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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.

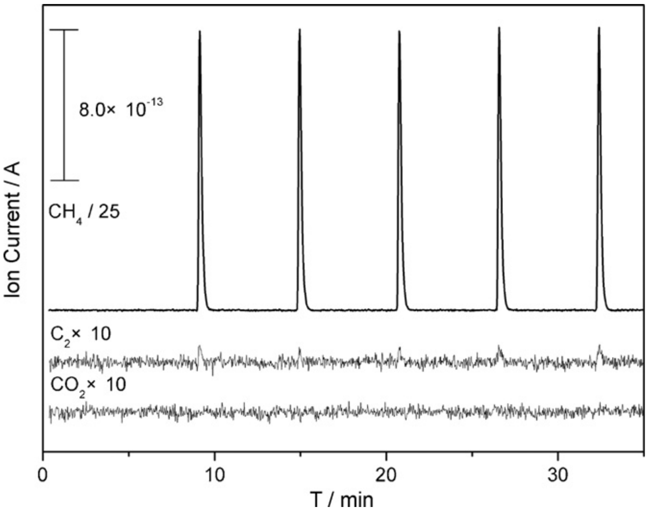

Fig. 1. Pulse reaction CH_4 over the He-pretreated SrF_2/Nd_2O_3 catalyst at 750 °C.

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

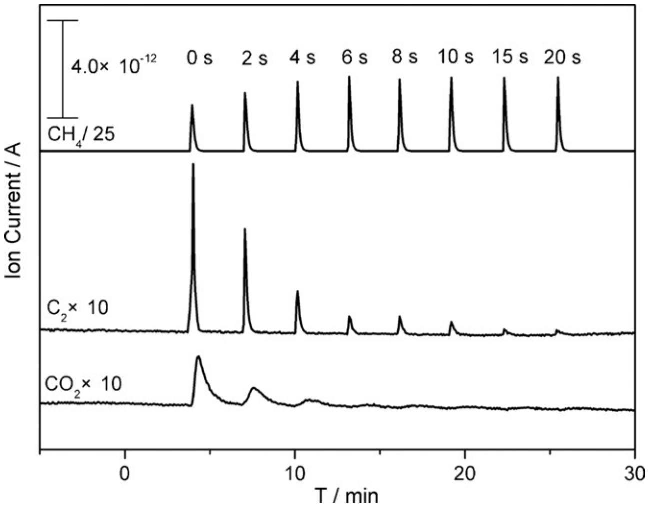

Fig. 2. Effect of time interval between O_2 and CH_4 pulses on the yields of OCM reaction products (C_2 hydrocarbons and CO_2) over SrF_2/Nd_2O_3 catalyst at 750 °C.