*Thermochimica Acta*, 47 (1981) 333—341
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

# COMPARATIVE STUDY OF THE BOND ENERGY OF OXYGEN AT THE SURFACE OF SUPPORTED SILVER CATALYSTS AND OF THE ACTIVITY OF THESE CATALYSTS FOR ETHYLENE EPOXIDATION

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(Received 12 March 1981)

## ABSTRACT

A heat-flow microcalorimeter equipped with a pulsed flow reactor has been used to study the reaction of oxygen, at 473 K, with a series of silica-supported silver catalysts. Combustion of impurities with the production of carbon dioxide and water was detected and allowed to correct the calorimetric data. At 473 K, adsorption of oxygen at the surface of silver is a fast process; incorporation of oxygen into deeper metal layers, though present, is a slow process. The differential heats of interaction decrease with increasing amounts of consumed oxygen but always exceed the heat of formation of bulk silver oxides. The average heat of formation of an oxygen monolayer varies from sample to sample and is correlated with the intrinsic activity of the catalysts for ethylene oxidation: surface oxygen species are apparently more catalytically active when they are less energetically bonded to the silver surface.

## INTRODUCTION

Oxidation of ethylene on silver to yield ethylene oxide is a good example of an industrial catalytic process with a good selectivity (~75%). It is well known, however, that the catalyst activity, selectivity and/or stability are very much dependent upon the mode of preparation and/or the reaction conditions. During the catalyst preparation, for instance, silver lactate is preferred to silver nitrate since, being less soluble, it will crystallize faster during the drying period and this will help to give a more even silver deposit, by reducing crystal growth, and thereby a more active catalyst [1]. Organic halogen compounds such as 1,2-dichloroethane or chlorobenzene are commonly added to the gas feed to increase the reaction selectivity towards ethylene oxide [2]. Moreover, several studies have demonstrated that the intrinsic activity of silver in this reaction (i.e. the activity expressed per unit metal area) is not constant, at a given temperature and for a given gas feed, but varies with the dispersion of the metal phase on the catalyst support [3,4]. This indicates that all the silver atoms, exposed at the metal surface, are not equivalent with respect to the reagents (ethylene and oxygen) and that the catalyst activity is regulated by some property of the surface metal atoms which, in turn, varies with the particle diameter.

In a recent study, Gravelle and co-workers [5] have confirmed the preceding observation but have moreover shown that the intrinsic activity does not monotonously follow the variation of particle size. It appears, indeed, that silver particles with an identical diameter can exhibit different intrinsic activities when they have been prepared or pretreated differently. However, from an analysis of the kinetic equation which fits the data obtained for all the catalysts, they have observed that the changes of intrinsic activity can apparently be associated with parallel changes of the equilibrium constant for oxygen adsorption. This suggests a possible correlation between the catalysts affinity towards oxygen and their activity in ethylene epoxidation. The object of the present study was to extend and generalize these preliminary observations. For this purpose, we have evaluated, at 473 K, the heat of interaction of oxygen with a series of silver catalysts which had been previously tested, at the same temperature, in the ethylene oxidation reaction [5,6].

## EXPERIMENTAL

The catalysts of the F series (Table 1) were prepared by adding formaldehyde, at 323 K, to aqueous solutions of ammonia containing silver nitrate and the support (silica, 340 $m^2\ g^{-1}$), in defined proportions. After 60 min, the solids were filtered, washed, dried at 393 K, crushed and sieved (50—100 μm grain size). In the case of catalyst 20-H-2 (Table 1), the support (silica, 340 $m^2\ g^{-1}$) was added to an aqueous solution of ammonia containing silver nitrate, at 293 K. After 30 min, the solid was filtered, dried at 393 K, crushed and sieved. Reduction of the silver complex ions, $Ag(NH_3)_2^+$, at the surface of the support, is achieved in situ, before any experiment with the 20-H-2 catalyst, by flowing hydrogen ($p = 10^5$ Pa) at 523 K during 14 h. A detailed description of the preparation and characterization of the different catalysts has been given by Jarjoui et al. [7].

Catalyst D-31-H is an industrial catalyst, kindly supplied by Degussa and tested for comparison purposes. Metal loading (in wt. % Ag), metal area and average diameter of the silver particles, determined by oxygen adsorption experiments and confirmed by electron microscopy, are given, for all catalysts, in Table 1.

Traces of carbonaceous impurities are always present at the surface of the catalysts and their reaction with oxygen at 473 K produces carbon dioxide and water. The contribution of these secondary reactions to the total heat produced by the interaction of oxygen with the silver surface may not be negligible [8]. For this reason, we have used, throughout this study, a heat-flow microcalorimeter associated with a pulsed reactor which allows a gas-chromatographic determination of the amounts of unreacted oxygen and secondary products. A description of the instrument combining both techniques, its operation and calibration have been presented elsewhere [9].

Prior to all oxygen-adsorption experiments, the catalyst samples (~0.1 g) are reduced by flowing hydrogen ($10^5$ Pa) at 523 K during 2 h (except for fresh sample 20-H-2, see above). The reactor is then flushed by helium and located in the calorimeter cell, maintained at 473 K. A continuous flow of

TABLE 1

Properties of silica-supported catalysts [5, 7]

| Catalysts | Metal loading (wt.% Ag) | Ave. diam. of metal particles (nm) | Metal area ($m^2\ g^{-1}$ Ag) | Ave. heat of formation of a AgO monolayer (kJ $mole^{-1}\ O_2$) | Catalytic activity ($10^{-8}$ mole $C_2H_4$ $s^{-1}\ m^{-2}$ Ag) | Selectivity (% $C_2H_4O$) |
|---|---|---|---|---|---|---|
| 20-H-2 | 2.15 | 5.3 | 107 | 325 | 211.6 | 62.4 |
| 50-F-2 | 2.20 | 15.0 | 38.2 | 217 | 419.0 | 66.5 |
| 50-F-5 | 4.68 | 17.3 | 33.0 | 206 | 437.0 | 70.4 |
| 50-F-9 | 8.62 | 21.5 | 26.5 | 266 | 354.6 | 71.5 |
| 50-F-17 | 16.65 | 24.8 | 23.7 | 342 | 238.6 | 72.8 |
| D-31-H | 10.00 | 32.5 | 17.5 | 383 | 158.2 | 75.8 |

helium (40 ml $\text{min}^{-1}$) is established through the reactor, and pulses of oxygen (0.38 $\mu$mole $O_2$) are injected in the inert carrier gas, at regular time intervals (40 min). The gas flowing out of the reactor is analyzed by means of a gas chromatograph, equipped with a catharometer.

## RESULTS AND DISCUSSION

Figure 1 summarizes the gas-chromatographic data, recorded during a run with the 50-F-2 catalyst. The first dose of oxygen reacts almost totally with the sample. However, the sample reactivity drops rapidly and, after 10 doses, a large fraction (~80%) of the injected oxygen is detected at the exit of the reactor. Both water and carbon dioxide are formed during the interaction of oxygen with the sample. The quantities of these products very much depend upon the catalyst pretreatment and, for instance, they decrease when the sample has been submitted to several oxidation—reduction pretreatments. Moreover, the amounts of both products decrease when the number of oxygen doses, injected during a given run, increases. From curves 1, 3 and 4 in Fig. 1 it is possible to calculate curve 2, representing the quantity of oxygen actually retained by the silver catalyst during the reaction of each dose.

In order to calculate the amount of heat evolved by the secondary reactions producing water and carbon dioxide and, thereafter, correct the calorimetric data, it should be required, in principle, to determine the nature of the chemical combination(s) in which carbon and hydrogen are engaged, before their reaction with oxygen. Fortunately, this is not necessary:

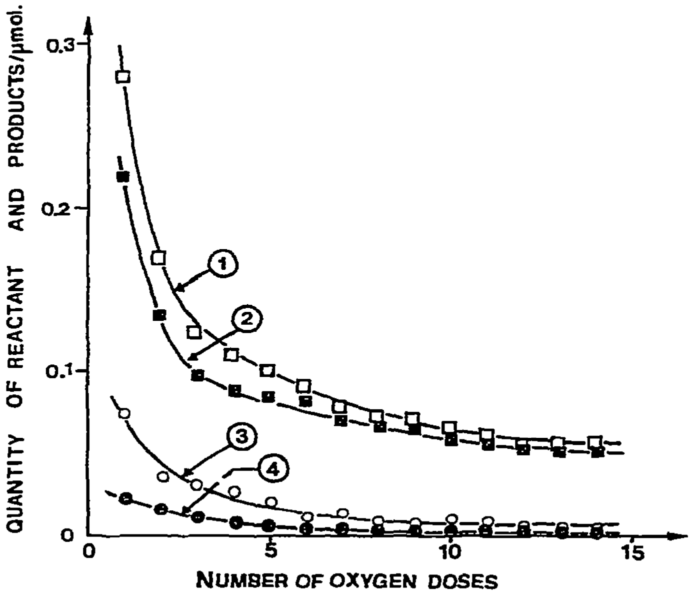

Fig. 1. Gas-chromatographic data for the interaction of successives doses of oxygen (0.38 $\mu$mole $O_2$) with a sample of the 50-F-2 silver catalyst at 473 K: oxygen consumed (1); oxygen retained by silver (2); water (3) and carbon dioxide (4) produced by the combustion of impurities.

because of the large exothermicity of the combustion of either carbon or molecular hydrogen, the final result is not modified, within experimental uncertainty, when different hypotheses on the origin of carbon and hydrogen in the sample are made. We compared, for instance, the two following possibilities: (i) elemental carbon and adsorbed hydrogen ($\Delta H_{\text{ads}} = -42$ kJ mole$^{-1}$), and (ii) long paraffinic chains, simulated by series of —$CH_2$— groups ($\Delta H$ formation = —20.5 kJ mole$^{-1}$) and adsorbed hydrogen. The variation of the corrected heat of adsorption of oxygen, in the case of the first dose of oxygen which reacted with the 50-F-2 catalyst and produced rather large amounts of water and carbon dioxide (Fig. 1), only amounts to 2 kJ mole$^{-1}$, when one set of hypotheses and the other are successively tried. The difference is not significant and, therefore, all following calculations were made with the hypothesis that the impurities are elemental carbon and adsorbed hydrogen.

The corrected calorimetric results are presented on Fig. 2. In all cases (except for the D-31-H sample), the curves summarize several experiments with different samples from the same batch and/or with the same sample reduced anew ($H_2$, $10^5$ Pa, 523 K, 2 h) after its reaction with oxygen. In all cases, when the introduction of doses of oxygen onto the sample was discontinued, the sample was still reactive with respect to oxygen and further doses could have reacted. The amount of oxygen which can be retained by silver, under the conditions selected for this study (473 K, doses of 0.38 $\mu$mole $O_2$, $P_{O_2} = 11.10^3$ Pa, 40 min intervals between doses), and which attained 25 × $10^{18}$ molec. m$^{-2}$ Ag in the case of the 50-F-17 catalyst (Fig. 2), exceeds the maximum amount of oxygen which apparently could be adsorbed during a preceding study with a pulsed reactor [7]. In the previous experiments, the apparent, maximum capacity of adsorption was, for all samples, limited to ~6.5 × $10^{18}$ molec. m$^{-2}$ Ag and this indeed justified the use of oxygen

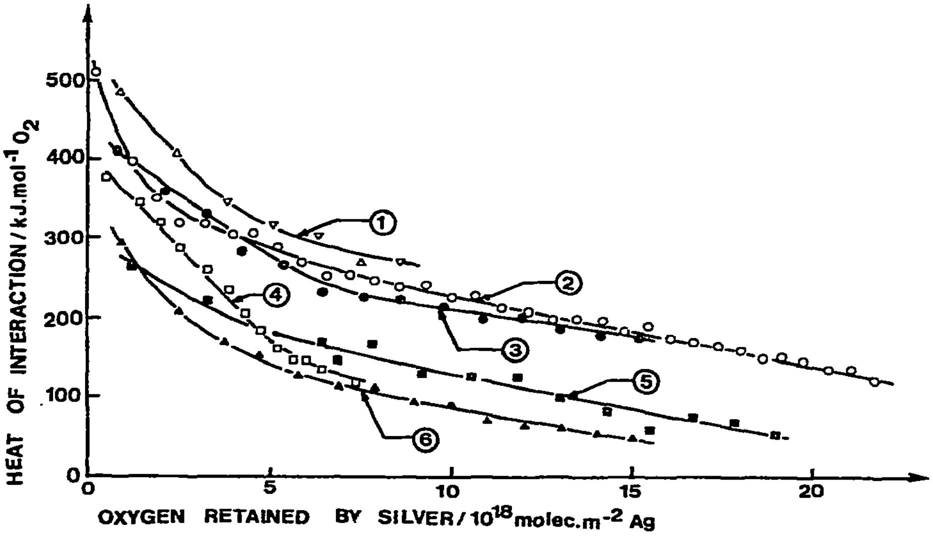

Fig. 2. Differential heats of interaction of oxygen at 473 K with a series of silica-supported silver catalysts: D-31-H (1), 50-F-17 (2), 20-H-2 (3), 50-F-9 (4), 50-F-2 (5) and 50-F-5 (6), as a function of the total amount of oxygen retained by the metal.

chemisorption experiments to determine the metal area [7]. It was then supposed, and indirectly confirmed by electron microscopy, that $6.55 \times 10^{18}$ molec. $O_2$ $m^{-2}$ Ag form a complete monolayer at the surface of silver. The corresponding average stoichiometry of adsorption corresponds to the formation of a AgO layer since, from the probable distribution of (100), (110) and (111) lattice planes at the particles surface [10], the number of silver atoms in the surface layer is generally assumed to be $1.31 \times 10^{19}$ atoms $m^{-2}$ Ag [11]. The quantity of oxygen retained by the samples, during the present study, always exceeds the monolayer capacity and, for instance, corresponds to the formation of four monolayers in the case of the experiment with the 50-F-17 sample (Fig. 2).

The origin of the different behavior of the silver—oxygen system during the two series of experiments with the pulsed reactor can easily be traced and associated with the different time intervals separating the injection of the oxygen doses: only 4 min in the previous study [7] and 40 min in the present one. At 473 K, adsorption of oxygen in the surface layer of the silver particles is a fast process which can take place as the pulse of oxygen passes though the sample (8 s). At 473 K, incorporation of oxygen into deeper silver layers seems to be a slow process. The 4 min-intervals which were used in the former study are not long enough for any substantial incorporation to take place and, consequently, the reaction of oxygen with the sample apparently comes to an end when the first monolayer is saturated. However, during the 40 min-intervals which were used in the present study, some surface oxygen is stabilized into deeper layers, creating free sites at the particle surface where oxygen from a further dose can react.

The $\bar{Q}$ vs. $\theta$ curves in Fig. 2 indicate that the initial heat of interaction of oxygen with all the samples is high (300—500 kJ $mole^{-1}$) but steadily decreases as the total amount of oxygen, retained by the metal, increases. The experimental heats always exceed the heat of formation of either $Ag_2O$ or $Ag_2O_2$ oxides (30.5 and 26.4 kJ $mole^{-1}$, respectively) [12]. Only surface oxidation took place during the experiments summarized in Fig. 2. Complete oxidation of the metal in the 50-F-17 sample, for instance, to form either $Ag_2O$ or AgO bulk oxides would have required, respectively, three or six times the amount of oxygen indicated in Fig. 2. The high heats of interaction of oxygen with silver which were experimentally recorded and which indeed are similar to those reported in previous studies with powdered silver [8,13] indicate that the surface of freshly reduced silver particles contains a large number of lattice defects. The silver atoms in the vicinity of these defects are more reactive with respect to oxygen than normal silver atoms. It is probable also that the result of the interaction is a disordered oxide layer, e.g. containing point defects and/or stacking faults, or even patches corresponding to different stoichiometric compositions ($Ag_2O$, AgO, ...).

There is no distinctive feature in the curves of Fig. 2 that would reveal the occurrence of different processes taking place successively during the reaction of doses of oxygen with the silver samples. The step in the $\bar{Q}$ vs. $\theta$ curve which had been tentatively interpreted by Ostrovskii and Temkin [13] as indicating a transition from $Ag_2O$ to AgO surface species, although it appears in the case of the 50-F-17 sample, is not a general characteristic of these

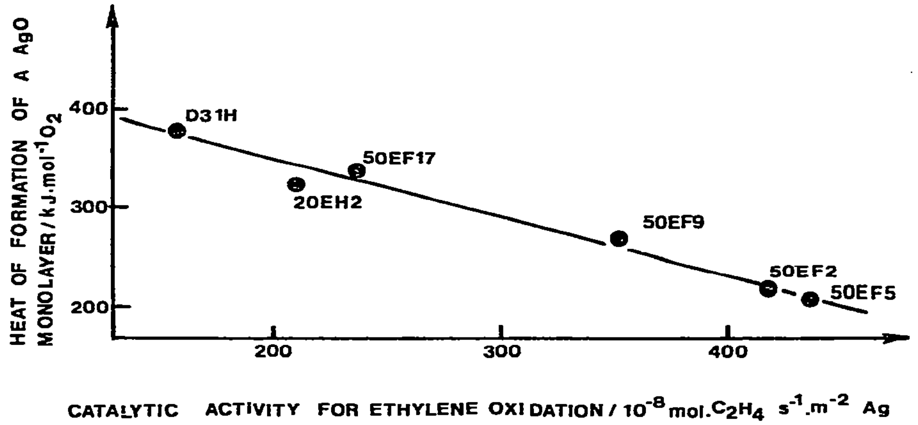

Fig. 3. Average heat of formation of a AgO monolayer at 473 K for a series of silica-supported silver catalysts, as a function of their intrinsic activity for the oxidation of ethylene at the same temperature.

curves. Therefore, the simplest method to quantitatively compare the calorimetric results for the different samples is to determine the average heat of interaction for a given amount of reacted oxygen, e.g. corresponding in all cases to a complete monolayer with a stoichiometry corresponding to AgO. The results of the calculations are given in Table 1.

The catalytic activity of these samples for oxidation of ethylene and their selectivity for the formation of ethylene oxide have been studied and described previously [5]. The results, summarized in Table 1, were obtained with the following experimental conditions: dynamic flow reactor; $P_{O_2} = 12.8 \times 10^3$ Pa; $P_{C_2H_4} = 21.9 \times 10^3$ Pa; $P_{\text{helium}} = 66.7 \times 10^3$ Pa; $T = 473$ K; total flow-rate = 25 ml min$^{-1}$; catalyst mass: 40 mg.

In all cases, the reactants conversion was less than 3% and the results in Table 1 were collected when the catalyst had reached stationary activity (~1 h).

Although, as indicated earlier, the intrinsic activity of the different catalysts changes with the metal particle size, there is no simple correlation between the values of these parameters (Table 1). There is, however, a linear correlation between the catalytic activity of the silver catalysts and the average heat of adsorption of oxygen on their surface, as shown in Fig. 3. It must be noted that the quality of the correlation is not significantly altered if slightly different oxygen coverages are selected for the calculation of the average heats of adsorption.

## CONCLUSIONS

Variation of the intrinsic activity of a catalyst with its dispersion occurs in the case of demanding reactions [14], i.e. reactions which require particular arrangements at the catalyst surface to act as active sites. The number of these structural arrangements usually varies with the dispersion of the catalytic phase, i.e. with the diameter of the particles, but it may also very much depend upon the catalyst preparation and/or pretreatment, when the particles have not attained a configuration corresponding to thermodynamic equilibrium. It now seems well established that ethylene epoxidation is a structure-sensitive reaction [3,5], but, until now, no simple correlation had been proposed to connect the surface structure of the silver catalysts (or some property related to it) and their activity.

The present calorimetric results allow such a correlation. They indicate (Fig. 3) that the intrinsic activity of silver (expressed by the number of moles of ethylene converted at 473 K per unit time and metal area) increases when the average heat of adsorption of oxygen, at 473 K, decreases. The correlation is demonstrated for six catalysts, prepared according to three different methods. A prima facie interpretation of this result could be that the most (catalytically) active sites are also those which are least reactive with respect to oxygen. Thus, the correlation would simply be a method for titrating the most active sites. But oxygen is also a reactant in the epoxidation reaction, and most previous kinetic studies of the reaction have indicated that surface oxygen species take part in the reaction mechanism [1]. Therefore the correlation, presented in Fig. 3, may also mean that the reactivity of the surface oxygen species, with respect to ethylene, increases when they are less strongly bonded to the metal surface. This interpretation is indeed supported by our previous observation of the existence of a correlation between the activity of the catalysts and the equilibrium constant for the adsorption of oxygen on their surface [5].

Partial oxidation of ethylene to ethylene oxide and complete oxidation to carbon dioxide follow independent reaction paths and, most probably, take place on different sites, particularly when the conversion of the reactants is small [1], as in the case of the catalytic runs summarized in Table 1. It could have been hoped to characterize the sites respectively active in the partial and complete oxidation by means of oxygen chemisorption experiments. However, Fig. 2 shows that the $\bar{Q}$ vs. $\theta$ curves do not reveal the existence of different oxygen species and that, consequently, adsorption of oxygen at 473 K is not a sensitive test for separating different surface sites. Finally, the present calorimetric data support the existence of a correlation between the bond energy of oxygen at the catalysts surface and their total activity for ethylene oxidation but no correlation between the energetics of the oxygen adsorption and the selectivity of the catalysts for the production of ethylene oxide can be proposed.

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