

NOTES

Reactivity of Oxygen Adsorbed on Silver Powder in the Epoxidation of Ethylene

It has been recognized that in the oxidation of ethylene over a silver catalyst the selectivity to ethylene oxide is highly determined by the mode of adsorption of oxygen on silver (1-3). However, there is no general consensus as to which oxygen species is active in the epoxidation of ethylene. Recently, it has been shown by application of high-resolution electron energy loss spectroscopy (EELS) in conjunction with temperature-programmed desorption (TPD) that three different types of adsorbed oxygen can be distinguished on the (110) plane of silver after exposure to oxygen at pressures $<10^{-3}$ Pa (4). A single type of adsorbed diatomic oxygen was detected, which dissociated at -100°C and was shown to be the precursor of adsorbed monoatomic oxygen. At temperatures between -100 and $+310^{\circ}\text{C}$, two atomic states may coexist. In one of these states the atom is adsorbed in a fourfold coordinated site on the surface and desorbs at 310°C , while in the second state atomic oxygen is present below the surface and does not desorb at temperatures below 450°C . Occupation of subsurface sites takes place by diffusion of adsorbed atomic oxygen, which occurs above 100°C .

These observations are of interest in view of a model proposed by Temkin (5). He postulates that the presence of surface oxide is essential for the epoxidation of ethylene, the oxygen of this surface oxide being necessary but not active in the epoxidation reaction itself.

In order to clarify the role of subsurface oxygen we have done a number of temperature-programmed reaction experiments using C_2D_4 with oxygen adsorbed on silver

powder. Powders were used in order to ensure a high silver surface area. Oxygen was adsorbed at 20 and 200°C since TPD and EELS experiments (4) had indicated that at 20°C no subsurface oxygen is created at a (110) surface. It should be noted, however, that so far this has only been found for Ag surfaces which had been exposed to oxygen pressure not higher than 10^{-2} Pa.

The silver sample consisted of 10 g of silver powder, which before each measurement was cleaned by repeated oxidations and reductions, with a final hydrogen treatment at 300°C and 1 bar for 16 h, followed by evacuation for a few hours at 300°C . The amount of oxygen adsorbed at 200°C is plotted in Fig. 1 as a function of time. A very fast and a slow activated adsorption can be distinguished, in agreement with the findings of Kilty *et al.* (1). After 30 min an amount of $10\ \mu\text{mol O}_2$ is adsorbed, increasing to $10.2\ \mu\text{mol}$ after 45 min. Only a small amount (7%) of this oxygen is desorbed upon evacuation for 30 min at 200°C . Temperature-programmed desorption up to 300°C results in a single peak at 290°C analogous to the findings in TPD measurements on Ag (110) (4) and Ag (111) (6). The amount desorbed from the powder during evacuation at 200°C and the TPD experiment is $4.2\ \mu\text{mol}$, so in other words, $6.0\ \mu\text{mol}$ remains undesorbed. The EELS measurements have shown for the (110) surface that after desorption at 300°C no surface oxygen is present, so that we postulate that in the Ag powder the $6.0\ \mu\text{mol}$ are accommodated in the subsurface layers. That this subsurface oxygen is also present after adsorption for 30 min at 200°C is evidenced by

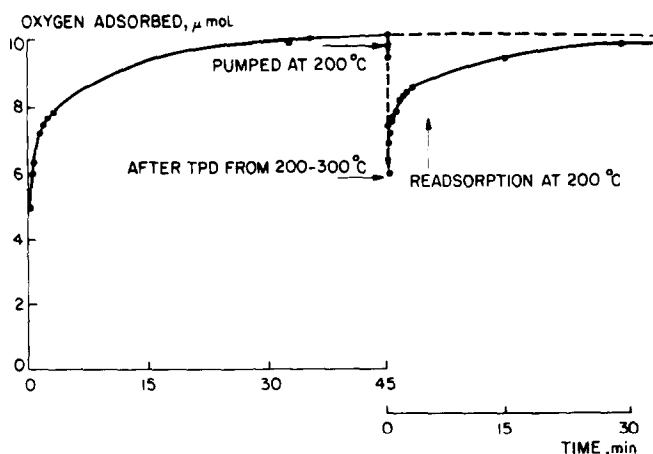


Fig. 1. Amount of oxygen adsorbed as a function of time and temperature.

the fact that after the treatment at 300°C re-adsorption at 200°C results in the same amount and the same kinetics of oxygen adsorption (Fig. 1). In another experiment oxygen was adsorbed at 200 and 20°C for 30 min at 100 Pa and the vessel containing the sample was evacuated at various temperatures. Subsequently 100 Pa C_2D_4 and 100 Pa Ar were admitted at $-80^\circ C$ and the reaction vessel closed. Then the silver was heated at a rate of $5^\circ C/min$, while every 3 min a small amount of the gas was analysed with a mass spectrometer, where the Ar signal served as a calibration for the pressure of EO and CO_2 in the vessel. Since the sampling of gas resulted in a small drop of the overall pressure in the vessel and therefore also of the pressure of Ar the amounts of CO_2 and EO are systematically too high by $\sim 15\%$ at temperatures above $200^\circ C$, the error becoming smaller towards lower temperatures, where less gas was removed for sampling. The amounts of CO_2 and ethylene oxide (EO) formed after adsorption of $10 \mu mol O_2$ at $200^\circ C$ and subsequent evacuation at $-80^\circ C$ are plotted in Fig. 2. A maximum amount of EO is obtained at $135^\circ C$; the subsequent decrease in EO shows that EO is further oxidized to CO_2 , as is also evidenced by an increase in CO_2 . As this consecutive reaction may also take place below $135^\circ C$ the quantity of EO ob-

served at this temperature is a lower limit for the quantity initially formed.

The amounts of CO_2 and EO detected at 300 and $135^\circ C$, respectively, after various oxygen pretreatments of the silver are given in the last two columns of Table 1. The first five columns show the temperature at which oxygen is adsorbed, the amount adsorbed in 30 min, the temperature at which the vessel was evacuated after the adsorption, the amount desorbed by evacuation and finally the amount of oxygen still present on the silver before C_2D_4 was admitted. Only in experiments 1 and 2 was EO detected, while the other oxygen pretreatments only resulted in the production of CO_2 . Since it has been indicated that several types of oxygen are found by adsorption at different temperatures, it can be concluded that the various types of oxygen lead to different selectivities. In column 6 the modes of the adsorbed oxygen are roughly classified in terms of surface (S) and subsurface (SS) oxygen. This classification is based on temperature-programmed desorption measurements of oxygen adsorbed on the (110) and the (111) plane of silver single crystals (4, 6). In Refs. (4) and (6) it was shown that desorption of surface oxygen takes place at $\sim 300^\circ C$, while the oxygen remaining on the surface was shown to be subsurface oxy-

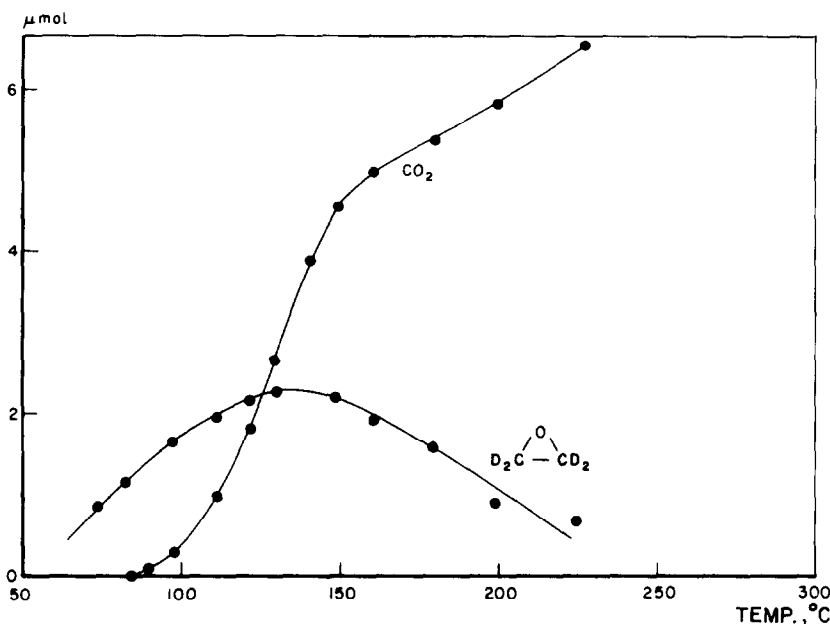


FIG. 2. Temperature-programmed reaction of 10 μmol O_2 chemisorbed on Ag with C_2D_4 .

gen, the diffusion of surface oxygen to subsurface sites occurring at temperatures above 100°C.

The data allow the following conclusions to be drawn:

—Of the oxygen adsorbed at 200°C (total 1.2×10^{15} atoms/cm²) about 50% is present as subsurface oxygen.

—EO is formed only if *both surface and subsurface oxygen* are present.

—Subsurface oxygen in the absence of

surface oxygen gives total combustion upon reaction with ethylene (Exps. 3, 4).

—Of the total number of oxygen atoms present on or below the surface (1.2×10^{15} atoms/cm²) in Exp. 1 at least 11% is active in the formation of EO.

—The active oxygen species resists evacuation at 200°C (Exps. 1, 2), which makes it accessible to modern surface analytical techniques.

The dependence of the selectivity on

TABLE I

The Adsorption, Desorption, and Reactivity of Oxygen on Silver Powder^a

Exp.	Adsorption-desorption of O_2					Mode ^b	Quantity produced	
	T_{ads} (°C)	O_2 ads (μmol)	$T_{\text{evac.}}$ (°C)	O_2 des. (μmol)	O_2 present (μmol)		CO_2 at 300°C (μmol)	EO at 135°C (μmol)
1	200	10	-80	0	10	S + SS	8.3	2.23
2	200	10	200	0.5	9.5	S + SS	7.7	1.90
3	200	10	300	4.8	5.2	SS	2.5	0
4 ^c	200	4.9	200	0	4.9	SS	2.6	0
5	20	3.6	20	0	3.6	S	2.4	0

^a $\text{O}/\text{Ag} = 1$ corresponds to $\approx 1.2 \times 10^{15}$ atoms/cm² or 10 $\mu\text{mol}/10$ g Ag.

^b S = surface; SS = subsurface; information derived from EELS (4).

^c In experiment 4 a pressure lower than 10^2 Pa has been used.

coverage, as shown in Table 1, is similar to that previously found by Gruver *et al.* (3). Below a coverage of $O/Ag = 0.35$ no ethylene oxide was formed, while at higher coverages the amount of EO increased with oxygen coverage. The degree of conversion of the adsorbed oxygen into ethylene oxide did not exceed 5% under their oxygen adsorption conditions. The higher maximum concentration of active oxygen found in our experiments (11%) is due to the higher oxygen coverage obtained at 200°C and possibly also to the fact that we used C_2D_4 instead of C_2H_4 (7).

The concentration of oxygen species observed to be active in ethylene oxide formation (>11%) is much higher than the O_2^- concentration (0.02%) detected by electron paramagnetic resonance spectroscopy (8), which so far is the only technique that has actually revealed the adsorption of a diatomic oxygen radical species at temperatures above 0°C. From this we may conclude either that the diatomic oxygen radical is not the active species in the epoxidation, or that the formal charge of the diatomic species is very small.

The present work is complementary to the recent work of Kagawa *et al.* (9), who measured the amount of EO and CO_2 formed after contacting 0.4 bar ethylene at 180°C with various amounts of oxygen pre-adsorbed on silver at a temperature of 180°C. The amount of oxygen adsorbed was derived from the amount of oxygen desorbing around 300°C, while in the present article both the amount adsorbed and the amount desorbed were measured. If this difference is taken into account, Kagawa *et al.* find that at maximum 20% of the oxygen adsorbed on the surface is active in the formation of EO.

We checked that the rate of epoxidation under catalytic conditions is of the same order of magnitude as that found in our surface reaction experiment by comparing data from Imre (10) with data derived from Fig. 2. The chance γ that an ethylene molecule impinging on the oxygen-covered

silver surface reacts to give ethylene oxide may be estimated from the slope, at 75°C, of the curve representing the amount of ethylene oxide formed in Fig. 2. A value of 10^{-10} is found for γ at 75°C. Imre (10) found that at 300°C and an oxygen pressure of 0.25 bar the rate of EO formation was 6×10^{-10} mol/cm² · s, which gives a γ of 1.3×10^{-8} . In order to compare this γ with the one found from the TPR experiments, we normalized both to a temperature of 200°C by making use of an activation energy of 34 kJ/mol (10). This is the lowest activation energy reported so far (11). In this way we obtained values of 2.2×10^{-9} and 3.0×10^{-9} for the γ 's found from this work and that of Imre, respectively.

Our results lead to the tentative conclusion that EO is formed if both surface and subsurface oxygen are formed. The overlayer formed by silver and oxygen ions, containing subsurface oxygen, may be similar to the surface oxide proposed by Temkin (5), to which the oxygen species active in the epoxidation reaction becomes adsorbed.

Experiments are in progress to verify this model via a spectroscopic investigation of the oxygen species adsorbed on silver at a pressure of 100 Pa and 200°C.

Our results imply that in further experiments directed towards elucidating the mechanism of ethylene epoxidation, it will be essential to establish a surface overlayer simulating the steady-state surface composition. The finding that the oxygen species responsible for epoxidation is stable with respect to evacuation makes study of this surface layer accessible to modern surface techniques.

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