A TRANSIENT KINETIC STUDY OF ETHYLENE EPOXIDATION OVER Ag/SiO$_2$

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Abstract—Transient kinetics of ethylene epoxidation over a Ag/SiO$_2$ catalyst has been studied at relatively low temperatures (110-130°C) using an automated square pulse cyclic reactor. It is observed at this low temperatures that the formation of CO$_2$ and H$_2$O was retarded compared to epoxide formation. The 100% selectivity toward ethylene oxide was obtained after hydrogen treatment of the catalyst surface. It indicates that maximum selectivity of 6/7 based on classical molecular oxygen hypothesis should be carefully reviewed. The participation of both atomic and molecular oxygen to epoxide formation was postulated, but the former probably after recombination with subsurface oxygen.

INTRODUCTION

The mechanism of the epoxidation of ethylene with oxygen over silver catalyst has been largely studied as this reaction is not only of industrial importance but also of fundamental interests in surface science. Although the subject has been extensively reviewed [1-4], the question on the identity of the epoxidizing species, i.e. chemisorbed atomic oxygen or chemisorbed molecular oxygen is still under considerable discussion. One model is based on the molecular oxygen hypothesis claiming that molecular oxygen participates to ethylene oxide (EO) formation while atomic oxygen leads only to CO$_2$ [1,5-8], but the other attributes both EO and CO$_2$ production to atomic oxygen [9-12]. The maximum selectivity of 6/7 (85.7%) according to classical prediction [1,13] is based on the molecular oxygen hypothesis.

It is well known that the study of transient phenomena occurring on the catalyst surface offers many interesting informations for defining the elementary steps of the reaction [14-16]. Therefore the automated square pulse cyclic reactor coupled with G. C. [16] was employed in the present study, where we now investigate the effect of hydrogen treatment and EO adsorption on the mechanism of this reaction.

EXPERIMENTAL

1. Catalyst

The supported silver catalyst was prepared using incipient wetness technique described previously [17].

The catalyst support used in this study was silica supplied by Prolabo (Spherosil XOB 030, surface area 63 m^2/g). This catalyst contained 25 wt % of silver and 2 wt % of barium. Transmission electron micrographs of the catalyst particles showed that silver was present as spherical particles of about 250 Å in diameter.

2. Apparatus and procedure

The automated square-pulse cyclic reactor system described in the previous paper [16] was used to study the performance of the silver catalyst under transient conditions. After pretreatment of the supported silver catalyst by hydrogen at 270°C for 4h, and then reactant mixture (C$_2$H$_4$ = 38%, O$_2$ = 12%, N$_2$ = 50%) at 180°C for 24 h the catalyst was stable and ready for operation. The amount of catalyst packed in the U-type stainless-steel reactor (I.D. = 4.7 mm, L = 30 cm) was 1.2g and the total flow rate of gases was 3 l/h.

A typical experiment was conducted in the following way. First the conditioned catalyst was cleaned by an oxygen pulse (O-pulse) followed by a hydrogen pulse (H-pulse) and then another oxygen (O-pulse) was allowed to adsorb onto the clean catalyst surface. Then ethylene pulse (E-pulse) was admitted to react with the preadsorbed oxygen. Four main pulses, namely, ethylene (E), oxygen (O), hydrogen (H) and oxygen (O) were separated by nitrogen (N) pulses. This 8-pulse cycle is called E-N-O-N-H-N-O-N cycle.

After a pseudo steady state condition is obtained, the reactor effluent is analyzed by on-line G.C. at any chosen time from the beginning of the cycle [16]. For ease of the observation of transient behavior, we have conducted our experiments at relatively low tempera-
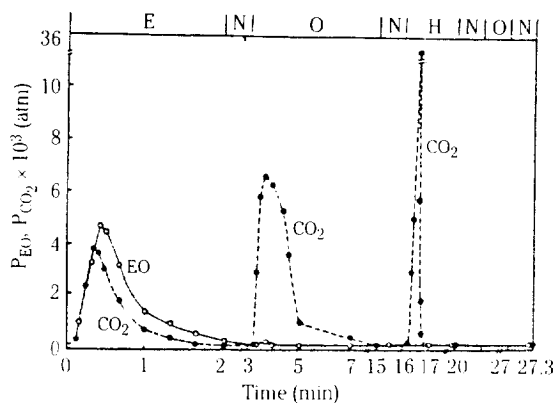
Fig. 1. A cyclic response of E-N-O-N-H-N-O-N cycle (2-1-12-1-4-1-6-0.3 in minutes) at 130°C.
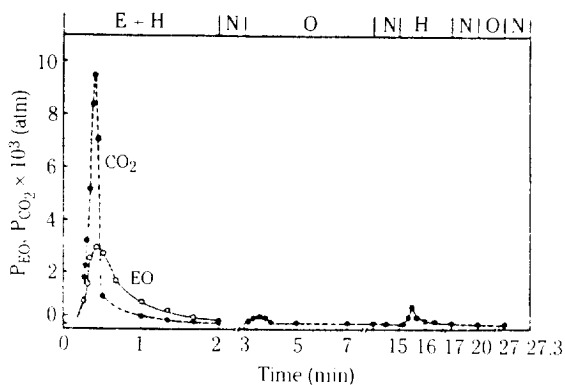

Fig. 2. A cyclic response of (E+H)-N-O-N-H-N-O-N cycle where (E+H)-pulse was composed of 2% H_2 and 98% C_2H_4.

The other conditions are the same as in Fig. 1.

tures (110-130°C).

RESULT

A typical transient response of EO and CO_2 with E-N-O-N-H-N-O-N cycle at 130°C was shown in Figure 1. It could be noted firstly that the evolution of EO and CO_2 with time was much slower and easier to observe compared with that of actual high temperature process (180 to 250°C). Two types of reaction intermediates desorbed as CO_2 were observed in the oxygen and hydrogen pulse. These could not be detected at steady state operation. They are reaction intermediates irreversibly chemisorbed on catalyst surface (deposits). The CO_2 desorbed in the O-pulse by combustion of the deposits is probably due to reaction intermediates of an alkoxide or acetate type and that desorbed in the H-pulse is due to mono- or bidentated carbonate [3,16,18]. Figure 1 shows that the rate of epoxidation and total combustion decreases sharply as long as the reaction intermediates cover the catalyst surface inhibiting the adsorption of ethylene and oxygen. At steady state operation the silver catalyst surface would always be partially covered with the deposits.

Figure 2 shows the results obtained when 2 vol % of hydrogen was added in the pure ethylene pulse. The hydrogen accelerated the desorption of CO_2 and inhibited ethylene oxide formation as shown in (E+H)pulse. The quantity of the deposits desorbed as CO_2 in O-pulse and H-pulse was very small compared with Figure 1. The large amount of CO_2 production within at about first 30 seconds is mainly due to the desorption of some deposits before their build-up to strongly chemisorbed species. After that, as long as epoxidation proceeds, the oxygen atom produced by epoxidation participates to the fabrication of deposits
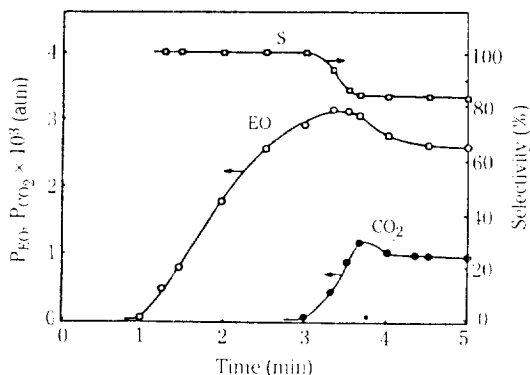

Fig. 3. A cyclic response in E-pulse with E-N-O-N-H-N cycle (5-1-10-1-1-1 in minutes) at 110°C.

and it results to the decrease of both epoxidation and total combustion rate.

Another series of experiments was carried out with E-N-O-N-H-N cycle and R-N-O-N-H-N cycle, the reactant pulse (R-pulse) in the latter case was composed of 80% ethylene and 20% oxygen. Figure 3 shows the response of E-N-O-N-H-N cycle at 110°C where pre-adsorbed oxygen was evacuated in nitrogen pulse followed by hydrogen pulse. It could be assumed that after this treatment chemisorbed surface oxygen would probably be sufficiently eliminated producing H_2O with hydrogen, and that only subsurface oxygen rests on the catalyst. Then pure ethylene pulse was allowed to pass onto the catalyst of chemisorbed subsurface oxygen. It is clearly shown that the epoxidation reaction occurs firstly and the production of CO_2 and H_2O starts more lately.

Another very important observation is that the selectivity of EO is maintained at 100% not producing
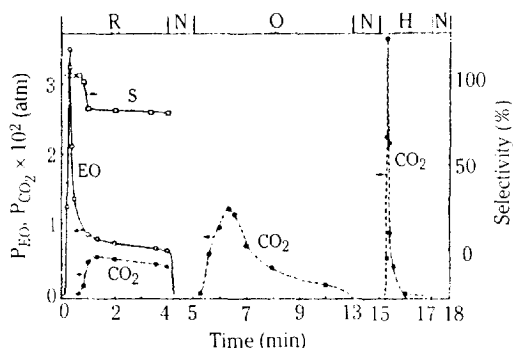
Fig. 4. A cyclic response of R-N-O-N-H-N cycle (4-1-8-2-2-1 in minutes) at 130°C.
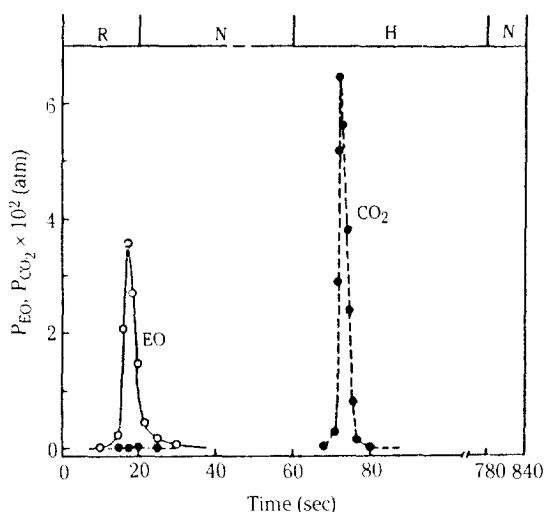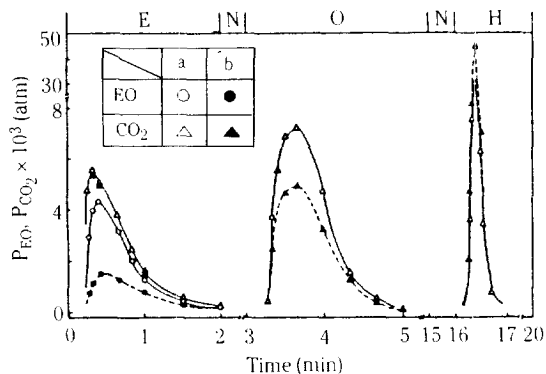

Fig. 6. The effect of ethylene oxide adsorption.

(a); E-N-O-N-H-N-O-N cycle (2-1-12-1-4-1-6-5 in minutes) without introduction of EO, (b); E-N-O-N-H-N-O-N-(N + EO)-N cycle (2-1-12-1-4-1-6-1-1-3 in minutes) where (N + EO)-pulse was composed of 2% EO and 98% N_2.

Fig. 5. A cyclic response of R-N-H-N cycle (20-40-720-60 in seconds) at 130°C.

The short R-pulse was composed of 80% C_2H_4 and 20% O_2. The temperature in H-pulse was maintained at 180°C and other pulses at 130°C.

at 130°C for very short time (during 20 seconds). Figure 5 shows that in the reactant pulse only EO production was obtained, indicating that the deposit had not enough time to build up and react with oxygen to produce CO_2 in this short R-pulse. But the presence of carbonate type deposit was identified in H-pulse.

Figure 6 shows that the effect of ethylene oxide adsorption on EO and CO_2 production rate. At the end of E-N-O-N-H-N-O-N cycle 2 vol.% of EO in nitrogen was allowed to adsorb on the catalyst surface during 1 minute followed by nitrogen pulse of 3 minutes before passing ethylene pulse. The cyclic response with and without EO adsorption was presented together in this figure. It can be postulated from the result that adsorbed EO covers the silver surface inhibiting the epoxidation reaction. The amount of CO_2 produced is practically equal in two cases but it does not mean that EO adsorbed surface inhibits only epoxidation reaction, but it also inhibits total combustion reaction. About half of the CO_2 produced in the case of EO adsorption may probably result from the decomposition of adsorbed EO.
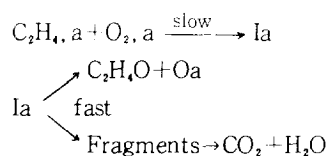
The selectivity of epoxide in E-pulse with EO adsorption was lower than that obtained without EO adsorption. But at the steady state operation, a slight increase of selectivity was observed in our earlier studies [16]. We have addressed this selectivity increase to the carbonate type deposit. The increase of CO_2 in H-pulse and the decrease in O-pulse was also observed in Figure 6.

CO_2 during about 2 minutes. It is a direct evidence that the maximum selectivity is not limited at 6/7 according to the classical molecular oxygen theory.

The experiment with R-N-O-N-H-N cycle (Figure 4) showed also the selectivity towards epoxide higher than 6/7 during about 40 seconds. But in this case the formation of CO_2 is not so largely retarded because the gas phase oxygen in the reactant pulse adsorbs on the surface of catalyst and participates in both epoxide and CO_2 formation.

One of the cyclic experiment with R-N-H-N cycle was conducted without use of oxygen pulse. Where hydrogen pulse was passed at 180°C for 12 minutes, but the reactant pulse (80% C_2H_4, 20% O_2) was passed

DISCUSSION

Oxygen adsorbs both molecularly and dissocia-

tively on silver although the nature of the oxygen species necessary in the epoxidation reaction is still under considerable discussion. But it is generally accepted that adsorbed oxygen is required to ethylene adsorption on silver and that the adsorbed ethylene participates in both the epoxidation and the complete combustion pathway [6,19].

The results of our pulse experiments clearly indicate that ethylene reacts firstly with adsorbed oxygen, whereas carbon dioxide and water are formed via some adsorbed reaction intermediates. It is consistent with our previously proposed reaction mechanism involving two types of deposits [16] and with that of other authors [3,4,20]. The epoxidation mechanism proposed by Campbell [21] after studying chlorine effect on reaction selectivity;

$$C_2H_4, a + O_2, a \xrightarrow{slow} Ia$$

$$Ia \begin{cases} \nearrow C_2H_4O + Oa \\ fast \\ \searrow Fragments \rightarrow CO_2 + H_2O \end{cases}$$

shows that the selectivity is determined by the branching ratio of fast step leading to the decomposition of this intermediate (Ia). Fragmentation of the intermediate seems to require larger ensembles of chlorine-free Ag sites than the epoxidation branch.

The 100% of initial selectivity to epoxide obtained in Figure 3 and 4 support the hypothesis of the recombination of the surface adsorbed atomic oxygen with the subsurface oxygen atom. If atomic oxygen participates only to the total combustion reaction, the selectivity should never exceed 6/7. Van Santen and De Groot [22] postulated the incorporation of atomic oxygen into epoxide by their oxygen isotope study and they exclaimed no selectivity limit for EO even though they did not observed it directly in their experiments.

The effect of hydrogen pretreatment on silver surface studied by Sandler and co-workers [23] showed that the presence of hydrogen (not completely desorbed after pretreatment) reduced the activation energy for the more weakly chemisorbed oxygen desorption. The activation of catalyst by hydrogen pulse in R-N-H-N cycle could be attributed to the increase of oxygen desorption.

The large decrease of deposits in O- and H-pulse with the use of 2 vol.% hydrogen in E-pulse (Fig. 2) could point out that the irreversibly chemisorbed deposits might be formed via several intermediate steps. Once the hydrogen desorbed certain initial deposit in form of CO_2 the ultimate quantity of deposit was largely decreased. With the results of the decrease of the deposit desorbable by hydrogen, the selectivity to

epoxide is much lower in Figure 2 compared with Figure 1. And these are in accordance with our steady state experiments [16,24]. We have observed that high selectivity was obtained with high ratio of ethylene to oxygen partial perssure and that the amount of deposits increased with this ratio of two reactant. The deposits inhibit more strongly the formation of CO_2 than EO production.

Our results on the effect of CO_2 [16] and EO on the deposit formation (Figure 6) showed the increase of carbonate type deposit, and other studies on the role of EO [19] and CO_2 [25] supported the increase of selectivity toward epoxide. Therefore, the introduction of small amount of CO_2 to reactant mixture in commercial EO plant would probably be based on the object of increasing certain quantity of deposit favorable for EO formation not so much decreasing the conversion of ethylene.

CONCLUSION

The transient kinetic study of ethylene epoxidation was carried out at relatively low temperatures (110-130°C) and the reaction mechanism was postulated with the aid of slower dynamic response.

The epoxidation reaction occurs fastly with chemisorbed molecular oxygen and the total combustion product was formed via several intermediate steps of deposit formation. The chemisorbed subsurface atomic oxygen could recombine with surface oxygen atom, therefore 100% of EO selectivity was obtained by the use of hydrogen treatment.

The role of reaction product on the increase of EO selectivity was due to the increase of the deposit build-up favorable to EO formation.

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