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The effect of oxygen vacancy of alkaline-earth metal Sr doped Sm₂Zr₂O₇ catalysts in the oxidative coupling of methane



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 A R T I C L E I N F O
 A B S T R A C T

 Keywords:
 A series of the Sr/Sm₂Zr₂O₇ catalysts with different Sr contents prepared by the coprecipitation method were used for OCM. The results revealed that the basicity and oxygen vacancies concentration on the surface of the Sm₂Zr₂O₇ catalysts were notably increased because of the addition of Sr. Activation of O₂ by the oxygen vacancies was responsible for the formation of C₂. Specifically, the 7.6% Sr/Sm₂Zr₂O₇ catalyst possessed 18.4% C₂ yield at 750 °C due to the presence of moderate basicity and the highest ratio of the oxygen species O₇ to lattice oxygen

1. Introduction

In the decade years, methane, as a main component of natural gas, is expected to be converted into different high-value chemicals, such as lower alcohols, olefins, and aromatics [1,2]. Among them, the oxidative coupling of methane (OCM, see Eq. (1)) to C₂ hydrocarbons, especially ethylene, is attractive route to convert natural gas directly [3]. Since Keller and Bhasin [4] published a paper on oxidative coupling of methane to ethylene in 1982, many researchers have done a lot of research on OCM [5].

$$CH4 + O2 \rightarrow C2H6 + C2H4 + COx + H2O$$
⁽¹⁾

It is well documented that the OCM reaction involves two typical steps, one is the heterogeneous catalytic step involving the activation of CH₄ on the catalyst surface to generate methyl (CH₃·) radicals [6], the other is combining two CH₃· radicals to form C₂H₆ molecule and then dehydrogenation to form C₂H₄ molecule [7,8]. The representative catalyst is Li/MgO with [Li⁺ O⁻] active site, where [Li⁺ O⁻] centers are formed to effectively generate CH₃· from CH₄ [9], but evaporation of Li from the bulk to the surface was observed for Li/MgO catalysts during the OCM reaction [10,11]. Wang et al.[12] reported a TiO₂-doped Mn₂O₃-Na₂WO₄/SiO₂ catalyst because the formation of MnTiO₃ triggered the low-temperature MnTiO₃ \leftrightarrow Mn₂O₃ chemical cycle for O₂ activation, thereby leading to a marked improvement of the low-

temperature activity [13].

O²⁻. More importantly, the 7.6%Sr/Sm₂Zr₂O₇ catalyst possessed high stability.

Mechanistic studies demonstrated that activating O_2 into desirable species on the catalyst surface is a pivotal step and OCM initiated by two possible active oxygen species were identified, namely: (I) molecular species such as O_2^- and O_2^{2-} for lanthanide oxides [14-16], and (II) dissociated oxygen species such as nucleophile ions O^- of the catalyst lattice. Schwach and coworkers [17] showed that polycrystalline MgO doped with Fe and Au can effectively activate O_2 to peroxide (O_2^{2-}) species, and thus enhanced the C_2 formation. According to the literature [18,19], for Ln₂Zr₂O₇ compounds, the surface electrophilic O_2^- species is a critical factor influencing the OCM reaction performance. Lattice oxygen anion on the perovskite oxides can be translated to the active sites for the OCM reaction [20]. It can be seen that the catalyst with oxygen vacancy can control the activation of oxygen and played an important role in OCM reaction [21,22].

The $A_2B_2O_7$ pyrochlore compounds generally own high thermal stability, intrinsic 8a oxygen vacancies and certain surface alkalinity, which is beneficial to OCM reaction [18,23]. The lattice defects change the adsorption and desorption properties of oxygen, which favors to increase the catalytic activity of pyrochlore catalysts for OCM [24,25]. If alkali and alkaline earth metals (such as Li, Na, Sr) are introduced to modify the catalyst, the increase of alkalinity will help to increase the number of active sites and inhibit the deep oxidation of methane to $CO_2[26,27]$. According to the literature [28], Mg²⁺, Ca²⁺, and Sr²⁺ into

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 CeO_2 as substitution ions on cerium created oxygen species on the oxide surface, leading to an abundance of electrophilic oxygen species on the catalyst surface. Song and co-workers [29] found that the addition of Sr changed the ratio of $(O_2^-+ O^-)/O^-$ and had a great influence on the performance of the catalyst. Therefore, the methane conversion and C_2 selectivity can be effectively improved.

In this study, we synthesized a series of $Sr/Sm_2Zr_2O_7$ catalysts with different Sr contents for OCM. The catalysts were characterized by using XRD, STEM, Raman, TPD, EPR and so on. It was found that the basicity and oxygen vacancy of the catalyst were changed in the case of Sr. The synergistic effect of the basicity and oxygen vacancy played an important role in the Sr/Sm_2Zr_2O_7 catalyst. Among the catalysts prepared, the 7.6%Sr/Sm_2Zr_2O_7 catalyst exhibited the best catalytic activity for OCM.

2. Experimental

2.1. Catalyst preparation

 $\rm Sm_2Zr_2O_7$ pyrochlore was synthesized by coprecipitation method using Sm (NO₃)₃·6H₂O (99.9%) and Zr (NO₃)₄·5H₂O (99.9%) as precursors. In a typical experiment, 15 mmol Sm (NO₃)₃·6H₂O and 15 mmol Zr (NO₃)₄·5H₂O were dissolved in 200 mL ddH₂O to form stable solutions. Then, the NH₃·H₂O solution (22–25 wt%) was slowly dripped in until the pH reached about 10. After that, the precipitate was filtered and thoroughly cleaned with ddH₂O. The resulting precipitates were dried overnight at 120 °C and then calcined in air at 800 °C for 4 h to obtain the Sm₂Zr₂O₇ catalyst.

The Sr/Sm₂Zr₂O₇ catalysts were prepared by using the incipient wetness method. Firstly, deionized water was added slowly to 1 g Sm₂Zr₂O₇ sample, then, white powder was continuously stirred during the dropping process to make the sample and water mixed evenly. The saturated water absorption of the sample was measured to be *m* g H₂O/g sample. Then, a certain amount of Sr (NO₃)₂ (99.9%) was weighed and dissolved in *m* g deionized water, and slowly dropped into 1 g Sm₂Zr₂O₇ sample. After the powder sample was mixed with Sr (NO₃)₂ solution, the Sm₂Zr₂O₇ samples were dried in vacuum oven at 60 °C for 12 h, then calcined at 800 °C for 4 h in an air atmosphere to obtain the x% Sr/Sm₂Zr₂O₇ catalysts.

2.2. Catalyst characterization

The crystalline structure of the catalyst was analyzed by Rigaku Ultima IV X-ray powder diffractometer, which was operated at 40 kV and 30 mA with a Cu target and K a irradiation. The scans were recorded in the 2 θ range from 10° to 90° with a step of 2°/min.

 $\rm N_2$ adsorption–desorption analyses were conducted at 77 K with ASAP 2420 physisorption analyser. And then the surface area was calculated by Brunauer-Emmett-Teller (BET) method.

The CO₂-TPD experiment was carried out on the Auto ChemII2920 chemisorption instrument. Typically, 50 mg sample was placed in a U-tube. Next, the sample was heated to 200 °C and then cooled to 50 °C and kept there for 1 h in flowing CO₂. After that, the sample was purged by a flowing He for 30 min. Subsequently, the CO₂ temperature programmed desorption was started from 50 °C to 800 °C in flowing He to get the CO₂ desorption amount.

The surface elements and oxygen species of the samples were analyzed by Thermo Fisher k-alpha X-ray photoelectron spectrometer with A1 KGC excitation source and accelerating voltage of 50 eV. The binding energy of each species was corrected by 284.6 eV of C 1 s.

EPR technique was used to characterize the oxygen vacancy and the oxygen species with electron paramagnetic activity. The sample was pretreated with 100 torr oxygen at 450 °C for 30 min, then cooled to room temperature and evacuated at the same temperature at 77 K in liquid N_2 , and then analyzed by EPR.

The HAADF-STEM images and elemental phase mapping were obtained by using a Hitachi s-4800 transmission electron microscopy (TEM) system that was equipped with a Brooke quanta X400 detector operated at 300 keV.

Raman spectra of the catalysts were measured using excitation wavelength of 514 nm in Renishaw in Via instrument. The measured Raman shift range was from 50 to 1600 cm^{-1} .

Thermogravimetric (TG) experiments were performed under 30 mL/min Air (20% $O_2+80\%\,N_2)$ with a heating rate of 5 $^\circ$ C/min on a Netzsch STA 449C thermoanalyzer.

2.3. Reaction performance

The OCM reaction was performed at atmospheric pressure in a quartz tube reactor with an inner diameter of 6 mm. In a typical experiment, 200 mg catalyst and the same weight of quartz sand was mixed into the reaction tube, and the reaction temperature was controlled by inserting the K-type thermocouple into the catalyst bed. The flow rates of CH₄, O₂ reactants and N₂ balance gas were controlled by three mass flow controllers and CH₄: O₂: N₂ volume ratio was 4:1:5. The total rate of the flow is 60 mL min⁻¹, respectively with GHSV 18000 mL h⁻¹ g⁻¹. The reactivity test generally started at 600 $^\circ C$ with a gap of 50 $^\circ C$ to 800 $^\circ C.$ In order to obtain stable kinetic data, all measurements were carried out at a certain temperature for 1 h. The mixed gas produced at the outlet of the reactor was cooled completely through the condenser to capture unreacted CH₄ and O₂. After drying, Inficon 3000 micro gas chromatograph was used to analyze H2, CO2, CO, C2H4 and C2H6 on-line automatically. In OCM reaction, methane conversion (X_{CH4}), C₂ selectivity (S_{C2}), CO_X selectivity (S_{COX}) and C₂ yield (Y_{C2}) were calculated as follows:

$$XCH4(\%) = \frac{(CH4)in - (CH4)out}{(CH4)in} \times 100$$
(2)

$$SC2(\%) = \frac{2(C2H4 + C2H6)}{2(C2H4 + C2H6) + CO + CO2} \times 100$$
 (3)

$$SCOX(\%) = \frac{COX}{2(C2H4 + C2H6) + CO + CO2} \times 100$$
 (4)

$$YC2(\%) = XCH4 \times SC2 \times 100$$
(5)

3. Results and discussion

3.1. Textural properties

As shown in Fig. 1a, the $Sm_2Zr_2O_7$ catalyst showed the diffraction peaks at $2\theta = 29.4^{\circ}$, 34.1° , 49.0° , and 58.3° , corresponding to the features of the (111), (200), (220), and (311) planes of $Sm_2Zr_2O_7$ (JCPDS 78–1291) respectively. However, no impurity peaks corresponding to single Sm_2O_3 or ZrO_2 oxide were detected. These results suggested that pure pyrochlore phase was successfully prepared in this study.

In the case of Sr/Sm₂Zr₂O₇ catalysts, the diffraction peaks at $2\theta = 30.5^{\circ}$, 43.7° and 54.3° were attributed to the presence of SrZrO₃ phase. As displayed in Fig. 1b, the diffraction peak intensity of SrZrO₃ phase for Sr/Sm₂Zr₂O₇ catalysts was gradually enhanced with the increase in Sr content, but that of Sm₂Zr₂O₇ phase was significantly decreased. Specifically, the diffraction peak intensity of Sm₂Zr₂O₇ phase for 7.6%Sr/Sm₂Zr₂O₇ catalyst was the same as that of and SrZrO₃ phase. However, the diffraction peak intensity of SrZrO₃ phase for the Sr/Sm₂Zr₂O₇ catalyst was obviously stronger than that of Sm₂Zr₂O₇ phase when the Sr content was increased to 15.4%. Therefore, the diffraction peak intensity of Sr content, while that of Sm₂Zr₂O₇ phase was decreased, which may be due to the substitution of Sr for Sm.

To further investigate the structural information, Raman spectra of the $Sr/Sm_2Zr_2O_7$ catalysts were recorded at $50-1600 \text{ cm}^{-1}$ in Fig. S1. For $Sm_2Zr_2O_7$, the F_{2e} modes at 395, 520, 601 cm⁻¹ were most likely due



Fig. 1. X-ray diffractograms of (a) fresh Sm₂Zr₂O₇ and Sr/Sm₂Zr₂O₇ catalysts, and (b) fresh Sm₂Zr₂O₇ and Sr/Sm₂Zr₂O₇ catalysts from 27.5° to 32°.

to the mixed Zr-O and Sm-O bond stretching with O-Zr-O bending vibrations [30]. Based on group theory, an ordered pyrochlore typically had six active Raman modes distributed as $A_{1g} + E_g + 4F_{2g}$ [31,32]. Only the F_{2g} peak was still detected with the disappearance of other bands, testifying that the Sm₂Zr₂O₇ pyrochlore phase was still present but become less ordered [33]. With Sr doping in Sm₂Zr₂O₇, the bands at 304 cm⁻¹ were most likely due to Sr-O bond vibration. This was consistent with the results of XRD.

As illustrated in Fig. 2, the distribution of Sm, Zr or O elements in the $Sm_2Zr_2O_7$ samples was very homogeneous, which proved the formation of homogeneous and chemically stable $Sm_2Zr_2O_7$ pyrochlore oxide. Similarly, the Sr was uniformly distributed on the surface of 7.6%Sr/ $Sm_2Zr_2O_7$ catalyst. Besides, according to the N₂-BET analysis results in Table S1, compared with the fresh catalysts, all the spent catalysts had only insignificant surface area drop, indicating that these Sr/Sm_2Zr_2O_7 catalysts were physically stable, which can stand the high temperature impact during the OCM reaction process.

3.2. CO2-TPD measurement

As shown in Fig. 3a, the temperature-programmed desorption (TPD) of CO_2 was performed. Based on the literature [34], there were three types of basic sites: the weak, medium and strong basic sites, which were

associated with desorption of CO2 at the temperatures 100 °C, 300–600 °C and >600 °C, respectively. These curves in Fig. 3a provided information on the strength of basic sites on the catalysts. For the Sm₂Zr₂O₇ catalyst, the desorption peak of CO₂ was at 500-600 °C. However, incorporation of Sr significantly altered the CO₂ desorption behavior compared to Sm₂Zr₂O₇. The low temperature CO₂ desorption was not increased, and CO_2 mainly desorbed between 300 $^\circ C$ and 800 °C. The 7.6%Sr/Sm₂Zr₂O₇ based materials showed a broad desorption peak around 400 $^\circ$ C, and the intermediate basic sites of the catalyst surface reached the maximum. When the Sr content exceeded 7.6 wt%, the desorption peak of CO₂ increased significantly at 600-800 °C. Whereas the strong alkaline sites were not conducive to the OCM reaction, which was easily to capture CO₂ and form stable carbonate [35]. The quantity of CO₂ evolved, as well as the temperatures of desorption indicated that doping the Sm₂Zr₂O₇ with Sr greatly affected the strength and the amounts of basic sites.

3.3. EPR study

As displayed in Fig. 3b, the oxygen vacancies of $Sm_2Zr_2O_7$ and $Sr/Sm_2Zr_2O_7$ were characterized by EPR. Firstly, the samples were pretreated with 100 Torr oxygen at 450 °C for 30 min, then cooled to room temperature and evacuated at the same temperature, finally analyzed by



Fig. 2. HAADF STEM mapping images of $Sm_2Zr_2O_7$ and $7.6\%Sr/Sm_2Zr_2O_7$.



Fig. 3. (a) CO2-TPD profiles of pure Sm2Zr2O7 and Sr/Sm2Zr2O7 catalysts; (b) EPR spectra of the Sm2Zr2O7 and Sr/Sm2Zr2O7 catalysts.

EPR. It can be observed from Fig. 3b that the $Sm_2Zr_2O_7$ catalysts showed two evident peaks at g = 1.997, 2.009. With increasing the loading content of Sr, the EPR signals were gradually strengthened, which indicated the concentration of oxygen vacancies was gradually increased. The results showed that the key step to prepare $Sr/Sm_2Zr_2O_7$ with the more concentration of oxygen vacancies was to change the amount of Sr (NO₃)₂ in the synthesis process. It was obvious that the peak intensity of g value for the catalysts followed the sequence of 7.6% $Sr/Sm_2Zr_2O_7 > 12.1\%Sr/Sm_2Zr_2O_7 > 15.4\%Sr/Sm_2Zr_2O_7 > 3.8\%Sr/$ $Sm_2Zr_2O_7 > Sm_2Zr_2O_7$, which was consistent with the performance of the catalyst.

3.4. XPS analysis of catalyst

As displayed in Fig. 4, the surface oxygen species on the catalyst were investigated by XPS analyses. The O 1s spectra of $Sm_2Zr_2O_7$ catalyst was fitted with three peaks, which were superoxide species O_2^- , carbonate

oxygen species CO₃²⁻, and lattice oxygen species O²⁻. According to the literature, the researchers [36,37] suggested that the electron deficient oxygen species O_2^- were responsible for the C_2 selectivity of OCM, whereas the lattice oxygen species O^{2-} promoted the complete oxidation of the reaction. Therefore, the ratio of electron deficient oxygen species to lattice oxygen (O_2^-/O^{2-}) can reflect the catalytic performance of OCM catalyst. The ratio of the peak intensities of the electron deficient species to lattice oxygen, O_2^- / O^{2-} can be calculated using the 80% Gaussian-20% Lorentzian peak shape (Fig. 4). In Table 1, as can be seen, the ratio of O_2^-/O^{2-} on the surface of $Sm_2Zr_2O_7$ catalyst was 0.08. With the increase of Sr content in Sr/Sm₂Zr₂O₇ catalysts, the ratio of $O_2^-/O_2^$ gradually increased. However, the ratio of O_2^-/O^{2-} decreased gradually when the content of Sr was increased from 7.6% to 15.4%. As can be seen from Fig. 4f, it should be noted that the 7.6%Sr/Sm₂Zr₂O₇ catalyst had the highest O_2^-/O^{2-} ratio and possessed the highest C_2 yield at 750 °C.



Fig. 4. XPS O 1s spectra of the $Sm_2Zr_2O_7$ and $Sr/Sm_2Zr_2O_7$ catalysts: (a) $Sm_2Zr_2O_7$, (b) 3.8%Sr/Sm_2Zr_2O_7, (c) 7.6%Sr/Sm_2Zr_2O_7, (d) 12.1%Sr/Sm_2Zr_2O_7, (e) 15.4% Sr/Sm_2Zr_2O_7, (f) C₂ yield at 750 °C vis O_2^{-}/O^{2-} ratios.

Table 1

Curve-Fitting results from XPS Data.

Catalyst	O 1s bindir	O 1s binding energies (eV)				
	1) O ²⁻	2) CO ₃ ^{2–}	3) O ₂			
Sm ₂ Zr ₂ O ₇	528.5	530.3	533.09	0.08		
3.8%Sr/Sm2Zr2O7	528.51	530.45	532.58	0.16		
7.6%Sr/Sm2Zr2O7	528.43	530.32	532.16	0.54		
12.1%Sr/Sm2Zr2O7	528.32	530.62	533.16	0.31		
15.4%Sr/Sm2Zr2O7	528.38	530.64	532.78	0.30		

3.5. Catalytic activity test

As shown in Table 2, the catalytic activity of $Sr/Sm_2Zr_2O_7$ catalysts for OCM performance was tested at 750 °C of reaction temperature. It was found that the addition of Sr into $Sm_2Zr_2O_7$ catalyst significantly increased the methane conversion, indicating the presence of promoting effect in Sr-modified $Sm_2Zr_2O_7$ catalysts [29]. Among the catalysts tested, the 7.6%Sr/Sm_2Zr_2O_7 exhibited the highest methane conversion of 39.1%. However, further increases in Sr loading notably decreased the methane conversion. Regarding to the product selectivity, the $Sm_2Zr_2O_7$ catalyst showed 21.7% C₂ selectivity at 750 °C. When the Sr species was added to the $Sm_2Zr_2O_7$ catalyst, the C₂ selectivity was remarkable enhanced. For example, in the case of 3.8%Sr/Sm_2Zr_2O_7 catalyst, the C₂ selectivity was increased to 36.3%. But it should be pointed out that the Sr/Sm_2Zr_2O_7 catalysts with high contents of Sr displayed similar C₂ selectivity, stabilizing at about 47%.

It can be observed from Table 2 that the C₂ yield of Sm₂Zr₂O₇ at 750 °C was only 3.6%. The reason was that the deep oxidation of methane produced a lot of CO and CO_2 , which deteriorated the C_2 selectivity. It had been proposed in the literature [35] that the formation of CO₂ reaction product took place on acid type as well as on amphoteric sites showing low affinity for CO₂. According to the results of CO₂-TPD in Fig. 3a, the amount of CO₂ desorption increased with the addition of Sr, indicating that there were more basic sites on the surface of the Sr/ Sm₂Zr₂O₇ catalysts than Sm₂Zr₂O₇ catalyst. When the Sr species was introduced into Sm₂Zr₂O₇ catalyst, the selectivity of CO and CO₂ decreased, thus the yield of C2 gradually increased. In addition, it was pointed out that the surface alkalinity was closely related to the chemisorption of oxygen anions such as O_2^- , O_2^{2-} , O^- and surface defects [35,38,39]. The results of XPS O1s curve fitting confirmed that the addition of Sr increased the ratio of O_2^-/O^{2-} on the surface of Sr/ Sm₂Zr₂O₇ catalyst.

It was generally believed that the higher the oxygen vacancy concentration on the surface of the catalyst, the more favorable it was for OCM to generate C_2 hydrocarbons. To encourage the formation of oxygen vacancies, the inclusion of a dopant can be used to introduce lattice defects, the nature of which varied with dopant and its concentration [40]. According to the results of EPR, the addition of Sr into Sm₂Zr₂O₇ catalyst increased oxygen vacancies concentration. The ability of materials to uptake oxygen was governed by the concentration of defect sites/vacancies in which an increase in vacancies resulted in an increase

Table 2

The performance of OCM reaction over $Sm_2Zr_2O_7$ and $Sr/Sm_2Zr_2O_7$ at 750 °C (Reaction conditions: 200 mg catalysts, CH4: O_2 : $N_2=4{:}1{:}5$ flow rate, WHSV = 18 000 mL h^{-1} g_{c1}^{-1}).

Catalyst	X _{CH4} (%)	S _{COx} (%)	S ₂ (%)	C ₂ H ₄ / C ₂ H ₆	C ₂ yield (%)
Sm ₂ Zr ₂ O ₇ 3.8%Sr/Sm ₂ Zr ₂ O ₇ 7.6%Sr/Sm ₂ Zr ₂ O ₇ 12.1%Sr/ Sm ₂ Zr ₂ O ₇ 15.4%Sr/ Sm ₂ Zr ₂ O ₇	16.7 27.4 39.1 32.9 25.3	78.3 63.7 53.0 52.0 53.4	21.7 36.3 47.0 48.0 46.6	0.3 0.7 1.1 0.9 0.7	3.6 9.9 18.4 15.8 11.8

in the oxygen uptake [41]. The role of oxygen vacancy was to activate oxygen into ideal species, so as to promote methane activation to methyl radical and subsequent oxidative dehydrogenation of ethane [13]. Therefore, the increase of oxygen vacancy content was helpful for the better OCM catalytic performance of the catalyst. Besides, according to XRD results, with the increase of Sr content, SrZrO₃ perovskite phase was formed. According to the OCM reaction performance of SrZrO₃ in Fig. S3, SrZrO₃ had little contribution to the reaction.

Among the Sr/Sm₂Zr₂O₇ catalysts tested, the 7.6%Sr/Sm₂Zr₂O₇ catalyst possessed the highest C₂ yield 18.4% at 750 °C of reaction temperature. The reason was that the 7.6%Sr/Sm₂Zr₂O₇ catalyst possessed the highest intrinsic oxygen vacancies concentration and the ratio of O_2^{-}/O^{2-} which were favorable for activation of CH₄ and production of C₂. According to the TGA results in Fig. S4, no obvious weight loss was detected in the spent 7.6%Sr/Sm₂Zr₂O₇ catalyst, suggesting no carbon formed. Therefore, it can be understood that the 7.6%Sr/Sm₂Zr₂O₇ catalyst displayed best OCM performance.

Fig. 5 displayed the catalytic performance for OCM on Sr/Sm₂Zr₂O₇ catalysts with a WHSV of 18000 mL h⁻¹ g⁻¹. By increasing the temperature from 600 °C to 800 °C, CH₄ conversion, C₂ product selectivity, and yield of Sr/Sm₂Zr₂O₇ catalysts gradually improved. Besides, with the increase of temperature, the selectivity of CO and CO₂ decreased gradually. The rise of temperature inhibited the deep oxidation of methane to CO and CO₂, which contributed to the formation of methyl radical and C₂ production. In all cases, X_{CH4}, S_{C2} and Y_{C2} showed a progressive increase with increasing reaction temperature up to 750 °C. The growth rate of the reaction selectivity and yield to C₂ decreased between 750 and 800 °C, most likely because of kinetic limitations. In a conventional packed bed continuous feed reactor, the upper limit of OCM yield was determined by the enthalpy of hydrogen adsorption of CH₄ and the enthalpy of oxygen dissociation [42].

3.6. Stability test

As displayed in Fig. 6, the Sm₂Zr₂O₇ and 7.6%Sr/Sm₂Zr₂O₇ catalysts was selected to study the stability. In the case of Sm₂Zr₂O₇ catalyst, the methane conversion and C₂ selectivity was remarkably decreased after 76 h time on stream. Conversely, the 7.6%Sr/Sm₂Zr₂O₇ catalyst had a relatively stable catalytic performance for OCM. After 100 h time on stream, the methane conversion and C₂ selectivity were still higher than 35% and 43% respectively. This indicated that the 7.6%Sr/Sm₂Zr₂O₇ catalyst possessed good stability, which may be due to the lattice distortion caused by the increase of oxygen vacancy concentration, thus improving the temperature stability of the sample.

4. Conclusion

In summary, the Sr-doped Sm₂Zr₂O₇ catalysts provided an enhanced activity and selectivity in combination with good stability for the OCM reaction. Incorporation of Sr²⁺ ions into Sm₂Zr₂O₇ as substitution ions on Sm created more oxygen species on the oxide surface, leading to an abundance of electrophilic oxygen species on the catalyst surface. OCM reaction performance of Sr/Sm₂Zr₂O₇ with different Sr contents was controlled by the relative amount of electrophilic oxygen species to lattice oxygen on the surface of the catalyst. Among them, the 7.6%Sr/ Sm₂Zr₂O₇ catalyst with moderate basicity and the highest oxygen vacancies concentration had the best catalytic performance for OCM with 39.1% methane conversion and 47.0% C2 selectivity at 750 $^\circ$ C. Through the stability test at 750 °C for 100 h, the 7.6%Sr/Sm₂Zr₂O₇ catalyst showed good stability. It was apparent that alkali-doped pyrochlore catalysts exhibited a wide range of catalytic activities upon optimization. This, therefore, represented a major aspect that was worthy of further detailed study. It was anticipated that further investigation of the solid state and surface chemistry of such doped pyrochlore compounds, together with relationship between active oxygen species and C₂ yield, should provide the basis for the identification of improved activity



Fig. 5. OCM reaction performance over the $Sm_2Zr_2O_7$ and $Sr/Sm_2Zr_2O_7$ catalysts: (a) CH_4 conversion, (b) C_2 selectivity, (c) $CO + CO_2$ selectivity, and (d) C_2 yield. Reaction conditions: 200 mg catalysts under 60 mL min⁻¹ CH_4 : O_2 : $N_2 = 4:1:5$ flow rate, WHSV = 18 000 mL h⁻¹ g_{cat}^{-1} .



Fig. 6. Stability test for C₂ yield, selectivity and CH₄ conversion (Reaction conditions: 200 mg catalysts under T = 750 °C, CH₄: O₂: N₂ = 4:1:5, WHSV = 18 000 mL h⁻¹ g_{cal}⁻¹).

catalysts containing an enhanced concentration of active surface sites.

CRediT authorship contribution statement

Jie Hao: Investigation, Writing - original draft. Fufeng Cai: Data curation, Writing - review & editing. Jiyang Wang: Software. Yu Fu: Writing - review & editing. Jun Zhang: Conceptualization, Writing - review & editing. Yuhan Sun: Conceptualization, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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