
ATTI ACCADEMIA NAZIONALE DEI LINCEI
CLASSE SCIENZE FISICHE MATEMATICHE NATURALI
RENDICONTI

GIANFRANCO LIBERTI, ADRIANO MATTERA, FABRIZIO
PEDRETTI, NICOLA PERNICONE, SERGIO SOATTINI

**Pulse microreactor study of ethylene oxidation over
silver oxide**

*Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche,
Matematiche e Naturali. Rendiconti, Serie 8, Vol. 52 (1972), n.3, p. 392–397.*
Accademia Nazionale dei Lincei

<http://www.bdim.eu/item?id=RLINA_1972_8_52_3_392_0>

L'utilizzo e la stampa di questo documento digitale è consentito liberamente per motivi di
ricerca e studio. Non è consentito l'utilizzo dello stesso per motivi commerciali. Tutte le
copie di questo documento devono riportare questo avvertimento.

*Articolo digitalizzato nel quadro del programma
bdim (Biblioteca Digitale Italiana di Matematica)
SIMAI & UMI*

<http://www.bdim.eu/>

Chimica. — *Pulse microreactor study of ethylene oxidation over silver oxide* (*). Nota di GIANFRANCO LIBERTI, ADRIANO MATTERA, FABRIZIO PEDRETTI, NICOLA PERNICONE e SERGIO SOATTINI, presentata (**) dal Socio G. B. BONINO.

RIASSUNTO. — L'ossidazione dell'etilene su Ag_2O è stata studiata mediante microreattore a impulso, per accertare il decorso della reazione in presenza di specie superficiali O^- . Si ha soltanto ossidazione diretta a CO_2 ; ciò è in accordo con l'ipotesi che la formazione di $\text{C}_2\text{H}_4\text{O}$ derivi dall'interazione di C_2H_4 con specie ossigeno legate ad Ag meno fortemente di O^- e probabilmente molecolari [1].

La velocità della reazione tra C_2H_4 e Ag_2O è stata studiata in funzione della concentrazione di C_2H_4 , della velocità di flusso dell'impulso e della temperatura. I risultati sono stati interpretati sulla base della successione di due stadi lenti: chemisorbimento di C_2H_4 e diffusione dell'ossigeno verso la superficie.

È stata infine discussa la possibile esistenza di composti intermedi, in particolare CO.

Ethylene oxidation to ethylene oxide and carbon dioxide has been the subject of a number of investigations and some comprehensive reviews recently appeared [1], [2]. The existence of two parallel reactions has been firmly established; therefore it is probable that two different oxygen adsorbed species are working out. It has been suggested that a molecular, weakly chemisorbed oxygen species is responsible for epoxidation, and that an atomic strongly chemisorbed oxygen is involved in deep oxidation [3-6]. To get further insight into this problem, we have carried out a kinetic study of ethylene oxidation by the solid phase oxygen of Ag_2O , using a pulse microreactor.

EXPERIMENTAL

The experimental apparatus is sketched in fig. 1. The flow rates of C_2H_4 and N_2 are measured by means of precision flowmeters. By rotation of the valve V_1 , a reacting gas pulse (1 cc) is led to the reactor with a selected flow rate. By the subsequent rotation of the valve V_2 (when the pulse is passing through the 20 cc coil S 2) the reacted pulse is led to the chromatographic column. The time elapsed between the rotation of the two valves is, from 3 to 8 seconds, depending on the He 1 flow rate. No detectable broadening of the gas-chromatographic peaks was observed. This system has allowed a flow rate variation in the range 3-40 Nl/h without affecting the carrier gas flow rate in the chromatographic column (1 cc/sec).

Silver oxide was prepared by precipitation under CO_2 -free nitrogen, adding AgNO_3 1 M to KOH 1 M. The precipitate was washed with hot

(*) Istituto Ricerche « Guido Donegani » (Montecatini-Edison)-Novara.

(**) Nella seduta dell'11 marzo 1972.

CO_2 -free water and dried 40 hours at 80°C and 5 hours at 100°C . Free silver, determined by titration [7], was less than 0.05 %. Surface area was $0.8\text{ m}^2/\text{gr}$ and lowered to $0.6\text{ m}^2/\text{gr}$ after heating at 200°C for 10 hours. Thermogravimetric runs showed a first weight loss of about 0.2 % (due to silver carbonate decomposition) at 120°C ; oxygen loss began only at temperatures over 230°C .

The amount of catalyst loaded in the reactor was 1 gr, the catalytic bed length 6 mm, its section 0.67 cm^2 , void fraction about 0.4. Particle size was about 0.4 mm. Every 20–30 pulses, a standard run was made to test

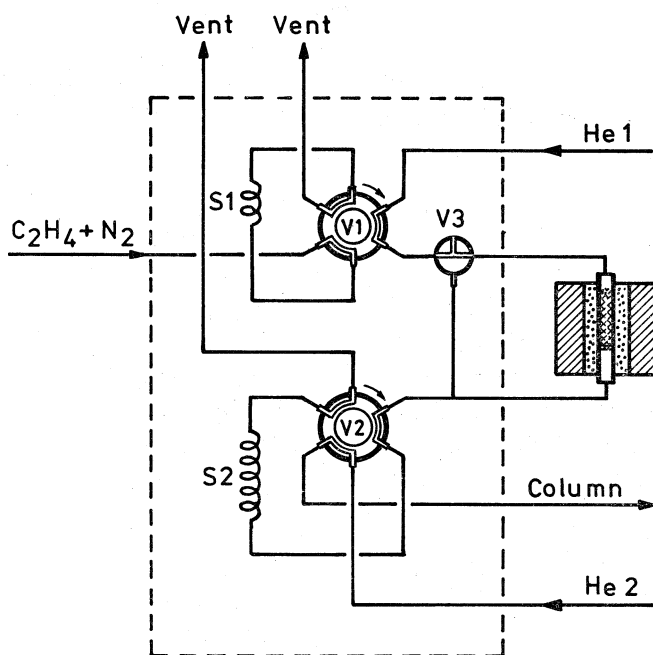


Fig. 1. – Scheme of the experimental apparatus.

the catalyst deactivation due to oxygen loss for both ethylene oxidation and Ag_2O decomposition (the latter very slow at our reaction temperatures). In fact in our reaction conditions reoxidation is not possible. The catalyst was changed when an activity loss greater than 10 % was detected. At 214°C it was possible to use the same catalyst for about 100 pulses before detecting an appreciable deactivation; at 250°C the same catalyst could not be used for more than 40–50 pulses. The reacting gas was high purity ethylene diluted with nitrogen. Gas chromatographic analysis was made by a 2 mt. Porapack R column, at 120°C , using helium as carrier gas.

A correction was made to account for the volume change of the pulse during the reaction. The estimated error of the reported data was less than $\pm 10\%$ (90 % probability level). The reaction rates were calculated considering

the reactor as a differential one. This procedure is justified by the low conversion (usually not higher than 30 %) and by the nearly rectangular shape of the pulse [8].

RESULTS AND DISCUSSION

Preliminary experiments showed that:

the use of oxygen instead of nitrogen as diluent gas did not change the conversion, therefore the reacting oxygen came from the solid phase only;

ethylene oxide was not oxidized by Ag_2O in the temperature range investigated (180–250°C);

the reaction between ethylene and Ag_2O gave practically CO_2 and H_2O only; however small amounts of ethylene oxide appeared at higher temperatures.

These results are in complete accordance with the existence of two parallel reactions. The formation of ethylene oxide should arise from interaction between ethylene and oxygen chemisorbed on Ag, (both molecular oxygen and silver coming from the decomposition of Ag_2O). Further information on the mechanism of the interaction between ethylene and Ag_2O were obtained by varying the working conditions.

In fig. 2 the amounts of disappeared ethylene (the difference between input and output ethylene) and produced CO_2 are reported versus the pulse

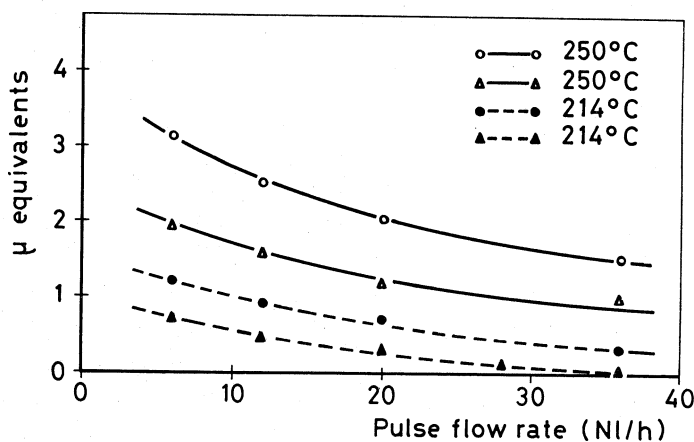


Fig. 2. - Amounts of C_2H_4 disappeared (\circ , \bullet) and of CO_2 formed (Δ , \blacktriangle) versus pulse flow rate.

flow rate. It may be seen that a defective mass balance occurs, that is an amount of substance remains adsorbed on the catalyst after the passage of the pulse. This seems to be a common phenomenon in pulse reactors [8]. From the results reported in fig. 2 an increase of the reaction rate with the

pulse flow rate can be deduced. It may be due, as previously discussed [9], to surface heterogeneity and/or to poisoning by products.

In fig. 3 the reaction rates calculated from C_2H_4 disappearance (*a*) and from CO_2 production (*b*) are reported versus inlet C_2H_4 concentration. The reaction is nearly first order in the former case, with an apparent activation energy of 13.5 kcal/mole, and tends to zero order in the latter, with an

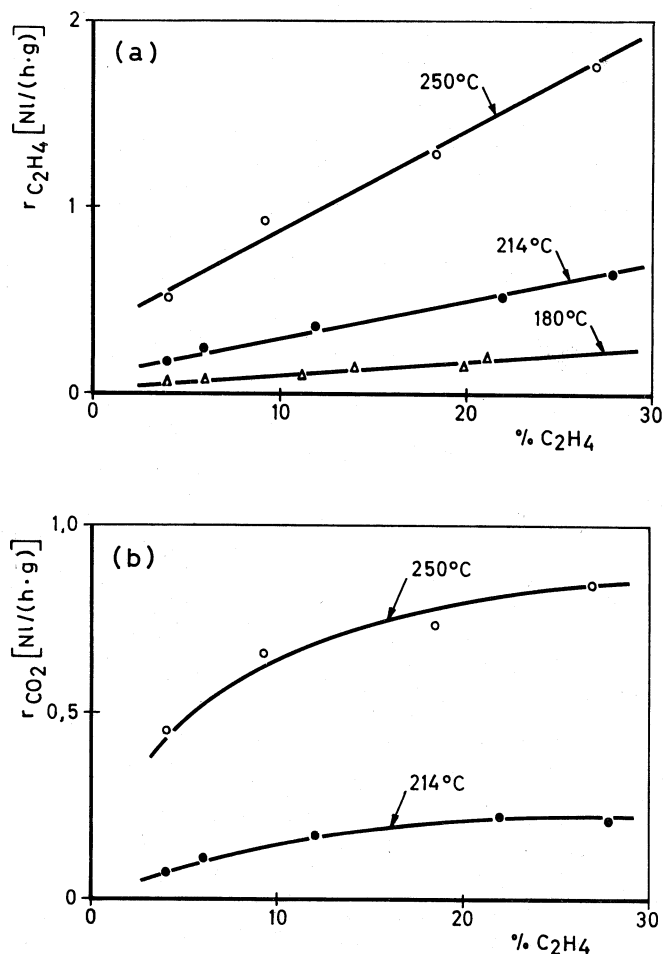


Fig. 3. — Reaction rate calculated from C_2H_4 disappeared (*a*) and from CO_2 formed (*b*) versus inlet C_2H_4 concentration.

apparent activation energy of 15 kcal/mole. This behaviour may be explained by supposing that C_2H_4 adsorption is a rather slow process and that a subsequent reaction step is slower, possibly oxygen diffusion from the bulk. Such a different kinetic behaviour obviously causes a dependence of the mass defect on C_2H_4 inlet concentration. Moreover, in fig. 4 a constant temperature correlation was found between the mass defect and the amount of disappeared ethylene. It may be seen that, for a given amount of disappeared ethylene,

the mass defect is higher at lower temperatures, irrespective of the pulse flow rate. This implies a dependence between temperature and amount of surface oxygen available for reaction. In our experimental conditions, without oxygen in the gaseous phase and at temperatures higher than that of oxide decomposition, surface oxygen should come from the bulk by diffusion. However the surface oxygen concentration could not be sufficient to oxidize all the chemisorbed ethylene, the excess of which in this case would stay in a chemisorbed state (may be as an intermediate species) after the passage of the pulse, as long as other oxygen will diffuse from the bulk.

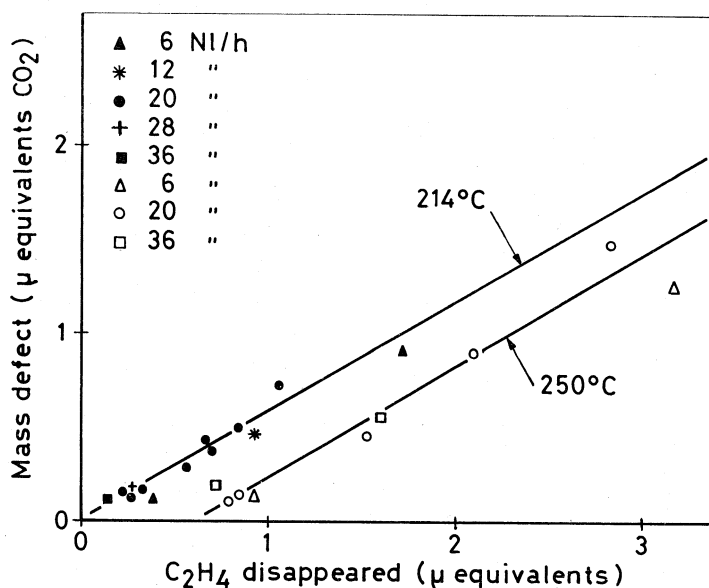


Fig. 4. - Mass defect versus C_2H_4 disappeared for various pulse flow rates.

The problem of the possible existence of intermediate compounds in C_2H_4 oxidation has been recently risen by Macdonald and Hayes [10] who have reported formaldehyde as a reaction intermediate in ethylene to CO_2 oxidation. In our experimental conditions, even at the highest pulse flow rates, we were not able to detect any additional chromatographic peak. On the contrary, by quickly cooling the reactor just after the passage of a pulse, then by slowly heating in helium stream, the presence of a small amount of CO was detected in the exit gas at about $170^\circ C$. This would lead to the conclusion that CO should be an intermediate reaction and that the oxidation of adsorbed CO to CO_2 would be the slowest step of the reaction. Keulks and Chang [11] have reported this step to be rate determining in the silver catalyzed CO to CO_2 oxidation. However, it remains to be explained why CO is not desorbed at the reaction temperature, though an answer might be found, supposing that the activation energy of the step leading to CO would be lower than that of the CO to CO_2 oxidation.

REFERENCES

- [1] H. H. VOGEL and C. R. ADAMS, «Advances in Catalysis», *17*, 151 (1967).
- [2] R. J. SAMPSON and D. SHOOTER, «Oxidation and Combustion Reviews» (C.F.N. Tipper Ed.), vol. I, Elsevier, Amsterdam 1965, p. 223.
- [3] S. KAGAWA, K. KONO, H. FUTATA and T. SEIYAMA, «Kogyo Kagaku Zasshi», *74*, 819 (1971).
- [4] J. MIKAMI, S. SATOH and H. KOBAYASHI, «J. Catal.», *18*, 265 (1970).
- [5] R. E. KENSON and M. LAPKIN, «J. Phys. Chem.», *74*, 1493 (1970).
- [6] W. HERZOG, «Ber. Bunsenges. physik. Chem.», *74*, 216 (1970).
- [7] J. C. LAGIER, «Thèse», Univ. Lyon, *26* (1970).
- [8] G. LIBERTI, N. PERNICONE and S. SOATTINI, «Rend. Accad. Naz. Lincei», ser. VIII, *49*, 124 (1970).
- [9] G. LIBERTI, N. PERNICONE and S. SOATTINI, J. Catal., in press.
- [10] R. W. MACDONALD and K. E. HAYES, «J. Catal.», *15*, 301 (1969).
- [11] G. W. KEULKS and C. C. CHANG, «J. Phys. Chem.», *74*, 2590 (1970).