

Deactivation of a commercial catalyst in the epoxidation of ethylene to ethylene oxide—basis for accelerated testing

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Abstract

An accelerated deactivation procedure for a commercial Ag-based catalyst for ethylene epoxidation was developed in a gradientless Berty-recycle reactor by increasing temperature and oxygen concentration which, however, were kept constant in the whole reactor for a single experiment. Thus, deactivation kinetics could be studied explicitly. The initial rates of both C₂H₄O and CO₂ formation and of ethylene consumption increase with reaction temperature and oxygen concentration. At 260 °C increasing O₂ concentration favors the rate of ethylene oxide over that of CO₂ formation. Above 260 °C the opposite is true. Catalyst activity decays faster at both higher reaction temperature and oxygen concentration. A correlation exists between the increase of the size of Ag particles and the catalyst activity decay, pointing to sintering as the main deactivation mechanism for this catalyst. Thus, by increasing these variables the catalyst deactivation process is accelerated.

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1. Introduction

With their unique ability of promoting selective against total oxidation of ethylene, supported silver catalysts are extremely important in ethylene oxide (EO) production. Catalyst deactivation has, however, a negative impact on process economy [1]. To keep catalyst activity and selectivity nearly stable despite deactivation, the reaction temperature is continuously increased over time; thus a nearly constant ethylene oxide output is maintained, as reported in the patent literature [2]. Over the years deactivation of Ag-based catalysts has been a subject of extensive research, with the aim of understanding its mechanism and of improving catalyst stability. Several possible causes for Ag-catalysts deactivation, such as catalyst poisoning either by impurities [3,4] or by an excess of chlorine-based promoters in the feed [5–7], accumulation of carbon deposits on the catalyst surface [8–12], and increase of both silver particles size [3,4,13–16] as well

as support crystallite size [16], have been discussed. Despite the wide list of possible causes for deactivation, it is broadly accepted that sintering of silver is the primary reason. In contrast to the commercial significance of the system, results reported on deactivation of Ag-based catalysts have been mostly related to model catalysts with just a few exceptions dealing with commercial catalysts [3,4].

The design of new EO catalysts or improvement of existing ones is often seen as overcoming the causes for their deactivation, with the final goal of increasing catalyst stability. These are expensive and time consuming investigations, especially when the assessment of catalyst lifetime is a task which may take months to years. In principle, there are two options in studying the problem of catalyst stability: (i) to run the catalyst in a pilot plant under process conditions over a time span close to the full anticipated catalyst life, or (ii) to perform accelerated deactivation tests in such a way that deactivation is mimicked under close-to-process conditions [17,18]. The second approach is favored for its shorter time and lower expenses.

In general, to study accelerated deactivation in a laboratory or bench-scale reactor, several important factors must be considered. The choice of the right process parameter(s) is crucial, since deactivation being deliberately caused must

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be of the same mechanism as the one in the industrial plant, but occurring during a shorter time span. The complexities in the design of such an accelerated deactivation test, resulting in genuine deactivation, have been addressed in the literature [17–23]. For example, if sintering is the proven mechanism of catalyst deactivation, its nature might still not be fully known. Often reaction temperature is assumed to be the main cause, but it is known, however, that other factors, like type and concentration of atmosphere surrounding the catalyst may also be very important. The predominance of one of two variables, temperature or concentration, may finally define the nature of sintering, i.e., being a *thermal* or *chemical* process [24]. Various mechanistic studies revealed that the presence of both atomic and subsurface oxygen in Ag/Al₂O₃ catalyst is essential for selective ethylene oxidation [8,25–28]. Oxygen is, however, also a factor that additionally influences deactivation of Ag/Al₂O₃ catalysts, since the rate of catalyst sintering does often depend on oxygen concentration [24]. Recently, reduced oxygen adsorption of a commercial catalyst, which was previously partially deactivated in a pilot plant, was recognized as one reason for its lower activity [29].

The design of an accelerated deactivation test should be based on an assumed catalyst deactivation mechanism. To focus on this, an accelerated deactivation experiment with a small number of possible deactivation causes is preferred in order to prevent their simultaneous contribution to the total effect. A favored scenario could be to have only one deactivation step at a time. However, the procedure is not always straightforward, since one accelerating parameter usually leading to the projected deactivation mechanism might unexpectedly cause additional ones [20,22]. Thus, an increase in space velocity, e.g., will eliminate concentrations of a specific compound due to high conversion as the cause for catalyst decay, but might cause major catalyst poisoning if some impurities are present in the feed [20]. Sulfur and fluorine, which are often present as impurities in the feed, were both claimed as being effective poisons for Ag catalysts operated under both commercial [3] and laboratory [4] conditions. Therefore, additional precautions, by means of checking the influence of space velocity on deactivation rate, must be undertaken to exclude interference of side-by-side poisoning mechanisms in the global picture of deactivation of the catalyst.

Although sintering has been regarded as the most probable mechanism of deactivation of an Ag-based catalyst, the effect of chlorine-based promoters is still quite controversial [6,25,26,30]. Generally speaking, chlorine promotes mobility of metals, hence leading to their redispersion in some cases [31], but also to their sintering in some others [24]. It has been discussed that chlorine might suppress dissociative O₂ adsorption, hence leading to less CO₂ production [30], or it can make adsorbed atomic oxygen less electronegative and hence enhancing electron transfer from ethylene to the former [25]. Another explanation of chlorine promotion was suggested by suppressing the formation of

multicoordinated strongly adsorbed O, presumably leading to total combustion of ethylene [26]. Chlorine over Ag(111) single crystals was also found to favor, to a smaller extent, a secondary reaction, i.e., ethylene oxide isomerization [6]. The side effect of poisoning by C₂H₄Cl₂, e.g., although reversible, often requires a “poison scavenger” in the reaction, like C₂H₆ [7]. Therefore, in the present deactivation studies it was also of interest to find an optimal chlorine concentration, and to minimize its poisoning effect as a factor influencing global catalyst deactivation.

2. Objectives

The aim of this study was to establish accelerated deactivation of an Ag-based prospective commercial catalyst by a change of parameters without changing the deactivation mechanism, which we define as *true deactivation*. If deactivation rates can be correlated with time of operation and variables influencing the deactivation process extracted from such experiments, then it is possible to predict catalyst behavior over extended periods of time of operation in a commercial reactor. Deactivation can be studied directly when variations in the rate of the catalytic reaction are solely due to the deactivation process [23]. This approach is also beneficial for studying deactivation kinetics [32,33], the results of which will be discussed in another publication (G. Boskovic et al., submitted).

3. Experimental

3.1. Methodology of experimentation

Assuming sintering as the main deactivation mechanism of an alumina-supported Ag catalyst [3,4,13–16], and due to the observation that the rate of catalyst sintering often depends on oxygen concentration [24], both high reaction temperatures and different oxygen concentrations were chosen as parameters supposed to bring accelerated and true deactivation. Given that reduced capacity for oxygen adsorption on Ag-based catalyst and its deactivation seem to be directly related [29], the decrease of the rates of oxygen conversion besides ethylene consumption and EO formation was chosen as a measure of catalyst deactivation during time on stream. In order to obtain true deactivation conditions for studying deactivation directly, the concept of “deactivation compensation” was applied [33]; for this O₂ conversion was kept constant over the time of operation of a gradientless recycle reactor. The time when the catalyst started to deactivate was defined as *zero time of deactivation*.

The chosen set of variables, i.e., temperature and O₂ concentration in the reactor being equal to outlet concentration, was kept constant throughout a single experiment. The initial space velocity was adjusted to 25,000 h⁻¹, and was gradually decreased over time on stream depending on the

rate of catalyst deactivation. The space velocities were significantly higher than those usually applied in commercial operation [1] in order to keep the concentrations of ethylene and oxygen at intermediate levels characteristic of the commercial process.

3.2. Equipment and operational procedure

The experiments were conducted in the equipment shown in Fig. 1, consisting of an internally back-mixed reactor (Berty), a manifold system for supply of reactants, an analytical part, and a unit for process control. The Berty reactor, ascertaining almost no mass and temperature gradients in the catalyst layer, and the high mass flow through the catalyst layer similar to industrial operation, is a simple means of determining reaction rates [34]. An ideal mixing regime was verified by the criterion of constant conversion versus variable turbine speed [35], and established by applying 1300 rpm of the impeller. The reaction temperature was measured by two Ni–Cr–Ni thermocouples (according to DIN IEC-584-2), below and above the catalyst layer; temperature was controlled by a respective unit (Eurotherm 2404). A third thermocouple was utilized for indicating the oven temperature.

Ethylene, oxygen, carbon dioxide, nitrogen, and a mixture of ethyl chloride and N₂ could be provided indepen-

dently by five mass-flow controllers (MFC) (Brooks 5850S) and premixed before entering the reactor. The product line leaving the reactor was equipped with three pressure regulators (GO, Inc.) allowing first adjustment of the working pressure in the reactor up to 50 bar, and second splitting of the exit flow in such a way that only a small part of the gas was passed to analysis.

An essential part of the equipment was a PC for data acquisition, automatic regulation of feed flow, and process control. By Field Point modules (National Instruments) the PC obtains information on temperature and pressure, and through a Bus interface it communicates with peripherals controlling these parameters. In addition, a program for automatic process control and regulation, based on a BridgeView software package (National Instruments), was integrated in the system. Process control and regulation are based on effluent gas composition by means of a software algorithm comparing a targeted value of a desired component concentration (which by our choice was the concentration of O₂) with its value at zero time of deactivation. Constancy in O₂ concentration is achieved by decreasing the total flow rate executed by MFCs. By adjusting PID values of the MFCs, response time to catalyst deactivation was varied from 15 min to 1 h, depending on the deactivation rate in the particular phase of the experiment and imposed by applied reaction parameters.

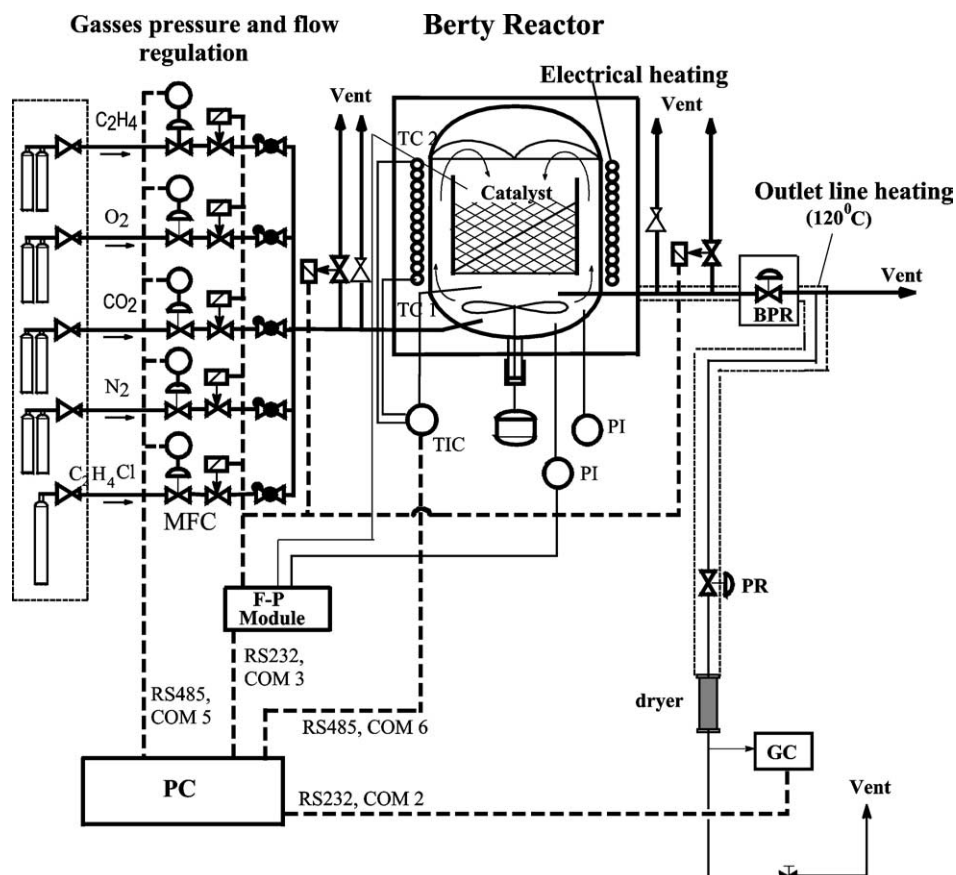


Fig. 1. Computer-controlled equipment for catalyst-deactivation studies.

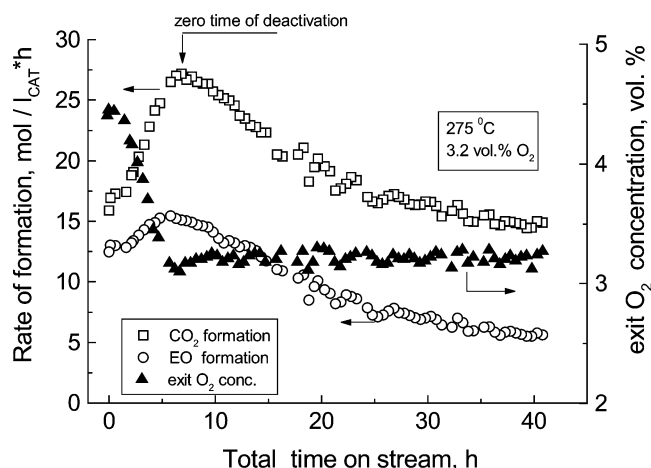


Fig. 2. Pattern of a typical deactivation experiment illustrated by the reaction rates and oxygen concentrations as a function of total time on stream. (TOS includes the times of activation and subsequent deactivation of the catalyst; starting at time “zero” of deactivation the constant oxygen concentration is a consequence of the compensation approach applied.)

In a typical experiment, the catalyst sample was first activated in the reaction mixture excluding O_2 , by heating up to $190^\circ C$, and then by additional heating with a temperature ramp of 3 K/h up to the working temperature. Once the desired temperature was reached, O_2 was gradually introduced to the feed for a period of several hours. The activation period lasted up to 40 h depending on the reaction temperature. After several hours upon first contact of the catalyst with oxygen the first catalyst activity was usually noted. During the next 5–10 h, rates of formation of both ethylene oxide and CO_2 continued to increase depending on the severity of applied conditions (Fig. 2). Rising of catalyst activity went along with a drop of O_2 concentration in the reactor. The maximum rate of formation of both ethylene oxide and CO_2 usually was reached simultaneously, and this point coincides with the minimum of O_2 concentration in the reactor. From that point, the catalyst started to deactivate, which led to a decrease of both ethylene oxide and CO_2 concentration, and increase of O_2 concentration. The very same point was taken as *zero time of deactivation* and corresponds to the “initial” rates of ethylene oxide and CO_2 formation and “initial” catalyst selectivity. Starting from zero time of deactivation the action of deactivation compensation was carried out, by means of decreasing the total feed flow and keeping the corresponding O_2 concentration in the reactor constant. Both relative stability of the O_2 concentration during time on stream of a typical accelerated deactivation run and continuous catalyst deactivation during experiments lasting as long as 120 h and representing long-term aging (Fig. 2) support the approach.

3.3. Safety precautions

Several safety measures were applied. Line plugging by polymerization of ethylene oxide resulting in a pressure rise above the safety limit was prevented by heating the exit

line to $120^\circ C$. Values for maximal temperature and pressure were defined as alarm functions, and connected to electromagnetic ON/OFF valves, providing the shutoff of all inlet flows in an emergency case and the simultaneous release of pressure in the reactor to the vent. Additional safety features included one-way valves preventing reverse gas flows leading to uncontrolled mixing of ethylene and oxygen, and spring valves limiting the maximal allowed pressure in the reactor.

3.4. Chemical analysis of effluent

A small fraction of the effluent was efficiently dried in a column filled with $CaSO_4$, although considerable amounts of water were produced throughout the experiment at high temperatures. A micro-GC (Varian-Chrompack CP-2002) provided with two channels and a TC detector was used to detect O_2 and N_2 (Mol sieve 5A) and C_2H_4 , CO_2 , and C_2H_4O (Poraplot Q), which took about 2 min per analysis. A flow of $3\text{ cm}^3\text{ min}^{-1}$ of 99.997% Ar, additionally purified by a moisture filter (Chrompack), was used as a carrier gas.

3.5. Type of catalyst and its characterization

The catalyst used in this study was provided by an industrial supplier. Its preparation corresponds closely to the state of the art. Such catalysts for ethylene epoxidation consist generally of silver particles (0.1 to $1\ \mu\text{m}$) supported on $\alpha\text{-Al}_2\text{O}_3$. Usually, they contain between 7 and 20 wt% of silver and are prepared by impregnation of the support with an organic silver complex compound. Supports with a low surface area ($< 2\text{ m}^2/\text{g}$) are used to suppress total oxidation and enhance EO selectivity. For the same purpose, promoters such as alkali compounds (in particular, cesium salts) are added during the manufacturing procedure [36].

At the end of their performance the size of Ag particles of some selected catalyst samples was examined by transmission electron microscopy (TEM). Micrographs were recorded by a CM20 (Philips) microscope equipped with an EDX facility (EDAX PV9900). The powdered samples were dispersed on a Cu grid (300 mesh) coated with a Lacey carbon film. The acceleration voltage used for the measurement was 200 keV.

3.6. Experimental conditions

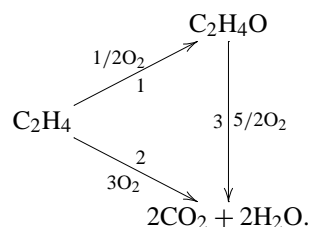
Reaction temperatures ranged from 260 to $280^\circ C$. The pressure was kept constant at 20 bar. The inlet flow consisted of 25 vol% C_2H_4 , 5.5 vol% CO_2 , 1.5 to 7.5 vol% O_2 , 1.8 ppm of chlorine (as ethyl chloride), the balance to 100 vol% being N_2 . The maximal inlet O_2 concentration was limited in order to be outside of the explosive range for ethylene–oxygen mixtures. In total, 15 runs were performed with different O_2 concentrations and temperatures, but keeping both parameters constant during a single run. A single experiment lasted from 40 to 120 h. A commercial

silver-based catalyst was used in the form of Raschig rings. The volume of the catalyst and the total flow of reactants were chosen in such a way that an initial space velocity of $25,000 \text{ h}^{-1}$ was achieved.

4. Results and discussion

4.1. General aspects

The reaction proceeds essentially to EO and carbon dioxide whereby the total oxidation of EO is almost negligible under the conditions chosen:



The experiments delivered rates of $\text{C}_2\text{H}_4\text{O}$ and CO_2 formation,

$$R_i = \frac{F_{\text{tot}} \cdot (C_i - C_i^0)}{V_{\text{CAT}}} \text{ mol/L}_{\text{CAT}} \text{ h},$$

and of ethylene consumption,

$$R_{\text{C}_2\text{H}_4} = \frac{F_{\text{tot}} \cdot (C_{\text{C}_2\text{H}_4}^0 - C_{\text{C}_2\text{H}_4})}{V_{\text{CAT}}} \text{ mol/L}_{\text{CAT}} \text{ h},$$

which were measured nearly continuously during time on stream. The reactor selectivity to ethylene oxide amounts to

$$S_{\text{EO}} = \frac{R_{\text{EO}}}{R_{\text{EO}} + 0.5 R_{\text{CO}_2}} \text{ \%}.$$

The initial reaction rates correspond to the reaction temperature, and to the O_2 concentration within the reactor at zero time of deactivation. The O_2 concentration within the reactor was varied from 0.87 to 4.80 vol%. The influence of the reaction variables on the initial rate of formation of ethylene oxide and CO_2 and on the initial selectivity is discussed. Their particular profiles during time on stream, i.e., related deactivation rates, are communicated elsewhere (G. Boskovic et al., submitted). During the first 50 h of time on stream a drop of the rate of ethylene oxide formation was observed; it is related to concentrations of O_2 and ethylene. Finally, the decrease of the ethylene oxide rate of formation depends on the size of the metal particles of the deactivated catalyst discharged from the reactor at the end of the experiment.

4.2. Optimization of chlorine addition to the feed

The rates of ethylene oxide and CO_2 formation and ethylene consumption as well as selectivity to ethylene oxide were influenced by the chlorine content in the feed (Fig. 3). Experiments were performed at 200°C and 20 bar, and with a reaction mixture containing 0 to 3.7 ppm chlorine,

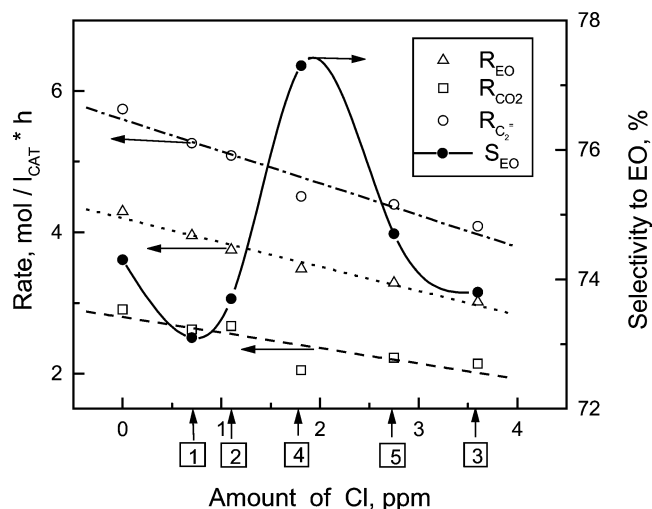


Fig. 3. Rates of ethylene consumption as well as ethylene oxide and CO_2 formation and selectivity as a function of chlorine concentration; 200°C ; 20 bar; 7.5 vol% O_2 in the feed; numbers in squares indicate the order of introducing of a new chlorine concentration.

30 vol% ethylene, 5.5 vol% CO_2 , 7.5 vol% O_2 ; the balance to 100 vol% was N_2 . The results shown in Fig. 3 were acquired over the same catalyst sample and refer to pseudo-steady-state conditions obtained after several hours after the chlorine concentration had been changed. In order to avoid doubtful conclusions as having no fresh catalyst sample for every single concentration, the selection of chlorine concentration in the limits of the stated range was rather random and then increased monotonically (numbers in squares below x axis in Fig. 3 indicate the order of introduction of every single chlorine concentration). In such a way, a possible cumulative effect of chlorine, left over on the catalyst surface from the previous experiment with certain chlorine concentration, can be avoided. As seen from Fig. 3, chlorine inhibits the rates of production of both ethylene oxide and CO_2 , but in the particular region of concentrations the production of CO_2 is more strongly inhibited.

The maximum of ethylene oxide selectivity was obtained at 1.8 ppm of chlorine in the feed; therefore, this concentration was used in all subsequent experiments. Since this selectivity was achieved following the removal of the highest chlorine concentration introduced in the row (3.7 ppm of chlorine was introduced as a third portion in the line, resulting in the lowest selectivity—Fig. 3), a reversible poisoning of silver by chlorine might be speculatively assumed, which is in line with claims in the literature [7]. Some authors claim that poisoning by chlorine is reversible only when certain impurities in the feed are present, like ethane. Its role as a scavenger might explain the reversible nature of Ag-catalyst poisoning by chlorine in commercial applications [4,7].

4.3. Effect of oxygen concentration and temperature on deactivation

The effect of oxygen concentration and reaction temperature on the rate of ethylene oxide and CO_2 formation and

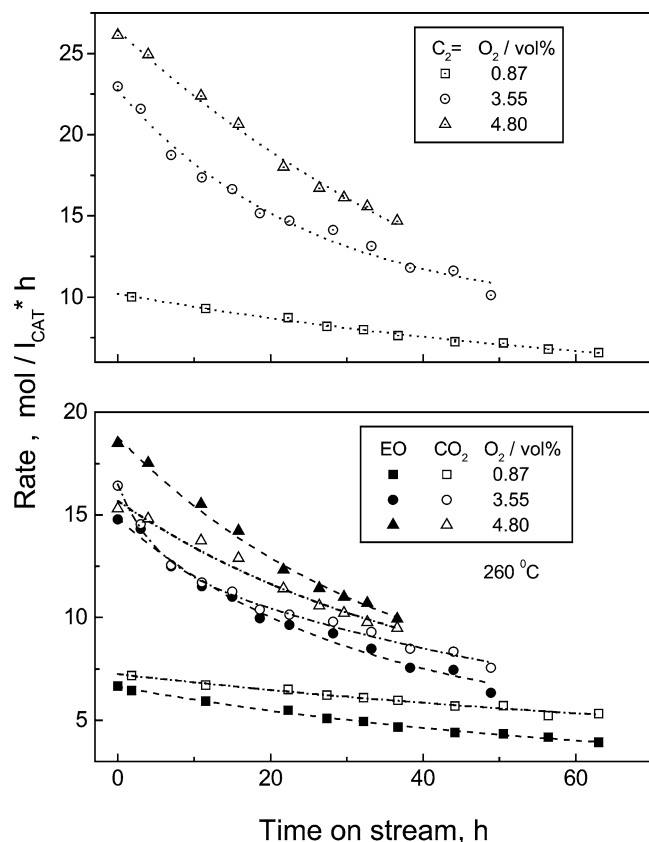


Fig. 4. Rates of C₂H₄O (■, ●, ▲) and CO₂ (□, ○, △) formation and of ethylene consumption (□, ○, △) as function of time on stream, at 260 °C for different O₂ concentrations in the reactor.

rate of ethylene consumption during time of operation is presented in Figs. 4 to 7.

At 260 °C the rates of formation of ethylene oxide and of CO₂ depend on the O₂ concentration in the reactor: at a very high O₂ concentration of 4.8 vol% EO formation rate dominates over that of CO₂, while at the lowest O₂ concentration applied (0.87 vol%) the opposite is true (Fig. 4). The nominal values of the corresponding rates of formation, for both ethylene oxide and CO₂, are directly proportional to O₂ concentration; i.e., the higher the exit concentration of O₂ the higher the rates. Regardless of the level of O₂ concentration, the drop of the rate of ethylene oxide formation is always more marked than the one for CO₂ formation (Fig. 4). When reaction temperature was increased to 270 °C, the rate of CO₂ formation dominates over ethylene oxide formation rate for the whole range of O₂ concentrations (Fig. 5). Again, the higher the exit O₂ concentration the higher the drop of the rate of formation of both products, among which the drop of the ethylene oxide rate is always more pronounced (Fig. 5). Finally, at the highest reaction temperature applied (280 °C) the drop of the rate of ethylene consumption is dramatically influenced by the highest O₂ concentration; however, the profiles of both ethylene oxide and CO₂ formation rates as a function of time on stream are more or less parallel for the whole range of applied O₂ concentration (Fig. 6).

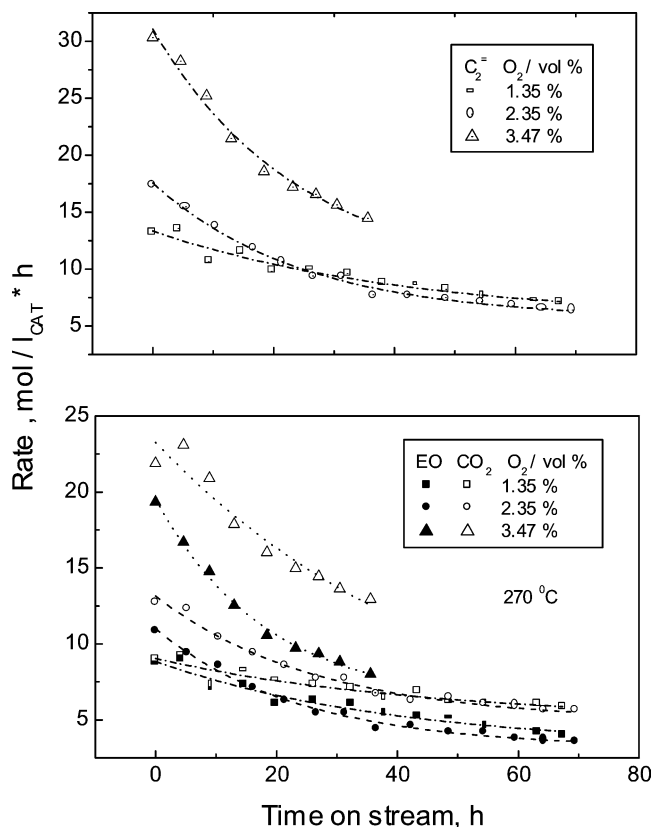


Fig. 5. Rates of C₂H₄O (■, ●, ▲) and CO₂ (□, ○, △) formation and of ethylene consumption (□, ○, △) as function of time on stream, at 270 °C for different O₂ concentrations in the reactor.

The reaction temperature influences the rates of consumption and formation significantly (Fig. 7). For nearly constant O₂ concentration, an increase of the reaction temperature causes an increase of the initial rate of CO₂ production. However, the initial rate of ethylene oxide formation is not a simple function of the temperature increase, since ethylene oxide production passes through a maximum at a reaction temperature of 270 °C. For high O₂ concentrations and temperatures within the range from 260 to 280 °C the formation of ethylene oxide and CO₂ is differently effected by temperature. Production rates of CO₂ are favored by temperature over the whole range of temperatures, but the increase in ethylene oxide rate is limited up to a temperature of 270 °C probably due to a consecutive total combustion pathway. From the temporal profiles of the production rates of both CO₂ and ethylene oxide it is obvious that O₂ concentration favors deactivation (Figs. 4–6). The same conclusion is valid when the reaction temperature is increased at constant O₂ concentration (Fig. 7). However, profiles of both rates of formation of ethylene oxide and CO₂ during time on stream are more or less parallel once the critical values of variables effecting deactivation are reached, i.e., either the reaction temperature (280 °C) (Fig. 6) or the O₂ concentration (O₂ concentration above 3 vol%) (Fig. 7). Catalyst decay as defined by the decrease of the rates of ethylene consumption and products formation is fastest when both the

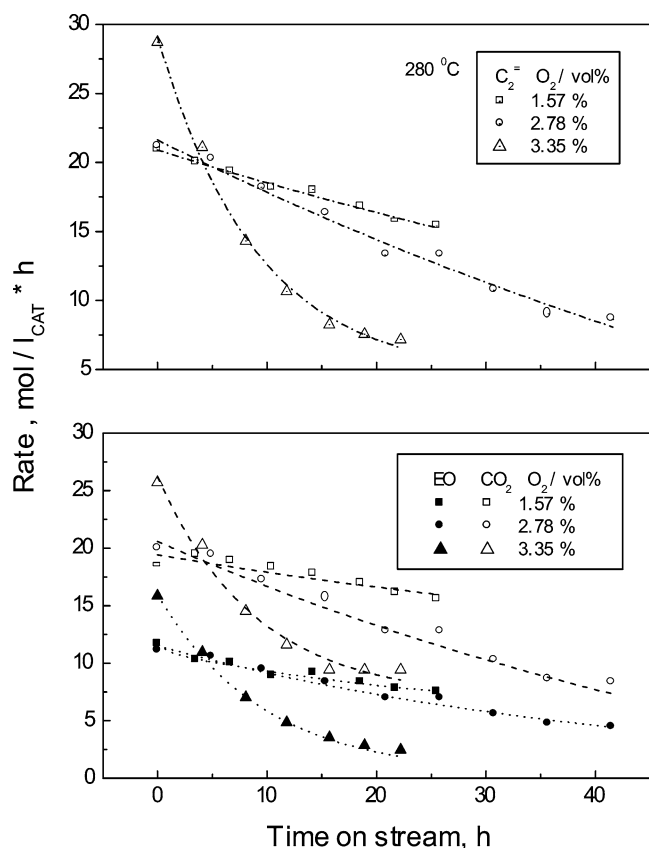


Fig. 6. Rates of C₂H₄O (■, ●, ▲) and CO₂ (□, ○, △) formation and of ethylene consumption (□, ○, △) as function of time on stream, at 280 °C for different O₂ concentrations in the reactor.

highest reaction temperature and the highest O₂ concentration are applied.

The effect of O₂ concentration on the initial selectivity to ethylene oxide at different reaction temperatures is presented in Fig. 8. At the lowest temperature of 260 °C, an increase of O₂ concentration favors the rate of ethylene oxide formation over the rate of CO₂ formation, resulting in increased selectivity to ethylene oxide. At higher temperatures, the influence of O₂ concentration is the opposite. It shows the predominant influence of high reaction temperature over O₂ concentration. These results are an indication of a certain synergism of these two parameters when involved in the deactivation process.

The negative effect of high temperature on Ag-based catalyst stability is a well-known problem in its commercial application [1]. It is usually manifested as a selectivity, rather than an activity problem. Thus, it is obvious from Figs. 6 and 7 that both reaction temperature and oxygen concentration are responsible for the performance of Ag catalysts.

As outlined in the Introduction, there is a possibility that deactivation may be caused by poisons in the feed, or poisoning by-products. Therefore, an additional experiment was carried out in order to check the possibility of significant poisoning of the catalyst by impurities in the feed. The initial space velocity was set two times as high as in the standard

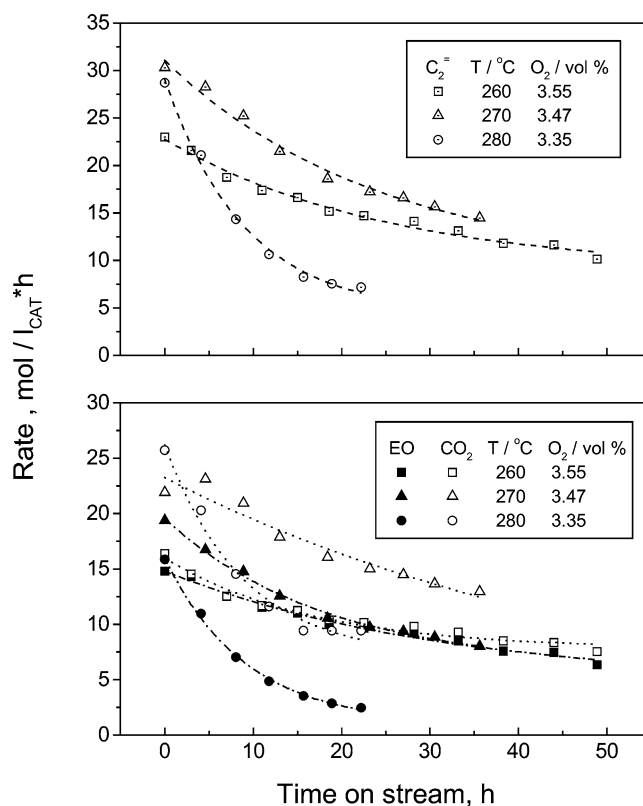


Fig. 7. Rates of C₂H₄O (■, ●, ▲) and CO₂ (□, ○, △) formation and of ethylene consumption (□, ○, △) as a function of reaction temperature for high oxygen concentrations in the reactor.

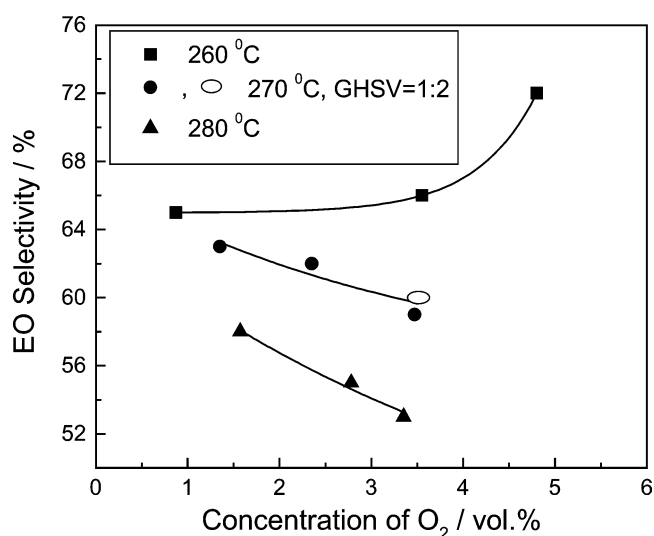


Fig. 8. Initial selectivity as a function of reaction temperature and O₂ concentration (filled, initial GHSV = 25,000 h⁻¹; blank, initial GHSV = 49,000 h⁻¹).

experimental setup. It turned out that no such cause of deactivation prevailed.

A very high initial space velocity resulted in some increase of R_{EO} , R_{CO_2} and rate of ethylene consumption; however, the deactivation rate was similar to that obtained in the experiment with standard initial space velocity of

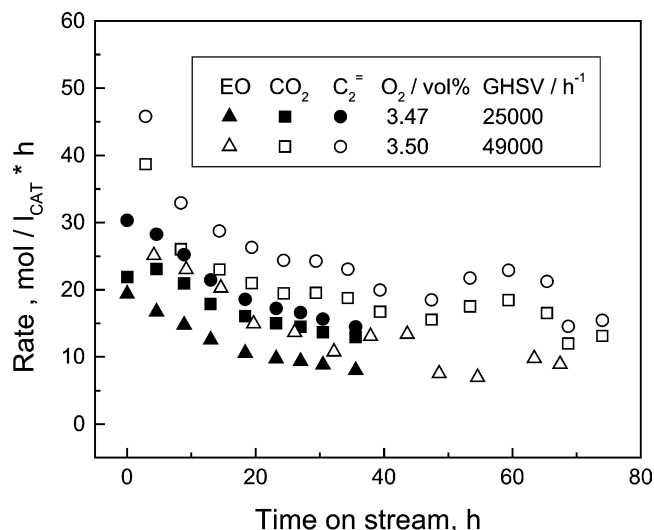


Fig. 9. Rates of formation of C_2H_4O (\blacktriangle , \triangle) and CO_2 (\blacksquare , \square) and ethylene consumption (\bullet , \circ) in time on stream at 270 °C as a function of different initial space velocities.

25,000 h^{-1} as shown in Fig. 9. The increased rates were due to higher concentrations of oxygen and ethylene caused by their lower degrees of conversion. This result eliminates the possibility of poisoning by reactants and impurities as a cause for the deactivation, indicating sintering as its most probable cause. Initial selectivity to ethylene oxide, as well as its temporal profile, is not influenced by the magnitude of space velocity, indicating that selectivity does not depend on the degree of conversion within the range covered in these experiments (blank symbols in Fig. 8); catalyst samples exposed to the same reaction temperature of 270 °C, and similar O_2 concentration of about 3.5 vol%, but initial space velocity differing by a factor of roughly two, resulted in the same selectivity, as shown on Fig. 8.

As can be derived from Figs. 4 to 6, catalyst decay, defined as the decrease of rate of formation of ethylene oxide, amounts to 30–70% after some 50 h of time on stream,

depending on the severity of the applied conditions. Obviously, deactivation of the catalyst could be accelerated on the laboratory scale in the range of reaction conditions applied. A drop in reaction rates of only 25% in the first 50 h of time on stream has been reported for the same epoxidation reaction using also a Berty reactor at 270 °C [4]. The difference as compared to the results presented is possibly induced by the difference in reaction conditions and the catalyst itself. The activity decay for 260 and 280 °C together with the corresponding degrees of conversions of O_2 and ethylene is presented in Fig. 10. Regardless of the applied reaction temperature a higher rate of deactivation was obtained on lowering O_2 conversion, which is a further proof that increased oxygen concentration enhances deactivation of the silver catalyst.

TEM micrographs after discharging the catalysts from the reactor at the end of an experiment, are shown in Fig. 11 in comparison to the same catalyst after activation. Corresponding values of the decay of activity (Δa , %) and of selectivity (ΔS , %) as a function of reaction conditions and time on stream are also given. After catalyst activation and prior to exposure to the epoxidation reaction, rather uniform Ag particles of 50–70 nm were observed (Fig. 11a). After being exposed to an O_2 concentration of 5.08 vol% at 260 °C for 70 h of time on stream, Ag particles agglomerate. Besides particles of the original which are still remaining, a certain amount of considerably larger particles were observed (Fig. 11b). The activity under these conditions dropped to about 50% from the initial activity of the activated fresh catalyst. A temperature increase to 275 °C, even at lower O_2 concentration, leads to a dramatic growth of the Ag particles after only 40 h, concomitant with an activity decline to 65% (Fig. 11c). This clearly shows the dominant influence of reaction temperature compared to oxygen concentration, as already pointed out. The maximum reaction temperature applied amounted to 275 °C, and was still 70 °C lower than the Tamman temperature of silver [37], which is necessary for migration of atoms through the silver lattice causing par-

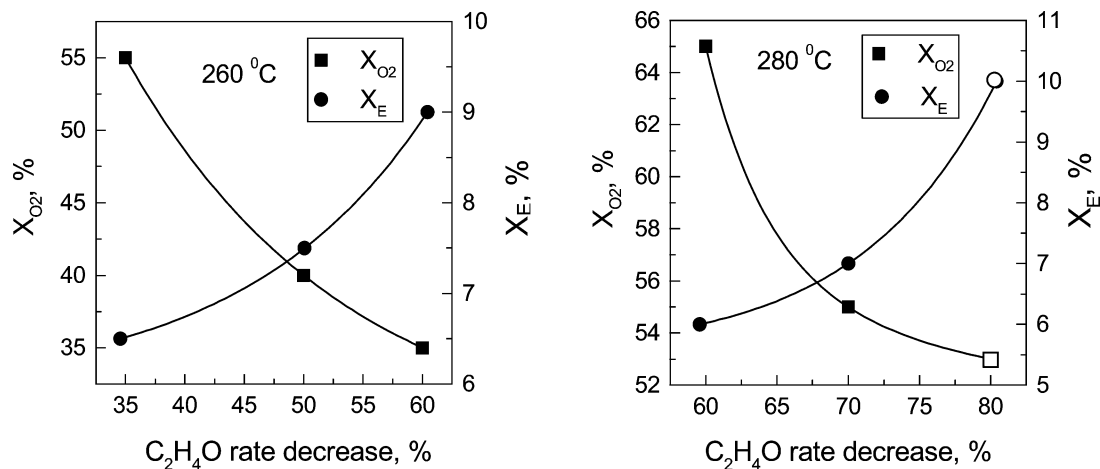


Fig. 10. C_2H_4O rate decrease estimated after some 50 h of time on stream at 260 °C (left) and 280 °C (right), as a function of O_2 conversion (left axis) and ethylene conversion (right axis) (blank symbols at 280 °C are values after only 20 h).

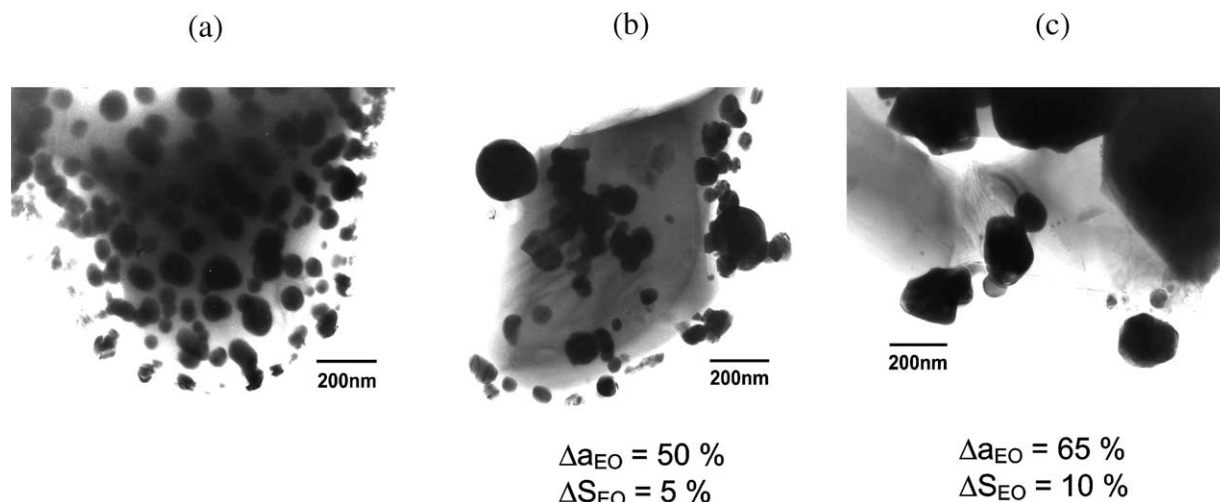


Fig. 11. TEM micrographs of (a) the activated catalyst, (b) after 70 h at 260 °C ($\text{CO}_2 = 5.08 \text{ vol}\%$), (c) after 40 h at 275 °C ($\text{CO}_2 = 3.2 \text{ vol}\%$). Related drops of catalyst activity, Δa_{EO} , and ethylene oxide selectivity, ΔS_{EO} , are indicated in the figure.

ticle growth. It is, however, more than twice as high as the Hüttig temperature, at which surface migration of atoms is possible.

Some preliminary thoughts are put forward on the effect of silver-particle size on catalyst selectivity referring further to Fig. 11. Only a minor change in selectivity has been observed for an activity drop of 50 or 65%, respectively (Fig. 11). Similar to these results, no change of selectivity has been reported in an aging experiment of a silver-catalyst model system of rather large Ag particles [38]; in a 7-day experiment carried out in a Bertly reactor at 270 °C, 19 bar, and a space velocity of 8000 h^{-1} , agglomeration of Ag particles from 300 to 500 nm brought an activity decrease to 60%, but the selectivity remained constant.

The correlation between the size of Ag particles and the extent of the catalyst activity drop is a general feature and has been discussed extensively in the literature [15,16,39]. The epoxidation reaction over Ag-based catalysts appears to be structure sensitive, since the rate of ethylene oxide formation was often found to increase with increasing size of the Ag particles. However, an influence of the reaction rate by particles as big as 70 nm is not common, since structure sensitivity is usually related to much smaller particles [40]. The phenomenon has, therefore, been explained by a change of particle morphology and a support effect [15], but also as a decrease of defects on the surface necessary for adsorption of covalent oxygen ions [41]. Our TEM results revealed, however, no significant differences in the outer appearance of Ag particles of different size. For this reason it is likely that additional reasons contribute to the activity decay. A different extent of metal support interactions to the change of Ag-particle size might be responsible.

5. Conclusions

In the epoxidation of ethylene to ethylene oxide an activation period exists. Initial formation rates of both $\text{C}_2\text{H}_4\text{O}$

and CO_2 increase with increasing reaction temperature and oxygen concentration in the reactor, the first variable being of higher importance. At constant oxygen concentration, initial production of CO_2 is favored by high temperature for the whole range of temperatures applied. An increase of the initial formation rate of ethylene oxide at constant high O_2 concentration, however, is limited to temperatures ≤ 270 °C. Below 270 °C an increase of O_2 concentration leads even to an increase of ethylene oxide selectivity. At temperatures of ≥ 270 °C the influence of the oxygen concentration and reaction temperature is equal, leading to a selectivity decrease in ethylene oxide with increasing severity of these variables.

Acceleration of the deactivation process of a commercial Ag/ Al_2O_3 catalyst could be achieved by increasing reaction temperature and oxygen concentration within the applied range of reaction conditions. The catalyst declines fastest at the highest reaction temperature and oxygen concentration applied, indicating a cooperative effect in the deactivation process. Hence, both high reaction temperature and high oxygen concentration are responsible for Ag catalysts in the commercial deactivation process.

The loss in catalyst activity amounts to 30 to 70% in 50 h of time on stream depending on the severity of conditions applied. The catalyst activity decay is related to the degree of agglomeration of Ag particles; this points to sintering as the main deactivation mechanism of the catalyst. The time for particle growth and hence deactivation depends on reaction temperature and O_2 concentration to which the catalyst is exposed during operation.

Notations

C_i^0 concentration of component i in the feed (vol%),
 C_i concentration of component i in the reactor (vol%),
 R_i reaction rate of formation of component i [mol/($\text{L}_{\text{CAT}} \text{ h}$)],

F_{tot} total molar flow rate (mol/h),
 $C_{2=}^0$ concentration of ethylene in the feed,
 $C_{2=}$ concentration of ethylene in the reactor,
 $RC_{2=}$ reaction rate of ethylene consumption [mol/(L_{CAT} h)],
 S selectivity (%),
 V_{CAT} catalyst volume (l).

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