



The preparation effect on activity and thermal stability of $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_3$ perovskite honeycombs dispersed by MgAl_2O_4 spinel washcoat for catalytic combustion of dilute methane



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ABSTRACT

$\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_3$ perovskite (LCF) honeycombs stabilized by MgAl_2O_4 spinel (MgAl) washcoat have been developed for the first time and applied in catalytic combustion of air diluted CH_4 (0.5 vol.%). The honeycombs were prepared by washcoating the $\alpha\text{-Al}_2\text{O}_3$ monoliths in sequence with the slurries of MgAl and LCF precursors, intermediated by calcination at corresponding temperatures. The effects of LCF powder preparation method, the calcination temperature and thickness of MgAl washcoat, and the loading of LCF were investigated. Meanwhile, the first order reaction rate constants (k) were calculated and activation energy (E_a) regressed for powder and honeycomb LCF catalysts.

The LCF prepared by a modified co-precipitation method was found more active and stable than that made by citrate method in literature. Calcination of bulk LCF powder at 700–800 °C led to a linear deactivation proportional to S_{BET} . For LCF honeycombs immediately washcoated on $\alpha\text{-Al}_2\text{O}_3$ substrates, k and E_a values are comparable to that measured with LCF powder, which is almost inert upon calcination at 1000 °C. When supported on MgAl washcoat, activity of LCF honeycombs is enhanced by folds, and the effect is more pronounced at higher calcination or reaction temperatures. Meanwhile, performance of the honeycombs is very sensitive to the washcoat preparation, with the optimum calcination temperature and proper thickness of the MgAl washcoat identified as 850 °C and 40 μm , respectively. Conversion of CH_4 goes up with LCF loading of honeycombs, but the values of k and E_a vary in different way. When LCF loading is low, k is the highest, accompanied by a lowest $E_a \sim 99$ kJ/mol; for intermediate loadings, k and E_a are both medium and constant; in cases of overloaded LCF, k reduces and E_a rises to 132 kJ/mol, approaching to that measured with bulk LCF (135 kJ/mol). The change of E_a with LCF loadings reflects the modification of active sites due to the interaction of LCF with MgAl, and the proper mass ratio of LCF/MgAl is at the range of 0.8–0.9. Finally, thermal resistance of LCF honeycombs supported by MgAl or MgO were compared after thermal aging at 1000 °C for 4 h. The MgAl supported LCF is about 200 °C more stable than MgO supported, indicating a much improved thermal resistance.

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1. Introduction

Methane released during coal mining is not only greenhouse gas, but also a valuable source of green energy, once exploited properly. The amount of coal mine methane released is huge, around 25 million ton/year worldwide, 70% of which is highly diluted (0.1–1.0 vol.%) ventilation air methane (VAM) [1]. China alone releases over 20 billion Nm^3 VAM annually, which causes severe air pollution and wastes lots of energy [2].

Compared to thermal combustion, use of catalysts can significantly decrease combustion temperature of methane, and can oxidize methane of any concentration almost completely to CO_2 and H_2O at high GHSV (>20000/h), without generation of the secondary pollutants like NO_x and CO. Due to the high combustion heat of methane, the threshold concentration of VAM for auto-thermal catalytic combustion is only 0.06 vol.% [3]. Therefore, combustion with honeycomb catalysts, which can stand high temperatures and run efficiently at high GHSV with low pressure drop, is most fitted for combustion of VAM [3–6].

So far, four categories of catalysts were developed in catalytic combustion of methane, namely, noble metals, mixture of transient metal oxides, perovskite, and hexaaluminates. Among them, noble metal is the most active one with the lowest light-off

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temperature around 350 °C [7], but the price is too high for large-scale implementation. Transition metal oxides are blamed by thermal stability at working conditions, while hexaaluminates, only active at high temperature range, are not fit for highly diluted methane combustion. In comparison, perovskite catalysts, like LaCoO₃, LaMnO₃, LaFeO₃, etc., as well as their modified or composite materials have demonstrated good activity and stability under medium temperature range around 600 °C [8–15].

The main unsolved drawback with the practical application of bulk perovskite is their low surface area and strong tendency to sintering [13]. To improve surface area and thermal stability of catalysts, various supports were investigated to disperse perovskite for methane combustion, but most of the studies concern the powder catalysts, only few examples of the perovskite honeycombs have been reported. Cimino et al. have introduced La stabilized γ -Al₂O₃, MgO and ZrO₂ [12–14] washcoat as the secondary support, and dispersed on which, LaMnO₃ perovskite has demonstrated better activity as well as excellent thermal stability above 1000 °C. Variations in values of E_a and in some cases even detected the presence of new phases, indicated the change of active sites in LaMnO₃ upon being supported on MgO and La stabilized Al₂O₃ [13]. Saracco et al. [16] prepared the Mg substituted LaMn_{1-x}Mg_xO₃ perovskite, with excess amount of MgO (molar ratio 17:1 to perovskite) added as the textural promoter, a reduction in crystalline size (80 nm vs 25 nm) was detected upon calcination at 800 °C. Laura Fabbrini et al. [15] introduced Al₂O₃ or La₂O₃ washcoat to disperse the active phase La_{0.9}Ce_{0.1}CoO_{3±d}, a high initial activity with Al₂O₃ and a much improved thermal stability with La₂O₃ were reported.

In previous studies, different refractory washcoat made of stabilized Al₂O₃, MgO, ZrO₂, or La₂O₃, etc., was examined to obtain better thermal resistance or higher activity, but none of them has optimized the preparation procedure, such as the preparation conditions of the washcoat, and the loading of active phase, which factors, as found in this study, play important roles on performance of the honeycomb catalysts. Meanwhile, the methods of impregnation and deposition–precipitation, which were previous adopted to disperse the active phase onto the preformed washcoat of honeycombs, were either difficult to control the quality of dispersion or troublesome and hard to scale-up. By comparison, washcoating is a matured technique widely used in industry, but to ensure an effective dispersion, the proper loading of the active phase on a preformed washcoat should be identified. On the other hands, instead of taking the values of T_x (temperature at which to attain $x\%$ conversion) for unreliable comparison of catalyst activity, quantification of reaction kinetics is needed, for assessment of performance of various catalysts in forms of honeycomb or powder, meanwhile to shed light on the interaction of support and active phase through the values of E_a .

In this paper, MgAl₂O₄ spinel (MgAl), an effective support once reported by Mariti et al. to stabilize powder La_{0.8}Sr_{0.2}MnO₃ perovskite in combustion of methane [17], was first prepared as washcoat to stabilize La_{0.8}Ca_{0.2}FeO₃ perovskite (LCF) honeycombs, and with the promotion effect compared to that MgO supported and unsupported LCF. The optimum calcination temperature and proper thickness of the MgAl washcoat were investigated in experiment. The dispersion and loading effect of LCF were examined to identify a proper range to balance the conversion of CH₄ and effective dispersion of LCF. The relevant physicochemical properties of both honeycomb and powder LCF catalysts are characterized for comparison, with kinetics parameters regressed in order to shed light on the interaction mechanism between MgAl and LCF.

2. Experimental

2.1. Preparation of LCF and MgAl₂O₄ powder

La_{0.8}Ca_{0.2}FeO₃ perovskite (LCF) was prepared by co-precipitation method, where ethanol (25 wt%) aqueous solution of the mixed La(NO₃)₃· n H₂O, Ca(NO₃)₂·4H₂O and Fe(NO₃)₃·9H₂O (unless otherwise stated, all chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd.) at a prescribed molar ratio (La:Ca:Fe = 0.8:0.2:1) and total concentration as 0.1N, was mixed with 10% excess of stoichiometric amount of 0.1N (NH₄)₂CO₃ aqueous solution as precipitant under vigorous stirring. The precipitation was performed at room temperature at a constant pH about 10 then kept for 6 h under stirring before the precipitate was filtered, and washed with 25 wt% of ethanol aqueous solution to a constant conductivity. After drying overnight at 110 °C in air, the precursor was grinded and screened. The particle size of 80–100 mesh was collected and heated in air at 2 °C/min to 800 °C or 1000 °C and kept for 4 h, used later for powder tests, while the fine particle below 100 mesh was calcined at 500 °C and collected for preparation of the honeycomb catalyst.

Similar to LCF preparation, the ethanol aqueous solution of Al(NO₃)₃·9H₂O and Mg(NO₃)₂·6H₂O at a total concentration of 0.1N was precipitated with 10% excess amount of 0.1N (NH₄)₂CO₃ aqueous solution at 65 °C and aged at the same temperature for 4 h under vigorous stirring. The prepared precipitate was dried at 110 °C and calcined at prescribed temperatures for dip-coating, and the spinel-phased MgAl₂O₄ was nominated as MgAl in this paper.

2.2. Preparation of LCF honeycombs

The α -Al₂O₃ substrates were purchased from Sanyuan ceramic honeycomb company in China (properties were shown in Table 1), on which the honeycomb structured LCF catalysts were prepared as described above. The substrate was immersed in 1 wt% nitric acid solution for 4 h at room temperature, rinsed thoroughly and dried in oven at 110 °C before dip-coating of the washcoat.

The slurry for dip-coating was made by mixing the powder of LCF or MgAl, solvent, surfactant, organic and inorganic binders in prescribed ratios, ball-milled for 24 h to meet the requirements of viscosity and suspension stability before applying on the substrate. Immerse the substrate in slurry for 2 min, then blew off the excess slurry with air knife. The honeycomb was kept at room temperature for over 12 h, before drying overnight at 110 °C and calcined in a muffle furnace at prescribed temperatures for 4 h. The attached mass of LCF or MgAl washcoat was quantified after calcination. The loading amount was controlled by adjusting the solid content in the slurry, and/or adding the times of immerse and blowing-off during preparation. Several dips were needed in cases to attain the desired high loadings.

Table 1
Fundamental properties of ceramic substrate modules.

Index	Parameter	Index	Parameter
Channel shape	Regular triangle	δ	0.2 mm
Channel density	400 cpsi	ε	65.4%
D	25 mm	S_{BET}	1.0 m ² /g
H	12 mm	$T_{calcin.}$	1350 °C
Mass	6–8 g	Crystal	α -Al ₂ O ₃
E wt%	Al 45.38, Si 8.25, Mg 2.16, Cr 0.97, O 43.24		

δ —thickness of channel wall; D —diameter of module; H —height of module, ε —percentage of open area; E wt%—weight percentage of elements.

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