

## Modeling of Diffusion Process in the Isotopic Oxygen Exchange Experiments of $Ce_xZr_{(1-x)}O_2$ Catalysts

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The oxygen mobility processes during the temperature programmed oxygen isotopic exchange is considered by proposed kinetic model. The model includes simple and complex heteroexchange reactions and bulk diffusion processes. The diffusion process is introduced considering monolayers in each separate particle of nanopowder taking into account the decrease of monolayer area with depth inside particle. The model is applied to fit experimental curves of  $Ce_xZr_{1-x}O_2$  catalysts with different composition in order to calculate reaction rates and diffusion coefficients, and activation energies of those processes. From the best fit the rates of chemical reactions and diffusion coefficients are found for each composition of catalyst. The dependences of activation energies (reaction and diffusion) and diffusion coefficients versus composition are obtained for  $Ce_xZr_{1-x}O_2$  catalysts. Obtained dependencies show nonlinear behavior with passes the maximum values at certain percentage of Ce (or Zr) in  $Ce_xZr_{1-x}O_2$  oxide.

*Keywords:* kinetics, catalysis, modeling, diffusion, isotopic oxygen exchange.

### INTRODUCTION

Cerium oxide is widely used as a promoter in the so-called “three-way catalysts” (TWC) for the elimination of toxic exhaust gases in automobiles [1]. The primary function of ceria in TWC is to provide oxygen storage capacity (OSC) in order to allow the catalyst to operate over a wider range of air/fuel ratios [2]. There are mainly two regimes for the engine operation: (1) fuel rich and (2) fuel lean. As a consequence, the catalyst should be active under both oxidizing and reducing conditions [3]. Oxygen storage capacity is associated with the fast  $Ce^{4+}/Ce^{3+}$  redox process and the exceptional ability of ceria to stabilize anionic vacancies [4]. However, the temperature in a close-coupled catalyst converter can rise above 1000 °C and  $CeO_2$  readily sinters at elevated temperatures resulting in catalyst deactivation. The addition of zirconium and formation of Ce–Zr mixed oxides prevents the ceria from sintering [5]. Insertion of  $ZrO_2$  into the  $CeO_2$  lattice, leading to formation of a  $CeO_2$ – $ZrO_2$  solid solution, has been shown to dramatically increase both thermal stability and OSC [6]. Indeed, a 10 at.% zirconium substitution in cerium oxide markedly increases the oxygen storage capacity compared to ceria-only systems [7].

The oxygen mobility on the surface and in the bulk of such catalysts plays a major role in the catalytic process. To investigate the oxygen mobility and to better understand the oxygen pathways, oxygen isotopic  $^{18}O$ – $^{16}O$  exchange reactions were studied [8, 9]. Adsorption of reactants on the support followed by diffusion of reactive species to the metal sites and vice versa has been proposed to explain support effects in catalysis [10]. From the course of the oxygen exchange reaction, conclusions can be drawn about

the way in which oxygen takes part in the catalytic processes [11]. Isotopic exchange is generally carried out in a recycle, close reactor coupled to a mass spectrometer [12]. The curves of exchange are registered which shows the changes, with time, of the partial pressures of  $^{16}O_2$ ,  $^{16}O^{18}O$  and  $^{18}O_2$  during the process. The adsorption of a probe molecule at low temperature, and subsequent monitoring of its desorption/reaction characteristics with temperature, is a way to characterize surface properties of catalysts and adsorbents [13, 14]. This is the basis of temperature-programmed analysis methods in which, for a linear increase in temperature, the concentration of the reacting/desorbing particles is recorded as a function of temperature [15]. The temperature programmed isotopic exchange method has an important application in the field of catalytic oxidation reactions involving lattice oxygen [16].

In general three types of exchange of dioxygen on oxide catalysts can occur: the homo-exchange between adsorbed atoms, the simple hetero-exchange between a molecule of dioxygen and an atom of the solid and the multiple hetero-exchange between a molecule of dioxygen and two atoms of the solid [17, 18]. Information on the mechanism of exchange may be obtained from the relative evolution of oxygen isotopomers partial pressures at the beginning of reaction. In fact, the formation of isotopomer  $^{16}O^{18}O$  as a primary product indicates that exchange process via a simple hetero-exchange mechanism while isotopomer  $^{16}O_2$  reveals a multiple exchange mechanism [19].

Very important parameter is oxygen exchange surface of catalyst. The high-surface area samples provide more active oxygen, tight contact condition is also critical to provide more contact probability for active oxygen to transfer from catalyst [20]. Specific surface area plays an important role in oxygen storage/release process for pure ceria since the oxygen storage capacity is attributed mainly

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to the release of surface oxygen. In this work the influence of mass and surface of catalyst is analyzed.

In the presented work the main attention is done on bulk diffusion of oxygen atoms in  $Ce_xZr_{(1-x)}O_2$  catalysts during the temperature programmed isotopic oxygen exchange experiments.

## EXPERIMENTAL PROCEDURE

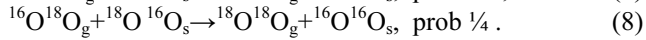
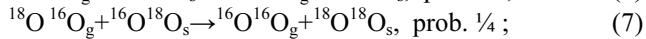
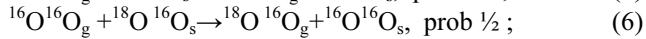
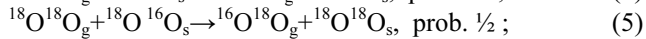
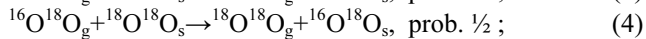
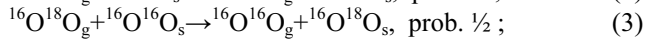
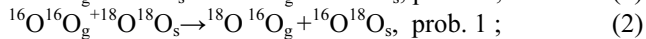
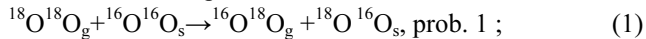
Cerium-zirconium mixed oxides were supplied by RHODIA and prepared by isomorphous substitution of  $Ce^{4+}$  cations with  $Zr^{4+}$  cations. The materials studied are noticed  $Ce_xZr_{(1-x)}O_2$  where  $x$  represents the molar ratio of cerium on zirconium. Three mixed oxides were studied with  $x = 0.15, 0.5$  and  $0.63$ .

Temperature-Programmed Isotopic Exchange (TPIE) experiments were performed in a recycling closed reactor of  $60\text{ cm}^3$  coupled to a mass. Around  $20\text{ mg}$  of sample were introduced in a U-form reactor and pre-treated from room temperature up to  $600^\circ\text{C}$  under oxygen flow with a temperature ramp rate of  $10^\circ\text{C}/\text{min}$  and maintained at  $600^\circ\text{C}$  during  $1\text{ h}$ . After outgassing at the same temperature during  $30$  minutes, the sample was cooled down to  $300^\circ\text{C}$  and a pure dose between  $53\text{ mbar}$  and  $55\text{ mbar }^{18}\text{O}_2$  (Isotec,  $99.9\%$ ) was introduced in the system. The temperature is finally increased from  $300^\circ\text{C}$  to  $600^\circ\text{C}$  with a ramp rate of  $2^\circ\text{C min}^{-1}$  while the evolutions versus time of the concentrations of  $^{18}\text{O}_2$ ,  $^{18}\text{O}^{16}\text{O}$ ,  $^{16}\text{O}_2$  isotopomers were continuously followed by collecting every  $3\text{ s}$  the  $36, 34$  and  $32\text{ m/z}$  values respectively.  $28\text{ m/z}$  value was also monitored to detect any possible leak in the system. The recycling pump permitted to prevent any problem of gaseous diffusion whereas a thermoregulated valve enabled a constant  $10^{-6}\text{ mbar}$  pressure in the ionization chamber and a very little decrease of the pressure (around  $1\text{ mbar}$  per hour) in the closed system.

## KINETIC MODEL

It is assumed in this model that during isotopic oxygen exchange of oxide surface the two mechanisms of exchange take place: simple hetero-exchange and complex (or multiple) heteroexchange [9, 11, 19]. Simple hetero-exchange occurs with participation of one oxygen atom from the structure of oxide. In complex hetero-exchange two oxygen atoms participate simultaneously.

In the case of simple hetero-exchange the following reactions can take place:



Here indexes  $g$  and  $s$  means compounds in gas phase and on the surface of oxide.

Considering reactions written in the form above the probabilities to change composition is not equal for all of them. Generally, for each reaction there are four

possibilities to exchange atoms. In reaction (1) and (2) all four possibilities give composition change. So, reactions probability to form reaction products is equal to 1. In reactions (3) – (6) there are cases when reaction does not change composition, e.g. if atom  $^{16}\text{O}$  from gas phase exchanges with atom  $^{16}\text{O}$  from the surface it does not change composition and molecules remain the same. So, those reactions probability to form reaction products is  $1/2$ . In the same way considering reactions (7) and (8) the probability for each reaction to occur is  $1/4$ . This aspect is taken into account writing below rate equations of reactions (1) – (8).

For calculations of isotopic composition changes in gas phase and on the surface of oxide the volume concentrations ( $\text{mol}/\text{m}^3$ )  $n_{32}$ ,  $n_{34}$  and  $n_{36}$  in gas phase and surface concentrations  $c_{32}$ ,  $c_{34}$  and  $c_{36}$  ( $\text{mol}/\text{m}^2$ ) of compounds  $^{16}\text{O}^{16}\text{O}$ ,  $^{16}\text{O}^{18}\text{O}$  and  $^{18}\text{O}^{18}\text{O}$ , respectively are defined [21, 22]. For calculations of those concentrations the mass action law is used:

$$\left(\frac{dn_{32}}{dt}\right)_s = k_s \left( \frac{1}{4} n_{34} c_{34} - n_{32} c_{36} + \frac{1}{2} n_{34} c_{32} - \frac{1}{2} n_{32} c_{34} \right), \quad (9)$$

$$\left(\frac{dn_{34}}{dt}\right)_s = k_s \left( n_{36} c_{32} + n_{32} c_{36} - \frac{1}{2} n_{34} c_{34} - \frac{1}{2} n_{34} c_{32} + \right. \\ \left. - \frac{1}{2} n_{34} c_{36} + \frac{1}{2} n_{32} c_{34} + \frac{1}{2} n_{36} c_{34} \right), \quad (10)$$

$$\left(\frac{dn_{36}}{dt}\right)_s = k_s \left( \frac{1}{4} n_{34} c_{34} - n_{36} c_{32} + \frac{1}{2} n_{34} c_{36} - \frac{1}{2} n_{36} c_{34} \right), \quad (11)$$

where:  $k_s$  is the rate constant for simple hetero-exchange reactions expresses by Arrhenius law:

$$k_s = A_s \exp(-Q_s/RT), \quad (12)$$

where  $A_s$  and  $Q_s$  is pre-exponential term and activation energy of simple hetero-exchange.  $R$  and  $T$  is gas constant and temperature, respectively.

The surface concentrations changes are expressed as:

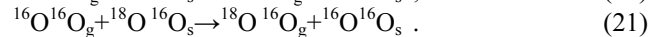
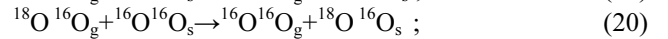
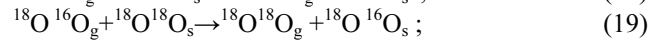
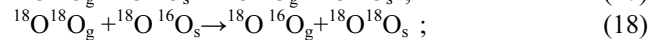
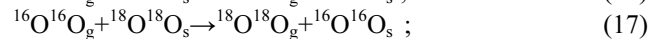
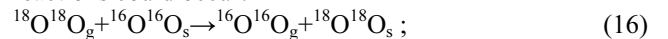
$$\left(\frac{dc_{32}}{dt}\right)_s = \frac{V}{S} k_s \left( \frac{1}{4} n_{34} c_{34} - n_{36} c_{32} - \frac{1}{2} n_{34} c_{32} + \frac{1}{2} n_{32} c_{34} \right), \quad (13)$$

$$\left(\frac{dc_{34}}{dt}\right)_s = \frac{V}{S} k_s \left( n_{36} c_{32} + n_{32} c_{36} - \frac{1}{2} n_{34} c_{34} + \frac{1}{2} n_{34} c_{32} + \right. \\ \left. \frac{1}{2} n_{34} c_{36} - \frac{1}{2} n_{32} c_{34} - \frac{1}{2} n_{36} c_{34} \right), \quad (14)$$

$$\left(\frac{dc_{36}}{dt}\right)_s = \frac{V}{S} k_s \left( \frac{1}{4} n_{34} c_{34} - n_{32} c_{36} - \frac{1}{2} n_{34} c_{36} + \frac{1}{2} n_{36} c_{34} \right), \quad (15)$$

where  $V$  and  $S$  represent the volume of the reactor and the surface area of catalyst, respectively.

In the case of complex hetero-exchange (with participation of two solid oxygen atoms) the following reactions could occur:



Considering reactions (16)–(21), the gas phase composition changes enable us to written the following rate equations:

$$\left(\frac{dn_{32}}{dt}\right)_C = k_C (n_{36}c_{32} + n_{34}c_{32} - n_{32}c_{34} - n_{32}c_{36}), \quad (22)$$

$$\left(\frac{dn_{34}}{dt}\right)_C = k_C (n_{32}c_{34} + n_{36}c_{34} - n_{34}c_{32} - n_{34}c_{36}), \quad (23)$$

$$\left(\frac{dn_{36}}{dt}\right)_C = k_C (n_{32}c_{36} + n_{34}c_{36} - n_{36}c_{32} - n_{36}c_{34}), \quad (24)$$

where  $k_C$  is reaction rate constant of complex hetero-exchange expresses by Arrhenius law:

$$k_C = A_C \exp(-Q_C / RT), \quad (25)$$

where  $A_C$  and  $Q_C$  is pre-exponential term and activation energy of complex hetero-exchange.

The rate equations for composition change on the surface in this case are following:

$$\left(\frac{dc_i}{dt}\right)_C = -\frac{V}{S} \left(\frac{dn_i}{dt}\right)_C, i = 32, 34, 36. \quad (26)$$

Considering composition changes of both simple and complex heteroexchange the composition in gas phase is calculated from the following expression:

$$\frac{dn_i}{dt} = \left(\frac{dn_i}{dt}\right)_S + \left(\frac{dn_i}{dt}\right)_C, i = 32, 34, 36. \quad (27)$$

In the same way the composition variations on the surface is expressed as:

$$\frac{dc_i}{dt} = \left(\frac{dc_i}{dt}\right)_S + \left(\frac{dc_i}{dt}\right)_C, i = 32, 34, 36. \quad (28)$$

Process of diffusion is involved following the second Fick's law  $\delta c / \delta t = D(\partial^2 c / \partial x^2)$  expressed in finite increments:

$$\left(\frac{dc_{18}^{(k)}}{dt}\right)_{dif} = [B^{(k-1)}(c_{18}^{(k-1)} - c_{18}^{(k)}) - B^{(k)}(c_{18}^{(k)} + c_{18}^{(k+1)})], \quad (29)$$

where  $h$  is thickness of one atomic monolayer,  $c_{18}^{(k)}$  is concentration of  $^{18}\text{O}$  atoms in  $k$ -th monolayer,  $D$  is diffusion coefficient expressed by Arrhenius law:

$$D = A_{dif} \exp(-Q_{dif} / RT), \quad (30)$$

where  $A_{dif}$  and  $Q_{dif}$  is preexponential term and activation energy of diffusion, respectively.

Eq. (29) describes diffusion of  $^{18}\text{O}$  atoms. It is assumed that diffusion of  $^{18}\text{O}$  atoms takes place by replacing  $^{16}\text{O}$  atoms. So, equation for  $^{16}\text{O}$  atoms keeping balance between diffusion fluxes and taking into account eq. (29) is:

$$\left(\frac{dc_{16}^{(k)}}{dt}\right)_{dif} = -\left(\frac{dc_{18}^{(k)}}{dt}\right)_{dif}, k \geq 2. \quad (31)$$

Coefficient  $B^{(k)}$  in eq. (29) describes the decrease of layer area going deeper to the center of cubic shape particle of powder catalyst (detail explanation on this is done in ref.[23]). Values of coefficient  $B^{(k)}$  are found from relations:

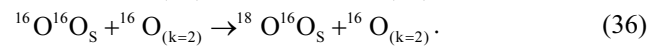
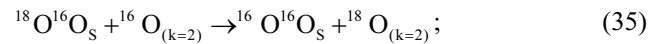
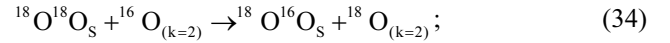
$$B^{(k)} = \begin{cases} \frac{S^{(k+1)}}{S^{(k)}}, & \text{if } (c_i^{(k)} - c_i^{(k+1)}) \geq 0 \\ \frac{S^{(k)}}{S^{(k+1)}}, & \text{if } (c_i^{(k)} - c_i^{(k+1)}) < 0 \end{cases}, \quad (32)$$

where  $S^{(k)}$  are area of  $k$ -th monolayer obtained for cubic particles form relation:

$$S^{(k)} = S_{OX} \left(1 - 2(k-1) \frac{h}{d_{OX}}\right)^2, \quad (33)$$

where  $S_{OX}$  is total surface of oxide,  $h$  is thickness of one monolayer and  $d_{OX}$  is size of oxide powder particle.

Eqs. (29) and (30) describe diffusion starting from second layer  $k \geq 2$ . Diffusion for first monolayer is expressed by mass action law because oxygen atoms in first monolayer according above model are formally grouped into species  $^{16}\text{O}^{16}\text{O}$ ,  $^{16}\text{O}^{18}\text{O}$  and  $^{18}\text{O}^{18}\text{O}$  with surface concentrations  $c_{32}$ ,  $c_{36}$  and  $c_{34}$ , respectively and direct use of Fick's law is impossible. Diffusion flux between first and second layer is mathematically described as chemical reaction with reaction rate constant  $k_d$  between surface oxygen species and oxygen atoms from second layer:



The rate equations of those reactions take the following form:

$$\left(\frac{dc_{32}}{dt}\right)_{dif} = \frac{D}{h^2} k_d (c_{18}^{(1)} - c_{18}^{(2)}) \left(\frac{1}{2} c_{34} - c_{32}\right) c_{16}^{(2)}, \quad (37)$$

$$\left(\frac{dc_{34}}{dt}\right)_{dif} = \frac{D}{h^2} k_d (c_{18}^{(1)} - c_{18}^{(2)}) \left(c_{36} + c_{32} - \frac{1}{2} c_{34}\right) c_{16}^{(2)}, \quad (38)$$

$$\left(\frac{dc_{36}}{dt}\right)_{dif} = -\frac{D}{h^2} k_d (c_{18}^{(1)} - c_{18}^{(2)}) c_{36} c_{16}^{(2)}, \quad (39)$$

where  $c_{18}^{(1)}$  is atomic surface concentration of  $^{18}\text{O}$  oxygen atoms on the surface  $k = 1$  which is found from molecular species  $^{16}\text{O}^{18}\text{O}$  and  $^{18}\text{O}^{18}\text{O}$  on the surface by relation:

$$c_{18}^{(1)} = c_{36} + \frac{1}{2} c_{34}. \quad (40)$$

For temperature programming exchange the temperature  $T$  in eqs. (12) and (25) is time dependant. In experiment considering here temperature was increased linearly, and  $T(t)$  is expressed as line function:

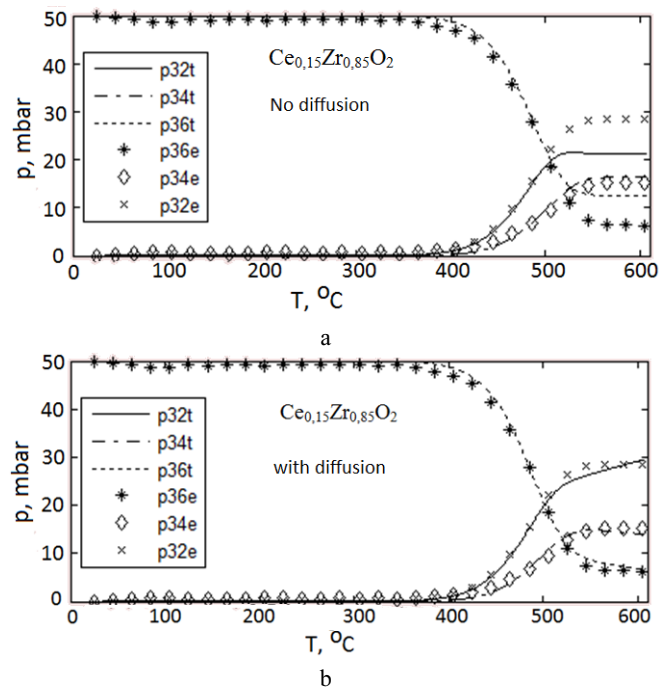
$$T(t) = T_0 + bt. \quad (41)$$

$T_0$  is initial temperature and  $b$  the rate temperature increase,  $t$  is time (in the experiment considered here  $T_0 = 298 \text{ K}$ ,  $b = 2 \text{ K/min}$ ).

## RESULTS AND DISCUSSION

Experimental results of temperature programmed isotopic oxygen exchange are presented in Figs. 1–3 (points). There are dependencies of oxygen species  $^{16}\text{O}_2$ ,  $^{16}\text{O}^{18}\text{O}$  and  $^{18}\text{O}_2$  partial pressures versus temperature. Temperature linearly increases with time with speed  $2^\circ\text{C/min}$ . The experiments are done for  $\text{Ce}_x\text{Z}_{1-x}\text{O}_2$  catalysts at various values of  $x$  from 0 to 1. Initially only oxygen  $^{18}\text{O}_2$  gas was introduced into reactor. After exchange start oxygen from gas phase react with oxygen atoms from catalyst oxide and other species  $^{16}\text{O}_2$ ,  $^{16}\text{O}^{18}\text{O}$  are formed by reactions described in eqs. (1–8) and (16–21). As a result pressure of  $^{18}\text{O}_2$  decreases and  $^{16}\text{O}_2$ ,  $^{16}\text{O}^{18}\text{O}$  increases approaching steady state value. From presented results it is seen that exchange starts at around  $400^\circ\text{C}$  temperature. However, it can be seen that exchange starts a little early

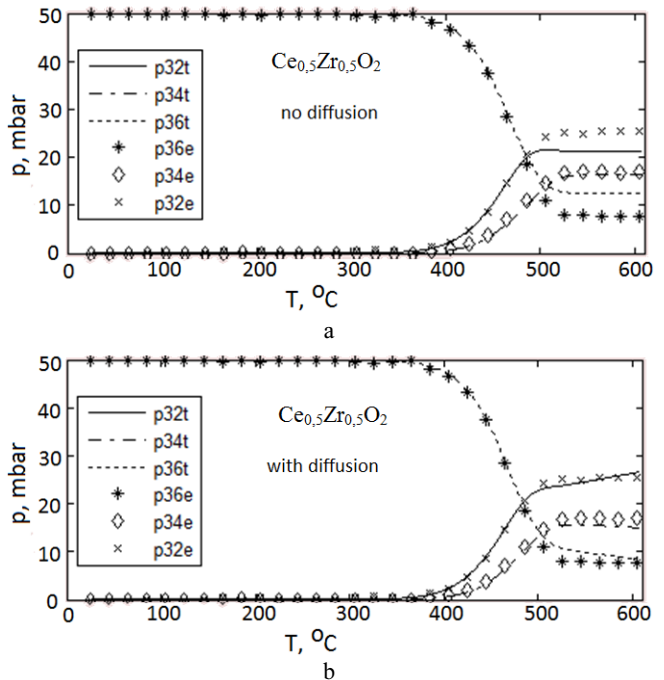
(at lower temperature) when concentration of Ce increases. Comparing the Figs. 1 and 3, one can notice that exchange starts at around 350 °C for  $Ce_{0.63}Zr_{0.37}O_2$  whereas it begins at 400 °C for the  $Ce_{0.15}Zr_{0.85}O_2$ . Another important observation is the first isotopomer molecule present in the gas phase after the exchange: for both solids  $Ce_{0.63}Zr_{0.37}O_2$  and  $Ce_{0.15}Zr_{0.85}O_2$ , it is  $^{16}O_2$ . It indicated that complex exchange mechanism which is described by eqs. (16–21) prevails for  $Ce_xZr_{1-x}O_2$  catalysts. From the point of the above presented model the exchange rate of complex exchange  $k_C$  is higher than exchange rate of simple exchange  $k_S$ :  $k_C > k_S$ . Value of reaction rate constant according to the Arrhenius law is defined by preexponential term and activation energy, but for the case of  $k_C > k_S$  it can be expected that for activation energies of complex and simple hetero-exchange the following inequality is valid for  $Ce_xZr_{1-x}O_2$  catalysts:  $Q_C < Q_S$ . Exact values of reaction rate constants, preexponential terms and activation energies can be found by fitting of experimental results by calculated curves using above presented model.



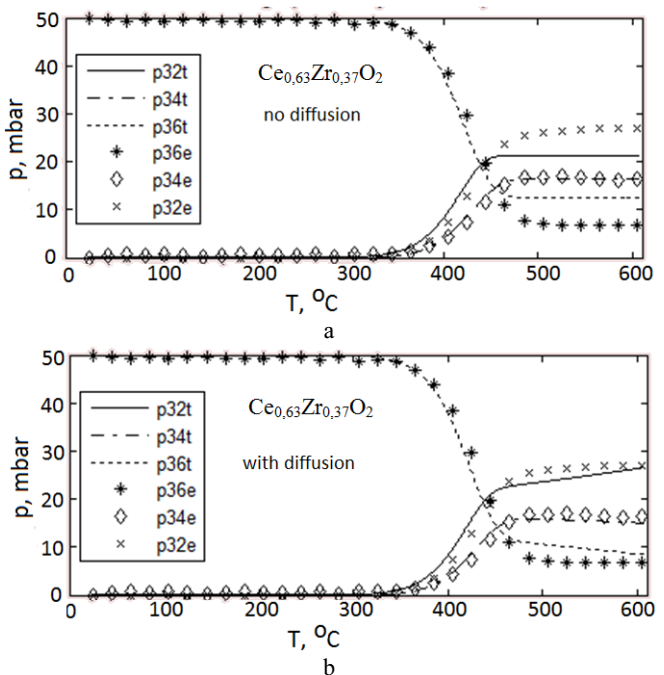
**Fig. 1.** Experimental (points) and calculated (lines) dependencies of partial pressures of oxygen species on exchange temperature for catalyst  $Ce_{0.15}Zr_{0.85}O_2$ : (a) the diffusion is not included in calculations (b) diffusion is included. p32t(e), p34t(e) and p36t(e) are the curves of partial pressures of oxygen species  $^{16}O_2$ ,  $^{16}O^{18}O$  and  $^{18}O_2$ , respectively, where (t) denotes theoretical and (e) experimental curves (the same in Figs. 1 and 2)

Calculated results according to the above presented model are presented in Figs. 1–3 (lines). The first goal was to analyze the influence of diffusion for the oxygen exchange process. Calculated results of the best fit of experimental points in the case when diffusion process is not included into calculations are presented in Figs. 1–3, a. In Figs. 1–3, b, there are results of the same calculation but with diffusion process included. Comparing figures (a) and (b) for all catalyst it is seen that the including diffusion process into calculations gives much better fit of the experimental results. From this it can be

concluded that diffusion process is important for all composition catalysts from 15 % to 63 % of Ce. The coefficient of diffusion depends on percentage Ce (or Zr) in  $Ce_xZr_{1-x}O_2$  catalyst. The values of preexponential term and activation energies of diffusion found from the best fit of experimental points  $A_{dif}$  and  $Q_{dif}$  are presented in Table 1 together with the same values of reaction rates. From those values diffusion coefficients calculated at temperature 500 °C are:

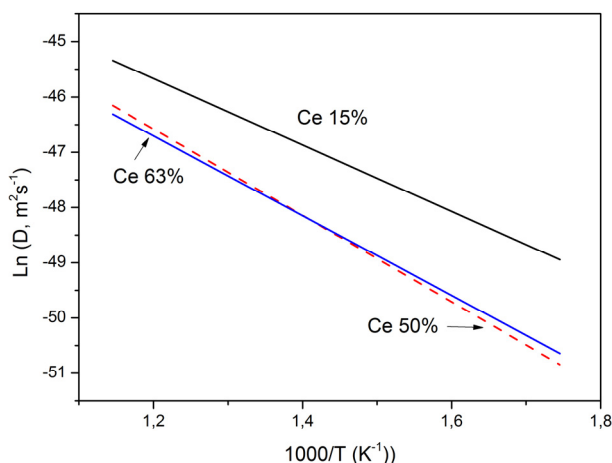


**Fig. 2.** Experimental (points) and calculated (lines) dependencies of partial pressures of oxygen species on exchange temperature for catalyst  $Ce_{0.5}Zr_{0.5}O_2$ : (a) the diffusion is not included in calculations (b) diffusion is included



**Fig. 3.** Experimental (points) and calculated (lines) dependencies of partial pressures of oxygen species on exchange temperature for catalyst  $Ce_{0.63}Zr_{0.37}O_2$ : (a) the diffusion is not included in calculations (b) diffusion is included

$D_{0.15} = 8.4 \cdot 10^{-21} \text{ m}^2/\text{s}$  for  $\text{Ce}_{0.15}\text{Zr}_{0.85}\text{O}_2$ ;  $D_{0.5} = 2.8 \cdot 10^{-21} \text{ m}^2/\text{s}$  for  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  and  $D_{0.63} = 2.7 \cdot 10^{-21} \text{ m}^2/\text{s}$  for  $\text{Ce}_{0.63}\text{Zr}_{0.37}\text{O}_2$ . These results show that diffusion coefficient decreases with increase of content of Ce until around 50 %, and then remains almost the same. Obtained values of diffusion coefficients are in good agreement with results of other authors: it was noted in ref. [24] that at temperature 300 °C diffusion coefficient of oxygen in  $\text{Ce}_{15}\text{Zr}_{85}\text{O}_2$  is  $D = 53 \cdot 10^{-23} \text{ m}^2 \text{ s}^{-1}$  and in ref. [25] it was found  $D = 1.6 \cdot 10^{-18} \text{ m}^2 \text{ s}^{-1}$  for the same catalyst at temperature 850 °C.



**Fig. 4.** Arrhenius plots of diffusion coefficients obtained from fitting of experimental results for different content of Ce in  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts

**Table 1.** The values of preexponential term and activation energies of complex Exchange (C), simple Exchange (S) and diffusion (dif) found from the best fit of experimental results for  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts at different content of Ce (values x)

Ce content x	$A_C, \text{m}^2/\text{s}$	$A_S, \text{m}^2/\text{s}$	$A_{\text{dif}}, \text{m}^2/\text{s}$
0.15	$3 \cdot 10^{-11}$	$6.8 \cdot 10^{-10}$	$2 \cdot 10^{-17}$
0.50	$8 \cdot 10^{-12}$	$6 \cdot 10^{-11}$	$7 \cdot 10^{-17}$
0.63	$5 \cdot 10^{-11}$	$5.4 \cdot 10^{-10}$	$3 \cdot 10^{-17}$
Ce content x	$Q_C, \text{kJ/mol}$	$Q_S, \text{kJ/mol}$	$Q_{\text{dif}}, \text{kJ/mol}$
0.15	147	177	50
0.50	143	177	65
0.63	138	165	60

In Fig. 4 there are presented Arrhenius plots of diffusion coefficients obtained from fitting of experimental results for different content of Ce in  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts. The diffusion coefficient for content of cerium 50 % and 60 % is almost the same in all temperature interval. But at lower amount of cerium (higher zirconium) diffusion coefficient is higher. This result is in agreement with OSC (Oxygen Storage Capacity) measurements [19] which show that with that increase of Ce content in  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  the OSC increases until 60 % of Ce and the slowly decreases. The change of Ce content changes lattice changes the structure of mixed oxide from cubic (Ce less than 50 %) to tetragonal (Ce more than 50 %) with continuous change of

lattice parameter [26]. The surface concentration of oxygen is also changed with content of Ce from 13.7 atoms  $\text{nm}^{-2}$  for pure  $\text{CeO}_2$  till 14.2 atoms  $\text{nm}^{-2}$  [26] for  $\text{Ce}_{63}\text{Zr}_{37}\text{O}_2$  indicating that oxygen storage takes place not only surface but also in the bulk of oxide. Participation of bulk oxygen is resulted by bulk diffusion process which is influenced by structural changes at different content of Ce.

## CONCLUSIONS

1. Considering two exchange mechanisms simple exchange and complex exchange the complex exchange mechanism is dominating for  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts .
2. Fitting of experimental results by proposed model is much better when process of diffusion is I included into calculations. This indicates that process diffusion is significant during oxygen exchange in  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts.
3. Diffusion coefficient for  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts depends on content of Ce and is highest at around 15 % of Ce.

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