Surface oxygen species and their reactivities in the mild oxidation of ethylene on cerium oxide studied by FT-IR spectroscopy

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Surface oxidation of ethylene on cerium oxide was studied at mild temperatures (293–473 K) by using *in situ* FT-IR spectroscopy, and isotopic technique. Ethylene oxidation took place even at around 330 K on a well outgassed cerium oxide independent of the presence of gaseous O_2. At mild temperatures, the surface adsorbed product was mainly formate species. Adsorbed superoxide (O_2^-) species was definitely observed at temperatures up to 373 K when gaseous oxygen was present. However isotopic experiment confirmed that the superoxide was not the active form of oxygen due to the mild oxidation of ethylene. The principal oxygen species participating in the mild oxidation of ethylene was surface lattice oxygen which is supposed to be in O^--like form created by an outgassing at high temperatures. The mild oxidation of ethylene could be also initiated by surface peroxide (O_2^{2-}) and O^- species which were formed via the adsorption of O_2 on a partially reduced cerium oxide.

Keywords: Cerium oxide; mild oxidation; oxygen species; rare earth oxide; FT-IR; ethylene oxidation; isotopic technique

1 Introduction

Cerium oxide has been extensively used in heterogeneous catalysis [1,2]. In particular, cerium oxide possesses active oxygen species both on the surface and bulk [3,4] and has been employed as active component of the catalysts for reducing exhaust emissions. The oxygen species on cerium oxide have been studied and surface superoxide (O_2^-) species were well identified by e.s.r. [5–7]. In our previous work [8,9], the adsorbed superoxide species were safely detected by FT-IR sectroscopy when an outgassed CeO_2 was in contact with O_2. Moreover, FT-IR results demonstrated that both adsorbed superoxide and peroxide (O_2^{2-}) species could be formed on a partially reduced cerium oxide and these dioxygen species could be observed even up to 373 K. In this letter, we report a further study of the surface oxygen species and their reactions with ethylene on

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CeO_2. The aim of the present study is therefore to investigate the reactivities of the surface oxygen species in the oxidation of ethylene at mild temperatures (293–473 K), hoping to understand the nature of the various oxygen species and their roles played in the oxidation of hydrocarbons on CeO_2.

2. Experimental

Cerium oxide (CeO_2, BET surface area, 20 m^2/g) used in this study was prepared by decomposing the cerium hydroxide gel at 773 K. The CeO_2 sample was pressed into a self-supporting wafer for IR study, and the sample wafer was outgassed in a quartz IR cell at 1000 K and then oxidized at 873 K with O_2 in an internal cycle system until surface contaminant species were completely removed prior to adsorption or reaction experiment. After the repeated pretreatment the sample was cooled down to room temperature under vacuum while the background IR spectra of the sample were recorded at given temperatures. Ethylene, O_2 or their mixture were first introduced in the IR cell at room temperature and then the sample was heated in a stepwise way. Surface species produced from adsorption and reaction were detected by FT-IR spectroscopy during the temperature elevation. A partially reduced cerium oxide was prepared by treating the sample wafer using H_2 at 673 K in the internal cycle system.

IR spectra were recorded on a Perkin-Elmer 1800 FT-IR spectrometer equipped with a liquid-nitrogen-cooled MCT detector at resolution of 4 cm^{-1}, and scans was set at 8. The purities of C_2H_4 and O_2 are better than 99.9%, and isotope $^{18}O_2$ is enriched more than 98%.

3. Results and discussion

Fig. 1 shows the IR spectra of adsorbed oxygen and of oxygen and ethylene co-adsorbed on a well outgassed CeO_2 at 293 K. The band at 1126 cm^{-1} that appeared for O_2 adsorption can be assigned to superoxide (O_2^-) species [8,10,11]. The adsorbed O_2^- species on CeO_2 were confirmed by e.s.r. spectrum which showed the similar g tensors as reported in [5–7, 12]. The band at 990 cm^{-1} (fig. 1c) originated from the ethylene adsorption and is reasonably attributed to adsorbed ethylene species. The spectrum of adsorbed superoxide is scarcely affected by coadsorption of ethylene indicating that there are no evident chemical interactions between adsorbed O_2^- and C_2H_4 on CeO_2 at room temperature. The IR results substantiated that no reaction between the adsorbed O_2^- and C_2H_4 happens at 293 K because there are no any additional species produced even after a prolonged standing under the atmosphere of $O_2 + C_2H_4$.

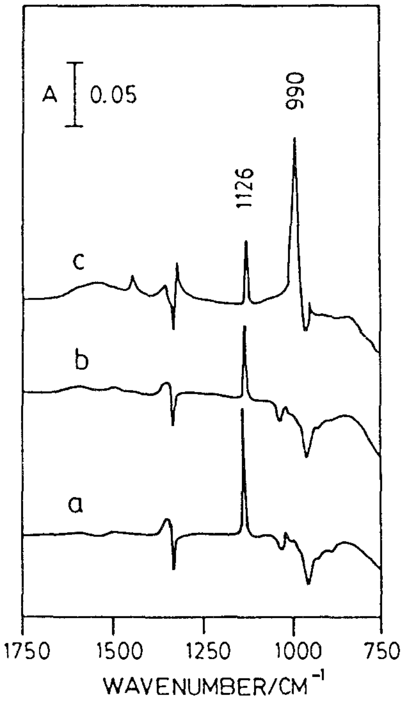

Fig. 1. IR spectra of adsorbed species formed from: (a) adsorption of O_2 for 1 min, (b) 60 min, and (c) coadsorption of O_2 and C_2H_4 at room temperature on well outgassed CeO_2.

The CeO_2 sample in contact with O_2 and C_2H_4 was warmed slowly and the surface species were followed by *in situ* FT-IR. Fig. 2 displays the IR spectra recorded in the temperature range of 293–373 K. With the elevation of temperature, IR bands at 1126 and 990 cm^{-1} gradually vanished while some new bands in 4000–1300 cm^{-1} region appeared at near 330 K as shown in fig. 2b. This indicated that some surface species derived from the oxidation of C_2H_4 even at 330 K on CeO_2. At 373 K IR bands at 1126 and 990 cm^{-1} disappeared but the bands in the 4000–1300 cm^{-1} region became prominent and developed with time as can be seen in figs. 2c and 2d. The bands at 2933, 2842, 1544, 1371, 1355 cm^{-1} are readily attributed to surface formate species [13]; in addition, weak bands at ~ 1560, ~ 1450 cm^{-1} due to acetate species [14] were also observed. The bands at ~ 3600 cm^{-1} are due to surface hydroxyls. The major species on the surface are formate and the bands of surface formate species grew significantly when the sample was heated to 473 K in the presence of C_2H_4 and O_2. The surface formate species were partly oxidized to surface carbonate species having bands at ~ 1455, ~ 1355, 854 cm^{-1} [15] at temperatures above 573 K.

To distinguish the active oxygen species for the mild oxidation of ethylene, a separate experiment was performed in the absence of O_2. A well outgassed CeO_2 was exposed to ethylene alone at room temperature and then the sample

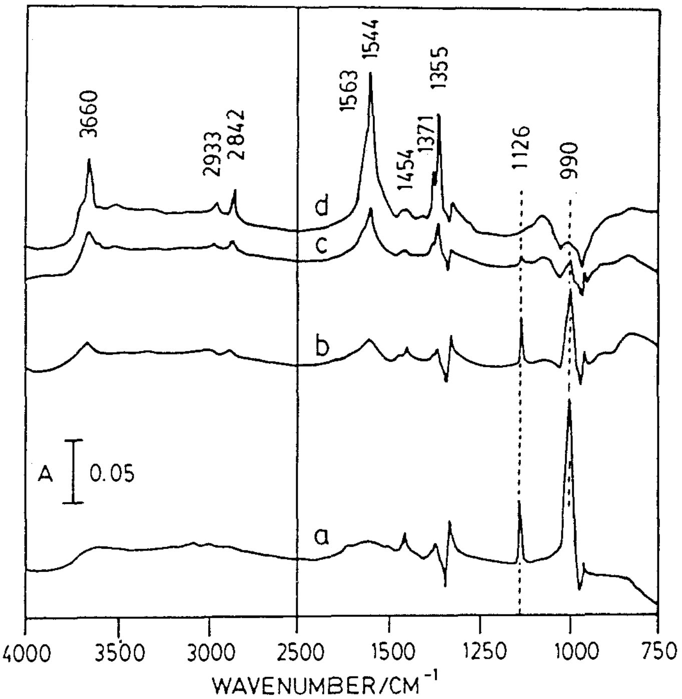

Fig. 2. IR spectra recorded during the oxidation of ethylene on well outgassed CeO_2 in the presence of O_2: (a) at room temperature, (b) at 333 K for 10 min, (c) at 373 K for 1 min and (d) at 373 K for 90 min.

was gradually heated in the same way as described above. The IR spectra recorded during the temperature course and showed in fig. 3. With the elevation of temperature, the bands at 3655 cm^{-1} due to surface hydroxyls and at 2933, 2842, 1544, 1371, 1355 cm^{-1} due to surface formate species also appeared at mild temperatures and grew considerably at 473 K. The oxidation of ethylene could be initiated on cerium oxide at temperatures below 373 K either in the presence of O_2 or not. A conclusion may be reached that the mild oxidation of ethylene on CeO_2 is independent of the presence of adsorbed O_2^-. A comparative experiment by using isotope $^{18}O_2$ was designed to confirm if the adsorbed O_2^- species are reactive or not at mild temperatures. A well outgassed CeO_2 sample was exposed to a mixture of $^{18}O_2$ and C_2H_4 and subsequently the sample was also heated to 473 K slowly. At temperatures below 373 K IR band at 1063 cm^{-1} due to adsorbed $^{18}O_2^-$ species was observed similarly as shown in fig. 1. The IR spectrum recorded at 473 K for $^{18}O_2 + C_2H_4$ is compared with that for $^{16}O_2 + C_2H_4$ as illustrated in fig. 4. The two spectra are almost identical and not any isotopic shift is found in fig. 4b for oxygen-18. The results clearly demonstrated that the adsorbed O_2^- species did not participate in the formation of formate species, neither could they exchange with surface lattice oxygen. Accordingly, the surface lattice oxygen species of cerium oxide must be

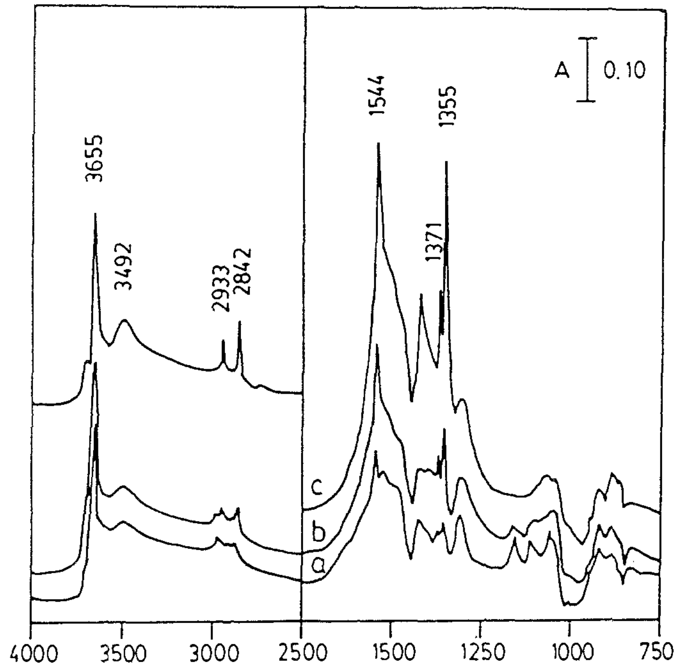

Fig. 3. IR spectra recorded during the oxidation of ethylene on well outgassed CeO_2 in the absence of O_2: (a) at 373 K for 10 min, (b) at 473 K for 1 min and (c) at 473 K for 120 min.

principal species contributing to the formation of formate species. Isotopic shifts in the IR spectrum for $^{18}O_2 + C_2H_4$ on CeO_2 could only be obviously observed at temperatures above 573 K.

There are discrepancies about the reactivity of O_2^- species although the dioxygen species have been extensively investigated. For example, Iwamoto and Lunsford [16] found that O_2^- species on MgO were much less reactive than O^- and O_3^- species, however O_2^- species could react with propylene and propane at 445 K. IR results [17,18] showed that O_2^- species on CoO-MgO catalyst were able to oxidize ethylene and propylene even at room temperature. Sass et al. [19] proposed that O_2^- was the active form of oxygen in the low-temperature oxidation of CO on ceria-noble metal catalysts. This study believed that adsorbed O_2^- species on CeO_2l do not seem to be active enough to react with ethylene at temperatures below 473 K.

It has also been found that surface lattice oxygen showed reactivity toward ethylene at mild temperatures only after the cerium oxide was well outgassed at high temperatures. If the surface was covered with carbonate and hydroxyls the mild oxidation of ethylene was remarkably inhibited. In our early paper [15] it was reported that CO could be easily oxidized to surface carbonate species on well outgassed cerium oxide even at room temperature. This leads us to a

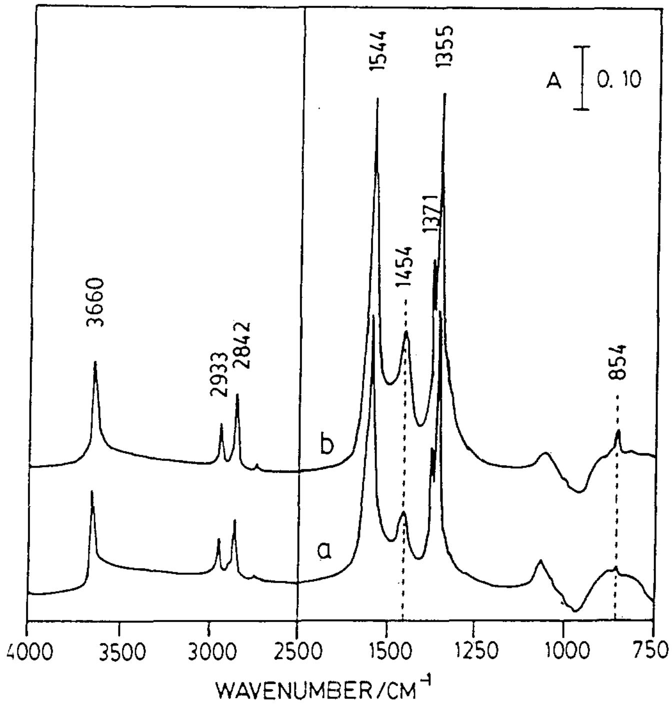

Fig. 4. A comparison of IR spectra of surface species derived from ethylene oxidation on well outgassed CeO_2 in the mixture of: (a) $^{16}O_2 + C_2H_4$ and (b) $^{18}O_2 + C_2H_4$, at 473 K for 90 min.

speculation that the surface lattice oxygen species having the high reactivity are maybe in a special active form only created by outgassing at high temperatures. Common aspects may be expected for other basic metal oxides some of whose extraordinary surface properties only appear after the removal of the strongly adsorbed carbonate and hydroxyl species at high temperatures.

We have firstly reported that both the superoxide (O_2^-) and peroxide (O_2^{2-}) species could be formed on a partially reduced cerium oxide [9]. To examine the reactivities of adsorbed O_2^{2-} species, a partially reduced cerium oxide was prepared by treating CeO_2 in H_2 at 673 K. The surface product species were not detected when the partially reduced cerium oxide was warmed in the presence of ethylene alone at mild temperature indicating that the surface active oxygen species were reduced by the H_2-treating. When the partially reduced cerium oxide was exposed to O_2, IR bands due to adsorbed O_2^- (1126 cm^{-1}) and O_2^{2-} (883 cm^{-1}) were observed. After introducing C_2H_4 on to the oxygen-preadsorbed surface the sample was heated slowly and the surface formate species were safely detected at mild temperatures too as shown in fig. 5. If isotope $^{18}O_2$ was employed, every IR band due to formate species splitted into two or three, e.g., 1544 cm^{-1} → 1544, 1534, 1522 cm^{-1}; 1371 cm^{-1} → 1371, 1369, 1361 cm^{-1}; 1355 cm^{-1} → 1355, 1334, 1319 cm^{-1}. This means that the formate

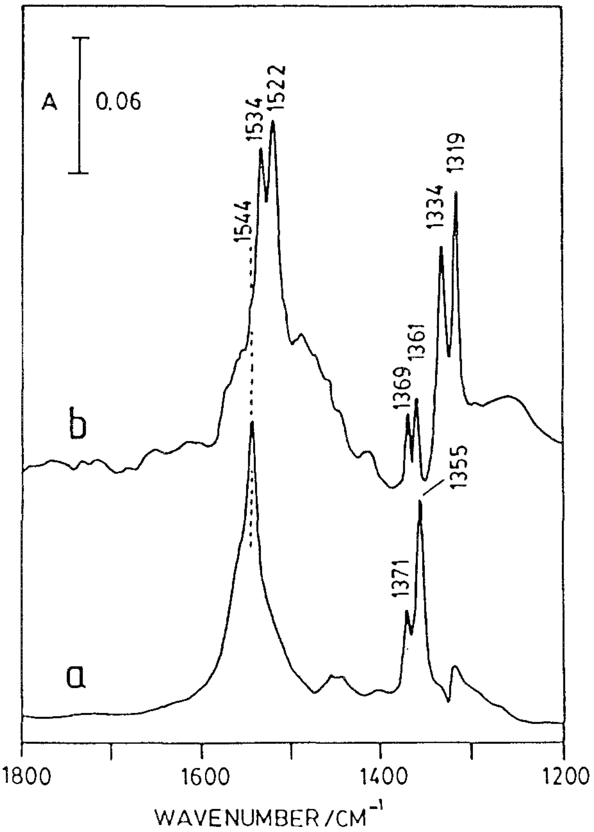

Fig. 5. IR spectra of surface species derived from ethylene oxidation in the mixture of $^{18}O_2 + C_2H_4$ at 373 K for 60 min: (a) on well outgassed CeO_2 and (b) on partially reduced cerium oxide.

species involved with oxygen-18 were formed. These bands can be attributed to $HC^{16}O^{16}O^-$ (1544, 1371, 1355 cm^{-1}), $HC^{16}O^{18}O^-$ (1534, 1369, 1334 cm^{-1}), and $HC^{18}O^{18}O^-$(1522, 1361, 1319 cm^{-1}), respectively. Of these bands, the bands due to $HC^{16}O^{16}O^-$ are relatively weak. The surface was dominated by $HC^{16}O^{18}O^-$ and $HC^{18}O^{18}O^-$ species which contain oxygen-18. Taking into account of that the adsorbed O_2^{2-} can easily convert into adsorbed O^- at elevated temperatures, we believed that both O_2^{2-} and O^- species are responsible for the production of formate species from the mild oxidation of ethylene on partially reduced cerium oxide. These results are consistent with the general consensus that the O_2^{2-} and O^- species are most active species among the surface oxygen species.

From the contrast between figs. 5a and 5b, it can be seen that the surface lattice oxygen species exhibit almost the same reactivity as adsorbed O_2^{2-} and O^- species. The surface lattice oxygen for the mild oxidation of ethylene, possibly coordinatively unsaturated caused by the outgassing at high temperatures, may transfer an electron to the bulk and accordingly become O^--like species as suggested for MgO [20–22]. Therefore the surface lattice oxygen species manifest the similar reactivity as adsorbed O_2^{2-} and O^- species. The O^--like species orignated from surface lattice oxygen may be in some covalence with cerium cations instead of a free ionic species like adsorbed O^- since the e.s.r. signals of O^--like species have not been obviously observed. However, two e.s.r. signals at 1.964 and 1.946 due to quasi free electron [5–7] always appeared for the well outgassed CeO_2. The appearence of the g tensors of quasi free electron is in accordance with the formation of surface O^--like species as proposed.

4. Conclusions

The active oxygen for the mild oxidation of ethylene on CeO_2 are mainly the surface lattice oxygen species which can be activated by outgassing at high temperatures. The activated surface lattice oxygen are assumed to be O^--like species. Adsorbed O_2^- species on CeO_2 was proved to be inert to ethylene at mild temperatures. While adsorbed O_2^{2-} and O^- species can initiate the mild oxidation of ethylene and produce the same surface species as those formed from the surface active lattice oxygen species.

Acknowledgements

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