Modification of Manganese Dioxide Catalyst Owing to the Change in Gas Composition

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Abstruct

Modification of the electrolytic manganese dioxide surface during oxidation of carbon monoxide was studied experimentaly by purterbing the reaction steady state with a stepwise change in the concentration of carbon monoxide. The transient behavior of the oxidation activity corresponded exactly to that of the amount of surface oxygen species having a higher oxidation power, O_s^{h*}, and moreover the apparent first order rate constant predicted by the steady state kinetics varied in proportion to the amount of O_s^{h*}. It was shown that the modification of catalyst surface owing to he change in gas composition affected the oxidation activity through the change of the amount of O_s^{h*} which was catalytically active for oxidation of cabon monoxide.

1. Introduction

It has been pointed out[1-3] that the original composition of solid catalysts is modified as a result of the equilibration processes of the solid-gas system and the catalytic activity of the surface is thereby changed corresponding to the composition of the gas phase. In our previous paper,[4] it was found that the surface structure of manganese dioxide during oxidation of carbon monoxide changed to manganese sesquioxide at certain partial pressure of carbon monoxide with an accompanying discontinuous change in the catalytic activity. In addition, it was shown that two different kinds of oxygen species exist on the surface during the reaction, one of which is the surface oxygen spcies of higher oxidation power O_s^{h*} which is catalytically active, and the other is that of lower oxidation power O_s^l.

In the present study, the modification of the catalyst activity was further studied with respect to the change in the amount of both surface oxygen species O_s^{h*} and O_s^l owing to the change of reaction gas composition. The electrical conductivity of manganese dioxide catalyst and the rate of the oxidation of carbon monoxide were investigated over the extended partial pressures of carbon monoxide and reaction temperatres. In addition, the transient behavior of the production of carbon dioxide and the amount of both surface oxygen pecies O_s^{h*} and O_s^l was also followed simultaneously by the application of the transient response technique[5].

2. Experimental

An electrolytic manganese dioxide was used as the catalyst. The compositions of the catalyst was $MnO_{1.84}$ and the BET surface area with nitrogen was 31 m^2/g. The Hall effect measured in air at room temperature showed that the electrolytic manganese dioxide was an n-type semiconductor.

The purification of the gas, the experimental system and the procedure of transient

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response method were exactly the same as described in the previous papers[4,5]. The catalyst (1.05 g) was packed in a reactor consisting of a quartz tube immersed in a fluidized bed. The total flow rate of the gas was kept constant at 343 ml/min and the concentrations of carbon monoxide and oxygen were varied by changing the concentration of nitrogen as a diluent. The intraparticle diffussion resistance of the catalyst was found to be negligible by examining the rate data for catalysts of different sizes, 60–80 and 80–100 mesh, at 50°C. The reaction conditions were chosen in such a way that the total conversion did not exceed 5%.

The surface oxygen species were analysesed by the KI method (pH $\geqq$ 10.5 for O_s^{h*} and $7.1 \leqq \mathrm{pH} \leqq 10.5$ for O_s^l) which was described in the previous paper[4]. The conductivity of the electrolytic manganese dioxide during the reaction was measured by using a D. C. bridge.

3. Experimental Results and Discussion

The rate of carbon monoxide oxidation was the first order with respect to the partial pressure of carbon monoxide, however the apparent rate constant changed anomalously at about $P_{co}^o = 0.08$ atm as shown in Fig. 1. As presented in the previous paper, we again designated two regions 1 and 2, respectively, as shown in Fig. 1.

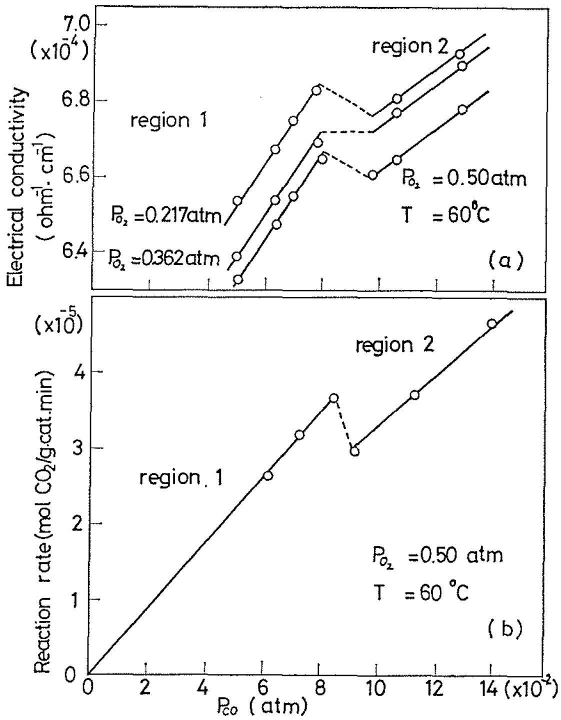

Fig. 1 The reaction rate and the electrical conductivity as a function of P_{co}.

Activation energies in both regions were exactly the same i.e. E_1(region 1) $= 22.2$ and E_2(region 2) $= 22.0$ kcal/mol. However, the apparent rate constant in region 1 is larger than that in region 2 and hence the number of active sites on the surface in the region 1 should be larger than that in the region 2.

As shown in Fig. 1 (a), the electrical conductivity of the catalyst during the reaction increased linearly with the increasing concentration of carbon monoxide within either region 1 or region 2, but an anomalous change in the electrical conductivity could be observed at the same partial pressure of carbon monoxide where an abrupt change in the reaction rate appeared.

We will consider first the change in electrical conductivity in each region. On the basis of the experimental findings described in the previous papers[5] in which we reported that carbon monoxide was not adsorbed on to the manganese dioxide surface and the electrical conductivity of the catalyst was not changed by the introduction of carbon dioxide into the reaction gas stream. It may be considered that the conductivity change during the reaction is caused by the change in the amount of surface oxygen species which are ionized. Since this catalyst is an n-type semiconductor, the increases in conductivity observed in Fig. 1 (a) may be due to the decrease in the amount of ionized surface oxygen. As was discussed earlier[4], there are two kinds of oxygen species, O_s^{h*} and O_s^l, on the surface. Since the amount of O_s^{h*} in either region 1 or region 2 is constant without depending on the partial pressure of carbon monoxide, we may reasonably assume that the increase in conductivity would be ascribed to the decrease in the amount of O_s^l which is strongly bound to the surface. The decrease in the amount of O_s^l during the reaction will be due to the very slow reaction with gaseous carbon monoxide as

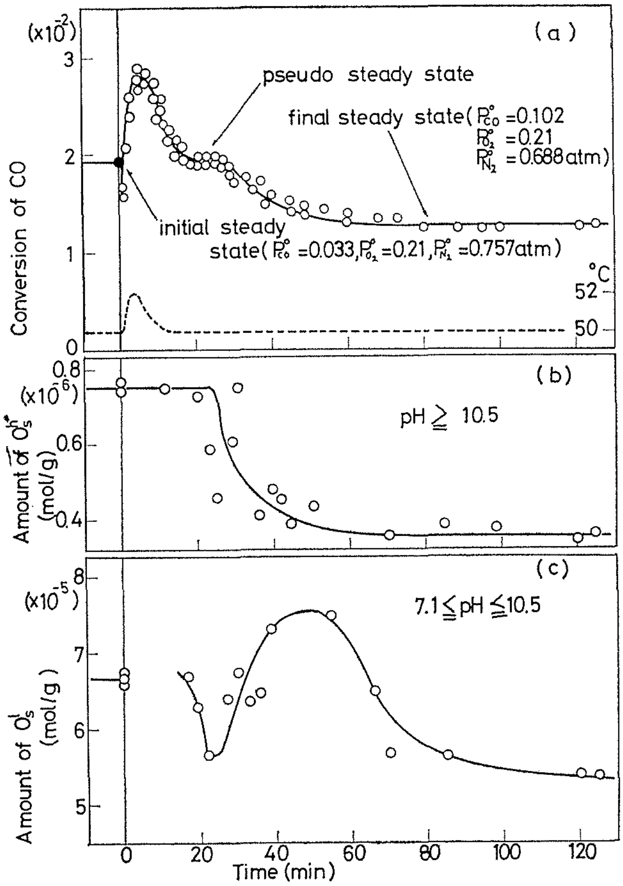

Fig. 2 Response of conversion, O_s^{h*} and O_s^l to step increase in partial pressure of carbon monoxide

discussed previously[4]. The experimental results in which the response of the electrical conductivity to the stepwise change in the partial pressure of carbon monoxide within the same region is very slowly compared with that of the reaction rate will also support this conclusion.

Now we will discuss the transition between two regions. After the reaction reached a steady state with a gas composition of (P_{co}=0.033, P_{O_2}=0.21 and P_{N_2}=0.753 atm (region 1)), the reaction gas stream was switched over to a different gas composition (P_{co}=0.102, P_{O_2}=0.21 and P_{N_2}=0.688 atm (region 2)). The amount of O_s^{h*} and O_s^l and the concentration of carbon dioxide produced by the reaction were analysed simultaneously and the results were presented in Fig. 2.

As Fig. 2 (a) shows, the extent of the conversion of carbon monoxide passed through a maximum and reached a pseudo steady state after about 15 min and then decreased monotonously and reached a final steady value after 70 min. Although a peak can be observed in the initial period of the conversion response curve, this may be ascribed to the spontaneous rise in the catalyst bed temperature as shown by the dotted line. In view of the first order with respect to the partial pressure of carbon monoxide, the conversion under a new gas composition is exactly the same as that at the initial steady state as shown by the pseudo steady state. If, therefore, the surface state of the catalyst does not change under the new gas composition, this pseudo steady state will be the true final state. However, due to the gradual modification of the catalyst surface, the conversion decreases gradually untill a new steady state is reached after 75 min. This mode of modification corresponds exactly to that of the change in the amount of O_s^{h*} as shown in Fig. 2 (b). This result clearly indicates that the oxygen species, O_s^{h*} are responsible for the catalytic activity and the modification of the catalyst surface from region 1 to region 2 affects the reaction rate through the change of the amount of O_s^{h*}.

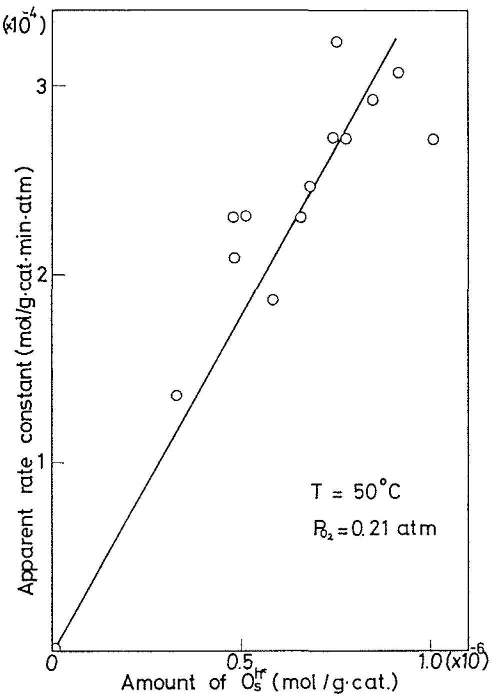

Fig. 3 Linear relationship between the apparent rate constant and the amount of O_s^{h*}

The apparent rate constants were plotted against the amount of O_s^{h*} on the catalysts of various activities. The results showed a good proportionality as shown in Fig. 3, which is quite similar with that obtained at a low temperature of (−15.5°C) which was discussed in the previous paper[5].

A similar response of the amount of O_s^l are presented in Fig. 2 (c). The mode of the response is quite different from those presented in Fig. 2 (a) and (b). This will also suggest that the oxygen species O_s^l does not play an important role in this catalytic reaction.

4. References

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