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TEMPERATURE PROGRAMMED DESORPTION OF CARBON MONOXIDE ADSORBED ON MAGNESIUM OXIDE

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The nature of adsorbed CO on MgO was investigated by temperature programmed desorption technique. Magnesium oxide outgassed at 500°C gave one desorption peak at 190°C while MgO outgassed at 1000°C gave two distinctive desorption peaks at 185°C and 300°C. Carbon-13 labeled study indicates that two types of the adsorbed species on MgO outgassed at 1000°C do not exchange each other.

Magnesium oxide exhibits characteristics both in catalytic properties and in surface properties when outgassed at high temperatures.[2-8)] The surface properties have been investigated by measuring the nature of adsorbed molecules by ESR, IR, and UV spectroscopies. When CO is adsorbed on well-degassed MgO, several types of adsorbed species are formed. Lunsford and Jayne observed the formation of paramagnetic species which was believed to be bonded to the surface in a manner similar to the bonding of metal carbonyls.[9)] Morris et al reported the formation of $(CO)_2^{-\bullet}$ on MgO on the basis of ESR studies of adsorbed CO and ^{13}CO.[10)] In addition to the paramagnetic species, non-paramagnetic species could be observed by IR.[10)] Guglielminotti et al found by IR technique that CO was adsorbed in clusters; one of which could be bescribed as $(CO)_n^{x-}$, where x=2 or4 and n 2.[11)] They also suggested that the adsorbed species could be classified into two main groups. Stone and Zecchina measured reflectance spectra of MgO exposed to CO and reported the formation of $(CO)_2^{2-}$ and $(CO)_n^{x-}$ anion species.[6)] In the present study, temperature programmed desorption of CO adsorbed on MgO was carried out, and it was found that two distinctive desorption peaks appeared when CO was adsorbed on MgO outgassed at 1000°C.

Magnesium oxide was obtained by thermal decomposition of $Mg(OH)_2$ (Kanto Chemical Co. Ltd.) under vacuum. Before decomposition, $Mg(OH)_2$ was sieved into 24-35 mesh. Carbon monoxide was purchased from Seitetsu Kagaku Co. Ltd., and purified by passage through a column packed with well-degassed 4A molecular sieves and MgO kept at dry ice-acetone temperature. Labeled ^{13}CO was obtained from Stohler Isotope Chemicals and its isotopic purity was 90%.

The $Mg(OH)_2$ sample (0.5 g) was placed in a quartz adsorption vessel fitted with a stop cock and heat treated under vacuum at 500°C for 3 h or at 1000°C for 2 h. The sample was then cooled to room temperature and exposed to about 200 Torr

of CO for 10 min. The sample was outgassed for 30 min and subjected to temperature programmed desorption. The rate of temperature increase was 10°C/min. Desorbed CO was monitored with mass spectrometer. As the sensitivity of the spectrometer varied with a pressure in a system, a small amount of Ar was constantly leaked into the system. The relative amount of CO was determined as a relative peak height of m/e=28 for CO to that of 40 for Ar.

The temperature programmed desorption chromatograms are shown in Fig. 1 for the MgO outgassed at 500°C, and in Fig. 2 for the MgO outgassed at 1000°C. For the MgO outgassed at 500°C, the maximum desorption was observed at 190°C with a small shoulder at about 300°C. For the MgO outgassed at 1000°C, there appeared distinctive two maxima at 185°C and at 300°C. The total amount of CO desorbed was much larger than that for the MgO outgassed at 500°C. It is obvious that there are

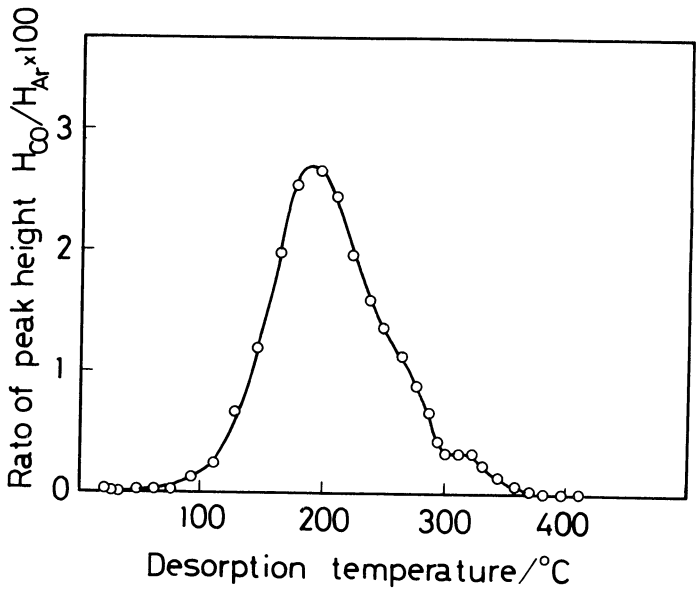

Fig.1 Temperature programmed desorption chromatogram of CO adsorbed on MgO outgassed at 500°C

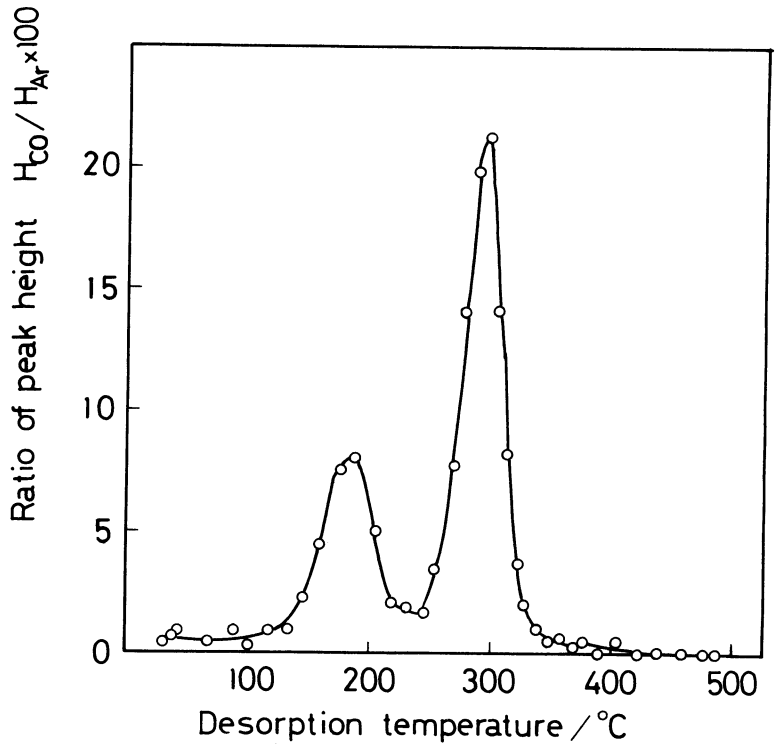

Fig.2 Temperature programmed desorption chromatogram of CO adsorbed on MgO outgassed at 1000°C

two types of adsorbed species on the MgO outgassed at 1000°C. The one which desorbed at lower temperature seems to be the same species as that observed for the MgO outgassed at 500°C. It is suggested that on thermal treatment at 1000°C under vacuum, the adsorption sites are generated which hold CO more strongly than those on the MgO outgassed at 500°C do.

To examine if two types of adsorbed species exchange each other, ^{13}CO-labeled experiment was done as follows. First, ^{12}CO was adsorbed on the MgO outgassed at 1000°C and temperature programmed desorption was performed up to 230°C, at which most of the one type of adsorbed species were desorbed (Fig. 3(A), S point). The sample was quickly cooled to room temperature and exposed to ^{13}CO. After evacuation, the subsequent temperature programmed desorption was carried out and the curve is shown in Fig. 3(B). The CO desorbed at lower

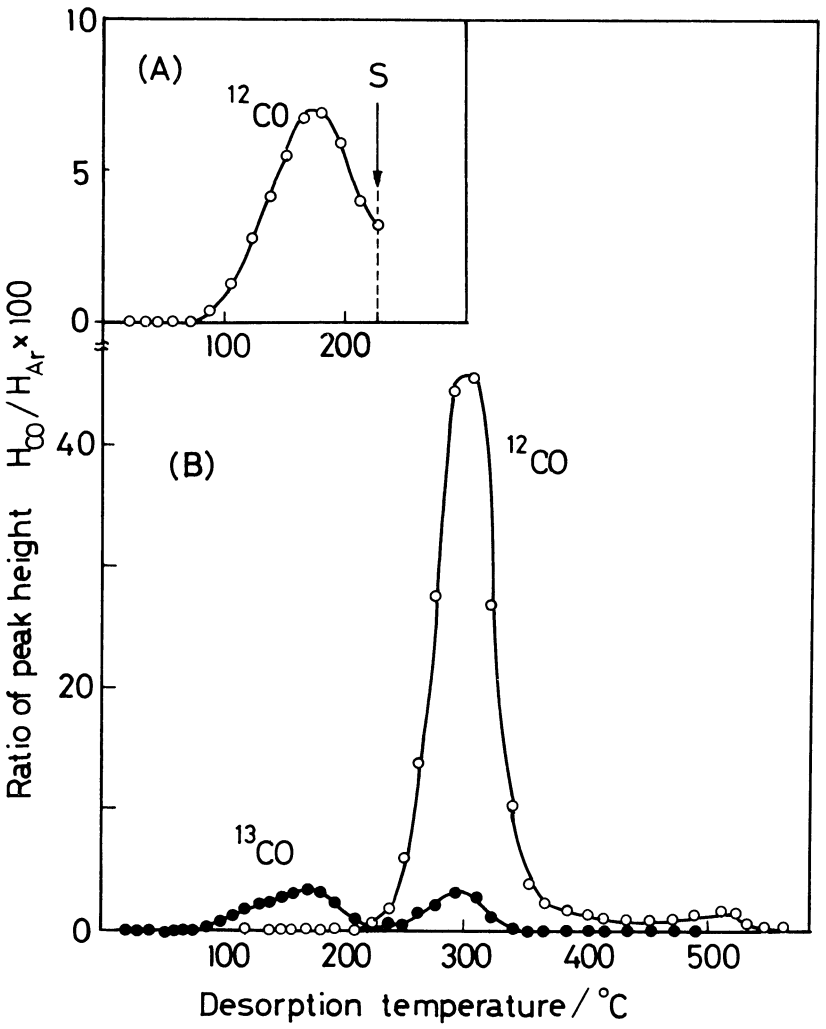

Fig 3 Temperature programmed desorption chromatograms of ^{12}CO and ^{13}CO on MgO outgassed at 1000°C
(A) First run; ^{12}CO was adsorbed and desorption was stopped at the point S.
(B) Successive run; ^{13}CO was adsorbed

temperature consisted exclusively of ^{13}CO, and the CO desorbed at higher temperature consisted mostly of ^{12}CO, though a small quantity of ^{13}CO was contained in the second peak. This result indicates that the exchange between two types of adsorbed species does not occur.

The chemical structures of the two types of the surface species are not definite in the present experiments. Combination with other techniques will clarify the chemical structures.

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