



Methane abatement under stoichiometric conditions on perovskite-supported palladium catalysts prepared by flame spray synthesis

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ABSTRACT

Three-way catalysts (TWC) are the key technology to reduce emissions of pollutants from stoichiometric engines. Perovskite-type catalysts of general formula $ABO_{3\pm\delta}$ (A = La, Y; B = Mn, Fe) containing 2 wt% Pd were produced by flame spray synthesis (FSS) using metal nitrate precursors. The structural properties of the catalysts were characterized by X-ray diffraction (XRD), surface area determination (BET) and transmission electron microscopy (TEM). Crystalline metal oxide nano-particles of 20 nm average size were accompanied by minority La_2O_3 and Y_2O_3 phases. The state of Pd in the catalysts was characterized using X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge spectroscopy (XANES) and CO adsorption by infrared spectroscopy. Metallic Pd coexisted with Pd in oxidation state +2 and higher on all fresh samples. TEM confirmed the presence of dispersed Pd particles 2–5 nm in diameter. Therefore, under the chosen synthesis conditions, FSS provides supported palladium nano-particles rather than a solid solution. PdO was the dominant Pd species after calcination at 700 °C. The TWC activity was tested in a simulated stoichiometric gas mixture comprising CH_4 , CO, NO_x and O_2 . PdO in combination with $YFeO_{3\pm\delta}$ exhibited the lowest temperature for CH_4 oxidation ($T_{50} = 450$ °C), which was ca. 100 °C lower than that of the sample obtained by the conventional wet-chemical method. After cycling under reaction conditions up to 850 °C, a large improvement of catalytic activity for CH_4 oxidation was observed which associated with the formation of metallic Pd particles (ca. 20 nm) and the hexagonal → orthorhombic phase transition of $YFeO_{3\pm\delta}$.

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1. Introduction

Natural gas and biogas are attractive alternative fuels to gasoline and diesel for motor vehicles. This calls for material design of suitable catalytic converters for pollution control in order to comply with the stringent emission regulations. Current aftertreatment technologies for stoichiometric engines fuelled by compressed natural gas (CNG) are based on palladium containing three-way catalysts (TWC) that are most efficient at stoichiometric

air-to-fuel ratio ($\lambda = 1$) [1]. Palladium (Pd) is relatively cheap among the platinum group metals (PGM) and is considered as the most active for total oxidation of methane [2]. Though conventional TWC are very efficient, they suffer from the deactivation caused mainly by sintering of Pd and the metal oxide support as a result of severe redox reaction conditions and high temperature surges within the catalytic converter [3]. Perovskite-type oxides have been indicated as potential components of TWC due to the possibility to stabilize the PGM through its interaction with the perovskite lattice [4,5]. In response to the periodic reducing and oxidizing reaction conditions, Pd seems to be capable to segregate and re-dissolve into the ABO_3 lattice, respectively, thus preventing extensive particle sintering under prolonged operation and at high temperatures. This controversial self-regenerative function [6] has

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Table 1
Physico-chemical properties of the catalysts.

Sample	Entry name	SSA (m ² /g)		Pd content ^b		XRD ^c	OSCC ^d μmol O ₂ /g
		Fresh	Calc ^a	wt%	at%		
LaFeO _{3±δ}	LFO	28	17	–	–	o + La ₂ O ₃	173
LaMnO _{3±δ}	LMO	18	17	–	–	o + La ₂ O ₃	490
YFeO _{3±δ}	YFO	27	19	–	–	h + Y ₂ O ₃	416
YMnO _{3±δ}	YMO	34	31	–	–	h + Y ₂ O ₃	875
La(Fe,Pd)O _{3±δ}	LFPO	22	17	1.82 ± 0.03	0.84	o + La ₂ O ₃	176
La(Mn,Pd)O _{3±δ}	LMPO	32	18	1.79 ± 0.01	0.82	o + La ₂ O ₃	597
Y(Fe,Pd)O _{3±δ}	YFPO	36	19	1.75 ± 0.02	0.64	h + Y ₂ O ₃	504
Y(Mn,Pd)O _{3±δ}	YMPO	33	31	1.71 ± 0.01	0.62	h + Y ₂ O ₃	961
YFeO _{3±δ}	YFO _{CM} ^e	–	9	–	–	h	–
Y(Fe,Pd)O _{3±δ}	YFPO _{CM} ^e	–	12	2.37 ± 0.01	0.86	h	505

^a Conditions: 700 °C for 2 h, in air.

^b By ICP-OES.

^c Fresh samples. o: orthorhombic; h: hexagonal. LMPO undergoes orthorhombic to rhombohedral phase transition upon calcination.

^d Oxygen storage capacity complete at 400 °C (by TG analysis).

^e Prepared by the amorphous citric acid method.

been extensively described with respect to gasoline stoichiometric engines, whereas the research is rarely undertaken with natural gas fuel and methane [7]. Tzimpilis et al. [8] reported the TWC activity of La–Mn–O substituted with low amounts of Pd. Catalyst activation was observed, which was ascribed to the segregation of Pd as a result of the high-temperature hydrothermal conditions experienced during operation.

It has been recognized that the activity of especially La-based perovskite-type (ABO_{3±δ}) oxidation catalysts is largely governed by their defect chemistry and oxygen diffusion properties [9,10]. However, the nature and size of the A-site rare-earth element play a crucial role to determine the physico-chemical properties of the mixed oxides. Replacement of La³⁺ (1.17 Å) by smaller size ions like Y³⁺ (1.04 Å) [11] introduces a large structural distortion that can change interatomic distances and microstructural properties. As a result, both oxygen content and mobility and consequently catalytic activity can be strongly affected. A few studies have demonstrated the potential of Y-based perovskite-type catalysts. Orthorhombic YFeO₃ and YMnO₃ exhibit weak ferromagnetic behaviour [12] and possess good photocatalytic properties [13]. Orthorhombic YCo_{0.5}Mn_{0.5}O₃ exhibited superior catalytic activity for methane oxidation compared to corresponding La and Er based catalysts [14]. Furthermore, the metastable hexagonal structure of YFeO₃ can be easily formed in the presence of Pd, which showed high catalytic activity for CO [15] and CH₄ oxidation [16]. Despite its different crystal structure, which ultimately affects the possible coordination environment of Pd at Fe sites, this material possesses ‘self-regenerative’ properties [15].

The activity and stability of catalyst nano-particles is strongly dependent on their size, shape, surface structure as well as the bulk and surface composition. These parameters can be tuned by the choice of appropriate synthesis methods. Flame-spray synthesis (FSS) is a well-established single step method to provide high yield of nano-materials using economic precursors [17–23]. Small crystal size and a sufficient thermal resistance against sintering are the key properties of a perovskite catalyst [18], which can be obtained by FSS. Additionally, the potential of FSS to produce novel and metastable phases with unusual properties, which may not be reproducible by conventional wet chemical methods is also known [24]. However, the particle formation mechanism is largely dependent on synthesis parameters and the homogeneity of the particles depends on the selection of the metal precursors [25,26]. FSS is a suitable method to produce perovskite-type oxides for the flameless methane oxidation [17,27–29].

In this work, we use a unique high temperature acetylene flame to produce Pd-substituted perovskite-type oxides from metal nitrate precursors of La and Y as the A-site cations and of Fe and Mn

as the B-site cations and of Pd. The aim is the single step synthesis of potential TWC components for the exhaust aftertreatment of stoichiometric engines fuelled with natural gas. The materials are tested under stoichiometric air-to-fuel ratio and their performance is compared with that of a conventional model TWC.

2. Experimental

2.1. Catalyst preparation

Perovskite-type oxides of the general composition A(B,Pd)O₃ (A = La or Y; B = Mn or Fe) containing nominally 2 wt% Pd were prepared by flame spray synthesis (FSS). Metal nitrates, La(NO₃)₃·6H₂O (99%, Auer Remy), Mn(NO₃)₂·4H₂O (97%, Fluka), Fe(NO₃)₃·6H₂O (98–101%, Fluka), Y(NO₃)₃·6H₂O (99.9%, ABCR) and Pd(NO₃)₂ (4.424 wt% Pd solution, Alfa Aesar) were dissolved in a 1:3 mixture of deionized water and *N,N*-dimethylformamide (DMF, 99%, Sigma–Aldrich) [23]. The total metal nitrate concentration was kept constant at 1 mol/l. DMF serves as a fuel with a high boiling point (153 °C) and high combustion enthalpy (–1941.9 kJ/mol), which increases the flame temperature to facilitate the conversion of non-volatile precursors into oxides [23].

The detailed FSS setup has been described elsewhere [21,30]. Briefly, each of the precursor solutions was pumped at 20 ml/min by double syringes through a capillary, atomized by a flow of 35 l/min O₂ and ignited by six circularly arranged acetylene/oxygen flamelets (13/17 l/min), resulting in a ca. 20 cm long flame. The acetylene/oxygen flame exhibits a higher heat capacity (44 kJ/mol) than the commonly used CH₄ flame (36 kJ/mol) thus enabling the decomposition of non-volatile nitrates into oxides and sustaining the presence of water. The nano-powders were collected on glass fiber filters (Whatman GF1) via a vacuum pump. A calcination treatment in air at 700 °C for 2 h was chosen after TGA analysis of the freshly prepared powders (Fig. S1). In the following, the catalysts are labelled as reported in Table 1.

For comparison, the best perovskite-type catalyst in terms of TWC activity was also prepared by the conventional amorphous citric acid method and calcined at 700 °C [16]. The reference conventional powder TWC was composed of Pd, alumina and ceria-zirconia (Pd/ACZ; 1.6 wt% or 0.3 at% Pd; SSA = 135 m²/g) and was kindly provided by Umicore.

2.2. Characterization

The Pd content of the catalysts was determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent 7500cx) (for details see [31]).

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