

# *In situ* Confocal Microprobe Raman Spectroscopic Studies on Defective La-based Complex Oxides \*

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The adsorption of  $O_2$  over defective  $La_2O_3$ -based OCM catalysts with anionic vacancies, and the reaction of surface oxygen species with  $CH_4$  were studied by means of *in situ* confocal microprobe Raman spectra. The partially reduced oxygen species  $O_2^-$ ,  $O_2^{2-}$ ,  $O_2^{\delta-}$  ( $0 < \delta < 1$ ) and even the lattice oxygen ion  $O^{2-}$  can be detected on the surface of  $O_2$ -pretreated  $La_2O_3$ -based catalysts. At lower temperatures ( $< 573$  K) it is peroxide species  $O_2^{2-}$  or  $O^-$  that is more essential for the coupling of methane, while at higher temperatures the superoxide  $O_2^-$  and lattice oxygen species  $O^{2-}$  are rather important. It is easier for fluoride-containing  $La_2O_3$ -based catalysts to induce the oxygen species with fewer negative charges and the basicity of the catalyst surface is weakened, so that the  $C_2$  selectivity for OCM reaction is improved. **Keywords** Methane oxidative coupling, Oxygen adspecies, Defective  $La_2O_3$ -based catalyst, *In situ* confocal microprobe Raman spectra

## Introduction

The oxidative coupling of methane (OCM) to ethene and ethane has been attracting worldwide attention in recent years. Since the pioneering work of Keller & Bhasin<sup>[1]</sup>, various types of catalysts have been studied, the great majority of which are mixed metal-oxides, or complex metal-oxides<sup>[2-4]</sup>. The heterogeneous-homogeneous OCM reactions over any of these catalysts are generally believed to be performed *via* H-abstraction from  $CH_4$  by certain active oxygen-species to form methyl radicals as the rate-limiting step; followed by the subsequent coupling of them and further reactions in the gaseous phase, or on the catalyst surface, then leading to the formation of  $C_{2+}$  hydrocarbons and  $H_2O$ , along with side-products  $CO_x$  ( $CO_2$  and  $CO$ ). Much attention has been focused on the nature of the active and  $C_2$ -selective oxygen-species, the knowledge of which may serve as an important guide to develop better OCM catalysts.

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For the catalysts with stable cationic valences, certain oxygen-adspecies, partially reduced surface oxygen species, *e. g.*,  $O^-$ ,  $O_2^{2-}$ ,  $O_2^-$  and even  $O_3^-$ , have been supposed as the active oxygen species for OCM reactions. The alkali-doped AEO (alkaline-earth-oxide) catalysts, especially the  $Li^+/MgO$  catalysts, have been extensively studied by Lunsford and coworker<sup>[3,5]</sup>, and based upon the results of matrix isolation and EPR characterization,  $O^-$  or  $Li^+O^-$  has been supposed as the active oxygen-species for OCM reactions. For the REO-based (rare-earth-oxide) OCM catalysts, diatomic-species,  $O_2^{2-}$  or/and  $O_2^-$ , were suggested as the active oxygen-species based on kinetics arguments<sup>[6]</sup>. The remarkably high activity and thermal stability together with fairly good OCM selectivity of the REO-AEO based catalysts, especially those with defective fluorite structure (DFS)<sup>[7-9]</sup> or layer-type structure, make this type of OCM catalysts particular interest for further development. The presence of  $O_2^-$  in REO-based catalysts at lower temperature has been shown by EPR<sup>[10]</sup>. Recently, Raman bands at  $863\text{ cm}^{-1}$  (and  $813\text{ cm}^{-1}$ ),  $853\text{ cm}^{-1}$  and  $863\text{ cm}^{-1}$  ascribed to active  $O_2^{2-}$  species from *in situ* Raman spectra of  $La_2O_3$ ,  $Na^+/La_2O_3$ , and  $Sr^{2+}/La_2O_3$  catalysts, respectively, have been reported by Mestl *et al.*<sup>[11]</sup>, and that at  $1140\text{ cm}^{-1}$  ascribed to  $O_2^-$  species on  $ThO_2-La_2O_3$  catalyst under OCM reaction conditions has been reported by Liu *et al.*<sup>[12]</sup>. On the other hand, based mainly on the results of the XPS studies of lanthania-based OCM catalysts and an apparent correlation between the  $C_2$ -selectivity-promoter efficiencies of AEO and the thermal stabilities of the corresponding carbonates, Cameron *et al.*<sup>[13]</sup> have postulated that  $O^-$  or  $O_2^{2-}$  might be the dominant active-oxygen species for OCM, while  $O_2^-$  might lead to the deep oxidation of  $CH_4$ .

Another effective REO-based OCM catalyst  $LaO_{1.5}-SrF_2$  has been reported by Wan and his coworkers<sup>[14]</sup>. With the anionic/cationic exchange between the oxides and fluorides lattices, it is possible to form a catalyst containing oxygen vacancies and  $F^-$ , which can be more conducive to the formation of some oxygen species with fewer negative charges.

There is no doubt that  $O_2^{2-}$  and  $O^-$  are active oxygen species at OCM reaction temperature<sup>[6,11,15]</sup>, but their contributions to  $C_2$ -selectivity are still unknown, so is the contribution of the precursor  $O_2^-$  species to OCM activity and  $C_2$ -selectivity. To resolve the controversies about the nature of the active and  $C_2$ -selective oxygen-species and about the effect of surface carbonates on the  $C_2$ -selectivity of these two types of REO-based catalysts, it is highly desirable in the present work to obtain more information from the *in situ* spectroscopic characterization of oxygen-adspecies and surface carbonates on CaO doped  $LaO_{1.5}-BaCO_3$  and  $LaO_{1.5}/SrF_2(1/4)$  catalysts under OCM reaction conditions, as well as under other chemical treatments.

# Experimental

## 1 The Preparation of the Catalysts

$\text{LaO}_{1.5}\text{-(Ba}_{0.5}\text{Ca}_{0.5})\text{(O, CO}_3\text{)}$  catalyst was prepared by coprecipitation with ammonium carbonate as precipitant, followed by being washed, dried and calcined in air (800 °C, 5 h), crushed and sieved.  $\text{LaO}_{1.5}/\text{SrF}_2(1/4)$  catalyst was synthesized by mixing  $\text{LaO}_{1.5}$  and  $\text{SrF}_2$  and being carefully ground. The mixture was then stirred with a certain amount of deionized water to a paste, which was dried at 120 °C for 4 h and calcined at 900 °C for 6 h, the resultant solid was then crushed and sieved. XRD powder patterns of the samples were taken by means of a Rigaku Rotflex D/Max C X-ray diffractometer. The BET surface areas of these samples were in the range of 2.5 to 3.5  $\text{m}^2/\text{g}$ .

## 2 Raman Spectroscopic Study

The Raman spectra of the samples ignited in air were taken at room temperature. In each case, the sample (0.20 mL, 40–60 mesh) was mounted between quartz chips of about the same mesh in a specially designed quartz-tubular Raman sample-cell in the form of a quartz-tubular microreactor (4 mm i. d.) capable of *in situ* treating the sample as described in Fig. 1<sup>[16]</sup>.

The Raman scattering back-ground (a very weak and broad band around 805–810  $\text{cm}^{-1}$ ) of quartz was determined by a blank test with the sample-cell filled only with quartz chips, and was automatically deduced from the Raman spectra of the samples. The sample was warmed in air to 1023 K, purged with He and treated with  $\text{O}_2$  at this temperature for 10 min. It was cooled down to room temperature, then the sample was heated gradually under He or  $\text{CH}_4$  atmosphere respectively from 298 to 1023 K at a rate of 30 K/min.

At each specified temperature point, the Raman spectrum was obtained using a confocal microprobe Raman system (LabRam I from Dilor, France) equipped with CCD cameras having essentially photon noise-notch filter<sup>[17]</sup>. The elastically scattered laser radiation could be filtered out by a holographic notch filter, the throughput efficiency was significantly improved as compared with that of traditional Raman systems with double or triple monochromators enabling to detect a relatively weaker surface signal, *e. g.*, oxygen ad-species at higher temperatures. The microscope attachment was based on an Olympus BX40 system and

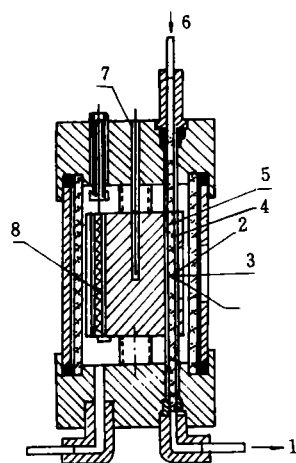


Fig. 1 The diagram of the oscillating-tubular Raman cell and microreactor.

1. outlet;
2. scattering light;
3. laser beam;
4. quartz tube;
5. furnace;
6. inlet;
7. thermocouple;
8. heater.

it used a 50x long working-length objective (8 mm). An air cooled  $1024 \times 256$  pixels CCD(Wright, UK) operating in the MPP mode at 213 K was used as a detector. The exciting wavelength of 488.0 nm Ar-ion laser line with a power of 20 mW and a spot of *ca.* 3  $\mu\text{m}$  on the surface was used to avoid any luminescence of samples. Ten scans were accumulated(each scan required 1 s) per spectrum.

Unless otherwise stated, the gas flow rate was 30 mL/min. He(99.995%) was purified by passing it through 5 A molecular sieve and 401 deoxidiser.  $\text{O}_2$  (99.5%) was purified with 5 A molecular sieve. The purified  $\text{CH}_4$  was better than 99.5%.

## Results

After the Ca-containing  $\text{LaBa}_{0.5}\text{Ca}_{0.5}(\text{O},\text{CO}_3)$  catalyst sample was pretreated with  $\text{O}_2$  at 1023 K, the Raman bands at  $1052\text{ cm}^{-1}$  and  $690\text{ cm}^{-1}$ (m) due to surface carbonate were found, which were attributed to  $\nu_2(\text{A}_1)$  and  $\nu_3(\text{A}_1 \delta_{\text{OCO}})$  of monodentate of  $\text{BaCO}_3$  phase<sup>[18]</sup>, besides these a strong band centered at  $418\text{ cm}^{-1}$  for the La—O lattice vibration of  $\text{La}_2\text{O}_3$  molecule was also observed<sup>[19]</sup>, and it caused even the complete removal of  $1082\text{ cm}^{-1}$  and  $740\text{ cm}^{-1}$  bands corresponding to surface carbonate with lanthania phase(not shown) under the same treatment.

When the sample was cooled down to ambient temperature, then exposed to  $\text{CH}_4$  stream and warmed up gradually, the *in situ* Raman spectra were recorded (Fig. 2). It showed at 773 K predominantly the bands at  $1052\text{ cm}^{-1}$  and  $690\text{ cm}^{-1}$  for  $\text{BaCO}_3$  with the concomitant appearance of two shoulders at  $1076$ (m)  $\text{cm}^{-1}$  and  $715\text{ cm}^{-1}$ (w), showing the formation of mixed carbonate (Ca, Ba) $\text{CO}_3$ . There was also a peak around  $1135\text{ cm}^{-1}$  which can be assigned to the stretching vibration frequency of superoxide species  $\text{O}_2^-$  on the  $\text{LaBa}_{0.5}\text{Ca}_{0.5}(\text{O},\text{CO}_3)$  surface<sup>[12]</sup>. A weak band around  $810\text{ cm}^{-1}$  due to  $\text{O}_2^-$  species and a peak around 940

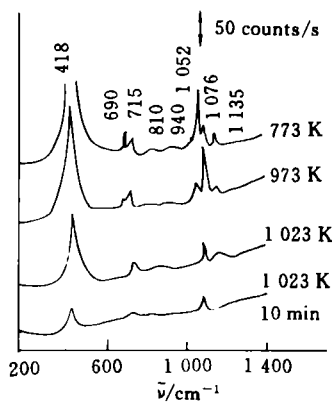


Fig. 2 Microprobe Raman spectra of  $\text{O}_2^-$  pretreated  $\text{LaBa}_{0.5}\text{Ca}_{0.5}(\text{O},\text{CO}_3)$  catalyst in  $\text{CH}_4$  atmosphere.

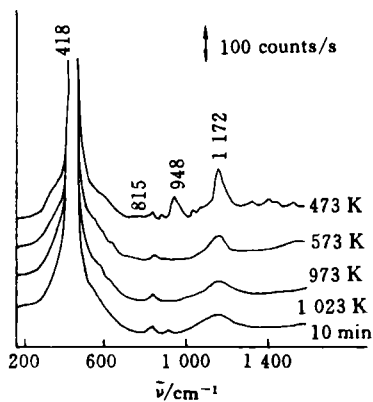


Fig. 3 Microprobe Raman spectra of  $\text{O}_2^-$  pretreated  $\text{LaO}_{1.5}/\text{SrF}_2(1/4)$  catalyst in He atmosphere.

$\text{cm}^{-1}$  were also detected. At 973 K the band centered at  $1076 \text{ cm}^{-1}$  associated with  $(\text{Ca},\text{Ba})\text{CO}_3$  mixed carbonate phase increased in intensity, while the peaks at  $1052 \text{ cm}^{-1}$  and  $690 \text{ cm}^{-1}$  decreased in intensity, indicating the steady formation of  $(\text{Ca},\text{Ba})\text{CO}_3$  solid solution. Peroxide species  $\text{O}_2^{2-}$  (*ca.*  $810 \text{ cm}^{-1}$ ) was found to vanish at 973 K, superoxide  $\text{O}_2^-$  ( $1135 \text{ cm}^{-1}$ ) decreased, then disappeared at 1023 K for 10 min, and the  $418 \text{ cm}^{-1}$  La—O lattice vibration band significantly decreased after the same treatment.

When the  $\text{LaO}_{1.5}\text{-SrF}_2$  (1/4) catalyst was heated up to 1023 K in the flow of  $\text{O}_2$ , then cooled down to room temperature, purged with He and heated up again to 1023 K, the Raman spectra of which are shown in Fig. 3. At 473 K, the  $1172 \text{ cm}^{-1}$  ( $\text{O}_2^-$ ),  $815 \text{ cm}^{-1}$  ( $\text{O}_2^{2-}$ ) and  $948 \text{ cm}^{-1}$  bands of diatomic species were observed, as well as the La—O lattice stretching vibration band around  $418 \text{ cm}^{-1}$ , the  $E_g$  Raman active mode of  $\text{La}_2\text{O}_3$ .

These bands decreased in intensity but did not disappear until 1023 K except for the  $948 \text{ cm}^{-1}$  peak, which had been vanished at 573 K. After the  $\text{O}_2$ -pretreated  $\text{LaO}_{1.5}\text{-SrF}_2$

catalyst was heated in the flow of  $\text{CH}_4$ , the peroxide species ( $815 \text{ cm}^{-1}$ ) and superoxide species ( $1165 \text{ cm}^{-1}$ ) were all disappeared at 973 K, but the La—O vibration peak ( $415 \text{ cm}^{-1}$ ) still remained, even at 1023 K for 10 min (Fig. 4). There was another intriguing observation during the course of the reaction, the bands due to surface carbonate species ( $1050\text{--}1100 \text{ cm}^{-1}$ ) were not detected which would be formed by the interaction between the catalyst and  $\text{CO}_2$  (the by-product of the OCM reaction), indicating that the surface basicity of the  $\text{LaO}_{1.5}\text{-SrF}_2$  catalyst was weak.

## Discussion

It is known that  $\text{BaCO}_3$  and  $\text{CaCO}_3$  are miscible to form a solid solution in a wide range of composition,  $(\text{Ba},\text{Ca})\text{CO}_3$  is expected to give off  $\text{CO}_2$  at considerably lower temperatures than pure  $\text{BaCO}_3$ , but still higher than the decomposition temperature of  $\text{Ca}^{2+}$ -doped  $(\text{LaO})_2\text{CO}_3$  phase. Thus the ignition of  $\text{LaBa}_{0.5}\text{Ca}_{0.5}\text{-(O,CO}_3\text{)}$  sample in  $\text{O}_2$  would produce  $\text{BaCO}_3$  phase together with  $(\text{Ba},\text{Ca})\text{CO}_3$  mixed carbonate phase. By heating the  $\text{O}_2$ -pretreated  $\text{LaBa}_{0.5}\text{Ca}_{0.5}\text{-(O,CO}_3\text{)}$  sample in  $\text{CH}_4$  atmosphere at an elevated temperature, most of the  $\text{CaO}$  will be carbonated and dissolved in the  $\text{BaCO}_3$  phase to form a  $(\text{Ba},\text{Ca})\text{CO}_3$  solid solution. As a result, at 973 K the  $1052 \text{ cm}^{-1}$  and  $690 \text{ cm}^{-1}$  bands due to  $\text{BaCO}_3$

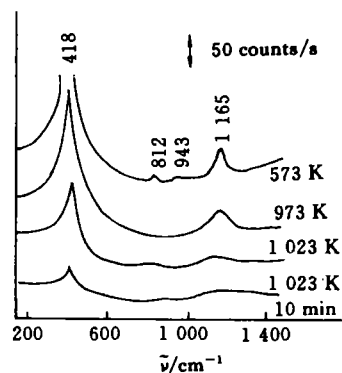


Fig. 4 Microprobe Raman spectra of  $\text{O}_2$ -pretreated  $\text{LaO}_{1.5}/\text{SrF}_2$  (1/4) catalyst in  $\text{CH}_4$  atmosphere.

phase would be almost vanished, while the mixed carbonate  $(\text{Ba}, \text{Ca})\text{CO}_3$  increased the intensity of the bands at  $1076\text{ cm}^{-1}$  and  $715\text{ cm}^{-1}$ , but they were eventually decomposed at higher temperatures. The  $\text{Ca}^{2+}$  can also destabilize the surface carbonate associated with  $(\text{LaO})_2\text{CO}_3$  as shown by the absence Raman peaks at  $1082\text{ cm}^{-1}$  and  $740\text{ cm}^{-1}$  for  $\text{LaBa}_{0.5}\text{Ca}_{0.5}(\text{O}, \text{CO}_3)$  sample. From the relative magnitudes of the cations radii ( $0.099\text{ nm}$  for  $\text{Ca}^{2+}$ ,  $0.106\text{ nm}$  for  $\text{La}^{3+}$  and  $0.134\text{ nm}$  for  $\text{Ba}^{2+}$ ), the  $\text{La}_2\text{O}_3$  phase of  $\text{LaBa}_{0.5}\text{Ca}_{0.5}(\text{O}, \text{CO}_3)$  sample will take up much more  $\text{Ca}^{2+}$  than  $\text{Ba}^{2+}$  as dopant cations, and thus to produce more anionic vacancies for  $\text{O}_2$  adsorption, this explains the increase in  $\text{CH}_4$  conversion activity for the catalyst, indicating that the Ca-containing La—Ba—O catalyst would have a considerably lower "light-off temperature". It can be obviously observed also from Fig. 2 that  $\text{O}_2^-$  ( $1135\text{ cm}^{-1}$ ) and  $\text{O}_2^{2-}$  ( $418\text{ cm}^{-1}$ ) had more OCM activity when the reaction temperature was above  $973\text{ K}$ , under which peroxide species ( $810\text{ cm}^{-1}$ ) was the principle active oxygen species for OCM reaction.

Molecular oxygen is activated at the anionic vacancies by gaining partial negative charges from the solid surface to form  $\text{O}_2^-$ ,  $\text{O}_2^{2-}$ ,  $\text{O}^-$  species *etc.*. Over pure  $\text{La}_2\text{O}_3$ , EPR measurement showed that the  $\text{O}_2^-$  superoxide species was detected after oxygen adsorption<sup>[20]</sup>. The  $\text{O}_2^-$  ( $1122\text{ cm}^{-1}$ ) species was also reported on  $\text{LaO}_{1.5}/\text{SrF}_2$  by *in situ* IR spectra under the OCM reaction condition<sup>[14]</sup>. In this work, over the  $\text{LaO}_{1.5}/\text{SrF}_2$  sample, anionic vacancies may be inducted by exchange between ions in the process of catalyst preparation (XRD results)<sup>[14]</sup>. Oxygen species, such as  $\text{O}_2^-$ ,  $\text{O}_2^{2-}$ ,  $\text{O}^-$  would form as gaseous oxygen which are adsorbed on the catalyst. This was supported by the aforementioned microprobe Raman spectra. Owing to the stronger electronegativity of F than O, oxygen species with fewer negative charges leading to higher amounts of  $\text{O}_2^-$  ( $1122\text{ cm}^{-1}$ ) species than those of  $\text{O}_2^{2-}$  species ( $815$  or  $948\text{ cm}^{-1}$ ) can be formed as shown in Fig. 3. When the sample was warmed to  $1023\text{ K}$  in the flow of He, the intensities of the diatomic adspecies peaks were all found to decrease more or less, but the species remained present on the  $\text{LaO}_{1.5}/\text{SrF}_2$  surface. It indicated that some of the diatomic adspecies had desorbed from the surface of the catalyst.

When  $\text{O}_2$ -pretreated  $\text{LaO}_{1.5}/\text{SrF}_2$  was warmed from  $298$  to  $1023\text{ K}$  in a flow of methane,  $\text{CH}_4$  was found to react only with peroxide species  $\text{O}_2^{2-}$  ( $815\text{ cm}^{-1}$ ) at a rather lower temperature (about  $573\text{ K}$ ), and as the temperature was increased to  $1023\text{ K}$ , the reaction between  $\text{CH}_4$  and superoxide species took place, leading to a decrease in the intensity of the band at  $1165\text{ cm}^{-1}$  (Fig. 4). At the same time, lattice oxygen  $\text{O}^{2-}$  also partially reacted with  $\text{CH}_4$ , thus decreased the intensity of  $\text{La}_2\text{O}_3 E_g$  peak.

The failure to detect any carbonate bands in  $1050\text{--}1100\text{ cm}^{-1}$  wavenumber range (Fig. 4) implied that the presence of surface fluoride ions decreased the basicity of the catalyst. This may be beneficial for preventing the poisoning of the

catalyst by CO<sub>2</sub> and increasing the C<sub>2</sub> selectivity in OCM reaction.

## Conclusion

Doped with lower valence cations in La<sub>2</sub>O<sub>3</sub>, *e. g.*, LaBa<sub>0.5</sub>Ca<sub>0.5</sub>(O,CO<sub>3</sub>), or with La<sub>2</sub>O<sub>3</sub> in alkaline earth fluoride, *e. g.*, LaO<sub>1.5</sub>/SrF<sub>2</sub>(1/4), some defective structural compounds with oxygen vacancies can be created, which adsorbed O<sub>2</sub> and activated it to partially reduce oxygen species O<sub>2</sub><sup>-</sup>, O<sub>2</sub><sup>2-</sup>, O<sup>-</sup> *etc.*. They are all active oxygen species for the oxidative coupling of methane(OCM) and can be obviously detected with confocal microprobe Raman spectra.

Considering that OCM usually took place beyond 973 K, only the superoxide species O<sub>2</sub><sup>-</sup> and lattice species O<sup>2-</sup> would be more important for the conversion of CH<sub>4</sub> in the OCM reaction, while at lower temperatures(around 573 K) it is peroxide species O<sub>2</sub><sup>2-</sup> or O<sup>-</sup> that plays the principle role for LaBa<sub>0.5</sub>Ca<sub>0.5</sub>(O,CO<sub>3</sub>) and La<sub>1.5</sub>/SrF<sub>2</sub> OCM catalyst systems.

Because of the stronger electronegativity of F than O, oxygen species with fewer negative charges O<sub>2</sub><sup>-</sup>, even O<sub>2</sub><sup>δ-</sup> (0<δ<1) would be formed, and the presence of surface fluoride ions decreases the basicity of LaO<sub>1.5</sub>/SrF<sub>2</sub> catalyst. These are the reasons to make the fluoride-containing catalysts more effective for the OCM reaction.

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