

# Modeling of Diffusion Process in Nanosized Perovskite LaCoO<sub>3</sub> Powder Catalysts

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Catalytic properties of nanosized perovskite LaCoO<sub>3</sub> powders are considered experimentally and theoretically. For the purpose of the use of those catalysts in automotive exhaust gas conversion the kinetics of oxygen atom transport processes from/to gas phase and catalyst are experimentally analyzed by isotopic oxygen exchange method. Molecular oxygen isotope <sup>18</sup>O<sub>2</sub> gas is introduced into reactor with powder of catalyst. The process of exchange is performed at temperature 400°C. As a result of oxygen exchange between gas as catalyst the molecular species of oxygen <sup>18</sup>O<sub>2</sub>, <sup>18</sup>O<sup>16</sup>O and <sup>16</sup>O<sub>2</sub> appears in gas phase which kinetics is registered by mass spectrometer. Three types of LaCoO<sub>3</sub> samples differently prepared [1,2] are considered. The S<sub>bet</sub> and powder particle size of those samples were following: first type 3.9 m<sup>2</sup>/g, 1000 nm, second type 3.8 m<sup>2</sup>/g, 11nm and third type 66 m<sup>2</sup>/g, 11nm. Small surface area and small powder size of second type catalyst shows that each powder particle contains grains which size is around 11 nm and can be considered as polycrystals. First and third type powder particles can be considered as monocrystalline.

The obtained experimental kinetic curves of partial pressures of oxygen species are fitted by proposed real time kinetic model based on rate equations. Model includes processes of chemical reactions (complex and simple heteroexchange) and diffusion of oxygen inside powder nanoparticles. The diffusion process is introduced considering the bulk diffusion adapted for powder catalysts [3] and diffusion by grain boundaries (for second type catalyst).

Considering possible reactions of type <sup>I</sup>O<sup>J</sup>O<sub>g</sub> + <sup>I</sup>O<sup>J</sup>O<sub>s</sub> = <sup>I</sup>O<sup>J</sup>O<sub>s</sub> + <sup>I</sup>O<sup>J</sup>O<sub>g</sub> where I and J = 16 and/or 18 the concentration variation of <sup>18</sup>O<sub>2</sub>, <sup>16</sup>O<sub>2</sub> and <sup>16</sup>O<sup>18</sup>O species in the gas phase and on the catalyst oxide surface is described by rate equations using mass action law  $dn_i / dt = k \sum_r n_i c_j$  (where  $n_i$  is the concentration of i-th type species in gas phase,  $r$  is

the number of reactions and  $c_i$  is surface concentration) with reaction rate constant  $k$  determined by Arrhenius law  $k = A \exp(-Q / kT)$ .

Considering bulk diffusion for powder catalysts with cubic shape grains it is necessary to take into account the fact that the area of each layer ( $S^{(K)}$ ) decreases and tends to zero as one goes deeper and deeper into the oxide bulk. So, these areas were calculated according to the following expression:  $S_B^{(K)} = S_{ox} (1 - 2(K-1)a / d_{ox})^2$  ( $K$  is number of monolayer,  $a$  is monolayer thickness and  $d_{ox}$  is size of grain). The variation of the atomic concentration in oxygen atoms in one given layer  $K$  of the oxide is calculated according to the second Fick's law.  $dc_i / dt = (D / a^2) (B^{(K-1)} (c_i^{(K-1)} - c_i^{(K)}) - B^{(K)} (c_i^{(K)} + c_i^{(K+1)}))$ , where  $D = D_o \exp(-Q_D / kT)$  is the diffusion coefficient and coefficients  $B$  describe

geometrical factor of monolayers  $B^{(K)} = S^{(K+1)} / S^{(K)}$ , if  $c_i^{(K)} - c_i^{(K+1)} \geq 0$  or  
 $B^{(K)} = S^{(K)} / S^{(K+1)}$ , if  $c_i^{(K)} - c_i^{(K+1)} < 0$ .

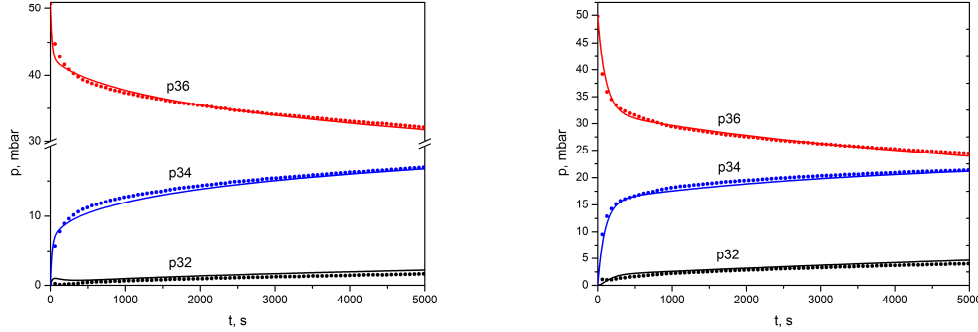


Fig. 1. Experimental (points) and calculated (lines) time dependencies of partial pressures of oxygen species  $^{18}\text{O}_2$  (p36),  $^{18}\text{O}^{16}\text{O}$  (p34) and  $^{16}\text{O}_2$  (p32) in gas phase during isotopic oxygen exchange process: left - for second type catalysts (see text) and right - for third type catalysts.

Calculated curves are in a good agreement with experimental points for all three types of catalysts. In Fig. 1 the experimental (points) and calculated (lines) time dependencies of partial pressures of oxygen species  $^{18}\text{O}_2$ ,  $^{18}\text{O}^{16}\text{O}$  and  $^{16}\text{O}_2$  in gas phase during isotopic oxygen exchange process is presented. Two figures represent the cases of polycrystalline (left) and monocrystalline (right) powder particles. In the case of polycrystalline powder particles both bulk and grain boundary diffusion takes place, while in monocrystalline case only bulk diffusion occurs. This assumption is realized in model. From the calculated results the kinetic (exchange rate constants, diffusion coefficients of bulk and grain boundary diffusion) and thermodynamic (activation energies of exchange reactions and diffusion) parameters are obtained.

#### Acknowledgement:

This research was funded by a grants (No.: TAPLZ 04/2012 and No.: MIP 118/2011) from the Research Council of Lithuania.

#### References:

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