Catalytic combustion of methane over $Ce_{1-x}La_xO_{2-x/2}$/Al_2O_3/FeCrAl catalysts

Fengxiang Yin, Shengfu Ji [*], Biaohua Chen, Zhongliang Zhou, Hui Liu, Chengyue Li [*]

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology,
15 Beisanhuan Dong Road, P.O. Box 35, Beijing 100029, China

Abstract

A series of the $Ce_{1-x}La_xO_{2-x/2}$/Al_2O_3/FeCrAl monolithic catalysts ($x = 0$–1) were prepared. The structure of the catalysts was characterized by X-ray powder diffraction (XRD), scanning electron microscope (SEM) and temperature-programmed reduction (TPR). The catalytic activity of the catalysts for the methane combustion was evaluated with a fixed bed reactor. The results showed that in the $Ce_{1-x}La_xO_{2-x/2}$/Al_2O_3/FeCrAl catalysts the phase structure was the $Ce_{1-x}La_xO_{2-x/2}$ solid solutions, α-Al_2O_3 and γ-Al_2O_3. The molar ratio of Ce to La in the $Ce_{1-x}La_xO_{2-x/2}$ solid solutions significantly influenced the surface particle shape and size of the catalysts. The catalytic activity for the methane combustion strongly depended on the La component of the $Ce_{1-x}La_xO_{2-x/2}$/Al_2O_3/FeCrAl catalysts, and the order of the catalytic activity in terms of x was $0.7 > 0.9 > 0.5 > 0.3 > 0 > 1$. TPR analyses of the catalysts revealed the existence of a strong interaction among the $Ce_{1-x}La_xO_{2-x/2}$ solid solutions, the Al_2O_3 washcoats and the FeCrAl support. This interaction remarkably enhanced the redox properties of the catalysts resulting in the higher catalytic activity.
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1. Introduction

During the last decades, the catalytic combustion of methane and other light hydrocarbons has attracted much attention due to its providing new technological solutions for reducing emissions of air pollutants and high burning efficiency [1–6]. In particular, the interest in new materials for methane catalytic combustion has boosted research in this area. The objective is to find suitable materials with high activity at low temperature and stability at high temperature, as well as low-cost for methane catalytic combustion. Though noble metal catalysts exhibit the highest activity (per site) for methane catalytic combustion, they suffer from some disadvantages, such as higher volatility and poor economics/availability [7–9]. The hexaaluminate materials seem to be the most promising candidates due to their thermal stability for high temperature catalytic combustion of methane. However, they suffer from much lower activity and higher light-off

temperatures [10–12]. The perovskite-type oxide catalysts show a good catalytic performance in methane combustion [13–16]. However, the low surface area of the catalysts leads to less activity per unit mass catalyst. It has been reported that the ceria exhibits very high catalytic activity and thermal stability in methane combustion using lanthana and praseodymia as promoters. The high catalytic activity relates to the synergistic effect between ceria and promoters [17]. Later, the promoter action is confirmed in an initial work by Liu and Flytzani-Stephanopoulos [18]. This study is extended by Kundakovic and Flytzani-Stephanopoulos [19]. It has been pointed out that ceria modified by doping with lanthanum shows the higher catalytic activity and thermal stability. The higher activity achieved with lanthana as dopant is attributed to various factors, including smaller ceria crystal size due to doping with lanthanum, increased reducibility, the introduction of extrinsic oxygen vacancies, and increased oxygen mobility in the defective fluorite structured mixed oxides. Recently, Wilkes et al. [20–23] prepared $Ce_{1-x}La_xO_{2-x/2}$ ($x = 0$–1) solid solution catalysts by co-precipitation. Their catalytic performance for methane combustion and CO oxidation as well as the surface and bulk structure was investigated. It is found that these solid solution

* Corresponding authors. Tel.: +86 10 64412054; fax: +86 10 64419619.
  E-mail addresses: jisf@mail.buct.edu.cn (S. Ji),
licy@mail.buct.edu.cn (C. Li).

catalysts show the higher activity related to synergistic action between ceria and lanthana. Cerium contributes a redox capability to the reaction, whilst the basicity of lanthanum activates adsorbed methane. However, a great number of the fixed-bed reactors used in industry are randomly packed with catalyst particles with different shapes. These systems, especially for strongly exothermic reactions with high gas hourly space velocity (GHSV) and heat effect, such as methane catalytic combustion reaction, present some disadvantages, such as much higher pressure drops across the catalyst bed and much higher temperature gradients in reactors, resulting in lower energy efficiency and local overheating of the catalysts.

Nowadays, a novel monolithic structured catalyst/reactor, especially which of using the FeCrAl alloy foils as the catalyst substrate/support, has increasingly drawn the attention of researchers [24–26]. The monolithic catalyst consists of thousands of small parallel channels or honeycombs, with metal walls between them. The channels are commonly square or triangular in cross-section and have a diameter of 0.5–4 mm. Moreover, the channel geometry and shape of the monolith can be adapted to the needs of the specific application. On the walls of the channels, the active materials are deposited in a typically 10–100 μm thick porous washcoat. The reactants diffuse into the washcoat and react on the active sites. Hereby, compared to conventional packed beds of catalyst pellets or slurry reactors, monolithic catalysts have distinct advantages: the much lower pressure drops, the lower capacity of mass and heat transfer, the higher resistance to thermal shocks [27–29]. So, for process intensification and strongly exothermic reactions such as methane combustion with high GHSV and heat effect, the metal monolithic catalysts have a promising application.

In our previous works, modeling and simulation based on computational hydrodynamics and heat transfer as well as mass transfer for the metal monolithic reactor are carried out to predict the flow field and temperature field, and to evaluate its performance in transport aspect with CFD software [30,31]. It is found that the metal monolithic reactor is quantitatively proved to have much better performance in heat transfer and mass transfer and much lower pressure drops in comparison with the conventional pellet packed bed. Usually, the channel walls of metal monoliths are covered by a porous oxide layer/washcoat (mainly alumina), on which the catalytic phase is deposited. The oxide washcoat has a large specific surface area, which is supposed to allow a good dispersion of the active phase. There are some reports on how to deposit Al_2O_3 washcoat onto the channel walls of monoliths which are made of FeCrAl alloy foils [32–35]. However, at present how to support an active phase onto the metal substrate has been less investigated [26]. Recently, we prepared a series of the $Ce_{1-x}Cu_xO_{2-x}/Al_2O_3/FeCrAl$ ($x = 0$–1) monolithic catalysts, and preliminarily understood the structure and catalytic performance for methane combustion [36]. In this study, a series of $Ce_{1-x}La_xO_{2-x/2}$ ($x = 0$–1)-based metal monolithic catalysts on supports made of the FeCrAl alloy foils, with Al_2O_3 washcoats, were prepared. The aim is to entirely understand the structure and the catalytic properties for methane combustion.

2. Experimental

2.1. Preparation of the $Ce_{1-x}La_xO_{2-x/2}/Al_2O_3/FeCrAl$ samples

The $Ce_{1-x}La_xO_{2-x/2}/Al_2O_3/FeCrAl$ ($x = 0$–1) metallic monolithic samples were prepared using the FeCrAl alloy foils (OC404, Sandvik Steel, Sweden) as supports. In order to remove the oil, primary oxides and other superficial impurities on the surface, the foils were cleaned in ethanol, basic and acidic solution, successively, then thoroughly rinsed in de-ionized water, and then, the surface treated foils were calcined at 950 °C for 15 h in air. A boehmite primer sol was used as intermediate layer to improve the adhesion between the γ-Al_2O_3 washcoats and the heat-treated metallic supports. The heat-treated metallic supports were immersed in the sol, then dried at room temperature in air and thereafter at 120 °C for 3 h, and then calcined at 500 °C for 4 h. Then, the metallic supports coated the boehmite primer sol were immersed in the slurry of γ-Al_2O_3, then dried at room temperature in air and thereafter at 120 °C for 3 h, and then calcined at 500 °C for 4 h, and then the monolithic supports ($Al_2O_3/FeCrAl$) was formed [32–35]. The mixing slurry of the $Ce_{1-x}La_xO_{2-x/2}$ ($x = 0$–1) solid solution oxides and γ-Al_2O_3 was deposited on the monolithic supports ($Al_2O_3/FeCrAl$), dried at room temperature in air and thereafter at 120 °C for 3 h, and then calcined at 500 °C for 4 h. Finally, the $Ce_{1-x}La_xO_{2-x/2}/Al_2O_3/FeCrAl$ metal support monolithic catalysts were obtained. The weight of the solid solution oxides layers and Al_2O_3 layers is ca. 8 wt.% and ca. 10 wt.%, respectively.

$Ce_{1-x}La_xO_{2-x/2}$ ($x = 0$–1) solid solution oxides were prepared by the urea–nitrate combustion method [37]. Briefly, Cerium(III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) and lanthanum(III) nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$) were used as the precursors and urea as combustion agent. $Ce(NO_3)_3 \cdot 6H_2O$, $La(NO_3)_3 \cdot 6H_2O$ and urea were mixed at the desired molar ratio, then the mixture was mulled at room temperature for about 30 min, finally, it was combusted at 650–850 °C for 10–30 min and the $Ce_{1-x}La_xO_{2-x/2}$ solid solutions powder was obtained. The BET area was ca. 40 m^2/g and the particle size was ca. 0.1 μm.

2.2. Characterization of $Ce_{1-x}La_xO_{2-x/2}/Al_2O_3/FeCrAl$ samples

The phase structure of the samples was characterized by X-ray powder diffraction (XRD) using a Rigaku D/Max 2500 VB2+/PC diffractometer with a Cu Kα radiation operating at 200 mA and 40 kV. The morphology of the samples was observed by Cambridge Instruments Streoscan 250 MK3 scanning electron microscope (SEM). Temperature programmed reduction (TPR) experiments were performed using a Thermo Electron Corporation TPDRO 1100 series Catalytic Surfaces Analyzer equipped with a TC detector. Samples were preheated with 10 vol.% O_2/He mixtures heating 20 °C/min up to 500 °C, and then cooling in flowing N_2 down to room temperature, and thereafter reduced with 5 vol.% H_2/N_2