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Synthesis and analysis of adaptive Pd-integrated perovskite catalysts for effective NO_x-reduction

G.C. Mondragón-Rodríguez *, B. Saruhan, W. Grünert [1], S. Geisler [2], M. Berndt [2]

DLR, Institute of Materials Research, D-51147 Cologne, Germany

[1] Ruhr-University Bochum, Dept. of Technical Chemistry

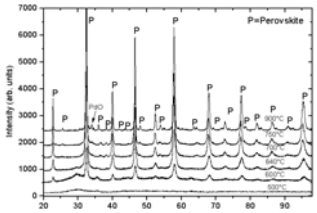
[2] INTERKAT Catalyst GmbH, Königswinter

•Corresponding author: Phone: + 49 2203 601 3869, Fax: + 49 02203 696480, Email: guillermo.mondragon-rodriguez@dlr.de

Introduction:

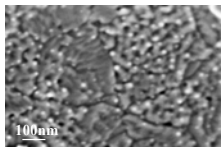
The purpose of the present work is to develop a catalyst with improved NO_x-reduction capacity for lean-burn applications. The main idea is to chemically bond palladium ions into the perovskitic crystal structure to create oxygen vacancies and reduce the amount of the PGM. Palladium ions may reversibly diffuse in and out of the perovskite structure depending on the redox conditions [1]. This reversible movement may hinders sintering effects (i.e. particle growth) that otherwise cause deactivation of the catalyst during long-term service resulting in improved catalyst performance.

Results:



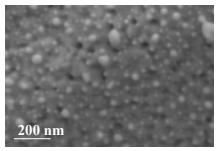
Evolution of phase(s) in $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ as detected by XRD after calcination in air [2].
-Only the perovskite with orthorhombic phase was found.
- PdO not found after calcination in air up to 700°C
- After treatment at 900°C tetragonal PdO was observed.

SEM and TEM study



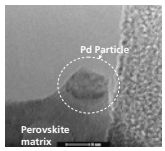
SEM-micrograph of $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ reduced in 5 vol. % H_2 in N_2 at 600°C/3h

- Particle sizes 10 - 15 nm.
- Possible diffusion of Pd out of the perovskite lattice?



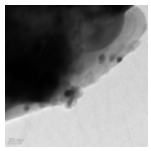
SEM-micrograph of Pd-$LaFe_{0.65}Co_{0.35}O_3$ reduced in 5 vol. % H_2 in N_2 at 600°C/3h.

- Pd particles supported on the perovskite surface.
- Particle sizes 50 – 80 nm



TEM-image of $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ reduced in 5 vol. % H_2 in N_2 at 600°C/3h.

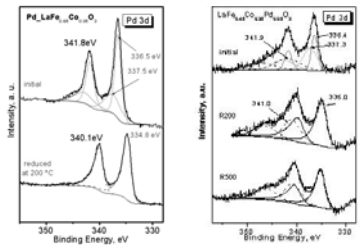
- Homogeneous distribution of Pd in the perovskite matrix.
- 5 nm Pd-particle.



TEM-image of Pd-$LaFe_{0.65}Co_{0.35}O_3$ reduced in 5 vol. % H_2 in N_2 at 600°C/3h.

- Pd on the perovskite surface
- 20 nm Pd-particles.

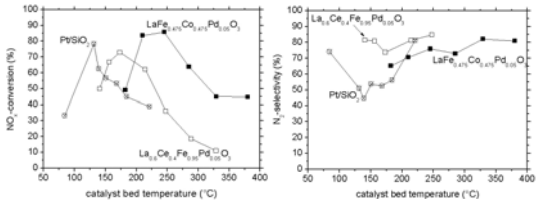
XPS analysis



Pd 3d XPS lines of Pd-integrated $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$-700°C/3h and Pd-$LaFe_{0.65}Co_{0.35}O_3$-700°C/3h, and after reduction treatments in 4.2 vol. % H_2 + Ar at 200°C and at 500°C/1h.

- Three Pd-states are found in the perovskite surfaces: Pd^{3+}, Pd^{2+} and Pd°,
- Only Pd° is found on Pd-$LaFe_{0.65}Co_{0.35}O_3$ upon reduction at 200°C,
- Pd° and Pd^{3+} are found even after reduction at 500°C on $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$,
- Asymmetry of the XPS signals as indicator for Pd in the lattice?

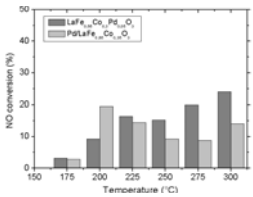
H_2-SCR of NO_x



NO_x-conversion (left) and N_2-selectivity (right) of the perovskites $LaFe_{0.475}Co_{0.475}Pd_{0.05}O_3$, $La_{0.6}Ce_{0.4}Fe_{0.95}Pd_{0.05}O_3$-900°C/3h and 1 wt.% Pt/SiO_2.
Reaction conditions: 300 mg of catalyst, gas composition = 0.072 vol.% NO + 5 vol.% O_2 + 1 vol.% H_2 + 7.2 vol.% H_2O + 7.2 vol.% CO_2 + He, W/F = 0.065 g.s.ml^{-1}.

- Perovskite composition affects the NO_x-conversions and N_2-selectivity of Pd,
- The different Pd-states in the perovskites caused a positive effect to the NO_x-conversion and N_2-selectivity,
- Pt/SiO_2 catalyst produced higher amount of N_2O.

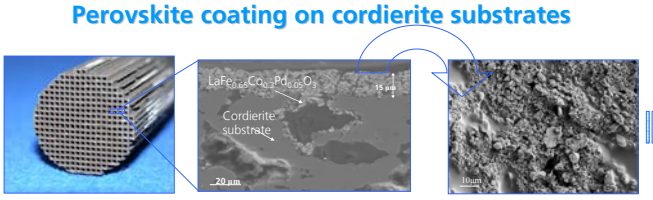
C_3H_6-SCR of NO_x



Reaction conditions: 75 mg of catalyst, gas composition = 0.05 vol.% NO + 0.05 vol.% C_3H_6 + 5 vol.% O_2 + Ar, W/F = 0.015 g.s. ml^{-1}.

- NO_x-conversion is affected by the state of Pd in the perovskites,
- $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ display higher NO_x-reduction than Pd-$LaFe_{0.65}Co_{0.35}O_3$ specially at higher temperatures.

Perovskite coating on cordierite substrates



Cross-section | Catalytic converter | Coating top-surface

Peak C_3H_6-SCR of NO_x-conversions of the catalytic converter

Gas mixture composition				Temp (°C)	NO_x-conv (%)
NO (ppm)	C_3H_6 (ppm)	H_2O (vol.%)	O_2 (vol.%)		
510	515	----	1	300-400	18
510	520	3.9	1.1	350-450	20
510	520	----	5	400-450	15
460	495	4.7	4.7	450	18

Temperature measured in front of the catalytic converter
Heating rate = 10°K.min^{-1}
SV = 60 000 h^{-1}

Conclusions:

- Finer Pd-particles are obtained in the Pd-integrated perovskite $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ than in the Pd-supported perovskite Pd-$LaFe_{0.65}Co_{0.35}O_3$,
- TEM investigation suggests homogeneous distribution of Pd in the perovskite $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$-700°C,
- XPS study indicates that Pd diffuses partially out of the perovskite lattice upon reduction treatment as some lattice bonded Pd remains,
- Less production of N_2O of the perovskite based catalysts is related to the new Pd-sites (Pd-states, i.e. Pd^{3+}),
- Creation of new Pd-sites (Pd-states, i.e. Pd^{3+}) shift the NO_x-conversions to higher temperatures (C_3H_6-SCR of NO_x) of $LaFe_{0.65}Co_{0.3}Pd_{0.05}O_3$ in comparison to the NO_x-conversions of the Pd-supported perovskite Pd-$LaFe_{0.65}Co_{0.35}O_3$.

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References:
[1] H. Tanaka, M. Misono, Current Opinion in Solid State and Materials Science **5** (2001) 381-387.
[2] G.C. Mondragón Rodríguez, R. Ochrombel, B. Saruhan, Journal of European Ceramic Society **28** (2008) 2611-2616.