Catal Lett (2007) 118:238–243
DOI 10.1007/s10562-007-9176-8

Isotopic Oxygen Exchange and EPR Studies of Superoxide Species on the SrF_2/La_2O_3 Catalyst

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Received: 30 January 2007 / Accepted: 22 June 2007 / Published online: 17 July 2007

Abstract By using the in situ IR spectroscopy, the superoxide species (O_2^-), characterized by the O–O stretching peak at 1130 cm^{-1}, was detected on the SrF_2/La_2O_3 catalyst at temperatures up to 973 K. The introduction of $^{18}O_2$ isotope caused the 1130 cm^{-1} peak to shift to lower wavenumbers (1095 and 1064 cm^{-1}), consistent with the assignment of the spectra to the superoxide species. A good correlation between the rate of the disappearance of the O_2^- species and that of the formation of C_2H_4 was observed, suggesting that O_2^- was the active oxygen species responsible for the oxidative coupling of methane (OCM) on the SrF_2/La_2O_3 catalyst. This conclusion was reinforced by the EPR experiments ($g_{xx} = 2.0001$, $g_{yy} = 2.0045$, $g_{zz} = 2.0685$), showing that O_2^- was the only paramagnetic oxygen species detectable on the O_2-preadsorbed SrF_2/La_2O_3 catalyst. These results suggest that superoxide O_2^- can be a stable active oxygen species, whose role in the OCM reaction cannot be overlooked.

Keywords Isotopic oxygen exchange · In situ IR · EPR · Superoxide species · Methane oxidative coupling

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1 Introduction

As one of the important potential routes to convert an abundant hydrocarbon resource to more useful chemicals, the oxidative coupling of methane (OCM) to C_2 hydrocarbons has been intensively studied since the pioneer work of Keller and Bhasin [1] (For some reviews we refer to references [2–6]). The reaction mechanism has now been well established. The reaction is initiated by the hydrogen abstraction from CH_4 to liberate CH_3, using the active oxygen species on the surfaces of the metal oxide catalysts; followed by the coupling of the methyl radicals in the gas phase to give ethane as the primary product, which is then dehydrogenated to form ethylene. However, consensus has not yet reached on the nature of the active oxygen species.

Lunsford and co-workers established many of the generally accepted principles concerning the nature of the active sites [7, 8]. In their work on the OCM reaction over Li/MgO, surface O^- species have been concluded as the active species based on the EPR results [7, 8].

In the case of pure alkaline earth or rare earth oxides or their composite compounds, there are evidences pointing to the surface peroxide O_2^{2-} ions as the active species. Otsuka et al. found that Na_2O_2, SrO_2 and BaO_2 were capable of converting CH_4 into C_2H_6 at temperature below 673 K in the presence of O_2 [9]. Lunsford et al detected a major Raman peak at 842 cm^{-1}, which was ascribed to the O–O stretching mode in BaO_2 over the 0.5 mol% Ba/MgO catalyst [10]. X-ray photoelectron spectroscopy (XPS) on the same catalysts showed a good correlation between the near-surface concentration of the peroxide ions and the intrinsic catalytic activity [11].

No single active site appears to be generally applicable to all kinds of OCM catalysts. The formation and the role of the active oxygen species is complicated by the metal oxides used as the catalysts (i.e. valence-stable or valence-variable cations [6], n-type or p-type semiconductors [4], basicity and conductivity [5], etc) and/or by the choice of the oxidants (i.e. N_2O or O_2 [3], etc). Under many circumstances, the superoxide O_2^- species has also been observed [12–15]. In our view, however, the role of O_2^- has been downplayed or even unfortunately ignored [16, 17]. People are concerned at the thermo stability and the reactivity of the superoxide species. Cordischi et al found that O_2^- could only survive up to 373 K [18]; whereas Lunsford et al claimed that O_2^- was stable around 473 K [12]. Earlier studies of the reaction of light alkanes with O_2^- on MgO showed that this form of oxygen species was unreactive with CH_4 at the temperatures up to 473 K [12]. This claim was substantiated by the experiments of Otsuka et al [9], which showed that the O_2^- species was unable to react with CH_4 even at 673 K. Nevertheless, it is known that the reactivity of O_2^- increases with the temperature [12] and Osada et al. were able to show that the O_2^- species could be stable up to 1023 K to react with CH_4 over the Y_2O_3–CaO catalysts [19]. In fact, two independent groups in our key laboratory have observed the superoxide species by using in situ Raman and IR under the OCM reaction temperatures for the Th–La–O_x catalysts [20] and the fluoride-containing rare earth-based catalysts [21, 22], respectively.

Considering the probability of laser-induced formation of the peroxide species [23], we believe that IR spectroscopy is particularly suitable for the characterization of the surface oxygen species. The O–O stretching vibration mode is IR active, and the in situ technique is well-suited for observing samples at the elevated temperatures. Therefore, the present study was focused on the $^{18}O_2$ isotopic exchange experiment using in situ IR spectroscopy. We provided here the direct evidence of the stable existence of the O_2^- species at 973 K, and showed a good correlation between the rate of disappearance of the O_2^- species and that of formation of C_2H_4. The EPR experiment substantiated the sole existence of the O_2^- species, such that the issue concerning the role of the O_2^- species for the OCM reaction over the SrF_2/La_2O_3 catalyst is now ascertained [21, 22]. Our results implicate the role that the superoxide species might play in the OCM reaction, as well as other oxidative processes over the metal oxide catalysts.

2 Experimental

SrF_2 and La_2O_3 (SrF_2 to La_2O_3 ratio = 1:4) were physically mixed for about 90 min with a small amount of distilled water to form a paste. The paste was dried at 383 K in the oven and then was calcined in the muffle furnace under static air at 1073 K for 6 h. The XRD results indicated that there were cubic SrF_2 ($2\theta = 26.568°$, 30.807°, 44.122°), hexagonal La_2O_3 ($2\theta = 26.094°$, 29.111°, 29.947°, 39.489°, 46.035°, 52.132°, 53.659°, 55.397°, 55.896°, 60.329°, 62.261°, 67.307°) and a few percent of rhombohedral LaOF ($2\theta = 26.921°$) phases in the fresh SrF_2/La_2O_3 catalyst.

The in situ FTIR experiments were performed with a Nicolet Nexus FTIR spectrometer. Raman spectra were recorded using a Dilor LabRam I Raman spectrometer with He-Ne laser (632.8 nm line, 10 mW) as excitation source. The catalyst was pressed into a self-supporting disk and was then placed in a homemade quartz high temperature in situ IR cell with ZnS windows. The spectra were scanned in the range of 4000–700 cm^{-1} with a resolution of 4 cm^{-1}. 32 scans were accumulated for a spectrum. All IR spectra were recorded in situ at the indicated temperatures.

The EPR experiment was conducted in the quartz EPR sample tube. The catalyst was pretreated with oxygen at 1073 K for 30 min and was then quenched from 1073 K by transferring it into liquid N_2 at 77 K in the presence of O_2. When the temperature was cooled down to 77 K, the sample was purged by helium to remove the gas phase O_2, which could lead to dipolar magnetic broadening of the signal. The EPR spectrum was recorded at 10 K with a Bruker E500 spectrometer operating in the X-band. The microwave power and the modulate amplitude were 10 mW and 4 G, respectively.

3 Results and Discussion

3.1 In Situ IR and Raman Characterization

Before the introduction of adsorbates to the catalyst, the sample disk was treated in the IR cell under gas phase O_2 (99.995%, Linde) at 973 K for 60 min. This was to ensure that the carbonate impurities on the catalyst were removed. For the experiment of O_2 adsorption, the sample was treated with H_2 at 973 K and was then evacuated briefly before $^{16}O_2$ was added. After being treated with $^{16}O_2$, a peak at 1120 cm^{-1} was detected at 973 K. This peak was ascribed to $(^{16}O–^{16}O)^-$. As the temperature of the cell was decreased to 323 K in the presence of $^{16}O_2$, the position of the major peak shifted to 1130 cm^{-1} (see Fig. 1). The frequency shift with respect to temperature is a well-known phenomenon of solids relating to the lattice relaxation at high temperature. Similar effect was also observed in the in situ Raman spectroscopy of the peroxide ions on the Ba/MgO catalyst [10].

To confirm the identification of the IR spectra, $^{18}O_2$ isotopic exchange experiment was carried out. When $^{18}O_2$ (97 atom % ^{18}O, Aldrich Chemical Company, Inc.) was introduced to the cell at 973 K, it was difficult to assign exactly the positions of the band maxima since the line was

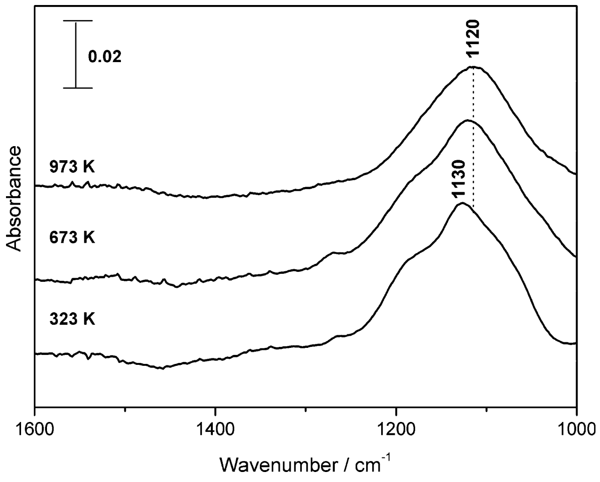

Fig. 1 In situ FTIR spectra for the O_2-preadsorbed SrF_2/La_2O_3 catalyst at the indicated temperatures

broadened. Thus the temperature of the cell was decreased to 323 K in the presence of $^{18}O_2$, and the difference spectrum was shown in Fig. 2. The result showed that peak at 1130 cm^{-1} was decreased, which was accompanied by a simultaneous increase for peaks at 1095 and 1064 cm^{-1} after $^{18}O_2$ was introduced to the cell. A simple calculation based on the diatomic harmonic oscillator model gave a band position at 1096 cm^{-1} for the $(^{18}O–^{16}O)^-$ superoxide ion, and that at 1062 cm^{-1} for $(^{18}O–^{18}O)^-$. Thus the experimental results were in quite reasonable agreement with the calculated values, when factors such as the anharmonicity, the width of the band, and the uncertainty in assigning the position of the band maximum, etc were taken into account [10]. These results unambiguously showed that the bands of $(^{18}O–^{16}O)^-$ and $(^{18}O–^{18}O)^-$ were detected, such that the peak at 1130 cm^{-1} can be attributed to the O_2^- species with confidence.

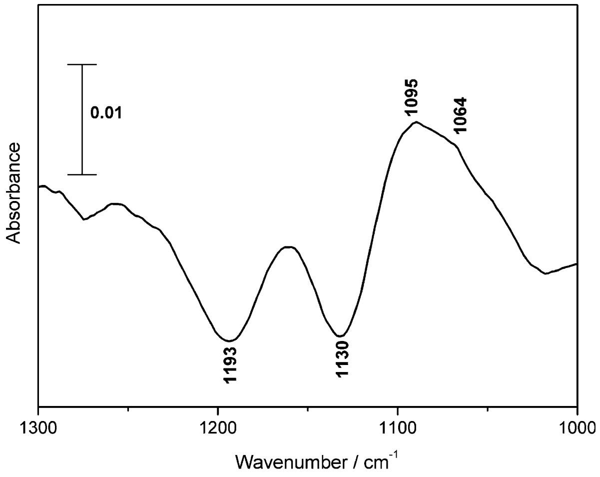

Fig. 2 In situ FTIR difference spectrum of O_2^- after $^{18}O_2$ isotopic exchange experiment over the SrF_2/La_2O_3 catalyst

As is seen from Fig. 2, there is a band at 1193 cm^{-1} that also decreases as a result of the isotopic exchange. We believe that this band could also be assigned to the superoxide species, which were located in a chemical environment different from that associated to 1130 cm^{-1} [24, 25]. With $^{18}O_2$ isotopic exchange, a simultaneous increase of the $(^{18}O–^{18}O)^-$ band should be observed. The theoretical value for the $^{18}O–^{18}O$ stretching mode is 1121 cm^{-1}. Such a band was, however, buried in the broad peak of 1130 cm^{-1}.

The formation of $(^{18}O–^{16}O)^-$ suggested that the isotopic exchange between ^{18}O and ^{16}O occurred. Figure 3 showed a Raman spectrum of the SrF_2/La_2O_3 catalyst recorded at 298 K after $^{16}O_2$ pretreatment and $^{18}O_2$ exchange at 973 K. A main peak at 407 cm^{-1} may be assigned to the La–^{16}O stretching mode of La_2O_3, which was shifted to 387 cm^{-1} upon isotopic exchange of $^{18}O_2$. (The theoretical value for the La–^{18}O stretching mode is 383 cm^{-1}.) These results demonstrated that the lattice oxygen was involved in the isotopic exchange of ^{18}O. There were review articles discussing the detailed mechanisms of isotopic exchange reaction, where O_2 dissociation or O_3 intermediate formation might happen [26]. We noticed that depending on the partial oxygen pressure and other kinetic parameters, the temperature for the isotopic exchange of ^{18}O between the gaseous phase and the La_2O_3 catalysts was within 483–723 K [26]. This is significantly lower than the typical OCM temperature (923—1153 K [3]). In the literature, it is well-documented that O^- and O_3^- are more reactive than O_2^- [7]. Hence we expect that O_2^- is more selective oxygen species in the OCM conditions.

From the IR experimental results shown in Fig. 2, it was clear that O_2^- was the only dioxygen adspecies detected at

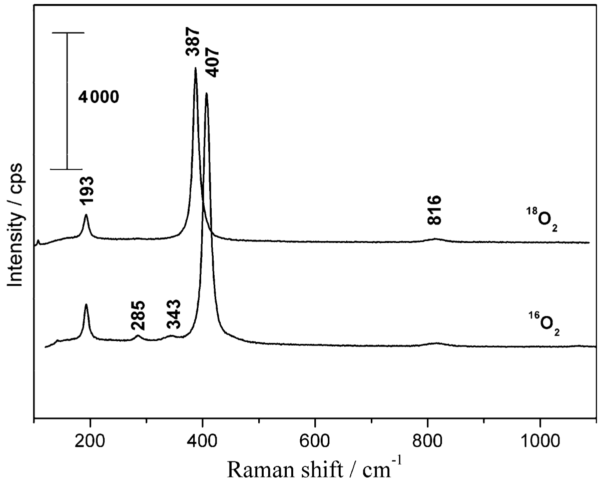

Fig. 3 Raman spectrum of the SrF_2/La_2O_3 catalyst at 298 K after $^{16}O_2$ pretreatment and $^{18}O_2$ exchange at 973 K. The main peaks of 407 and 387 cm^{-1} correspond to the La–^{16}O and La–^{18}O stretching modes, respectively, of La_2O_3

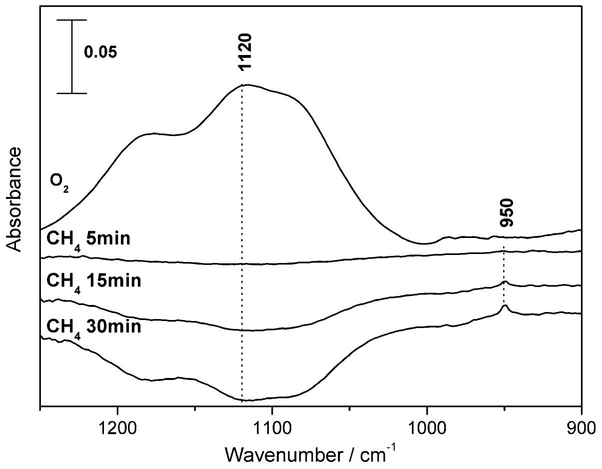

Fig. 4 In situ FTIR spectra of the SrF_2/La_2O_3 catalyst at 973 K after O_2 pretreatment for 30 min, followed by reaction with CH_4 after 5, 15 and 30 min, respectively. Peak at 1120 cm^{-1}, associated to the O_2^- species, gradually decreases, whereas peak at 950 cm^{-1}, associated to C_2H_4, gradually increases with the increase of reaction time. See the text for details

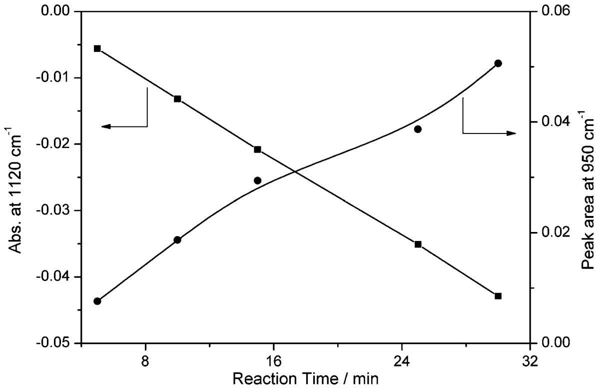

Fig. 5 Correlation between the absorbance at 1120 cm^{-1} (O_2^-) and the peak area of 950 cm^{-1} (C_2H_4) along the reaction time of 5, 10, 15, 25 and 30 min, respectively

973 K over the SrF_2/La_2O_3 catalyst. No peaks related to the peroxide O_2^{2-} ions (~800 cm^{-1} [10]) were observed on this catalyst. To prove that the as-generated O_2^- species could react with CH_4, the interaction of O_2^- with CH_4 was investigated. Figure 4 showed a sequential change in the IR spectra when pure CH_4 (99.99%, Linde) was introduced to the catalyst, which has been pretreated with O_2 at 973 K followed by a brief evacuation at the same temperature to remove the gas phase O_2. As can be seen from Figure 4, the absorbance around 1120 cm^{-1} gradually decreased with the increase of reaction time. In the meantime, a band at 950 cm^{-1}, which was ascribed to the bent vibration of CH_2 of the gas phase C_2H_4 [27], gradually increased in intensity. From the change of the IR absorbance at 1120 cm^{-1}(O_2^- species) and that of the peak area of the band at 950 cm^{-1}(gas phase C_2H_4) with the reaction time, a corresponding relationship between the O_2^- species and the gas phase C_2H_4 was established (Fig. 5). The absorbance of O_2^- decreased linearly with the reaction time, accompanied by a steady increase of the peak area corresponding to C_2H_4. The peak area of C_2H_4 was seen to diverge below the initial linearity. This is understandable. The prolonged the reaction time increased the possibility of side reactions such as the deep oxidation, the selectivity to C_2H_4 was decreased accordingly. The clear corresponding relationship shown in Fig. 5 strongly suggests that the superoxide O_2^- was an active oxygen species responsible for the OCM reaction to give C_2H_4 over the SrF_2/La_2O_3 catalyst.

In order to obtain more information on the active oxygen species under the OCM reaction condition, the interaction between the CH_4/O_2 co-feed mixture and the catalyst sample was studied. The IR spectra recorded under a stream of CH_4/O_2 on the O_2-preadsorbed SrF_2/La_2O_3 catalyst, were shown in Fig. 6. Gas phase CH_4 (1307 cm^{-1}) and surface CO_3^{2-} (860 cm^{-1}, 1450 cm^{-1}) [28] were observed at 673 K. When the reaction temperature was increased to 773 K, gas phase CH_4, surface CO_3^{2-} (860, 1060, 1450, 1760 cm^{-1}) [28], gas phase CO_2 (2330, 2360 cm^{-1}) and gas phase CO (2110, 2175 cm^{-1}) were detected. Besides gas phase CH_4, surface CO_3^{2-}, gas phase CO_2 and gas phase CO, the absorption band of C_2H_4 (950 cm^{-1}) [27] was observed at 873 K on the working catalyst. These results demonstrated that the OCM reaction did happen on the catalyst at 873 K. The intensity of C_2H_4 was increased when the reaction temperature was increased to 973 K, and the intensity of the adsorbed O_2^- band at ~1127 cm^{-1} was increased simultaneously, showing that the O_2^- species was maintainable under the OCM condition. Comparing with the IR spectra in Fig. 4, the IR band of the gas phase C_2H_4 in Fig. 6 was much stronger.

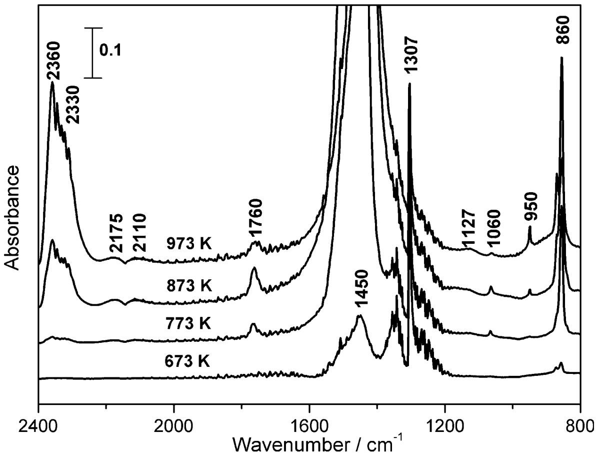

Fig. 6 In situ FTIR spectra for the O_2-preadsorbed SrF_2/La_2O_3 catalyst under the OCM reaction conditions at the indicated temperatures

Control experiment was performed on the same catalytic system but in the absence of O_2. Little conversion of methane was detected in this condition, showing that the lattice oxygen O^{2-} hardly played any role in the OCM reaction at 973 K over the SrF_2/La_2O_3 catalyst. We noticed that Neurock et al. [16] provided a theoretical evidence, showing that hydrogen abstraction by using the lattice O^{2-} in La_2O_3 is too endothermic (uphill by 91.6 kcal/mol) to be possible.

3.2 EPR Characterization

The EPR spectrum of the SrF_2/La_2O_3 catalyst was shown in Fig. 7. The sample was first treated with oxygen at 1073 K for 30 min and then quenched to 77 K in the presence of O_2. We observed EPR signals at $g_{xx} = 2.0001$, $g_{yy} = 2.0045$, $g_{zz} = 2.0685$ (The z direction is taken to be parallel to the O–O internuclear axis). These g values can be compared favorably with those of O_2^- reported by Lunsford et al ($g_{xx} = 1.994$, $g_{yy} = 2.006$, $g_{zz} = 2.040$ on La_2O_3 [13]) and Osada et al ($g_{xx} = 2.001$, $g_{yy} = 2.003$, $g_{zz} = 2.040/2.070$, coordinated to Ca^{2+} and Y^{3+}, respectively [19]). We noticed that EPR did not detect other paramagnetic species such as O^- ($g_{\perp} = 2.054$, $g_{||} = 2.004$ for $[Li^+O^-]$ on Li/MgO [7, 8, 14]) and O_3^- ($g_1 = 2.0172$, $g_2 = 2.0100$, $g_3 = 2.0014$ on MgO [29]) in our catalytic system, solidifying the conclusion that the O_2^- species was the only active oxygen species observable over the SrF_2/La_2O_3 catalyst.

Lunsford et al made similar observation of O_2^- over La_2O_3 [13, 14]. They claimed that no O^- and O_3^- were detectable even when Li^+ was added to La_2O_3 as done in the Li/MgO system [13]. They suggested that O_2^- can activate a methane molecule, but provided the other alternative that a transient O^- species may indeed be formed via O_2^-, and, in the presence of CH_4, may give rise to the CH_3 radicals [14]. A similar explanation may be applicable to our system. Since there was no definite evidence of O^- species in our EPR studies, we share with Osada [19] that the participation of O_2^- species in the selective formation of C_2 compounds from methane is most likely.

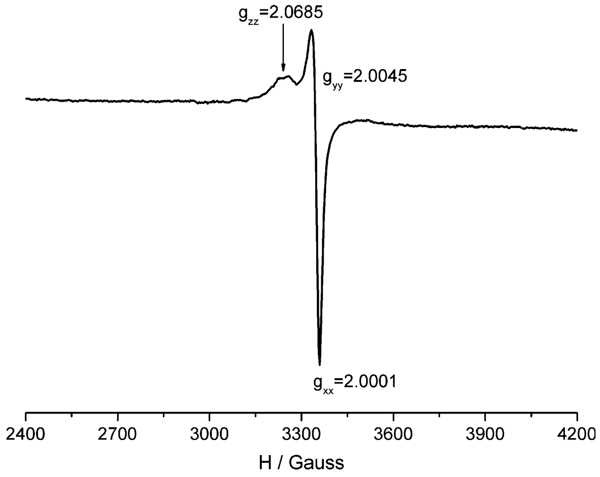

Fig. 7 EPR spectrum of O_2^- over the SrF_2/La_2O_3 catalyst at 10 K

4 Conclusion

Understanding the nature of the active oxygen species is not only the key to improve the activity and the selectivity of the catalyst for the OCM reaction, but also of general significance in many other important processes, such as ODH (oxidative dehydrogenation) of lighter alkanes to alkenes, POM (partial oxidation of methane) to methanol or formaldehyde, and the catalytic $DeNO_x$ science and technology, etc. While oxygen species such as O^-, O_3^-, O_2^{2-}, and O_2^- have been detected in many circumstances, the role of the superoxide O_2^- as a selective active species has sometimes been overlooked. People have been worrying about the stability and the reactivity of the O_2^- species. Based on the in situ IR spectroscopy results, we showed that O_2^- was the only dioxygen species present on the SrF_2/La_2O_3 catalyst at temperatures up to 973 K. The substitution of $^{18}O_2$ isotope for $^{16}O_2$ caused the peak at 1130 cm^{-1} to shift to lower wavenumbers (1095 and 1064 cm^{-1}), consistent with the assignment of the spectra to the O_2^- species. At 973 K, the as-generated O_2^- species was found to react with CH_4, leading to the formation of the gas phase C_2H_4. There existed a parallelism between the rate of disappearance of O_2^- species and the rate of formation of the gas phase C_2H_4, suggesting that O_2^- is the active species responsible for the OCM reaction. The EPR results ($g_{xx} = 2.0001$, $g_{yy} = 2.0045$, $g_{zz} = 2.0685$) provide support to the sole existence of the paramagnetic O_2^- species on the O_2-preadsorbed SrF_2/La_2O_3 catalyst. Similar results have been observed on La_2O_3 [13, 14], Y_2O_3/CaO [19], SrF_2/Nd_2O_3 [30], BaF_2/La_2O_3 [30], and other fluoride-containing rare earth (alkaline earth)-based catalysts [21, 22], reinforcing our conclusion that the superoxide O_2^- species could not be neglected as the active oxygen species for the OCM reaction.

Acknowledgments This work was supported by the Ministry of Science and Technology of China (Grant No. 2005CB221408, 2004CB719902) and NSFC (20433030, 20525311, 20533030, 20423002).

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