

The influence of the state of Pd on methane combustion in Pd-doped LaFeO₃ perovskites

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Introduction

“Intelligent catalysts” [1] promise long term stability and activity for the abatement of NO_x, CO and hydrocarbons through their capability of incorporating in the lattice and segregating on the surface noble metals in cycles of oxidative and reductive atmosphere typical of automotive catalysts. This was successfully shown for the La-Fe-Pd-O perovskite system [2]. The perovskite phase enables keeping high dispersion of the noble metal under the fluctuating conditions of a car exhaust. Fast redox cycles prevent the agglomeration of noble metal particles on the perovskite that is usually observed on conventional catalysts.

Stimulated by these reports we synthesized Pd-doped LaFeO₃-perovskites with the aim to engineer the position of the metal on the surface or within the lattice for their possible use in the exhaust aftertreatment of CNG vehicles.

Materials and Methods

Perovskites with the general formula LaFe_{1-x}Pd_xO₃ (x = 0.05, ~2 wt.% Pd) were synthesized by the citrate method [3] by mixing the required amounts of metal nitrates in the precursor solution with stoichiometric (LaFe_{0.95}Pd_{0.05}O₃) and non-stoichiometric Pd content (LaFePd_{0.05}O₃). The obtained gels were dried and calcined in air for 2h at 700°C. Additionally, 2 wt.% Pd/LaFeO₃ was synthesized by impregnation of LaFeO₃. All samples were characterized using XRD, XRF, BET, H₂-TPR (10 vol.% H₂/He), CO-DRIFT, TEM and XAS. CH₄ combustion runs were performed in a lab scale plug-flow reactor between 200 and 700°C by heating at 10°C/min in a mixture of 1 vol.% CH₄ and 4 vol.% O₂ (bal. He) at a flow rate of 100 ml/min.

Results and Discussion

X-ray fluorescence analysis showed highest intensity of the Pd-L_α-signal for Pd/LaFeO₃ and lowest intensity for LaFe_{0.95}Pd_{0.05}O₃. The XANES region of calcined LaFe_{0.95}Pd_{0.05}O₃ showed an edge characteristic of Pd in higher oxidation state than Pd²⁺, whereas Pd/LaFeO₃ showed the typical edge of PdO. The FT-EXAFS spectrum of LaFe_{0.95}Pd_{0.05}O₃ showed only Pd-O but no Pd-Pd bonds of PdO nanoparticles. Additionally, some contribution from likely Pd-Fe and Pd-La distances was found.

H₂-TPR indicated that reduction of Pd/LaFeO₃ is facile and occurs already at room temperature, whereas reduction of LaFe_{0.95}Pd_{0.05}O₃ is difficult. CO-DRIFT spectra (Fig. 1) demonstrate that after reduction at 300°C more Pd is available on Pd/LaFeO₃ than LaFe_{0.95}Pd_{0.05}O₃ for CO adsorption. Pd nanoparticles appear smaller on LaFe_{0.95}Pd_{0.05}O₃ following reduction. The XANES data under H₂-TPR conditions suggest that Pd in LaFe_{0.95}Pd_{0.05}O₃ is still in the oxidized state under these conditions. All data support the

incorporation of Pd within the ABO₃ lattice of LaFe_{0.95}Pd_{0.05}O₃. Therefore, according to the time of addition of Pd during synthesis, different catalysts with same composition but different structure can be obtained.

Methane combustion tests (Fig. 1) showed highest catalytic activity for the impregnated perovskite where most of Pd is present as PdO on the surface of LaFeO₃. LaFe_{0.95}Pd_{0.05}O₃ and LaFeO₃ exhibited the lowest catalytic activity for CH₄ conversion. Incorporation of Pd in the lattice does not provide sufficiently active catalysts, and PdO species still appear required for best catalytic performance.

On-going reduction-oxidation cycles during methane combustion will provide information to assess whether the possible self-regenerating function of LaFe_{0.95}Pd_{0.05}O₃ can improve the performance compared to impregnated catalysts.

Significance

Growing awareness of environmental protection, stricter governmental regulations for the abatement of exhaust gases and the shortage of crude oil resources are setting CNG engines into the focus of research. Pd-doped perovskites are promising catalysts as alternative to conventional three-way catalysts typical of gasoline vehicles.

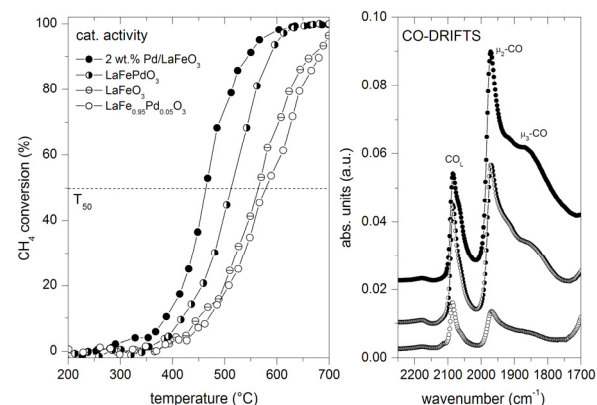


Figure 1: Catalytic data of CH₄ abatement and CO-DRIFTS spectra of Pd/LaFeO₃, LaFePd_{0.05}O₃ and LaFe_{0.95}Pd_{0.05}O₃ after reduction at 300°C for 30 min and CO-adsorption at room temperature.

References

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