

Supplementary Material (ESI) for RSC Advances

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Electronic Supporting Information

Vertical and in situ growth of hexaaluminate embedded in alumina intermediate layer with high stability

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Synthesis of $\text{Al}_2\text{O}_3/\text{FeCrAl}$. The FeCrAl alloy (FeCrAlloy) foil with a thickness of 0.1 mm and a chemical composition of 6.1 wt. % Al, 25.1 wt. % Cr and Fe (balance) was supplied by Shanghai Daoda Electric Alloy Material Co., Ltd., PRC. Firstly some FeCrAlloy foils were pretreated as described in ref. [1] and used as the structural substrate to support the $\gamma\text{-Al}_2\text{O}_3$ coating by a dip-coating process with a Al_2O_3 hydrosol prepared from the pseudo-boehmite.² The FeCrAlloy foil coated with the Al_2O_3 hydrosol was dried at 120 °C for 1 h and calcined at 500 °C for 1 h. The coating and drying were repeated for 2 times with a weight increase of approximately 1 wt.%, the monolithic substrate ($\text{Al}_2\text{O}_3/\text{FeCrAl}$) was thus formed.

Synthesis of LHA- $\text{Al}_2\text{O}_3/\text{FeCrAl}$. LaMn-based hexaaluminate (LHA) was synthesized using an in situ process on the $\text{Al}_2\text{O}_3/\text{FeCrAl}$ substrate. Solutions of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$ and NH_4NO_3 , with a total metal ion concentration of 0.1 M, were mixed in a beaker according to the $\text{La}^{3+}/\text{Mn}^{2+}/\text{NH}_4^+$ atomic ratio equal to 1:1:12. After pH value of the immersing solution was adjusted to 8 by adding dilute aqueous ammonia solution (1%), the FeCrAlloy foil coated with $\gamma\text{-Al}_2\text{O}_3$ were vertically immersed in the solution without any Al^{3+} salts for a certain period of time at 60 °C. Subsequently, these foils were washed and dried at 60 °C for 24 h and then calcined at 1100 °C for 5 h.

Synthesis of $\alpha\text{-Al}_2\text{O}_3/\text{FeCrAl}$. In order to compare with LHA- $\text{Al}_2\text{O}_3/\text{FeCrAl}$ on the adhesion performance, $\text{Al}_2\text{O}_3/\text{FeCrAl}$ was finally calcined at 1100 °C for 5 h to obtain $\alpha\text{-Al}_2\text{O}_3/\text{FeCrAl}$.

Synthesis of LHA/LHA- $\text{Al}_2\text{O}_3/\text{FeCrAl}$ and LHA/ $\text{Al}_2\text{O}_3/\text{FeCrAl}$ monolithic catalysts. The ball milling slurry of the LHA particles was deposited on LHA- $\text{Al}_2\text{O}_3/\text{FeCrAl}$ and $\text{Al}_2\text{O}_3/\text{FeCrAl}$ by a dip-coating method. After dried at 100 °C for 2 h and calcined at 800 °C for 1 h, then repeated for 3 times with a weight increase of approximately 3 wt. %. Finally, the samples were calcined at 1100 °C for 5 h to obtain the LHA/LHA- $\text{Al}_2\text{O}_3/\text{FeCrAl}$ and LHA/ $\text{Al}_2\text{O}_3/\text{FeCrAl}$ monolithic catalysts respectively.

Characterization. The crystalline phases of the prepared samples were identified by X-ray diffraction (XRD) with a Japan Rigaku D/MAX 2500 v/pc X-ray diffractometer by 40 kV, 40 mA, Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) with a scan speed of $2\theta = 12^\circ \text{ min}^{-1}$. The surface morphological observations were performed with a Germany Zeiss Supra 55 scanning electron microscopy (SEM). The high-resolution transmission electron microscopy (TEM) images were taken using a Japan JEOL JEM-2100 transmission electron microscope by dispersing the samples scraped off from the FeCrAlloy in ethanol ultrasonically and then depositing them on a copper grid.

Adhesion tests. The processes of ultrasonic vibration and thermal shock tests are the same as described in ref. [3]. The ultrasonic vibration measurement was conducted by immersing the sample in petroleum ether inside a closed beaker and vibrating it in an ultrasonic vibration instrument (40 KHz/100W) for 5~100 min. After that, the sample

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was dried and weighed. The thermal shock test was performed by heating the sample at 800 °C in a muffle oven for 20 min, and then dropping it into water at room temperature, then the sample was dried and weighed. The mass loss due to ultrasonic vibration or thermal shock is calculated by the equation, $\text{mass loss} = (M_0 - M_1)/M_0 \times 100\%$, in which M_0 and M_1 are the mass of sample before and after the tests.

Catalytic performance tests. The temperature catalytic combustion of CH₄ experiments were performed in a conventional flow system reactor under atmospheric pressure. The tests were carried out with 4 g of monolithic catalyst, and the feed consisted of a gas mixture of 1.5 vol. % CH₄ in air with a weight hourly space velocity (WHSV) of 1,500 ml/g_{cat}·h. The outlet products were measured on line with a SP-2100 gas chromatography (GC) equipped with a thermal conductivity detector (TCD) and a column packed with 5A molecular sieve. The reaction temperature was controlled with a K-type thermocouple placed in the vicinity of the catalytic bed. The activity of the catalyst is evaluated in terms of the temperatures at which the conversions attain 10% and 90% (i.e., T_{10} and T_{90} , respectively).

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Supplementary Figures

Fig. S1-Supporting information

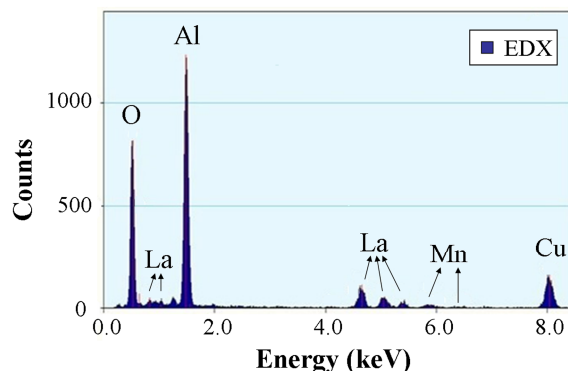


Fig. S1 Energy dispersive X-ray spectrometer (EDS) spectrum of a representative stick-like grain in Fig. 2a

The result of energy dispersive X-ray spectrometer (EDS) analysis at the region of one representative stick-like grain in Fig. 2a is shown in Fig. S1. As can be seen, elements of La, Mn, Al and O can be detected in the stick-like grains by EDS. To combine with other results in the article, we can further confirm that these stick-like grains are LHA grains.

Fig. S2-Supporting information

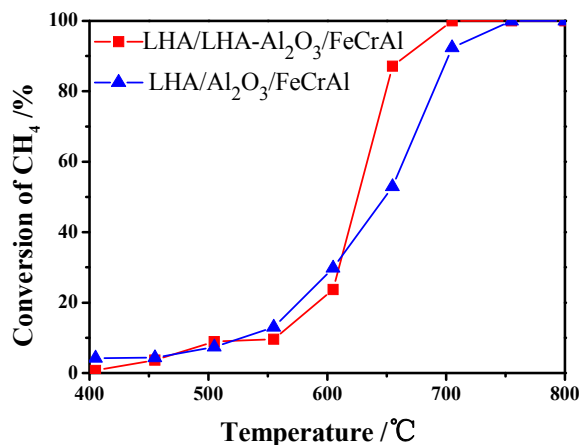


Fig. S2 Catalytic activity of CH₄ combustion over LHA/LHA-Al₂O₃/FeCrAl and LHA/Al₂O₃/FeCrAl monolithic catalysts. Reaction conditions: 1.5 vol.% CH₄ and 98.5 vol.% air; GHSV = 1,500 ml/g_{cat}·h.

The catalytic results of CH₄ combustion are given in Fig. S2. As can be seen, LHA/LHA-Al₂O₃/FeCrAl and LHA/Al₂O₃/FeCrAl monolithic catalysts obtain similar activities whose T₁₀ are 550 °C and 530 °C, T₉₀ are 665 °C and 705 °C, respectively. So it can be concluded that the new LHA/LHA-Al₂O₃/FeCrAl catalyst can not only achieve a better adhesion stability, but also maintain a good catalytic activity of CH₄ combustion, compared with LHA/Al₂O₃/FeCrAl.

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Fig. S3-Supporting information

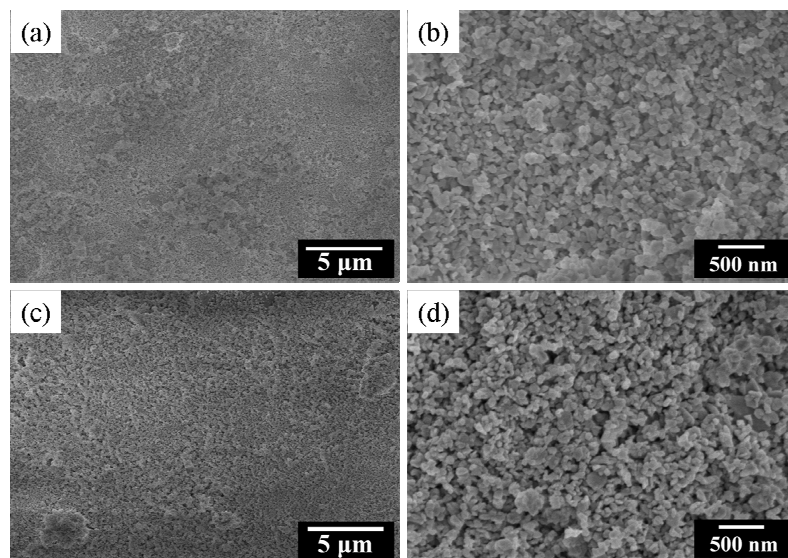


Fig. S3 Surface SEM micrographs of LHA/LHA-Al₂O₃/FeCrAl monolithic catalyst before (a, b) and after (c, d) CH₄ combustion. Reaction conditions: 1.5 vol.% CH₄ and 98.5 vol.% air; GHSV = 1,500 ml/g_{cat}·h.

The surface SEM micrographs of LHA/LHA-Al₂O₃/FeCrAl monolithic catalyst before and after CH₄ combustion are shown in Fig. S3. As can be seen, the catalyst surface is coated with LHA layer, and there is nearly no change for the surface coating after CH₄ combustion. It can be attributed to the lower reaction temperature compared to the calcination temperature. Further, and even more important, is due to the special structural stability of LHA and enhanced adhesion of multilayer oxide to metal by the in situ growth of LHA in Al₂O₃ layer. Based on the above-mentioned three facts, the catalyst could effectively retain its morphology of surface coating after CH₄ combustion.

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- 1 D. Zhang, L. H. Zhang, B. Liang and Y. D. Li, *Ind. Eng. Chem. Res.*, 2009, **48**, 5117.
 - 2 Y. Zhang, H. Liang, C.Y. Zhao and Y. Liu, *J. Mater Sci.*, 2009, **44**, 931.
 - 3 L. H. Zhang, T. Li, M. M. Zhang and Y. D. Li, *J. Rare Earth.*, 2011, **29**, 758.