

## Oxygen Exchange between Adsorbed CO<sub>2</sub> and MgO Surfaces

Yasunori Yanagisawa, Hirohumi Shimodama and Akinori Ito

Department of Physics, Nara University of Education, Takabatake-cho, Nara 630, Japan

By using temperature-programmed desorption gas analysis, thermal desorption of C<sup>16</sup>O<sub>2</sub> and C<sup>18</sup>O<sup>16</sup>O gases after C<sup>18</sup>O<sub>2</sub> adsorption on MgO powders was observed in the temperature range 350–1000 K, suggesting double oxygen exchange reactions to occur on the surfaces.

Magnesium oxide is recognised to be a catalyst for hydrogenation and oxidation of CO, and H–D exchange between CH<sub>4</sub> and D<sub>2</sub>, properties which are explained as resulting from the basic nature of the surface.<sup>1</sup> EPR measurements at room temperature have shown that CO<sub>2</sub> molecules interact with surface F-type centres on UV-irradiated MgO powder to form CO<sub>2</sub><sup>-</sup> adsorbates.<sup>2</sup> Recently, we have reported oxygen exchange reactions between CO and defect MgO surfaces<sup>3</sup> and between O<sub>2</sub> and UV-irradiated MgO.<sup>4</sup> More recently, CO<sub>2</sub> adsorption on an MgO (100) surface was investigated below room temperature under ultra-high vacuum, but only weakly physisorbed CO<sub>2</sub> was observed.<sup>5</sup> Thus, while it is possible that oxygen exchange reactions may occur between CO<sub>2</sub> and defect MgO surfaces, this kind of reaction on alkaline-earth oxides is hitherto unknown. In this work, we report on the thermal desorption (TD) of C<sup>18</sup>O<sub>2</sub>, C<sup>16</sup>O<sup>18</sup>O and C<sup>16</sup>O<sub>2</sub> from C<sup>18</sup>O<sub>2</sub> adsorbed on MgO powder.

MgO powder (Specpure; Johnson-Matthey) was preheated at 1150 K in a quartz tube of diameter 5 mm attached to a vacuum system. The base pressure was about  $7 \times 10^{-9}$  Torr. After being cooled to room temperature, the sample was exposed to C<sup>18</sup>O<sub>2</sub> gas (99% purity) for the desired time with an exposure in the range 10<sup>2</sup> to 10<sup>4</sup> L (1 L = 10<sup>-6</sup> Torr s) in the dark. Temperature programmed desorption (TPD) measurements were carried out up to 1150 K with a heating rate of 0.5 K s<sup>-1</sup> using a quadrupole mass spectrometer (ULVAC, MSQ-400). Peaks with *m/z* in the ranges 28–36 and 44–48 were repetitively scanned.

After several cycles of exposure and TPD, reproducible TD curves of C<sup>16</sup>O<sub>2</sub>, C<sup>16</sup>O<sup>18</sup>O and C<sup>18</sup>O<sub>2</sub> gases were obtained. The TPD profiles of C<sup>16</sup>O<sub>2</sub>, C<sup>16</sup>O<sup>18</sup>O and C<sup>18</sup>O<sub>2</sub> gases after 3000 L C<sup>18</sup>O<sub>2</sub> exposure at room temperature are shown in Fig. 1. TDs of C<sup>16</sup>O<sub>2</sub> and C<sup>16</sup>O<sup>18</sup>O have broad peaks at 800 and 750 K, respectively with shoulders at about 900 K, while the TD of adsorbed C<sup>18</sup>O<sub>2</sub> has a weak peak at about 370 K and almost negligible desorption above 800 K. Thus, thermal exchange of adsorbed CO<sub>2</sub> molecules with lattice oxygen atoms takes place on the MgO surface. A small amount of C<sup>16</sup>O TD (*ca.* 10% of the C<sup>16</sup>O<sub>2</sub> TD) was observed in the temperature range 700–900 K with a maximum at about 850 K, which seemed to be a fragment product of desorbed C<sup>16</sup>O<sub>2</sub>. No TD evidence for oxygen molecules was obtained with or without C<sup>18</sup>O<sub>2</sub> exposure. The temperature maximum of the C<sup>16</sup>O<sub>2</sub> TD peak did not change on increasing the exposure, suggesting that the TD may obey first-order kinetics. The TD amounts of C<sup>16</sup>O<sub>2</sub>

and C<sup>16</sup>O<sup>18</sup>O, which correspond to the areas under the respective TD peaks, increased linearly with exposure up to 2000 L, near-saturation being reached around 300 L. The ratio of C<sup>16</sup>O<sub>2</sub> and C<sup>16</sup>O<sup>18</sup>O TD amounts is about 1 : 0.25, and was almost independent of exposure above 2000 L.

The initial rise method based on the Arrhenius plot of the C<sup>16</sup>O<sub>2</sub> TD intensity leads to a rough estimate of the activation

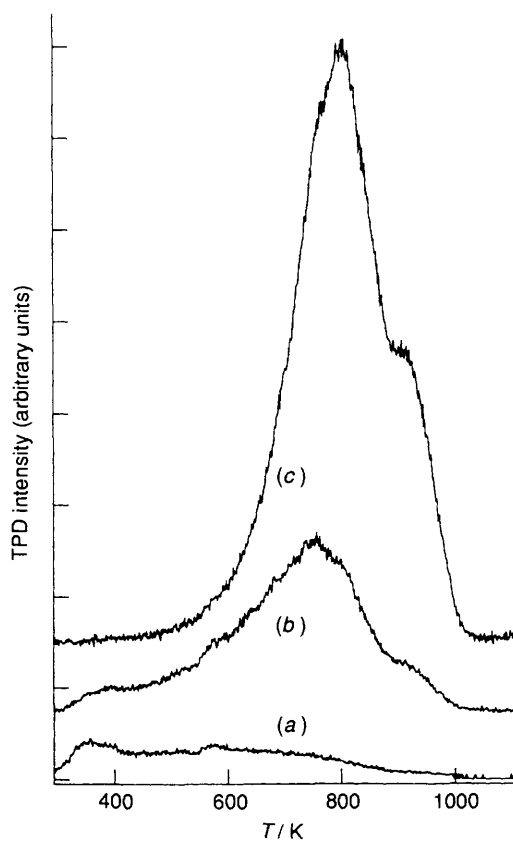


Fig. 1 TPD profiles of (a) C<sup>18</sup>O<sub>2</sub>, (b) C<sup>16</sup>O<sup>18</sup>O and (c) C<sup>16</sup>O<sub>2</sub> gases after 3000 L exposure to C<sup>18</sup>O<sub>2</sub> from MgO powder baked at 1150 K under ultra-high vacuum

energy for desorption ( $E_d$ ) of *ca.* 130 kJ mol<sup>-1</sup>. This large  $E_d$  suggests that the bond interchange causing the exchange may occur in the chemisorption state, giving the C<sup>16</sup>O<sub>2</sub> and C<sup>16</sup>O<sup>18</sup>O TD peaks.

For C<sup>18</sup>O<sub>2</sub> adsorbed on titania surfaces, no C<sup>16</sup>O<sub>2</sub> was desorbed in the temperature range 150–700 K.<sup>6</sup> Based on the present TPD results, the oxygen isotope exchange process between adsorbed C<sup>18</sup>O<sub>2</sub> molecules and surface <sup>16</sup>O atoms may take place as follows. Recently, Freund *et al.* reported that O<sup>2-</sup> anion may be converted into O<sup>-</sup> at cation vacancies in MgO crystals and form the peroxy anion O<sub>2</sub><sup>2-</sup> with the nearby O<sup>-</sup> anion without the need for ionization radiation.<sup>7</sup> Thus, one may suppose the generation of similar peroxy type ions, (O<sub>2</sub>)<sub>2</sub><sup>2-</sup>, on defect MgO surfaces, and adsorbed C<sup>18</sup>O<sub>2</sub> may interact with the peroxy ions to form tentative intermediate rolling carbonate ions during the exposure or thermal desorption run. Few peroxy-type anions seem to be present on a (100) flat surface, where only physisorbed CO<sub>2</sub> was formed.<sup>5</sup> The dissociation energy of the O<sub>2</sub><sup>-</sup>·CO<sub>2</sub> bond is about 90 kJ mol<sup>-1</sup>,<sup>8</sup> which seems to be comparable with the observed  $E_d$  value. A simple CO<sub>3</sub> type intermediate may not explain the

large TD of double exchanged CO<sub>2</sub> molecules. The actual exchange mechanism, however, is not yet clear.

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