High-temperature *in situ* FTIR spectroscopy study of LaOF and BaF_2/LaOF catalysts for methane oxidative coupling

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In situ FTIR spectroscopy was used to characterize the oxygen adspecies and its reactivity with CH_4 over LaOF and 15 mol% BaF_2/LaOF catalysts at OCM temperature (750–800 °C). It was found that gas-phase oxygen was activated on the surface of LaOF and 15 mol% BaF_2/LaOF, which had been pretreated under vacuum at 750 or 800 °C, forming O_2^- species at high temperature (750–800 °C). At 750 °C, the adsorbed O_2^- species can react with pure CH_4 accompanied by formation of gas-phase C_2H_4 and CO_2, and there is a good correlation between the rate of disappearance of surface O_2^- and the rate of formation of gas-phase C_2H_4. The O_2^- species was also observed over the catalysts under working condition, and it reacted with CH_4 in a manner that was consistent with its role in a catalytic cycle. These results suggest that O_2^- may be the active oxygen species for OCM reaction over these catalysts.

Keywords: *in situ* FTIR, oxygen species, LaOF, BaF_2/LaOF, methane oxidative coupling

1. Introduction

The oxidative coupling of methane (OCM) to ethylene and ethane is an attractive reaction to convert natural gas to more valuable chemicals. Since Keller and Bhasin reported their early work on the reaction in 1982 [1], OCM has become a subject of world-wide research in recent years. After more than a decade of study, many catalyst systems have been developed, which include supported transition-metal oxide catalyst system [1–5] partially stabilized with alkali, e.g., MnO_x–Na_2WO_4/SiO_2, reducible non-transition-metal oxides catalyst system [6–11] supported on basic carriers, e.g., PbO_x/MgO, and alkaline-earth-oxide (AEO)- and/or rare-earth-oxide (REO)-based irreducible metal oxides (and carbonate), mostly of the host-dopant type, catalyst system [12–31], and many catalysts in the latter system such as Li^+/MgO, Na^+/CaO, Sr^{2+}/La_2O_3 and ThO_2–La_2O_3–AEO–$BaCO_3$ have been intensively investigated.

In early studies, the goal of applied research is often to maximize C_2 yield by varying catalyst composition, reagent partial pressure, etc. However, economic evaluations have shown that C_2 selectivity is more important than yield. Therefore, much attention has also been focused on the nature of the active and C_2-selective oxygen species for OCM reaction, the knowledge of which may help in search of a better OCM catalyst. For an OCM reaction, running on an oxide or oxyfluoride catalyst with stable cation valence under the co-feed mode, mono- and diatomic anionic species such as O^-, or O_2^{2-}, and O_2^- have been proposed to be the active oxygen species for the reaction, based on both *ex situ* and *in situ* experimental evidence from techniques such as EPR, XPS, IR and Raman [20,32–42]. Unfortunately, the nature of the oxygen species responsible for the selective conversion of methane to C_2 hydrocarbons has not yet been clarified.

In the last five years, we have reported a series of fluoride-containing rare-earth/alkaline-earth-metal-oxide-based catalysts for the selective conversion of light alkanes in the presence of oxygen. Among these catalysts, the BaF_2/LaOF prepared based upon the principles of structurally directed constituent selection, i.e., doping the tetragonal LaOF of defective fluorite structure with metal fluoride of lower cationic valence, demonstrated excellent catalytic performance for both OCM [43,44] and ODE [44,45]. For example, under the conditions of 770 °C and $GHSV = 15000\ h^{-1}$ with $CH_4/O_2 = 6$ and 9, CH_4 conversions of 19.5 and 16.5% with C_2 selectivities of 81.2 and 84.6% were obtained, respectively. In this study, *in situ* FTIR spectroscopy is used to characterize the oxygen adspecies and its reactivity with CH_4 over LaOF and 15 mol% BaF_2/LaOF catalysts at OCM temperature (750–800 °C). The IR spectra of the catalysts when they are treated with a CH_4/O_2 (3.4/1) mixture at OCM temperature are also presented. These results will provide very useful information for the understanding of the active oxygen species for the OCM reaction over the corresponding catalysts.

2. Experimental

The LaOF and 15 mol% BaF_2/LaOF catalysts were prepared by the method of grinding and calcining as described elsewhere [44]. The starting materials used to prepare the LaOF and 15 mol% BaF_2/LaOF were of analytical grade. The transmittance IR spectra were recorded

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on a Perkin-Elmer Spectrum 2000 system equipped with a liquid-nitrogen-cooled MCT detector and a home-built transmittance IR cell designed to treat the sample *in situ*. The cell was fitted with a furnace, cooling water jackets, gas inlet and outlet, and with BaF_2 windows. The gas inlet and outlet of the IR cell were connected to a two-way and a three-way valve, respectively. By proper switching these valves, the sample in the IR cell can be treated under vacuum, exposed to different gas atmosphere or reacted with a flow of CH_4/O_2 mixture. The sample holder of the cell can be heated up to 800 °C. The catalyst was pressed into a self-supported disk. Before the introduction of adsorbates or reactants to the catalyst, the sample disk was treated in the IR cell under O_2 at reaction temperature (750 or 800 °C) for 30 min and then evacuated (10^{-3} Torr) at the same temperature for more than 5 h, until surface contaminants such as carbonate species were completely removed.

For the experiments of CO_2 or O_2 adsorption, LaOF or BaF_2/LaOF sample was exposed to 1 atm of CO_2 or O_2 at 750 °C for a certain time followed by evacuation at the same temperature. To study the reaction of surface oxygen adspecies with CH_4, 1 atm of the CH_4 was added in a batch mode to the IR cell to react with the oxygen species adsorbed on the LaOF at 750 °C. To study the OCM reaction over the catalysts, 1 atm of the $CH_4/O_2 = 3.4$ mixture was introduced and shut up in the IR cell to react on the LaOF or BaF_2/LaOF sample at 750 °C for a certain time. The catalyst was then switched to a flow of $CH_4/O_2 = 3.4$ mixture to carry on the reaction under working state. The adsorption or reaction process was continuously followed at reaction temperature by the IR spectrometer. All of the IR spectra reported in this paper were recorded at reaction temperature (750–800 °C) with 36 scans at the resolution of 4 cm^{-1} over 0.5–1 min. The reported absorbances were obtained from spectra referenced to the background spectra, which were taken under vacuum prior to the introduction of absorbates or reactants to the catalyst.

O_2 (99.5%) was purified by passing through a NaOH column and a 5 A molecular sieve column to remove small amounts of CO_2 and H_2O. CO_2 was purified with a 401 deoxidiser column to remove the O_2 impurity. CH_4 (99.99%) and CH_4/O_2 (3.4/1) were used without further purification.

3. Results

3.1. CO_2 adsorption over LaOF and BaF_2/LaOF

Since the position of the IR bands of surface carbonates is very close to that of dioxygen adspecies such as O_2^{2-} and O_2^-, experiments of CO_2 adsorption were first performed in order to identify the adsorption bands which resulted from the surface carbonates.

Figure 1 (a)–(c) displays the sequential change of IR spectra of LaOF when it is exposed to 1 atm of CO_2 at 750 °C. After the sample was in contact with CO_2 for 1 min, IR bands at 852, 942, 983, 1047, 1088, 1361, 1453 and 1512 cm^{-1} were observed (figure 1(a)). Among them, the bands at 852, 1361, 1453 and 1512 cm^{-1} gradually increased in intensity as the adsorption time increased and could be assigned to the surface carbonate species. Other bands (at 942, 983 1047 and 1088 cm^{-1}) remained unchanged with time and could be easily removed by brief evacuation (figure 1(d)); they were, therefore, attributed to the absorption from gas phase, probably from the impurity in CO_2. It is worth to mention that the intensities of surface carbonate bands are rather weak, even when the sample is under 1 atm of CO_2, indicating that the basicity of LaOF is very weak. After exposure to CO_2 at 750 °C for 30 min, the sample was switched to a vacuum line; the corresponding IR spectra during the evacuation are shown in figure 1 (d)–(f). As can be seen, most of the surface carbonate is removed within 10 min of evacuation.

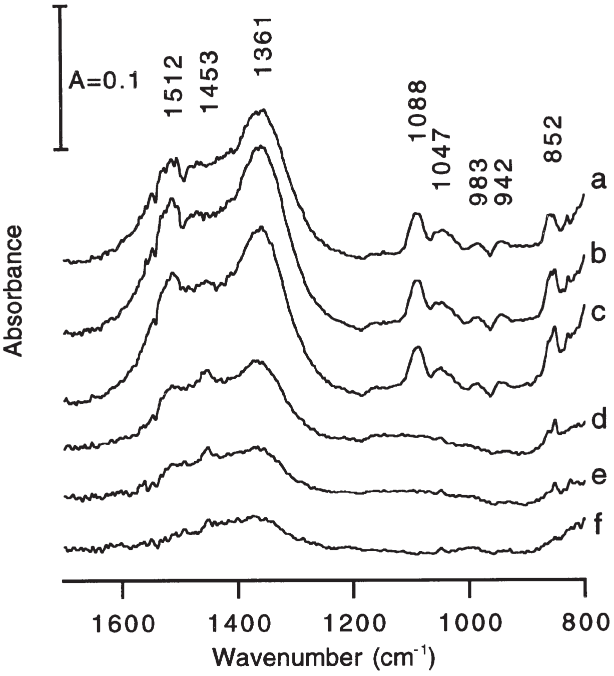

Figure 1. IR spectra of CO_2 adsorption on LaOF at 750 °C. The spectra were recorded after the sample was exposed to 1 atm of CO_2 at 750 °C for (a) 1 min, (b) 10 min and (c) 30 min, and then evacuated at the same temperature for (d) 1 min, (e) 10 min and (f) 60 min.

Similar IR spectra were observed when a 15 mol% BaF_2/LaOF sample was exposed to 1 atm of CO_2 at 750 °C (figure 2). Two strong IR bands at 856 and ca. 1422 cm^{-1}, and four weak bands at 942, 983, 1052 and 1091 cm^{-1} were observed after the catalyst was exposed to CO_2 for 1 min. As the time increased, the bands at 856, 1052 and 1422 cm^{-1} gradually increased in intensity. Therefore, they were assigned to the surface carbonate species. The other bands (at 942, 983 and 1091 cm^{-1}) might be attributed to the absorption from gas phase. It is interesting to note that, under similar experimental conditions, the band intensity of surface carbonate over 15 mol% BaF_2/LaOF is much stronger than that over LaOF, which indicated that the surface of the former is more basic than that of the latter. After exposure to CO_2 for 5 min, the catalyst was evacuated at

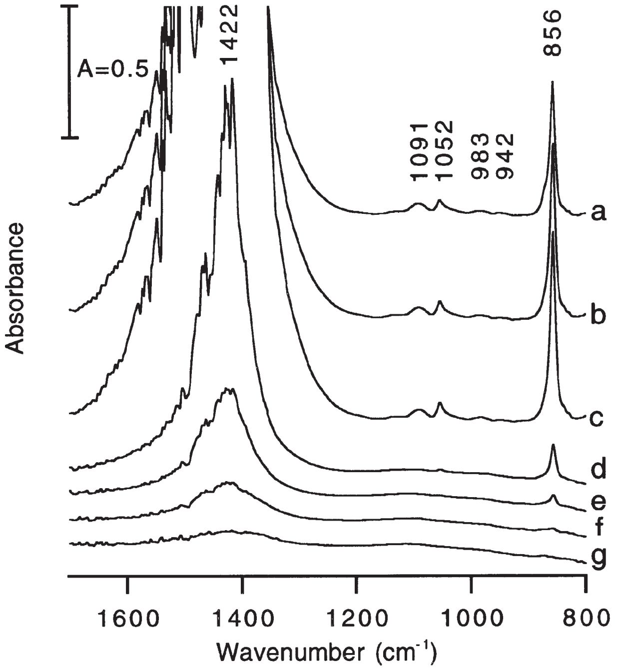

Figure 2. IR spectra of CO_2 adsorption on 15 mol% BaF_2/LaOF at 750 °C. The spectra were recorded after the sample was exposed to 1 atm of CO_2 for (a) 1 min, (b) 3 min and (c) 5 min, and then evacuated at the same temperature for (d) 1 min, (e) 5 min, (f) 10 min and (g) 30 min.

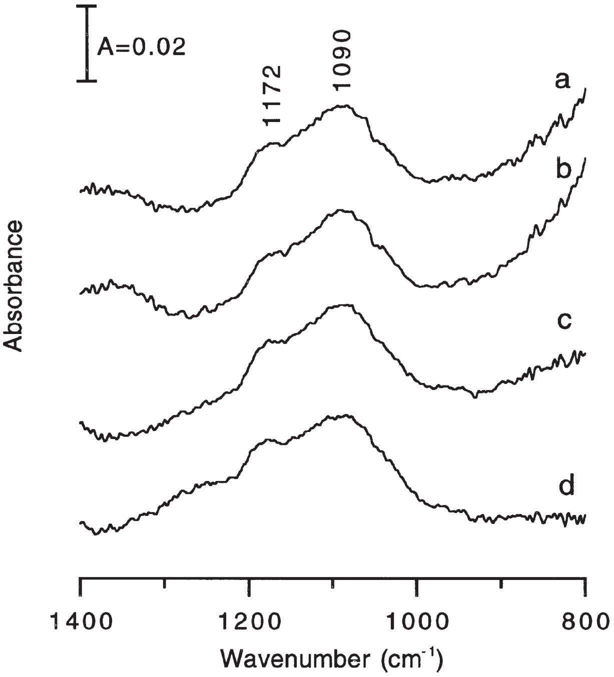

Figure 3. IR spectra of O_2 adsorption on LaOF at 750 °C. The spectra were recorded after the sample was exposed to 1 atm of O_2 at 750 °C for (a) 1 min and (b) 12 min, and then evacuated at the same temperature for (c) 1 min and (d) 40 min.

750 °C; the corresponding IR spectra during evacuation are shown in figure 2 (d)–(g). Most of the surface carbonate species were removed within 30 min of evacuation.

3.2. O_2 adsorption over LaOF and BaF_2/LaOF

After a LaOF sample was treated as described in section 2 followed by exposure to O_2 at 750 °C, two broad bands with maximum at 1090 and a shoulder at 1180 cm^{-1} were observed (figure 3(a)). These bands were relatively stable under the experimental conditions. Their intensities were almost not affected by increasing contact time with O_2 (figure 3(b)) or by evacuating the sample under vacuum for ca. 40 min (figure 3 (c), (d)). By comparing with the IR spectra of the CO_2-pretreated sample recorded at 750 °C (figure 1), the possibility of attributing these bands to surface carbonate species can be excluded. Since the positions of the bands are consistent with those of superoxide ligands in the matrices [46–48], complex [49,50] and CeO_2 surface [51], they were assigned to the adsorbed superoxide species (O_2^-) located in two different micro chemical environments.

Figures 4 and 5 show the IR spectra of an O_2-pretreated 15 mol% BaF_2/LaOF sample at 750 and 800 °C, respectively. The spectra were quite similar to that of the O_2-pretreated LaOF. Two broad IR bands with maximum at 1098 cm^{-1} and a shoulder at 1168 (1162) cm^{-1} were detected. These bands can also be assigned to the superoxide species. When an O_2-pretreated 15 mol% BaF_2/LaOF was heated under H_2 atmosphere at 600 °C for 30 min followed by brief evacuation at 750 °C, the IR bands of superoxide

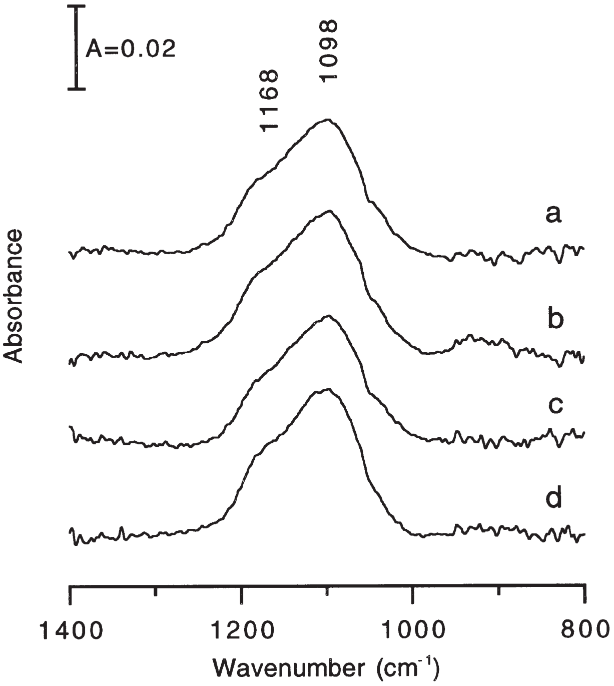

Figure 4. IR spectra of O_2 adsorption on 15 mol% BaF_2/LaOF at 750 °C. The spectra were recorded after the sample was exposed to 1 atm of O_2 at 750 °C for (a) 1 min and (b) 10 min, and then evacuated at the same temperature for (c) 1 min and (d) 60 min.

species significantly decreased in intensity, suggesting that this species could react with H_2 under the experimental conditions. The intensity of O_2^- bands would also gradually decrease if the sample was continuously heated at

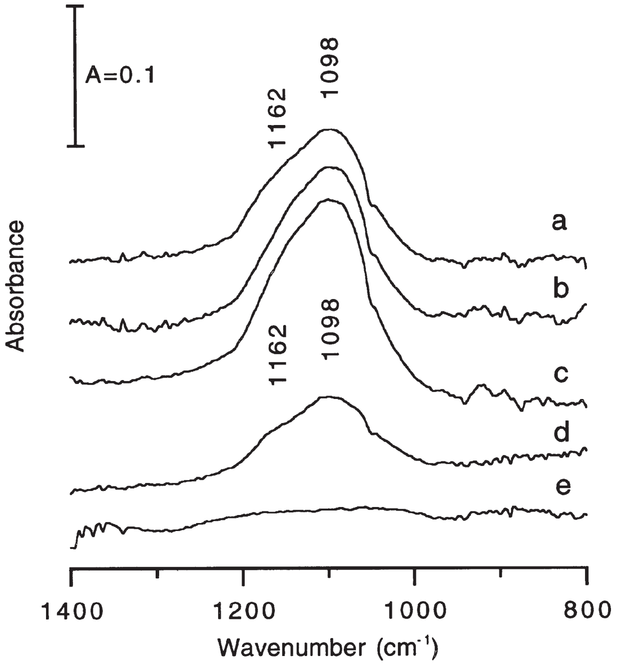

Figure 5. IR spectra of O_2 adsorption on 15 mol% BaF_2/LaOF at 800 °C. The spectra were recorded after the sample was exposed to 1 atm of O_2 at 800 °C for (a) 1 min and (b) 30 min, and then evacuated at the same temperature for (c) 3 min, (d) 30 min and (e) 120 min.

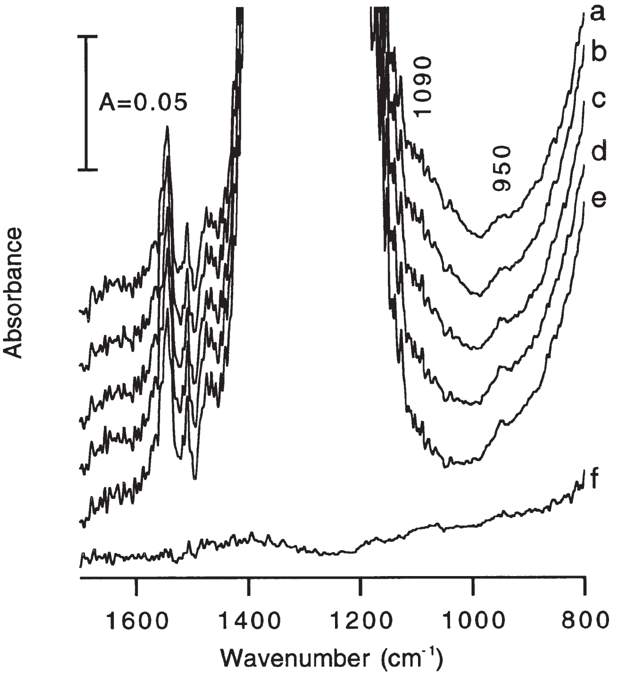

Figure 6. Change of IR spectra at 750 °C when 1 atm of CH_4 was added in a batch mode to O_2-preadsorbed LaOF for (a) 1 min, (b) 5 min, (c) 10 min, (d) 20 min and (e) 30 min, and then evacuated for (f) 5 min.

800 °C under vacuum (figure 5(d)), and they were found to disappear after about 120 min (figuer 5(e)).

The peroxide species (O_2^{2-}), which was detected by Lunsford et al. [32,36] over OCM catalysts such as La_2O_3, Na^+/La_2O_3, Sr^{2+}/La_2O_3 and Ba^{2+}/MgO at high temperature, and was expected to appear at ca. 850 cm^{-1}, was not detected under the experimental conditions.

3.3. Interaction of adsorbed oxygen species with CH_4 at OCM temperature

From the experimental results shown in figures 3, 4 and 5, it is clear that O_2^- is the only dioxygen species detected at temperature above 750 °C over the LaOF and 15 mol% BaF_2/LaOF catalysts. To ensure that the generating O_2^- species will react with CH_4, we investigated the interaction of O_2^- with pure CH_4 over LaOF at 750 °C. Figure 6 shows a sequential change in IR spectra when 1 atm of CH_4 is added in a batch mode to the LaOF sample which has been preadsorbed with O_2 at 750 °C followed by brief evacuation at the same temperature to remove the gas-phase O_2. As can be seen from figure 6, the absorbance around 1090 cm^{-1} gradually decreased with the increase of reaction time. In the meantime, a band at 950 cm^{-1}, which was characteristic of CH_2 wagging of gas-phase ethylene [52], and the bands of gas-phase CO_2 at 2310 and 2340 cm^{-1} (not shown) gradually increased in intensity. After the LaOF sample was exposed to CH_4 at 750 °C for 30 min and the gas-phase products were removed by evacuation, it was found that the bands of O_2^- disappeared from the surface. If we plot the changes of the IR absorbance at 1090 cm^{-1} (surface O_2^-) and that of the peak area of the band at 950 cm^{-1} (gas-phase C_2H_4) versus the reaction time, a parallelism between the decrease of IR absorbance of surface O_2^- and the increase of IR band of gas-phase C_2H_4 was observed (figure 7). Since the reaction was performed under an atmosphere of pure CH_4, O_2^- was the only possible dioxygen species on the LaOF catalyst to react with CH_4. A good correlation between the rate of consumption of surface O_2^- and that of formation of C_2H_4 indicates that O_2^- is responsible for the conversion of CH_4 to form the OCM product such as C_2H_4, therefore it may be the active oxygen species for the OCM reaction over the corresponding catalyst.

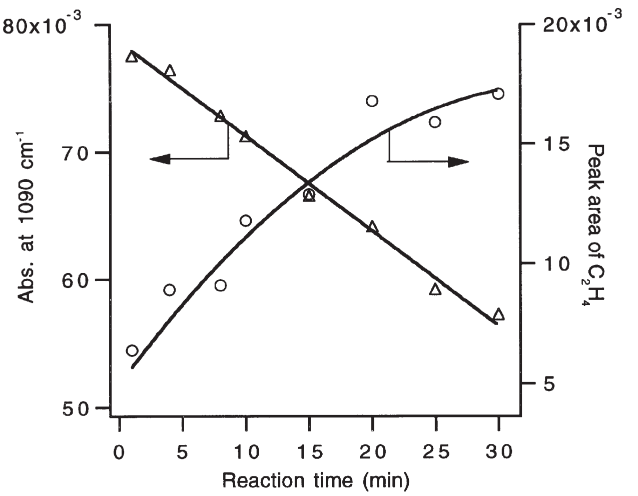

Figure 7. Plots of absorbance at 1090 cm^{-1} (O_2^-) and peak area of C_2H_4 versus reaction time for the reaction shown in figure 6.

The formation of carbonate on the surface of the catalyst during the reaction was not very serious, as no bands at 852 and 1052 cm^{-1} were observed. The very intense bands of gas-phase CH_4 at 1304 cm^{-1} make it difficult to identify the strong bands of surface carbonate at 1361, 1453 and 1512 cm^{-1}. However, from the IR spectra recorded after the sample had been evacuated for 5 min (figure 6(f)), it is clear that the surface carbonate was unstable at 750 °C.

3.4. Interaction of LaOF and 15 mol% BaF$_2$/LaOF with CH$_4$/O$_2$

In order to obtain more information on the oxygen adspecies under OCM condition, the interaction between the CH_4/O_2 mixture and the catalyst sample was studied at 750 and 800 °C, and the change of the catalyst surface during the reaction was followed by IR spectrometer.

Figure 8 shows the change of IR spectra when 1 atm of $CH_4/O_2 = 3.4$ mixture is added in a batch mode to the LaOF sample, which has been evacuated at 750 °C for more than 5 h. Although no clear band appears at ca. 1090 cm^{-1}, the change of absorbance at 1090 cm^{-1} during the reaction can still be followed by IR spectrometer. As the reaction time increased (figure 8 (a)–(d)), the absorbance near 1090 cm^{-1} gradually decreased, while the band of C_2H_4 at 950 cm^{-1} and that of the surface carbonate at 854 cm^{-1} became prominent and developed with time. Comparing with the IR spectra in figure 6, the IR band of gas-phase C_2H_4 in figure 8 is much stronger since the reaction between CH_4 and O_2^- is carried out in presence of O_2 and the consumed O_2^- species can be regenerated, which will enable the OCM reaction to proceed for more than one catalytic cycle to generate more C_2H_4. After the sample was exposed to CH_4/O_2 for 60 min and the reactants and products in gas phase were removed by brief evacuation at 750 °C, the IR spectra displayed only a broad band of surface carbonate at 1432 cm^{-1}, while the band of O_2^- species was no longer observed (figure 8(f)), indicating that this species was completely consumed in the reaction.

Figure 9 (a)–(d) shows the sequential change of IR spectra when 1 atm of $CH_4/O_2 = 3.4$ mixture is added in a batch mode to 15 mol% BaF$_2$/LaOF at 750 °C. After the reactant was introduced to the sample for 1 min, a broad band with maximum at 1113 cm^{-1}, which was assignable to an O_2^- species, and a band at 870 cm^{-1}, which was attributed to a surface carbonate species, were detected (figure 9(a)). During the first 3 min (figure 9 (a), (b)), the band of O_2^- increased slightly. After that, the intensity of O_2^- gradually decreased with increasing reaction time (figure 9 (b)–(d)). In the meantime, the bands of gas-phase C_2H_4 (at 950 cm^{-1}) and that of surface carbonate (at 870 and 855 cm^{-1}) continued to increase.

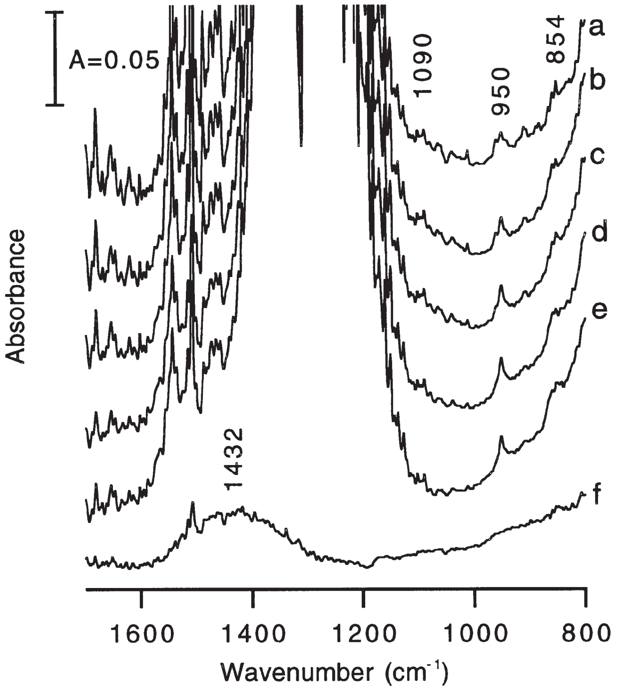

Figure 8. Change of IR spectra at 750 °C when 1 atm of $CH_4/O_4 = 3.4$ was added in a batch mode to LaOF for (a) 1 min, (b) 5 min, (c) 10 min, (d) 30 min and (e) 60 min, and then evacuated for (f) 2 min.

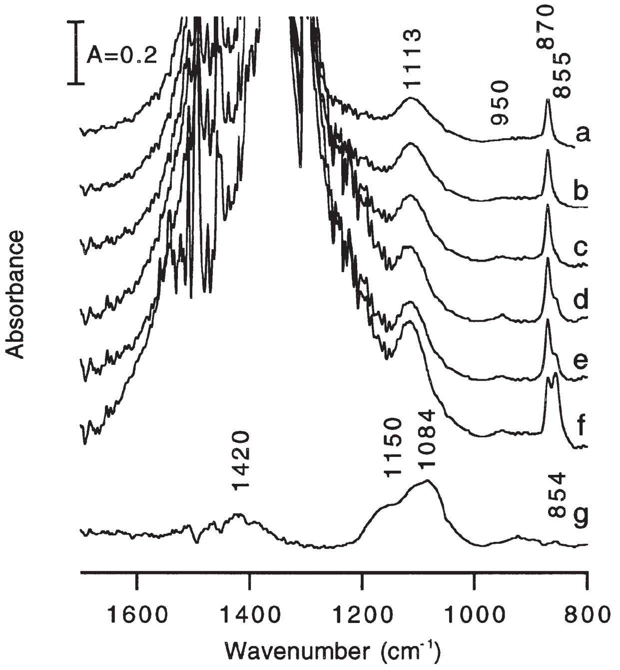

Figure 9. Change of IR spectra of 15 mol% BaF$_2$/LaOF at 750 °C when the sample was exposed to 1 atm of $CH_4/O_2 = 3.4$ for (a) 1 min, (b) 3 min, (c) 5 min and (d) 12 min, followed by switching to a flow of $CH_4/O_2 = 3.4$ (15 ml/min) for (e) 1 min and (f) 30 min, and evacuated for (g) 2 min.

After the batch mode reaction went on for ca. 12 min, the catalyst was switched to a flow of $CH_4/O_2 = 3.4$ (flow rate 15 ml/min), and the reaction continued at the same temperature for another 30 min. The IR spectra, recorded after the catalyst was switched to a flow of CH_4/O_2 mixture for 1 and 30 min, are shown in figure 9 (e) and (f), respectively. Due to the dilution effect of CH_4/O_2 flow to the gas-phase atmosphere in IR cell, the IR band of gas-phase C_2H_4 in figure 9(e) significantly decreased in intensity. If the sample was continued to interact with a CH_4/O_2 flow

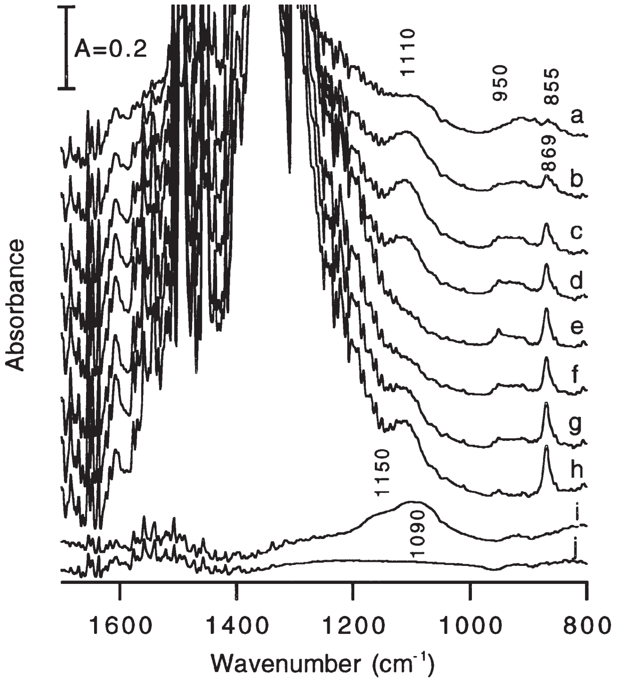

Figure 10. Change of IR spectra of 15 mol% BaF_2/LaOF at 800 °C when the sample was exposed to 1 atm of $CH_2/O_2 = 3.4$ for (a) 0.5 min, (b) 1 min, (c) 3 min, (d) 5 min and (e) 10 min, followed by switching to a flow of $CH_4/O_2 = 3.4$ (15 ml/min) for (f) 1 min, (g) 7 min and (h) 12 min, and evacuated for (i) 2 min and (j) 30 min.

at 750 °C for ca. 30 min, the IR band of gas-phase C_2H_4 slightly increased, and that of O_2^- (at 1113 cm^{-1}) also increased apparently (figure 9(f)).

Comparing with the IR band of surface carbonate species shown in figure 8, the intensity of the surface carbonate band in figure 9 is much stronger under comparable conditions. This is understandable since the basicity of BaF_2/LaOF is stronger than that of LaOF. However, the carbonate species formed on BaF_2/LaOF is also not very stable at 750 °C. Most of them were readily removed by brief evacuation, and only the bands of O_2^- species at 1084 and 1150 cm^{-1} remained on the catalyst (figure 9(g)).

Figure 10 shows the sequential change of IR spectra for the reaction of $CH_4/O_2 = 3.4$ mixture over a 15 mol% BaF_2/LaOF sample at 800 °C. The reaction was first performed in a batch mode in which 1 atm of $CH_4/O_2 = 3.4$ mixture was added to a 15 mol% BaF_2/LaOF sample, which had been treated in the similar way under vacuum as described above and maintained at 800 °C.

Spectrum (a) in figure 10 was recorded after CH_4/O_2 was added to the IR cell for ca. 0.5 min. As can be seen, the IR bands of O_2^- species (at 1100 cm^{-1}) and surface carbonate (at 855 and 869 cm^{-1}) were observed. As the reaction time increased, the band of surface carbonate continued to grow in intensity (figure 10 (a)–(e)), while the band of O_2^- species passed through its maximum intensity at ca. 3 min (figure 10(c)), and almost vanished after ca. 10 min (figure 10(e)). During this period, the band of gas-phase C_2H_4 (at 950 cm^{-1}) kept increasing (figure 10 (a)–(e)). After the batch mode reaction went on for ca. 10 min, the catalyst was switched to a flow of $CH_4/O_2 = 3.4$ (flow rate 15 ml/min) and the reaction continued (figure 10 (f)–(h)). The disappeared superoxide band was found to be gradually restored in the flow of CH_4/O_2, indicating that the O_2^- species over the catalyst reacted with CH_4 in a manner that was consistent with its role in the catalytic cycle. This result provides additional experimental evidence for our previous suggestion that O_2^- may be the active oxygen species for the OCM reaction over LaOF and BaF_2/LaOF catalysts. After reacting in the flow of CH_4/O_2 for ca. 12 min, the catalyst was briefly evacuated at reaction temperature. The IR spectrum recorded after evacuation showed only the bands of O_2^- species at 1090 and 1150 cm^{-1} (figure 10(i)), while the bands of surface carbonate were completely removed. If the sample was continuously evacuated at 800 °C for ca. 30 min, the band of O_2^- also disappeared.

Comparatively, the evolution of the IR band of O_2^- species under CH_4/O_2 at 800 °C (figure 10) is quite similar to that at 750 °C (figure 9), but the reaction goes faster at higher temperature. This is consistent with the results of catalytic performance evaluation, which shows that the best C_2 yield over 15 mol% BaF_2/LaOF is obtained at ~800 °C.

4. Discussion

The identification of oxygen species on metals and oxides has long been of interest [53], especially for studies of the reaction mechanisms of selective and complete oxidation. For the OCM reaction performed over a metal oxide or complex oxide with stable cationic valence, oxygen species such as O^-, O_2^{2-} and O_2^- have been proposed to be the active oxygen species. The early discovery of Li^+/MgO as an effective OCM catalyst focused attention on $[Li^+O^-]$ centers or O^- ions as sites or species for CH_4 activation [12,20]. However, the theoretical studies on the interaction of O^- center with CH_4 indicated a barrier of only 25 kJ/mol for hydrogen abstraction reaction, which is much less than the experimental value of 96 kJ/mol for $CH_3\cdot$ radical formation [54,55]. There is also experimental evidence which shows that O^- will act as a non-selective oxidant enhancing the formation of CO_2 at high temperature (720 °C) [56]. Latterly, O_2^{2-} was also proposed to be the active species, and there is also considerable evidence indicating that O_2^{2-} plays a role in the activation of CH_4 over certain catalysts. Sinev et al. [57] and Otsuka et al. [58] found that Na_2O_2 and BaO_2 are capable of converting CH_4 into C_2H_6 at the temperature above 400 °C. Yamashita et al. [59] studied the Ba^{2+}/La_2O_3 catalyst by means of XPS and concluded that BaO_2 was present on the surface and O_2^{2-} or O^-, derived from the peroxide, was responsible for the catalytic activity. Lunsford et al. [60] demonstrated that a phase separation occurred and BaO/BaO_2 decorated the surface during the OCM reaction over $BaPbO_3$ and $BaBiO_3$ catalysts, and found that there was a good correlation between the activity for CH_4 conversion and the concentration of O_2^{2-}

on the surfaces of a series of Ba^{2+}/MgO catalysts [61]. Lunsford and Knözinger et al. [36] have also used high-temperature *in situ* Raman spectroscopy to characterize the La_2O_3, Na^+/La_2O_3, Sr^{2+}/La_2O_3 and Ba^{2+}/MgO catalysts. The results show that the peroxide species is observed at 700–800 °C, and it is the only dioxygen species detected on these catalysts. At OCM temperature, this peroxide species was reactive when the samples were exposed to CH_4/O_2 mixture. In this experiment, however, *in situ* FTIR spectroscopy indicated the existence of only O_2^- species at the temperature above 750 °C for the O_2-pretreated LaOF and 15 mol% BaF_2/LaOF as well as for the 15 mol% BaF_2/LaOF catalyst under CH_4/O_2 atmosphere. No IR band assignable to the O_2^{2-} species is observed around 850 cm^{-1}, which is the position expected for O_2^{2-} species over the many oxides containing Ba^{2+} [36].

It is well known that the molecular oxygen species is activated at anionic vacancies of the catalyst by gaining partial negative charge from the solid surface to form O_2^-, O_2^{2-} and O^- species. Conceivably, due to the stronger electronegativity of F than O, the presence of F^- in the catalyst will be conducive to decrease the electron donating ability of the catalyst. As a result, fluoride-containing catalysts will have higher work function than the corresponding oxide catalysts (e.g., alkaline-earth/rare-earth-based complex oxide (carbonate), for which the signal of O_2^- adspecies is much weaker and can only be detected on few catalysts under co-feed mode [31,39]) and will, therefore, be more favorable to adsorb oxygen species which are less electron-rich [62] such as O_2^-. A similar phenomenon was also observed in our previous studies on the oxygen adspecies over several other fluoride-containing oxide catalysts such as BaF_2/CeO_2 [42], SrF_2/La_2O_3 [33] and SrF_2/Nd_2O_3 [63], for which the O_2^- is the only dioxygen adspecies detected by IR or Raman spectroscopy at OCM temperature.

According to the literature, there are discrepancies about the thermal stability of O_2^- species over the oxide surface. For example, Li et al. [51] used FTIR and found that the O_2^- species over CeO_2were unstable at temperature above 200 °C. Similar results were also reported by Cordischi et al. [64] and Ito et al. [65] on the O_2^- species over H_2-preadsorbed MgO. Nevertheless, there was also ample experimental evidence which showed that O_2^- species could be formed over the oxides at the temperature above 600 °C [31,66,67]. Louis et al. [68] used the EPR method to study the O_2^- species over La_2O_3 and found that, at room temperature, O_2^- species were located on the La_2O_3 surface and, at 650 °C, 85% of O_2^- species were on the surface and 15% were between the $(LaO)_2^{2+}$ layers of La_2O_3. After OCM reaction, the O_2^- species were no longer observed. Comparing with O_2^{2-} and O^- species, the reactivity of O_2^- toward CH_4 was relatively weak as proved by the experiments of Otsuka et al. [69], which indicated that the O_2^- species over BaO_2 and Na_2O_2 would not react with CH_4 at 400 °C. This, however, does not rule out the possibility of O_2^- as an active oxygen species for methane oxidative coupling, since the reaction usually takes place at temperature above 650 °C. The early experiments of Osada et al. [67] showed that the O_2^- species over a Y_2O_3–CaO catalyst could react with CH_4 at 750 °C. The results of these experiments also indicated that O_2^- species over LaOF can react with pure CH_4 to form C_2H_4 and CO_2. A good correlation between the rate of consumption of surface O_2^- and the rate of formation of gas-phase C_2H_4 suggests that surface O_2^- is not only a reactive oxygen species, but also is responsible for the selective conversion of CH_4 to form OCM product such as C_2H_4. Since the O_2^- species was also observed over the working catalyst and the IR spectra in figure 10 clearly indicated that the evolution of surface O_2^- species during OCM reaction was consistent with its role in the catalytic cycle, it may be the active oxygen species for the OCM reaction over the LaOF and BaF_2/LaOF catalysts. It is necessary to mention that, with the experimental method used in this experiment, it is unable to detect the O^- species, and, therefore, the possibility of co-existence of O^- on the LaOF and 15 mol% BaF_2/LaOF catalysts and the possibility of its participating in OCM reaction cannot be completely ruled out. However, in consideration of its high reactivity, it is reasonable to infer that, for the OCM reaction performed at 750–800 °C over the LaOF and BaF_2/LaOF catalysts, O_2^- should be a more selective oxygen species than O^- for the conversion of CH_4 to C_2 hydrocarbons.

5. Conclusions

Based on the above FTIR spectroscopy results, it can be reasonably concluded that gas-phase oxygen was activated on the surface of LaOF and 15 mol% BaF_2/LaOF, which had been pretreated under vacuum at 750 or 800 °C, and formed O_2^- species at high temperature (700–800 °C). The O_2^- species was also observed over the 15 mol% BaF_2/LaOF catalyst under working condition, and was the only dioxygen adspecies over the catalysts. At 750–800 °C, the adsorbed O_2^- species could react with CH_4 accompanied by formation of gas-phase C_2H_4, CO_2 and surface carbonate, and there is a parallelism between the rate of disappearance of surface O_2^- and the rate of formation of gas-phase C_2H_4. When a 15 mol% BaF_2/LaOF catalysts was treated with a CH_4/O_2 mixture at OCM reaction temperature, O_2^- species over the catalyst reacted with CH_4 in a manner that was consistent with its role in the catalytic cycle. These results suggest that O_2^- may be the active oxygen species for OCM reaction over these catalysts.

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