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Dual Routes of the Reaction between Nitrous Oxide and Carbon Monoxide over SnO_2 as Revealed by the Transient-Response Method

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The mechanism of the reaction between nitrous oxide and carbon monoxide over SnO_2 was studied by the transient-response method. It was concluded that at higher temperatures the reaction proceeded by catalyst redox mechanism with nitrous oxide and carbon monoxide over the catalyst in more reduced states. However, the reaction between adsorbed carbon monoxide and gaseous nitrous oxide was also involved in the reaction paths when the temperature was decreased or the surface of the catalyst was in more oxidized states.

INTRODUCTION

A number of papers have been published on the mechanism of the reaction between nitrous oxide and carbon monoxide over a variety of metal oxides (*1–9*). It has been concluded that the reaction proceeds by the redox mechanism over CuO (*1, 2*), ZnO (*3*), $CoFe_2O_4$ (*4*), and SnO_2 (*5*), where surface oxygen or O^- species is abstracted by carbon monoxide and the generated reduced sites are successively oxidized by nitrous oxide. On the other hand, the reaction between nitrous oxide and carbon monoxide either or both adsorbed on the catalyst was reported to be predominant over Fe_2O_3/Cr_2O_3 (*6*), MoO_3/SiO_2 (*7*), NiO (*8*), and MnO (*9*).

The transient-response method has been applied for various catalyzed reactions (*10*) and it was shown that this method was potentially effective for elucidation of the mechanism of heterogeneous catalytic reactions. In the present work, the reaction between carbon monoxide and nitrous oxide over SnO_2 is studied with the aid of this method to show how the mechanism of the title reaction is affected by the reaction conditions.

EXPERIMENTAL

The catalyst was prepared according to a method similar to that employed by Fuller and Warwick (*5*). Hydrous stannic oxide gel was prepared by addition of an aqueous solution of ammonia to a solution which contained 116 g of stannic chloride. The gel was separated from the solution by centrifugation, dried at room temperature, and immersed in 1 dm^3 of nitric acid solution (1 mol/dm^3). Thereafter, it was washed with distilled water until the pH of the solution attained 4. The gel was further filtered, dried again at 473 K for 3 h, and calcined in a stream of nitrogen–oxygen mixture ($N_2 : O_2 = 4 : 1$) for 10 h at 723 K. A part of the catalyst (9.3 g) thus prepared was packed in the catalyst bed and experiments were carried out at a total flow rate of 150 cm^3/min and at 109.4 kPa using an apparatus similar to that adopted in the previous work (*10*). After the concentrations of gaseous components at the inlet of the catalyst bed had been changed stepwise, the change in the outlet concentrations of the reactants and products was followed by gas chromatography with which automatic gas sampling devices were equipped. The air-driven valves attached to sampling tubes were able to open and close automatically according to a program which was laid out beforehand by means of a programmable sequence controller (Ohkura R 2016). The gases at the outlet were, therefore, taken and held in the sampling tubes at any time for any length of time, so that they were

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admitted to gas chromatography at any time for analysis.

The surface area of the catalyst was estimated to be 35 m^2/g according to the BET method (*11*) and the number of reduced sites on the catalyst surface was determined by titration with nitrous oxide at 420 K. As Fuller and Warwick (*5*) observed, SnO_2 was found to readily undergo reduction by carbon monoxide and oxidation by nitrous oxide at this temperature. During the course of the reduction carbon dioxide was formed, while by the oxidation nitrogen was evolved. However, no oxygen was detected in the outflow during the course of the oxidation, so that all the nitrogen formed was attributable to the oxidation of the catalyst. The catalyst surface was oxidized by a stream of nitrous oxide–helium mixture (mole fraction of nitrous oxide: $f_{N_2O} = 0.12$) at 420 K until no nitrogen was detected in the outflow. The mixture was then switched over to a helium stream and the catalyst was kept in the stream until no more gas was desorbed. After this catalyst had been reduced by carbon monoxide in any given amount and then all gases held on the surface such as carbon monoxide and carbon dioxide were flushed with helium, nitrous oxide–helium mixture was again admitted over the catalyst at 420 K until no nitrogen was detected in the outflow. It was found that the amount of nitrogen totally evolved was practically the same as that of carbon dioxide formed by the previous reduction with carbon monoxide. This was always valid irrespective of the extent of the previous reduction, suggesting strongly that the reduced sites were fully oxidized with nitrous oxide when the nitrous oxide–helium mixture was admitted at 420 K until no nitrogen was detected in the outflow. The numbers of the reduced sites were, therefore, estimated from the total amount of nitrogen evolved by titration with nitrous oxide at this temperature.

It was assumed for convenience that the (001) plane was preferentially exposed on the SnO_2 surface. On the basis of the crystal structure of SnO_2 (*12*), 2.83×10^{21} nitrogen molecules were, therefore, assumed to evolve when a monolayer of the surface of the present catalyst was fully reduced. The fraction θ_v of the reduced sites was defined as the ratio between the numbers of nitrogen molecules determined by titration and those which were assumed to be evolved when a monolayer of the surface was fully reduced. In some cases, the catalyst was subjected to reduction with a stream of carbon monoxide–helium mixture ($f_{CO} = 0.064$) for various periods of time and was then flushed with helium for conditioning the catalyst at different reduced states. The initial fraction θ_v of the reduced sites was varied by these procedures.

RESULTS AND DISCUSSION

Transient Response to the Addition or Cutoff of CO or N_2O

Figure 1 illustrates the results obtained when carbon monoxide was admitted over the fully oxidized surface at 420 K. The

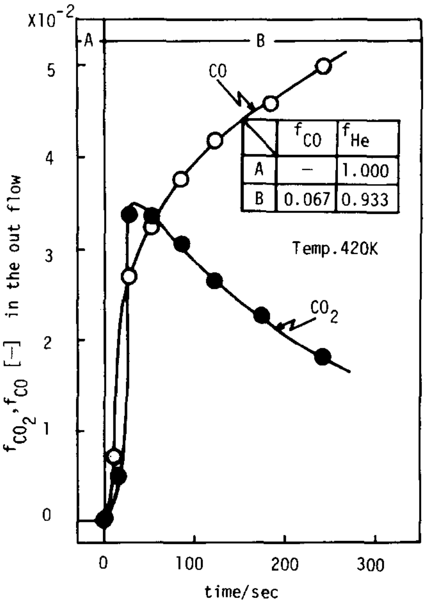

FIG. 1. CO_2 formation by addition of CO over the fully oxidized surface. A stream (He) was switched over to B stream (CO + He) stepwise at the inlet of the catalyst bed. f_{CO_2}, etc.: mole fraction of CO_2, etc.

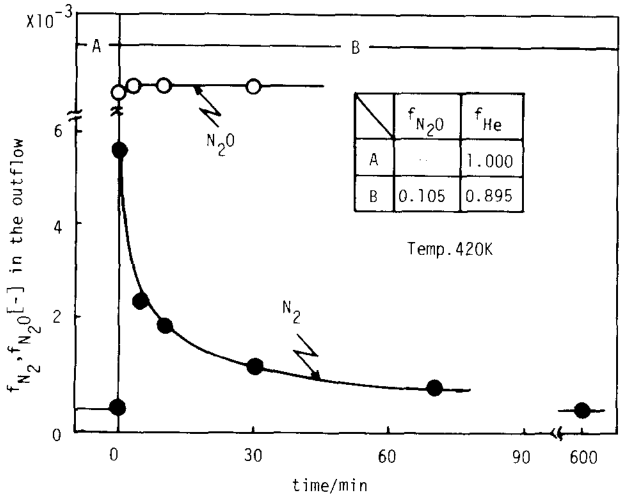

FIG. 2. N_2 formation by addition of N_2O over partially oxidized surface. A stream (He) was switched over to B stream (N_2O + He) stepwise at the inlet of the catalyst bed. f_{N_2}, etc.: mole fraction of N_2, etc. The fraction θ_v of the reduced sites: 0.48.

mole fraction f_{CO_2} of carbon dioxide at the outlet of the catalyst bed initially increases steeply with time, attains a maximum at 33 sec, and then decreases gradually. When the supply of carbon monoxide was switched back to that of helium, the outflow of carbon monoxide could be observed for 1 min, and that of carbon dioxide lasted for more than 5 min. The results indicate that carbon monoxide is reversibly adsorbed on the surface, and also the reaction between adsorbed carbon monoxide and surface oxygen on the catalyst is not so fast at this temperature since a finite amount of carbon monoxide could be desorbed. According to the time required for complete disappearance of carbon dioxide from the outflow, the desorption of carbon dioxide is likely to be rather slow. Since the outflow of carbon dioxide continued after complete disappearance of desorbed carbon monoxide, the desorption of carbon dioxide seems to be much slower than the formation of adsorbed carbon dioxide due to the reaction between adsorbed carbon monoxide and surface oxygen. Separate experiments on the desorption of carbon dioxide simply adsorbed from a carbon dioxide–helium mixture also substantiated this conclusion.

Figure 2 illustrates the results obtained at 420 K after nitrous oxide was admitted over the partially reduced surface (θ_v = 0.48). Nitrogen formation overshoots immediately after nitrous oxide was admitted. As described in the previous section no oxygen was detected in the outflow so that the reduced sites should be oxidized by nitrous oxide. The height of the overshoot multiplied by total flow rate gives the initial rate of nitrogen formation under the present experimental conditions. Figure 3 illustrates the results obtained at 420 K on the catalyst with various fractions of the reduced sites (θ_v). It is seen that the initial rates obtained are proportional to the fraction θ_v. It was also found that nitrogen was formed at the rates proportional to the partial pressures of nitrous oxide. When the supply of nitrous oxide was switched over to that of helium, nitrous oxide slowly desorbed as seen from Fig. 4. In contrast to the slow desorption of nitrous oxide, the nitrogen formation immediately ceased when the supply of nitrous oxide was cut off. On the basis of these results, it is, therefore, concluded that adsorbed nitrous oxide does not participate in the nitrogen formation and nitrous oxide in the gas phase must attack directly the reduced sites to form nitrogen.

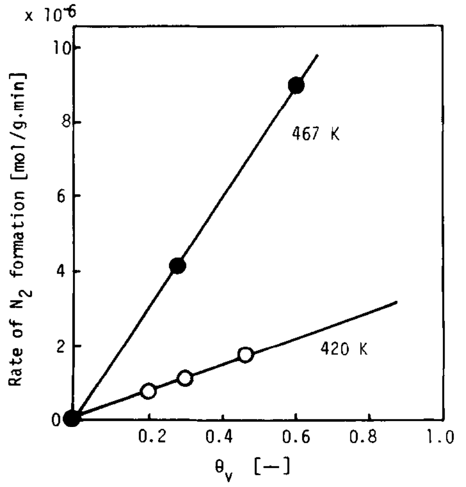

FIG. 3. Initial rate of N_2 formation versus the fraction θ_v of the reduced sites. N_2O was admitted over the catalyst with various θ_v values. Mole fraction f_{N_2O} of nitrous oxide admitted = 0.11.

Transient Response to the Addition of CO–N₂O Mixture

Figure 5 illustrates the results obtained at 420 K after a carbon monoxide–nitrous oxide mixture was admitted over the partially reduced surface (θ_v = 0.48). Immediately after the admission of the mixture, the nitrogen formation overshoots but carbon dioxide slowly appears in the outflow as the reduced sites are increasingly oxidized. Similar experiments were carried out over the fully oxidized surface. As Fig. 6 shows, the nitrogen formation overshoots immediately after the admission of the mixture even on such an oxidized surface. The carbon dioxide formation increases fairly steeply but not abruptly, attains a maximum, and decreases with time. The solid curve in Fig. 7 shows the initial rate of nitrogen formation at 420 K against the fraction θ_v of the reduced sites. The rate decreases until θ_v values decrease to 0.2. However, when the fraction θ_v is lowered below 0.2, it increases. As compared to the results in Fig. 3 at the same temperature, it is evident that the initial rates obtained are always greater than those obtained by the admission of nitrous oxide alone. The differences between these values are shown by the broken curve in Fig. 7. The differ-

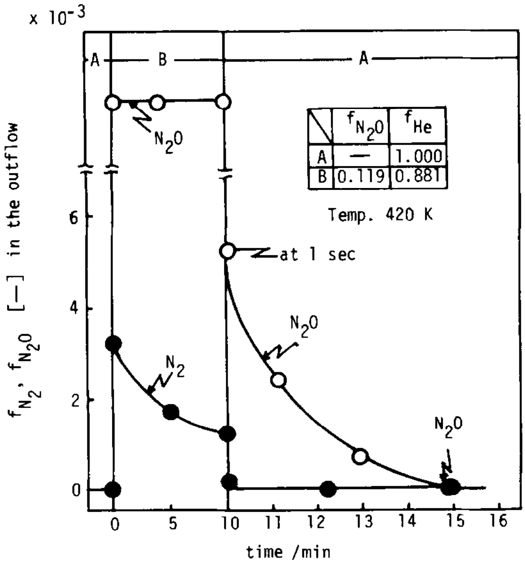

FIG. 4. Transient responses of N_2O and N_2 accompanied by cutoff of N_2O supply. A stream (N_2O + He) was switched over to B stream (He) stepwise at the inlet of the catalyst bed. f_{N_2}, etc.: mole fraction of N_2, etc.

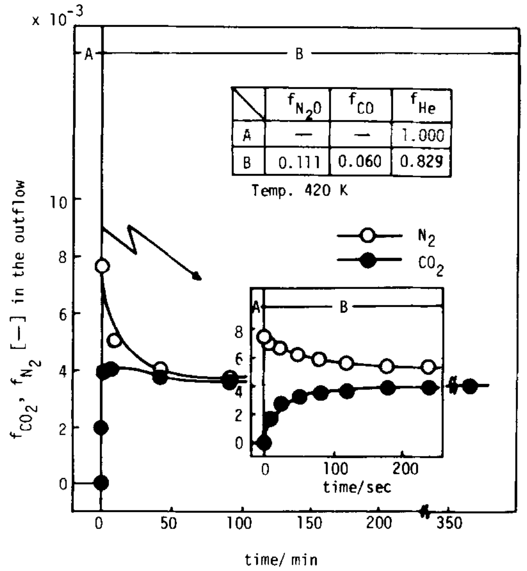

FIG. 5. N_2 and CO_2 formations accompanied by the supply of a CO–N_2O mixture over partially reduced surface. A stream (He) was switched over to B stream (N_2O + CO + He) at the inlet of the catalyst bed. f_{CO_2}, etc.: mole fraction of CO_2, etc. The fraction θ_v of the reduced sites: 0.48.

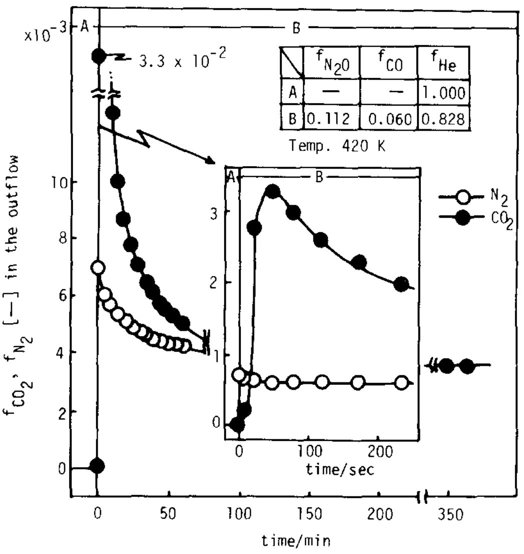

FIG. 6. N_2 and CO_2 formations accompanied by the supply of a CO–N_2O mixture over the fully oxidized surface. A stream (He) was switched over to B stream (N_2O + CO + He) stepwise at the inlet of the catalyst bed. f_{CO_2}, etc.: mole fraction of CO_2, etc.

ence between these values decreases with increasing values of the fraction θ_v. Namely, the rate of nitrogen formation obtained by the admission of the mixture approaches that obtained by the admission of nitrous oxide alone when the catalyst surface is in more reduced states. This indicates that nitrogen is mainly formed by oxidation of the reduced sites with nitrous oxide irrespective of the presence or the absence of carbon monoxide when the surface is in more reduced states. In these respects, it is, therefore, concluded that when the title reaction is occurring, the redox mechanism (mechanism I) is always operating over the catalyst surface but another mechanism (mechanism II) is also operating in parallel on the oxidized surface. Since nitrogen is produced over a reduced surface by mechanism I and on an oxidized surface by mechanism II, the relative contribution of these two mechanisms for the production of nitrogen depends on the oxidation state of the catalyst surface. Mechanism I prevails over the catalyst in more reduced states and mechanism II becomes predominant over that in more oxidized states.

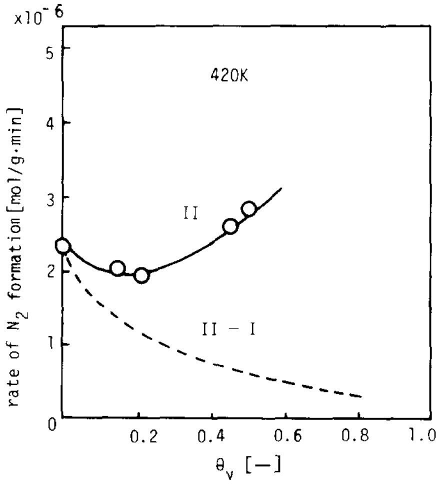

FIG. 7. Initial rate of N_2 formation versus the fraction θ_v of the reduced sites. A N_2O–CO mixture (f_{N_2O} = 0.11 and f_{CO} = 0.064) was admitted over the catalyst with various θ_v values. Broken curve is the difference of the initial rates of N_2 formation from N_2O–CO mixture (II) and N_2O alone (I).

Effect of Temperature upon Nitrogen Formation

Figure 8 shows the results when the nitrous oxide–carbon monoxide mixture was admitted with the helium stream over the fully oxidized surface at 467 and 352 K.

The response curves obtained at 467 K are markedly different from those obtained at 420 K (Fig. 6). Carbon dioxide overshoots when the mixture was admitted but no overshoot-type response is seen in the nitrogen formation. It is readily seen that the total amount of carbon dioxide formed exceeds that of nitrogen appreciably, indicating that the catalyst surface is reduced with time to a considerable extent. At a very initial period when the catalyst surface is fully oxidized, nitrogen is abruptly formed ($f_{N_2} = 2.8 \times 10^{-3}$) by mechanism II upon admission of the carbon monoxide–nitrous oxide mixture. As the oxidized surface is increasingly reduced with carbon monoxide, gaseous nitrous oxide attacks the generated reduced sites and the nitro-

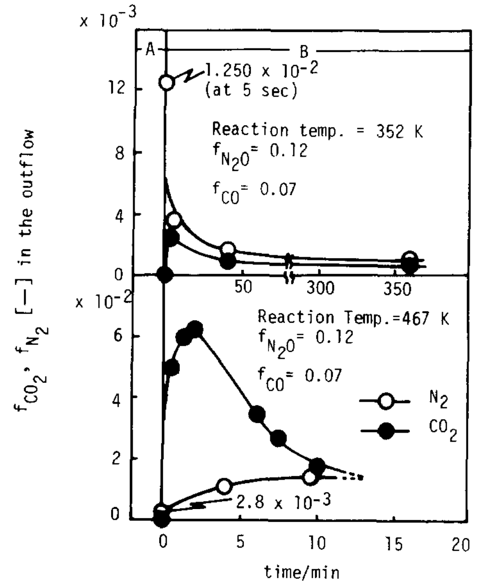

FIG. 8. N_2 and CO_2 formations accompanied by the supply of a N_2O–CO mixture over the fully oxidized surface at various temperatures. A stream (He) was switched over to B stream (N_2O + CO + He) stepwise at the inlet of the catalyst bed. f_{CO_2}, etc.: mole fraction of CO_2, etc.

gen formation by mechanism I, therefore, slowly increases over the later period. The initial rate of nitrogen formation at 467 K which is obtained by admission either of nitrous oxide alone or the nitrous oxide–carbon monoxide mixture is determined as a function of the fraction θ_v of the reduced sites. When nitrous oxide alone was admitted, no nitrogen was formed at $\theta_v = 0$. On the other hand, when the nitrous oxide–carbon monoxide mixture was admitted, the appreciable amount of nitrogen ($f_{N_2} = 2.8 \times 10^{-3}$) was evolved immediately after admission of the mixture as can be seen from Fig. 8. The initial rates obtained by admission of the mixture were always greater than those obtained by admission of nitrous oxide alone over the whole θ_v region studied. At 467 K, however, in marked contrast to the results obtained at 420 K, the former values obtained were almost equal to the latter values above $\theta_v = 0.1$. From these results, it is suggested at 467 K that nitrogen is formed by mechanism II at θ_v = 0 while at θ_v larger than 0.1 it is formed mostly by mechanism I, and that mechanism I tends to prevail at higher temperatures.

When the experiments are carried out at 352 K over the fully oxidized surface, the response curves obtained are similar to those obtained at 420 K for which both nitrogen and carbon dioxide formations overshoot and decrease gradually with time. However, the formation of nitrogen exceeds that of carbon dioxide, indicating that the latter species desorbs slowly at this temperature. When mechanism II is operating, the nitrogen formation is suppressed presumably by adsorbed carbon dioxide as will be shown in the next section.

Figure 9 illustrates the plots of the initial rate of nitrogen formation obtained by admission either of nitrous oxide–carbon monoxide mixture (curve II) or nitrous oxide alone (curve I) against the reciprocal of the temperature. It is demonstrated that when the temperature is raised, the rate obtained by the mixture decreases but that obtained by nitrous oxide alone increases.

On the basis of these observations, it is, therefore, concluded that in the presence of

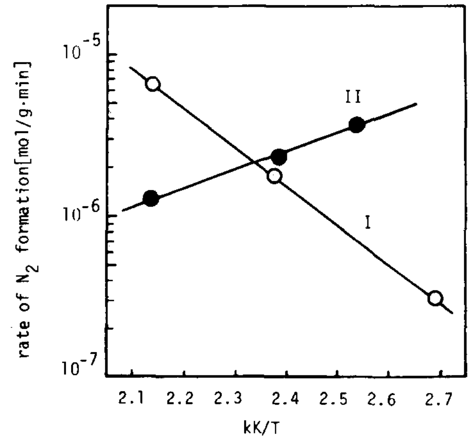

FIG. 9. Temperature dependence of the initial rates of N_2 formation. (I) N_2 formation from N_2O alone at θ_v = 0.48. Mole fraction of N_2O admitted: f_{N_2O} = 0.12. (II) N_2 formation from the N_2O–CO mixture at θ_v = 0. Mole fractions of N_2O and CO: f_{N_2O} = 0.11 and f_{CO} = 0.064.

TABLE 1

Initial Rate of Nitrogen Formation (mol/min)[a]

$\theta_v = 0$		$\theta_v = 0.48$	
In the presence of CO_2	In the absence of CO_2	In the presence of CO_2	In the absence of CO_2
1.34×10^{-5}	4.69×10^{-5}	3.61×10^{-5}	5.09×10^{-5}

[a] Obtained at 420 K.

carbon monoxide nitrogen is formed by mechanism I at higher temperatures but mechanism II becomes involved as the temperature is lowered.

Effect of Carbon Dioxide upon the Reaction

To study the effect of carbon dioxide upon the nitrogen formation, a carbon dioxide–helium stream was allowed to flow over the catalyst for a while and then switched over to the mixture composed of nitrous oxide, carbon monoxide, and carbon dioxide. In Table 1, the initial rates of nitrogen formation obtained either in the presence or the absence of carbon dioxide are listed. When the catalyst was fully oxidized ($\theta_v = 0$), the rate obtained in the presence of carbon dioxide was decreased by 79% as compared to that obtained by the carbon dioxide-free mixture. Since adsorbed carbon dioxide was estimated to occupy only 2% of the surface (2.25 cm^3 STP) under this condition, it is highly probable that the reaction through mechanism II is taking place on a very small part of the oxidized surface. When the experiments are carried out over a partially reduced catalyst at the fraction $\theta_v = 0.48$, the rate was decreased by 29% in the presence of carbon dioxide. In a like manner, a nitrous oxide–helium mixture was admitted with carbon dioxide. In marked contrast to the above results, the nitrogen formation from nitrous oxide alone was unaffected by the presence of carbon dioxide.

We may conclude from these results that the adsorption of carbon dioxide takes place on the oxidized surface and hence the rate of nitrogen formation through mechanism I which is taking place at reduced sites is not affected by the preadsorption of carbon dioxide. On the other hand, the nitrogen formation through mechanism II which is taking place over the oxidized surface is strongly retarded by the preadsorption of a small amount of carbon dioxide due to the blocking of particular active sites on the oxidized surface for the operation of mechanism II.

Reaction between N_2O and Adsorbed CO

When 2 cm^3 carbon monoxide which corresponds to nearly 2% of surface oxygen was dosed on the fully oxidized surface as a pulse at 420 K, no products were detected in the outflow. The whole carbon monoxide was held on the catalyst and existed presumably as adsorbed carbon monoxide or surface carbonate species (*13*). A nitrous oxide–helium stream was then admitted stepwise over the catalyst at given intervals after the carbon monoxide pulse injection. Nitrogen was evolved immediately after the admission of nitrous oxide. Curve I in Fig. 10 shows a plot of the initial rate of nitrogen formation against the time intervals. It is seen that the rate of nitrogen formation decreases as the time intervals are prolonged. By setting the time intervals close to zero, the rate obtained is found to be more than ten times as large as that estimated from Fig. 3 as the rate due to mechanism I with the assumption that carbon monoxide admitted previously had been all consumed for the formation of the reduced sites. Therefore, it is reasonable to assume that under this condition mechanism II should prevail and nitrogen was formed rapidly by the reaction between adsorbed carbon monoxide and nitrous oxide. As the time intervals are prolonged, however, previously adsorbed carbon monoxide presumably transformed into carbonate species by the reaction with surface oxygen so that the nitrogen formation decreased with the time intervals. Curve II in Fig. 10 shows a plot of

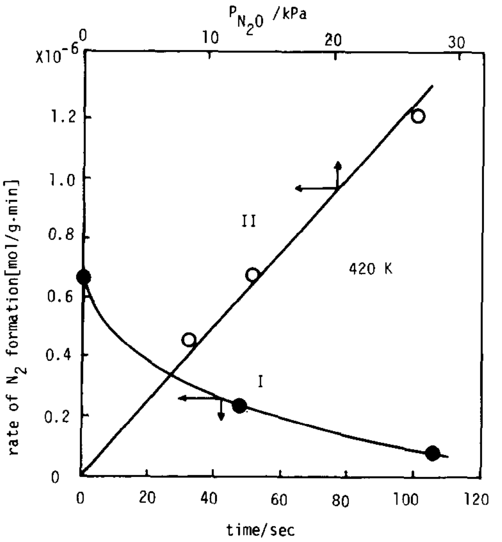

FIG. 10. Initial rate of N_2 formation from adsorbed CO and gaseous N_2O. Mole fraction N_2O admitted: $f_{N_2O} = 0.12$. (I) Rates versus time intervals between CO and N_2O admissions. (II) Effect of N_2O upon N_2 formation.

the initial rates of nitrogen formation which are estimated by extrapolation of the time interval to zero against the partial pressure of nitrous oxide. It is seen that the rate is proportional to the partial pressure of nitrous oxide, suggesting that gaseous nitrous oxide takes part in the reaction.

In a like manner, experiments were carried out in which carbon monoxide was admitted over the catalyst which had been previously covered by nitrous oxide but no nitrogen was detected in the outflow. On the basis of these results, it is, therefore, concluded that nitrous oxide in gaseous phase attacks short-lived carbon monoxide adsorbed on a small part of the oxidized surface when mechanism II operates. The amount of carbon monoxide held on the surface would greatly decrease as the temperature increased. This presumably compensates the increase in the rate constant so that the rate decreases when the temperature is increased under the reaction conditions where nitrogen formation is taking place predominantly through mechanism II.

The Reaction under the Steady State

At the steady state of the reaction, the rate was found to be greatly decreased in the presence of carbon dioxide at lower temperatures. On the other hand, its effect was practically negligible at higher temperatures, as previously observed by Fuller and Warwick (*5*). Figure 11 shows the results obtained when carbon monoxide supply was cut off during the course of the steady state of the reaction. When this experiment is done at lower temperature, the nitrogen and carbon dioxide formations decrease to an appreciable extent immediately after the supply of carbon monoxide is cut off, followed by the slow decrease in their rates. When the reaction was carried out at higher temperatures, no such abrupt decrease was observed and the formation rate of the products gradually decreased with time.

These results substantiate the conclusion that the formation of nitrogen due to the reaction between nitrous oxide and carbon monoxide is taking place through two different mechanisms which are operating in parallel, one (mechanism I) is producing nitrogen on the reduced surface and the other, producing it over the oxidized surface (mechanism II). At higher temperatures or when the catalyst is in more re-

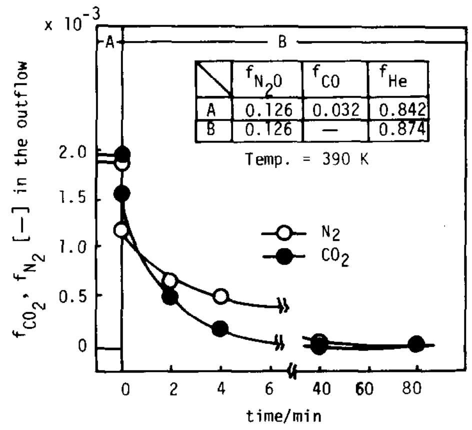

FIG. 11. Transient response of N_2 and CO_2 accompanied by cutoff of CO supply at the steady state of the title reaction. f_{N_2O}, etc.: mole fraction of N_2O, etc.

duced states, mechanism I prevails, while at lower temperatures or when the catalyst is in a more oxidized state the participation of mechanism II becomes more important where the retardation effect of carbon dioxide becomes appreciable.

RELEVANCE TO THE WORK PREVIOUSLY PUBLISHED

Fuller and Warwick (*5*) studied the title reaction over SnO_2 in the temperature range of 463 to 493 K and concluded that the reaction proceeded through the redox mechanism. No effect of carbon dioxide upon the reaction was observed. In these respects, the present results obtained by the transient-response method were practically in accord with these results particularly at higher temperatures. In contrast to these results, however, it was revealed that the reaction between gaseous nitrous oxide and adsorbed carbon monoxide was involved when the reaction was carried out at lower temperatures or over the catalyst in more oxidized states. In these respects, it would be interesting to note the results obtained by Tanaka and Blyholder for the same reaction over ZnO (*3*). They concluded that the reaction proceeded by the redox mechanism over stabilized ZnO. On the other hand, they briefly showed that when nitrous oxide alone was admitted on the fresh ZnO, the decomposition occurred sluggishly but by addition of carbon monoxide nitrogen was abruptly evolved. The latter process was reported to be strongly inhibited by the presence of carbon dioxide. This seems to be closely related to the present observations which were obtained over the oxidized surface or at lower temperatures.

SUMMARY

The mechanism of the reaction between carbon monoxide and nitrous oxide was studied by the transient-response method over SnO_2 under various reduced states of the catalyst surface and at various temperatures. It was concluded that the reaction proceeds through redox of the catalyst with nitrous oxide and carbon monoxide at higher temperatures or on the surface in partially reduced states. The mechanism through the reaction between gaseous nitrous oxide and adsorbed carbon monoxide was also concluded to occur on a small portion of oxidized surface particularly at lower temperatures.

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