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The Mechanism of the Action of BaO_2 and $BaCO_3$ as Additives to Silver Catalysts in the Oxidation of Ethylene to Ethylene Oxide

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The mechanism of the action of BaO_2 and $BaCO_3$ used as additives to silver catalysts (2–36 wt %) in the oxidation of ethylene to ethylene oxide and CO_2 has been studied. As starting material for the silver component AgO was used. Two different effects exerted by these additives have been distinguished. On the one hand, an effect termed the "primary effect," as exerted by the almost inert $BaCO_3$ additive, consists in stabilizing the catalyst matrix, which is made up of a loosely bound network of interlaced silver rods and lumps. The resulting catalysts had a somewhat increased activity and good selectivity. On the other hand, BaO_2, being not stable under reaction conditions, completely transforms into $BaCO_3$ of highly increased surface area. The carbonate is covering the silver matrix with a semiconducting film containing Ag atoms as donors and is considered to be the actual catalyst. This effect was termed the "secondary effect." The resulting catalysts have largely increased activity with a maximum around 8 wt % BaO_2, but a lower selectivity compared to a proper standard silver catalyst. Besides catalytic studies carried out in a reactor where both thermal effects and longitudinal diffusion were absent, the catalysts have been investigated by X-ray analysis, thermogravimetry, BET studies, and scanning electron microscopy. The results, as obtained in this study, can be generalized, to some extent, to additives other than $BaCO_3$ and BaO_2.

NOMENCLATURE

A	integral activity of catalyst (%); A = [(volume of E oxidized to EO, CO_2, and H_2O)/(volume of E in feed gas)] × 100
C	integral conversion of catalysts (%); C = [(volume of E oxidized to EO)/(volume of E in feed gas)] × 100
S	integral selectivity of catalysts (%); S = [(volume of E oxidized to EO)/(volume of E oxidized to EO and CO_2/H_2O)] × 100
E	ethylene
EO	ethylene oxide
E_0	vol % E in feed gas
M	mass of catalyst (g)
M_t	total mass of catalyst (g)
M_{Ag}	mass of silver component in catalyst (g)
F	volumetric flow rate (cm^3 at NTP/sec)
s_t	specific surface area of total catalyst (m^2/g)
s_{Ag}	specific surface area of silver component in catalyst (m^2/g)
T	temperature (°C)
T_m	temperature of maximum conversion (°C)

INTRODUCTION

Additives to silver catalysts are well known to have a marked influence on both activity and selectivity with respect to the oxidation of ethylene to ethylene oxide and CO_2. There are papers devoted to this subject. A literature survey has been given recently by Voge and Adams (*1*). Nevertheless, it is not easy to correlate unambiguously the data of different authors due to differences in catalyst preparation, catalyst configuration and experimental conditions applied. The interpretation of the data is based essentially on selectivity and activity of the catalysts. However, selectivity and activity do not depend only on the modifying action of the additives, but to a pronounced extent on the catalyst configuration, especially its porosity. This clearly has been shown for catalysts supported on alumina-silica- and kieselguhr-type carriers (*2, 19*) and for beds packed with granular silver catalysts or skeletal catalysts (*3*). Further difficulties arise in the definition of a standard pure silver catalyst with properly defined characteristics over a wide range of experimental conditions.

Nevertheless, it is generally accepted that small amounts of additives which are more electronegative with respect to silver, such as Cl, S, Se, and Te, increase selectivity and decrease activity, the reverse being true for more electropositive additives (group I and II elements) (*4, 5*). The electropositive or negative character of the additives has been related to changes in work function with respect to a "pure" silver catalyst (*1, 6*). However, the reference state of a pure silver catalyst is not very well defined, although there have been attempts to clarify this point (*7*). The work of Ostrovskii *et al.* (*5*) indicates that there are distinct ranges in concentration of certain additives, inevitably present in any silver catalyst, where there is an increase or decrease in activity and/or selectivity. Too high concentrations of these elements always decrease both activity and selectivity. From these findings, however, it is surprising that most commercial catalysts prepared with less care and certainly containing higher amounts of Cl or S have good activity and selectivities as high as 70%. It is felt that these catalysts are properly modified by accident. From the additives mentioned above and which should be present in very small concentration, only Cl and probably Te are of commercial importance (*1*).

There is another group of moderators added to the silver in much higher concentrations and which are of commercial importance. These additives essentially are the oxides, hydroxides, peroxides, and carbonates of the alkaline earth metals, preferably Ca and Ba. In the patent literature, a wide range up to 50 wt % of the additives is reported, although the range between 2 and 15% seems to be preferred (*8, 9*). There exists also some work in the current literature dealing with silver catalysts modified by these additives (*2, 10–14*). Though the promoting effect of these moderators has been well established, there exists no unambiguous interpretation of the real action of these additives. In principle, the additives may change either the electronic properties of the catalyst or stabilize the "active" silver surface. The reason why there exists no convincing theory for the action of the additives certainly lies in the lack of a systematic study of these catalysts, covering the range from small to larger amounts of the additives.

This is the first part of a series of papers devoted to the study of the properties of silver catalysts containing modifying additives of the above mentioned type. This paper deals especially with BaO_2 and $BaCO_3$ used as additives. In a forthcoming paper, the studies made with peroxides, carbonates, formates, and oxalates of the alkaline earth metals will be reported. A standard silver catalyst is defined, relative to which the properties of the modified catalysts are compared. Besides catalytic studies (activity, selectivity) under varying experimental conditions (gas composition, temperature, flow rates), the catalysts are characterized by surface area measurements, X-ray analysis, thermogravimetric studies, work function measurements, and scanning electron microscopy.

EXPERIMENTAL METHODS

Materials

The starting materials for the catalysts were AgO, $BaO_2 \cdot 8H_2O$ and commercial A.R. grade $BaCO_3$. Some informal runs have been made using $BaSO_4$, $Ba(N_3)_2$, γ-Al_2O_3 and Ba-acetate as moderators.

AgO was prepared according to (*15*) by pouring a solution of A.R. grade $AgNO_3$ into an alkaline solution of A.R. grade $K_2S_2O_8$ at 85°C. The black precipitate of well-established AgO crystals (mean particle size 1–3 μ, cf. Fig. 3a) has been thoroughly washed to remove K^+ and SO_4^{2-}-ions and stored over P_2O_5 in an opaque desiccator. The reason for the use of AgO instead of some other silver compound is discussed below. $BaO_2 \cdot 8H_2O$ was prepared from unstabilized H_2O_2 and A.R. grade $Ba(OH)_2 \cdot 8H_2O$ in a glove box free of CO_2. The precipitate was dehydrated *in vacuo* over P_2O_5 at room temperature to give BaO_2. Ethylene from Fluka (Switzerland) of the following composition was used: C_2H_4, >98%; C_2H_6, 1.2%; CH_4, 0.21%; CO_2, 0.06%; traces of CO; no C_2H_2. Ethylene and air of any desired composition have been premixed in steel cylinders at a pressure of about 70 atm.

Methods

Catalytic Experiments

A flow apparatus made of Pyrex glass was used for studying activity, conversion, and selectivity of the catalysts. Before entering the reactor the premixed gases of known composition passed a series of appropriate packed towers to remove residual CO_2, H_2O and other impurities. A portion of the gas stream at constant flow was passed through a 1 ml sampling valve of a Perkin–Elmer gas chromatograph (model F6/T3). The lines from the reactor exit and the sampling valve were held at constant temperature (50°C). The components of the reacted gas were separated in a Poropak S or Q column, using He as carrier gas. In case of very high conversions, H_2O was preabsorbed in a tower packed with Drierite ($CaSO_4$ from Fluka), a drying agent which does not affect the other components (*16*). This was necessary due to the pronounced tailing of the H_2O peak. A very sensitive katharometer was employed for detection. The peak areas were determined by a ball-and-disc integrator. The flows were measured by rotameters or a soap-bubble flowmeter. All flow rates have been corrected to NTP (cm^3/sec).

An integral type reactor was employed. From preliminary tests it became obvious that any standard packed bed reactor is unsuitable for a laboratory study of the ethylene oxidation, due to its marked exothermicity. In all cases, both large transverse and longitudinal temperature gradients arose at even low conversions. This had a deleterious consequence for selectivity. In order to study accurately activity and selectivity differences of the catalysts, good temperature constancy across the catalyst bed must be maintained at even high conversions. This has been accomplished with a reactor section which essentially consisted of a set of 14 rectangular sheets of silver (6 × 3 × 0.05 cm, total geometric area about 500 cm^2). The sheets were held at two sides in a frame of parallel grooves a distance of 0.15 cm apart from each other. The catalyst was sprayed in a thin layer over both sides of the sheets. Temperature constancy has been maintained by means of a proportional temperature controller (Varian Aerograph, model 328) to an accuracy of about 1°C. Due to the excellent heat conductivity of both the catalyst and the silver carrier sheets, only minor temperature gradients (1–2°C) occurred across the reactor section. This was checked by soldering a series of silver and constantan wires along the central and the outer sheets and measuring the small thermo-voltages between them. During an experiment the temperature was controlled by a thermocouple in direct contact with the upper end of the central sheet. The gas before entering the reactor section passed a preheater zone filled with small glass beads. Pressure gradients in this arrangement were negligible in the range of flow rates employed (2–20 cm^3/sec), operation at atmospheric pressure having been ascertained. Although this type of reactor guarantees good temperature constancy even at high conversions, there are some problems concerning diffusion processes (due to the relatively large free space between the carrier sheets), which might adversely affect the results. These problems have been considered in some detail and the experimental conditions and reactor dimensions where there is no diffusion controlling influence on conversion were determined. It was found that, for the reactor used in this study, longitudinal diffusion is negligible at flow rates larger than about 3 cm^3/sec.

Catalyst Preparation and Conditioning

An alcoholic suspension of the components (AgO + varying amount of the additive) was vibrated for 2 hr to arrive at complete mixing. The suspension under permanent shaking was then sprayed over both sides of the silver sheets resulting in a very good adhering film. By this method, constant amounts of the catalysts could be homogeneously and reproducibly distributed over the sheets. Between 1 and 1.5 g of the catalyst have been employed, covering an area of about 400 cm^2 of the sheets. The thickness of the catalyst layer was less than 0.010 cm.

There exists a variety of methods used in catalyst conditioning, and contradictory opinions as to the time of the conditioning period are reported in the literature. From a series of preliminary experiments the following process was adopted for all catalysts in this investigation. A standard ethylene/air mixture (3–4 vol % ethylene) was passed over the raw catalysts at a constant flow rate (3.5 cm^3/sec). The temperature was raised at a rate of about 2°/min up to 300°C and then held constant for 12 to 15 hr. This temperature is about 20° higher than any used in the following experiments. It was found that, after this treatment, the catalyst had constant activity and selectivity over the whole period of the following tests, covering the temperature range from about 180 to 280°C, ethylene/air mixtures from 1.5 to 12 vol % ethylene and volumetric flow rates from 3 to 20 cm^3/sec. This has been checked using a standard ethylene/air mixture, flow rate, and a reference temperature of 220°C. However, when using feed compositions of higher oxygen contents, alterations in activity and selectivity occurred due to slow processes at the catalyst surface. These processes have been studied in some detail by Orzechowski and McCormack (*17*).

By the procedure used in this investigation, a standard silver catalyst having reproducible activity and selectivity over the range of experimental conditions employed was defined. The properties of catalysts containing BaO_2 or $BaCO_3$ (from 2 to 30 wt %) and subject to the same procedure could definitely be compared to those of the standard.

Analysis

The silver and Ba contents of the catalysts have been determined by flame photometry. It has been found that there were only slight changes in composition compared to the values expected from the initial mixture. Thus there were no changes in catalyst composition during the preparation process. By fluorescence analysis traces of sulfur have been detected in the catalyst. Sulfur, probably present as So_4^{2-}, was to be expected due to the method of AgO preparation. These traces of sulfur probably have a favorable effect on selectivity.

X-Ray and Thermogravimetric Studies

X-Ray patterns have been taken from the catalysts at various stages of the process. Using an X-ray diffractometer with a heating attachment the chemical changes of the catalyst components have been followed during the conditioning period. The experiments have been carried out both in a stream of N_2 and C_2H_4/air, either isothermally or dynamically at constant heating rates. The homogeneity in composition of the compound catalysts has also been checked by X-rays.

Thermogravimetric studies during the conditioning process have been carried out in a Linseis thermobalance. Again, both N_2 and C_2H_4/air atmospheres over the catalyst samples have been employed. The heating rates were between 0.5 and 5°/min.

Surface Area Measurements

The surface areas of the catalysts have been determined immediately after the catalytic studies using a standard BET method with krypton. A procedure has been worked out to determine the surface areas of the components (Ag and additive) separately. The catalysts have been treated several times with acetic acid (1:1) at room temperature. The additive easily dissolved leaving the pure silver component. After washing with H_2O and acetone and drying at 100°C, the surface area of the silver residue has been determined. It has been proved that the dissolving procedure does not change the surface area of the silver to any considerable extent by treating pure silver catalysts in the same way. From scanning electron microscopy, it is also seen that the characteristic structure of the silver matrix is not affected by this procedure (compare Fig. 3c and h). The outgassing temperature in the BET apparatus was 250°C, i.e., 50° below the conditioning temperature.

Additional Experiments

A number of additional investigations on the catalysts have been made, including photoelectric work function measurements (*18*), and a systematic study of the catalysts by scanning electron microscopy covering the range of magnification from 20× to 20000×. Reference is made only to some of the results immediately related to the subject of the present paper. Details of these investigations are to be published elsewhere.

RESULTS

Catalyst Preparation and Conditioning

From X-ray studies, it was found that the compound catalysts after the process of homogenization in alcohol essentially consisted of AgO and BaO_2, a small portion of the AgO having been reduced to Ag_2O, Ag–acetate, and metallic silver. Some of the BaO_2 has been found as Ba–acetate but no $BaCO_3$ was detected.

The processes taking place on heating the catalyst components in a stream of N_2 or C_2H_4/air are summarized in Figs. 1 and 2. Figure 1 shows thermograms of pure AgO and a mixture of AgO with 20 mole % BaO_2 obtained at heating rates of 2 and 0.5°/min, respectively, in a stream of pure N_2 and C_2H_4/air. In N_2, AgO (surface area, 1.0 m^2/g) decomposes into metallic Ag in two distinct steps. The first step

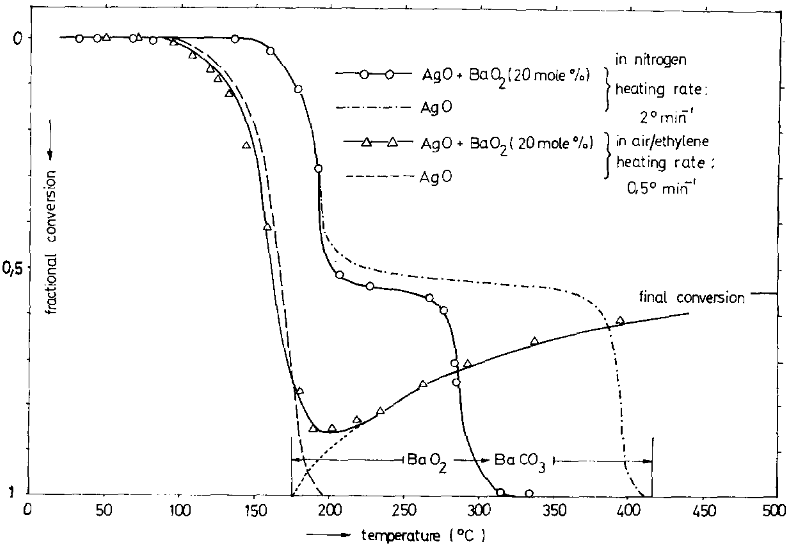

FIG. 1. Thermograms of the decomposition of AgO and AgO + 20 mole % BaO_2 in N_2; in C_2H_4/air: The fractional conversions are given with respect to AgO. For better distinction, curves are given for different heating rates.

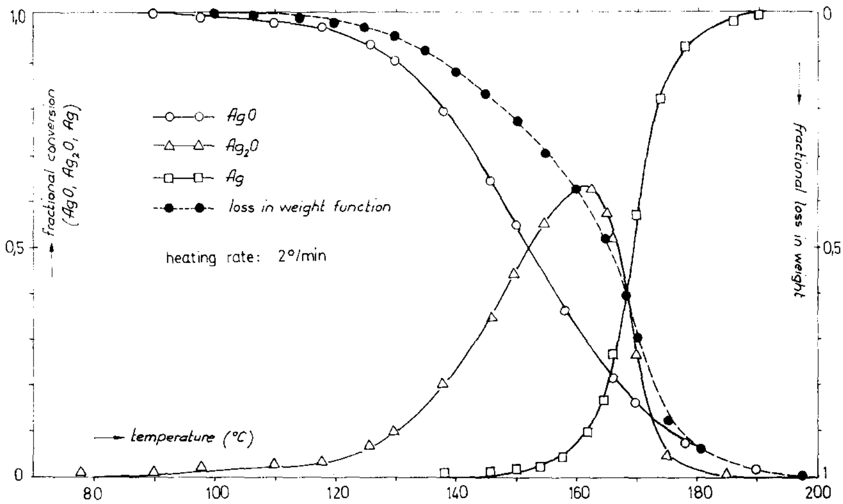

FIG. 2. Decomposition of AgO → Ag_2O → Ag in C_2H_2/air as followed by X-ray analysis. The loss in weight function has been calculated from the fractional amounts of the individual species.

($AgO \rightarrow Ag_2O + \frac{1}{2}O_2$) occurs around 170°C (depending on the heating rate); whereas Ag_2O decomposes into Ag only above 350°C. The specific surface area of the resulting Ag was 0.30 m^2/g, that of the Ag_2O intermediate, 1.8 m^2/g. Ag_2O (surface area 3.3 m^2/g) on thermal decomposition yielded metallic silver with a surface area of only 0.06 m^2/g. Addition of BaO_2 decreases the temperature of the second step down to about 280°C. The first step, however, is not markedly influenced by the presence of BaO_2. BaO_2 itself in N_2 is not affected at temperatures below about 600°C.

The situation is quite different in a stream of C_2H_4/air, as met in the conditioning process adapted in this work for all catalysts. In case of pure AgO, there is no step in the thermogram. The presence of C_2H_4 does not alter the onset of decomposition, and the first step ($AgO \rightarrow Ag_2O + \frac{1}{2}O_2$) again takes place purely thermally. The intermediate Ag_2O now is quickly reduced to metallic silver by C_2H_4. This could be proved by analyzing the product gases in the gas chromatograph. Up to about 140–150°C neither CO_2 nor C_2H_4O have been detected; whereas above this temperature at first large amounts of CO_2 and H_2O, and later, even C_2H_4O were found. The transformation of AgO into Ag has been followed also in the X-ray diffractometer, the results being summarized in Fig. 2. It is clearly shown that Ag_2O is present as an intermediate although the loss in weight function as calculated from the three fractional amounts of AgO, Ag_2O, and Ag yields a stepless function as observed in the thermograms, formally masking the presence of the Ag_2O intermediate.

If BaO_2 is present (20 mole % in this case) there is no change in the transformation of AgO into Ag. However, above about 170°C (depending on the heating rate) an increase in weight is observed (Fig. 1). From X-ray studies it has been shown that at this stage BaO_2 transforms into $BaCO_3$, a process which obviously can take place in presence of Ag and C_2H_4/air (CO_2/H_2O atmosphere). From X-ray studies, we have evidence that $Ba(OH)_2 \cdot H_2O$ is an intermediate in this transformation process. The first step probably is hydrolysis of the BaO_2. Transformation of BaO_2 into $BaCO_3$ under these conditions is completed in less than 1 hr at 300°C.

From these data, the following scheme can be proposed for the processes occurring during the conditioning period (the temperatures given cover the range of different heating rates):

$$\begin{array}{lrcl} 140\text{–}170^\circ\text{C} & \text{AgO} & \rightarrow & \text{Ag}_2\text{O} + \tfrac{1}{2}\text{O}_2 \text{ (thermally)} \end{array}$$

$$\left.\begin{array}{lrcl} 140\text{–}170^\circ\text{C} & 6\text{Ag}_2\text{O} + \text{C}_2\text{H}_4 & \rightarrow & 2\text{CO}_2 + 2\text{H}_2\text{O} + 12\text{Ag} \\ >180^\circ\text{C} & x\text{C}_2\text{H}_4 & \underset{(\text{Ag})}{\rightarrow} & y\text{C}_2\text{H}_4\text{O} + z(\text{CO}_2 + \text{H}_2\text{O}) \end{array}\right\} \text{(reaction with C}_2\text{H}_4\text{)}$$

$$\begin{array}{lrcl} 180\text{–}300^\circ\text{C} & \text{BaO}_2 + 2\text{H}_2\text{O} & \underset{(\text{Ag})}{\rightarrow} & \text{Ba(OH)}_2\cdot\text{H}_2\text{O} + \tfrac{1}{2}\text{O}_2 \\ & \text{Ba(OH)}_2\cdot\text{H}_2\text{O} + \text{CO}_2 & \rightarrow & \text{BaCO}_3 + 2\text{H}_2\text{O}. \end{array}$$

In the absence of Ag, BaO_2 is stable in C_2H_4/air up to 300°C.

Scanning electron micrographs of the catalysts were taken before and after various stages of the conditioning process. Two methods of preparation were employed, differing in that in one case the components were vibrated in alcohol

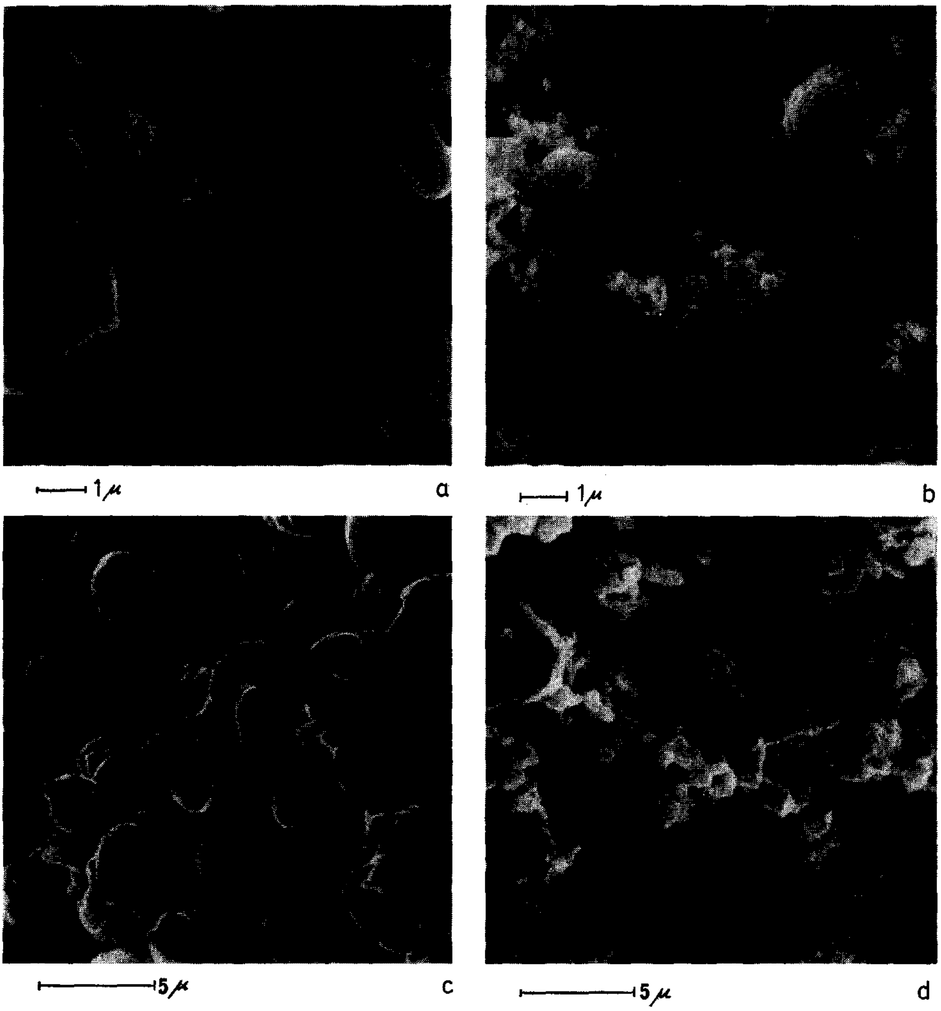

FIG. 3. Scanning electron micrographs of different catalysts before and after a 15 hr conditioning period at 300°C: type I: vibrated in alcohol; type II: vibrated in acetone. (a) AgO + 8 mole % BaO_2 (type II), before conditioning; (b) AgO + 8 mole % BaO_2 (type I), before conditioning; (c) pure Ag catalyst (type II), conditioned; (d) pure Ag catalyst (type I), conditioned; (e) catalyst with 8 mole % $BaCO_3$ from BaO_2 (type II), conditioned; (f) catalyst with 8 mole % $BaCO_3$ from BaO_2 (type I), conditioned; (g) silver matrix after removal of $BaCO_3$ by acetic acid from a catalyst originally containing 8% $BaCO_3$ from BaO_2 (conditioned, type II); (h) pure silver catalyst (type II) after treating with acetic acid for 1 hr; (i) catalyst with 6 mole % $BaCO_3$ added directly to AgO (type II, conditioned).

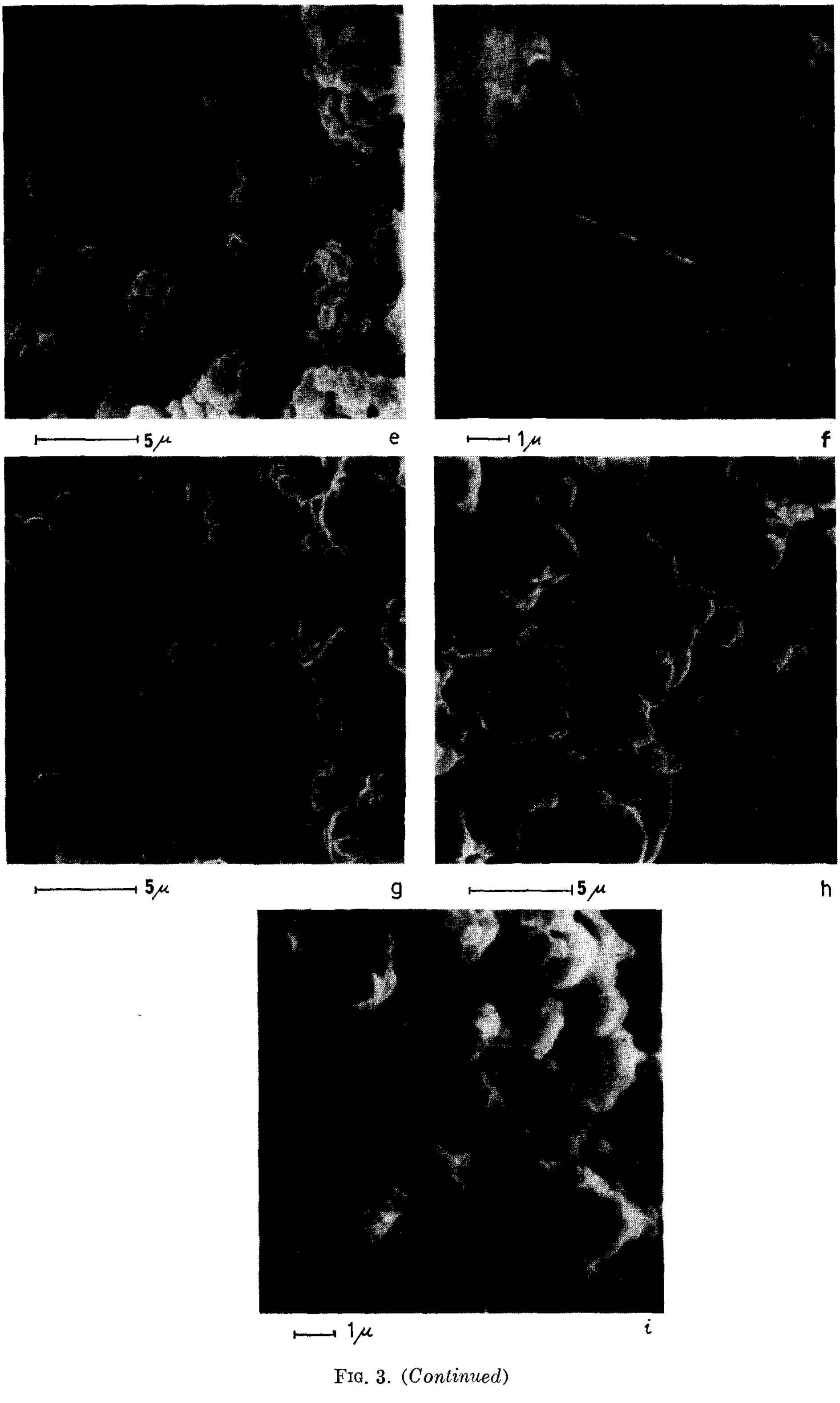

FIG. 3. (*Continued*)

(type I catalysts), in the other the same procedure has been carried out in an acetone suspension (type II catalysts). Figure 3a shows that acetone does not affect at all the AgO crystals; whereas, in case of alcohol, there is some reaction with the peripheral parts of the crystals (formation of Ag_2O, Ag, and Ag–acetate) resulting in the more attacked structure of Fig. 3b. In Fig. 3a, BaO_2 is well distinguished from the AgO crystals but this is no longer the case for Fig. 3b, both mixtures containing 8% BaO_2. The structure of pure silver catalysts conditioned for 15 hr at 300°C in C_2H_4/air are shown in Fig. 3c (type II) and Fig. 3d (type I). The size of the interlaced silver rods and lumps during the first 5 to 10 hr markedly increases and then remains constant over long periods of operation (investigations up to 90 hr have been made). There is some difference in the structure of the two types of catalysts, the alcohol-vibrated samples having a less regular and somewhat looser structure than have the acetone-vibrated catalysts. The size of the silver rods is very sensitive to temperature. Up to about 200°C, besides some interlacing, there is no essential increase in particle size; whereas, at higher temperatures, the structure becomes more and more massive by combining individual branches by diffusion and sintering. Heating in C_2H_4/air for 15 hr at 350°C results in a structure similar to that of Fig. 3c and d, but with a three- to fourfold increase of the size of the silver particles. However, a structure produced at 300°C does not alter at lower operating temperatures for long periods of time. From stereograms, it has been seen that the loosely packed silver matrix contains no closed pores and extends over the whole depth of the catalyst layer down to the carrier sheets. Thus the total mass of the catalyst is involved in the oxidation process.

Addition of BaO_2 has a very pronounced influence on the resulting catalyst matrix as shown in Fig. 3e and f showing type II and type I catalysts each containing 8% BaO_2. The typical network of branching and interlacing silver has altered, leaving a more or less ragged structure. The character of the resulting catalyst matrix is very similar in the range of 2 to 10% BaO_2; at higher BaO_2 contents, the surface becomes more compact. The compound catalysts often show small needles of $BaCO_3$ (Fig. 3f) indicating high mobility of the ions over the surface during the transformation $BaO_2 \rightarrow BaCO_3$. Thus the typical structure of the catalyst matrix is due to the transformation of BaO_2 into $BaCO_3$ at the BaO_2/Ag interface. As BaO_2 essentially transforms *after* the decomposition of AgO, the nascent $BaCO_3$ covers the Ag-matrix with a thin coating and fills out part of the large pores leaving a highly porous structure. This is clearly seen by comparing Fig. 3e and f with Fig. 3g where $BaCO_3$ had been removed from the catalyst by acetic acid. The original silver matrix, reappears, although the rods are somewhat smaller and less compact as in case of pure silver (Fig. 3c and d). Figure 3h shows a pure silver catalyst after treatment with actic acid (1:1) for 1 hr. There is no change of the structure and character of the silver matrix, the acetic acid treatment therefore being well suited for the separation of the two components.

If $BaCO_3$ is added directly to the AgO, a structure similar to that of pure silver is obtained (Fig. 3i), although the catalyst matrix seems to be more disintegrated and less compact due to the presence of the diluting $BaCO_3$. The effect of coating the silver, however, is hardly observed.

These observations point towards two different effects exerted by addition of BaO_2 or $BaCO_3$ to silver catalysts. The first effect which we shall call the "primary effect" is exerted by the inert $BaCO_3$ and consists mainly in preventing the silver somewhat from sintering and collapsing into the more or less massive network of Fig. 3c and d. The effect increases with increasing amounts of the additive and is well known in the art of catalyst preparation. An additional effect is met in the case of BaO_2, which we shall call the "secondary effect." This effect has its origin in the complete transformation of BaO_2 into $BaCO_3$ under reaction conditions and the formation of a thin carbonate coating of the silver matrix due to the high mobility of the ions during this transformation process. This coating stabilizes the catalyst matrix and is well integrated to the silver forming some kind of semiconductor/metal contact. The secondary effect, as described above, is well established even at BaO_2 contents of only 2 mole %.

Surface Area Measurements

The total surface areas s_t (m^2/g) of a series of catalysts are summarized in Table 1. In the first column, the amount of the additive is given on the basis of wt % $BaCO_3$ present in the catalyst instead of the initial BaO_2. The total surface area markedly increases from 0.49 m^2/g (pure Ag) up to 7.5 m^2/g for a catalyst containing about 18 wt % $BaCO_3$. The surface areas of the starting materials were 1.0 m^2/g (AgO) and 2.85 m^2/g (BaO_2). The surface areas of the silver catalysts remain constant over long periods of use, a result consistent with the microscopic observations.

From selective surface area measurements the data given in columns 3 and 4 of Table 1 have been obtained. The surface area of the silver component s_{Ag} increases only slightly with increasing BaO_2-contents from around 0.5 to 0.9 m^2/g. This result again is consistent with the information obtained from the micrographs Fig. 3c and g, showing somewhat smaller silver particles for the compound catalyst. Therefore, the large increase in surface area is mainly due to the transformation of BaO_2 into $BaCO_3$ during conditioning. The data for the $BaCO_3$ component are collected in column 4 of Table 1. The specific surface area of the additive had increased from 2.85 up to a mean value of 32 m^2/g. The data of column 4 have been obtained by subtracting the surface area of the silver component measured after removal of $BaCO_3$ from the total surface area and dividing through by the mass of the additive.

TABLE 1

TOTAL AND INDIVIDUAL SPECIFIC SURFACE AREAS OF AgO/BaO_2 CATALYSTS (ALCOHOL PREPARATION) CONDITIONED IN A STREAM OF C_2H_4/AIR AT 300°C FOR 18 hr

Wt % $BaCO_3$ in catalyst	s_t (m^2/g)	s_{Ag} (m^2/g)	s_{BaCO_3} (m^2/g)
2.2	1.10	0.58	24.0
2.4	1.30	0.73	23.8
4.3	1.88	0.73	27.4
4.7	2.00	0.79	26.6
7.1	3.00	0.66	33.7
7.3	3.30	0.73	35.9
9.2	3.98	0.76	35.8
9.3	3.98	0.87	34.3
9.8	4.03	0.88	33.1
11.5	4.95	0.79	37.0
12.1	5.48	1.05	37.7
17.3	7.59	0.79	40.1
		Mean	32.4

Some additional information has been obtained to support the interpretation given above. A known amount of either BaO_2 or AgO has been added to a conditioned catalyst followed by a full conditioning period. It was found that again BaO_2, as expected, completely transformed into $BaCO_3$ with a surface area of 29 m^2/g, whereas the surface area of the additional silver was 0.51 m^2/g. Pure BaO_2 is hardly affected by a C_2H_4/air stream at 300°C. This has been found from X-ray and thermogravimetric studies, and has been confirmed from the slight changes in surface area which only occur after an 18 hr exposure to the reacting gases at 300°C (decrease in surface area from 2.85 to 2.75 m^2/g). Therefore the transformation of BaO_2 into $BaCO_3$ does take place only in the presence of metallic silver.

If $BaCO_3$ is added directly to the AgO, the resulting catalyst has a much smaller surface area as compared to an equivalent amount of BaO_2. A catalyst with 34.7 wt % $BaCO_3$ had a surface area of 0.92 m^2/g only, with $s_{Ag} = 0.52$ m^2/g and $s_{BaCO_3} = 1.68$ m^2/g.

The data from surface area measurements support and complete the interpretation of the processes occurring during the conditioning period. $BaCO_3$ has only a small influence on both the catalyst matrix and the surface area exerting only the "primary effect" and probably a minor "secondary effect." On the other hand, BaO_2, by its transformation into $BaCO_3$ of largely increased surface area and coating the silver matrix, completely alters the surface structure of the catalysts.

Catalytic Studies

Activity, conversion, and selectivity of the catalysts have been measured immediately after the conditioning period which endowed them with constant properties. Several series of measurements have been made with the standard silver catalyst to define accurately its properties at various experimental conditions. The parameters varied in this study were the temperature (180 to 280°C), the feed composition (ethylene contents from 1.5 to 11 vol %, oxygen content slightly varying from 18 to 19.5 vol %, balance being nitrogen) and the reciprocal flow rate $1/F$. However, as integral data have been obtained, it is more appropriate to use the ratio M/F instead of $1/F$ as independent variable.

From the rather extended program of this study, covering about 100 different catalysts and widely varying experimental conditions, the following functions which best characterize the catalysts have been selected:

standard silver catalyst:

$A,C,S = f(M/F)$ at 220°C, $E_0 = 2.79$ vol %
$A,C,S = f(E_0)$ at 220°C, varying M/F
$A,C,S = f(T)$ at $M/F = 0.335$ g cm^{-2} sec, $E_0 = 3.40$ vol %

catalysts with varying amounts of BaO_2 and $BaCO_3$:

$A,C,S = f(M/F)$ at 220°C, $E_0 = 2.79$ vol %
$A,C,S = f(T)$ at $M/F = 0.335$ g cm^{-3} sec, $E_0 = 3.40$ vol %
$A,C,S = f(BaCO_3)$ at 220°C, $M/F = 0.335$ g cm^{-3} sec, $E_0 = 3.40$ vol %

The results are shown graphically in Figs. 4 to 10 and can be summarized as follows:

i. Activity increases with increasing M/F and decreasing E_0 for all catalysts (Figs. 4 and 5). The same is true for conversion.

ii. Selectivity is not very sensitive to variations in M/F and E_0. This is true for all catalysts (Figs. 4 and 5).

iii. The absolute amount (cm^3 of E at NTP/min) of ethylene oxidized increases with increasing E_0 and decreasing M/F (increasing F), as shown in Fig. 6.

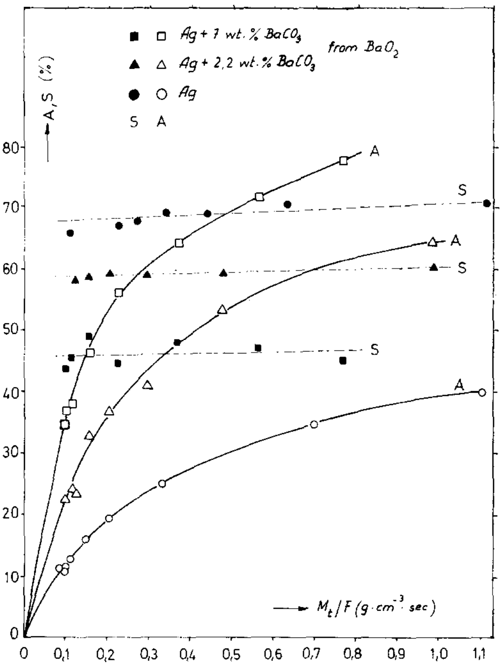

FIG. 4. Activity and selectivity vs M/F for a standard pure silver catalyst and two compound catalysts ($E_0 = 2.79\%$, $T = 220°C$).

iv. Activity strongly increases with increasing temperature for all catalysts (Fig. 7).

v. Conversion increases with increasing temperature for the pure silver catalyst, but has a pronounced maximum for catalysts containing BaO_2 (Fig. 7). The temperature of maximum conversion decreases with increasing amounts of BaO_2 (Fig. 8).

vi. Selectivity decreases with increasing temperature for all catalysts (Fig. 7).

vii. Activity increases with increasing amounts of BaO_2 up to a maximum around 8% BaO_2, and then slightly decreases. The same is true for conversion; whereas selectivity decreases with increasing BaO_2 (Fig. 9).

In case of temperature and M/F variation, the experiments have been carried out at both rising and falling arguments to control establishment of equilibrium. In all cases, the experiments have been carried out

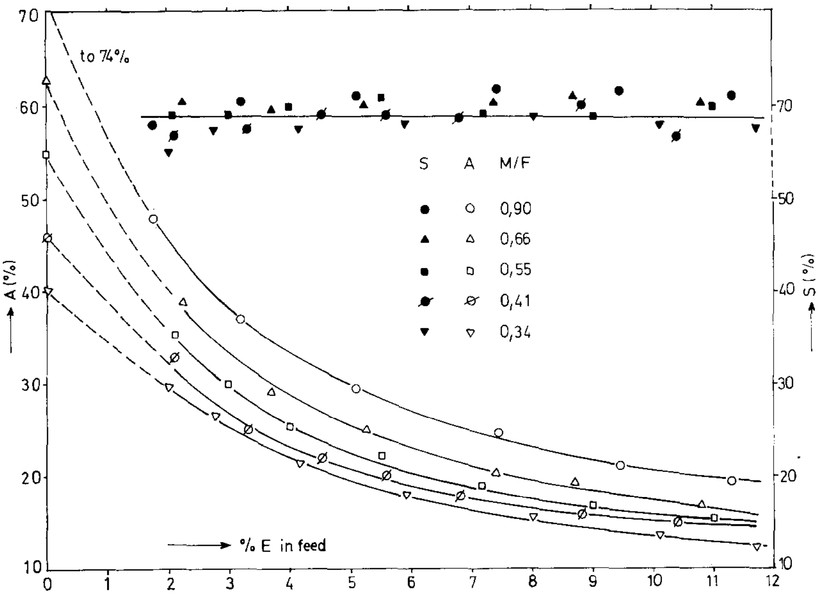

FIG. 5. Activity and selectivity of a pure standard silver catalyst at varying E_0 and M/F; $T = 220°C$.

such that equilibrium conditions have been met. A step of 10° upwards or downwards required about 15 to 20 min to reach equilibrium.

A comparative survey of the catalysts containing varying amounts of BaO_2 is given in Fig. 9. The figure has been drawn using $T = 220°C$, $E_0 = 3.40$ vol % and $M/F = 0.335$ as reference state. Any other reference state could have been used for comparison, without altering the general characteristics. Instead of BaO_2, the amount of $BaCO_3$ (wt %) actually present in the catalyst has been used as abscissa. Activity and conversion rapidly increase with increasing BaO_2 up to about 4 wt %. There is

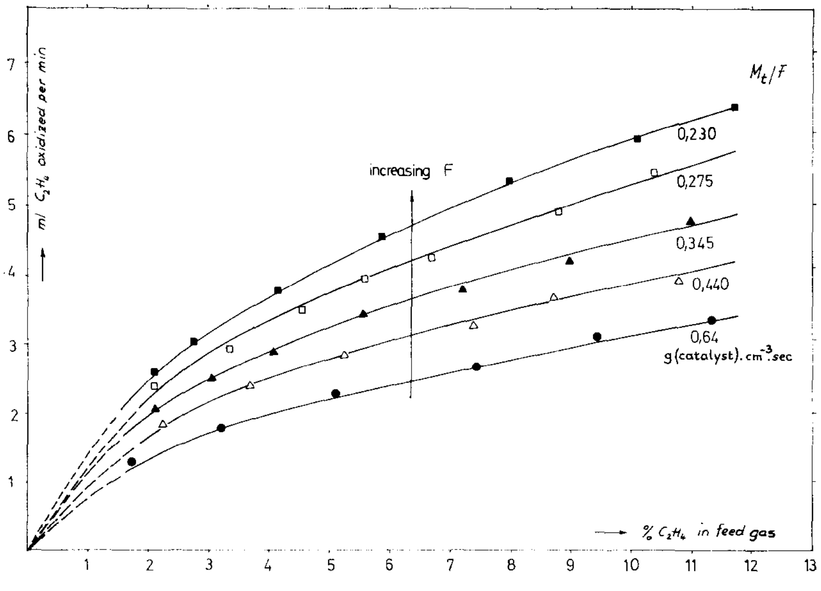

FIG. 6. Absolute amount of E oxidized (cm^3 at NTP/min) at varying E_0 and M/F for a standard pure silver catalyst ($T = 220°C$).

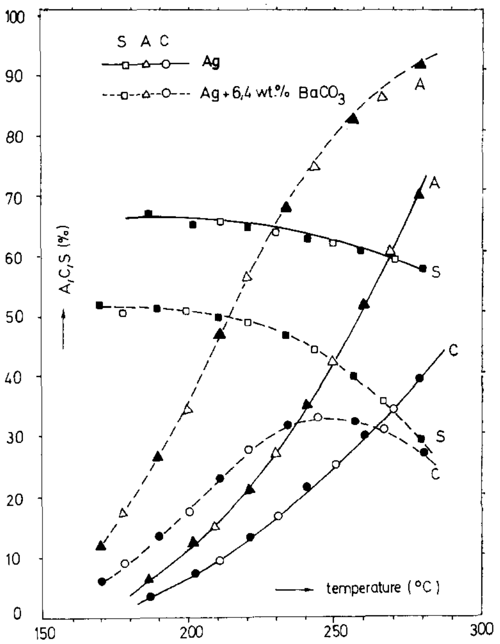

FIG. 7. Activity, conversion and selectivity vs T for a standard pure silver catalyst and a catalyst with 6% BaO_2 (given in terms of $BaCO_3$): $M/F = 0.335$ g cm^{-3} sec; $E_0 = 3.40$ vol %.

a flat maximum around 6–8 wt % BaO_2 and a steady decrease beyond this value. Selectivity rapidly and steadily decreases with increasing BaO_2. If activity and conversion are normalized with respect to the mass of silver M_{Ag} in the catalyst, i.e., comparison is made at $M_{Ag}/F = 0.335$ instead of the former M_t/F, the broken curves of Fig. 9 are obtained. It is interesting to note that with this normalization there is no considerable decrease in activity at higher BaO_2 contents. Conversion, of course, again decreases due to the corresponding decrease in selectivity. The plot of the temperature of maximum conversion vs wt % $BaCO_3$ (Fig. 8) shows a characteristic similar to that for activity: there is no considerable change in T_m beyond 10 wt % of the additive.

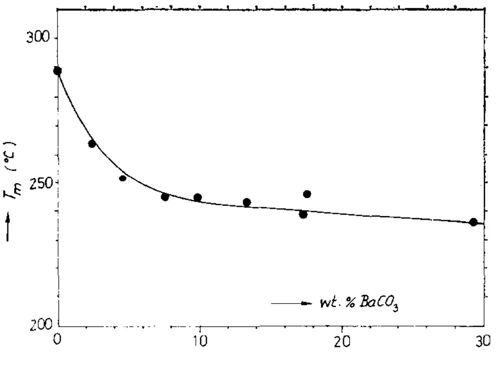

FIG. 8. Temperature of maximum conversion vs amount of BaO_2 (given in terms of $BaCO_3$): $M/F = 0.335$ g cm^{-3} sec; $E_0 = 3.40$ vol %.

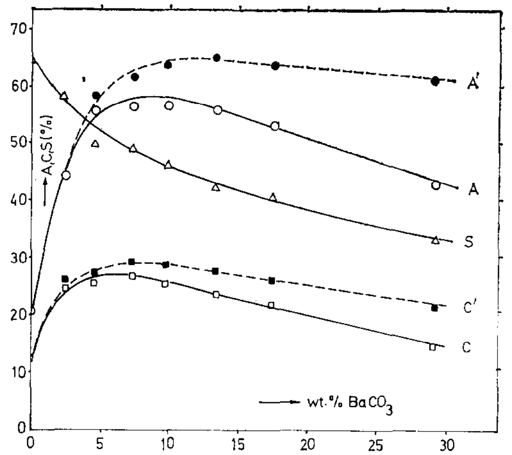

FIG. 9. Activity, conversion and selectivity vs amount of BaO_2 (given in terms of $BaCO_3$): A,C,S: normalization with respect to $M_t/F = 0.335$ g cm^{-3} sec; A',C': normalization with respect to $M_{Ag}/F = 0.335$ g cm^{-3} sec; ($T = 220$°C; $E_0 = 3.40$ vol %).

DISCUSSION

From the results presented above, the main features of the action of BaO_2 added to silver catalysts have been elucidated. A silver catalyst prepared from AgO and subject to a defined conditioning process has been used as a standard, relative to which the promoting action of BaO_2 was studied. The standard catalyst had a relatively high activity and an excellent selectivity compared to catalysts referred to as "pure" silver catalysts in the literature (*1*). The high selectivities probably are due to the presence of some sulfur in the AgO from the preparation method. However, photoelectric work function measurements of the resulting silver gave constant values between 4.40 and 4.47 eV (*18*) coinciding well with a value of 4.48 eV given by Suhrmann and Wedler (*20*) for pure polycrystalline silver, though there are much smaller values reported in the literature. Unfortunately, as far as we know, there exist no absolute work function data for pure silver used as catalyst, only relative values from contact potential measurements being available (*4*, *6*). Nevertheless, the relatively high work function of our standard silver catalyst fits well in the current conception of the selectivity–work function relationship (*1*, *4*). Concerning activity, it is hardly possible to make comparison with literature data because, in the case of integral reactor studies, activity strongly depends on the M/F ratio at a given temperature.

As outlined above, there are two effects exerted by BaO_2 if present in the starting catalyst mixture. First, BaO_2 suppresses the silver matrix from agglomerating and sintering into a more massive structure. This effect is also observed for inert additives like $BaCO_3$, and has been termed the "primary effect." Second, by its transformation into $BaCO_3$ during the conditioning period, BaO_2 stabilizes the silver matrix by coating it with a thin layer of $BaCO_3$ having a highly increased surface area. The work function of compound catalysts decreases from 4.40 (standard silver catalyst) to 3.80 eV for a catalyst containing 10 mole % BaO_2, which is attributed to the existence of the $BaCO_3$ coating having semiconductor properties with Ag atoms acting as donors. The coating has been imitated by preparing it from coprecipitation of $Ag_2CO_3 + BaCO_3$ from the nitrates. The resulting matrix after conditioning had a work function of 3.8 eV and oxidation properties similar to those of the compound catalysts. The electrical conductivity was found to be as low as $2 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$ (*18*). Thus the properties of the compound catalysts are no longer those of a coherent silver matrix but must be attributed to Ag atoms or groups of Ag atoms embedded in the carbonate coating. The increased activity therefore is due

i. to the increased surface area
ii. to the decreased work function of the actual catalyst matrix.

The matrix of the metallic silver reappears after removing the $BaCO_3/Ag$ coating (cf. Fig. 3c and g), but the size of the silver particles is somewhat smaller due to the primary effect exhibited by the additive, and the fact that a small portion of the silver incorporated into the $BaCO_3$ has dissolved too. This has been proved from chemical analysis of the acetic acid after filtration, where small amounts of Ag^+ ions have been detected. This, however, was not the case with pure silver catalysts subject to the same procedure. Therefore, it can be said that the silver matrix acts something like a support to the actual catalyst with close electric contact to it. The forming of this catalyst structure by BaO_2 has been termed the "secondary effect."

In a recent study Harriott (*19*) has tied activity and selectivity with particle size of the silver on high surface area supports. He concludes that a decrease in selectivity due to particle size must come from particles less than 30–50 Å due to increased consecutive oxidation of ethylene oxide. There is no evidence for the existence of such small silver particles on the carbonate layer of the compound catalysts described in this study. Our rejection of the idea of small silver particles on the outer surface of the carbonate layer does not come from immediate observation of the surface (because the 100–200 Å resolution of the instrument is not sufficient) but from the observation that the electric conductivity of the surface of compound catalysts is very poor (this can well be observed in the scanning electron microscope). Furthermore, after dissolving the carbonate from the catalysts there reappear completely smooth silver particles without any of the "dust" which should be observed if smaller particles had been present on the original surface (cf. Fig. 3g). A possible support/metal interaction for Ag on alumina catalysts is also put forward in Harriott's study. Electron doping is held responsible for the high activity of modified silver catalysts (of not specified composition) by Feller-Kniepmeier *et al.* (*21*) due to a Ag_2O_3 layer covering the silver particles.

Although in this study we dealt with

catalysts prepared from alcoholic suspension of the components (type I catalysts), reference should be made to some properties of catalysts prepared from acetone suspension (type II catalysts), to support the interpretation as given above. Under otherwise constant conditions, type II catalysts have smaller surface areas than have type I catalysts (e.g., 0.30 m^2/g compared to 0.50 m^2/g for pure Ag), smaller activity (15% at 220°C compared to 20%), and somewhat higher selectivity (around 70%). Addition of BaO_2 has the same influence on activity and selectivity as with type I catalysts although the effects are less pronounced compared with the alcohol preparation. The reason for this difference lies in the fact that during vibration in alcohol the components are chemically affected to some extent, AgO being reduced to Ag_2O, Ag-acetate, and Ag; and BaO_2 to Ba-acetate. Part of the silver so formed is incorporated into the additive already at this stage. The difference in the outer appearance of the AgO and BaO_2 particles after vibration in acetone and alcohol is clearly shown in Fig. 3a and b. Formation of the silver-doped $BaCO_3$ semiconductor surrounding the silver matrix thus will be facilitated in the case of alcohol vibration; whereas, for vibration in acetone, the catalyst components are not affected at all and incorporation of the silver into the $BaCO_3$ occurs only by diffusion during the conditioning period. The color of the alcohol-prepared catalysts changes from light grey (pure silver) to dark brown or even black with increasing BaO_2 addition. This change in color is less pronounced in case of type II catalysts.

After addition of about 6–8 wt % BaO_2 the most favorable situation concerning activity is met, the proper $BaCO_3$/Ag coating being fully established. The actual catalyst matrix not only has an altered geometric structure (highly increased surface area) but also has changed electronic properties compared with the pure silver (*18*). Addition of more than the optimal amount of BaO_2 does not essentially change activity (per g of silver), but it has an unfavorable effect on selectivity, probably due to stronger consecutive oxidation of the ethylene oxide.

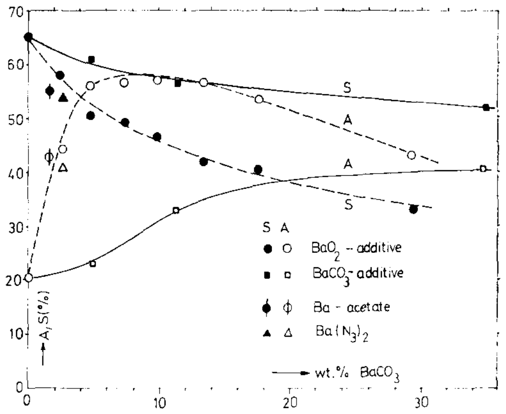

FIG. 10. Activity and selectivity of catalysts containing varying amounts of different additives ($T = 220°C$; $E_0 = 3.40\%$; $M/F = 0.335$ g cm^{-3} sec).

If $BaCO_3$ is added directly to the AgO there is only a slight increase in activity up to about 40% at 36 wt % $BaCO_3$. Selectivity decreases correspondingly more slowly (Fig. 10). This behavior is certainly to be expected from the above interpretation, as $BaCO_3$ essentially exhibits only the primary effect, a secondary effect being exerted only to some degree (*18*).

As to the kinetics of the oxidation reaction, from the data presented in this paper, only some qualitative conclusions can be drawn. As shown in Fig. 5, activity increases with decreasing concentration of C_2H_4 in the feed. This points towards an inhibiting effect of the reaction products adsorbed to some extent at the active surface of the catalyst, the inhibiting action certainly being less pronounced at low C_2H_4 concentration. The absolute amount of C_2H_4 oxidized increases with increasing E_0 and increasing M/F (Fig. 6). From this, it follows that only part of the catalyst surface is active in the range of variables investigated, the active part increases with increasing ethylene supply.

From the fact that there is a pronounced maximum in the conversion vs temperature curve (Fig. 7) it follows that considerable consecutive oxidation of C_2H_4O occurs at high catalyst activity. The height of the conversion maximum and its temperature decreases with increasing BaO_2 (Fig. 8), showing that more active catalysts are also more active with respect to the consecutive oxidation of ethylene oxide. This may be due partly to increasing porosity of catalysts with larger amounts of BaO_2.

There is a distinct relationship between activity and selectivity for all catalysts investigated. The higher the activity, the smaller the selectivity. Furthermore, it has been established that equal activities of different catalysts correspond to equal selectivities. Although selectivity decreases with increasing amounts of BaO_2, activity increases correspondingly faster. This is seen clearly from a plot of the space-time-yield (amount of ethylene oxide produced in unit time) vs wt % BaO_2. The function obtained is similar to that of Fig. 9 for activity with a maximum around 6–8 wt % BaO_2. The commercial advantage of using compound silver catalysts thus would lie in the threefold increase of the amount of ethylene oxide produced per unit time per unit catalyst mass as compared to a pure silver catalyst.

The results can be generalized to some extent. We expect, from the interpretation given in this paper, that any additive which decomposes or transforms into the corresponding carbonate in the range of experimental conditions should act in a way similar to BaO_2; whereas additives, which are inert under these conditions essentially should act like $BaCO_3$. That this, in principle, is true has been shown by adding $BaSO_4$, γ-Al_2O_3 on the one hand, and Ba-acetate, Ba-azide, and Ba-formate on the other hand to the AgO. It has been found, indeed, that the first two additives did not alter activity and selectivity to any considerable amount; whereas the latter three additives behaved in almost the same way as did BaO_2 (Fig. 10).

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