Journal of the Taiwan Institute of Chemical Engineers 000 (2018) 1–10

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

# Effect of MOx (M = Ce, Ni, Co, Mg) on activity and hydrothermal stability of Pd supported on $ZrO_2$–$Al_2O_3$ composite for methane lean combustion

Yang Wu[a], Guangxia Li[b], Wei Hu[b], Fujin Huang[b], Jianjun Chen[a], Lin Zhong[b,*], Yaoqiang Chen[a,c,*]

[a] *Institute of New Energy and Low-Carbon Technology, Sichuan University, Chengdu 610065, Sichuan, China*
[b] *College of Chemical Engineering, Sichuan University, Chengdu 610064, Sichuan, China*
[c] *College of Chemistry, Sichuan University, Chengdu 610064, Sichuan, China*

ARTICLE INFO

*Article history:*
Received 26 November 2017
Revised 26 January 2018
Accepted 27 January 2018
Available online xxx

*Keywords:*
Palladium
$ZrO_2$–$Al_2O_3$ composite
Methane combustion
Lean burn
Natural gas vehicles

ABSTRACT

$Zr_{0.5}Al_{0.5}O_{1.75}$ (ZA) was modified by metal oxide (Ce, Co, Ni or Mg oxide) *via* double solvent method. The Pd nanoparticles were supported on the modified ZA and then tested for methane lean combustion. The textural, structural and redox properties, surface Pd oxidation states and stability of the samples were investigated systematically. The modified catalysts were aged in the 750 °C humid air (10 vol.% water vapor) for 10 h, namely aging treatment. It was found that the activity and hydrothermal stability of the Pd/ZA catalyst was enhanced after the addition of NiO, MgO or $Co_3O_4$. Particularly, the Pd/NiO/$Zr_{0.5}Al_{0.5}O_{1.75}$ (Pd/NiO/ZA) catalyst exhibited the best performance for methane combustion in the presence of water vapor, regardless of aging treatment. X-ray diffraction (XRD) patterns showed that the presence of spinel phase in the Pd/NiO/ZA. CO-chemisorption results demonstrated the highest Pd dispersion on the fresh and aged Pd/NiO/ZA. $H_2$-temperature-programmed reduction ($H_2$-TPR) measurements indicated that the Pd/NiO/ZA catalyst possessed the best reducibility regardless of aging treatment. X-ray photoelectron spectroscopy (XPS) analysis and temperature-programmed oxidation (TPO) experiments revealed that the Pd/NiO/ZA catalyst possessed the highest active phase PdO content and stability. Consequently, the Pd/NiO/ZA catalyst would be promisingly applied to exhaust after-treatment for lean-burn natural gas vehicles.

## 1. Introduction

Natural gas has been regarded as a cleaner and cheaper energy form compared with coal and oil, and recent years have witnessed extensive industrial and domestic application of natural gas [1]. Particularly, vehicles fueled by natural gas are presently considered as an effective alternative to those fueled by diesel and gasoline due to: 1) the emission of thermal NOx is low due to comparatively lower combustion temperatures in natural gas vehicles (NGVs), 2) the emission of $CO_2$ from NGVs is also lower than the one in diesel and gasoline-fueled vehicles due to the C:H ratio and 3) particulate pollutants produced by NGVs are about ten times less than diesel vehicles', and mainly composed of volatile materials [2–5]. Nevertheless, a significant concern for the widespread implementation of NGVs is the unburned methane, a very strong potent greenhouse gas [4].

Catalytic combustion on Pd-supported catalysts has been proved to be the most efficient solution for the removal of the unburned methane [6–12]. It was found that the catalytic activity of the Pd-supported catalysts for methane combustion was determined by the surface Pd oxidation state and the Pd dispersion and reducibility of Pd catalyst [4,9,10,13–15]. Pd/$Al_2O_3$ normally displays good performance for the removal of methane in exhaust emissions of NGVs. However, main problems in practice include poor activity at low temperature (below 400 °C), and its rapid deactivation, especially under hydrothermal conditions [4,9,10,16]. Therefore, it is very challenging to develop Pd supported on $Al_2O_3$-based materials with excellent activity and hydrothermal stability for methane combustion [4,17]. Promoters have been added to the Pd/$Al_2O_3$ catalyst to improve its performance in methane combustion. Ceria or doped-ceria show special abilities of oxygen storage and donation [10,18,19]. Thus, the additive ceria can provide oxygen for the catalytic combustion at low temperatures by

---

* Corresponding authors.
*E-mail addresses:* zhonglin@scu.edu.cn (L. Zhong), nic7501@scu.edu.cn (Y. Chen).

https://doi.org/10.1016/j.jtice.2018.01.038

Please cite this article as: Y. Wu et al., Effect of MOx (M=Ce, Ni, Co, Mg) on activity and hydrothermal stability of Pd supported on $ZrO_2$-$Al_2O_3$ composite for methane lean combustion, Journal of the Taiwan Institute of Chemical Engineers (2018), https://doi.org/10.1016/j.jtice.2018.01.038

transferring oxygen to Pd, and improve the stability of the active PdO phase at high temperatures [20,21]. Recently, Cargnello *et al.* has reported a Pd@$CeO_2$/H-$Al_2O_3$ catalyst which shows excellent catalytic activity for methane combustion due to the strong metal-support interaction [17]. Generally, strong acidity of the support $Al_2O_3$ would make supported Pd particles prone to sintering under high temperature condition and causes loss of activity [22]. The significantly beneficial effect of MgO promoter on Pd/$Al_2O_3$ catalyst has been found, and there was a conclusion that a support material with moderate acid strength offers maximum conversion of methane [4]. Liu and co-workers investigated the effect of metal oxides (Mn, Fe, La, Mg and Ni) on Pd/$Al_2O_3$ catalysts, and they found that the formation of $NiAl_2O_4$ and $MgAl_2O_4$ spinel phases would be beneficial to the catalytic activity for methane combustion [14]. They further demonstrated that Pd on Ni-modified alumina material showed enhanced hydrothermal stability for methane combustion under lean conditions. This outstanding performance was associated with high Pd dispersion resulting from the stable effect of the support and the least lattice mismatch between $NiAl_2O_4$ and Pd [23]. Yuji Mahara *et al.* developed a Pd/Co/$Al_2O_3$ catalyst prepared by a galvanic deposition method (GD), which provided high quantity of interfaces between PdO and $CoO_x$ as well as appropriate PdO particle size around 8.5 nm. The notable activity for methane oxidation over the catalyst was attributed to its higher reducibility of PdO [24]. Also, Giuliana Ercolino *et al.* reported that cobalt oxide helped to remove hydroxyl species from the PdO surface and supplied lattice oxygen to the PdO phase, contributing to the recreation of the active sites [25].

Recently, due to its unique properties, $ZrO_2$ has attracted considerable attention and has been used as the support of Pd catalysts for methane oxidation [4,11–13,15,19,26,27]. Basically, $ZrO_2$ can improve the resistance of Pd catalysts to water during methane combustion [26,27]. However, Pd supported on single $ZrO_2$ suffers from low activity and hardly meets the requisition of emission standards [3–5]. It was found that Pd supported on $ZrO_2$–$Al_2O_3$ composite could realize considerable enhancement in catalytic activity and stability for the reaction [28,29]. Recently, we have added $La_2O_3$, ZnO, $Y_2O_3$ or BaO to the Pd/$Zr_{0.5}Al_{0.5}O_{1.75}$ catalyst to further improve the catalytic performances for methane oxidation [30]. The results demonstrated that ZnO and $Y_2O_3$ promoters enhanced the catalytic activity remarkably. However, the hydrothermal stability of these catalysts was not good, which might be due to the poor metal dispersion. Recently, a new double solvent (DS) method has been developed to synthetize supported catalysts. With the method, the desired salt solution with a more favorable wetting property can replace the apolar solvent such as n-hexane in the pores of the support, which would result in homogeneously dispersed metal (oxide) catalysts [31]. Very recently, we have found that Pd supported on $ZrO_2$–$Al_2O_3$ composite *via* the new DS method showed improved catalytic activity and hydrothermal stability for methane combustion under lean conditions compared with the catalyst prepared by a convenient incipient wetness impregnation method [32]. The enhancement could be linked to higher Pd dispersion of the catalyst. However, this catalyst' performance is still not excellent enough to meet the *increasingly* stringent emission standards [5]. It seems that there is a possibility of significantly improving the catalytic performance of the catalyst by modification of the $ZrO_2$–$Al_2O_3$ support with metal oxides reported in literature [10,14,17,19–25].

Here, Pd/MOx/$Zr_{0.5}Al_{0.5}O_{1.75}$ (M = Ce, Ni, Co, Mg) catalysts were developed by the double solvent method. The textural, structural and redox properties, surface Pd oxidation states and stability of the samples were investigated systematically. The catalysts displayed significantly enhanced activity and hydrothermal stability for methane lean combustion in a gas mixture simulating the exhaust of lean-burn NGVs.

## 2. Experiment

### 2.1. Preparation of support

The $Zr_{0.5}Al_{0.5}O_{1.75}$ support material was prepared by co-precipitation method. The precursor $ZrOCO_3$ (48.00 ± 0.01 g) was dissolving in concentrated nitric acid (68 wt.%, 10.30 ± 0.01 ml) and $Al(NO_3)_3$•$9H_2O$ (53.80 ± 0.01 g) in distilled water (100 ± 1 ml), respectively. After mixing the two solutions thoroughly, the mixed solution was diluted to 500 ± 5 ml by distilled water. Then the diluted solution was coprecipitated with an ammonia solution under vigorous stirring and the pH was kept at around 8.5–8.8. After being digested in the mother liquor at 98 ± 1 °C for 6 h, the obtained precipitate was subsequently filtered and washed with distilled water, followed by drying at 120 ± 5 °C overnight and calcining at 950 ± 5 °C in air for 3 h to finally obtain the $Zr_{0.5}Al_{0.5}O_{1.75}$ material which was denoted as ZA. The support's photograph and micrographs were shown in Fig. S1.

Modified $MO_x$/ZA (M = Ce, Co, Ni and Mg) materials were prepared by the double solvent method, which had been used in our previous work [32]. The schematic representation was shown in Fig. S2(a). Typically, 5.00 ± 0.01 g of the as-prepared ZA was suspended in 200 ± 2 ml *n*-hexane as hydrophobic solvent and the mixture was stirred for 30 min until a homogeneous mixture was obtained. A desired loading content of $Ce(NO_3)_2$•$6H_2O$, $Co(NO_3)_3$•$6H_2O$, $Mg(NO_3)_2$•$6H_2O$ and $Ni(NO_3)_2$•$6H_2O$ precursors was respectively dissolved in 1.65 ± 0.01 ml distilled water, whose quantity is equal to the pore volume of the support determined by $N_2$ adsorption–desorption. Then, each hydrophilic salt solution was added dropwise to the hydrophobic n-hexane suspending ZA with constantly vigorous stirring, respectively. The resulting turbid liquid was continuously stirred for 3 h. After careful filtration, the powders were dried in air at room temperature. These synthesized samples were further dried at 120 ± 5 °C for 2 h, and then calcined in air at 900 ± 5 °C for 3 h to finally get the $MO_x$/ZA materials. The modified support materials were denoted as $CeO_2$/ZA, $Co_3O_4$/ZA, NiO/ZA and MgO/ZA, respectively. Here, we assigned the content of ZA as a, the loading content of $MO_x$ as b and the content of $MO_x$ in the $MO_x$/ZA as c, then $c = b/(a + b)$. The nominal loading of metal oxide for all the sample is 5 wt.%.

### 2.2. Catalyst preparation

The corresponding Pd-based catalysts were also prepared by double solvent impregnation method (as described above) and the Schematic representation was shown in Fig. S2(b). Specifically, 4.50 ± 0.01 g of the modified ZA was suspended in 200 ± 2 ml n-hexane and the mixture was stirred for 30 min until a homogeneous mixture was obtained. 1.40 ± 0.01 ml aqueous solution of $Pd(NO_3)_2$ containing a desired amount of Pd was added dropwise to the above mixture with constant vigorous stirring. The resulting mixture was continuously stirred for 3 h. After careful filtration, the powders were dried and calcined by the way described above. The nominal loading of Pd for all the modified ZA is 1.5 wt.%. After that the catalyst samples were ball-milled with a certain amount of deionized water to obtain homogeneous slurries, and then the resulting slurry was coated onto honeycomb cordierite monoliths (Jiangsu Yixing, 400/6 cordierite material, 2.5 $cm^3$). The excessive slurry was blown away with compressed air. Thereafter, the coated catalysts were dried overnight at 120 ± 5 °C and calcined at 550 ± 5 °C in air for 3 h and eventually the fresh monolithic catalysts (Fig. S3) were obtained. They were denoted as Pd/ZA,

Please cite this article as: Y. Wu et al., Effect of MOx (M=Ce, Ni, Co, Mg) on activity and hydrothermal stability of Pd supported on $ZrO_2$-$Al_2O_3$ composite for methane lean combustion, Journal of the Taiwan Institute of Chemical Engineers (2018), https://doi.org/10.1016/j.jtice.2018.01.038