

In Situ* Confocal Microprobe Raman Spectroscopy Study of the Oxygen Species over Cerium Oxide

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Abstract: *In situ* confocal microprobe Raman spectroscopy results showed that O_2^{2-} , O_2^- and $O_2^{\delta-}$ ($0 < \delta < 1$) adspecies formed on the O_2 pretreated cerium oxide sample when the temperature was below 423 K. At 1023 K, only $CeO_2 F_{2g}$ peak (at 449 cm^{-1}) and O_2^- species (at 1159 cm^{-1}) were observed on the surface. The reactivity of methane with the oxygen species was lower than that of ethane with the oxygen species.

Cerium oxide, as a nonstoichiometric rare earth oxide, has been extensively used as catalysts or promoters in heterogeneous catalysis [1]. A study of surface oxygen species at high temperature is desirable for understanding the oxidation mechanism. In this paper, we will report the adsorption of oxygen and the reactions of oxygen species with methane and ethane on cerium oxide at the temperature range of 298-1023 K by means of *in situ* confocal microprobe Raman spectroscopy.

Raman spectra were recorded using a confocal microprobe Raman system (LabRam I, Dilor, France) equipped with CCD cameras having essentially photon-noise-limited signal detection, confocal microscope and holographic notch filter. Since the elastically scattered laser radiation can be filtered out by a simple single spectrograph together with a holographic notch filter, the throughput efficiency has been significantly improved as compared with the traditional Raman systems with double or triple monochromators. The exciting wavelength was 514.5 nm from an Ar^+ laser with a power of 20 mW and a spot of ca. 3 μm on the surface. The spectra were obtained *in situ* with the collection time of 1 s for one scan and the accumulation times of 10 scans.

The sample was treated successively with He and O_2 at 1023 K, and then cooled down to room temperature. A strong Raman peak at 456 cm^{-1} and five peaks at 952, 1176, 1329, 1428, and 1468 cm^{-1} were detected on the surface of CeO_2 sample (Fig. 1). The former three bands might be attributed to the $CeO_2 F_{2g}$, O_2^{2-} and O_2^- species, respectively [2, 3], and the other bands above 1300 cm^{-1} could be assigned to $O_2^{\delta-}$ ($0 < \delta < 1$) adspecies [4]. This result suggested that the adsorption equilibria of $O_2(g) = O_2(a) = O_2^{\delta-}(a) = O_2^-(a) = O_2^{2-}(a)$ might exist on the surface of O_2 -pretreated cerium oxide. As the sample was warmed to 423 K in a flow of He, the intensities of the above dioxygen adspecies peaks were all found to decrease more or less but remain existing on the cerium oxide surface. The O_2^{2-} and

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$O_2^{\delta-}$ ($0 < \delta < 1$) adspecies peaks were found to disappear at 573 °K. During the temperature elevation, the $CeO_2 F_{2g}$ and O_2^- peaks were found to broaden and shift to lower wavenumbers. The frequency shift with respect to temperature is a well known phenomenon in Raman spectroscopy of solids and it is related to the thermal expansion of lattice parameters. At 1023 °K, the O_2^- adspecies (at 1159 cm^{-1}) and $CeO_2 F_{2g}$ (at 449 cm^{-1}) peaks were found to remain existing on the surface of cerium oxide.

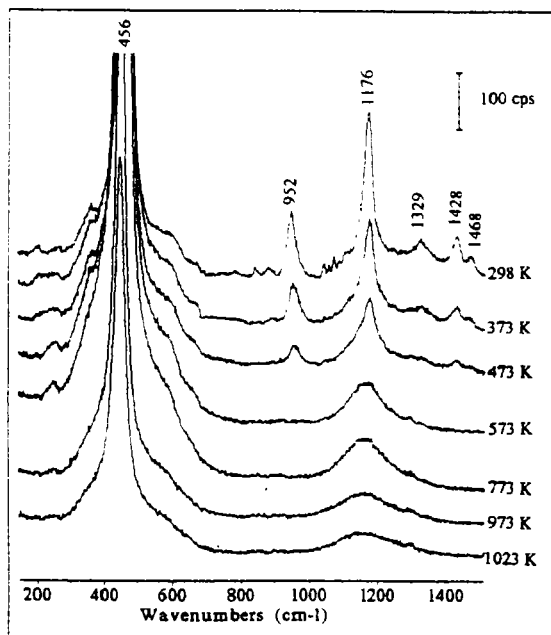


Fig. 1 Microprobe Raman spectra of O_2 -pretreated CeO_2 sample at the indicated temperature under He atmosphere.

indicating that the interaction between gaseous ethane and these dioxygen adspecies began to take place. At 473 °K, almost no Raman bands attributed to dioxygen adspecies were detected. The reaction between lattice oxygen and ethane also happened below 373 °K, and the peak at 449 cm^{-1} was found to vanish at 1023 °K. These results indicated that the reactivity of methane with oxygen species was lower than that of ethane with oxygen species on cerium oxide, which might be related to the fact that the bond energy of C-H in CH_4 molecule (104 kcal/mol) is higher than that in C_2H_6 molecule (98 kcal/mol).

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When the O_2 -pretreated CeO_2 sample was warmed successively in a flow of CH_4 , the reactions of CH_4 with lattice oxygen and O_2^- species were found to take place at 1023 °K, leading to the decrease of the intensities of $CeO_2 F_{2g}$ and O_2^- adspecies peaks. After the sample was heated at 1023 °K in a flow of CH_4 for about 60 min, only a very weak $CeO_2 F_{2g}$ peak (at 449 cm^{-1}) was observed on the cerium oxide surface. When the cerium oxide was exposed to O_2 atmosphere at 1023 °K for 5 min and cooled down to room temperature, the Raman peaks attributed to $CeO_2 F_{2g}$ and dioxygen adspecies were found to appear again. After the O_2 -pretreated sample was switched to C_2H_6 atmosphere and heated to 373 °K successively, the Raman peaks of dioxygen adspecies including O_2^{2-} , O_2^- and $O_2^{\delta-}$ were found to decrease in intensity conspicuously,