

Application of Transient Response Method to the Study of Heterogeneous Catalysis

II. Mechanism of Catalytic Oxidation of Carbon Monoxide on Manganese Dioxide

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The mechanism of the oxidation of carbon monoxide over manganese dioxide was studied by a transient response method. To follow the transient behavior, measurements were made on the time dependencies of the reaction gas composition and of the electrical conductivity of the catalyst. The analyses of the response curves showed that the gaseous carbon monoxide reacts directly with the surface oxygen species, which is negatively charged, to form some intermediates, which successively decompose to form carbon dioxide. It was found that the amount of carbon dioxide existing on the surface during the reaction under steady states was larger than the equilibrium amount, which was calculated from the adsorption isotherm specified by the Langmuir equation, and it was suggested that the desorption step of carbon dioxide is one of the slower steps in the overall reaction.

INTRODUCTION

The mechanism of the catalytic oxidation of carbon monoxide over manganese dioxide has been studied extensively by many investigators. Roginskii and Zel'dovitch (1) proposed that the oxidation of carbon monoxide on manganese dioxide is preceded by the reaction between chemisorbed carbon monoxide and gaseous oxygen. Brooks (2) also suggested a Rideal-type mechanism due to the reaction between reactive radical species of carbon monoxide on the surface and gaseous oxygen. Bruns and Shurmovskaya (3), however, suggested that the reaction takes place in two stages: the reduction of manganese dioxide by carbon monoxide and the subsequent oxidation of the surface by gaseous oxygen. In recent years, Davydov, Shchekochikhin and Keier (4) revealed more directly by using IR that the reaction takes place with participation of adsorbed oxygen and gaseous carbon monoxide.

In our previous work (5), we showed,

with the aid of a transient response method, that the reaction took place with the participation of gaseous carbon monoxide and the surface oxygen species which consists of only a fraction of total adsorbed oxygen. This active oxygen, designated as O_s^h , was also shown to be negatively charged.

In this study, the transient response method was further applied to obtain additional information on the behavior of other components and also on the events on the surface, which will contribute to reveal the detail of the mechanism and eventually to provide a sound basis for the kinetic analysis of this reaction.

EXPERIMENTAL METHODS

The methods used in this study were exactly the same as that described earlier (5).

RESULTS AND DISCUSSION

The response of component B in the outlet gas mixture to a stepwise change in the

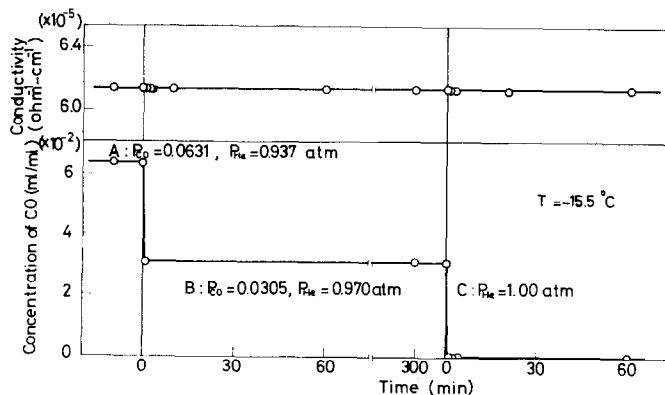


FIG. 1. The CO-CO and the CO-conductivity response.

concentration of A in the inlet gas stream is designated as the A-B response.

1. Behavior of Carbon Monoxide

With the catalyst in use for the reaction under steady state at -26°C , the CO-CO response was instantaneous and indicated no appreciable adsorption of carbon monoxide, and even if taking place at all, it seemed to be at a very slow rate or to a very limited extent. Since the adsorption of carbon monoxide on metal oxides are considered to take place either on metal ions or anion vacancies, the CO-CO response was measured also with a catalyst which was previously reduced for 48 hr in a carbon monoxide-helium mixture. Even with this reduced catalyst, the results again showed an instantaneous response and no appreciable adsorption of carbon monoxide was observed as shown in Fig. 1. The subsequent introduction of oxygen produced no detectable amount of carbon dioxide and, moreover, no desorbed carbon dioxide was detected even when this catalyst was heated up to 90°C in a helium stream.

Since the catalyst was proved to be a *n*-type semiconductor, if carbon monoxide is adsorbed on the catalyst surface as an electron donor as has been frequently observed in the adsorption of carbon monoxide on the semiconductor catalysts (6), the electrical conductivity of the catalyst should be changed during this procedure. The electrical conductivity of the catalyst,

however, remained unchanged as shown in Fig. 1.

The results of CO-CO₂ response are presented in Fig. 2. After a catalyst was kept under a steady state, the gas mixture was switched over to either pure helium ($9 \times 10^{-7} \text{ O}_2$) or helium containing oxygen (20.7%). If carbon monoxide was adsorbed on the surface as suggested by Roginskii and Zel'dovitch (1) and Brooks (2), the response obtained in the stream of helium containing a large amount of oxygen should be higher than that obtained in the stream of pure helium due to the reaction between gaseous oxygen and adsorbed carbon monoxide. The response curves of carbon di-

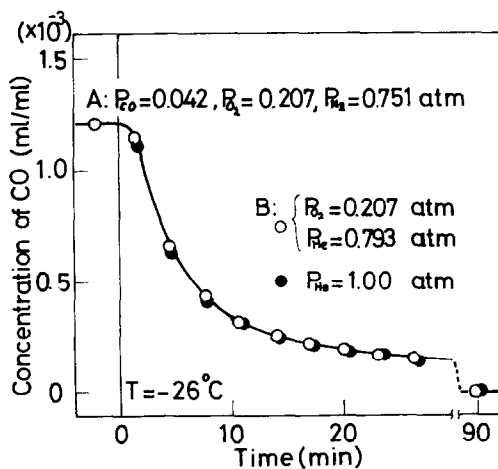


FIG. 2. The CO(dec., 0)-CO₂ response.

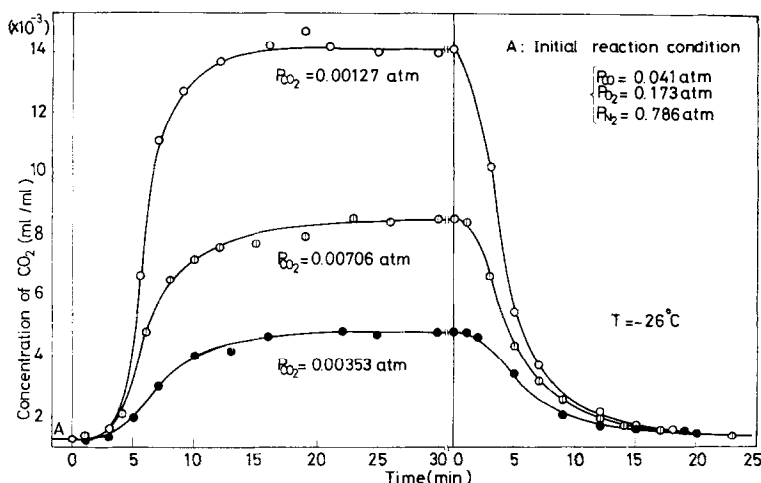


Fig. 3. The CO_2 - CO_2 response during the reaction.

oxide obtained, however, were exactly the same as shown in Fig. 2.

The results obtained so far in this study gave no evidence which suggests the adsorption of carbon monoxide. It is reasonable to conclude, therefore, that the gaseous carbon monoxide reacts directly with the oxygen species on the surface.

2. Transient Adsorption Studies of Carbon Dioxide

The CO_2 - CO_2 response during the reaction at -26°C was relatively slow in contrast to the CO - CO response and a transient state was observed over an extended period of time as shown in Fig. 3. This result clearly indicates the adsorption of carbon dioxide on the catalyst surface. The graphical integration of the $\text{CO}_2(\text{inc.})$ - CO_2 response curve gives the amount of adsorbed carbon dioxide and that of the $\text{CO}_2(\text{dec.})$ - CO_2 response curve also gives the amount of desorbed carbon dioxide. As may readily be seen from the figure, the amount of desorbed carbon dioxide is less than that of adsorbed carbon dioxide. This fact suggests that a fraction of carbon dioxide is adsorbed irreversibly. The amount of irreversibly adsorbed carbon dioxide was calculated to be in a range 2 - 6×10^{12} molecule/ cm^2 depending upon the partial pressures of carbon dioxide in the gas phase. Elovitch (7) demonstrated that a

fractional amount of adsorbed carbon dioxide on manganese dioxide was very strongly adsorbed, and Klier and Kuchynka (8) also found tightly bound carbon dioxide on manganese dioxide and the amount of which was estimated to be 6×10^{12} molecule/ cm^2 at 20°C . These results are in good agreement with those obtained in the present study.

The amount of reversibly adsorbed carbon dioxide was estimated from the $\text{CO}_2(\text{dec.})$ - CO_2 response curves measured in three different gas atmospheres, O_2 , He and a reaction mixture, and the results are presented in Fig. 4. As shown in the figure, the amount of reversibly adsorbed carbon dioxide was the same regardless of the existence of oxygen or other gases and varied only with the partial pressure of carbon dioxide in the inlet gas stream.

As shown in Fig. 4, the reaction rates are not influenced by the partial pressure of carbon dioxide in the gas phase, as was observed previously by Roginskii and Zel'dovich (1). As already stated, the reaction proceeds through the reaction between gaseous carbon monoxide and the active surface oxygen. Therefore, if carbon dioxide is adsorbed reversibly on the sites where it is formed, the rate of carbon monoxide oxidation should be affected by the adsorption of carbon dioxide depending on the partial pressure of carbon dioxide in the gas phase.

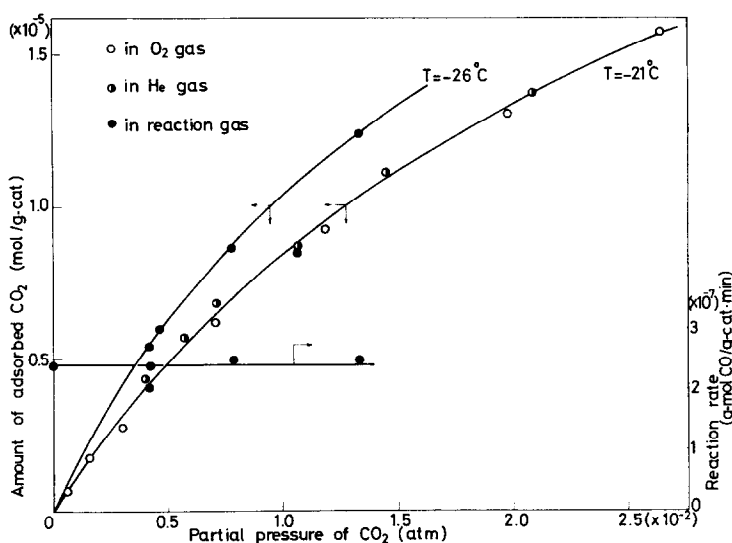


FIG. 4. Adsorption isotherm of CO_2 and the reaction rate as a function of P_{CO_2} .

It would be, therefore, reasonable to assume that the sites on which carbon dioxide is reversibly adsorbed are different from the sites where carbon dioxide is formed, i.e., the sites where active oxygen species exist. Presumably, carbon monoxide reacts with active oxygen on the surface to form some sort of intermediate and this intermediate releases carbon dioxide onto another different site where carbon dioxide can be reversibly adsorbed.

Since the overall rate of the reaction is of a first order with respect to the partial pressure of carbon monoxide and the amount of active oxygen on the surface is unchanged regardless of the partial pressure of carbon monoxide in the reaction mixture, the rate of the release of carbon dioxide from the intermediate should be very rapid compared with that of the formation of this intermediate. Because, unless this is otherwise, the amount of active oxygen on the surface should decrease with the increased partial pressure of carbon monoxide due to the accumulation of this intermediate and this would lead to a kinetics other than a simple first order in partial pressure of carbon monoxide.

No appreciable change could be observed in the electrical conductivity during the course of CO_2 - CO_2 response. Elovitch and

Margolis (10) observed changes in electrical conductivity upon adsorption of carbon dioxide over manganese dioxide at 20°C and suggested a donor type adsorption of carbon dioxide. This is not the case in our experiment. Carbon dioxide, therefore, must be adsorbed without any charge transfer as was suggested by Yenikev (11) for the adsorption of carbon dioxide over zinc oxide at room temperature.

3. The CO - CO_2 Response

After the catalyst was kept under steady state with a flow of reaction gas mixture, the CO - CO_2 response was followed upon changing the concentration of carbon monoxide in the gas mixture. The results are presented in Fig. 5. The mode of the response was similar to that of the CO_2 - CO_2 response but the transition to a new steady state was rather slow. When the carbon monoxide concentration returned to the initial value, a complete recovery of the initial steady state was seen; namely the response was reversible.

The amount of adsorbed carbon dioxide at steady state B and C in excess to that at state A can be estimated by the graphical integration of the $\text{CO}(\text{dec.})$ - CO_2 response curves with the base line at the level of steady state A. These amounts were

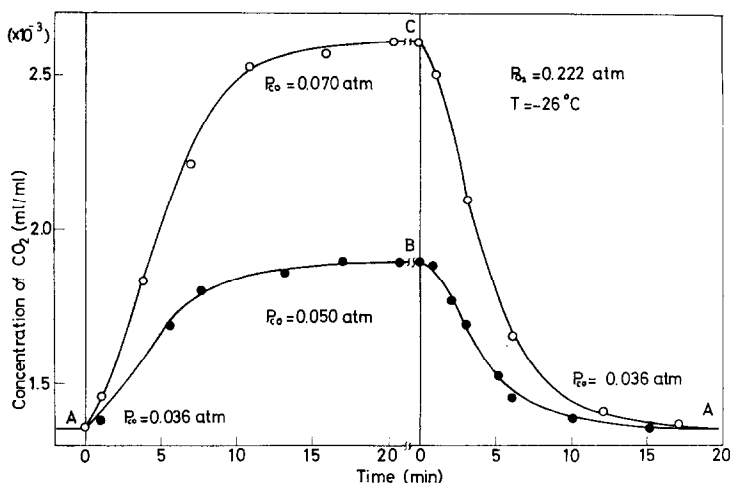


Fig. 5. The CO-CO₂ response during the reaction.

plotted against the partial pressures of carbon monoxide at corresponding states and the intersection of the ordinate obtained by extrapolation was taken as the amount of reversibly adsorbed carbon dioxide at steady state A. The amount of adsorbed carbon dioxide thus estimated from the CO-CO₂ response data is plotted in Fig. 6 as represented by straight line 1. On the other hand, the amount of adsorbed carbon dioxide was calculated from Fig. 4 and the results are shown in Fig. 6 as represented by straight line 2. In this calculation, the partial pressure of carbon dioxide in the gas phase was considered to increase linearly along the catalyst bed. Because of the low conversion, this linearization can be made without introducing serious errors.

As shown by these lines, the amount of adsorbed carbon dioxide estimated from the CO-CO₂ response is larger than that estimated from the CO₂-CO₂ response by about 20%. This means that the amount of adsorbed carbon dioxide during the reaction is in excess to that equilibrated with the carbon dioxide in the gas phase and it suggests that the desorption of carbon dioxide from the catalyst surface is one of the slower steps in the overall reaction.

4. Mechanism of the Reaction

According to the results and discussion presented so far together with that pre-

sented in the previous paper, it would be possible to single out the following conclusions regarding the mechanism of carbon monoxide oxidation over manganese dioxide at the temperatures around -26°C.

1. There are two types of adsorbed oxy-

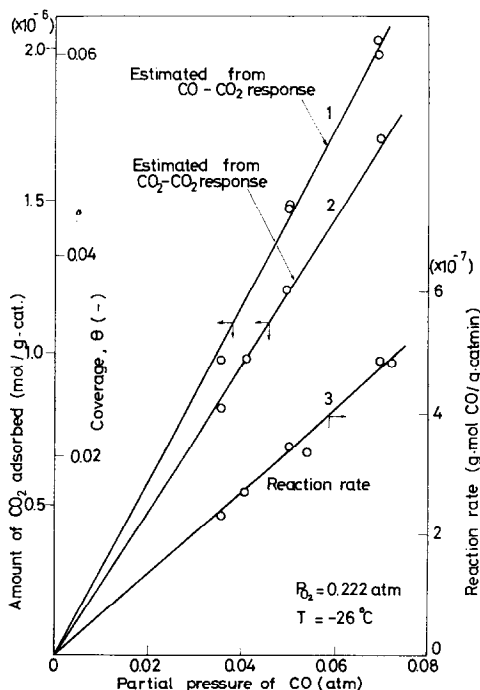


Fig. 6. The amount of adsorbed CO₂ and the reaction rate as a function of P_{CO} .

gen species on the catalyst surface, O_s^i and O_s^h . O_s^h consists of only a small fraction of the total adsorbed oxygen and is negatively charged, probably in the form of O_2^- . This active oxygen can be readily regenerated with gaseous oxygen.

2. Carbon monoxide is not adsorbed on the surface but reacts directly from the gas phase with active oxygen on the surface to form a certain intermediate, which successively decomposes to form carbon dioxide.

3. Most of the carbon dioxide formed is adsorbed reversibly on the sites which are different from the sites where the intermediate is formed. The reversibly adsorbed carbon dioxide is electrically neutral.

4. The amount of the adsorbed carbon dioxide during the reaction is in excess by 20% to the equilibrium amount estimated from the concentration of carbon dioxide in the gas phase.

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