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Probing possible structure sensitivity in the exchange of isotopic oxygen with the surface of MgO

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Abstract

The possibility of structure sensitivity in the heterolytic exchange of isotopic oxygen with the surface of a series of magnesium oxide samples has been probed. Two general approaches have been adopted: (i) variation in particle size for MgO samples exhibiting the {100} termination plane and (ii) variation in termination plane by alteration of the preparation method. In the former case, the surface area normalised exchange rate is found to vary insignificantly for the samples tested, despite a variation in their surface areas of nearly an order of magnitude. In addition, at the temperatures employed, only a fraction of a monolayer of the available oxygen is found to exchange, and, once exchanged, sites can be re-exchanged back with very similar reaction kinetics. It is proposed that the mechanism of reaction may involve the formation and decomposition of intermediate ozonide species generated on reaction of gas-phase O_2 with surface O^-, or is associated with the presence of ensembles of reactive low coordinate $Mg^{2+}O^{2-}$ pairs. Studies involving samples prepared via different routes have demonstrated the order of activity to be {111} or {110} *mean* surface planes > {100} > {111}, suggesting a beneficial role for ensembles of low coordinate $Mg^{2+}O^{2-}$ ion pairs. In addition, it has been found that samples prepared from hydroxide-based precursors exhibit activity in the exchange process involving two lattice ions (R_2). This has been rationalised in terms of the exchange of diatomic surface species, such as peroxide ions and/or superoxide ions.

Keywords: Magnesium oxide; Isotopic oxygen exchange; FTIR; Photoluminescence spectroscopy; UV–visible diffuse reflectance spectroscopy

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1. Introduction

Over the years, the isotopic oxygen exchange reaction with metal oxides has been the subject of much interest [1–4]. This has been due predominantly to the relationship between this reaction and activity for oxidation catalysis. For example, direct correlations of exchange activity have been documented in the literature for reactions involving the transfer of oxygen, such as methane combustion, hydrogen oxidation, nitric oxide decomposition, methanol oxidation, and nitrosobenzene oxidation [3,5]. Frequently, studies of this reaction have taken the form of comparisons of the activities over a range of different materials. More recently, these activity patterns have been used, with some degree of success, in attempts to design oxidation catalysts from first principles [6,7].

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Within the literature, two general approaches to the study of the exchange reaction have been adopted:

(i) homomolecular exchange in which a non-isotopically equilibrated $^{36}O_2/^{32}O_2$ mixture is equilibrated over a catalytic surface, and
(ii) heterolytic exchange in which one isotope is exchanged with the surface or lattice oxygen of a catalyst. This process has been subdivided into two further processes, which refer to whether there is transfer of one lattice oxide ion (R_1) or two lattice ions (R_2) in a single reaction event.

In this study, we concentrate on magnesium oxide and particularly on whether structure–function relationships can be observed in the heterolytic exchange process. The heterolytic reaction is of greater interest to us because it more closely resembles the Mars–van Krevelen oxidation mechanism [8], in which oxygen is transferred between the lattice and the substrate. Magnesium oxide is a good model oxide, since it has a simple rock salt structure, and its morphology and resultant catalytic activity can be easily altered by variation of the preparation method. The surface structures exhibited are reasonably well understood and easily characterised, as is its defect chemistry. Although the isotopic oxygen exchange properties of MgO have been widely studied [1,2,9–12], to our knowledge no attempt has been made to elucidate potential structure sensitivity in this system. Furthermore, we have previously demonstrated structure sensitivity in the MgO-catalysed oxidative coupling of methane reaction [13]. In that case, it was concluded that selectivity for higher hydrocarbons was not associated with the 3 and 4 coordinated sites on cubic morphology MgO, since it was invariant with changing catalyst particle size under conditions of constant conversion. However, enhanced selectivity was observed with samples exhibiting {110} and {111} *mean* index surface planes. A preliminary report on our studies of structure sensitivity in oxygen isotopic exchange on MgO has already appeared [14].

2. Experimental

Four magnesium oxide samples kindly supplied by the Ube company were used in this study, specified as having crystallite sizes of 100 Å (MgO 100 Å), 500 Å (MgO 500 Å), 1000 Å (MgO 1000 Å), and 2000 Å (MgO 2000 Å). Before reaction, samples were subjected to an overnight pretreatment at 733 K, as described later in the text, to remove contaminant traces of magnesium hydroxide and magnesium carbonate that were evident in powder X-ray diffraction patterns of some of these materials, as discussed elsewhere [14]. The resultant samples had surface areas of 98, 31, 26, and 12 $m^2\,g^{-1}$, respectively, for MgO 100, 500, 1000, and 2000 Å, which was considered a wide enough surface area variation to detect any significant structure-sensitivity. XPS analyses of these samples, both before and subsequent to reaction, did not indicate any impurities above the levels of detection. In addition to the Ube samples, MgO was prepared by a further three routes: (i) burning magnesium ribbon (Aldrich) in air followed by calcination in air at 1073 K for 3 h to remove traces of the nitride, (ii) thermal decomposition of magnesium hydroxide (Merck) in air at various temperatures for 3 h, and (iii) thermal decomposition of magnesium hydroxycarbonate (Merck) in air.

Surface area was determined by nitrogen physisorption in a semi-automated BET apparatus, and transmission electron microscopy was performed with a Jeol 2000EX microscope operated at 200 kV with samples prepared by dispersion in ethanol and deposition on holey carbon grids.

Microreactor testing was performed in a re-circulating closed-loop reactor fabricated from 1/4″ stainless-steel tubing. The section housing the catalyst consisted of a quartz-lined 1/2″ stainless-steel tube. Magnesium oxide sample reactor beds, which were typically 25–100 mg, corresponding to a surface area of 2 m^2, were held centrally between silica wool plugs in the heated zone of a vertical LPC Elements tube furnace. Materials were tested in powder form. The temperatures reported in this paper correspond to set-point temperatures. The reactor was operated under sub-ambient pressure. In a typical experiment, a quantity of $^{36}O_2$ (CK Gas Products 99.2 at% balance $^{32}O_2$) was dosed to correspond to a final reactor pressure of either 20 or 80 Torr at room temperature, as described later in the text. On-line gas-phase composition analysis was performed with a Hiden 201.5 quadrupole mass spectrometer with a very low leak rate to ensure that the pressure change during the course of the reaction, typically 8 h, was very small. In addition to 32, 34, and 36, m/z values of 28, 18, and 14 were also scanned to ensure that data were not influenced by leaks. Background experiments confirmed that exchange did not occur in the absence of MgO.

For infrared spectroscopy, samples were pressed into thin self-supporting wafers weighing ca. 10 mg, and measurements were performed with an ATI RS1 Fourier transform spectrometer equipped with an in situ stainless-steel cell with calcium fluoride windows, capable of a base pressure of $<10^{-7}$ mbar. Samples could be heated to 1073 K in various atmospheres. Typically 20 scans were co-added. The spectra presented are baseline-corrected absorbance spectra.

For UV measurements, the samples were placed in a cell with an optical quartz window, allowing the thermal treatment to be carried out in situ, after attachment to a conventional vacuum line (residual pressure 1×10^{-6} Torr). Diffuse-reflectance spectra were recorded with a Perkin–Elmer Lambda 19 spectrometer, equipped with an integrating sphere, with $BaSO_4$ as a reference powder. Photoemission spectra were recorded with a Spex FL212 spectrofluorimeter.

Table 1
Specific rates of isotopic exchange on the Ube samples at 80 Torr

Pretreatment	Temperature (K)	Specific rate of isotopic oxygen exchange ($\times 10^{13}$ atoms s^{-1} m^{-2})			
		100 Å	500 Å	1000 Å	2000 Å
Vacuum at 733 K	688	1.41 ± 0.32	2.34 ± 0.35	1.18 ± 0.54	1.02 ± 0.50
	708	3.61 ± 0.33	3.73 ± 0.37	1.94 ± 0.23	1.73 ± 0.26
	723	3.74 ± 0.37	6.12 ± 0.55	2.69 ± 0.30	2.35 ± 0.33
	733	6.22 ± 0.44	8.52 ± 0.60	5.74 ± 0.40	4.96 ± 0.45
Oxygen at 733 K	688	1.45 ± 0.20	2.59 ± 0.31	1.06 ± 0.24	1.07 ± 0.43
	708	3.16 ± 0.22	4.52 ± 0.32	1.42 ± 0.23	1.46 ± 0.48
	723	4.51 ± 0.32	6.01 ± 0.42	1.98 ± 0.24	2.25 ± 0.10
	733	6.03 ± 0.30	9.66 ± 0.48	5.52 ± 0.39	4.55 ± 1.41

3. Results and discussion

3.1. *Effect of variation of crystallite size*

The heterolytic isotopic oxygen exchange reaction has been studied over the Ube 100, 500, 1000, and 2000 Å MgO samples in the temperature range of 688–733 K. As described elsewhere [14], the Ube samples comprise MgO crystallites terminated by {100} faces, although high-resolution transmission electron microscopy has demonstrated that the crystallite surfaces are highly faceted [15]. In all cases, the R_1 mechanism was exclusively observed, with the rate of loss of $^{36}O_2$ exactly compensated for by the corresponding rate of production of $^{34}O_2$. It was also observed that, in all cases, the exchange reaction had halted before the whole surface monolayer had been exchanged, and typical values of exchange were 8% of a monolayer. Previously, Kalenik and Wolf reported that only 7% of the total lattice oxygen of MgO was exchangeable at the much higher reaction temperature of 1023 K [11]. Table 1 presents the results of surface area normalised initial rate measurements. These were determined within the first 2.8 h of reaction by fitting of data to a pseudo-first-order expression that assumes the kinetics of reaction to be first order in concentration of sites, as we have described elsewhere [14]. Table 1 also shows the influence of variation of pretreatment regime. Two procedures, which mimic methods described in the literature, have been adopted: overnight annealing at 733 K in an oxygen atmosphere (120 Torr) or in vacuo. In agreement with earlier work by Winter [1], it was observed that there was no difference between oxygen or vacuum pretreated samples at this temperature. However, we have observed that pretreatment in vacuo at higher temperature (1023 K) causes an induction period of 5.5 h on reaction, where the lattice takes up gas-phase oxygen, before the commencement of the exchange process, which proceeds with kinetics similar to those of the samples pretreated at lower temperature. The data in Table 1 have been used to construct the Arrhenius plots given in Fig. 1. We determined the error bars by taking into consideration the effects of variation in the mass spectrometer response and the accuracy of the surface area and reaction temperature measurements. When account is taken of the different temperatures used in the various studies, it is worth noting that the specific rates reported in Table 1 are similar to those reported by Boreskov [2] and Karasuda and Aika [16]. However, the two different stages of activity, apparently relating to the exchange of two different types of oxygen species, as reported by the latter authors, were not observed in our study, and the similarity of rates is observed with the lower activity species. There are two orders of magnitude difference between our exchange rates and those reported by Martin and Duprez [10], despite the fact that they performed their studies on Ube 100 Å MgO material. We suggest the origin of this discrepancy lies in the fact that, in the latter case, the samples tested evidently contained a contaminant hydroxide phase and were also subjected to a hydrogen pretreatment stage before reaction. The activity reported by Winter [1] is around an order of magnitude higher than ours; however, we are unable speculate on the reason for this.

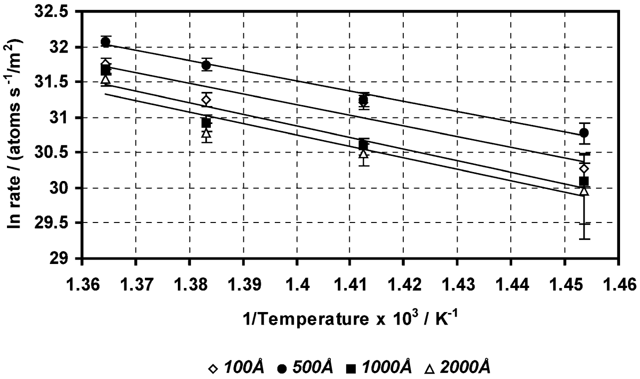


Fig. 1. Arrhenius plots for Ube MgO samples of varying surface area following pretreatment in vacuo.

With the exception of the 500 Å material, despite possessing nearly an order of magnitude spread in surface area, the Ube samples exhibit activation energies and surface area normalised specific rates that are the same within experimental error. This implies that there are energetically homogeneous exchange sites that vary in number in direct proportion to surface area. In the case of the 500 Å material, the activation energy is the same within experimental error as for the other samples, which implies that the higher activity observed with this sample is most likely due to a higher concentration of exchange sites. Although we have

Table 2
Table showing the ratios of each different co-ordination site type from the experimental data and calculated ratios based on the assumption of perfect morphology

Ratio	3 Coordinated			4 Coordinated			5 Coordinated	
	Experimental[a]	Experimental[b]	Calculated	Experimental[a]	Experimental[b]	Calculated	Experimental	Calculated
100:500	1.27	3	30	0.9	2.3	5	–	0.97
100:1000	1.66	3	100	1.24	3.25	11	–	0.96
100:2000	3.38	10.2	600	1.46	3.84	21	–	0.96

[a] Taken from photoluminescence measurements.
[b] Taken from UV/VIS/NIR diffuse reflectance measurements.

Table 3
Specific rates of isotopic exchange on the 100 and 2000 Å Ube samples at 20 Torr following vacuum pretreatment at 733 K

Temperature (K)	Specific rate of exchange ($\times 10^{13}$ atoms s^{-1} m^{-2})	
	100 Å	2000 Å
688	1.46 ± 0.20	1.35 ± 0.22
708	3.51 ± 0.35	2.27 ± 0.25
723	3.65 ± 0.40	3.23 ± 0.42
733	5.95 ± 0.65	4.69 ± 0.39

observed that the Ube samples do not exhibit a regular cubic morphology and well-defined size range, transmission electron microscopy studies indicate that the crystallites are terminated by the {100}-type planes, as described previously [14]. As noted elsewhere [15], high-resolution transmission electron microscopy has demonstrated that these surfaces can be highly faceted, most likely as a result of the formation and subsequent thermal decomposition of contaminant hydroxide and carbonate phases before reaction. Accordingly, we have applied photoluminescence and UV–visible diffuse-reflectance measurements to make a semi-quantitative determination of the relative differences in low (i.e., 3 and 4) coordinate ion population between the various Ube samples. The application of these techniques to oxides has been reported elsewhere [17,18]. The results for the samples in the present study are presented in Table 2. As anticipated, there is a wide variation in the relative numbers of these different sites, with the highest number of low coordinate sites being associated with the 100 Å sample.

Taken in conjunction with the reactivity data, our spectroscopic studies are indicative that either 3 or 4 coordinated ions *alone* on {100}-terminated faces of MgO are not responsible for the observed activity. Furthermore, the fact that such a small fraction of the monolayer is exchangeable suggests that neither are all 5 coordinated ions.

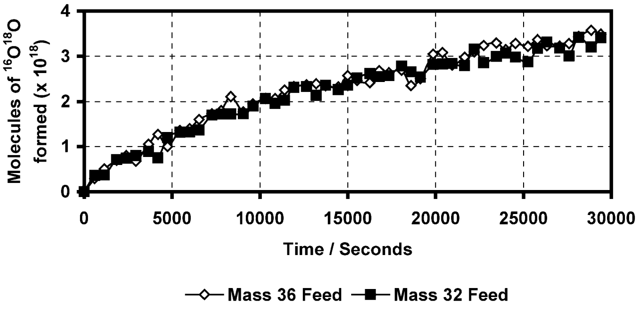


Fig. 2. Switching experiments at 733 K involving initial exchange with $^{36}O_2$ and its subsequent replacement with $^{32}O_2$ on Ube MgO.

Table 4
Specific rates of isotopic oxygen exchange from switching experiments on 100 and 2000 Å MgO

Ube MgO sample (Å)	Specific rate of oxygen exchange ($\times 10^{13}$ atoms s^{-1} m^{-2})	
	MASS 36 FEED	MASS 32 FEED
100	6.17 ± 0.435	6.43 ± 0.435
2000	4.72 ± 0.446	4.17 ± 0.446

The effect of variation of the initial pressure of $^{36}O_2$ between 20 and 80 Torr has been investigated, and the results of the 20 Torr study are listed in Table 3. By comparison with Table 1, it is evident that, to within experimental error, there is no influence of pressure on rate within these limits, which is consistent with previous reports of zero-order dependence [1]. This observation implies that the rate-determining step of the process is not related to the activation of O_2; rather, the desorption step is, as concluded by others [1]. Moreover, the linear nature of our activity plots further confirms our conclusion of energetically homogeneous exchange sites. In Fig. 2 and Table 4, data are presented for experiments on the 100 and 2000 Å samples in which initial isotopic exchange had been carried out to varying extents at 733 K, followed by switching to normal oxygen. The quantity of exchange for the two samples corresponds, respectively, to 8 and 9% of a monolayer. As shown, the exchanged sites were found to re-exchange with a rate very similar to the initial process. In view of the fact that we were re-exchanging such dilute systems, this result is somewhat surprising and has interesting implications when considered in conjunction with the results described above. As stated previously, the absence of apparent surface area sensitivity on the rate of reaction and the fact that only a small fraction of the monolayer exchanges indicate that the reaction is not exclusively confined to 3, 4, or 5 coordinated surface ions on MgO {100}-type faces. However, the switching experiments indicate that for the Ube samples, there are a fixed number of exchangeable sites that vary in direct proportion with surface area and are effectively labeled by the exchange process. Previously we have speculated that these may be hydroxyl groups, on the basis that others have observed similarity in the patterns of H_2–D_2 isotopic exchange and isotopic oxygen exchange activity on

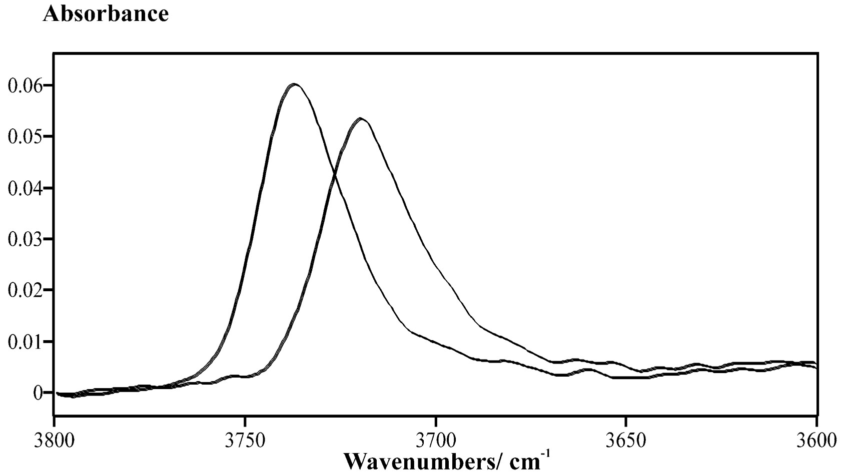
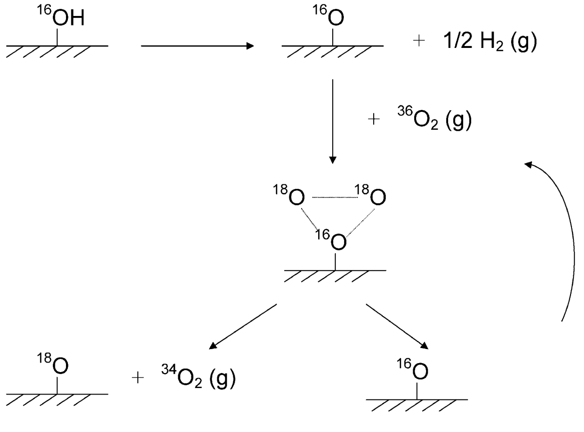


Fig. 3. Isotopic shift of hydroxyl groups on admission of $^{36}O_2$ at 80 Torr and 738 K on Ube 100 Å MgO.



Scheme 1.

alkaline earth oxides [19]. However, as shown in Fig. 3, we have subsequently performed in situ FTIR studies of the exchange process with terminal ^{16}OH groups of MgO at 738 K and 80 Torr and have observed that, although the extent of exchange is quantitative, the process occurs too rapidly to account for the kinetics observed in our microreactor studies. The observed shift of 17 cm^{-1} compares reasonably well with the 13 cm^{-1} shift calculated with the assumption of a harmonic oscillator. The process was observed to be complete within 1 min and, because of our sampling rate, would therefore not show up in our first-order plots. Comparison with temperature-programmed desorption studies of magnesium hydroxide [20] suggest that there could be a possible indirect role of hydroxyl group decomposition to yield O^- centres by loss of hydrogen under the pretreatment conditions used in the present study. A possibility is that these sites subsequently interact with gas-phase $^{36}O_2$ to form a three-centred ozonide ion intermediate, which isotopically scrambles on decomposition as shown in Scheme 1. A V1 centre comprising a triangular array of O^- sites on an MgO(111) facet on the surface has previously been proposed on the basis of ESR studies [27]; however, this interpretation has been controversial [28]. Our proposal does not necessarily invoke the presence of such V1 centres, since intermediate ozonide can be formed via reaction with isolated O^- sites. Ozonide intermediates have previously been observed to form by reaction of O^- with O_2 on MgO [21]. The fact that these intermediates are known to be fairly stable suggests that their decomposition may be the rate-limiting process, which is entirely consistent with the observed lack of $^{36}O_2$ pressure dependence upon reaction rate. On MgO 100 Å, an infrared band at 2180 cm^{-1} can be observed (Fig. 4). By comparison with similar bands in cerium oxide [22], we believe that this band can be attributed to either an O–O stretching vibration of a superoxide species, O_2^-, or an ozonide species. The vibrational frequency is typical of an O–O stretching vibration with a bond order of 1.5. We have also observed an infrared band at 846 cm^{-1}. This band has been attributed to ozonide species on MgO [21]. Note that in contrast to the ex OH species (as described in the next section), no band at 1060 cm^{-1} was observed and the band at 855 cm^{-1} shifted to 846 cm^{-1}. As oxygen exchange with $^{36}O_2$ leads to an isotopic shift very small in comparison with the literature (the minimum calculated shift for a ^{18}O–^{16}O shift being 62 cm^{-1}) on the time scale of the experiment, we conclude that these species exchange slowly. This is qualitatively consistent with the kinetics observed in the reactor experiments.

In conducting a study of the formation and reactivity of surface O^- and O_3^- species on MgO [23], Tench reported the isotopic exchange reaction to occur with ^{17}O-containing oxygen. A mechanism related to the one we are suggesting was proposed:

$$O_2 + O^- \rightarrow O_3^-,$$

$$2O_3^- \rightarrow 2O_2^- + O_2.$$

We believe this to be inconsistent with our observations, since it would lead to the occurrence of some R_2 products, which we have not observed for the Ube MgO samples. However, as reported by Che et al. [31], superoxide species can be active for R_1 exchange via the intermediacy of O_4^-

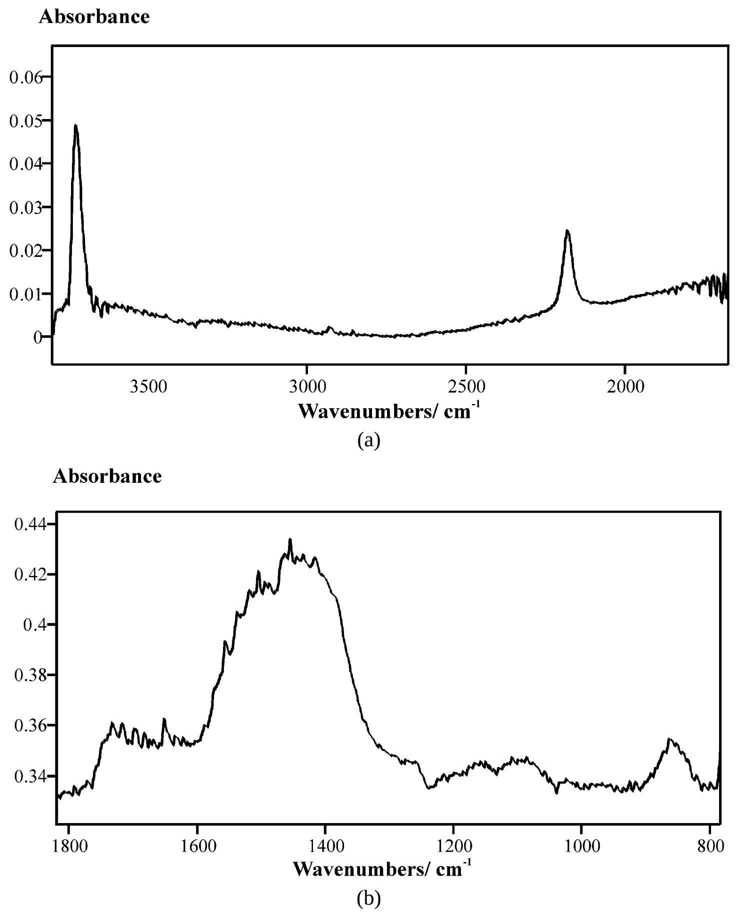


Fig. 4. (a) In situ FTIR spectrum of Ube 100 Å MgO. (b) Ex situ FTIR spectrum of Ube 100 Å MgO.

species. Therefore, the occurrence of the R_1 mechanism via such intermediate O_4^- centres cannot be ruled out.

An alternative possibility is that *ensembles* of low coordination sites could be associated with activity. As we have shown elsewhere, erosion of Ube MgO samples can lead to the formation of highly irregular surfaces on the unit cell scale [15]. Since erosion of the samples by CO_2 and H_2O is known to occur preferentially at sites of low coordination, it would be possible for the density of such ensembles to scale directly with surface area. As we have shown, there would not necessarily be a relationship between the density of the various sites explored by the experiments described in Table 2 and the density of ensemble sites.

The results of the high-temperature in vacuo outgassing studies, in which there is an apparent induction period, are intriguing. They clearly suggest that the exchange reaction cannot occur below a certain critical surface stoichiometry, which could indicate that the decomposition of intermediate ozonide, or the activity of ensembles of low coordinate sites, is suppressed until this is attained.

Table 5
Specific rates of isotopic oxygen exchange measured on the MgO catalysts, prepared from different precursors, at 708 K following vacuum treatment at 733 K

Catalyst	Ratio R_1:R_2	Specific rate of isotopic oxygen exchange ($\times 10^{13}$ atoms s^{-1} m^{-2})		
		R_1	R_2	Total
Ribbon	–	4.05 ± 0.81	–	4.05 ± 0.81
Hydroxide	8:5	3.12 ± 0.22	2.37 ± 0.28	5.49 ± 0.50
Basic carbonate	1:1	9.23 ± 1.85	11.9 ± 2.14	21.1 ± 3.99

3.2. *Effect of variation of morphology*

To investigate the influence of crystallographic face on the kinetics of the exchange reaction, we prepared MgO samples by a variety of methods. Although electrostatic considerations dictate that the MgO {100} termination plane is the most stable, it is known that intermediate metastable faces can be prepared. Common metastable faces are of {111} type, which is stabilised by the presence of high concentrations of terminal surface hydroxyl groups [24], and *mean* {111} and {110} faces, which are composed of micro-ensembles of cubeltes exposing {100} faces [25]. It has been demonstrated elsewhere that variation of preparation methods can lead to MgO samples exhibiting such metastable faces to varying degrees [13]. Accordingly, we have investigated the activities of MgO samples prepared by different methods designed to yield samples containing various proportions of different MgO termination plane. Table 5 shows

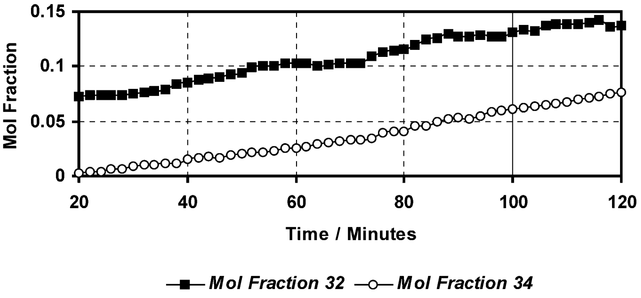
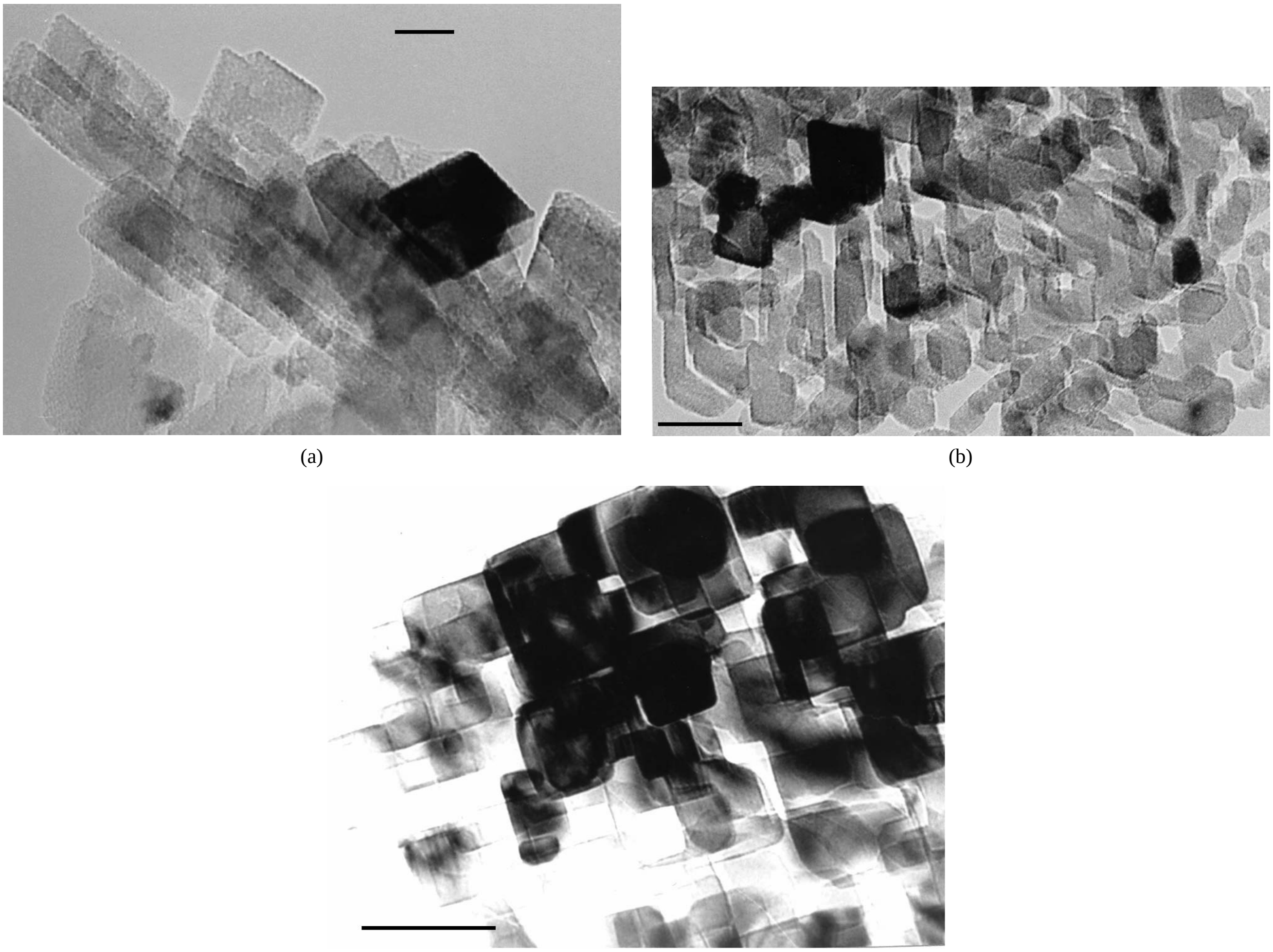


Fig. 5. Occurrence of the R_2 process over MgO derived from a basic carbonate precursor.

the activities of samples prepared by the thermal decomposition of magnesium basic carbonate (to produce a sample containing a relatively high proportion of mean {111} and {110} faces), burning magnesium ribbon in air (to produce exclusively {100}-terminated MgO), and thermal decomposition of magnesium hydroxide (to produce {111}- and {100}-terminated MgO in proportions dependent upon the temperature/duration of calcination). All samples were subject to a 16-h calcination stage at 1073 K in air before activity testing. Transmission electron microscopy of such samples confirmed our previous observations of morphology [13]. In all cases, powder X-ray diffraction demonstrated that MgO was the sole phase present, and XPS studies demonstrated the absence of impurities at the limit of detection. Caution must be exercised in the case of the thermal decomposition of magnesium basic carbonate derived materials, where the presence of sodium and calcium contaminants (which could enhance exchange activity) are well documented. However, we have shown previously that the role of impurities in this preparation route is minor in the structure sensitivity of MgO for oxidative coupling [13], where the role of mean {111} and {110} termination faces is dominant. It is noteworthy that there is a pronounced effect of preparation route on exchange kinetics and that in the case of MgO samples prepared via decomposition of a hydroxylated precursor, significant activity to the R_2 process in which $^{32}O_2$ is produced is apparent. An example is shown in Fig. 5 for MgO prepared from the hydroxycarbonate precursor. It is possible to relate the overall exchange kinetics to the occurrence of different crystallographic faces. As described previously [13], transmission electron microscopy studies show that magnesium oxide prepared from both the ribbon and hydroxide preparation routes exposes the {100} termination, whereas that prepared via magnesium hydroxycarbonate predominantly exposes the mean {111} and {110} termination. Mean {111} and {110} crystallographic faces are composed of high concentrations of the low coordinate $Mg^{2+}O^{2-}$ ion pair ensembles proposed to be of importance for the activity of the Ube samples. The effect of preparation route therefore further supports the potential role of such sites in determining O_2 exchange activity.

In the case of the R_2 process, it is possible that sequential exchange is occurring because of the presence of high local concentrations of active sites, resulting in an increased probability of sequential exchange of $^{34}O_2$, or that the mechanism proposed by Tench [23] detailed earlier is operative. Indeed, we have recently shown pronounced differences in the concentration of low coordination ensembles in Ube 100 Å MgO and MgO prepared via decomposition of the hydroxide [15]. Alternatively, R_2 exchange may occur in a single step with a diatomic surface oxygen species, such as peroxide and/or superoxide, which have been observed on some MgO surfaces [21]. In fact, the generation of peroxide has been suggested as an intermediate stage in O^- centre formation on decomposition of magnesium hydroxide [20]. In this context, it is also very interesting to note that MgO prepared via burning of ribbon in air has a specific activity comparable to that of the Ube materials. There is also no apparent R_2 activity, however, which is consistent with the fact that intermediate hydroxyl species are not involved in the genesis of this sample. Overall, the occurrence of the R_2 process on some samples and not others is a very interesting observation, since in previous literature this process has been reported by some authors and not others [26], despite similarities in their reaction regimes. This suggests that choice of preparation route exerts a major influence on the exchange activity pattern. Previously, Yanagisawa et al. [29] have observed the R_2 process to occur over MgO only after irradiation. This was initially ascribed to the formation of a non-square O_4^- intermediate, which was proposed to occur at kink sites on stepped {111} surfaces, which would clearly imply a potential influence of morphology. In a subsequent study, on the basis of ab initio molecular orbital calculations performed with defective {111} clusters, the same group postulated the importance of charged O_5 intermediates for R_2 exchange [30]. The absence of R_2 in nonirradiated MgO was stated to be due to the difficulty in the formation of such intermediates. As detailed above, Che et al. [31] proposed the intermediacy of square O_4^- species in the R_1 exchange process.

To further investigate the role of crystallographic plane on the exchange reaction kinetics, we prepared a series of magnesium oxide samples by the thermal decomposition of magnesium hydroxide in air at temperatures in the range of 623–1223 K. As mentioned previously, it is known that this procedure can generate MgO with differing proportions of the metastable {111} faces stabilised by terminal hydroxyl groups. It would be anticipated, and has been verified by the transmission electron micrographs presented in Fig. 6, that the preponderance of the {111} termination face would decrease with increasing temperature. Table 6 shows the surface area normalised activities of materials calcined at 623, 923, and 1223 K. Again, powder X-ray diffraction demonstrated that all materials comprised exclusively the MgO phase prior to reaction. It is worth noting that the activity of these materials is somewhat lower than their counterpart generated by prolonged calcination at 1073 K, as shown in Table 5, which indicates that, overall, the activity of {111}-type termination planes is lower than that of the {100}-type


(a)

(b)

(c)

Fig. 6. Transmission electron micrographs of MgO prepared by decomposition of $Mg(OH)_2$: (a) at 623 K scale bar corresponds to 200 Å, (b) 923 K scale bar corresponds to 400 Å, and (c) 1223 K scale bar corresponds to 500 Å.

Table 6
Specific rates of isotopic oxygen exchange measured on the MgO catalysts at 708 K prepared from decomposition of $Mg(OH)_2$ at various temperatures for 3 h

Decomposition temperature (K)	Ratio R_1:R_2	Specific rate of isotopic oxygen exchange ($\times 10^{13}$ atoms s^{-1} m^{-2})		
		R_1	R_2	Total
623	3:2	0.75 ± 0.19	0.57 ± 0.19	1.32 ± 0.39
923	6:1	3.08 ± 0.19	0.55 ± 0.25	3.63 ± 0.44
1223	2:3	0.92 ± 0.16	1.22 ± 0.26	2.14 ± 0.41

planes. It may be possible to rationalise this on the basis of the fact that the average coordination number of ions in the {111} surface plane is lower than for {100}, and consequently species are more tightly bound to the lattice and hence less reactive in the former case. It is also apparent that the intermediate calcination temperature yields the most active sample of the three, which may be a consequence of the decreasing concentration of the {111} plane coupled with the fact that reactive sites may be annealed at the higher temperature calcination. The variation of R_2 activity may merely reflect the stage of surface OH group decomposition. Weight is given to this suggestion by Fig. 7, which presents the FTIR spectrum of $Mg(OH)_2$ that has been decomposed at 723 K in vacuo. In this spectrum, it is worth noting that, in addition to absorptions in the range of 1260–1700 cm^{-1}, there are two bands at 1090 and 860 cm^{-1} that we attribute to peroxide species on the basis of previous literature [22]. For MgO 100 Å, on the other hand, we only observed a band at 846 cm^{-1} attributed to an ozonide species (see above). Furthermore, we cannot rule out the possible presence of superoxide species, which could be obscured by the broad absorption in the 1690–3000 cm^{-1} range.

4. Conclusion

A comprehensive investigation of the structure sensitivity of the exchange of isotopic oxygen with the surface of magnesium oxide samples was undertaken. Both the effect of crystallite size and surface plane termination have been investigated. In the former case, the surface area normalised

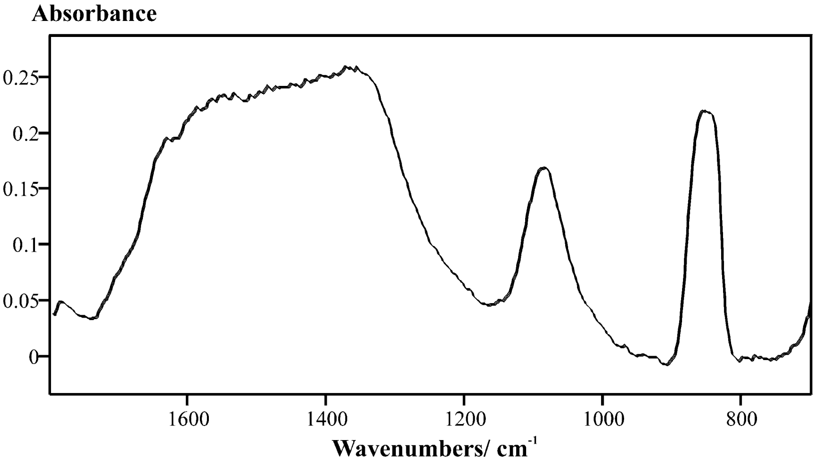


Fig. 7. In situ FTIR spectrum $Mg(OH)_2$ decomposed at 773 K in vacuo.

activity of a series of MgO samples exhibiting only {100}-type termination planes has not been found to vary significantly over a range of temperature, implying a structure insensitivity for this reaction. In all cases, exchange did not go to a complete monolayer, apparently stopping at a fraction equivalent to ca. 8%. The exchange process was found to be fully reversible, which indicated that discrete sites are effectively labeled in the reaction. By application of in situ FTIR measurements, it was demonstrated that these sites did not correspond to surface hydroxyl groups, and it is postulated that the intermediate of the reaction may be ozonide species generated by the reaction of gas-phase O_2, with surface O^- resulting from OH decomposition. An alternative possibility is that *ensembles* of low coordination sites could be associated with activity. Preparation of MgO samples by a variety of methods demonstrated the surface crystallographic plane to have an important influence on reaction. Most active surfaces corresponded to those consisting of mean {111}- and {110}-terminated planes, and the least active surfaces to those consisting of hydroxyl-terminated {111} planes, with {100}-terminated planes possessing an intermediate activity. In addition, it was found that samples prepared via hydroxylated precursors exhibited activity for the R_2 exchange process, in which two lattice surface species are exchanged with each molecule of gas-phase O_2. This observation suggests that the discrepancies in activity pattern reported in the literature for this reaction are likely to be due to influences of the precise preparation method. It was proposed that the occurrence of R_2 results from exchange with diatomic species documented to be generated from OH group decomposition.

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