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Studies on the Catalytic Oxidation of Ethylene by Means of the Pulse Technique

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By means of the pulse technique, the catalytic oxidation of ethylene and ethylene oxide over a supported silver catalyst were studied at 200°C. The results obtained for the adsorption and reaction of oxygen and other reaction components suggested that the reaction occurs between gaseous ethylene and the oxygen which is firmly adsorbed at the silver surface, and that among the firmly adsorbed oxygen less firmly bound oxygen is favorable to form ethylene oxide whereas the oxygen which is more firmly bound is favorable to form carbon dioxide. Carbon dioxide is adsorbed on the latter type of oxygen and inhibits the further formation of carbon dioxide.

1. INTRODUCTION

Catalytic oxidation of ethylene by a silver catalyst has been investigated by various researchers from different points of view. In order to explain the mechanism of this reaction, many studies on the adsorption of oxygen have been made (*1–4*, *7*). Margolis (*10*) suggested that both atomic and molecular oxygen coexist on a silver surface. On the other hand, Sandler and Hickam (*7*) showed that only one form of oxygen exists on the surface. Sandler and Durigon (*3*) extended the latter study to reveal that there are two different binding states of oxygen on the surface; they studied also the effect of hydrogen on the oxygen adsorption (*4*).

Investigations of the adsorption of the other reaction participants, C_2H_4, CO_2, and C_2H_4O are few, and many aspects of the relations between the adsorption of these components and that of oxygen remain unclear. Carbon dioxide adsorption onto the oxygenated surface was detected [cf. Ref. (*10*)], but its effect on selectivity has not been determined.

Furthermore, there are few studies which used the industrial catalyst, and its catalytic effect under commonly used reaction conditions has not been discussed.

With this in mind, this paper presents, in addition to the experimental results of the oxygen adsorption, the results of the adsorption of ethylene, carbon dioxide, and ethylene oxide over oxygenated or deoxygenated catalyst obtained from an alumina-supported silver catalyst. The adsorption measurements were carried out by means of the pulse technique. These adsorptions were also discussed in relation to the kinetic mechanism of this reaction under commonly used conditions.

2. EXPERIMENTS

2-1. Catalyst

The catalyst was prepared by reducing the silver oxide coated on α-alumina (16 ~ 24 Taylor mesh) with a flow of hydrogen for 12 hr at 50°C and subsequently for 12 hr at 100°C. The silver oxide used was prepared by adding a 10% solution of potassium hydroxide to a 10% solution of silver nitrate. The precipitate was washed thoroughly with a sufficient amount of distilled water and then mixed with a small amount of K_2SO_4 solution and dried. This was mixed well with α-alumina in the presence of a small amount of ethanol (*5*). The content of silver oxide in this catalyst was 23%. The activity of this catalyst was reported in a previous paper (*6*). In this experiment, at a temperature of 200°C with W/F equal to 10,000 g cat·hr/g mole of C_2H_4, 50% of C_2H_4 was converted to C_2H_4O, 25% to CO_2; and the selectivity was 66.7%, based on C_2H_4 reacted.

2-2. Apparatus

A stainless steel U-tube of 4-mm diameter was used as a reactor. 24 g of the catalyst was packed into this tube to a length of 20 cm. This reactor was immersed in an electrically heated fluidized bed, and the temperature difference between the entrance and the exit of catalyst bed, therefore, could be maintained within 1°C.

A six-way valve was provided just behind the reactor, followed by a gas chromatograph. "Porapack-R" was used as a column packed in a stainless steel U-tube of 75 cm length, 4 mm in diameter. Helium was used as a carrier gas with a flow rate of 60 ml/min. It was confirmed that the trace of oxygen in helium showed no appreciable effect on the reaction. By the six-way valve, the system could be readily changed from the steady state operation (C_2H_4–air mixture flows in the reactor) to the pulse operation (helium flows in the reactor) and vice versa. The catalyst activity was checked in the flow system at steady state with a standard gas mixture consisting of 4.5% ethylene and 95.5% air. The source of oxygen was laboratory air and the other gases were obtained from commerical cylinders. In the pulse operations, given amounts of gases were injected into the head of the reactor by using commercial injectors.

2-3. Experimental Method

The stabilization of catalyst activity was first established by a steady state operation in the flow system at a temperature of 200°C and a W/F of 10,000 g cat·hr/g mole of C_2H_4 with the standard reaction gas mixture. Upon establishing the stable activity, the flow of reaction gas mixture was switched to the helium flow by the six-way valve. All the reaction components in the effluent gas from the reactor, air, CO_2, C_2H_4, H_2O, and C_2H_4O, were analyzed by gas chromatography. After passing through all of these components, the pulse of given gas was injected. All experiments were performed at 200°C. Steady state activity of the catalyst was checked at the beginning of every run of the pulse operations confirming that no appreciable change took place.

3. RESULTS AND DISCUSSION

3-1. Adsorption of Oxygen and Its Reaction

When an ethylene pulse was injected during the operation described above, the formation of CO_2, H_2O, and C_2H_4O was observed. This fact indicates that the catalyst holds oxygen on its surface even after the reaction mixture is replaced by helium. When the ethylene pulses were injected repeatedly, the amount of products became small at every injection and finally no reaction was observed to take place. The catalyst in this state was designated as "deoxygenated catalyst."

When a given amount of air and then a 100-μl pulse of ethylene were injected to this deoxygenated catalyst, we could again observe the formation of products. The effect of the amount of initially injected air on the amount of products formed is shown in Fig. 1. Since the same results were obtained with any injection of air of more than 3 ml, the catalyst in this state is designated as "oxygenated catalyst."

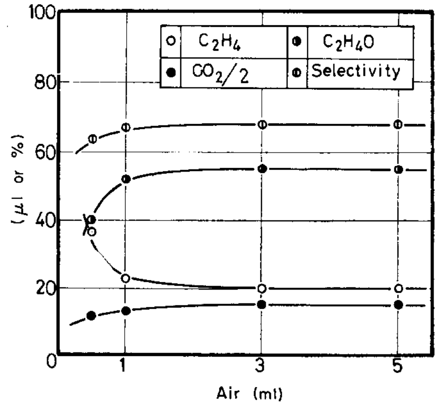

FIG. 1. Effect of the amount of initially injected air: Operation: deox.-cat. 3 min air (ml), 3 min C_2H_4 100 μl.

In Fig. 2 is shown the stability of the reactive oxygen on the oxygenated catalyst. The amount of products formed by the injection of a 100-µl ethylene pulse was plotted against the time interval between air injection and ethylene injection. No variation in the amount of products could be observed up to the time interval of 60 min. This fact suggests that the amount of reactive oxygen on the surface does not change even in the flow of helium, namely, the oxygen is very firmly bound on the silver surface and not readily desorbed, but it readily participates in chemical reactions.

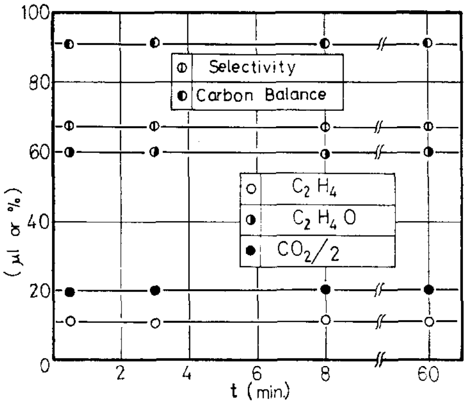

FIG. 2. Stability of the reactive O_2 on the oxygenated catalyst: Operation: deox.-cat. air, 5 ml (*t*) C_2H_4 100 µl.

This is in good agreement with the results of Sandler and Hickam (*7*) revealed in their isotopic exchange studies. Flank and Beachell (*8*) suggested that the adsorbed oxygen can readily migrate into the subsurface layers and that this oxygen does not readily participate in the reaction. Since the adsorbed oxygen formed the same amount of products even after 60 min, no appreciable amount of adsorbed oxygen could have migrated into the subsurface layers in our experiments, presumably due to the lower temperature (200°C) used in this study.

The results of the reduction of the oxygenated catalyst by repeated ethylene pulses are shown in Fig. 3 (100-µl ethylene pulses were injected every 9 min). At every injection, as the formation of ethylene oxide decreases, the selectivity decreases accordingly.

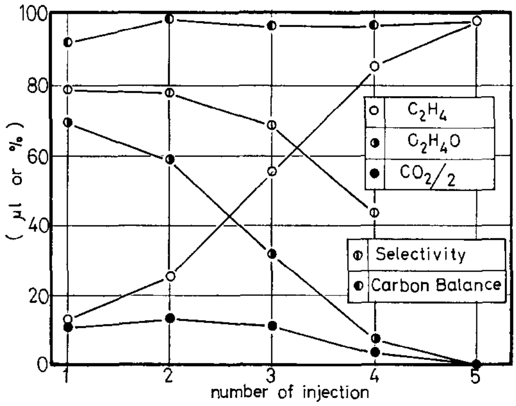

FIG. 3. Reduction of the oxygenated catalyst by repeated C_2H_4 pulses: Operation: ox.-cat. C_2H_4 100 µl (every 9 min).

When the ethylene pulse was injected into the oxygenated catalyst which had been partly reduced by various amounts of hydrogen, a similar mode of variation in the selectivity could be observed as shown in Fig. 4. These facts would suggest that the oxygen on the surface of the catalyst has different activities in forming either C_2H_4O or CO_2. When the oxygenated catalyst is reduced step by step, the oxygen which is likely to form ethylene oxide seems to be more easily reduced than the oxygen which oxidizes ethylene and ethylene oxide to form carbon dioxide. One may be led to conclude that less firmly bound oxygen is likely to form ethylene oxide,

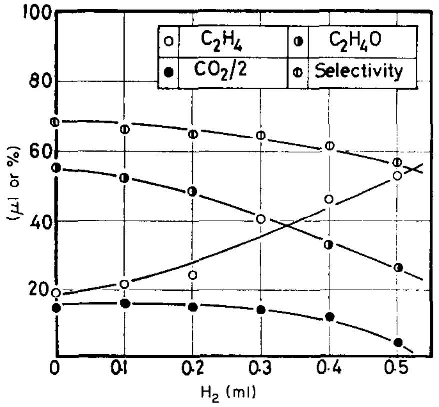

FIG. 4. Effect of the reduction by H_2: Operation: ox.-cat. 1 min H_2 (ml), 3 min C_2H_4 100 µl.

and firmly bound oxygen is likely to form carbon dioxide.

As shown in Figs. 3 and 4, the decrease in the selectivity in the case of a hydrogen-reduced catalyst is rather insensitive compared to the one reduced with ethylene. Sandler *et al.* (*4*) demonstrated the effect of hydrogen treatment on the oxygen adsorptive properties of a silver surface. The results indicated that hydrogen pretreatment reduced the activation energy of the desorption of oxygen by 8.5 kcal/mole. It suggests that the contact of hydrogen produces changes in the surface and loosens the bond energy of adsorbed oxygen. This might be one of the reasons why the selectivity did not fall rapidly in the case of a hydrogen-reduced catalyst.

Twigg (*9*) concluded from his kinetic studies that oxygen is chemisorbed as atoms on a silver surface and that the reaction of a gaseous ethylene molecule with one oxygen atom produces ethylene oxide, while the reaction with two oxygen atoms produces carbon dioxide. It was suggested, on the other hand, that the oxygen exists on the surface in two distinctly different states, molecular and atomic (*10, 11*). Hayes (*11*) thought that ethylene oxide is formed by the reaction of ethylene with atomic oxygen, whereas CO_2 is formed by the reaction with molecular oxygen. But this suggestion is questionable [(*3*), cf. Ref. (*12*)]. Sandler and Durigon (*3*) revealed that there are two different binding states of oxygen, but no evidence was found that one of these was in the undissociated form of molecules. In our experiments of flash desorption of oxygen from the oxygenated catalyst, no measurable amount of oxygen was detected in a temperature range from 200 to 280°C, even though this oxygenated catalyst could react with ethylene pulses as were shown in Fig. 3. Sandler and Durigon (*3*) showed that the adsorbed oxygen at 160°C could easily be desorbed at a temperature range from 160 to 190°C and that this oxygen involves one type of oxygen on the silver surface. However, this type of oxygen would not exist on the oxygenated catalyst which was used in our experiments, as indicated by the results described above. Therefore, the oxygen on the oxygenated catalyst which reacted with ethylene will involve more firmly bound oxygen at or near the surface. Taking into consideration all the facts mentioned above, it is reasonable to assume that the firmly bound oxygen at or near the surface shows a distribution of binding energy and this might be an essential factor determining the selectivity of the reaction.

From this point of view, among the firmly bound oxygen, the oxygen favorable to form ethylene oxide would be the one which is less strongly adsorbed at the oxygenated surface; whereas the oxygen which is more firmly adsorbed and exists in the strong field of the silver lattice is likely to form carbon dioxide. This interpretation is also supported by the results given in Fig. 1, which shows that oxygen is initially strongly adsorbed, leading to a lower selectivity for ethylene oxide, and also by Fig. 3, which shows that strongly held oxygen is not selective for ethylene oxide.

3-2. Adsorption of Ethylene and Its Reaction

When an ethylene pulse was injected into the deoxygenated catalyst, the same amount of ethylene was found in the effluent from the reactor. It can be concluded from this fact that the adsorption of ethylene does not take place on the deoxygenated catalyst.

When ethylene was introduced to the oxygenated catalyst, however, the reactions of ethylene to form ethylene oxide and carbon dioxide always took place, and the subsequent air injection did not give these products. From this result, it is seen that either ethylene is not adsorbed or that its adsorption, if it exists, is relatively unimportant. The reaction on the catalyst, therefore, is shown to be that of gaseous ethylene and the adsorbed oxygen, as has been generally accepted.

3-3. Adsorption of Carbon Dioxide

In Fig. 5 are shown the chromatograms obtained for carbon dioxide in the effluent from the reactor when a carbon dioxide

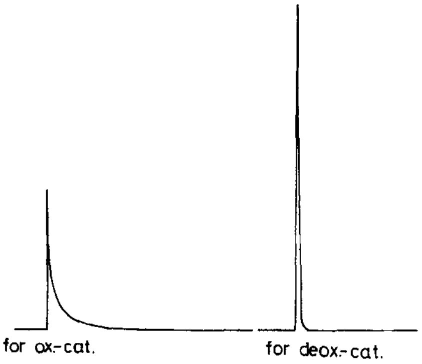

FIG. 5. Chromatograms of CO_2.

pulse was injected into either the oxygenated (left) or the deoxygenated catalyst (right). In the case of the deoxygenated catalyst, the whole amount of injected carbon dioxide appeared immediately in the exit gas without showing any noticeable tailing in its chromatogram; whereas, for the oxygenated catalyst, the strong tailing could be observed, and it took more than 6 min for the flowing out of the whole amount of injected carbon dioxide. This fact reveals that carbon dioxide can be adsorbed only on the oxygenated catalyst and that the adsorption is reversible. The adsorption of CO_2 onto the oxygenated catalyst was also detected at 250°C. Since Ag_2CO_3 can not exist in bulk at this temperature, adsorbed CO_2 on the oxygenated catalyst may exist as a very unstable Ag_2CO_3, which in turn decomposes to form CO_2.

The effect of the adsorption of carbon dioxide on the reaction between injected ethylene and oxygenated catalyst is shown in Fig. 6. The ethylene pulse was injected after the injection of carbon dioxide into the oxygenated catalyst, and the performances of the reaction of ethylene were plotted against the time interval of these two injections. The shorter the time interval, the higher is the selectivity; but for time intervals of more than 6 min, the performances are substantially the same. Holding in mind that injected carbon dioxide can be held on the oxygenated catalyst for about 6 min, initial higher values of selectivity to ethylene oxide may

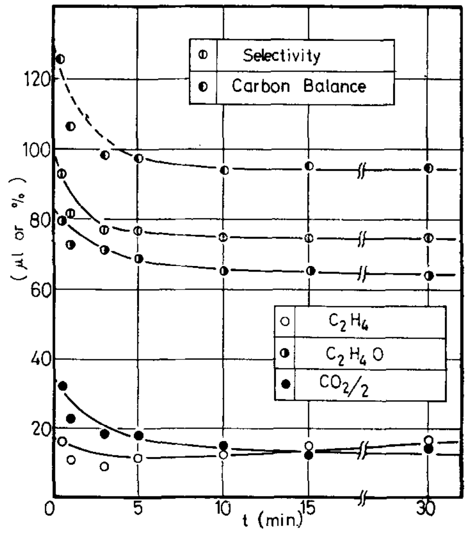

FIG. 6. Effect of CO_2 adsorption: Operation: ox.-cat. 1 min CO_2 100 μl, (*t*) C_2H_4 100 μl.

be attributed to the effect of adsorbed carbon dioxide. From this result we see that the adsorption of carbon dioxide is favorable for the formation of ethylene oxide, and that this might be due to the adsorption of carbon dioxide onto the oxygen which preferably produces carbon dioxide, as was discussed in Sect. 3-1.

The carbon balance, which exceeds 100% in Fig. 6, can be attributed to the desorption of adsorbed carbon dioxide resulting from the preceding injection of carbon dioxide.

3-4. Adsorption and Reaction of Ethylene Oxide

When an ethylene oxide pulse was injected into the oxygenated catalyst, carbon dioxide and water were observed as the product in the effluent, whereas by the subsequent injection of air, no products were observed. This fact suggests that neither ethylene nor ethylene oxide is adsorbed in its unreacted form on the oxygenated catalyst.

By the injection of ethylene oxide into the deoxygenated catalyst, the formation of ethylene took place in addition to the formation of carbon dioxide and water, and the conversion of this backward reaction exceeded the equilibrium value of the reaction, $C_2H_4O \rightleftharpoons C_2H_4 + \frac{1}{2}O_2$. This may be attributed to the separation of each component along the catalyst column due to the difference of moving velocities—a phenomenon frequently observed in the pulse reactor. However, the main reason for this phenomenon would be the complexity of the reactions on the surface, namely, the equilibrium formation of ethylene cannot be determined solely by the reaction shown above, but should be determined in a system including silver and silver oxide.

When an ethylene oxide pulse was injected into the deoxygenated catalyst, the subsequent injection of air produced carbon dioxide and water. The source of these products could be either ethylene or ethylene oxide remaining on the catalyst. Since ethylene cannot be adsorbed on the deoxygenated catalyst, as has been mentioned above, the substance remaining on the catalyst and serving as the source of the formation of these products must be assumed to be ethylene oxide. Thus it is shown that ethylene oxide can be adsorbed on the deoxygenated catalyst. But when a pulse of an ethylene oxide–air mixture was used, ethylene oxide could be adsorbed only when the air/C_2H_4O ratio was less than 5. In view of these facts, we may conclude that ethylene oxide cannot be adsorbed on the catalyst under the commonly used reaction conditions where the catalyst surface would be in a more oxidized state than this criterion allows, and therefore the reaction of ethylene oxide will take place only between gaseous ethylene oxide and adsorbed oxygen.

The effect of adsorption of carbon dioxide was also observed in the reaction of ethylene oxide. When an ethylene oxide pulse of 100 μl was injected into the oxygenated catalyst, 14 μl was converted to carbon dioxide; whereas, only 4 μl was converted when carbon dioxide had been injected 3 min prior to the injection of ethylene oxide. This fact would be due to the same effect as has been discussed in the case of ethylene oxidation.

4. Conclusion

In view of all the facts mentioned above, the catalytic oxidation of ethylene on the silver catalyst seems to take place in the following manner. The catalyst adsorbs oxygen strongly, and the gaseous ethylene reacts with surface oxygen to form either ethylene oxide or carbon dioxide. The oxygen which is likely to produce ethylene oxide is that which is less strongly adsorbed on the oxygenated surface, and the oxygen at or near the surface which is strongly affected by the field of the lattice of silver seems to react with ethylene and ethylene oxide to produce carbon dioxide. Carbon dioxide is adsorbed on the latter type of oxygen and inhibits the further formation of carbon dioxide.

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