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In situ IR and pulse reaction studies on the active oxygen species over SrF_2/Nd_2O_3 catalyst for oxidative coupling of methane

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Abstract

Pulse reaction method and *in situ* IR spectroscopy were used to characterize the active oxygen species for oxidative coupling of methane (OCM) over SrF_2/Nd_2O_3 catalyst. It was found that OCM activity of the catalyst was very low in the absence of gas phase oxygen, which indicated that lattice oxygen species contributed little to the yield of C_2 hydrocarbons. IR band of superoxide species (O_2^-) was detected on the O_2-preadsorbed SrF_2/Nd_2O_3. The substitution of $^{18}O_2$ isotope for $^{16}O_2$ caused the IR band of O_2^- at 1128 cm^{-1} to shift to lower wavenumbers (1094 and 1062 cm^{-1}), consistent with the assignment of the spectra to the O_2^- species. A good correlation between the rate of disappearance of surface O_2^- and the rate of formation of gas phase C_2H_4 was observed upon interaction of CH_4 with O_2-preadsorbed catalyst at 700 °C. The O_2^- species was also observed on the catalyst under working condition. These results suggest that O_2^- species is the active oxygen species for OCM reaction on SrF_2/Nd_2O_3 catalyst.

Keywords: Methane oxidative coupling; SrF_2/Nd_2O_3 catalyst; Superoxide species; $^{18}O_2$ isotopic exchange experiment; Pulse reaction; *In situ* IR

1. Introduction

The oxidative coupling of methane (OCM) to C_2 hydrocarbons has been intensively studied since the pioneering work of Keller and Bhasin [1], as one of the important potential routes to a possible future production of basic chemicals. In the OCM reaction, the nature of oxygen species participating in the reaction was not yet fully understood. Adsorbed oxygen species of electrophilic character (e.g. O_2^-, O_2^{2-}, O^-) [2–9], as well as lattice oxygen (O^{2-}) [10,11], were supposed to be responsible for C–H bond cleavage to produce methyl radicals.

In their early work on the oxidative coupling of methane reaction over Li–MgO, Lunsford and co-workers [7–9] established many of the generally accepted principles concerning the reaction mechanism and the nature of the active site. In Lunsford's proposed reaction scheme the active sites for CH_4 activation were assumed to be surface O^- species, which generated $CH_3\cdot$ radicals upon interaction with methane. The O^- species was believed to be present in the form of a [Li^+O^-] defect in the near surface region of the catalyst.

Nevertheless, in the case of pure alkaline earth or rare earth oxides or their composition compounds, a promising kind of catalysts which showed not only high methane conversion and C_2 selectivity but also good thermal stability, significant amounts of O_2^- ions and O_2^{2-} ions, instead of O^- ions, have been found by EPR [4,12,13], XPS [14,15] and Raman [5]. It was obvious that the active oxygen species and activation mechanism of methane on these catalysts were different from those on alkali-doped alkaline oxides.

SrF_2/Nd_2O_3 is one of the fluoride-containing rare earth–alkaline earth catalysts with good catalytic performance for OCM reaction [16]. In this study, pulse reaction method and *in situ* IR spectroscopy are used to characterize the oxygen species

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on SrF_2/Nd_2O_3 and its reactivity with CH_4 at OCM temperature (700 °C). It is expected that such experiments should provide with some useful information to understand the active oxygen species for OCM reaction over the corresponding catalysts.

2. Experimental

2.1. Catalyst preparation

SrF_2 and Nd_2O_3 (SrF_2 to Nd_2O_3 ratio = 1:1) were physically mixed for about 90 min with a small amount of distilled water. The paste was dried at 383 °C and then was calcined in static air at 800 °C for 6 h. The catalyst used for the reaction was pressed, sequently crushed and sieved to 40–80 mesh.

2.2. Catalyst characterization

Pulse reaction was carried out to investigate the reactivity of active oxygen species to CH_4. Before the collecting of the data, the catalyst (40–80 mesh, 400 mg) packed in a quartz reactor was pretreated *in situ* with a flow of He (20 mL min^{-1}, 99.999% in purity, Linde) at 800 °C for 30 min in order to remove the surface carbonate. CH_4 or O_2 pulses were then injected in He carrier (flow rate 20 mL min^{-1}) over the catalyst. The carrier gas and products were analyzed on-line by a Balzers OmniStar quadrupole mass spectrometer (QMS 200).

The *in situ* IR experiments were recorded on a Nicolet Nexus FTIR spectrometer. 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}. Thirty-two scans were accumulated for a spectrum. All the IR spectra were recorded *in situ* at the indicated temperatures.

3. Results and discussion

3.1. Pulse reaction

Fig. 1 shows the mass spectrum signals of C_2 hydrocarbons and CO_2 for the pulse reaction of CH_4 over SrF_2/Nd_2O_3 catalyst at 750 °C. Before the introducing of CH_4, the catalyst was pretreated with He at 800 °C for 30 min in order to remove carbonate and oxygen species on the catalyst surface. As shown in Fig. 1, both the signals of C_2 hydrocarbons and CO_2 are very weak, indicating that lattice oxygen species on the catalyst shows very low reactivity to CH_4 under the experimental condition.

To further demonstrate the importance of the active oxygen species in maintaining high C_2 hydrocarbon yield levels for the OCM reaction over SrF_2/Nd_2O_3 catalyst, additional pulse reaction studies were performed over the SrF_2/Nd_2O_3 catalyst in which each pulse of pure O_2 was followed by a pulse of pure CH_4, but the time intervals between O_2 and CH_4 pulses were varied from 0 to 20 s. As shown in Fig. 2, maxima yields of C_2 hydrocarbon and CO_2 were observed when CH_4 and O_2 were pulsed to the catalyst simultaneously. With the increasing of time interval between the initial O_2 pulse and the subsequent CH_4 pulse from 2 to 10 s, the yield of C_2 hydrocarbons over the catalyst decreased dramatically. When the time interval between O_2 and CH_4 pulses was increased to 15 s or longer, the signal of C_2 hydrocarbons was leveling off, but the yield of C_2 was still superior to that observed in the pulse reaction of CH_4 over He-pretreated catalyst shown in Fig. 1. These results suggest that the presence of the active oxygen species on the catalyst surface (i.e. gas phase oxygen adsorbed on the surface of the catalyst and then converted to the active oxygen species) is necessary to achieve high C_2 hydrocarbon yield for the reaction of CH_4 over SrF_2/Nd_2O_3 catalyst.

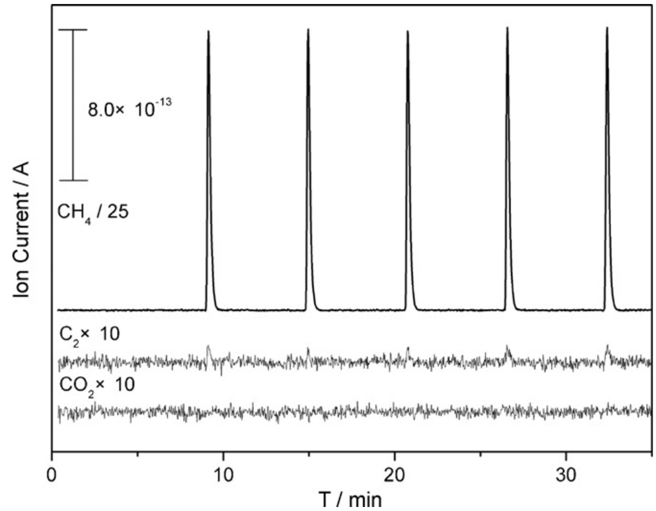

Fig. 1. Pulse reaction CH_4 over the He-pretreated SrF_2/Nd_2O_3 catalyst at 750 °C.

3.2. In situ IR characterization

By using *in situ* IR technique, superoxides species has been observed on several fluoride-containing rare earth (alkaline earth) based catalysts in the temperature range of OCM reaction or under the condition of OCM reaction [17]. To determine

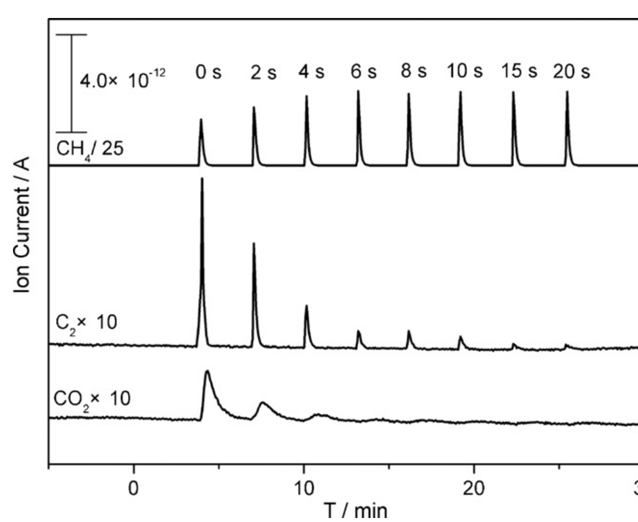

Fig. 2. Effect of time interval between O_2 and CH_4 pulses on the yields of OCM reaction products (C_2 hydrocarbons and CO_2) over SrF_2/Nd_2O_3 catalyst at 750 °C.

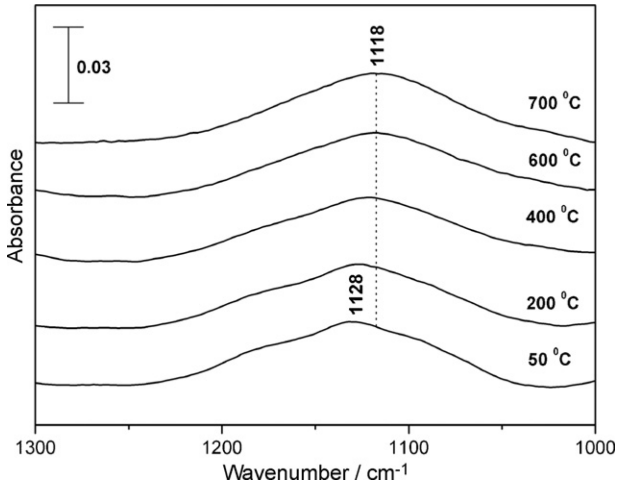

Fig. 3. *In situ* IR spectra of the O_2-preadsorbed SrF_2/Nd_2O_3 catalyst at the indicated temperatures.

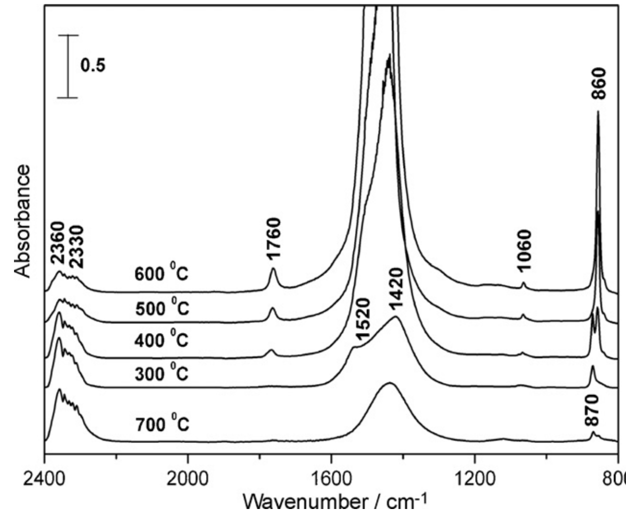

Fig. 4. *In situ* IR spectra of gas phase CO_2 and surface carbonate species formed by CO_2 adsorption on the SrF_2/Nd_2O_3 catalyst at the indicated temperatures.

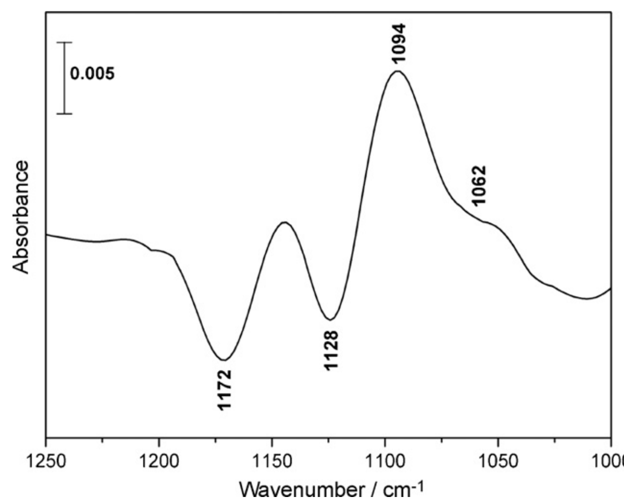

Fig. 5. IR spectrum of the SrF_2/Nd_2O_3 catalyst recorded at 50 °C after $^{18}O_2$ isotopic exchange reaction at 700 °C (with IR spectrum of $^{16}O_2$-preadsorbed catalyst recorded at 50 °C as background).

whether the superoxide species was indeed the active oxygen species formed on the SrF_2/Nd_2O_3 catalyst in the temperature range of OCM reaction, $^{16}O_2$ adsorption and $^{18}O_2$ isotopic exchange experiments were carried out in the *in situ* IR reaction cell. IR spectroscopy is particularly suitable for this type of investigation because the O–O stretching vibration mode in superoxide species is IR active, and the technique is well-suited for observing samples at the elevated temperatures.

After being treated with $^{16}O_2$ at 700 °C, a peak at 1118 cm^{-1}, which was ascribed to $(^{16}O–^{16}O)^-$ species, was observed on the SrF_2/Nd_2O_3 catalyst (Fig. 3). As the temperature of the cell was gradually decreased to 50 °C under $^{16}O_2$ atmosphere, the position of the $(^{16}O–^{16}O)^-$ peak was shifted to 1128 cm^{-1} (as shown in Fig. 3). The frequency shift with respect to temperature is a well-known phenomenon of solids relating to the lattice relaxation at high temperatures [5]. It was evident from these studies that O_2^- species was present on the SrF_2/Nd_2O_3 catalyst at considerably higher temperature under pure O_2 atmosphere.

The experiment of CO_2 adsorption was also performed at the indicated temperatures on the SrF_2/Nd_2O_3 catalyst. Before CO_2 was introduced, the sample was pretreated in vacuum in order to eliminate the carbonate species. Fig. 4 shows the IR spectra of the catalyst taken after 5 min exposure to CO_2 at the indicated temperatures. IR bands of surface carbonate species were observed at 860, 870, 1060, 1420, 1520 and 1760 cm^{-1} [18]. However, the peak at 1118 cm^{-1} was not found after exposure to CO_2. These results indicated that the peak at 1118 cm^{-1} was not from the surface carbonate. To further confirm the assignment of the IR bands shown in Fig. 3 to O_2^- species, $^{18}O_2$ isotopic exchange experiment was carried out.

When $^{18}O_2$ (97 atom % ^{18}O, Aldrich Chemical Company, Inc.) was introduced to the *in situ* IR cell at 700 °C, owing to the line broadening at high temperature, it was difficult to assign the positions of the band maxima exactly at 700 °C. The sample was then cooling down in the IR cell to 50 °C under $^{18}O_2$ atmosphere, and the corresponding spectrum was shown in Fig. 5. The result showed that the intensity of the peak at 1128 cm^{-1} decreased after the catalyst was exposure to $^{18}O_2$, and two new peaks were observed at 1094 and 1062 cm^{-1}. A calculation assuming a diatomic harmonic oscillator gave a band position at 1094 cm^{-1} for the $(^{18}O–^{16}O)^-$ superoxide species. Similarly, the $(^{18}O–^{18}O)^-$ superoxide species would be expected to have a band at 1060 cm^{-1}. Considering anharmonicity, the width of the band, and the uncertainty in assigning the position of the band maximum, the experimental wavenumber was in reasonable agreement with the calculated value. The result indicates that the bands of $(^{18}O–^{16}O)^-$ and $(^{18}O–^{18}O)^-$ species are detected on the catalyst after $^{18}O_2$ exchange experiment, and the peak at 1128 cm^{-1} can therefore be assigned to the O_2^- species confessedly.

In addition to the peak at 1128 cm^{-1}, a negative peak at 1172 cm^{-1} was also observed after $^{18}O_2$ exchange experiment (Fig. 5). We believe that the band of 1172 cm^{-1} can also be

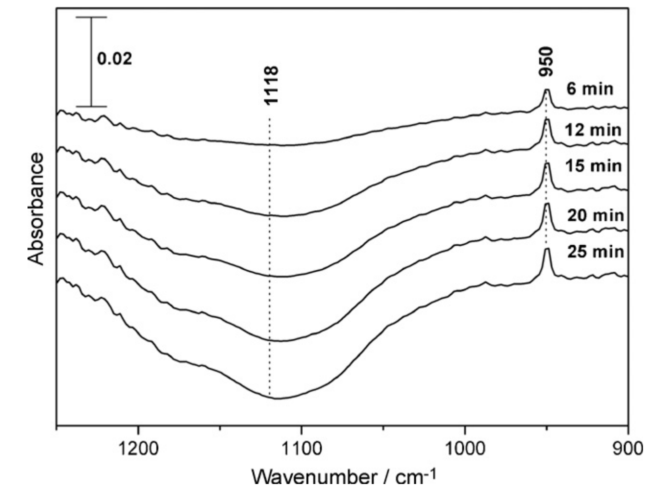

Fig. 6. *In situ* IR spectra for the reaction of CH_4 over O_2-preadsorbed SrF_2/Nd_2O_3 catalyst at 700 °C (with IR spectrum of the catalyst recorded immediately after the introducing of CH_4 as background).

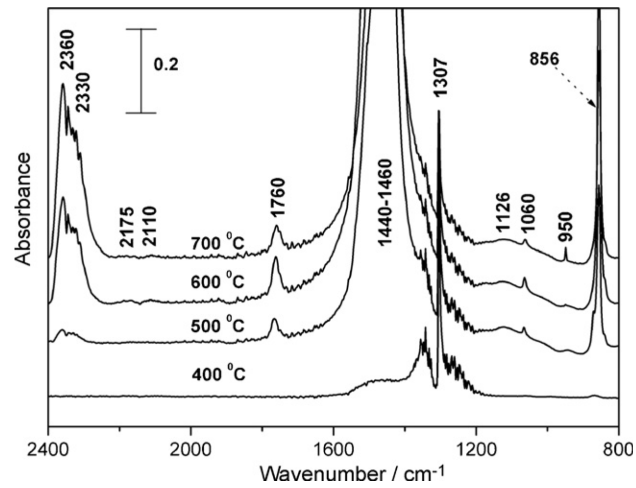

Fig. 7. IR spectra of the SrF_2/Nd_2O_3 catalyst recorded at the indicated temperatures in a stream of simulated OCM feed ($CH_4/O_2/Ar$ = 2/1/45) (with IR spectra of O_2-preadsorbed catalyst recorded at corresponding temperatures as backgrounds).

assigned to the superoxide species, which were located in a chemical environment different from that associated with 1128 cm^{-1}[2]. After $^{18}O_2$ isotopic exchange experiment, the decrease in the band at 1172 cm^{-1} $(^{16}O–^{16}O)^-$ should be accompanied by an increase in the intensity of the IR band of $(^{16}O–^{18}O)^-$ species. The theoretical value for the $(^{16}O–^{18}O)^-$ stretching mode is 1137 cm^{-1}. Such a band was, however, buried in the broad peak of 1128 cm^{-1}.

A sequential change in IR spectra was observed when CH_4 was introduced to the catalyst, which had been preadsorbed with O_2 at 700 °C followed by brief evacuation at the same temperature to remove the gas phase O_2. The absorbance around 1118 cm^{-1} was gradually decreased in intensity with the increase of reaction time. In the meantime, a band at 950 cm^{-1}, which was ascribed to the bent of vibration of CH_2 of gas phase C_2H_4 [19], gradually increased in intensity (see Fig. 6). If we plotted the changes of the IR absorbance at 1118 cm^{-1} (O_2^- species) 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 O_2^- species and the increase of IR band of gas phase C_2H_4 was observed. Since the reaction was performed under pure CH_4, O_2^- species was the only possible species on the catalyst to react with CH_4. A good correlation between the rate of consumption of O_2^- species and that of the formation of C_2H_4 indicated that O_2^- species was responsible for the conversion of CH_4 to form C_2H_4, therefore it was the active oxygen species for the OCM reaction over the SrF_2/Nd_2O_3 catalyst.

The IR spectra recorded in a stream of CH_4/O_2 on the O_2-preadsorbed SrF_2/Nd_2O_3 catalyst were shown in Fig. 7. At 400 °C, the IR bands of gas phase CH_4 (1307 cm^{-1}) and surface CO_3^{2-} (860 and 1450 cm^{-1}) [18] were observed. When the reaction temperature was raised to 500 °C, gas phase CH_4, surface CO_3^{2-} (856, 1060, 1440, 1460 and 1760 cm^{-1}) and gas phase CO_2 (2360 and 2330 cm^{-1}) were detected. Besides gas phase CH_4, surface CO_3^{2-} and gas phase CO_2, IR bands of gas phase CO (2110 and 2175 cm^{-1}) and C_2H_4 (950 cm^{-1}) [19] were observed at 600 °C on the working catalyst. With further increasing of the reaction temperature to 700 °C, the intensity of the band at 950 cm^{-1} increased. These results indicated that the OCM reaction did happen on the catalyst in the IR cell at the temperature above 600 °C. It should be noted that the IR band of O_2^- species did not decrease in intensity under the OCM reaction condition. These results indicate that O_2^- is the active oxygen species for OCM reaction over SrF_2/Nd_2O_3 catalyst.

4. Conclusion

SrF_2/Nd_2O_3 catalyst shows very low OCM activity in the absence of gas phase oxygen, indicating that lattice oxygen species on the catalyst contributed little to the yield of C_2 hydrocarbons. IR band of O_2^- at 1118∼1128 cm^{-1} was detected on the O_2-preadsorbed SrF_2/Nd_2O_3. The substitution of $^{18}O_2$ isotope for $^{16}O_2$ caused the band at 1128 cm^{-1} to shift to lower wavenumbers (1094 and 1062 cm^{-1}), consistent with the assignment of the IR band at 1128 cm^{-1} to the O_2^- species. At 700 °C, the O_2^- species was found to react with CH_4, leading to the formation of the gas phase C_2H_4. The O_2^- species was also observed on the SrF_2/Nd_2O_3 catalyst under working condition. Based upon these results, the superoxide species could not be overlooked as the active oxygen species for the oxidative coupling of methane on the SrF_2/Nd_2O_3 catalyst.

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