0^{x_e} \frac{dx}{R(x)} = f(x_E^0, x_e) \approx f(x_e).$$
$$(2)$$

In the catalytic oxidation of E two independent reactions occur with rate equations $R_1(x)$ (to EO) and $R_2(x)$ (to CO$_2$ + H$_2$O), whence

$$R(x) = R_1(x) + R_2(x). \qquad (3)$$

The equation corresponding to Eq. (2) for conversion reads:

$$\frac{1}{x_E^0} \cdot \left(\frac{M}{F}\right) = \int_0^{x_{e,1}} \frac{dx_1}{R_1(x_1)} = f_1(x_E^0, x_{e,1})$$
$$\approx f_1(x_{e,1}). \quad (4)$$

x_e and $x_{e,1}$ are the measured fractional integral A and C, respectively, at the outlet of the reactor. Equations (2) and (4) in their elementary form are applicable only if there is no considerable change in volume during reaction. In case of not too high x_E^0 this requirement is met.

The functions Eqs. (2) and (4), $f(x_E^0, x_e)$ and $f_1(x_E^0, x_{e,1})$, respectively, are experimentally obtained by measuring x_e and $x_{e,1}$ at, say, various flow rates F or, generally speaking, at various M/F at constant temperature for different x_E^0. Plots of $100x_e = A$ and $100x_{e,1} = C$ vs M/F are given in Fig. 6 for a catalyst containing 2 mole % SrO$_2$ (type II). As shown, $f(x_E^0, x_e)$ and $f_1(x_E^0, x_{e,1})$, are only slightly dependent on
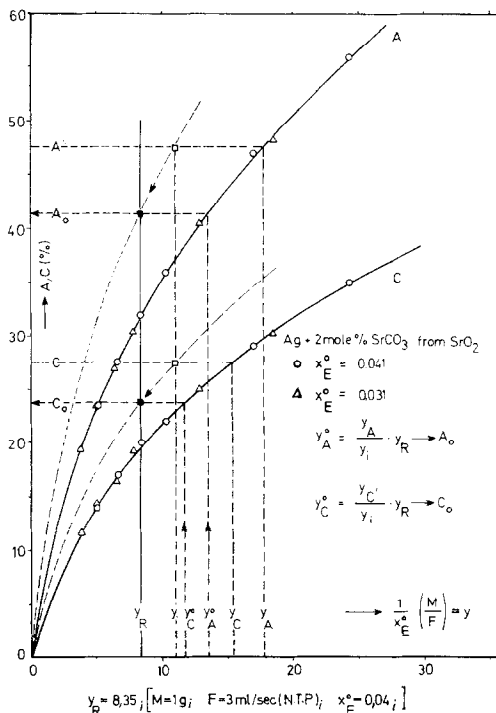

FIG. 6. A and C vs $y = 1/x_E^0 \cdot M/F$ at 220°C and varying x_E^0 for a Ag/SrO$_2$ catalyst (type II). Example for normalization.

x_{E}^0. To a good approximation we can substitute $f(x_{\mathrm{E}}^0, x_e)$ and $f_1(x_{\mathrm{E}}^0, x_{e,1})$ of Eqs. (2) and (4) simply by $f(x_e)$ and $f(\mathrm{x}_{e,1})$.

From these arguments it follows that A and C have definite values for any given $y = 1/x_{\mathrm{E}}^0 \cdot M/F$, where the three parameters x_{E}^0, M and F can be varied independently. This is the basis of the correlation method to be developed. The changes in the rate equations that might occur for different catalysts must be such that they enter as constant multipliers into $f(x_e)$ and $f(x_{e,1})$. This, e.g., will be the case if the dominant feature of changes in catalytic properties by the additives is a change in the active surface area. If the electronic properties of the catalysts are altered too, alteration in the activation energies and heats of adsorption are to be expected. The only requirement to make this correlation valid is that the basic catalytic mechanism, i.e., the type of the functions $R(x)$ and $R_1(x)$ are not altered by addition of different additives. To be sure of that, it is advisable to define a proper function $f(x_e)$ and $f(x_{e,1})$ for each series of the Ca, Sr and Ba additives separately.

If $f(x_e)$ and $f(x_{e,1})$ denote the respective functions for the standard catalyst, for any other catalyst in between the series we have to a good approximation

$$y_i = [1/x_{\mathrm{E}}^0 \cdot M/F]_i = \beta_A \cdot f(x_e) = \beta_A \cdot y_A$$
(5a)

$$y_i = [1/x_{\mathrm{E}}^0 \cdot M/F]_i = \beta_C \cdot f_1(x_{e,1}) = \beta_C \cdot y_C,$$
(5b)

where β_A and β_C are multipliers characteristic for the catalyst i. Thus, for any catalyst i there exists a function of type Eqs. (5a) and (5b), the ratios of the abscissas y_A/y_i and y_C/y_i being constant and equal to

$$y_A/y_i = 1/\beta_A, \qquad y_C/y_i = \beta_C. \quad (6)$$

The validity of Eq. (6) for not too high activities is seen from Fig. 7 where the corresponding ratios of the abscissas are calculated for two Ag/BaO$_2$ catalysts. On this basis, A and C for each catalyst obtained at any y_i can be correlated to a chosen standard state y_R; in our case a value $y_R = 8.35$ has been selected. An illus-
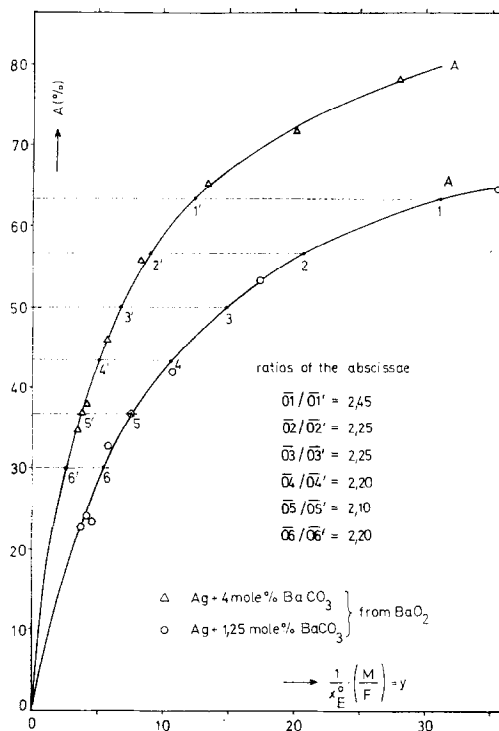

FIG. 7. A vs $y = 1/x_{\mathrm{E}}^0 \cdot M/F$ at 220°C for two Ag/BaO$_2$ catalysts showing constant ratios of the abscissas.

trative example for this correlation is given in Fig. 6 for a Ag/SrO$_2$ catalyst. At $y_i = 11$ this catalyst has activity A and conversion C. At the chosen reference state y_R this catalyst will have activity A_0 and conversion C_0, as seen from the construction in Fig. 6. A numerical example for SrO$_2$/Ag catalysts is summarized in Table 2. Table 3 contains the results as obtained for CaO$_2$/Ag catalysts correlated to pure Ag, Ag/SrO$_2$ and Ag/BaO$_2$ standards. The same results are obtained for each standard and thus, as assumed, the basic catalytic mechanism and type of rate equation $R(x)$ and $R_1(x)$ is the same for each series of catalysts.

If normalization with respect to s_t instead of M is desired, y^0 of Table 2 and Fig. 6 is to be replaced by $y^0/s_t = y^{0\prime}$. This is illustrated in the right hand portion of Table 2 for activity A'_0.

TABLE 2

NORMALIZATION OF CATALYTIC DATA $(Ag/SrO_2$, TYPE I)[a]

Additive (mole %)	M	y_i	A	C	S	y_A	y_C	y_A^0	y_C^0	A_0	C_0	s_t	$y_A^{0'}$	A'_0
2	1.031	8.05	37	18.5	50.5	10.9	7.5	11.3	7.76	37.5	18.8	1.10	10.3	35
4	0.677	5.30	37	18.0	49	10.9	7.2	17.2	11.40	46.5	23	2.36	7.3	29.5
6	0.617	4.80	33.5	15.3	45.5	9.0	5.6	15.8	9.70	45	21	3.09	5.1	24
8	1.052	8.20	44.5	15.5	35	15.5	5.7	15.8	5.80	45	15.5	3.79	4.2	21
8	1.439	11.20	54	16.5	30.5	22.8	6.3	16.9	4.70	46	13.5	3.50	4.8	22.5
12	0.977	7.60	46.5	14.5	31	17.0	5.1	18.5	5.60	48	15	5.94	3.1	17.5
12	0.789	6.15	35	11.5	32.5	9.9	3.8	13.5	5.15	42	14	6.80	2.0	13
20	1.025	8.00	42	11.0	26.5	13.9	3.6	14.5	3.75	43	11.5	9.35	1.55	10

$y_R = 8.35$ (i) $M = 1$ g, $F = 3$ ml NTP/sec, $x_E^0 = 0.04$

$y'_R = 8.35$ (ii) $s_t = 1$ m²/g, $F = 3$ ml NTP/sec, $x_E^0 = 0.04$

[a] $T = 220°C$; reference catalyst: $Ag/2$ mole % SrO_2 (Fig. 6).

TABLE 3

NORMALIZATION FOR Ag/CaO_2 CATALYSTS WITH RESPECT TO DIFFERENT STANDARDS

Standard:		Ag/BaO_2		Ag/SrO_2		Ag	
y_i	A	y_A^0	A_0	y_A^0	A_0	y_A^0	A_0
8.10	38.5	8.55	39	12.2	39	32	39
6.45	35	9.1	40.5	13	40.5	33	40
10.40	32	4.8	28	6.7	28	16.8	29
11.95	40	6.3	33.5	8.8	33	23.5	34
9.95	37	6.5	34	9.15	33.5	24.5	34.5
9.05	42	9.0	40	12.6	40	35	40.5

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