Full Length Article

Effects of preparation methods on CoAlO$_x$/CeO$_2$ catalysts for methane catalytic combustion

Xionghua Fan[a,b], Luming Li[a,b], Fangli Jing[a,b,*], Jing Li[a], Wei Chu[a,b,*]

[a] Department of Chemical Engineering, Sichuan University, Chengdu 610065, Sichuan, China
[b] Institute of New Energy and Low-carbon Technology, Sichuan University, Chengdu 610065, Sichuan, China

GRAPHICAL ABSTRACT

The plasma catalyst CoAlO$_x$/CeO$_2$-P shaw the better performance than that of other sample via one of other 3 preparation methods, for methane catalytic combustion. This CoAlO$_x$/CeO$_2$-P catalyst possessed the lower apparent activation energy (Ea was 92.2 ± 0.1 kJ/mol) and a reaction temperature of 415 °C for 50% methane conversion, while it was only 5% for the CoAlO$_x$/CeO$_2$-IWI sample.
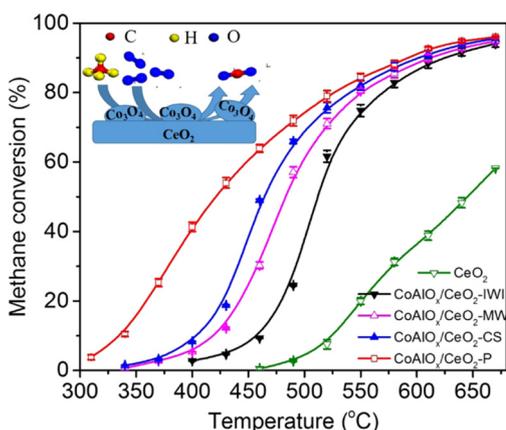
ARTICLE INFO

ABSTRACT

The novel supported CoAlO$_x$/CeO$_2$ catalysts have been synthesized via four preparation processes [impregnation (IWI), microwave in-situ grown (MW), impregnation-combustion (CS) and plasma treatment (P)], and investigated for methane catalytic combustion. The results indicated that preparation method played a vital role in controlling structural properties of the catalysts, resulting in a significant difference in catalytic performance. The activities of synthesized catalysts increased and optimised in the following order: CoAlO$_x$/CeO$_2$-IWI < CoAlO$_x$/CeO$_2$-MW < CoAlO$_x$/CeO$_2$-CS < CoAlO$_x$/CeO$_2$-P. The CoAlO$_x$/CeO$_2$-P catalyst possessed the lower apparent activation energy (Ea was 92.2 ± 0.1 kJ/mol) and a better performance with a lower reaction temperature at 415 °C for the 50% methane conversion, while the conversion was only 5% for the CoAlO$_x$/CeO$_2$-IWI sample at this temperature, as comparison. The samples were characterized by X-ray photoelectron Spectroscopy (XPS) and several other techniques. The CoAlO$_x$/CeO$_2$-P catalyst possessed a higher ratio of surface absorbed oxygen and lattice oxygen (O$_{ads}$/O$_{latt}$) which enabled the enhancement of its catalytic activity. The plasma method provided an effective path to develop the efficient combustion catalyst for higher performance.

* Corresponding authors at: Department of Chemical Engineering, Sichuan University, Chengdu 610065, Sichuan, China.
E-mail addresses: fangli.jing@scu.edu.cn (F. Jing), chuwei1965@scu.edu.cn (W. Chu).

1. Introduction

Natural gas is a promising alternative energy comparable to petroleum owing to its abundant reserves and the rapid development of exploration technology [1]. CH_4, the main component of natural gas, has been widely applied to power plants and natural gas powered vehicles. However, the greenhouse contribution of CH_4 to global warming is much higher than that of carbon dioxide (CO_2) [2]. Therefore, the post-treatment of CH_4 in tail gas is of vital importance in terms of the sustainable development and environmental protection. The low-temperature catalytic combustion of CH_4 has been considered as the best strategy to solve these problems because of its inherit advantage over conventional thermal combustion such as reducing the lower ignition temperature, complete combustion and avoiding the discharge of noxious NO_x, CO, and hydrocarbons [3–8]. When it comes to the catalytic combustion, the key issue is rational design of high-performance catalyst with an outstanding stability and anti-coke properties under relatively demanding conditions [9,10].

Up to now, Noble metal catalysts, especially palladium based catalysts, have been found to exhibit the best activities for CH_4 combustion rising from the formation of palladium oxide active phase during the reaction processes [10–14]. However, the limited abundance and high cost of the precious metal fade the possibility of further industrialization. So, there is a strong desire to design and synthesize non-noble metal catalysts, such as the reported transition metal oxides (CoO_x, NiO, CuO, Cr_2O_3 and MnO_x), spinel oxides and perovskite-type catalysts [15–21]. Among these candidate catalysts, cobalt-based oxides as type of earth-abundant materials are well known because of the structural and electronic properties of spinel type cobalt oxides with variable valence states (Co^{2+}/Co^{3+}) as well as the lower bonding energy of Co-O bonds, which have exhibited high activities for the catalytic combustion of lean methane [22].

To maximize the synergistic interaction, the active components are often highly dispersed on the surface of support material. CeO_2 can function as an important oxygen storage material mainly originated from the strongly reversible $Ce^{4+} \leftrightarrow Ce^{3+}$ redox reaction, which is known to be the potential oxidation catalyst support [23–29]. Di Sarli et al. reported that the exchange of oxygen atoms between the CeO_2 and O_2 produces highly reactive oxygen species at the catalyst surface (the so-called "activeoxygen"), which can oxidize soot very efficiently [30]. In general, the preparation method has a significant effect on the dispersion, reducibility and the interaction between active phases and support material, and further influence their catalytic performance [31]. Impregnation method has been widely used to prepare supported catalysts, but this method may result in poor dispersion or agglomeration of the catalyst [32]. In our previous study, it has been found that the plasma-assisted CoPt-Al_2O_3 catalyst has higher cobalt dispersion and better reducibility which contribute to high catalytic activity [33]. And Xu et al. found that the highly dispersed active surface Ni species prepared by the in situ grown method can greatly enhance the activation of methane. And the synergistic effects induced by γ-Al_2O_3 and the in-situ LDH precursor lead to the excellent catalytic stability [34]. Recently, Wang et al. reported that Co_3O_4/γ-Al_2O_3 prepared by a combination of impregnation and combustion synthesis exhibited excellent catalytic performance. It is noted that the Co_3O_4 dispersion could facilitate the migration of surface Co^{3+} and the redox cycle between Co^{2+} and Co^{3+} at a lower temperature [35]. And microwave synthesis has the advantage of simplicity. However, the detailed comparative information on the supported catalysts prepared by plasma treatment, impregnation-combustion method, microwave in-situ growth of and impregnation method is lacked and the effect of adsorption oxygen and lattice oxygen for methane catalytic combustion has not been addressed. Moreover, it is worth noting that the redox mechanistic studies of spinel-type cobalt oxides to understand the structure-activity relationships are still roused much attentions over the long term. And there is essential need to investigate the effects of

synergistic interaction between active components and support, which is generally regarded as the fundamental insights to improve the catalytic performances of cobalt based catalysts in oxidation processes.

Here, a series of $CoAlO_x$/CeO_2 catalysts were prepared by impregnation-combustion method, plasma treatment, microwave in-situ growth and impregnation method. And the carrier CeO_2 was prepared by solution combustion method. The synthesized catalysts were characterized by using the XRD, BET, TEM, TPR and XPS techniques. The aim of this study is to emphatically investigate the effect of different preparation methods upon catalytic activity as well as the relevance of the adsorption oxygen and lattice oxygen to the catalytic performance.

2. Experimental

2.1. Catalyst preparation

The carrier CeO_2 used in this experiment was prepared by solution combustion method. The supported $CoAlO_x$/CeO_2 catalysts were prepared by impregnation, microwave in-situ grown, impregnation-combustion and plasma treatment. Impregnation method: adequate amounts of $Co(NO_3)_3 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were added into deionized water and mixed with the appropriate amount of CeO_2 powder. After being aged at room temperature for 4 h, the mixture was dried at 100 °C for 24 h. The solid was then crushed and calcined in air at 600 °C for 5 h, denoted as $CoAlO_x$/CeO_2-IWI. Microwave in-situ grown method: 2 g CeO_2 powder was impregnated in an aqueous solution of $Co(NO_3)_3 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and urea with a mixed solution solvent of ethylene glycol and deionized water at a ratio of 7: 1, at a molar ratio of urea to total metal cations of 6:1. After being stirred for 30 min and ultrasound for 20 min, the mixture was kept in microwave reactor at 140 °C for 30 min. Then the particles was washed with deionized water. The obtained samples were dried at 80 °C overnight and calcined at 600 °C for 5 h, denoted as $CoAlO_x$/CeO_2-MW. Impregnation-combustion method: 2 g CeO_2 powder was impregnated in an aqueous solution of $Co(NO_3)_3 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and glycine with deionized water, at a molar ratio of glycine to total metal cations of 1: 2. After aged at room temperature for 4 h, the mixture was heated up to 80 °C in water bath until a sol gel state. Then the mixture was dried at 80 °C and was heated in the muffle furnace until the temperature reached 250 °C. Subsequently, the obtained samples were calcined at 600 °C for 2 h, denoted as $CoAlO_x$/CeO_2-CS. Plasma treatment: $Co(NO_3)_3 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were added into deionized water and mixed with the appropriate amount of CeO_2 powder. After aged at room temperature for 4 h, the mixture was dried at 100 °C for 24 h. The solid was then crushed and exposed at ambient temperature to glow-discharge nitrogen plasma for 15 min, denoted as $CoAlO_x$/CeO_2-P. The Co and Al content at a ratio of 3:1 was fixed at 30 wt% in all mixed oxides.

2.2. Characterization of catalysts

The powder X-ray diffraction (XRD) patterns were obtained using a 40 kV, 30 mA Cu target ray on a DX-2700 diffractometer (China Hao Yuan Company) of the Institute of New Energy and Low Carbon Technology of Sichuan University. 2θ ranges from 5° to 80° with a scan step of 0.03° per second. The average grain size of the Co_3O_4 spinel structure was calculated using the half-width of the strongest peak according to the Scherrer equation.

The N_2 adsorption-desorption curves were measured using an automatic specific surface area and pore size analyzer (Quantachrome NOVA 1000e device) at a liquid nitrogen temperature (77 K). Prior to testing, the sample was degassed at 200 °C for 3 h under vacuum condition. The specific surface area of the catalysts was calculated by the BET equation, and the pore volume and pore size distribution and the average pore size were calculated using the desorption curve according to the BJH method.

The transmission electron microscopy (TEM) pictures were obtained