

# The Active Oxygen Species for Oxidative Coupling of Methane over CeO<sub>2</sub>/BaF<sub>2</sub> Catalyst by *in Situ* Confocal Microprobe Raman Spectroscopy\*

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(Received July 3, 1996)

**Keywords** Oxygen species, Oxidative coupling, Methane, *In situ* Raman spectroscopy

## Introduction

In the past decade, significant advances have been made in oxidative coupling of methane (OCM)<sup>[1]</sup>. Much attention has been focused on the nature of the active and C<sub>2</sub> selective oxygen species, the knowledge of which may be served as an important guide in searching for a better OCM catalyst. Mono- and diatomic anionic species, *e.g.* O<sup>-</sup>, O<sub>2</sub><sup>-</sup>, O<sub>2</sub><sup>2-</sup> as well as lattice oxygen O<sup>2-</sup> at low coordination sites, have been proposed as the OCM active oxygen species based on both *ex situ* and *in situ* experimental results<sup>[1]</sup>. While the nature of the active oxygen species responsible for the activation of methane has not been clarified, recently, Zhou *et al.*<sup>[2]</sup> have reported that the addition of BaF<sub>2</sub> significantly improved C<sub>2</sub> selectivity and yield over CeO<sub>2</sub> catalyst for OCM. In this paper, we will report the adsorption of oxygen on the surface of CeO<sub>2</sub>/BaF<sub>2</sub>(1/4) catalyst and the interactions between oxygen species and methane at high temperatures by means of *in situ* confocal microprobe Raman spectroscopy.

## Experimental

CeO<sub>2</sub>/BaF<sub>2</sub>(1/4) catalyst was prepared by the method of grinding and calcining as described elsewhere<sup>[2]</sup>, and then was pressed to a slice and laid in a self-designed quartz microprobe Raman sample cell<sup>[3]</sup> which could be heated from room temperature to 1023 K. Raman spectra were obtained using a confocal microprobe Raman system (LabRam from Dilor, France) equipped with a charge couple detector (CCD), a confocal microscope and a holographic notch filter. The microscope attachment was based on an Olympus BX40 system and a 50X

\* Supported by the National Natural Science Foundation of China.

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long working-length objective (8 mm) was used. The exciting wavelength was 514.5 nm from an Ar<sup>+</sup> laser with a power of 20 mW and a spot of *ca.* 3 μm on the surface. Ten scans were accumulated (each scan required 1 s) for a spectrum.

In the experiment, the gas flow rate was 20 mL/min unless otherwise stated. He (99.995%) was purified by passing it through the columns of 5A molecular sieve and 401 deoxidizer. CH<sub>4</sub> (99.99%), O<sub>2</sub> (99.5%) and H<sub>2</sub> (98.5%) were purified with 5A molecular sieve column.

## Results and Discussion

After CeO<sub>2</sub>/BaF<sub>2</sub>(1/4) catalyst was pretreated in a flow of H<sub>2</sub> for about 30 min at 1023 K, only a very weak Raman band at 451 cm<sup>-1</sup> was found on the catalyst surface in the region of 150—1550 cm<sup>-1</sup> (not shown). When the sample was purged with He and adsorbed O<sub>2</sub> at 1023 K, and then cooled down to room temperature, a very strong Raman peak at 465 cm<sup>-1</sup> and twelve relatively weaker peaks at 243, 883, 948, 1040, 1059, 1073, 1089, 1172, 1329, 1431, 1474 and 1550 cm<sup>-1</sup> were observed, respectively (Fig. 1). The band centering at 465 and 451 cm<sup>-1</sup> may result from the *F*<sub>2g</sub> Raman active mode characteristic of fluorite structure CeO<sub>2</sub>, and the weak band at 243 cm<sup>-1</sup> coincides with the location of the normally Raman inactive (but infrared active) zone-center transverse optical (TO) mode<sup>[4]</sup>. The peaks at 883 and 948 cm<sup>-1</sup> can be attributed to peroxide adspecies (O<sub>2</sub><sup>2-</sup>) at two different micro-chemical environments<sup>[5]</sup>; while the bands between 1040 cm<sup>-1</sup> and 1172 cm<sup>-1</sup> may be assigned to the surface superoxide ions (O<sub>2</sub><sup>-</sup>) adsorbed at different sites<sup>[5,6]</sup>; the other bands above 1300 cm<sup>-1</sup> could be assigned to O<sub>2</sub><sup>δ-</sup> (0 < δ < 1, at 1329, 1431 and 1474 cm<sup>-1</sup>) and molecular O<sub>2</sub> (at 1550 cm<sup>-1</sup>) adspecies<sup>[7,8]</sup>. The Raman band attributed to BaF<sub>2</sub> lattice vibration (at 287 cm<sup>-1</sup>, resulted in our experiment) was not observed because of its weak intensity. As O<sub>2</sub>-pretreated CeO<sub>2</sub>/BaF<sub>2</sub>(1/4) sample was warmed in a flow of He, the intensities of the above peaks were found to decrease, indicating that a lot of dioxygen adspecies and some of the lattice oxygen

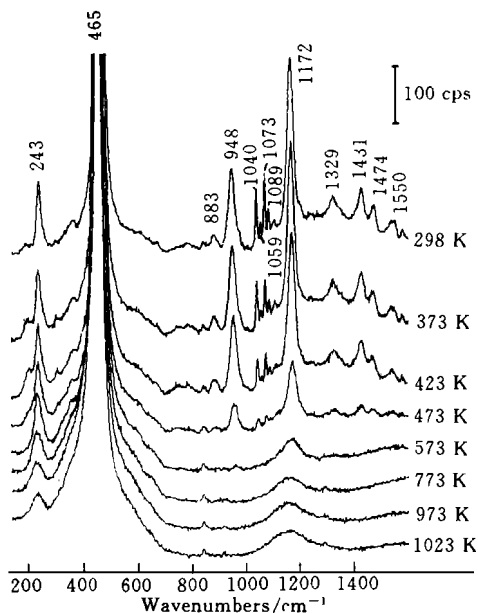


Fig. 1 Microprobe Raman spectra of O<sub>2</sub>-pretreated CeO<sub>2</sub>/BaF<sub>2</sub>(1/4) catalyst at the indicated temperature under He atmosphere.

desorbed from the catalyst surface. At 1023 K, the  $O_2^-$  adspecies (at  $1165\text{ cm}^{-1}$ ),  $CeO_2\text{ TO}$  (at  $238\text{ cm}^{-1}$ ) and  $F_{2g}$  (at  $451\text{ cm}^{-1}$ ) peaks were found to remain existing on the catalyst (Fig. 1). During the temperature elevation, the above three 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<sup>[1]</sup>.

At 1023 K, when the  $O_2$ -pretreated  $CeO_2/BaF_2(1/4)$  sample was exposed to  $CH_4$  atmosphere, the intensities of  $O_2^-$ ,  $CeO_2\text{ TO}$  and  $F_{2g}$  peaks were found to decrease, indicating that the reactions of partial lattice oxygen ( $O^{2-}$ ) and  $O_2^-$  species with  $CH_4$  took place. The consumption of partial lattice oxygen will lead to the change of partial  $CeO_2$  lattice structure and thus to the decrease in the intensities of  $CeO_2\text{ }F_{2g}$  and  $TO$  peaks. After the sample was heated for 40 min at 1023 K in a flow of  $CH_4$ , only a very weak Raman band at  $451\text{ cm}^{-1}$  was found on the catalyst surface. After switching  $CH_4/O_2(3.4/1)$  mixture (in a flow rate of  $50\text{ mL/min}$ ) to the catalyst, the Raman bands due to  $O_2^-$  adspecies (at  $1153\text{ cm}^{-1}$ ),  $CeO_2\text{ TO}$  (at  $233\text{ cm}^{-1}$ ) and  $F_{2g}$  (at  $449\text{ cm}^{-1}$ ) peaks appeared again. During the course of the reaction, no bands due to the surface carbonate species were detected, indicating that the surface basicity of the catalyst was weak.

Based on the above results, it can be reasonably concluded that gaseous oxygen was activated on the surface of  $CeO_2/BaF_2(1/4)$  OCM catalyst which had been pretreated with  $H_2$  and  $He$  at high temperatures, and  $O_2^{2-}$ ,  $O_2^-$ ,  $O_2^{\delta-}$  ( $0 < \delta < 1$ ) and adsorbed  $O_2$  species were formed at room temperature. As the temperature was raised, some of the oxygen adspecies desorbed from the sample surface. At 1023 K,  $O_2^-$ ,  $CeO_2\text{ TO}$  and  $F_{2g}$  peaks were detected on the cerium oxide surface in a flow of  $He$ . In the absence of gaseous oxygen,  $O_2^-$  and partial lattice  $O^{2-}$  species could react with  $CH_4$  at 1023 K. These oxygen species were also detected on the working  $CeO_2/BaF_2(1/4)$  catalyst. These results suggest that the lattice  $O^{2-}$  and  $O_2^-$  species may be the active oxygen species over the catalyst for OCM. However, which oxygen species is responsible for the more selective conversion of  $CH_4$  to  $C_2$  hydrocarbons needs to be identified by further experiments.

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