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Ethylene Adsorption on Oxygenated Silver: Evidence for Two Types of Chemisorbed Oxygen

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The adsorption of ethylene on supported 13 weight percent silver was measured by frontal chromatography at 25, 135 and 285°C. Both a "new" catalyst (as prepared) and a "used" catalyst (one which was tested under epoxidation conditions) were studied. It was found that two types of adsorption sites exist on the oxygenated silver. On one site ethylene is held irreversibly and on the other it is held reversibly. This behavior leads to the conclusion that two different types of adsorbed oxygen, corresponding to the two different ethylene adsorptions, exists on the silver surface since reduced silver does not adsorb any ethylene.

INTRODUCTION

Epoxidation of ethylene over silver catalysts has been investigated by both industrial and academic workers for more than three decades. A considerable number of these studies dealt with the chemisorption of oxygen on both silver catalysts and silver films. The work of Czanderna (*1*, *2*), Kummer (*3*), and Sandler *et al.* (*4*, *5*) represents some of the more recent studies. The primary goal of these chemisorption studies was to gain a more complete understanding of the mechanism by which the ethylene epoxidation reaction to yield ethylene oxide takes place. A significant conclusion which resulted from these investigations is that two different types of adsorbed oxygen exist on the silver surface; a view which is now generally accepted. By comparison with the oxygen chemisorption, investigations of the adsorption of the other reactants, principally C_2H_4, or reaction products C_2H_4O, CO_2, and H_2O on silver films or catalysts are few, and many aspects of the relationships between the adsorption of these components and that of oxygen on silver surfaces remain unclear. This study deals with an investigation of the chemisorption of ethylene on oxygenated silver; on reduced silver (*6*, *7*) it is well known that no ethylene adsorption occurs. From this work we hope to gain a better understanding of the interaction between ethylene and the chemisorbed oxygen on the silver surface.

EXPERIMENTAL

Frontal chromatography coupled with a flame ionization detector gauge served as the experimental method (*8*, *9*). The principle of the method is illustrated schematically in Fig. 1. A supported silver sample is brought to the desired temperature in the oxygenated form with nitrogen passing over it. The feed is then switched to a gas mixture which consists of a saturated hydrocarbon, methane, ethylene and nitrogen which is fed over the catalyst at a uniform rate. The retention time of the nonadsorbing methane is a measure of the column void volume or holdup. Its appearance in the outlet gas causes the first "step" in the figure. Ethylene is adsorbed by the catalyst, hence it does not reach the detector until the available surface for ethylene adsorption is depleted at which point C_2H_4 breaks through the column and is detected by the sensor along with the methane hence the second step in the figure.

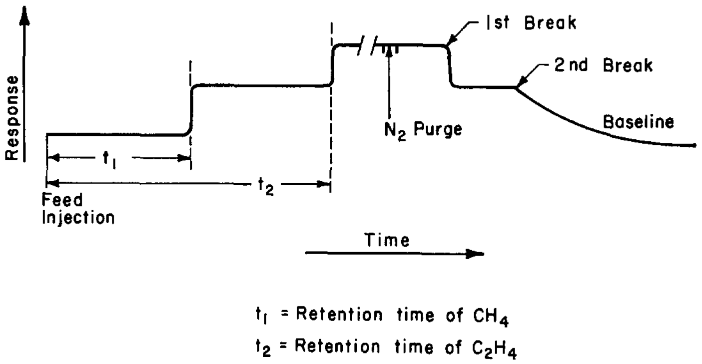

FIG. 1. A typical frontal chromatogram obtained by feeding a gas mixture of C_2H_4/CH_4 over a silver catalyst.

The total volume of ethylene adsorbed, V_E, at room temperature and pressure is given by the following equation:

$$V_E = F \times \Delta T \times C \qquad (1)$$

where F = gas flow through the column at 25°C and atmospheric pressure ($cm^3\ sec^{-1}$);

$\Delta T = t_2 - t_1$, the retention times in seconds of C_2H_4 and CH_4, respectively;

C = volume fraction of C_2H_4 in the feed gas.

Once equilibrium has been established the concentration of organic in the effluent remains constant. When nitrogen replaces the feed gas (N_2-purge introduced) the "first break" represents the point at which all the gaseous hydrocarbon has been displaced from the system. The response, however, does not drop to zero indicating that an organic component is desorbing at a uniform rate (horizontal length) until the "second break" is reached at which point a slow depletion of the organic in the effluent ensues and continues until the base line is eventually reached. At this point the so-called cycle 1 is completed. By reintroducing the feed gas a second cycle is started. At the same linear velocity as before, t_1 remains the same as before but t_2 will be different. This is because while t_1 depends only on the column and flow rate which are constant, t_2 depends on the nature of the silver catalyst surface and the amount of oxygen which remains. Each time feed gas is admitted without reoxidizing the catalyst the cycle count is increased and a new $t_2 - t_1$ is obtained.

The experimental equipment consisted of a standard applications 8-port pneumatic valve operated in the "selector" position. The packed columns, 36 in. in length, were bent in the form of a double U-tube and were made of ¼ in. o.d. stainless-steel tubing. While under test, the tubes were jacketed by a tube furnace 16 in. long which contained a 2-⅛ in. i.d. Alundum core. The column was connected to the nitrogen and feed supply through the valve and in turn to the flame ionization gauge where response was monitored on a strip chart recorder. The feed gas, 0.14, 0.11 and 99.75% C_2H_4, CH_4 and N_2, respectively, was premixed in a single cylinder which was analyzed by mass spectrometry. Gas flow through the column was determined with a soap bubble flow-meter. The two columns, one packed with "new" 13% silver on a α-alumina support and one packed with the "used" catalyst had surface areas of 1.26 and 1.60 m^2/g, respectively. The amount of material in each tube was 22.4 and 21.3 g, respectively, for the "used" and "new" catalysts. The dispersion of silver throughout the porous support, by microscopic examination, appeared very uniform.

Each catalyst was initially oxidized by heating at 285°C for a period of time, >2 hr, with air flowing over it. After a sequence of experiments called cycles were carried out, the catalyst was again reoxidized in a stream of air as before.

In order to carry out an experiment at other temperatures, the catalyst was reheated to 285°C in a stream of air, held at this temperature for >2 hr and then cooled to the desired temperature before cycle 1 was recommenced.

RESULT AND DISCUSSION

The ethylene adsorption results for the "new" and "used" catalyst expressed as μl of ethylene adsorbed at room temperature and pressure (RTP) per gram of catalyst are given in the table.

The desorption behavior for both catalysts at 25 and 135°C is essentially as shown in Fig. 1. Two breaks occurred, the first representing the retention time of the gas in the column and the second when the desorbing species began decreasing in concentration. At 285°C no second break during desorption was noticeable, i.e, all organic was swept out of the column at the same time. It will be shown later that at the 285°C the silver catalyst is actually reduced by the ethylene feed.

For the "new" catalyst at 25°C, 20.8 μl/g catalyst was adsorbed in cycle 1 before ethylene broke through the column; the "used" catalyst adsorbed 27.2 μl/g catalyst. For cycle 1, the ethylene breakthrough while sharp is never complete at this point. To reach equilibrium which represents an increase of about 15% more in response relative to its breakthrough value may require ca. 30 min longer. This behavior is common for both "new" and "used" catalysts for the first cycle experiment at all temperatures. This may be due to (a) a slow adsorption rate of ethylene onto the oxygenated silver or (b) the result of a competitive adsorption by CH_4 similar to that observed by Verna and Ruthven (*10*) in the adsorption of CO on a Ni catalyst when H_2 is the carrier gas instead of He gas. For this case they found H_2 adsorbs competitively, but He does not; hence CO is adsorbed more slowly from H_2. In future work the question of possible competitive adsorption of CH_4 and C_2H_4 on Ag will be checked by running ethylene in N_2 gas over the catalyst without the CH_4 marker gas in which case the holdup time will be determined separately.

After the catalyst has attained equilibrium with the ethylene, the feed gas is shut off and the column purged with N_2. This is called the desorption portion of the cycle. The first break occurs when all the hydrocarbon gas in the column has been swept out. The plateau which follows (Fig. 1) represents a steady-state type of desorption which is presumably C_2H_4 desorbing at 25°C and quite probably also other reaction products at higher temperature, especially for the first cycle desorption. At 25°C, the pattern of desorption is similar for the "new" or "used" catalyst. The desorption for the "new" and "used" catalyst at 135°C is similar and comparable to the 25°C results. Continuation of these studies will be directed toward an understanding of the desorption products from these experiments.

In cycle 2 the ethylene breakthrough is sharp at which point organic concentration in the effluent becomes invariant with time. In higher cycles, ethylene breakthrough is likewise always sharp, however, the amount of adsorbed ethylene on the second and subsequent cycles is always much smaller than during the first cycle. Thus at 25°C for the "used" catalyst the first cycle adsorbed 27.2 μl/g catalyst and the second cycle adsorbed 18.4 μl/g catalyst.

During cycle 6 (new catalyst at 25°C), the gas effluent was sampled in the region where all the ethylene feed is considered adsorbed by the catalyst. The analysis for C_2H_4 and CH_4 clearly showed no ethylene present in the sample, only CH_4, thus verifying the schematic shown in Fig. 1.

At 135°C, cycle 1, the "new" catalyst adsorbed 12.3 μl/g catalyst and the "used" catalyst adsorbed 10.9 μl/g catalyst. The behavior was similar to that observed for cycle 1 at 25°C. For cycle 2 and higher cycles at 135°C, ethylene breakthrough is sharp and adsorption is essentially complete at t_2. At cycle 2 the "new" catalyst adsorbs 1.23 μl/g catalyst.

Total ethylene adsorption, for both the "new" and "used" catalyst, obtained from cycle 1 versus temperature passes through a minimum between about 135 and 200°C. This appears to be a typical curve for an adsorption isobar when some chemisorption is taking place (*11*). By subtracting the adsorbed volume of the average (limiting value) of succeeding cycles, Nos. 3, 4, and 7, from the volume adsorbed in cycle 1 the amount irreversibly adsorbed is obtained. Inspection of the results shows a significantly lower ethylene readsorption at 135°C for the higher numbered cycles compared to that adsorbed at 25°C. By this method, of going from 25 to 135°C, the amount of irreversible adsorption significantly increases for the "new" (7.0 μl at 25°C to 11.3 μl at 135°C) and decreases for the "used" (12.2 μl at 25°C to 9.7 μl at 135°C) catalysts. The ethylene adsorbed during cycle 2 and all subsequent cycles for both the "new" and "used" catalyst is reversible. Furthermore, the volume of the reversibly adsorbed ethylene decreases with increasing temperature. This difference represents chemisorption which is of the reversible type or physical adsorption (*11, 12*).

The amount of ethylene adsorbed irreversibly increases with temperature thus signifying that an activation process typical of chemisorption is involved. This chemisorption is of the irreversible type where presumably a chemical bond is formed between the ethylene and the surface which is sufficiently strong (*12*) that the adsorbate cannot be removed by a simple nitrogen purge, i.e., an electron has probably been transferred between adsorbent and adsorbate. Final distinction as to whether the reversibly adsorbed ethylene is physisorbed or chemisorbed must await heat of adsorption measurements.

The ethylene adsorption-desorption results at 285°C for both the "new" and "used" catalysts are markedly different from that observed at 25 and 135°C. The amount of ethylene adsorbed in the first cycle is 40.1 μl/g catalyst for the "new" versus 18.3 μl/g catalyst for the "used" catalyst. It is interesting to note that the "new" catalyst at this high temperature adsorbs much more ethylene before breakthrough than the "used" catalyst which may explain why a "new" catalyst burns ethylene rather than converting it to oxide. This point will be investigated further as the study continues.

At 285°C, during the desorption phase of cycle 1, no second break as noted in Fig. 1 occurred for either "new" or "used" catalyst. In subsequent cycles the silver did not adsorb any measurable amounts of ethylene as noted in Table 1. This observation is interpreted to mean that all the adsorbed oxygen was stripped away by the ethylene in the first cycle, i.e., the catalyst was reduced, since it is known that ethylene is not adsorbed on reduced silver (*6, 7, 13*). Conformation of this view was obtained in a separate experiment in which the silver was initially reduced with hydrogen gas in which case it also showed no adsorption. Upon reoxidizing the catalyst, ethylene is

TABLE 1

ETHYLENE ADSORPTION ON SUPPORTED SILVER

State of supported silver	Temp. (°C)	Volume C_2H_4 adsorbed at RTP (μl/g)				
		Cycle No. 1	Cycle No. 2	Cycle No. 3	Cycle No. 4	Cycle No. 7
New[a]	25	20.8	16.0	13.1	13.9	14.5
Used[b]	25	27.2	18.4	17.5	14.6	12.9
New	135	12.3	1.20	1.04	1.04	1.04
Used	135	10.9	1.23	1.26	1.21	1.21
New	285	40.1	Essentially no detectable adsorption, i.e., oxygen was removed by chemical reaction in first cycle			
Used	285	18.3				

[a] New = supported silver on alumina after preparation.

[b] Used = supported silver used as a catalyst in ethylene epoxidation.

again adsorbed as before. One striking difference between the "new" and "used" catalysts at 285°C is that the amount of ethylene adsorbed by the "used" catalyst is much lower than that adsorbed by the "new." The difference between these two catalysts is that the "used" catalyst was exposed to the ethylene epoxidation reaction in which a trace of organic chloride, ca. 1 ppm, was used as inhibitor and the other was not. The paper by Meisenheimer and Wilson (*14*) deals with effect of chloride inhibitor on Ag catalysts. They found that chloride on the Ag surface at moderately high surface concentrations inhibits the rate of O_2 adsorption. Since ethylene adsorbs only on oxygenated Ag it may be, in this case, that the chloride on the "used" Ag is responsible for the observed effect. The results at 135°C demonstrate a similar behavior. This conclusion is considered tentative since the above authors also state that ethylene at room temperature can adsorb on a chlorinated Ag surface though adsorption was not detected at 200°C.

One other interesting point concerning the first cycle ethylene adsorption results at 285°C versus 135°C is that a larger amount of ethylene is adsorbed at the higher temperature for both the "new" and "used" catalyst. This behavior indicates that some type of interaction, i.e., CO_2 or the epoxidation reaction, is taking place at 285°C which is not taking place at the lower temperature. As far as can be ascertained from the literature the lowest temperature at which the ethylene expoxidation reaction takes place has not yet been clearly established.

This study has shown that there are two types of sites on the oxygenated silver catalyst surface which adsorb ethylene. On one site the ethylene is chemisorbed and is held irreversible and on the other site it is held reversibly where it could either be held by physical forces or by weak chemisorption forces. Previous workers (*15, 16*) who have reported on ethylene adsorption on oxygenated silver surfaces have apparently underestimated the significance of this behavior. From an alternate view this behavior could be thought of as indicating two different types of adsorbed oxygen. By comparing the chemisorption of oxygen on silver with that of ethylene on oxygenated silver it becomes apparent that here is proof of a chemical nature for the claim, which up to now is based strictly on physical methods, that two types of adsorbed oxygen actually exist on the silver surface (*1, 4, 17, 18*). These sites are present in both the "new" and "used" catalysts. Attempts to distinguish the two oxygen sites by chemical means have already been tried by several workers, among them being Sandler and Durigon (*19*) who carefully adsorbed oxygen on silver powders at room temperature and then looked for an acceleration in the parahydrogen conversion which would be expected from the existence of paramagnetic O_2-ions. No such effect was observed. Isotopic exchange experiments were first interpreted by Margolis (*17*) and Meisenheimer *et al.* (*20*) as showing one mode of oxygen adsorption is nondissociative but these claims have not been verified by the recent work of Sandler and Durigon (*4*).

The complete differentiation of these sites and a deeper understanding of their nature could help in furthering the understanding of the ethylene epoxidation mechanism (*21, 22, 23*), which involves also a burning reaction to produce CO_2 and water.

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