Carbon Monoxide Oxidation over Chromium Sesquioxide. II. Adsorption Behavior of CO and CO_2

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The adsorption behavior of carbon monoxide and carbon dioxide on oxidized and reduced surface of α-Cr_2O_3 catalyst was studied experimentally by the application of a transient response method. From the analysis of response curves obtained for the concentration of effluent gas component and for the electrical conductivity of catalysts, it was shown that neither carbon monoxide nor carbon dioxide can be adsorbed on the oxidized surface, but they are adsorbed on the reduced surface without electron transfer between adsorbates and the catalysts. Adsorption of carbon monoxide is almost reversible, but that of carbon dioxide is both reversible and irreversible. Oxygen markedly accelerates the desorption of both carbon monoxide and carbon dioxide. It is concluded that this can be attributed to the effect of adsorbed oxygen in lowering the degree of coordinative unsaturation of Cr^{3+} ions.

The adsorption of carbon monoxide and carbon dioxide on Cr_2O_3 surface has been studied by many investigators.[1-3] It was found that the adsorption behavior of both gases on Cr_2O_3 surface is strongly affected by the oxidation state of the surface as pointed out by Dawden and Garner.[1] In recent years, IR spectroscopy has been successfully applied to reveal the surface properties of Cr_2O_3 and the adsorbed states of CO and CO_2 on its surface.[4,5] It was demonstrated in this line of studies that the degree of coordination unsaturation of Cr^{3+} ions plays as important role in the adsorption behavior of these gases. Zecchina, Colluccia, Guglielminotti and Ghiotti[5] concluded that CO is adsorbed on coordinatively unsaturated (coord. unsatd.) Cr^{3+} ions and CO_2 is adsorbed mainly on Cr^{3+} (coord. unsatd.)–O^{2-} (coord. unsatd.) couples resulting in the formation of bidentate carbonate, and partly on Cr^{3+} (coord. unsatd.) ions or O^{2-}(coord. unsatd.) ions forming linearly bonded CO_2 or monodentate carbonate, respectively. The forms of adsorbed CO_2 and the strength of their bonding to the surface are strongly dependent on the coordination heterogeneity as well as on the ligand heterogeneity. Because of the variety of the adsorbed states it will be worthwhile to reveal the dynamic behavior of the surface complexes and the effect of oxygen on the dynamic behavior.

In the present study, the transient response method[6-8] was utilized for this purpose.

Experimental

α-Cr_2O_3 samples and the method of experiments are the same as described in part I.[9]

The responses of the electrical conductivity, σ, of the catalyst and of the concentration of component Y in the outlet gas stream to a step change in the concentration of component X in the inlet gas mixture are denoted by X–σ and X–Y, respectively. When X is increased from nil, X(inc., 0)–σ and X(inc., 0)–Y; when decreased down to nil, X(dec., 0)–σ and X(dec., 0)–Y.

Results and Discussion

Behavior of CO and CO_2 on the Oxidized Surface

After the catalyst had been completely oxidized in a stream of O_2(20%)–N_2 mixture at 131 °C, CO_2 was introduced stepwise into the feed stream without changing the concentration of oxygen, and the CO_2(inc., 0)–CO_2 and the CO_2(inc., 0)–σ responses were followed simultaneously. Subsequently, the CO_2 in the feed stream was cut off and the CO_2(dec., 0)–CO_2 and the CO_2(dec., 0)–σ responses were followed. The CO_2–CO_2 responses obtained in both runs were instantaneous and the CO_2–σ responses showed no appreciable change in conductivity (Fig. 1). The CO–CO and the CO–σ responses were also measured in the same way and exactly the same results were observed. The results indicate that neither CO_2 nor CO can be adsorbed on the oxidized surface when prepared in the way used in this experiment. The oxidized sample used in our experiments contains saturated amounts of oxygen on the surface, and hence the oxidized surface has no activity for the additional adsorption of CO and CO_2.

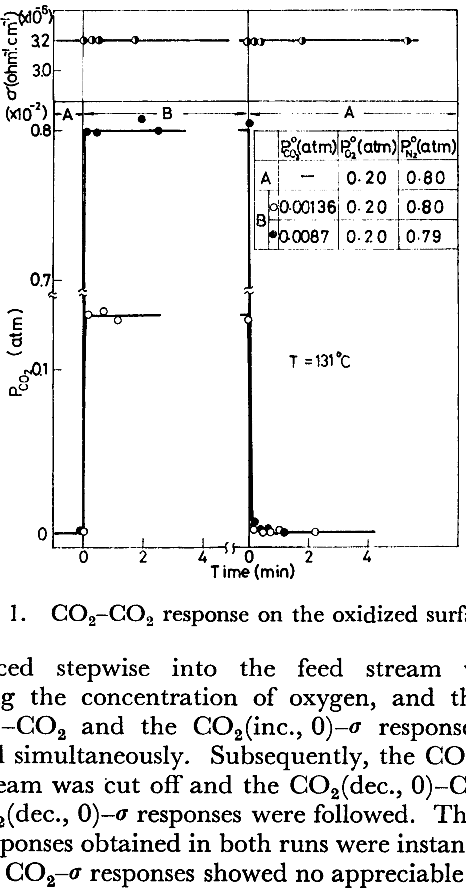

Fig. 1. CO_2–CO_2 response on the oxidized surface.

Behavior of CO_2 on the Reduced Surface. For the preparation of a reduced surface, a stream of CO(6%)–N_2 mixture was allowed to flow through the catalyst bed at 131 °C until no carbon dioxide was detected in the effluent stream. The electrical conductivity of the catalyst fell down to as low as 1×10^{-8} ohm^{-1} cm^{-1}. Carbon dioxide (0.85%) was then introduced into the

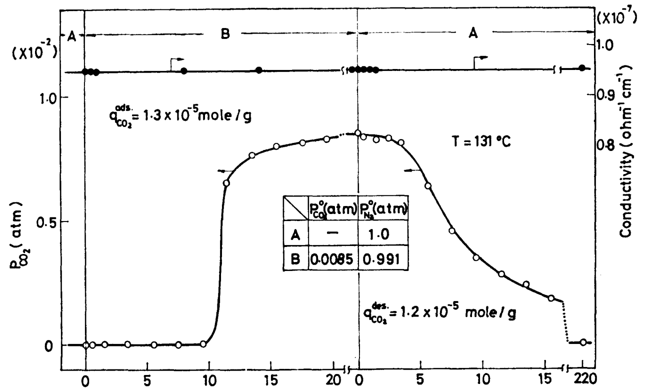

Fig. 2. CO_2–CO_2 response on the reduced surface.

inlet gas stream and the CO_2(inc., 0)–CO_2 and the CO_2(inc., 0)–σ responses were followed until a steady state was reached. Subsequently, the CO_2 in the feed stream was cut off and the CO_2(dec., 0)–CO_2 and the CO_2(dec., 0)–σ responses were followed. The results are shown in Fig. 2. The transient state of the CO_2–CO_2 response was observed in both cases for 30—220 min, indicating the adsorption of CO_2 on the reduced surface. The integrated amount of adsorbed CO_2 is estimated to be 1.3×10^{-5} mol/g from the CO_2 (inc., 0)–CO_2 response and that of desorbed CO_2 is estimated to be 1.2×10^{-5} mol/g from the CO_2(dec., 0)–CO_2 response. Both amounts are nearly the same. It seems that the adsorption of CO_2 under the present conditions is almost reversible.

During these response periods, the electrical conductivity of the catalyst remained constant (Fig. 2), indicating that no electron transfer is accompanied by the adsorption of carbon dioxide, *i.e.* the adsorbed carbon dioxide is electrically neutral.

After the CO_2(inc., 0)–CO_2 response had been followed as described above, the feed stream of CO_2(0.85%)–N_2 mixture was switched over to a stream of O_2(20%)–N_2 mixture instead of pure nitrogen and the CO_2-(dec., 0)–CO_2 response was followed. The results are shown in Fig. 3. A large amount of carbon dioxide was desorbed at the initial period of the response, it decreased steeply and then tailed until no carbon dioxide was detected after 220 min. No carbon monoxide was detected in the effluent stream during the course of response. The integrated amount of the desorbed CO_2 during this run was estimated to be 6.2×10^{-5} mol/g. Since the amount of desorbed CO_2 estimated in the foregoing run was 1.2×10^{-5} mol/g, the desorbed amount of CO_2 estimated in this run is much larger than that in the nitrogen stream. Since the adsorbed CO does not react with gaseous oxygen, the difference in the two amounts can be attributed to the existence of irreversibly adsorbed CO_2 which had been produced during the course of reduction of the surface with CO and remained during the subsequent treatment in the pure nitrogen stream. This suggests that the desorption of the irreversibly adsorbed CO_2 can be attributed to the competitive adsorption of oxygen onto Cr^{3+} (coord. unsatd.) ions. The amount of irreversibly adsorbed CO_2 is estimated to be 5.0×10^{-5} mol/g. This value is in good agreement with that estimated in Part I.

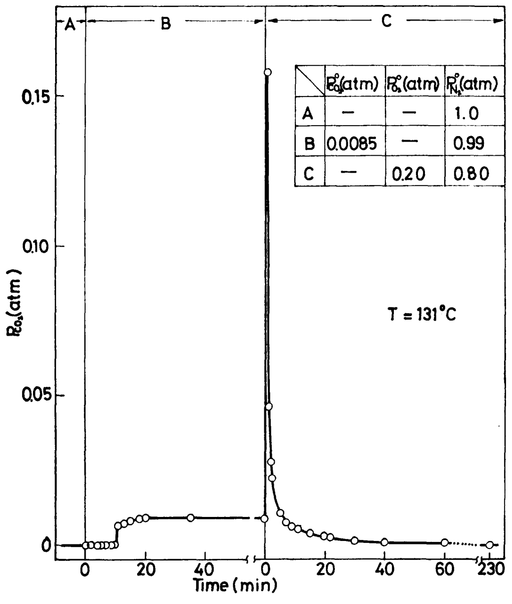

Fig. 3. CO_2–CO_2 response.

It was suggested in Part I that the carbon dioxide produced on site S_I is irreversibly adsorbed while that produced on site S_{II} is reversibly adsorbed. Since the adsorption of oxygen onto site S_I is very rapid, the desorption of the irreversibly adsorbed carbon dioxide from S_I due to the competitive adsorption of oxygen should also be rapid. Comparing the period of the initial rapid desorption of carbon dioxide (Fig. 3) with the time required for the initial rapid adsorption of oxygen (Fig. 6, Part I), we see that the time required for both processes are consistent with each other.

We might conclude that when oxygen is present in the gas phase, the site S_I is always free from retardation by adsorbed carbon dioxide, and $O^- \cdot S_I$, which is very active for CO oxidation, is rapidly regenerated, contributing substantially to the reaction. This might explain the fact that the amount of $O^- \cdot S_I$ remains constant in the steady state of the reaction with a variety of P_{CO}.

The rate of oxygen adsorption on S_{II} is very small and the same effect of oxygen can not be expected for the carbon dioxide produced on S_{II}. Eventually the amount of $O^- \cdot S_{II}$ is lowered at a steady state with higher partial pressure of CO where the rates of CO_2 formation on S_{II} are higher.

According to the results obtained by Zecchina *et al.*[5] the irreversibly adsorbed CO_2 observed in this study will probably be in the form of bidentate carbonate produced by the adsorption of CO_2 on the Cr^{3+} (coord. unsatd.)–O^{-2} (coord. unsatd.) couples which are present on the highly reduced surface. Another possibility is that the bicarbonate ions produced by the adsorption of CO_2 on hydroxyl ions remain on the surface. The reversibly adsorbed CO_2, on the other hand, will mainly correspond to CO_2 coordinated to Cr^{3+} (coord. unsatd.) ions in the linear form which is predominant when the degree of coordinative unsaturation of Cr^{3+} is low.

Behavior of CO on the Reduced Surface. After the

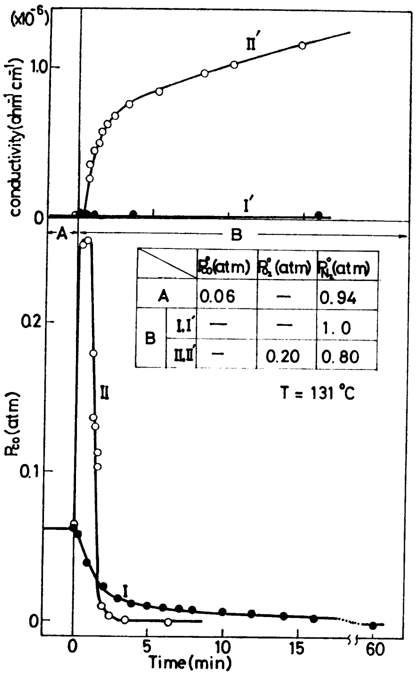

Fig. 4. CO–CO and CO–σ responses.

catalyst had been reduced in the same way as described in the foregoing section, the feed stream was switched over to a stream of either pure nitrogen or a mixture of $O_2(20\%)$–N_2, and the CO–CO and the CO–σ responses were followed simultaneously. The results are shown in Fig. 4.

When the feed stream was replaced by the stream of pure nitrogen, the desorption of CO was observed for about 60 min as shown by curve I in Fig. 4. From the graphical integration of curve I, the total amount of adsorbed carbon monoxide is estimated to be 3.0×10^{-5} mol/g. During the same run, the electrical conductivity of the catalyst was kept entirely constant (line I′, Fig. 4). These results imply that CO can be adsorbed on the reduced surface without electron transfer between the adsorbed CO and the catalyst. Since the adsorption of CO can take place only on the reduced surface, the sites for the adsorption should be Cr^{3+} (coord. unsatd.) ions.

When the feed stream was replaced by a stream of $O_2(20\%)$–N_2 mixture, on the other hand, the desorption of a large amount of CO took place at the initial stage of the response and the desorption was completed within 3 min (curve II in Fig. 4). The integrated amount of desorbed CO is estimated to be 3.6×10^{-5} mol/g, being slightly higher than the amount of CO desorbed into the pure nitrogen stream. If the carbon monoxide adsorbed on the surface can react with the oxygen introduced, the amount of the desorbed CO in the $O_2(20\%)$–N_2 stream should be lower than the amount of the desorbed CO in the pure nitrogen stream. The results suggest that the adsorbed CO does not react with the introduced oxygen.

The difference in the amounts of desorbed CO into the $O_2(20\%)$–N_2 stream and the pure N_2 stream may also be ascribed to the same reason as in the case of CO_2. It has been stated by Zecchina *et al.*[5] that the adsorption of CO on the reduced surface is reversible. Presumably, however, the adsorption of CO under the conditions in this study will not be completely reversible, and the adsorbed CO at a very low coverage will remain on highly coordinatively unsaturated Cr^{3+} ions, and these residual adsorbed CO molecules will be desorbed only by the adsorption of oxygen onto Cr^{3+} (coord. unsatd.) ions, with which the degree of coordinative unsaturation of Cr^{3+} (coord. unsatd.) ions is lowered and eventually the desorption of CO is enhanced.

The change in the electrical conductivity was observed (curve II′, Fig. 4). Since no electron transfer takes place in the case of CO desorption into the pure nitrogen stream, the change in the electrical conductivity in this case should be due to the adsorption of oxygen.[9]

So far we have discussed the nature of adsorption sites on the surface only in terms of coordinative heterogeneity of Cr^{3+} ions, but ligand heterogeneity may also play some role in characterizing the nature of those sites. OH^- on the surface might have some effects on the behavior of CO and CO_2 on the surface.

Behavior of CO and CO_2 during the CO Oxidation at Steady States. When a mixture of CO–O_2–N_2 is allowed to flow through the bed of oxidized catalyst, oxidation of CO takes place, the reaction rate varying

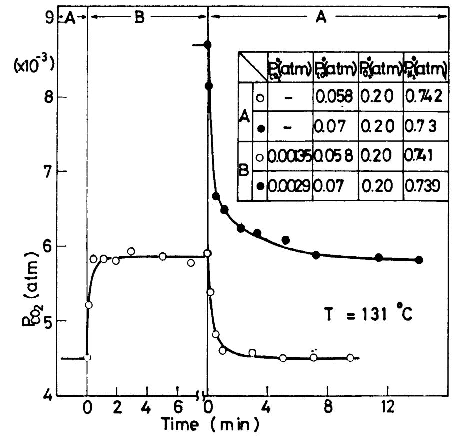

Fig. 5. CO_2–CO_2 response during the reaction.

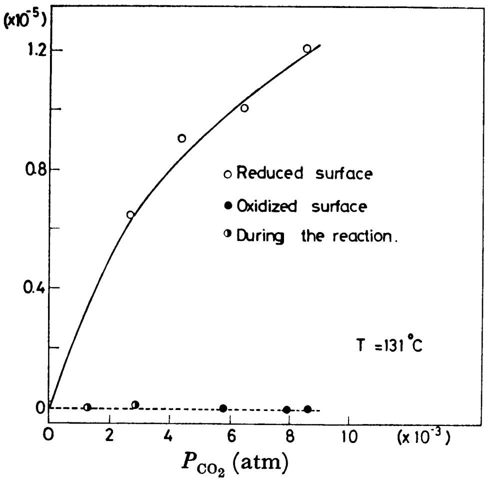

Fig. 6. Adsorption isotherm for CO_2.

very slowly until it reaches a steady state after 15 h. After the steady state was attained, the CO in the feed was cut off and CO(dec., 0)–CO response was followed. The response was instantaneous, indicating that no carbon monoxide was adsorbed on the surface in the steady state during the course of reaction. On the other hand, the CO_2(inc., 0)–CO_2 and the CO_2(dec., 0)–CO_2 responses obtained in the same steady state indicates the occurrence of adsorption and the desorption of CO_2 on the same surface (Fig. 5). The amount of adsorbed CO_2 estimated from the graphical integration of the CO_2(dec., 0)–CO_2 response curve was presented in Fig. 6 with those on the reduced surface and on the oxidized surface. As can be seen from Fig. 6, the amount of CO_2 adsorbed on the surface during the reaction was two orders of magnitude smaller than that adsorbed on the reduced surface and rather close to that on completely oxidized surface. From the result, it can be concluded that the catalyst surface during the course of reaction in the steady state is in highly oxidized state.

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