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Ce_{0.45}Zr_{0.45}Y_{0.07}La_{0.03}O_{1.95}/La-Ba-Al₂O₃质量比对整体式铁基催化剂上稀薄甲烷燃烧的影响

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摘要: 采用共沉淀法和胶溶法分别制备了高性能的储氧材料 Ce_{0.45}Zr_{0.45}Y_{0.07}La_{0.03}O_{1.95} (OSM)和耐高温高比表面的 La-Ba-Al₂O₃, 并以它们为载体, 制备了一系列整体式铁基催化剂. 考察了该系列催化剂对甲烷稀薄燃烧的催化性能. 并用低温 N₂吸附-脱附, 储氧量(OSC)测试, X射线衍射(XRD)和 H₂程序升温还原(H₂-TPR)等测试手段考察了不同 Ce_{0.45}Zr_{0.45}Y_{0.07}La_{0.03}O_{1.95}/La-Ba-Al₂O₃ 质量比对催化剂特性的影响. 活性测试结果表明, 当 Ce_{0.45}Zr_{0.45}Y_{0.07}La_{0.03}O_{1.95}/La-Ba-Al₂O₃质量比为 1:1 时新鲜和老化催化剂的活性均最好, 新鲜催化剂可在 50000 h⁻¹的高空速条件下使含量为 1% (体积分数)的甲烷在 446 °C 起燃, 553 °C 完全转化; 低温氮气吸附-脱附测试结果和 H₂-TPR 表明, 不同的 Ce_{0.45}Zr_{0.45}Y_{0.07}La_{0.03}O_{1.95}/La-Ba-Al₂O₃ 质量比使催化剂表现出不同的织构性能和还原性能; XRD 测试结果表明, OSM 以均一固溶体存在, Fe 高度分散在载体上. 综合以上表征手段得出: 合适的 Ce_{0.45}Zr_{0.45}Y_{0.07}La_{0.03}O_{1.95}/La-Ba-Al₂O₃质量比导致催化剂具有优异的稀薄甲烷催化燃烧活性和热稳定性.

关键词: Fe₂O₃基整体式催化剂; OSM/La-Ba-Al₂O₃质量比; 稀薄甲烷催化燃烧

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Effect of Ce_{0.45}Zr_{0.45}Y_{0.07}La_{0.03}O_{1.95}/La-Ba-Al₂O₃ Mass Ratio on the Activity of Fe-Based Monolithic Catalysts for the Combustion of Thin Methane

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Abstract: Ce_{0.45}Zr_{0.45}Y_{0.07}La_{0.03}O_{1.95}, an oxygen storage material (OSM), and La-Ba-Al₂O₃ have been prepared by co-precipitation and peptization, respectively, to be used as supports for Fe₂O₃ catalysts. The Fe₂O₃ catalysts were obtained by impregnation methods and then coated on the monolith. The catalytic combustion of low concentration (thin) methane was investigated over the prepared catalysts. The effect of the OSM/La-Ba-Al₂O₃ mass ratio on the physicochemical properties of the catalysts was investigated using nitrogen adsorption-desorption, oxygen storage capacity (OSC) measurements, X-ray diffraction (XRD), and H₂-temperature-programmed reduction (H₂-TPR). The highest catalytic activity of both fresh and aged Fe₂O₃ catalysts for thin methane combustion was observed when the mass ratio of OSM/La-Ba-Al₂O₃ was 1:1. At this OSM/La-Ba-Al₂O₃ mass ratio, methane started to convert at 446 °C and completely converted at 553 °C, with 1% (volume fraction) CH₄ and a gas hourly space velocity (GHSV) of 50000 h⁻¹. The

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Fe-based monolithic catalysts with different mass ratios of OSM to La-Ba-Al₂O₃ had different specific surface areas and reducibilities. XRD results showed that OSM existed in uniform solid solution and Fe₂O₃ was well dispersed on the binary supports. Based on the characterizations, the high catalytic activity and thermal stability of the catalysts can be attributed to the proper coordination of OSM and La-Ba-Al₂O₃ for thin methane combustion.

Key Words: Fe₂O₃ based monolithic catalyst; OSM/La-Ba-Al₂O₃ mass ratio; Catalytic combustion of thin methane

1 Introduction

The catalytic combustion of methane has attracted considerable attention in recent years. Good catalysts must be able to totally convert methane in low concentration and at high gas velocity, and should also have high thermal stability because of the high temperatures under reaction conditions. Initially, the noble metal catalysts that were studied showed high catalytic activities but had poor thermal stability and were expensive due to the sintering of the active sites of the catalyst.^{1,2} As an alternative, transition metal oxide catalysts have been studied.³⁻⁵ At present, the research on Fe₂O₃-based catalysts for the catalytic combustion of methane has mainly focused on perovskite^{6,7} and hexaaluminate.^{8,9} In addition, Fe₂O₃ is widely applied as a catalyst promoter.^{10,11} However, only a few studies on the catalytic combustion of thin methane on supported Fe₂O₃-based monolithic catalysts have been reported.^{12,13}

One of the Fe₂O₃ catalyst supports is γ -Al₂O₃, which is the most common support for monolithic catalysts. The specific surface area and pore volume of γ -Al₂O₃ decrease in water-thermal conditions and at high temperatures due to the formation of α -Al₂O₃. However, doping γ -Al₂O₃ with alkali, alkaline-earth, and rare-earth metals can increase the thermal stability and suppress the decrease in specific surface area of the catalysts.¹⁴⁻¹⁶

Another common Fe₂O₃ catalyst support is CeO₂-ZrO₂ oxygen storage material, which is widely used in the three-way catalysts of gasoline vehicles. CeO₂-ZrO₂ solid solutions not only disperse the active components but also improve the catalytic activity, owing to their oxygen storage capability. However, when methane combusts the local temperature of the catalyst surface can become very high, resulting in sintering of the CeO₂-ZrO₂ solid solution which has poor thermal stability. Turko,¹⁷ Zhang,¹⁸ Lv¹⁹ *et al.* found that CeO₂-ZrO₂ solid solutions doped with La³⁺, Y³⁺, Ba²⁺, Nd³⁺, Pr³⁺, or Sm³⁺ had large oxygen storage capacities (OSCs), large specific surface areas, and high thermal stabilities.

Liu *et al.*²⁰ studied Fe₂O₃/Ce_{0.67}Zr_{0.33}O₂-Al₂O₃ catalysts with a mass ratio of Ce_{0.67}Zr_{0.33}O₂ to Al₂O₃ of 1:2 for methane catalytic combustion at GHSVs around 15000 h⁻¹. When the loading amount of Fe₂O₃ was 8% (w, mass fraction), the catalyst showed the highest activity, the best temperature specialty, and the highest thermal stability. However, the catalyst was not studied at high gas velocities.

In our early work, Fe/Ce_{0.45}Zr_{0.55}La_{0.05}O_{1.95}-Al₂O₃ monolithic catalysts were prepared for the catalytic combustion of thin methane at a GHSV of 50000 h⁻¹,²¹ and the catalyst with $x=0.7$ showed the highest activity. Using this catalyst, methane started to convert at 465 °C and completely converted at 615 °C. We have also studied Fe-based catalysts supported on Ce_{0.35}Zr_{0.55}Y_{0.07}La_{0.03}O_{1.95} (OSM) and La-Al₂O₃,²² and found that methane started to convert at 474 °C and completely converted at 565 °C on the monolithic catalyst of Fe/OSM + La-Al₂O₃ with a GHSV of 50000 h⁻¹. However, the catalytic activity and thermal stability of the catalysts need to be improved.

In this work, to improve the thermal stability, Ba has been introduced into La-Al₂O₃ to form La-Ba-Al₂O₃, and the Ce ratio in the compound oxide CeZrYLaO has been increased to improve its oxygen storage capacity. Fe₂O₃ monolithic catalysts coated by mixed catalysts of Fe/Ce_{0.45}Zr_{0.45}Y_{0.07}La_{0.03}O_{1.95} and Fe/La-Ba-Al₂O₃ were prepared for the catalytic combustion of methane with 1% (volume fraction) CH₄ at a GHSV of 50000 h⁻¹. The effect of the OSM/La-Ba-Al₂O₃ mass ratio on the physicochemical properties of the catalysts was investigated by nitrogen adsorption-desorption, OSC measurements, XRD, and H₂-TPR.

2 Experimental

2.1 Catalyst preparation

Ce_{0.45}Zr_{0.45}Y_{0.07}La_{0.03}O_{1.95} was prepared by co-precipitation and was then calcination at 600 °C for 3 h. Fresh La-Ba-Al₂O₃ (5% (w) La₂O₃, 5% (w) BaO) was prepared by peptization and then calcination at 1000 °C for 3 h. All aged samples were calcined at 1050 °C for 5 h in an air atmosphere.

The catalysts were prepared by wet impregnation. The loading of Fe₂O₃ was 8% (w). In a typical preparation, the support was impregnated with the desired amount of Fe(NO₃)₃ solution. The resulting powder was dried at 120 °C for 2 h and calcined in air at 600 °C for 2 h. The dried powder was then ball-milled with distilled water to form a slurry. The slurry was coated on cordierite (62 cell · cm⁻², $\Phi=9$ mm, $L=24$ mm) and the excess slurry was blown off. Finally, the catalyst was dried and calcined in air at 600 °C for 2 h to give the fresh catalyst. Catalysts were prepared with Fe/(OSM + La-Ba-Al₂O₃($m_1:m_2$)) ratios of $m_1:m_2=0:1$, 1:1, 2:1, 1:2, 1:0 (mass ratio of OSM to La-Ba-Al₂O₃). The aged samples were obtained by calcining the fresh catalysts in air at 1050 °C for 5 h. The catalyst load-

ing amount of all the samples on cordierite was 140 mg·mL⁻¹.

2.2 Activity measurements

Catalytic activity tests were carried out on the monolithic samples in a multiple fixed-bed continuous flow microreactor with a gas mixture composed of 1% CH₄, 4% O₂, and 95% N₂. The GHSV was 50000 h⁻¹. Before the reactions, all of the catalysts were treated at 600 °C for 1 h in a N₂ atmosphere regulated by a mass-flow controller. The reaction temperature range was 450–800 °C. The reactants and products were separated by a carbon molecular sieve 601 column (stainless steel, 120 °C) through pulse injection with an entrance temperature of 100 °C and detected by an on-line GC-2000 II gas chromatography equipped with a thermal conductivity detector (TCD), using H₂ as the load gas with a flow speed of 50 mL·min⁻¹ at 120 °C.

2.3 Characterization of the catalysts

The specific surface area and pore size of the catalysts and supports were determined by N₂ adsorption-desorption at -196 °C on a ZXF-06 automatic surface analyzer (Xibei Chemical Institute, China). Before the measurements, the samples were degassed in vacuum at 350 °C for 1 h.

The crystal structures of the samples were determined by XRD on a Netherland Phillip X'Pert Por MPD diffractometer with Cu K_α radiation ($\lambda = 0.15406$ nm) at 40 kV and 40 mA. The XRD data were recorded for 2θ values from 25° to 80° at an interval of 0.03° and the results were processed using Jade-6.

H₂-TPR experiments were performed on a quartz tubular microreactor, equipped with a TCD. A 100 mg sample was pretreated in the flow of a 10% O₂ and 90% N₂ gas mixture (20 mL·min⁻¹) at 600 °C for 45 min, and then cooled to room temperature in N₂ (30 mL·min⁻¹). The reduction was carried out in a flow of a 5% H₂ and 95% N₂ gas mixture (20 mL·min⁻¹) from room temperature to 1000 °C with a heating rate of 8 °C·min⁻¹, and detected by a TCD at 120 °C.

Oxygen pulse-adsorption was used to measure the OSC of the samples by gas chromatography in pure N₂ flow (20 mL·min⁻¹) for a 200 mg sample at 200 °C. Prior to the measurements, the samples were reduced in pure H₂ at 550 °C for 45 min, and then cooled to 200 °C in pure N₂ flow. Finally, pulses of oxygen (20 mL·min⁻¹) were injected into the sample in intervals of 5 min until no further oxygen consumption could be detected by the TCD at 120 °C.

3 Results and discussion

3.1 Catalytic activity of the catalysts for methane combustion

The effects of the OSM/La-Ba-Al₂O₃ mass ratio of the Fe-based monolithic catalysts for the combustion of thin methane are shown in Fig.1.

As shown in Fig.1, the activity of the catalysts depends on the mass ratio of OSM to La-Ba-Al₂O₃. The activity of the fresh catalysts is in the order of 1:1>2:1>1:2>1:0>0:1, and the activity of the aged catalysts is in the order of 1:1>2:1>1:2>0:1>1:0. This indicates that OSM increases the activity of the Fe-based monolithic catalyst. Furthermore, it is possible that OSM releases oxygen, which can decrease the conversion temperature. When OSM is used, the optimum mass ratio of OSM to La-Ba-Al₂O₃ is 1:1. At this ratio, the catalyst has the highest activity for both aged and fresh catalysts. The temperatures (T_{10} , T_{50} , and T_{90}) at which 10% (T_{10}), 50% (T_{50}), and 90% (T_{90}) of methane are converted are listed in Table 1.

From Table 1, it can be seen that on the fresh Fe/(OSM+La-Ba-Al₂O₃(1:1)) catalyst methane starts to convert at 446 °C and is completely converted at 553 °C, with 1% CH₄ and GHSV of 50000 h⁻¹. The difference (ΔT) between the light-off temperature (T_{10}) and the complete-conversion temperature (T_{90}) is 107 °C. The activity of the fresh catalyst Fe/(OSM+La-Ba-Al₂O₃(2:1)) is slightly higher than that of Fe/(OSM+La-Ba-Al₂O₃(1:2)), indicating that OSM slightly improves the catalytic activity. However, aged Fe/(OSM+La-Ba-Al₂O₃(1:2))

Fig.1 Catalytic activity of fresh (A) and aged (B) catalyst samples for thin methane combustion

(a) Fe/La-Ba-Al₂O₃, (b) Fe/(OSM+La-Ba-Al₂O₃(1:2)), (c) Fe/(OSM+La-Ba-Al₂O₃(1:1)), (d) Fe/(OSM+La-Ba-Al₂O₃(2:1)), (e) Fe/OSM. reaction conditions: feed 1%CH₄-4%O₂-95%N₂; catalyst concentration: 140 g·L⁻¹; GHSV: 50000 h⁻¹

Table 1 Catalytic activity of fresh and aged samples

Sample	$T_{10}/^{\circ}\text{C}$		$T_{50}/^{\circ}\text{C}$		$T_{90}/^{\circ}\text{C}$		$\Delta T/^{\circ}\text{C}$	
	fresh	aged	fresh	aged	fresh	aged	fresh	aged
Fe/La-Ba-Al ₂ O ₃	480	558	558	648	623	705	143	147
Fe/(OSM+La-Ba-Al ₂ O ₃ (1:2))	454	560	525	638	578	697	124	137
Fe/(OSM+La-Ba-Al ₂ O ₃ (1:1))	446	519	517	624	553	673	107	154
Fe/(OSM+La-Ba-Al ₂ O ₃ (2:1))	450	529	522	638	568	685	118	156
Fe/OSM	480	580	538	667	669	747	189	167

$$\Delta T = T_{90} - T_{10}$$

shows higher catalytic activity than aged Fe/(OSM + La-Ba-Al₂O₃(2:1)) in the reaction temperature range from 600 to 680 °C, indicating that La-Ba-Al₂O₃ is the better anti-aging component in the catalysts. The catalyst Fe/(OSM+La-Ba-Al₂O₃(1:1)) shows the lowest light-off temperature and the smallest ΔT value for both aged and fresh catalysts, which can be attributed to the coordinating effect of OSM and La-Ba-Al₂O₃ on the catalyst.

3.2 Textural properties and OSC

Specific surface area and pore volume play an important role in the performance of catalytic supports, especially in high space velocity catalytic reactions. Thus, the supports must have suitable specific surface area and pore volume. The textural properties and OSC of the catalytic supports and catalysts are shown in Table 2.

As seen in Table 2, the OSM calcined at 1050 °C for 5 h retains a high specific surface area (37 m² · g⁻¹), large pore volume (0.20 mL · g⁻¹), and large oxygen storage capacity (342.5 $\mu\text{mol} \cdot \text{g}^{-1}$). The BET specific surface area and BJH pore volume for La-Ba-Al₂O₃ are 137 m² · g⁻¹ and 0.48 mL · g⁻¹, respectively. The textural properties indicate that the good thermal stability of La-Ba-Al₂O₃ can improve the dispersion of active sites and enhance anti-sintering of the catalysts.¹⁵ Therefore, these materials are good catalytic supports. As expected, the specific surface areas of fresh and aged catalysts decrease with increasing OSM/La-Ba-Al₂O₃ ratio, while the OSC of the catalysts increases. From Table 2, the OSC of Fe/OSM is larger than that of OSM, because adding iron increases the oxygen vacancies in the OSM structure after impregnation and improves the oxidizing capability and oxygen storage capacity of the OSM. In the OSC testing procedure, the samples were pre-reduced with hydrogen at 550 °C for 45 min, with the iron oxides reduced to elementary substances by hydrogen and then oxidized to oxides during the testing. Therefore, the OSC of Fe/OSM tends to be larger than that of OSM. Fe/La-Ba-Al₂O₃ has the largest specific surface area (S_{BET}) and pore volume, but no OSC. While Fe/OSM has the largest OSC, but its textural properties are poor. From Fig.1, the catalytic activities of Fe/La-Ba-Al₂O₃ and Fe/OSM are lower than the other catalysts, indicating that for a catalyst to have good activity it should have both good textural properties and large OSC.

3.3 XRD characterization

X-ray diffraction (XRD) was used to determine the bulk crystalline phases of the catalysts. The diffraction patterns of

Fig.2 XRD patterns of fresh (A) and aged (B) samples

(a) Fe/Al₂O₃, (b) Fe/La-Ba-Al₂O₃, (c) Fe/(OSM+La-Ba-Al₂O₃(1:2)), (d) Fe/(OSM+La-Ba-Al₂O₃(1:1)), (e) Fe/(OSM+La-Ba-Al₂O₃(2:1)), (f) Fe/OSM

the fresh and aged catalysts are shown in Fig.2.

As shown in Fig.2, OSM exists in uniform CeO₂-ZrO₂ solid solution.¹⁷ The crystalline structure of La-Ba-Al₂O₃ calcined at 1000 °C retains the γ -Al₂O₃ phase, which indicates that La₂O₃ and BaO stabilize γ -Al₂O₃. The crystalline structure of Fe₂O₃ was not observed in any of the catalysts, indicating that Fe₂O₃ is well dispersed on the support matrix.

As shown in Fig.2(A), the catalysts with OSM:La-Ba-Al₂O₃ mass ratios of 1:2 (c), 1:1 (d), and 2:1 (e) have well-defined peaks, corresponding to the CeO₂-ZrO₂ solid solution structure and the γ -Al₂O₃ phase. From Fig.2(B), the crystalline structures of all the fresh catalysts change after being calcined at 1050 °C. The XRD peaks become sharper and more intense, indicating that the structures are more crystalline. The α -Al₂O₃ phase is also observed. Mixed OSM and La-Ba-Al₂O₃ improves the dispersion and thermal stability of the supports towards Fe₂O₃, which maintains a high catalytic activity for the conversion of methane.

3.4 H₂-TPR analysis

TPR curves for Fe-based monolithic catalysts with various OSM/La-Ba-Al₂O₃ ratios are shown in Fig.3. From Fig.3(A), the fresh catalysts have a large peak (γ) in the range of 400–480 °C, which corresponds to Fe₂O₃ → Fe₃O₄.²³ The shoulder peak (α) of Fe/(OSM+La-Ba-Al₂O₃) and Fe/OSM catalysts in the range of 470–500 °C can be attributed to the reduction of Ce⁴⁺ on the surface. The peak at 800 °C is due to the reduction of the lattice Ce⁴⁺,^{24,25} which is the same as the reduction of Ce_{0.33}Zr_{0.53}Y_{0.10}La_{0.04}O_{1.93}.¹⁷ These peaks become more intense and

Table 2 Textural properties and OSC of fresh and aged samples

Sample	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$		$V_p/(\text{mL} \cdot \text{g}^{-1})$		OSC/ $(\mu\text{mol} \cdot \text{g}^{-1})$	
	fresh	aged	fresh	aged	fresh	aged
La-Ba-Al ₂ O ₃	170	137	0.50	0.48	0.0	0.0
Ce _{0.45} Zr _{0.45} Y _{0.07} La _{0.03} O _{1.95} (OSM)	126	37	0.27	0.20	530.2	342.5
Fe/La-Ba-Al ₂ O ₃	133	94	0.26	0.21	76.3	3.7
Fe/(OSM+La-Ba-Al ₂ O ₃ (1:2))	118	73	0.25	0.19	273.0	155.8
Fe/(OSM+La-Ba-Al ₂ O ₃ (1:1))	96	66	0.23	0.16	466.0	253.0
Fe/(OSM+La-Ba-Al ₂ O ₃ (2:1))	87	48	0.21	0.11	518.2	281.3
Fe/OSM	77	31	0.20	0.09	805.3	706.4

Fig.3 H₂-TPR profiles of fresh (A) and aged (B) catalysts
(a) Fe/La-Ba-Al₂O₃, (b) Fe/(OSM+La-Ba-Al₂O₃(1:2)), (c) Fe/(OSM+La-Ba-Al₂O₃(1:1)), (d) Fe/(OSM+La-Ba-Al₂O₃(2:1)), (e) Fe/OSM.
The main peaks are signed as α, β, and γ.

the area of the peaks increase as the OSM/La-Ba-Al₂O₃ mass ratio increases. It is known that the peak area is related to the amount of reducible species on the surface of the catalyst. The larger the peak area, the greater the amount of reducible species and the stronger the reducing capability. This is consistent with the activity of the catalysts increasing in the order of 0:1 < 1:2 < 1:1 for the OSM/La-Ba-Al₂O₃ mass ratio. When the mass ratio of OSM/La-Ba-Al₂O₃ is 1:1, there is overlap between the Fe₂O₃→Fe₃O₄ and Ce⁴⁺→Ce³⁺ reduction peaks and its intensity significantly increases, which indicates that there is interaction between the two components and that the interaction increases the reduction of Fe³⁺ and Ce⁴⁺ on the surface.

The overlap of the reduction peaks Fe₂O₃→Fe₃O₄ and Ce⁴⁺→Ce³⁺ on the surface improves the catalytic activity and oxygen storage capacity of Ce_{0.45}Zr_{0.45}Y_{0.07}La_{0.03}O_{1.95}, and thus improves the catalytic activity of Fe/(OSM+La-Ba-Al₂O₃) for methane combustion. The temperature of the Fe₂O₃→Fe₃O₄ peak reflects the activities of the samples.²⁶ Among the catalysts, Fe/(OSM+La-Ba-Al₂O₃(1:1)) has the lowest peak temperature of 406 °C, which is in agreement with it having the lowest light-off and total conversion temperatures (Fig.1).

For the aged samples in Fig.3(B), the reduction peaks are at higher temperatures than the corresponding peaks for the fresh samples. The specific surface area of the samples decreased, the pore canal collapsed, and active components were sintered, resulting in the TPR peak of the samples moving to a higher temperature. Compared with Fig.3(A), the change of the reduction temperature for aged Fe/La-Ba-Al₂O₃ is less than that for aged Fe/OSM, indicating that the thermal stability of Fe/La-Ba-Al₂O₃ is greater than that of Fe/OSM. With increasing La-Ba-Al₂O₃ content (from (e) to (a) in Fig.3), the γ peak temperature decreases, which indicates that La-Ba-Al₂O₃ resists aging. The ΔT for the γ peak temperature between fresh and aged Fe/(OSM+La-Ba-Al₂O₃(1:1)) of 134 °C is the smallest among all the Fe/(OSM+La-Ba-Al₂O₃) samples, which indicates that it has the best thermal stability due to the balance of OSM and La-Ba-Al₂O₃.

4 Conclusions

Ce_{0.45}Zr_{0.45}Y_{0.07}La_{0.03}O_{1.95} prepared by co-precipitation has a high oxygen storage capacity, while La-Ba-Al₂O₃ made by peptization has excellent texture and high thermal stability. Ce_{0.45}Zr_{0.45}Y_{0.07}La_{0.03}O_{1.95} can improve the OSC and redox ability of the catalyst, both of which are important factors of fresh catalysts for methane combustion. La-Ba-Al₂O₃ increases the dispersion of the active species of the catalysts and their thermal stability. Fe/(OSM+La-Ba-Al₂O₃) monolithic catalysts supported by a mixture of Ce_{0.45}Zr_{0.45}Y_{0.07}La_{0.03}O_{1.95} and La-Ba-Al₂O₃ have good catalytic activities and high temperature stabilities. When the mass ratio of Ce_{0.45}Zr_{0.45}Y_{0.07}La_{0.03}O_{1.95} to La-Ba-Al₂O₃ is 1:1, methane starts converting at 446 °C and is completely converted at 553 °C, which shows the highest activity for the combustion of thin methane of the catalysts studied. These catalysts show potential for the use in practical applications.

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