

# The effects of specific features of the defect structure on the bonding and mobility/reactivity of oxygen in ceria-based nanomaterials

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## Introduction

Oxygen bonding strength and reactivity in the catalysts control the rates and direction of the processes in oxidation catalysis. It is well-known that fluorites based upon ceria are promising catalysts for various oxidation processes due to their high oxygen mobility [1]. Specific features of their defect structure and microstructure, especially for nanomaterials, strongly depend upon the type and concentration of promoters [2]. Distortions of Ce coordination sphere due to dopants (Zr, Ln) effect favor appearance of weakly bound surface oxygen species and enhance lattice oxygen mobility. The specific features of the defect structure of the surface affect the state of supported Pt which is stabilized as cations, mixed metal oxide clusters and small (20-40 Å) metal clusters. A higher degree of the surface/bulk disordering favors stabilization of mixed Pt clusters in the vicinity of extended defects as well as in the subsurface layers of fluorite-like oxide support.

In the given work the energy features and effective diffusion parameters of the surface and bulk oxygen in Ce-Zr(Sm)-O solid solutions with fluorite structure including Pt supporting ones are discussed on the based of models defect structure of those nanomaterials (distortion of Ce environment, anion vacancies and interstitial oxygen) and state of Pt species.

## Materials and Methods

Ce<sub>1-x</sub>Sm<sub>x</sub>O<sub>y</sub> (x=0.05-0.4) and Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> have been prepared by complex polymerized method (CPM) [1] or co-precipitation from solutions of Ce<sup>3+</sup>/ Sm<sup>3+</sup> nitrates and ZrOCl<sub>2</sub> followed by calcination at 700°C. Pt (1.4 wt%) is supported by wetness impregnation. TPD O<sub>2</sub> is carried out in the flow of He. Constants of diffusion exchange rate between surface and subsurface layer (V<sub>D</sub>) and diffusion coefficient (D) are estimated by reduction by CO and CH<sub>4</sub> (1% in He) according to procedure described in [1].

## Results and Discussion

The enthalpy of the removal of oxygen from the lattice of pure ceria (800-1100 kJ/mol) in contrast to the energy barrier of its lattice migration (~100 kJ/mol) is rather high and could be reduced by formation of defects and/or distortions in cerium environment [2]. As is estimated by TPD O<sub>2</sub> data in the range of 20-900°C, for ceria doped by Sm or Zr (up to 50 mol%) up to 1.4 monolayer (M) coverage of oxygen are desorbed being presented by two forms of oxygen: weakly bound surface oxygen with E<sub>d</sub> ~ 40 kJ/mol (desorbed up to 500°C) and stronger bound oxygen c E<sub>d</sub> ~100-120 kJ/mol. Their ratio depends on the type and amounts of promoter and grows with increasing the distortions in Ce environment, as it is estimated by UV-Vis and Raman spectra. The largest amounts of the first form (0.25 M) is observed for Ce-Zr-O sample with the most pronounced distortions (with homogeneous distribution of cations) prepared by CPM. In this sample, cation sublattice network consists of the structural modules

comprised of the Zr<sub>4</sub> species (as in initial Zr salt) surrounded by Ce cations. For less homogeneous Ce-Zr-O sample prepared by coprecipitation (with admixture of extended defect regions possessing the Ce<sub>n</sub>O<sub>m</sub> structure), the amount of this form decreases by 10 times. Similar amounts of the first oxygen form are observed for Ce-Sm-O samples characterized by the same Ln<sub>n</sub>O<sub>m</sub> structure of extended defects. The removal of weakly bound oxygen and formation of anion vacancies facilitate subsequent migration of oxygen from subsurface layers. The amounts of desorbed O<sub>2</sub> at higher temperatures depend on the structural features of solid solutions. For Ce-Zr-O fluorites, the rate of O<sub>2</sub> desorption at 900°C grows with enhancement of distortions in the Ce-O sphere as well. For ceria doped by Sm, the rates of O<sub>2</sub> desorption at 900°C grow with increasing concentration of interstitial oxygen the in subsurface layers, going through the maximum at a low (10 mol% Sm) doping level. Diminishing the rates with increasing doping level could be explained by increasing concentration of trimer clusters Me<sub>3</sub>Ce' VO••Me<sub>3</sub>Ce' which can hamper oxygen migration in the lattice. Desorption of O<sub>2</sub> for samples with supported Pt is determined by the specific features of defect structure of fluorite and state of supported Pt depending on those features. The increase of the total amount of desorbed O<sub>2</sub> (up to 2.5 M) could be explained by additional distortions in Ce environments caused by Pt incorporation (producing no changes in E<sub>d</sub>) and stabilization of oxidic Pt species. The formation of those species of Pt improves the bulk diffusion of oxygen at higher temperatures due to formation of additional anion vacancies in the subsurface layers.

The specific character of activation of reductant can control the values of effective diffusion parameters in the fluorites along with features of defect structure and states of Pt (Table 1). For CO reduction, the low values of D could be caused by higher concentrations of trimer clusters hindering oxygen migration in the small particles of fluorite in comparison with the larger ones. For Pt supported samples, a higher ratio of oxidic Pt species for more homogeneous fluorite favors CO activation and subsequent diffusion of oxygen. For CH<sub>4</sub> reduction, the same factor decreases the efficiency of activation of reductant and diffusion of oxygen. A higher value of D is observed for sample with a higher share of Pt<sup>0</sup> species. The V<sub>D</sub> weakly depends on the sizes of fluorite particles and its homogeneity.

**Table 1. Diffusion parameters estimated by CO and CH<sub>4</sub> reduction (500°C) of Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> and 1.4 wt%/ Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> samples (CPM).**

Particle size, Å	Pt, wt%	CO		CH <sub>4</sub>
		V <sub>D</sub> , s <sup>-1</sup>	D 10 <sup>21</sup> , m <sup>2</sup> s <sup>-1</sup>	D 10 <sup>21</sup> , m <sup>2</sup> s <sup>-1</sup>
50 (homogen.)	0	1.8	0.30	
	1.4	1.5	14.0	1.0
200 (less homogen.)	0	2.3	11.4	
	1.4	1.3	3.3	1.9

## Significance

New insight into effect of the real structure of doped ceria on the energy characteristics of surface/lattice oxygen is given.

## References

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