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Mechanism of reduction of dinitrogen monoxide by carbon monoxide over magnesium oxide–role of surface formate species [1]

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With the help of infrared spectroscopy and the transient response method, it was revealed that surface formate species were involved in the title reaction over magnesium oxide. This contrasted to the results obtained over reducible metal oxides on which the catalyst redox was operating.

Keywords: N_2O-CO reaction; MgO; formate species

1. Introduction

It has been reported that the title reaction proceeds by the catalyst redox over CuO [2], $CoFe_2O_4$ [3], SnO_2 [4] and Fe_2O_3 [5] whereas over MoO_3/SiO_2 [6], Fe_2O_3/Cr_2O_3 [7], NiO [8] and MnO [9] the reaction proceeds through a pathway involving the reaction between dinitrogen monoxide and carbon monoxide in the adsorbed state. These results were based upon the steady state kinetics. In our recent work, the transient response method was applied to this reaction over magnesium oxide [10]. The kinetics under the transient state was found to be greatly different from those over other metal oxides in which the catalyst redox was operating [11]. Adsorbed carbon monoxide was suggested to react with dinitrogen monoxide over magnesium oxide.

In the present work, the title reaction was studied over magnesium oxide by the use of infrared spectroscopy. We show that surface formate species participate in the reaction.

2. Experimental

Magnesium oxide (Kishida Chem. Co., extra pure grade) was calcined at 773 K for 3 h in a stream of a helium-oxygen mixture containing 20 vol.% of oxygen.

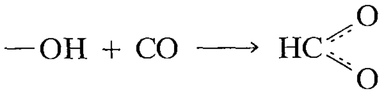
All the spectra were obtained at 589 K and at 101.3 kPa in a flow system. In infrared spectral measurements, the mixture of dinitrogen monoxide and carbon monoxide at various compositions flowed through an infrared cell [12,13] in which a thin wafer of magnesium oxide was placed. The spectra were recorded on a Hitachi 260-50 infrared spectrophotometer.

The experimental setup for the transient response method was similar to that used by Kobayashi et al. [14]. Gases from the outlet of the catalyst bed were collected with autosampling devices [15] at computer controlled intervals and analyzed by gas chromatography. Helium was used as diluent.

3. Results and discussion

When carbon monoxide alone was fed over magnesium oxide, no reaction occurred. The outlet partial pressure of carbon monoxide increased with time in a monotonic manner and attained a constant value. When the stream of the carbon monoxide was switched over to that of helium, the outlet partial pressure of carbon monoxide decreased with time, attaining to nil in 10 min. During the processes of these procedures, no other species were detected in the effluent. This suggested that carbon monoxide was reversibly adsorbed on magnesium oxide.

Fig. 1 illustrates how the infrared spectra of magnesium oxide vary, when carbon monoxide is fed over the catalyst. The absorptions ascribed to surface hydroxyls are seen at 3716 and 3550 cm^{-1} over magnesium oxide. Upon feeding carbon monoxide, the intensity of the absorption at 3716 cm^{-1} decreases and a new absorption appears at 3580 cm^{-1}. In a lower wave number region, absorptions appear at 2940, 2838, 2745, 2721, 1610, 1384, and 1340 cm^{-1}. By comparison with the spectra observed by previous authors [16,17], these absorptions were assigned to the surface formate species $\mathrm{HC}\begin{smallmatrix}\nearrow \mathrm{O}\\ \searrow \mathrm{O}\end{smallmatrix}$. When carbon monoxide was fed over the catalyst having deuteroxyl groups, the absorptions ascribed to $\mathrm{DC}\begin{smallmatrix}\nearrow \mathrm{O}\\ \searrow \mathrm{O}\end{smallmatrix}$ species appeared at 2147, 2111, 2020, 1600, 1378, 1339, 1315 and 1015 cm^{-1}. Table 1 lists the assignments of the absorptions of the surface formate species according to Hussein et al. [18]. As shown by Scholten et al. [16], the formate species were produced via the step



$$-\mathrm{OH} + \mathrm{CO} \longrightarrow \mathrm{HC}\begin{smallmatrix}\nearrow \mathrm{O}\\ \searrow \mathrm{O}\end{smallmatrix} \qquad (1)$$

in which surface hydroxyls and carbon monoxide were involved. When the stream of carbon monoxide was switched over to that of helium, all absorptions ascribed to the surface formate decreased in intensities simultaneously and

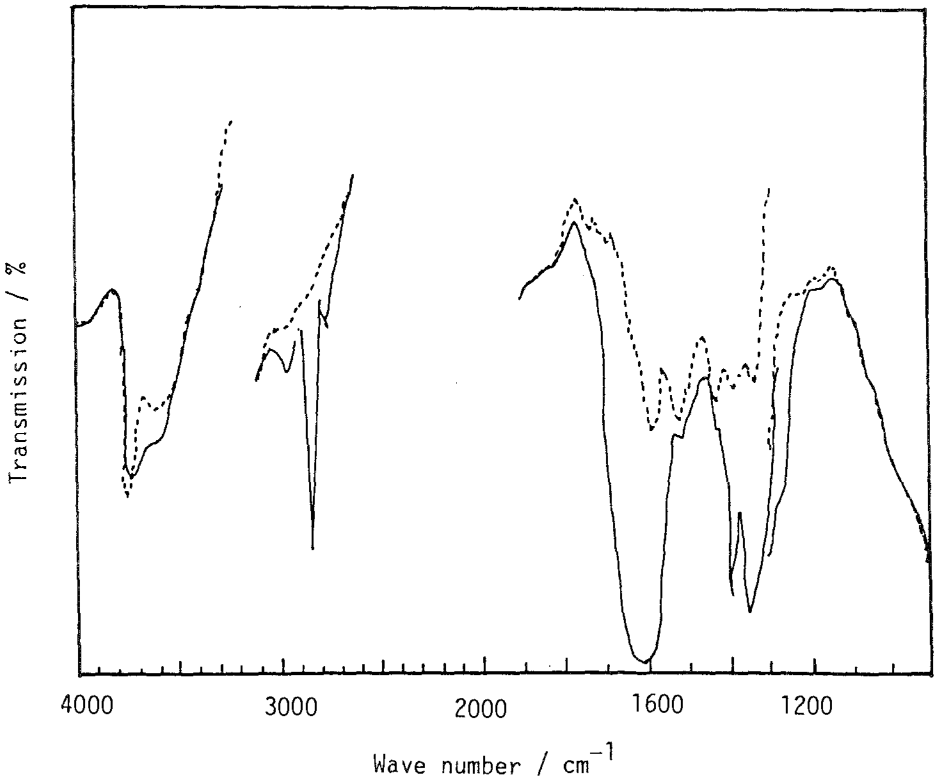


Fig. 1. Infrared spectra of formate species formed by adsorption of CO and MgO. - - - - - -, background spectra of magnesium oxide; ———, formate species formed by adsorption of CO at 589 K.

vanished in 10 min. As the intensities of the absorptions ascribed to the formate species decreased, those ascribed to the surface hydroxyls restored to their initial values. These findings strongly suggested that carbon monoxide was reversibly adsorbed as formate species.

When dinitrogen monoxide alone was fed over the catalyst, no reaction occurred. This species was also reversibly adsorbed on the surface, although its amount was much smaller than that of formate species. No absorption ascribed to adsorbed dinitrogen monoxide was discerned in the infrared spectra, possibly because of the small amount of the adsorbed dinitrogen monoxide or overlapping with absorptions due to gaseous dinitrogen monoxide. By contrast, on feeding of dinitrogen monoxide over the catalyst on which formate species were previously formed by reaction (1), nitrogen was produced along with carbon dioxide [11]. This strongly suggested that formate species was involved in the title reaction.

Under the steady state of the title reaction, the absorptions ascribed to formate species were evidently seen in the infrared spectra. No other absorptions which were ascribed to adsorbed carbon monoxide, adsorbed dinitrogen

Table 1

Assignments of $\mathrm{HC}\genfrac{}{}{0pt}{}{\nearrow\mathrm{O}}{\searrow\mathrm{O}}$ and $\mathrm{DC}\genfrac{}{}{0pt}{}{\nearrow\mathrm{O}}{\searrow\mathrm{O}}$ species formed on magnesium oxide

	Wave number (cm^{-1})	Assignment
$\mathrm{HC}\genfrac{}{}{0pt}{}{\nearrow\mathrm{O}}{\searrow\mathrm{O}}$	2940	$\nu\mathrm{C}\genfrac{}{}{0pt}{}{\nearrow\mathrm{O}}{\searrow\mathrm{O}}$ (sym) + δCH
	2838	νCH
	2745	2δCH
	2721	$2\nu\mathrm{C}\genfrac{}{}{0pt}{}{\nearrow\mathrm{O}}{\searrow\mathrm{O}}$ (sym)
	1610	$\nu\mathrm{C}\genfrac{}{}{0pt}{}{\nearrow\mathrm{O}}{\searrow\mathrm{O}}$ (asym)
	1384	δCH
	1340	$\nu\mathrm{C}\genfrac{}{}{0pt}{}{\nearrow\mathrm{O}}{\searrow\mathrm{O}}$ (sym)
$\mathrm{DC}\genfrac{}{}{0pt}{}{\nearrow\mathrm{O}}{\searrow\mathrm{O}}$	2111	νCD
	2020	2δCD
	1600	$\nu\mathrm{C}\genfrac{}{}{0pt}{}{\nearrow\mathrm{O}}{\searrow\mathrm{O}}$ (asym)
	1315	$\nu\mathrm{C}\genfrac{}{}{0pt}{}{\nearrow\mathrm{O}}{\searrow\mathrm{O}}$ (sym)
	1015	δCD

monoxide and carbonate species were discerned in the spectra. The title reaction was carried out, in which the partial pressure of dinitrogen monoxide was held constant and that of carbon monoxide varied. The amount of formate species present under the steady state of the reaction was estimated from the optical density of the absorption at 2838 cm^{-1}. Fig. 2 illustrates the relationship between the rate of the nitrogen formation and the amount of formate species estimated at the steady state of the reaction. It shows that the rate was practically proportional to the amount of formate species. On the basis of these findings, we conclude that formate species reacted with dinitrogen monoxide by reaction

$$\mathrm{HC}\genfrac{}{}{0pt}{}{\nearrow\mathrm{O}}{\searrow\mathrm{O}} + \mathrm{N_2O} \longrightarrow \mathrm{CO_2} + \mathrm{N_2} + -\mathrm{OH}$$

over magnesium oxide.

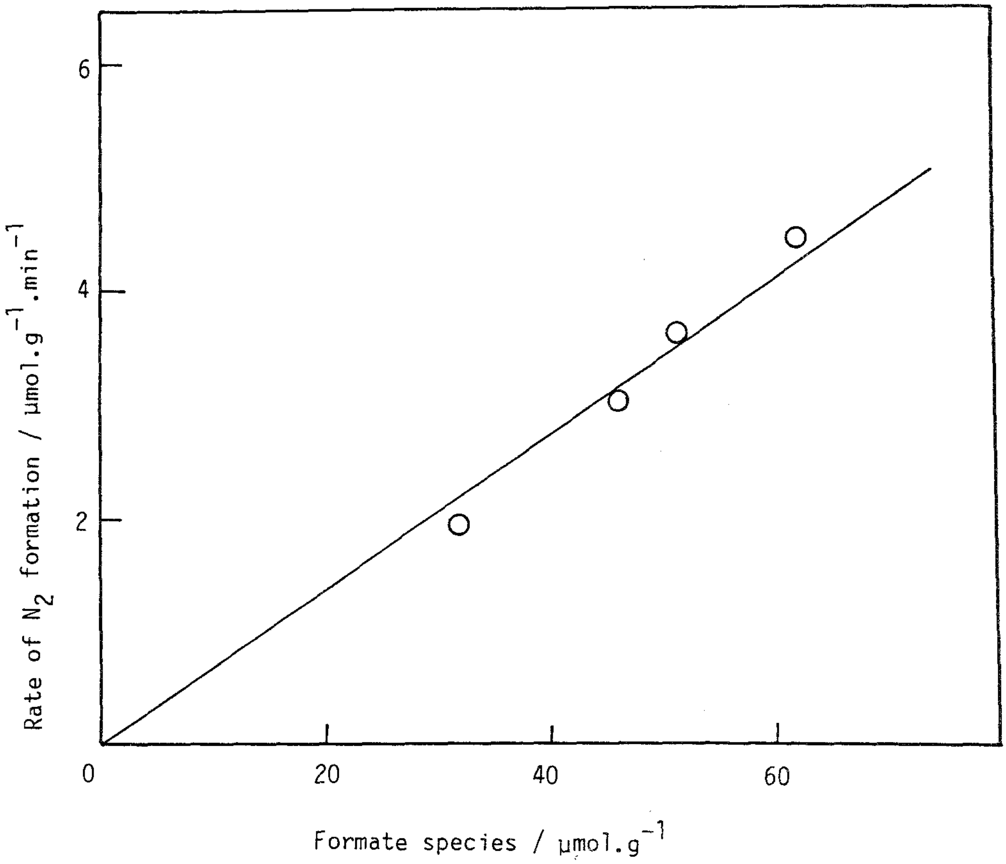


Fig. 2. The rate of nitrogen formation and the amount of formate species present under the steady state of the title reaction. Reaction temperature, 589 K. Partial pressure of N_2O was kept at 16.0 kPa whereas that of CO varied.

In our recent work, we showed that the title reaction proceeded through the catalyst redox over CeO_2 [11] by the transient response method and fluorescence spectroscopy. Over this metal oxide, surface oxygens were readily reduced by carbon monoxide to form carbon dioxide, and Ce(IV) was transformed into Ce(III). When dinitrogen monoxide was fed over the catalyst which was previously reduced by carbon monoxide, nitrogen was produced instantaneously and Ce(III) diminished. In great contrast to this, no carbon dioxide was formed by addition of carbon monoxide over magnesium oxide, and no reaction occurred with dinitrogen monoxide. However, surface hydroxyls reacted readily with carbon monoxide to form formate species, which was subsequently oxidized by dinitrogen monoxide. In these respects, it was highly probable that when the reducible metal oxide was employed for the title reaction, surface oxygens were rapidly reduced by carbon monoxide, and the reduced surface was oxidized by dinitrogen monoxide. The title reaction occurred prevailingly by the catalyst redox over these metal oxides. On the other hand, over irreducible metal oxides formate species were produced by reaction between carbon monoxide and surface hydroxyls, playing an important role in a process of the title reaction as a reaction intermediate.

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