A study of the structure sensitivity of the exchange of oxygen with the surface of magnesium oxide

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Abstract

The kinetics of exchange between $^{18}O_2$ and the surface of magnesium oxide have been studied for four samples with surface areas of between 10 and 100 m^2 g^{-1}. Less than 20% of the MgO oxygen monolayer undergoes exchange, and reaction is first order in exchangeable oxygen. Specific rate constants are very similar on all four samples, with all of the activation energies in the range 129 ± 9 kJ mol^{-1}, indicating that the exchange reaction is *structure insensitive*. After exhaustive exchange of the MgO surface with pure $^{18}O_2$, the gas phase was changed to $^{16}O_2$. Surprisingly, production of $^{18}O^{16}O$ restarted, at a rate identical to that originally observed between $^{18}O_2$ and the surface. This fascinating result indicates that, although the reaction kinetics show that heterolytic oxygen exchange is structure insensitive, there are nevertheless unique surface sites for the exchange reaction, which are not destroyed or randomised during the exchange process. Possible involvement of surface hydroxyl groups in the mechanism of exchange is discussed. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The exchange of gas phase oxygen with the surface and bulk of oxides has been of interest for many years, with important studies particularly due both to Winter [1] and Boreskov [2]. The reaction is of fundamental interest and is also of technological significance, since oxygen activation may be the rate determining step in oxidation catalysis, particularly where the Mars–van Krevelen mechanism occurs [3]. Two experimental approaches to the study of the exchange reaction have been adopted.

· Where a mixture typically of $^{18}O_2$ and $^{16}O_2$ is equilibrated over a catalytic surface, the process is referred to as *homomolecular* exchange.

· Where $^{18}O_2$ is exchanged with the oxygen of the catalyst, the process is referred to as *heterolytic* exchange. This has been divided into two mechanisms, the so-called R_1, where only one surface oxygen species is exchanged; and R_2, where two surface oxygen species are exchanged simultaneously.

Previous studies have generally compared the activities of series of different oxides, and we are not aware of any attempts to study whether

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or not oxygen exchange with oxide surfaces is structure sensitive. In this work, we concentrate on the exchange of $^{18}O_2$ with the surface of $Mg^{16}O$ magnesium oxide, seeking for structure sensitivity in the reaction by the now classical technique derived from catalysis by metals, of varying the catalyst particle size. [1] Magnesium oxide is a particularly appropriate material to study since its structural chemistry is simple—it normally exposes only the (100) crystal plane—and its defect chemistry has been well studied. We have previously demonstrated structure sensitivity in the oxidative coupling of methane reaction catalysed by magnesium oxide, although showing that reaction did not take place preferentially at sites of high coordinative unsaturation [5].

2. Experimental

The Ube Industries Company of Tokyo, Japan manufactures magnesium oxide samples which are intended to have uniform, well defined cube sizes. Four different samples of the Ube materials were obtained, with nominal cube sizes respectively of 100 Å, 500 Å, 1000 Å and 2000 Å. Surface area determination was performed using nitrogen physisorption at 77 K in a semi-automated 5-point BET apparatus. Transmission electron microscopy was carried out in a JEOL 2010 instrument, operated at 200 keV. Samples were prepared by dispersion in ethanol and deposition onto carbon coated copper grids. Measurements of the kinetics of oxygen exchange were performed in a closed loop reactor fabricated from 6.5 mm diameter stainless steel tubing. The section housing the catalyst consisted of a quartz lined 12.5 mm diameter stainless steel tube, and catalysts were tested in powder form. Catalyst beds, which were typically 5 mm long, were held between silica wool plugs centrally in the heated zone of a vertical

LPC Elements tube furnace. $^{18}O_2$ was obtained from CK Gas Supplies and was 99% pure. Analysis of isotopic oxygen mixtures was performed using a Hiden HAL 02/210 quadrupole mass spectrometer pumped by a turbomolecular pump, and connected to the reactor by a Balzers leak valve. The leak rate was chosen to ensure that the pressure change was small during the course of the reaction, 4–8 h. In a typical experiment to measure the kinetics of exchange, $^{18}O_2$ was admitted to give a pressure in the reactor of ca. 90 mbar. The extent of exchange was monitored by observing the increase of peaks at mass 34 ($^{16}O^{18}O$) and 32 ($^{16}O_2$), and the decrease of the mass 36 peak. To allow for any variations in the sensitivity of the mass spectrometer with time, the extent of exchange was calculated by expressing the concentration for example of $^{18}O^{16}O$ as a mole fraction of all of the three oxygen species present, namely $^{18}O_2$, $^{18}O^{16}O$, and $^{16}O_2$.

3. Results

The samples supplied by Ube Industries should have comprised well ordered magnesium oxide cubes of uniform size. Unfortunately, both powder X-ray diffraction (XRD) and electron microscopy indicated that there had been significant degradation of the samples during transit from Japan. In addition to magnesium oxide, XRD of the as-received materials showed the presence of magnesium hydroxide and carbonate phases. Consequently, all samples were heated in oxygen or vacuum at 735 K for 16 h

Table 1
Surface areas of the magnesium oxide samples

Nominal cube length (Å)	Surface area (m^2 g^{-1})
100	98
500	31
1000	26
2000	12

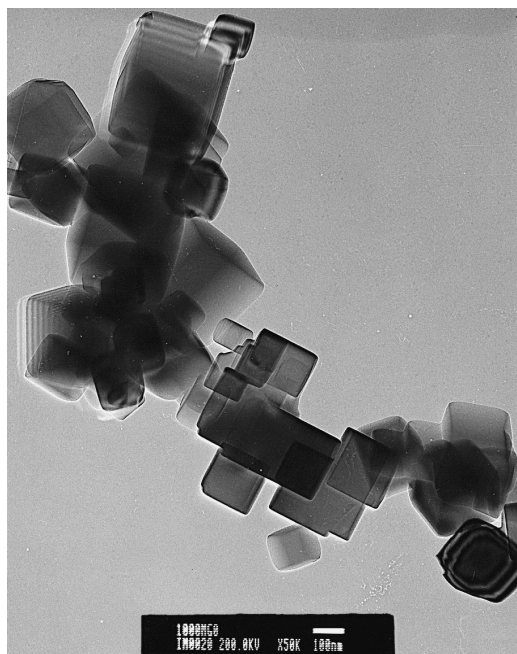
[1] See, e.g., discussion in Ref. [4].

Fig. 1. Electron micrograph at 50,000 magnification of a magnesium oxide sample with nominal cube size of 1000 Å.

prior to use, which eliminated the impurity phases. The surface areas of the four samples after this oxygen treatment are given in Table 1,

and these did not change following exchange with $^{18}O_2$ or heating in vacuo.

A representative transmission electron micrograph of the nominal 1000 Å material is shown in Fig. 1. As expected, all crystallites are terminated by (100) faces (see discussion in Ref. [5]), but the observed morphology is disappointingly ill-defined and the crystallite size range is quite broad. However, the surface areas vary by almost an order of magnitude over the four samples, which should be sufficient to reveal any marked structure sensitivity.

All samples were studied by X-ray photoelectron spectroscopy both before and after exchange, however no impurity species were observed other than the ubiquitous carbon. The limit of detection for possible impurities such as potassium or calcium is < 3% of the surface monolayer.

The exchange of $^{18}O_2$ with each of the four magnesium oxide samples was studied at temperatures of 690–740 K, a range chosen so that measurable rates were observed, but still much too low for significant exchange of lattice oxygen [6]. The initial product of the exchange
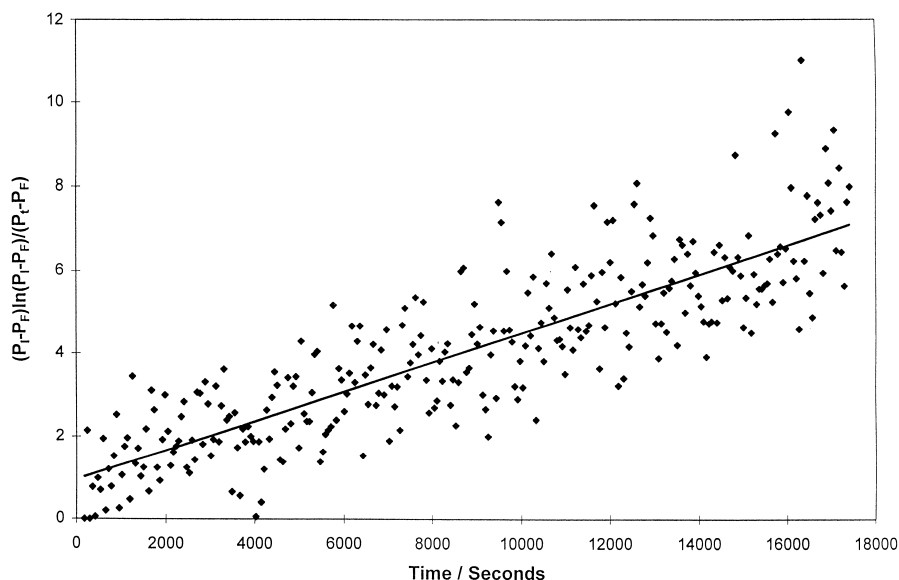

Fig. 2. First order rate plot for $^{18}O_2$ exchange with MgO having a nominal cube size of 2000 Å, obtained at 733 K with $^{18}O_2$ pressure of ca. 80 mbar. The linear nature of the plot shows the first order dependence on exchangeable surface oxygen concentration. For details, see text.

reaction was always $^{18}O^{16}O$, followed after some time by much smaller quantities of $^{16}O^{16}O$, indicating that only the R_1 exchange mechanism was occurring. Exchange was initially rapid, but the rate decreased with time and eventually became very slow. Since plentiful quantities of $^{18}O_2$ remained in the gas phase, the termination of the reaction indicates that the number of surface sites available for exchange is limited. If the exchange reaction is first order in the concentration of exchangeable surface species, and the pressure of $^{18}O_2$ remains constant, then the kinetics of exchange will be described by a straight line expression passing through the origin, of the form:

$$kt = (P_I - P_F)\ln[(P_I - P_F)/(P_t - P_F)] \qquad (1)$$

where P_I is the initial pressure of $^{18}O_2$, P_t is the pressure at time t, P_F is the pressure when exchange has ceased, and k is the first order rate constant. Since it is not possible to carry out the exchange reaction to completion, P_F must be treated as a disposable parameter.

Fig. 2 shows the first order plot obtained with MgO of nominal cube size 2000 Å, and is typical of the results for all four samples at each of the temperatures studied. A straight line is observed up to at least 90% of the exchange

Table 2
Activation energies for oxygen exchange

Nominal cube length (Å)	Activation energy (kJ mol^{-1})
100	127 ± 12
500	120 ± 6
1000	136 ± 28
2000	135 ± 27

capacity predicted by Eq. (1), the failure of the line to go exactly through the origin reflecting a small experimental error in the value of P_I. These linear first order kinetics establish that there is a finite pool of exchangeable surface oxygen species, and that reaction is first order in the concentration of this species. From the observed values of P_F, no more than 20% of the surface oxygen monolayer of any sample can be exchanged with ^{18}O.

Fig. 3 shows the Arrhenius plots obtained for all four MgO samples, using rate constants normalised to unit surface area of sample, (i.e., specific rate constants) and Table 2 lists the activation energies obtained. Although there are small differences in the Arrhenius plots for the four samples, all are very similar within experimental error, with the possible exception only of the nominal 500 Å sample. Similar specific
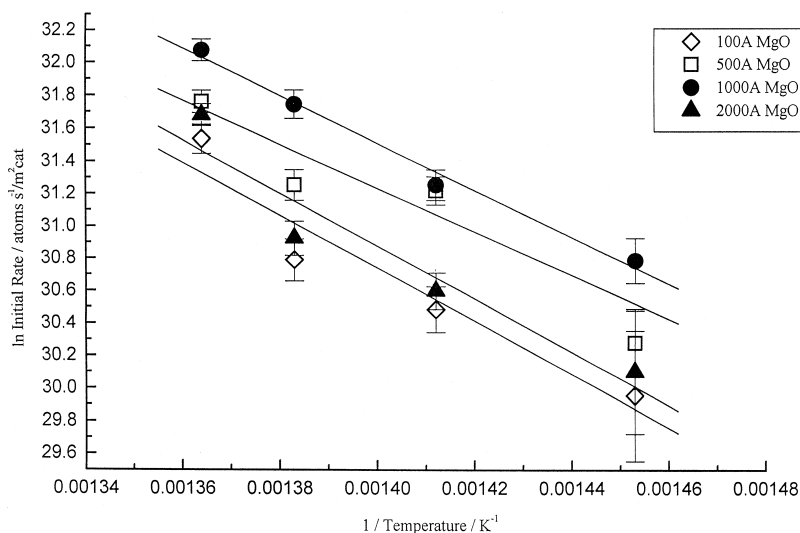

Fig. 3. Arrhenius specific rate plots for the four MgO samples studied.
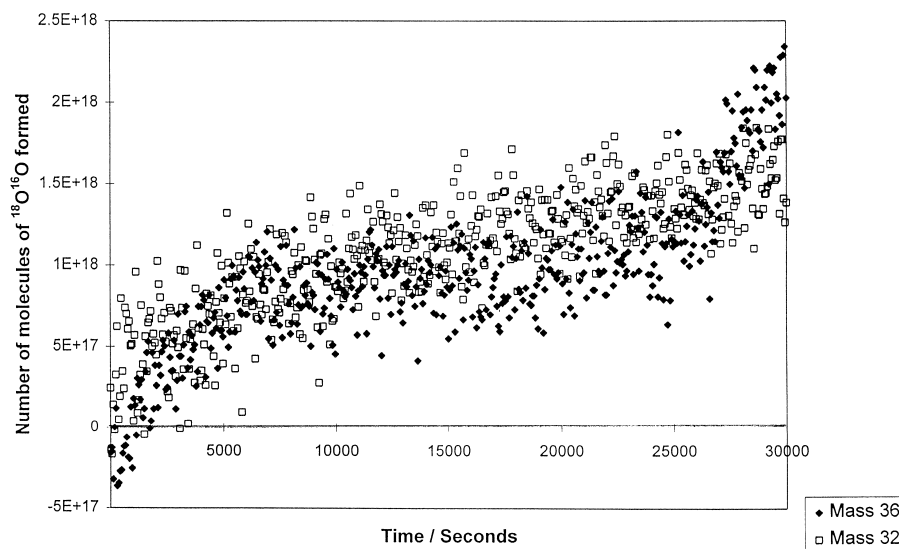
Fig. 4. The results of a switching experiment at 733 K. MgO was first exposed to $^{18}O_2$ for ca. 50 h, and the extent of exchange observed as a function of time is shown by the open squares. $^{18}O_2$ was then pumped away and replaced with normal oxygen, (99.5% $^{16}O_2$) and the rate of production of $^{18}O^{16}O$ was again monitored, as indicated by the closed diamonds.

rates are observed irrespective of whether the sample had been pre-treated in oxygen or vacuum. All of the activation energies are also similar, falling within range 129 ± 9 kJ mol^{-1}.

We have carried out experiments in which the MgO surface was first extensively exchanged with $^{18}O_2$, the gas phase was then pumped away, replaced with normal oxygen, ($> 99.5\%$ $^{16}O_2$), and the exchange reaction again monitored. Fig. 4 shows the results of such an experiment on the nominal 100 Å MgO at 733 K. The degree of exchange prior to the switch corresponded to ca. 15% of a monolayer. Yet, very surprisingly, the ^{18}O introduced by the initial exchange was found to re-exchange with kinetics almost identical to the initial process and to be almost wholly removed from the surface. Similar results were also observed using the nominal 2000 Å material.

4. Discussion

The observation of $^{18}O^{16}O$ as the initial product of exchange is in agreement with the early conclusions of Winter that R_I is the predomi-

nant exchange mechanism with magnesium oxide. Winter also found that the rate of the exchange reaction was unaffected by whether the sample was pre-treated in oxygen or in vacuum. Extrapolation of the rates which he observed to our conditions, however, gives values about ten times larger than those reported here, for reasons which are not understood. Our activation energies are a little lower than the previously reported values of ca. 160 kJ mol^{-1}. The extent of exchange which we have observed is in the range of 10–20% of the MgO surface monolayer, and is less than 20% of the monolayer for all samples. Equivalent figures have not been reported previously, but Kalenik and Wolf observed that only 7% of the lattice oxygen of MgO was exchangeable at the much higher temperature of 1023 K [6].

For the first time, our experiments compare the specific kinetics of oxygen exchange across a set of samples of markedly different surface areas. We observe that there are no significant differences in specific rates or activation energies, even though the surface areas of the four samples studied vary across the range by almost an order of magnitude (12–98 m^2 g^{-1}). Yet in

each case, up to about 20% of the surface oxygen monolayer appears to be capable of exchange with ^{18}O. The change in surface area corresponds to a variation of almost an order of magnitude in MgO particle size, and, taken with the constancy of the kinetics, indicates clearly that the exchange reaction is *structure insensitive*. Specifically, the change in particle size will lead to marked changes in the relative concentrations of 3- and 4-fold coordinated surface sites compared to the majority 5-fold coordinated surface site, so that we may conclude that these sites of high coordinative unsaturation are not involved in the exchange reaction. The invariance of the specific rates and activation energies over the range of materials tested also indicates that *only a single type of site is involved in the exchange, and that all sites are energetically homogeneous*.

The results of the switching experiments provide a very important insight into the exchange process. While the simple kinetic experiments show that no more than about 20% of the surface oxygen monolayer is exchangeable, the switching experiments demonstrate that exchange with $^{18}O_2$ effectively labels the exchange site. In the presence only of $^{18}O_2$, the exchange reaction appears to come to a halt, yet, on the replacement of $^{18}O_2$ by $^{16}O_2$ the exchange reaction appears to restart, and follows similar kinetics to those initially observed with $^{18}O_2$. The two sets of results taken together indicate that there is a fixed pool of exchangeable sites representing up to 20% of any MgO surface, and that their density appears to be independent of particle size. Thus, although the reaction kinetics show that heterolytic oxygen exchange is structure insensitive, the switching experiments indicate that there are nevertheless unique surface sites for the exchange reaction, which are not destroyed or randomised during the exchange process.

We believe, following Cunningham and Healy [7], that these results point to the involvement of surface hydroxyl groups in the exchange process. Infrared spectroscopy observa-

tions by Anderson et al. [8], and in this laboratory show that there are hydroxyl groups on MgO at these temperatures. The exchange reaction may be written:

$$^{18}O_2 + {}^{16}OH_{(s)}^- \rightarrow {}^{18}O^{16}O + {}^{18}OH_{(s)}^- \qquad (2)$$
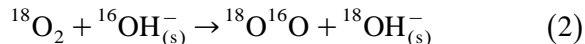
To explain the observation that interaction with $^{18}O_2$ effectively labels the exchange site, it is sufficient to postulate that the surface hydroxyl groups may participate in exchange *only* with a gas phase molecule, and not with the lattice oxygen of the MgO. To explain the structure insensitivity of the reaction, it only requires the reasonable assumption that the density of surface hydroxyl groups is independent of particle size. We are currently probing this by infrared spectroscopy [9].

Acknowledgements

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