The state of adsorbed oxygen species formed in the decomposition of N_2O on CaO

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Temperature programmed desorption, FT-IR spectra and hydrolysis of adsorbed oxygen species revealed that a considerable amount of adsorbed peroxide species were formed on CaO by decomposition of N_2O, whereas no adsorbed species were formed by molecular oxygen.

Keywords: Adsorbed peroxide species; CaO; N_2O decomposition

1. Introduction

It has been shown that a variety of adsorbed oxygen species, such as O_2^-, O^-, and O^{2-}, are produced by adsorption of molecular oxygen on metal oxides [1–3]. For reactions involving N_2O over metal oxides, the formation of adsorbed O^- species was frequently reported [4,5]. Adsorbed O^- and O_2^- species were characterized by the use of electron paramagnetic resonance technique (EPR) [1–3]. Reactivity of these oxygen species was studied in relation to the catalytic oxidation reactions [1–3].

In recent years, extensive work has been carried out for the oxidative dimerization of methane forming ethane and ethene with molecular oxygen [6–9]. Involvement of various adsorbed oxygen species was discussed in this reaction. Lunsford and co-workers previously showed that adsorbed O^- species participated in the oxidative dehydrogenation of methane over Li/MgO [6,10]. On the other hand, Sinev et al. [11] found that methane reacted with BaO_2, giving ethane. Otsuka et al. [12] also reported that the reaction of methane occurred with Na_2O_2, BaO_2 and SrO_2 at lower temperatures, giving C_2H_4 and C_2H_6. They further studied the reactions of ethane and propane with Na_2O_2 [13]. These findings suggested that peroxide species, O_2^{2-}, were also involved in the catalytic oxidative dimerization of saturated hydrocarbons over alkaline and

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alkaline earth metal oxides. However, the presence of adsorbed peroxide species is not well established. Metal peroxides are frequently prepared by reaction of metal oxides or hydroxides with H_2O_2 [14–16]. To our knowledge, for alkaline and alkaline earth metal oxides only BaO reacts with molecular oxygen at atmospheric pressure, forming BaO_2.

In the present paper, we show by temperature programmed desorption method, FT-IR spectroscopy and hydrolysis of adsorbed oxygen species, that a considerable amount of adsorbed peroxide species are formed by the decomposition of N_2O over CaO.

2. Experimental

CaO was prepared by decomposition of calcium carbonate (Nakarai Chemicals Ltd., extra pure grade) at 1073 K for 2 h in vacuum. The decomposition of N_2O was carried out in a conventional flow reactor at a total flow rate of 150 cm^3/min. The partial pressure of N_2O was kept at 15.2 kPa. The temperature programmed desorption (TPD) runs were carried out in a helium stream of 30 cm^3/min at heating rates of 2–24 K/min. Gases desorbed were analyzed by gas chromatography. FT-IR spectra of adsorbed peroxide species were recorded at room temperature on a Fourier-transform infrared spectrophotometer (JASCO FT-IR-5M). For analysis of H_2O_2 formed by hydrolysis of adsorbed peroxide species in a sulfuric solution, Ti(IV) species was used as an indicator, and UV/VIS spectra of peroxo Ti(IV) species formed were obtained by means of a UV/VIS spectrophotometer (Hitachi 330) [17,18]. The surface area of CaO was estimated to be 33.5 m^2/g by the BET method. CaO_2 was prepared from $Ca(OH)_2$ in a H_2O_2 solution (30 vol% H_2O_2) at room temperature [15,16,19,20]. The formation of CaO_2 was confirmed by X-ray diffraction [20,21].

3. Results and discussion

When N_2O was fed over CaO, the decomposition of N_2O occurred above 473 K. Under the transient state of the reaction, the outlet partial pressure of N_2 greatly exceeds that of O_2 expected from the stoichiometry of the decomposition reaction. This strongly suggested that adsorbed oxygen species were formed on CaO by the decomposition of N_2O.

Fig. 1a illustrates TPD profiles obtained after the decomposition of N_2O was carried out at 573 K for various periods of time. A strong peak of the oxygen desorption occurs at 643–740 K. No other species were desorbed in the course of the TPD runs. Unless N_2O was previously decomposed, no desorption of oxygen took place. For the catalyst exposed to N_2O at 573 K for 1 h, the amount of desorbed oxygen was estimated to be 2.40 cm^3. This corresponded to 27% of

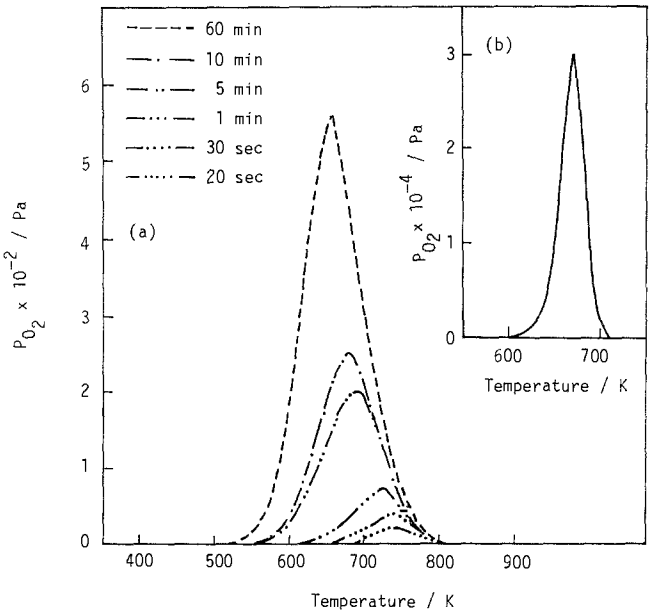


Fig. 1. (a) TPD profiles of adsorbed oxygen species formed on CaO by the decomposition of N_2O. The decomposition was carried out at 573 K for various periods of time described in the figure. Heating rate, 7 K/min. (b) TPD profile of CaO_2. Heating rate, 7 K/min.

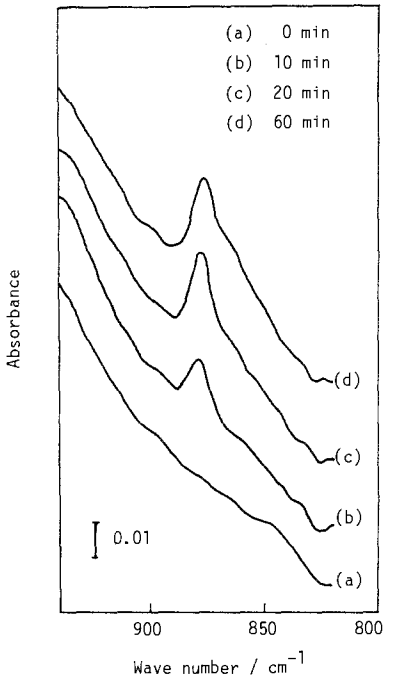


Fig. 2. FT-IR spectra of adsorbed oxygen species formed on CaO by the decomposition of N_2O. The decomposition was carried out at 573 K for various periods of time described in the figure.

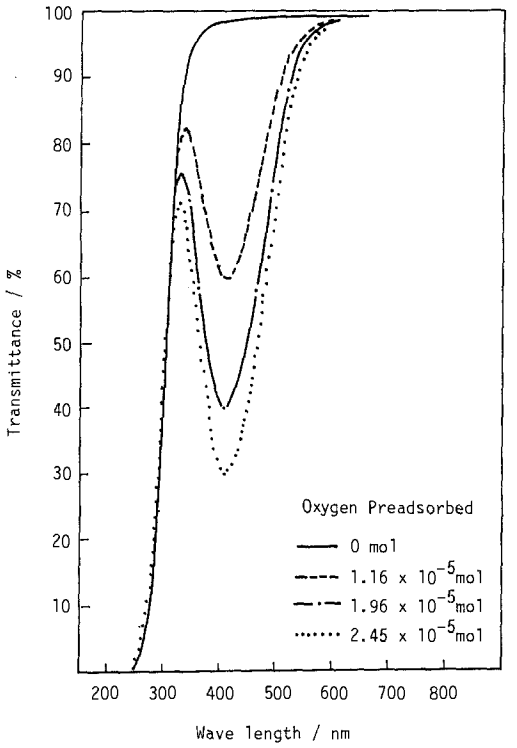
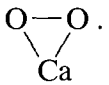


Fig. 3. UV/VIS spectra of peroxo Ti(IV) species formed by reaction between Ti(IV) and H_2O_2 formed by hydrolysis of adsorbed oxygen species in sulfuric acid solution. The amounts of oxygen species preadsorbed on 0.1 g of CaO are described in the figure.

the surface by assuming that adsorbed species were in molecular form. In contrast, no desorption occurred over the catalyst previously exposed to O_2 at this temperature.

Fig. 1b shows a TPD profile of CaO_2. The evolution of oxygen occurs at 663 K, as observed by Brunere and Kalina [20] in the thermal decomposition of CaO_2. The decomposition of CaO_2 occurs at the temperature where the adsorbed oxygen species desorbed. This suggests that adsorbed peroxide species are formed by the decomposition of N_2O.

Fig. 2 shows FT-IR spectra of adsorbed oxygen species formed on CaO. When the catalyst is subjected to the decomposition of N_2O, the absorption occurs at 880 cm^{-1}. The intensity of the absorption increases with the reaction time. According to the literature [3,22,23] the absorption at 880 cm^{-1} is assigned to peroxide species, most probably to the species in a side-on structure



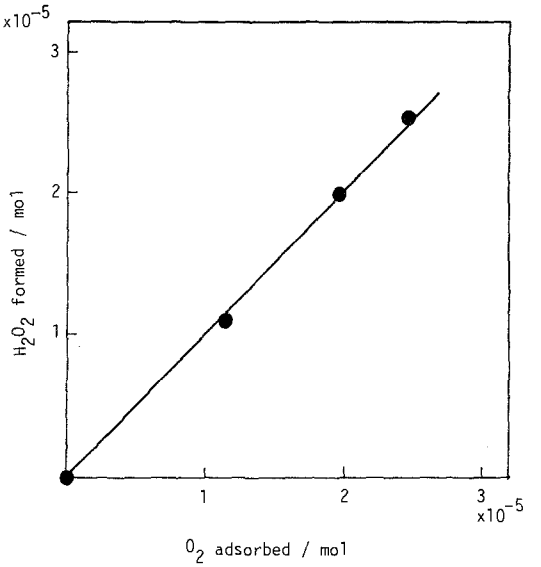


Fig. 4. Amounts of H_2O_2 species formed by hydrolysis of adsorbed oxygen species versus those of the adsorbed oxygen species.

The intensity of the absorption was unchanged upon heating up to 573 K where the desorption of adsorbed oxygen species commenced. The absorption decreased rapidly above 573 K and diminished at 773 K where the desorption of oxygen was completed.

In confirmation of these findings, the catalyst with preadsorbed oxygen species was added to a sulfuric acid solution, and the formation of H_2O_2 was tested by using Ti(IV) as an indicator [17,18]. A strong absorption ascribed to peroxo Ti(IV) species occurred at 407 nm in UV spectra of the solution (fig. 3). The intensity of the absorption increases with the increase of the amount of preadsorbed oxygen species. As fig. 4 shows, the amount of H_2O_2 formed was satisfactorily in accord with those of the adsorbed oxygen species. This indicates that H_2O_2 is formed by hydrolysis of adsorbed oxygen species in an acidic solution. These observations were quite similar to those observed for CaO_2 for which the reaction $CaO_2 + 2H_2O \rightarrow Ca(OH)_2 + H_2O_2$ occurred in an acidic solution, giving H_2O_2 [15,16].

Based upon these findings, we concluded that a considerable amount of adsorbed peroxide species were formed by the decomposition of N_2O over CaO.

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