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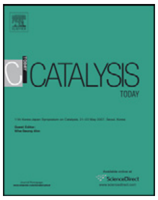

Pd-integrated perovskites for TWC applications: Synthesis, microstructure and N_2O-selectivity

G.C. Mondragón Rodríguez [a,*], K. Kelm [a], S. Heikens [b], W. Grünert [b], B. Saruhan [a]

[a] *German Aerospace Center, Institute of Materials Research, Cologne, Germany*
[b] *Ruhr University Bochum, Dept. of Technical Chemistry, Bochum, Germany*

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ABSTRACT

Two versions of Pd-doped perovskite based catalysts (Pd impregnated onto or integrated into perovskite: Pd–$LaFe_{0.65}Co_{0.35}O_3$ and $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$) were synthesized by applying a modified citrate route and analyzed by XRD, TEM and XPS. The catalytic properties of the perovskites were measured for NO reduction reactions occurring in three way catalysis, including lean, stoichiometric and rich conditions. The N_2O concentrations were measured and compared to the N_2O formation of a commercial three way catalyst. The perovskite-based catalysts produced significantly less N_2O than the TWC – ca. 75% under lean conditions at the temperatures of maximum N_2O-formation and ca. 60% less N_2O under stoichiometric conditions. Under rich conditions the Pd–$LaFe_{0.65}Co_{0.35}O_3$ catalyst produced ca. 58% less N_2O than the TWC, while no N_2O was detected at all on the Pd-integrated perovskite $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ under these conditions.

1. Introduction

The three way catalyst (TWC) is a well-established technology for exhaust treatment from automotive engines. Precious metal(s) such as Pd, Pt, and Rh, supported on mixed oxides (i.e. Al_2O_3, CeO_2, SiO_2, ZrO_2, etc.) represent the state of the art in this field. The TWCs are very effective in eliminating NO_x, CO and unburned hydrocarbons (UHCs) to the emission levels imposed by the actual legislation. Under stoichiometric combustion enough reducing agent (UHCs and/or CO) is present to eliminate NO and O_2 [1]. The global reactions occurring during NO_x-reduction on the TWCs are:

$$HC + O_2 \rightarrow CO_2 + H_2O \tag{1}$$

$$2CO + O_2 \rightarrow 2CO_2 \tag{2}$$

$$HC + NO \rightarrow 1/2\,N_2 + CO_2 + H_2O \tag{3}$$

$$CO + NO \rightarrow 1/2\,N_2 + CO_2 \tag{4}$$

These reactions imply a very clean catalytic system but, in reality the TWC produces significant amounts of N_2O. Particularly, the TWC in gasoline-fuelled cars produce considerably more N_2O (approx. 100 mg/km) than any other engine technology and cars without catalyst [2]. New catalytic technologies contribute to considerably less N_2O-formation which is strongly affected by the driving conditions and fuel quality [3]. The formation of N_2O may occur in the presence of excess NO with CO (reaction (5)) as reported by Granger et al. [4]. Depending on the reaction conditions, the catalyst composition, the stream composition and the temperature, the formed N_2O may react with CO to form N_2 and CO_2, see reaction (6) [5].

$$CO + 2NO \rightarrow N_2O + CO_2 \tag{5}$$

$$CO + N_2O \rightarrow N_2 + CO_2 \tag{6}$$

Nitrous oxide (N_2O) is a greenhouse gas and has 310 and 21 times the Global Warming Potential (GWP) of CO_2 and CH_4 respectively [6]. In 1998 only 5% of the total annual N_2O formation in the European Union was related to transport – the agricultural sector and chemistry industry were the highest N_2O producers with 57 and 29%. However, the strong growth of motorization may cause concern also related to N_2O when its output from catalytic converters cannot be reduced. To date N_2O is not yet regulated, but legislation and automobile producers will have to tackle this issue in the near future.

In the 1975s, perovskite based catalysts such as $LaCoO_3$ and $La_{0.8}K_{0.2}Mn_{0.94}Ru_{0.06}O_3$ were tested for NO reduction in streams containing H_2 and CO [7]. The molecular adsorption of NO and its dissociative adsorption on an oxygen vacancy were determined as the main mechanism of reduction of NO by CO and H_2. The combination of these two processes leads to the formation of N_2O.

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[*] Corresponding author. Tel.: +49 2203 601 3869; fax: +49 2203 696480.
E-mail address: guillermo.mondragon-rodriguez@dlr.de (G.C.M. Rodríguez).

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Small amounts of precious metals did not affect the NO conversions but the selectivity of the catalysts. For instance, Rh produced NH_3, Ru produced N_2 and Ni produced N_2O at low temperature. The importance of the transition metal in the binding and the reactions of the nitrogen-containing products after NO-dissociation was noted [7,8]. The surface oxygen vacancy has a very important role. A La–Sr-based perovskite with high binding energy of oxygen yielded less desorbed N_2 and N_2O than perovskites with low binding energy of oxygen. In general, Ru-doped perovskites i.e. $La_{0.8}K_{0.2}Mn_{0.94}Ru_{0.06}O_3$, $SrRuO_3$ had better selectivity than the Ru-supported catalyst Ru/γ-Al_2O_3 catalyst.

More recently, Japanese researchers reported a series of Pd-integrated perovskites that might display a self-regenerative effect [9]. Palladium ions are dissolved in the crystal lattice of ABO_3 (A = La, Ce, etc., and B = Fe, Co, Pd) perovskites. These metal ions emerge from the perovskite as Pd° metallic nanoparticles under reducing conditions and fully dissolve back into the structure under oxidizing conditions [9,10]. The $LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$ perovskite displayed 95% of NO_x conversion for NO vs. CO reactions compared to 80% achieved on a Pd/Al_2O_3 reference after catalyst treatment at 850 °C. Additionally, the TWC was strongly deactivated after exposition at 1050 °C, while the perovskite was able to withstand the thermal deactivation still achieving 85% of NO reduction. On the other hand, the N_2 selectivity (in other words the N_2O-formation) of the Pd-integrated perovskite for TWC applications has been scarcely studied. Uenishi et al. investigated the NO reduction ability of the $LaFe_{0.95}Pd_{0.05}O_3$ perovskite by applying pulses of NO and analysing the products with a Time of Flight Mass Spectrometer (TOF-MS). The formation of N_2 and N_2O was detected during these experiments but no selectivity values were given [11]. No oxygen release was observed in the products leading to an assumption that N_2O may be formed on the Pd° sites according to the following reaction;

$$2NO + Pd^{\circ} \rightarrow N_2O + PdO \qquad (7)$$

In the present investigations, La-based perovskite catalysts doped with Pd have been synthesized by the citrate route. The Pd-doped perovskites were characterized by means of XRD, XPS, TEM techniques and thoroughly tested for NO_x-reduction under slightly lean, stoichiometric and slightly rich conditions. Particular attention has been paid to the N_2O-formation of the catalysts. The N_2O-formation of the Pd-doped perovskites has been evaluated and compared with the N_2O-formation levels of a reference TWC catalyst.

2. Experimental

2.1. Synthesis method

Separate sols of lanthanum acetate ($La(COOCH_3)_3\cdot xH_2O$) (99.9%) dissolved in isopropanol, cobalt acetyl acetonate (98%) and iron nitrate ($Fe(NO_3)_3$) (99%) dissolved in distilled water were prepared. Concentrated nitric acid is needed to improve the solubility of La acetate and Co acetyl acetonate solutions. Palladium nitrate ($Pd(NO_3)_2$) was first added to the iron nitrate solution and then mixed with the cobalt source. The solution containing Fe and Co was mixed with a stoichiometric amount of citric acid. Ethylene glycol was also added to the solution at a mass ratio of 40:60% of the citric acid amount. The resulting solution was mixed with the lanthanum acetate sol under thorough stirring. Finally, the solvent was removed on a hot plate at 80 °C and the resulting solid was slightly ground in an agate mortar and calcined at temperatures up to 900 °C for 3 h [12]. The samples tested here were treated at 700 °C for 3 h to reduce the presence of PdO as we will discuss in Section 3. This sample will be labelled $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ – 700 °C/3 h.

Table 1
Reaction conditions during catalytic tests performed with Pd–$LaFe_{0.65}Co_{0.35}O_3$ – 700 °C/3 h and $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ – 700 °C/3 h. Catalyst mass 125 mg, total flow rate = 183 ml/min, W/F = 0.041 s g ml^{-1}.

Reaction	Stream composition
CO vs. NO	1000 ppm CO, 1000 ppm NO, balance He
Stoichiometric mixture	1.1% CO, 1000 ppm propene, 1000 ppm NO, 9500 ppm O_2, balance He
Lean mixture	1.1% CO, 1000 ppm propene, 1000 ppm NO, 10,500 ppm O_2, balance He
Rich mixture	1.1% CO, 1000 ppm propene, 1000 ppm NO, 8500 ppm O_2, balance He

For the TEM-analysis part of the material was reduced by heating in a mixture of N_2/H_2 (20:1) at 600 °C.

In addition, a Pd-supported perovskite was investigated. For this purpose the Pd-free perovskite ($LaFe_{0.65}Co_{0.35}O_3$) was synthesized applying the same synthesis route described in this section. The final solution was also dried and ground in an agate mortar and calcined at 700 °C for 3 h. The obtained powder was then mixed with a palladium nitrate aqueous solution. Finally, the resulting suspension was dried and calcined at 700 °C for 3 h. This sample will be labelled Pd–$LaFe_{0.65}Co_{0.35}O_3$ – 700 °C/3 h.

2.2. Structural characterization of the catalysts

The XRD analysis of the powder catalysts was carried out in a SIEMENS D5000 diffractometer in Bragg Brentano geometry applying Cu Kα radiation (λ = 1.54056 Å). The powder sample was slightly ground in anagate mortar and dispersed and fixed by adhesion only on the surface of a reflex-free silicon single crystal sample holder. Peak assignments were made with the JCPDS data base (EVA software package, Bruker).

The Transmission Electron Microscopy (TEM) study was made with a Phillips Tecnai F30 microscope equipped with an Energy Dispersive X-ray Spectrometer (EDAX) operated at 300 keV. For TEM-analysis the powder samples were dispersed on holey carbon films supported by TEM copper grids (LACEY) without applying any solvent to avoid any preliminary reduction of the sample.

The XPS spectra were taken with a Leybold LHS 10 spectrometer equipped with a Specs EA 10/100 electron analyzer with multi-channel detection. The perovskite samples were analyzed in as prepared state (after calcination at 700 °C), and after reduction in 4.5 vol.% H_2 in Ar at 200 °C and 500 °C. The reduced samples were transferred into the spectrometer avoiding any contact with air. The XPS spectra were recorded with Mg Kα radiation (1253.6 eV, 12 kV, 20 mA). The binding energies (BE) reported here are relative to the binding energy of carbon C 1s = 284.5 eV.

2.3. Catalytic tests

The catalytic tests were performed in a catalytic microflow reactor of 15 mm inner diameter with a weight/feed ratio W/F = 0.041 s g ml^{-1} (183 ml/min feed dosed on 125 mg catalyst). The catalyst was pressed, crushed and sieved, and the sieve fraction between 250 and 355 μm was used for the study. The feeds were prepared from premixed gases provided by Air Liquide. In the TWC model feeds, propene was employed to simulate unburned hydrocarbons. On this preliminary stage of the research, dry product mixtures were used. The compositions used in the experiments reported here are summarized in Table 1. All products were analyzed by a combination of calibrated mass spectrometry and non-dispersive IR photometry.