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# Oxygen Exchange Reactions over Cerium Oxide: An FT–IR Study

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Oxygen (site and isotope) exchange reactions over well-outgassed and partially reduced cerium oxide were examined in the temperature range 200–373 K by means of Fourier-transform infrared (FT–IR) spectroscopy. Isotopic exchange between gaseous $O_2$ and lattice oxygen of the cerium oxide does not occur at the temperature below 373 K. Site exchange via gaseous $O_2$ with adsorbed superoxide ($O^-_{2\,ads}$) species was found to be very fast on both the outgassed and partially reduced surfaces even at 200 K, but site exchange between gaseous $O_2$ and adsorbed peroxide ($O^{2-}_{2\,ads}$) species does not take place in the temperature range 200–373 K. The isotopically exchanged superoxide species ($^{16}O^{18}O^-_{ads}$) with characteristic IR bands at 2175 and 1095 cm$^{-1}$ are readily formed from a mixture of $^{16}O_2$ + $^{18}O_2$ adsorption over well-outgassed and partially reduced cerium oxides. It is concluded that isotope exchange reactions proceed via adsorbed superoxide species and the exchange reaction is presumed to involve a tetraoxygen intermediate as the result of the reaction of gaseous $O_2$ with adsorbed superoxide species. © 1990 Academic Press, Inc.

## INTRODUCTION

Oxygen exchange reactions on oxides have been extensively studied with reference to elucidating catalytic oxidations (*1–4*). However, the detailed mechanism of exchange reactions on most oxide surfaces still remains insufficiently understood due to the paucity of evidence on surface oxygen species (*5*). The oxygen exchange over cerium oxide has been investigated at high temperatures (*6, 7*), but studies of the reaction and related surface species at mild temperatures have not been done. Recently we have successfully identified the dioxygen species (both superoxide, $O_2^-$, and peroxide, $O_2^{2-}$) derived from oxygen adsorption on cerium oxide using FT–IR (*8, 9*). The IR study has been further extended in the present paper with a view to detecting the adsorbed surface oxygen species formed during isotopic exchange reactions and therefore to distinguish various possible oxygen exchange reactions over cerium oxide in the temperature range 200–373 K.

## EXPERIMENTAL

Cerium oxide used in this study was prepared by precipitation from a solution of cerium nitrate with aqueous ammonia followed by calcination in air at 773 K for 3 h (BET surface area = 20 m$^2$/g). A self-supported sample disk for IR study was evacuated at 1000 K for 1 h, then cooled *in vacuo* to the desired temperatures for adsorption experiment, and this well-outgassed sample is referred to as $CeO_2$ (1000 K). A partially reduced cerium oxide named $CeO_2$ (673-H) was obtained through a pretreatment of the sample disk in $H_2$ at 300 Torr at 673 K for the desired time prior to the above-mentioned procedure.

IR spectra were recorded on a JEOL JIR-100 FT–IR spectrometer with 256 scans at 4 cm$^{-1}$ resolution and plotted in absorbance. Background spectra were recorded before the admission of $O_2$ at correspondingly experimental conditions of the spectra. $^{16}O_2$ and $^{18}O_2$ (98%) were purified in a circulating system through a liquid nitrogen trap.

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## RESULTS

### $^{16}O_2$ *and* $^{18}O_2$ *Adsorption on Cerium Oxides*

Adsorption of $^{18}O_2$ on well-outgassed cerium oxide, $CeO_2$ (1000 K), gives rise to two sharp bands at 2112 and 1063 $cm^{-1}$ as shown in Fig. 1a. These bands are attributed to superoxide species, $^{18}O_2^-$, according to the characteristic frequency of 1063 $cm^{-1}$, which is estimated to be the vibration of dioxygen with a bond order of 1.5. Figure 1b displays the spectrum of adsorbed dioxygen species formed after admission of $^{18}O_2$ to partially reduced cerium oxide, $CeO_2$ (673-H). In addition to the two bands at 2114 and 1065 $cm^{-1}$ shown in Fig. 1a, one more band was clearly observed at 835 $cm^{-1}$ which is ascribed to peroxide species, $^{18}O_2^{2-}$. Spectra similar to those in Fig. 1 were obtained from adsorption of $^{16}O_2$ on $CeO_2$ (1000 K) and $CeO_2$ (673-H). All the IR bands derived from adsorption of $^{18}O_2$ and $^{16}O_2$ on well-outgassed and partially reduced cerium oxides together with isotopic ratios and assignments for these bands (*8*, *9*) are collected in Table 1. The assignments are in excellent agreement with results reported in the literature (*5*, *10–13*) and also confirmed by the isotopic ratios.

TABLE 1

IR Bands Derived from Adsorption of $^{16}O_2$ and $^{18}O_2$ on Cerium Oxide ($cm^{-1}$)

| Cerium oxide | $^{16}O_2$ | $^{18}O_2$ | $^{16}O_2/^{18}O_2$[a] | Assignment |
|---|---|---|---|---|
| $CeO_2$ (1000 K) | 1126 | 1063 | 1.059 | Superoxide, $O_2^-$ |
| | 2237 | 2112 | 1.059 | |
| $CeO_2$ (673-H) | 883 | 835 | 1.057 | Peroxide, $O_2^{2-}$ |
| | 1128 | 1065 | 1.059 | Superoxide, $O_2^-$ |
| | 2238 | 2114 | 1.059 | |

[a] Calculated value is 1.061.

### $^{16}O_2$ + $^{18}O_2$ *Adsorption on* $CeO_2$ *(1000 K) and* $CeO_2$ *(673-H)*

Figure 2 shows a series of IR spectra of adsorbed dioxygen species formed on $CeO_2$ (1000 K) in contact with a mixture of $^{16}O_2$ + $^{18}O_2$ (40 : 20, Torr) at elevated temperatures. Figure 2a presents the spectrum recorded after immediate admission of the $^{16}O_2$ + $^{18}O_2$ mixture to $CeO_2$ (1000 K). The same bands, at 2113 and 1063 $cm^{-1}$, 2237 and 1126 $cm^{-1}$, appear as listed in Table 1 for individual adsorptions of $^{18}O_2$ and $^{16}O_2$, respectively. It is noteworthy that a pair of

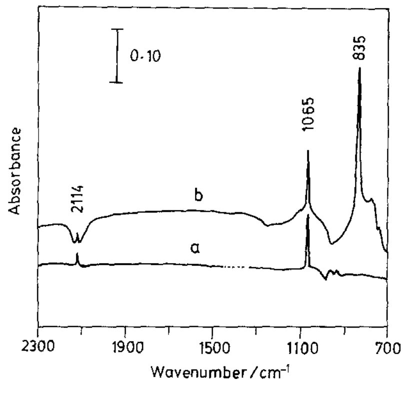

FIG. 1. IR spectra of adsorbed dioxygen formed from adsorption of $^{18}O_2$ (10 Torr) on (a) $CeO_2$ (1000 K) at 298 K and (b) $CeO_2$ (673-H) (reduced in $H_2$ for 15 h) at 210 K.

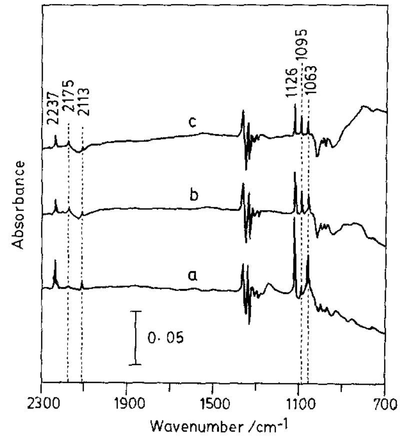

FIG. 2. IR spectra of adsorbed dioxygen species formed from adsorption of $^{16}O_2$ + $^{18}O_2$ (2 : 1, 60 Torr) on $CeO_2$ (1000 K) at elevated temperatures. (a) After admission of the gas at 200 K for 1 min; (b) at 306 K for 60 min after a; and (c) at 323 K for 15 min after b.

new weak bands at 2175 and 1095 $cm^{-1}$ was observed in Fig. 2. The two bands are growing with time and rising temperature (<320 K) of adsorption as exhibited in Fig. 2. From the bands in the region 1200–1000 $cm^{-1}$ of Figs. 2a and 2b, it is evident that the intensity of the band at 1095 $cm^{-1}$ increases while those of its two neighboring bands at 1126 and 1063 $cm^{-1}$ decrease. All the bands are gradually attenuated above 320 K and finally disappear simultaneously at 373 K in the presence of $^{16}O_2 + {}^{18}O_2$. The two new bands at 2175 and 1095 $cm^{-1}$ are just in the regions of 2237–2112 and 1126–1063 $cm^{-1}$, respectively, so that they are reasonably attributed to isotopically exchanged superoxide species, $^{16}O^{18}O^-$, and the assignment is supported by their isotopic shifts, which are consistent with the calculated results. The intensity ratio of the band at 1126 to 1063 $cm^{-1}$ is about 2 : 1, which is also the ratio of the partial pressures, $P(^{16}O_2) : P(^{18}O_2)$, and the ratio of the bands was unchanged from Fig. 2a to 2c. This indicates that the surface distribution of the species $^{16}O_2^-$ and $^{18}O_2^-$ is directly proportional to their pressure ratio.

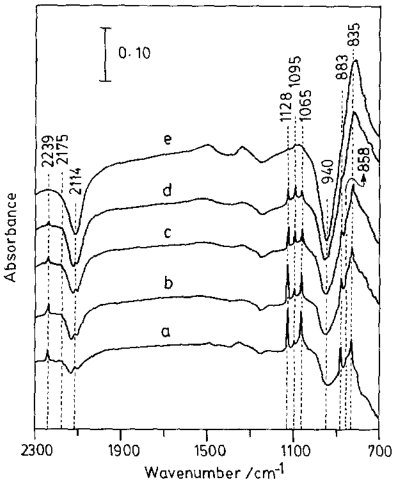

FIG. 3. IR spectra of adsorbed dioxygen species formed on $CeO_2$ (673-H) (reduced in $H_2$ for 3 h) in the presence of $^{16}O_2 + {}^{18}O_2$ (1 : 1, 37 Torr) at elevated temperatures (ca. 2.5 K/min). (a) After admission of the gas at 200 K for 1 min; (b) 268 K; (c) 301 K; (d) 323 K; and (e) 373 K.

Figure 3 gives spectra in a separate experiment for $^{16}O_2 + {}^{18}O_2$ (1 : 1, 37 Torr) adsorption on $CeO_2$ (673-H) at temperatures from 200 to 373 K. Figure 3a shows the spectrum recorded immediately after exposure of the $CeO_2$ (673-H) to $^{16}O_2 + {}^{18}O_2$ at 200 K in which nine bands at 2239 (w), 2175 (w), 2114 (w), 1128 (s), 1095 (w), 1065 (s), 883 (m), 858 (vw), and 835 (m) $cm^{-1}$ were observed, where s, m, w, and vw stand for strong, middle, weak, and very weak, respectively. By comparison with Table 1, it is notable that three new bands at 2175, 1095, and 858 $cm^{-1}$ appear in Fig. 3a, and the rest are due to $^{16}O_2^-$ (2239, 1128 $cm^{-1}$), $^{18}O_2^-$ (2114, 1065 $cm^{-1}$), $^{16}O_2^{2-}$ (883 $cm^{-1}$), and $^{18}O_2^{2-}$ (835 $cm^{-1}$), which have been summarized in Table 1. Obviously, the bands at 2175 and 1095 $cm^{-1}$ derived from $^{16}O^{18}O^-$ species as for $CeO_2$ (1000 K) and the shoulder band at 858 $cm^{-1}$ should be assigned to isotopically exchanged peroxide, $^{16}O^{18}O^{2-}$. Upon heating the sample in contact with the gas mixture, the indistinct band at 858 $cm^{-1}$ due to peroxide species is reduced markedly and it is therefore too weak to be detected in Figs. 3b–3e, whereas the band at 1095 $cm^{-1}$ becomes prominent.

The tendency for bands displayed in Fig. 3 is similar to those in Fig. 2 with warming of the sample. The same conclusion as that for $CeO_2$ (1000 K) can be deduced for $CeO_2$ (673-H), that the intensity ratio of 1128 to 1065 $cm^{-1}$ is dependent on the ratio of the partial pressure. The bands at 1128 and 1065 $cm^{-1}$ were weakened while the band at 1095 $cm^{-1}$ developed at elevated temperatures (Figs. 3a–3d), and all the bands vanished simultaneously above 373 K. The two reverse bands at 2115 and 939 $cm^{-1}$ and bands at around 1335 $cm^{-1}$ originate from cerium oxide (*7, 8*) and they are not shifted by the isotope oxygen adsorption.

IR spectra were recorded after introduction of $^{16}O_2$ to a partially reduced cerium oxide with preadsorbed oxygen-18 species

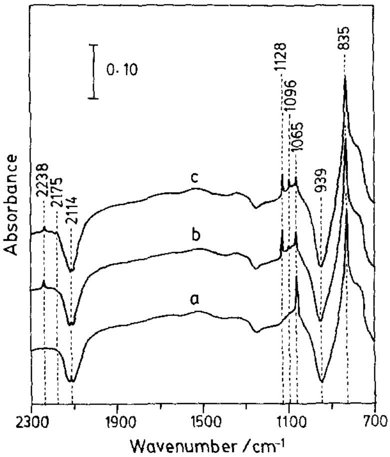

FIG. 4. IR spectra of adsorbed dioxygen species formed on $CeO_2$ (673-H) (reduced in $H_2$ for 15 h) from adsorption of $O_2$. (a) After admission of $^{18}O_2$ (40 Torr) for 30 min at 294 K; (b) then introduction of $^{16}O_2$ (65 Torr) after a at 298 K; and (c) for 15 min in the presence of the gas mixture at 323 K.

at 294 K, as shown in Fig. 4a. The three bands at 2114, 1065, and 835 $cm^{-1}$ in Fig. 4a have been attributed to adsorbed $^{18}O_2^-$ and $^{18}O_2^{2-}$ species, respectively. A spectrum displayed in Fig. 4b was taken when $^{16}O_2$ (40 Torr) was admitted to the surface which had been treated with $^{18}O_2$ (65 Torr) for 30 min. It is clearly found that the bands at 2238 and 1128 $cm^{-1}$ due to $^{16}O_2^-$ species appear while the bands at 2114 and 1065 $cm^{-1}$ due to $^{18}O_2^-$ species decline; meanwhile, a weak band at 1096 $cm^{-1}$ due to $^{16}O^{18}O^-$ species emerges. But the band at 835 $cm^{-1}$ is not affected by the new component of gas phase and the possible bands at 883 $cm^{-1}$ due to $^{16}O_2^{2-}$ and 858 $cm^{-1}$ due to $^{16}O^{18}O_2^{2-}$ are not observed. The band at 1096 $cm^{-1}$ grows somewhat; however, the bands at 1128 and 1065 $cm^{-1}$ are slightly reduced when the temperature is elevated from 298 (Fig. 4b) to 323 K (Fig. 4c). Although the equilibrium time was prolonged, bands at 883 and 858 $cm^{-1}$ were not detected. A similar result was obtained for $CeO_2$ (1000 K) in a separate experiment, in which the 1063 $cm^{-1}$ band was reduced while the 1126 $cm^{-1}$ was produced after admission of $^{16}O_2$ to oxygen-18 preadsorbed sample.

## DISCUSSION

Oxygen exchange reaction over oxides can be divided into two types; site exchange is distinguished by the adsorption sites where the adsorbed species are replaced isotopically *(14)*. Isotope exchange takes place involving the making and breaking of chemical bonds. Generally speaking, isotope exchange may occur between the following pairs: gas phase and the lattice oxygen of oxide, adsorbed species and the lattice oxygen of oxide, gas phase and adsorbed species (e.g., Eley–Rideal mechanism), and adsorbed species and adsorbed species (e.g., Langmuir–Hinshelwood mechanism). The first two kinds of exchange occur usually at higher temperatures, involving the lattice oxygen which has been considered an active participator in oxidation reactions at high temperatures *(2, 3)*, and the last two have been confirmed over some oxides at low temperatures *(15, 16)*.

The spectra in Fig. 1 permit us to deduce that the exchange involving oxygen of cerium oxide is impossible at temperatures below 373 K because no band due to isotopically exchanged dioxygen species, such as $^{16}O^{18}O^-$ or $^{16}O^{18}O_2^{2-}$, was detected and furthermore no $^{16}O^{18}O$ in gas phase was detected spectroscopically even after equilibrating the cerium oxide in $^{18}O_2$ at 373 K overnight. A large amount of $^{16}O^{18}O$ was produced after treating either $CeO_2$ (1000 K) or $CeO_2$ (673-H) in $^{18}O_2$ at 673 K. This indicates that the exchange reaction between $O_2$ and the lattice oxygen of cerium oxide can occur at high temperatures.

In Fig. 2, the bands due to adsorbed $^{16}O^{18}O^-$ species show direct evidence that the isotope exchange really proceeds on $CeO_2$ (1000 K) even at temperatures as low as 200 K. The fact that the bands at 2175 and 1095 $cm^{-1}$ due to $^{16}O^{18}O^-$ species grow with increasing temperature (Fig. 2a and

2b) indicates that the oxygen exchange is facilitated at higher temperatures. The intensities of the three bands at 1126, 1095, and 1063 $cm^{-1}$ vary with adsorption time and temperature (Figs. 2a–2c). This may indicate that the surface concentration of adsorption sites for superoxide species is constant or that the total number of electrons which can be transferred from the surface to the adsorbed oxygen is limited. The intensity increase in the band at 1095 $cm^{-1}$ accompanying the decrease in its two neighboring bands at 1126 and 1063 $cm^{-1}$ can be accounted for by the mechanism that the $^{16}O^{18}O^-$ species derives from $^{16}O_2^-$ and $^{18}O_2^-$, namely,

$$^{16}O^-_{2\,ads} + {}^{18}O_2 \rightarrow {}^{16}O^{18}O^-_{ads} + {}^{16}O^{18}O \quad (1)$$

$$^{18}O^-_{2\,ads} + {}^{16}O_2 \rightarrow {}^{16}O^{18}O^-_{ads} + {}^{16}O^{18}O \quad (2)$$

$$^{16}O^-_{2\,ads} + {}^{18}O^-_{2\,ads} \rightarrow 2{}^{16}O^{18}O^-_{ads}. \quad (3)$$

Figure 3 shows the same tendency for bands due to superoxide species as that in Fig. 2; thereby the same postulation for isotopic oxygen exchange on $CeO_2$ (673-H) as that on $CeO_2$ (1000 K) can be made. In addition, although the band at 858 $cm^{-1}$ is very weak, it leads us to infer possible isotopic exchange reactions which may take place through peroxide species on partially reduced cerium oxide,

$$^{16}O^{2-}_{2\,ads} + {}^{18}O_2 \rightarrow {}^{16}O^{18}O^{2-}_{ads} + {}^{16}O^{18}O \quad (4)$$

$$^{18}O^{2-}_{2\,ads} + {}^{16}O_2 \rightarrow {}^{16}O^{18}O^{2-}_{ads} + {}^{16}O^{18}O \quad (5)$$

$$^{16}O^{2-}_{2\,ads} + {}^{18}O^{2-}_{2\,ads} \rightarrow 2{}^{16}O^{18}O^{2-}_{ads}. \quad (6)$$

When the coexistence of the superoxide species with the peroxide on the partially reduced surface is taken into consideration, the following processes might be possible too:

$$^{16}O^-_{2\,ads} + {}^{18}O^-_{2\,ads} \rightarrow {}^{16}O^{18}O^{2-}_{ads} + {}^{16}O^{18}O \quad (7)$$

$$^{16}O^-_{2\,ads} + {}^{18}O^{2-}_{2\,ads} \rightarrow {}^{16}O^{18}O^{2-}_{ads} + {}^{16}O^{18}O^-_{ads} \quad (8)$$

$$^{18}O^-_{2\,ads} + {}^{16}O^{2-}_{2\,ads} \rightarrow {}^{16}O^{18}O^{2-}_{ads} + {}^{16}O^{18}O^-_{ads} \quad (9)$$

$$^{18}O^{2-}_{2\,ads} + {}^{16}O_2 \rightarrow 2{}^{16}O^{18}O^-_{ads} \quad (10)$$

$$^{16}O^{2-}_{2\,ads} + {}^{18}O_2 \rightarrow 2{}^{16}O^{18}O^-_{ads}. \quad (11)$$

All of the above isotopic exchange processes can be assumed to occur via negatively charged tetraoxygen complexes, viz., $O_4^{n-}$ ($n = 1$–4). Although there is a lack of direct spectroscopic evidence for the four-atom intermediate in the present study, the proposed isotopic exchanges are most likely to occur through the reaction between two dioxygen species in the light of the IR spectra of both adsorbed dioxygen and isotopically exchanged dioxygen species. The dimers of dioxygen species are so unstable that they have been reliably detected only at low temperatures in matrixes, such as $CsO_4$ (*17, 18*), $AgO_4$ (*19*), and $NaO_4$, $KO_4$, and $RbO_4$ (*18*). Spectroscopic and calculated data (*20*) for an $O_4^-$ in the matrix showed that a weak interbond is formed between two dioxygens while the intrabond of a dioxygen is slightly weakened. Our hypothesis is in accordance with this result as the isotropic exchange involves the breaking of the oxygen–oxygen bond. The four-atom intermediate ($O_4^-$) has been proposed to be involved in oxygen isotopic exchange over MgO (*14*), ZnO (*21*), and $TiO_2$ (*22*) on the basis of ESR observations.

It has been also suggested that oxygen exchange can proceed via ozonide species ($O_3^-$) which are formed from mononuclear oxygen species, $O^-$ species, according to ESR data (*23, 24*). The atomic oxygen species may be generated on adsorption of $O_2$ over cerium oxide, but the isotopically exchanged product was not evidently detected spectroscopically in the present study either over the surface or in the gas phase after equilibrating the oxygen-18 preadsorbed cerium oxide with $^{16}O_2$ at temperatures below 373 K.

On the other hand, ESR data (25–27)

proved that the adsorbed $O_2^-$ species instead of $O^-$ species is favored on cerium oxide. It is accordingly concluded that the isotopic exchange involving mononuclear oxygen species is not dominant over cerium oxide at the temperature range in the present study.

Since the oxygen exchange reactions are usually examined from analysis of products in gas phase, the site exchange cannot be easily discriminated from the total exchange process by ESR (*28*). The site exchange process via adsorbed $O_2^-$ species can be distinguished in the present study from the IR results given in Fig. 4, in which the decrease in the band at 1065 $cm^{-1}$ can be explained as a result of site exchange between $^{18}O^-_{2\,ads}$ and $^{16}O_2$,

$$^{18}O^-_{2\,ads} + {}^{16}O_2 \rightarrow {}^{16}O^-_{2\,ads} + {}^{18}O_2. \quad (12)$$

However, site exchange between $^{16}O_2$ with adsorbed peroxide, $^{18}O_2^{2-}$, seems to be impossible over $CeO_2$ (673-H) since the band at 835 $cm^{-1}$ remains unchanged and the band at 883 $cm^{-1}$ due to adsorbed $^{16}O_2^{2-}$ is not observed in Fig. 4. The site exchange between adsorbed $^{18}O_2^-$ species and $^{16}O_2$ is by nature a transfer of one electron from adsorbed species to adsorbing species from the gas phase. The site exchange between adsorbed peroxide species and $O_2$ in the gas phase is prohibited owing to the difficulty that the process will involve a transfer of two electrons.

Figure 4 also indicates that the isotopic exchange involving peroxide species does not proceed over partially reduced cerium oxide on the basis of the facts that the band at 835 $cm^{-1}$ is not reduced while the band at 1096 $cm^{-1}$ due to $^{16}O^{18}O^-$ species becomes stronger, and moreover the band at 858 $cm^{-1}$ due to isotopically exchanged peroxide species is absent in Fig. 4. It is recognized that reactions (4)–(6) and (8)–(11) are really not dominant contributions to the isotopic exchange. The formation of adsorbed $^{16}O^{18}O^{2-}$ species with the weak band at 858 $cm^{-1}$ in Fig. 3a is most probably ascribed to the disproportionation reaction (*7*). The isotopically exchanged surface species, $^{16}O^{18}O^-_{ads}$, are mainly derived from surface reactions (1)–(3). The possibility of readsorption of $^{16}O^{18}O$ is ruled out because the partial pressure of $^{16}O^{18}O$ is extremely low compared with those of $^{16}O_2$ and $^{18}O_2$ in the present investigation, and the site exchange of surface peroxide species has not been found to occur.

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