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Communication

$Ln_2Zr_2O_7$ compounds (Ln = La, Pr, Sm, Y) with varied rare earth A

sites for low temperature oxidative coupling of methane

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Graphical abstract



The replacement of Ln site with different rare earth cations alters the crystalline phases of $Ln_2Zr_2O_7$, which in turn influences the surface active oxygen and alkaline sites significantly. The abundance and the interaction of the two types of sites determine the OCM reaction performance.

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ABSTRACT

With the objective to develop catalysts having application potential for oxidative coupling of methane (OCM) at relatively lower temperature. A series of $Ln_2Zr_2O_7$ compounds with varied rare earth A sites have been prepared by a co-precipitation method. XRD and Raman have proved that pure $Ln_2Zr_2O_7$ compounds have been successfully prepared for all the catalysts. By decreasing the r_A/r_B ratio, their crystalline structure transform from an ordered pyrochlore ($La_2Zr_2O_7$) to a less ordered pyrochlore ($Pr_2Zr_2O_7$ and $Sm_2Zr_2O_7$) and eventually to a defective cubic fluorite phase ($Y_2Zr_2O_7$). H₂-TPR, O₂-TPD and XPS have testified that the amount of surface active O₂⁻ species follows the order of $La_2Zr_2O_7 > Pr_2Zr_2O_7 > Sm_2Zr_2O_7 > Y_2Zr_2O_7$, which is well consistent with the reaction performance, indicating that the abundance of surface O₂⁻ sites is a critical factor influencing the reaction performance. CO₂-TPD has demonstrated that a better catalyst generally possesses a larger amount of surface moderate alkaline sites, which is another factor to affect the reaction performance. It is concluded that the concerted interaction between the two types of surface active sites controls the reaction performance of the $Ln_2Zr_2O_7$ catalysts. In comparison with the state-of-the art Mn/Na₂WO₄/SiO₂, La₂Zr₂O₇, the best catalyst, exhibits much improved reaction performance below 750 °C

Keywords: Pyrochlore compounds Low temperature OCM A site substitution effects Surface superoxide sites Surface alkaline sites

Natural gas, which consists mainly of methane, is an important and cheap natural resource for the production of platform chemicals and as an energy source. Since 2010, several countries have made breakthroughs in the field of shale gas exploiting, thus a large amount of difficult-to-exploit methane can be extracted [1, 2]. Therefore, the utilization of methane has attracted even more attentions and interests. Oxidative coupling of methane (OCM) is regarded as an effective way to utilize methane with added-value, since it can transform methane into C₂ products, among which ethylene is a crucial platform organic compound for chemical industry. Up to now, several kinds of catalysts have been tried for this reaction [3-6]. It is commonly accepted that Mn/Na₂WO₄/SiO₂ is still the most promising catalyst for industrial application, on which 27% C₂ product yield can be obtained at 850 °C [7, 8]. Whereas, the industrially implement of this vital resource reaction is still limited by the one-way C₂ yield below 30%, which is regarded as the minimum requirement to industrialize this reaction economically and technically [9, 10]. Therefore, it is still of great necessity to develop more efficient catalysts for this reaction.

A₂B₂O₇ pyrochlore compounds generally own high thermal stability, intrinsic 8a oxygen vacancies and certain surface alkalinity, which fit to the active site requirements for a good OCM catalyst. Therefore, since late 1980s, some A₂B₂O₇ pyrochlores have been tested for this reaction preliminarily, and found to display certain reactivity [11-14]. But to date, only limited literatures are documented and people are still in short of deep understanding on the structure and reactivity relationship for the application of pyrochlore compounds for OCM reaction. Our former study has proved that La₂Ce₂O₇ displays very good reaction performance for OCM [15]. In particular, compared with the state-of-the-art Mn/Na₂WO₄/SiO₂ catalyst, it possesses much better low temperature reaction performance, though its highest C₂ product yield is still lower than that of Mn/Na₂WO₄/SiO₂. For instance, even at 650 °C, 15.3% C₂ yield can be achieved on La₂Ce₂O₇ demonstrates very potent resistance to sulfur and lead poisoning. It is revealed that the co-existence of both active electrophilic oxygen and alkaline sites and the synergistic interaction between them are the major reasons to control the reaction. With the target to develop better catalysts and gain deeper understanding on

structure and reactivity relationship, $Ln_2Zr_2O_7$ pyrochlore compounds (Ln = La, Pr, Sm and Y) with a fixed Zr^{4+} B site and varied rare earth A sites have been investigated for OCM reaction as a continued work. Indeed, it is found that the reactivity of the catalysts changes with the change of the A site cation. $La_2Zr_2O_7$ displays the best reaction performance among all the catalysts, on which 15.1% C₂ yield can be obtained even at 750 °C. Moreover, at low temperature region between 650-700 °C, it also exhibits much better reaction performance than Mn-Na₂WO₄/SiO₂. These finding could give people some new insights on how to develop OCM catalysts that can be operated at relatively lower temperature region. In addition, the bulk and surface structure changes of $Ln_2Zr_2O_7$ have been characterized by different means, and the relationship between the reactivity and structure has been elucidated.

The Ln₂Zr₂O₇ pyrochlore compounds have been prepared by a co-precipitation method. The detailed activity evaluation and characterization experiment procedures of the catalysts are described in the supporting information. For comparison purpose, a ZrO₂ sample was also prepared by precipitation method, and a Mn-Na₂WO₄/SiO₂ catalyst was prepared with a traditional impregnation method according to the references [18].

The reaction performance of the Ln₂Zr₂O₇ catalysts has been tested and shown in Fig. 1. Pure ZrO₂ displays very poor reaction performance for OCM, as evidenced by the very low methane conversion, C₂ product selectivity and yield in the whole tested temperature region. In comparison, all the Ln₂Zr₂O₇ catalysts exhibit significantly improved reaction performance, indicating the formation of pyrochlore structure generates the active sites required for OCM reaction. With the increasing of the reaction temperature from 650 °C to 750 °C, while the methane conversion improves, the C₂ product selectivity is nearly constant, proving that the C₂ yield increase is contributed mainly by the methane conversion change. In addition, the results imply that the C₂ product selectivity on the catalysts is not sensitive to the reaction temperatures. As shown in Fig. 1C, the C_2 product yields achieved over the catalysts follow the sequence of $La_2Zr_2O_7 > Pr_2Zr_2O_7 > Sm_2Zr_2O_7 \approx Y_2Zr_2O_7 > ZrO_2.$ Among all the catalysts, La_2Zr_2O_7 shows the best reaction performance, on which the highest C₂ yield around 15.1% can be achieved even at 750 °C. For clarification, the coupling product distribution on the catalysts collected at 750 °C is presented in Table S1 (Supporting information). It is revealed that over all the catalysts, the percentage of C_2H_6 is higher than that of C_2H_4 . However, $La_2Zr_2O_7$, the best catalyst in this study, owns the highest C_2H_4 selectivity in all the catalysts, testifying that this catalyst also has more abundant active sites favorable for C2H6 dehydrogenation.

For an OCM catalyst, the stability is an important parameter to estimate its application potential, since this reaction generally requires high temperature to proceed. Where upon, the long-term stability of La₂Zr₂O₇, the best catalyst, has been evaluated at 750 °C for 80 h. As demonstrated in Fig. 1D, the methane conversion, C₂ selectivity and yield remains constant during the time span without any decrease, testifying this catalyst possesses superior stability for the high temperature OCM process.

Currently, Mn-Na₂WO₄/SiO₂ is still the most promising OCM catalyst from the point of view of industrial application, on which the highest one way C₂ product yield close to 27% can be obtained at 850 °C [19]. However, this catalyst has very low activity below 700 °C. To reduce production cost, it is always desirable to find catalysts that can be operated at relatively lower temperatures region. As compared in Fig. S1 (Supporting information), La₂Zr₂O₇, the best catalyst in this study, displays much better reaction performance than Mn-Na₂WO₄/SiO₂ under the same condition in the temperature region of 650~700 °C. For instance, even at 650 °C, 5.4% C₂ yield has already been achieved over La₂Zr₂O₇, but the reaction over Mn-Na₂WO₄/SiO₂ is just started with an extremely low C₂ yield of 0.2%. At 700 °C, the C₂ yield over La₂Zr₂O₇ becomes about 1% lower than that over Mn-Na₂WO₄/SiO₂. In brief, Ln₂Zr₂O₇ pyrochlores possess surface active sites that can match the requirements of OCM reaction. With suitable element combination, La₂Zr₂O₇ and Pr₂Zr₂O₇ catalysts having outstanding low temperature reaction performance and high stability has been attained. This implies that with further optimization, pyrochlore type of OCM catalysts that can function at lower temperature could be eventually obtained.

The phase compositions of the catalysts have been analysed by XRD, with the patterns shown in Fig. 2. Pure ZrO₂ shows the typical diffraction feature of monoclinic phase structure, as also testified by the lattice parameters in Table S2 (Supporting information). In contrast, for all the Ln₂Zr₂O₇ catalysts, cubic pyrochlore is the only detectable crystalline phase, no any impurity diffraction belonging to the individual oxides can be observed, indicating that pure pyrochlore phase has been successfully synthesized. The intensive peaks observed indicate that all the smaples are well crystallized. With the decreasing of r_A/r_B ratio from La₂Zr₂O₇ to Y₂Zr₂O₇, the peak position of the Ln₂Zr₂O₇ pyrochlores shifts gradually to higher 2 θ angles, as dispalyed

in the enlarged Fig. 2B, and the side length becomes smaller, indicating the presence of cell shrinking effect caused by the decrease of the radii of the A site cations. It was reported formerly that with the decreasing of the r_A/r_B ratio, the crystalline structure of the samples could transform from ordered pyrochlore ($La_2Zr_2O_7$) to less ordered pyrochlore ($Pr_2Zr_2O_7$ and $Sm_2Zr_2O_7$) and eventually to defective cubic fluorite phase ($Y_2Zr_2O_7$) [20]. As a result, the surface oxygen property related to the 8a intrinsic oxygen vacancies could be changed, which subsequently influence the OCM reaction performance [14]. The XPS and O₂-TPD results indeed testify the change of the oxygen property, which will be discussed in more detail in the following sections.

The texture properties of the Ln₂Zr₂O₇ catalysts have also been analysed by N₂ adsorption-desorption, with the isotherms and pore size distribution profiles displayed in Fig. S2 (Supporting information). Pure ZrO₂ depicts a typical type IV isotherm with an H1-type hysteresis loop, and its pore size distribution profile shows a wide peak, which corresponds to an average pore size of 21 nm (Table S2), implying the presence of inter-particle pores. In contrast, all the Ln₂Zr₂O₇ catalysts possess also a typical type IV isotherm but with an H2-type hysteresis loop, indicating that they have the same texture structure with each other but which is different from that of the individual ZrO₂. However, the quantification results in Table S2 manifest that both Sm₂Zr₂O₇ and Y₂Zr₂O₇ have much higher pore volumes than that of La₂Zr₂O₇ and Pr₂Zr₂O₇. In addition, the surface areas of the former two catalysts are higher than the latter two. Theoretically, the higher pore volumes and surface areas are generally favourable for the reactants diffusion and contacting with the surface active sites, which might promote the reaction performance of the catalysts. Whereas, as depicted in Fig. 1, the reaction performance Sm₂Zr₂O₇ and Y₂Zr₂O₇ is much worse than La₂Zr₂O₇ and Pr₂Zr₂O₇, which indicates that the texture structure change is not the crucial factor to affect the OCM reaction performance on the catalysts.

Raman technique was adopted to investigate the structure change of Ln₂Zr₂O₇ compounds, with the profiles manifested in Fig. S3 (Supporting information). It is particularly noted here that the XRD patterns in Fig. 2 have indicated that all the Ln₂Zr₂O₇ samples are well crystallized due to high temperature calcination. Therefore, it is rational to propose that the change of Raman spectra can be ascribed to the phase change instead of crystalinity change of the samples. It is noticed that all the Ln₂Zr₂O₇ catalysts show complete different spectra from pure ZrO₂, which confirms the structure difference observed by XRD. A well-ordered cubic A₂B₂O₇ pyrochlore generally has six typical Raman peaks at 299, 395, 500, 520, 601 and 750 cm⁻¹[21, 22]. The Raman peaks at 520 cm⁻¹ is assigned to A_{1g} mode related to the O-B-O banding vibrations. The most intense Raman band at about 299 cm⁻¹ is assigned to E_g mode. Moreover, the Raman band at around 395, 500, 601 and 750 cm⁻¹ can be assigned to the F_{2g} mode. It is well known that Raman spectroscopy can provide explicit information to distinguish between a pyrochlore, biphasic mixture and a defect-fluorite material [23]. The presence of all the six Raman bands in the profile of La₂Zr₂O₇ testifies the formation of ordered pyrochlore phase in its bulk. In contrast, on the profiles of Pr₂Zr₂O₇ and Sm₂Zr₂O₇, only the strongest F_{2g} peak is still detected with the disappearance of other bands, testifying that the pyrochlore phase is still present but become less ordered [24]. On the profile of $Y_2Zr_2O_7$, all the Raman bands assigning to pyrochlore phase disappear completely, indicating the complete transformation of the crystalline phase. As discussed above for the XRD results, it is believed that a defective cubic fluorite phase could have eventually been formed in this sample.

H₂-TPR was used to investigate the redox properties of the Ln₂Zr₂O₇ catalysts, with the profiles shown in Fig. S4A (Supporting information). For all of the Ln₂Zr₂O₇ catalysts with different A site cations, a small reduction peak is observed in the temperature region of 300-500 °C, as better indicated by the enlarged profiles in Fig. S4B (Supporting information). It is noted that pure ZrO₂ shows also a minute reduction peak at ~345 °C. Theoretically, if all the lattice oxygen of a Ln₂Zr₂O₇ compound can be reduced, the O/(Ln+Zr) atomic ratio should be 1.75. However, the quantified results in Table S3 prove that on all the catalysts with varied A sites, the ratios are much lower than 1.75, proving the peak can be assigned to the reduction of a very small amount of surface deficient oxygen species. In addition, the oxygen amount follows the order of La₂Zr₂O₇ > Pr₂Zr₂O₇ > Sm₂Zr₂O₇ = Y₂Zr₂O₇, which is nearly in accordance to the reaction performance of the catalysts. Therefore, it is reasonable to believe that the amount of surface active oxygen sites could be important for the reaction performance.

To further understand the oxygen property of the catalysts, O₂-TPD experiments were also conducted for all the Ln₂Zr₂O₇ catalysts, with the profiles shown in Fig. S5 (Supporting information). Two groups of desorption peaks are observed for all the Ln₂Zr₂O₇ samples and the pure ZrO₂. The low temperature peak at ~100 °C, which is labbled as α peak, is assigned to the desorption of loosely bonded surface oxygen species [25]. The broad desorption peak above 200 °C, which is labelled as β peak, is obviously composed of two overlapped peaks. Therfore, it was deconvoluetd into two peaks at ~300 and ~410 °C, respectively. The peak at ~300 °C may correspond to the desorption of surface electrophilic oxygen species formed by the inducing

of the inherent 8a oxygen vacancies in the lattice [26], and the peak at ~410 °C could be assigned to the desorption of surface mobile lattice oxygen [27]. Since the β group oxygen sites are close to the OCM reaction temperature range, we hence believe that they should contribute mainly to the reaction. As quantified in Table S4 (Supporting information), the amount of β group oxygen sites follows the sequence of La₂Zr₂O₇ > Pr₂Zr₂O₇ > Sm₂Zr₂O₇ > Y₂Zr₂O₇, which is in line with the H₂-TPR results. It is worth noting here that La₂Zr₂O₇ possesses the largest amount of surface active oxygen species, thus having the highest OCM performance among all the catalysts. This testifies again that the amount of surface active oxygen species is an important factor to decide the OCM reaction performance.

To further investigate the impact of A site change on the surface oxygen property of the Ln₂Zr₂O₇ catalysts, XPS experiments were also performed, with the spectra shown in Fig. 3. For all the Ln₂Zr₂O₇ catalysts, including the comparison pure ZrO₂, two overlapped O 1s peaks are obviously observed. Fig. S6 (Supporting information) proves that carbonate is formed on the surface of all the catalysts, as indicated by the XPS peak at ~288.9 eV. Therefore, part of the surface oxygen could be contributed by surface carbonates, which is generally inert for any oxidation reaction [28]. Based on this, the O1s spectra of the samples are deconvoluetd into three peaks according to the typical binding energies. The major peak at ~529.0 eV can be assigned to surface lattice O²⁻, the peak at ~531.0 eV can be ascribed to oxygen species related to surface carbonates, and the peak at ~532.8 eV can be attributed to surface superoxide O₂⁻ cations [28]. Former studies have substantiated that superoxide O₂⁻ sites are important for the activation of methane molecules and the selective formation of coupling products during OCM reaction [29, 30]. Therefore, the surface superoxide O₂⁻ site percentages of the catalysts are quantified and listed in Table S5. Apparently, the percentages of the Ln₂Zr₂O₇ > Y₂Zr₂O₇ > Y₂Zr₂O₇ > Y₂Zr₂O₇ which is well consistent with the H₂-TPR and O₂-TPD results.

For better understanding, the surface superoxide O_2^- percentages of the catalysts and C_2 product yields achieved at 650, 700 and 750 °C are plotted in Fig. 3F. It is apparent that with the decreasing of the superoxide O_2^- percentages in the order of La₂Zr₂O₇ > Pr₂Zr₂O₇ > Sm₂Zr₂O₇ > Y₂Zr₂O₇, the C₂ product yields degrade with the same order. This strongly demonstrates again that the amount of surface active electrophilic oxygen species is a major factor to decide the OCM reaction performance of the La₂Zr₂O₇ catalysts.

It is particularly noted here that although ZrO_2 also possesses a small amount of surface active oxygen species, our reaction results in Fig. 1 have testified that it displays very poor reaction performance for OCM, with the formation of negligible amount of C_2 product due to the short of surface alkaline sites. Many previous studies have testified that both surface active electrophilic oxygen species and alkaline sites are indispensible for OCM reaction. The surface alkaline sites are active for methane molecules adsorption and activation, and the surface electrophilic oxygen sites are responsible for the formation of coupling products, although sometimes they are also involved into methane activation [29]. Our former work has also testified that the concerted interaction between surface alkaline sites and active oxygen species indeed controls the OCM reaction performance of a catalyst [31].

According to this discussion, the amount of surface alkaline sites could correlate to the OCM reaction performance of a catalyst intimately. Therefore, to probe the effect of the differed A sites on the surface alkalinity of the Ln₂Zr₂O₇ catalysts, they are subjected to CO₂-TPD analysis. As manifested by Fig. 4, pure ZrO₂ displays no observable CO₂ desorption in the tested temperature region, indicating the absence of alkaline sites on its surface, which explains its very low OCM activity with the formation of negligible amount of C₂ products. In contrast, all Ln₂Zr₂O₇ catalysts depict two CO₂ desorption peaks. The first peak emerges in the temperature region of 50-200 °C, which is assigned to weak surface alkaline sites. The second peak emerges in the temperature range of 200-500 °C, which is assigned to alkaline sites with moderate strength. It is worth noting here that the alkaline sites with moderate strength are particularly beneficial to the selective formation of C₂ coupling products [15, 31-33]. Therefore, the CO₂ desorption amount is quantified in Table S6 for all the catalysts, which indicates that the amount of the moderate alkaline sites of Ln₂Zr₂O₇ compounds affects not only its surface active oxygen amount, but also its surface alkaline sites quantity, which could eventually influencing the reaction performance of the catalysts.

For clarification, the amount of moderate surface alkaline sites is plotted against the C₂ product yields achieved at 650, 700 and 750 °C in Fig. 4B. It is typically observed that the C₂ product yields on the catalysts increase with the increasing of the moderate alkaline sites amount. Whereas, though $Y_2Zr_2O_7$ possesses a larger amount of surface moderate alkaline sites than $Sm_2Zr_2O_7$, it displays similar reaction performance to the latter. This proves again that surface alkalinity is not the only factor deciding the reaction

performance. Taking into account of the surface oxygen property explored by H₂-TPR, O₂-TPD and XPS, it is rational to propose that both the surface oxygen species and alkaline sites are critical for OCM reaction, and their concerted interaction determines the reaction performance. By tuning the combination of A and B sites of A₂B₂O₇ compounds, catalysts with suitable amount of both active sites could be achieved, thus developing catalysts having industrialization potential for OCM.

In conclusion, with the objective to develop catalysts having application potential for OCM, especially at relatively lower temperature region. A series of $Ln_2Zr_2O_7$ compounds with a fixed Zr^{4+} cation B sites but with varied rare earth A sites (Ln = La, Pr, Sm and Y) have been prepared by a co-precipitation method in this study. The surface and bulk properties of the catalysts have been characterized by different means, and correlated with their reaction performance.

- (1) XRD and Raman results have proved that pure Ln₂Zr₂O₇ compounds have been successfully prepared for all the catalysts. With the decreasing of the r_A/r_B ratio, the crystalline structure of the compounds transform from an ordered pyrochlore (La₂Zr₂O₇) to a less ordered pyrochlore (Pr₂Zr₂O₇ and Sm₂Zr₂O₇) and eventually to a defective cubic fluorite phase (Y₂Zr₂O₇).
- (2) As testified by H₂-TPR, O₂-TPD and XPS, the amount of surface active superoxide O₂⁻ species follows the order of La₂Zr₂O₇ > Pr₂Zr₂O₇ > Sm₂Zr₂O₇ > Y₂Zr₂O₇, which is well consistent with the reaction performance of the catalysts, and indicates that the abundance of surface active oxygen sites is a critical factor influencing the reaction performance. CO₂-TPD results have demonstrated a better catalyst generally possesses a larger amount of surface moderate alkaline sites, which is another factor to affect the reaction performance.
- (3) It is concluded that the concerted interaction between the two types of surface active sites controls the reaction performance of the Ln₂Zr₂O₇ catalysts. La₂Zr₂O₇ possesses the largest amount of both kinds of surface sites, hence displaying the optimal reaction performance among all the catalysts. In comparison with the state-of-the art Mn/Na₂WO₄/SiO₂, La₂Zr₂O₇ exhibits much better reaction performance at a low temperature region (<750°C). Therefore, the information included in this study could give people some new insights on how to develop improved OCM catalysts that can be operated at relatively lower temperatures.</p>

Acknowledgements

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Fig. 1. Reaction performance of the $Ln_2Zr_2O_7$ catalysts. (A) CH_4 conversion, (B) C_2 product selectivity, (C) C_2 product yield, (D) Stability test at 750 °C over $La_2Zr_2O_7$ catalyst.



Fig. 2. XRD patterns of the $Ln_2Zr_2O_7$ catalysts.



Fig. 3. Analyzing surface oxygen property of the $Ln_2Zr_2O_7$ catalysts by XPS. (A) O 1s of $La_2Zr_2O_7$, (B) O 1s of $Pr_2Zr_2O_7$, (C) O 1s of $Sm_2Zr_2O_7$, (D) O 1s of $Y_2Zr_2O_7$, (E) O 1s of ZrO_2 , (F) the relationship between surface active oxygen amount and C_2 product yields.



Fig. 4. CO₂-TPD profiles of the Ln₂Zr₂O₇ catalysts.