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Surface diffusion upon oxygen isotopic exchange on oxide-supported metal nanoclusters

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A newly developed real-time kinetic model is presented. The model was used for the characterization of supported metal catalysts' properties in the oxygen isotopic exchange reaction. This model is based on rate equations and includes several elementary processes: adsorption on the metal nanoclusters, reactions on the metal nanoclusters, desorption from the metal nanoclusters, surface and bulk diffusion on/in the oxide support and direct exchange with the gas phase. On the basis of this model, a computer code was developed to determine the kinetic and thermodynamic parameters of the oxygen isotopic exchange reactions. The characteristics of a Rh/CeO₂ catalyst were examined in the temperature range between 200 and 450 °C.

Keywords: Catalysis; Nanoclusters; Reactions; Kinetics; Surface diffusion; Oxide; Isotopic exchange

1. Introduction

The exhaust gases from car engines contain harmful components such as carbon monoxide, hydrocarbons, nitrogen oxides and carbon particulates. As a result, catalytic converters implemented on gasoline-fueled engines must combine three functions: oxidize the CO and the unburnt hydrocarbons to CO₂ and H₂O and reduce NO to N₂.

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. For that reason, ceria-based oxides must be used as supports [1]. Such supports may “absorb” the oxygen in excess and supply oxygen under reducing conditions. 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 exchange reactions were studied [2,3].

On oxide-supported metals, ¹⁸O/¹⁶O exchange occurs through a sequence of well-differentiated steps [4–7] as schematized in Fig. 1: (1) dissociative adsorption of ¹⁸O₂

on the metal nanoclusters; (2) transfer of ¹⁸O atoms from the metal particles to the oxide surface; (3) migration of ¹⁸O atoms on the oxide's surface; (4) exchange between ¹⁸O atoms and ¹⁶O from the oxide. Furthermore, depending on the reaction temperature, two other steps might be encountered: (5) internal (bulk) migration and exchange of ¹⁸O atoms with ¹⁶O from the oxide's bulk; (6) direct (nondissociative) exchange between ¹⁸O₂ molecules from the gas phase and dioxygen species on the support.

Depending on the experimental conditions (e.g. the temperature), two exchange regimes are distinguished [8]: (1) homoexchange, when only oxygen atoms from the gas phase participate in the exchange processes. Oxygen atoms from the oxide do not participate. In this case, the exchange processes exclusively take place on the metal particles. Homoexchange studies give profitable information on the oxygen activation step at the metal particles surface. (2) Heteroexchange, when oxygen atoms from the oxide do participate in the reaction. In this case, pure ¹⁸O₂ is introduced into the reactor and the formation of ¹⁶O₂ and ¹⁶O¹⁸O is followed as a function of time. Heteroexchange studies give direct information about the kinetics of the oxygen transportation on the catalyst.

In this paper a real-time kinetic model, based on rate equations, is presented [9]. Using this model, a computer code, named “Platina”, was built. It allows to model the

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Fig. 1. Schematic of the isotopic exchange mechanism between $^{18}\text{O}_2$ (g) and ^{16}O atoms from the oxide over supported metal catalysts.

exchange processes from the fitting of the experimental kinetic curves of the $^{16}\text{O}_2$, $^{18}\text{O}_2$ and $^{16}\text{O}^{18}\text{O}$ partial pressures evolutions as a function of time. Kinetic and thermodynamic parameters (reaction rate constants, surface and bulk diffusion coefficients and activation energies for reactions and diffusion) are obtained from the best fitting of the experimental curves.

2. Experimental

Oxygen isotope exchange experiments were carried out on a ceria-supported rhodium catalyst (0.3 wt.% Rh/CeO₂, $S_{\text{BET}} = 27 \text{ m}^2 \text{ g}^{-1}$, average oxide grain size = 260 Å, average metal nanocluster particle size = 15 Å, dispersion = 56%). About 20 mg of the catalyst was used for each experiment.

The oxide we used as a support, supplied by Rhodia Electronics and Catalysis (La Rochelle, France), was pre-calcined at 900 °C for 6 h. The catalyst was then prepared at room temperature by impregnation of the support, in excess water, with an aqueous solution of rhodium nitrate (Rh(NO₃)₃). After drying overnight at 120 °C, the catalyst was calcined in dry air (30 ml min⁻¹) at 450 °C for 4 h.

The experimental setup consisted in a re-circulated gas manifold consisting in a tubular quartz reactor, a re-circulating pump (Metal Bellows MB-41E) to circulate the gases over the catalyst and a mechanical pump to evacuate the system before and after each experiment [2,8]. An efficient re-circulating pump, operating under reduced pressure (50 mbar), is necessary to avoid any diffusion and mass transport effects in the gas phase. Such a phenomenon would limit the changes in the partial pressures and then distort the results. $^{16}\text{O}_2$, $^{18}\text{O}_2$ and $^{16}\text{O}^{18}\text{O}$ were monitored using a Quadrupole Mass Spectrometer (QMS 420 Blazers) connected to the reaction loop via thermo-valve (Balzers RVG 050 A). This valve was calibrated so that the total pressure in the ionization chamber was kept constant at 10^{-6} mbar. For the reactions, pure gases were used: $^{16}\text{O}_2 \geq 99.995\%$ pure (Air Liquide, Alpagaz1) and $^{18}\text{O}_2 \geq 99\%$ pure (Isotec).

3. Calculation of the diffusion coefficients

When surface migration is the rate determining step in the oxygen exchange reaction, the surface diffusion coefficient might be calculated using a simple model developed by Kramer and André [2,10]. This model assumes circular sources (metal nanoparticles) distributed on an infinite surface. Then, the amount of oxygen atoms diffusing on the support is given by:

$$N_e = \frac{2}{\sqrt{\pi}} C_m^{18} I_o \sqrt{D_s t} \quad (1)$$

The initial slope (S_1) of the kinetic curve N_e vs. $\sqrt{t}$ gives the surface diffusion coefficient:

$$D_s = \frac{\pi}{4} \left(\frac{S_1}{I_o C_m^{18}} \right)^2$$

with $S_1 = \left(\frac{dN}{d(\sqrt{t})} \right)_{t=0}$ (2)

and $I_o = \frac{\beta x_m D^2}{A}$

where x_m is the metal loading in the catalyst (wt.%), D is the dispersion of the metal nanoparticles (%), A is the surface area of the catalyst ($\text{m}^2 \text{ g}^{-1}$) and β is the surface atomic concentration in metal nanoparticles (at m^{-2}).

When the support exhibits a significant internal mobility of oxygen, the bulk diffusion coefficient (D_b) might be calculated as follows, using a model developed by Duprez [2] and Kakioka et al. [11]:

$$-\ln \frac{\alpha_g' - \alpha_s^0}{\alpha_g^\infty - \alpha_s^0} = \frac{\rho A}{N_g} \sqrt{\frac{4D_b t}{\pi}} \quad (3)$$

where ρ is the oxide density, N_g is the total amount of ^{18}O atoms in the gas phase and S_2 is the slope of the curve

$-\ln((\alpha_g^t - \alpha_s^0)/(\alpha_g^\infty - \alpha_s^0))$ vs. $\sqrt{t} \cdot \alpha_g^t$. α_g^∞ and α_s^0 are respectively the atomic fractions in ^{18}O in the gas phase (g) and in the solid (s) at time zero, at time t and at the equilibrium (∞). Then, the bulk diffusion coefficient is expressed as:

$$D_b = \frac{\pi}{4} \left(\frac{S_2 N_g}{\rho A} \right)^2 \quad (4)$$

When the elementary processes (surface and bulk diffusion) are well separated, these equations allow us to calculate the diffusion coefficients from the kinetic curves. In that case, only the initial time of the exchange process is taken into account for the calculations. Experimental curves cannot be fitted this way.

However, only the fitting of the entire experimental kinetic curves can indicate which elementary processes take place and which one is dominating upon catalysis. For that reason, a kinetic model had to be developed for a better understanding of the reaction schemes upon exchange on ceria-based mixed oxides with high oxygen mobility.

4. Kinetic model

4.1. Exchange on the metal nanoclusters

Generally, oxygen exchange on metal nanoclusters proceeds in three steps: (1) adsorption of dioxygen molecules and dissociation, (2) reaction between oxygen atoms and formation of dioxygen molecules, and (3) desorption of dioxygen molecules to the gas phase. The third one is not a limiting step as the activation barrier for desorption of molecular dioxygen is low. As a result, it is assumed that dioxygen molecules formed on the metal surface immediately leave the surface. The time variation of the concentration in the gas phase of the i th type of dioxygen molecule consist in two terms: the adsorption and the chemical reactions contributions.

$$\frac{dn_i}{dt} = \left(\frac{dn_i}{dt} \right)_{\text{Ad}} + \left(\frac{dn_i}{dt} \right)_{\text{Re}} \quad (5)$$

For the kinetic modeling of the surface processes [12], the adsorption term is usually represented by the Langmuir–Hinshelwood equation:

$$\left(\frac{dn_i}{dt} \right)_{\text{Ad}} = \alpha_i I_i c_m \quad (6)$$

where α_i is the sticking coefficient, I_i is the flux of particles to the surface, c_m is the relative atomic concentration of metal atoms in the first atomic layer at the metal nanoparticles surface. This concentration decreases when the coverage in

adsorbed oxygen isotopes (^{18}O and ^{16}O) increases. In fact, $c_m + c_{16} + c_{18}$ is kept equal to 1.

The flux of particles arriving to the surface is estimated from the expression:

$$I_j = p_j N_A (2\pi M_j RT)^{-1/2}$$

where p_j is the partial pressure of the j th type species, M_j is molecular mass of the j th type species and N_A is the Avogadro's number.

The flux of oxygen atoms to the surface is in the order of $10^{24} - 10^{25} \text{ m}^{-2} \text{ s}^{-1}$ when the total pressure is in the range of a few mbar. Furthermore, the relative flux to the surface, that is the number of oxygen atoms arriving from the gas phase per surface metal atom and per second ($i_j = I_j/c_m$) varies in the range $10^5 - 10^6 \text{ s}^{-1}$, when the surface concentration c_m is in the range of 10^{19} m^{-2} ($c_{\text{Rh}} = 1.33 \times 10^{19} \text{ m}^{-2}$).

The sticking coefficient for oxygen on noble metals (Pt, Pd, Rh, Ir, Ru) is close to 1.

In our case, the oxygen flux to the surface at 50 mbar is so high that the metal nanoclusters were considered as fully covered by oxygen atoms even at the very beginning of the experiment. Consequently, the oxygen isotopic composition on the metal surface was considered to be equal to the oxygen composition in the gas phase. Then, before each iteration during the calculation, the surface composition of the metal nanoclusters is obtained from the following expression:

$$c_i(t) = f_i(t) \left(c_m - \sum_j c_j(t) \right), \quad i, j = 16, 18 \quad (7)$$

where $f_i(t)$ is the fraction, at time t , of the i th type of oxygen isotope in the gas phase. The term in brackets gives the uncovered metal surface at time t after desorption of the dioxygen molecules (reaction).

The reactions between oxygen atoms taking place on the metal surface are as follows:

The time variations of the oxygen atoms concentrations at the metal nanoclusters surface, according to the mass action law, are expressed as:

$$\begin{cases} \left(\frac{dc_{18}}{dt} \right)_{\text{Re}} = -kc_{18} \left(\frac{1}{2} c_{18} + c_{16} \right) \\ \left(\frac{dc_{16}}{dt} \right)_{\text{Re}} = -kc_{16} \left(\frac{1}{2} c_{16} + c_{18} \right) \end{cases} \quad (9)$$

In the last equations, the factor of 1/2 accounts for the adsorption and the subsequent dissociation of the $^{16}\text{O}^{18}\text{O}$ molecules from the gas phase. In fact, as far as atomic concentrations are considered, and not molecular concentrations, a factor of 1/2 is need. After dissociation, one $^{16}\text{O}^{18}\text{O}$ molecule gives only one ^{16}O atom and one ^{18}O atom, while a $^{16}\text{O}_2$ molecule would give two ^{16}O atoms.

Finally, the reaction term in Eq. (5) is given by:

$$\begin{cases} \left(\frac{dn_{32}}{dt} \right)_{\text{Re}} = \frac{S_m}{2V} k c_{16}^2 \\ \left(\frac{dn_{36}}{dt} \right)_{\text{Re}} = \frac{S_m}{2V} k c_{18}^2 \\ \left(\frac{dn_{34}}{dt} \right)_{\text{Re}} = \frac{S_m}{V} k c_{16} c_{18} \end{cases} \quad (10)$$

with:

$$S_m = (N_A f_m m_{\text{cat}} D) / (c_m M_m) \quad (11)$$

where: S_m is the total surface area of the metal nanoclusters in the catalyst, f_m is the metal loading in the catalyst, m_{cat} is the catalyst sample mass, D is the dispersion of the metal nanoclusters (ratio between the number of surface metal atoms to the total number of metal atoms in the nanoclusters), M_m is the molar mass of the metal and V is the reactor volume.

$k = A \exp(-Q/RT)$ is the reaction rate constant ($\text{m}^2 \text{mol}^{-1} \text{s}^{-1}$), n_i and c_i , respectively, represent the volume and surface concentrations (mol m^{-3} and mol m^{-2} , respectively), Q is the reaction activation energy (J mol^{-1}), A ($\text{m}^2 \text{mol}^{-1} \text{s}^{-1}$) is the pre-exponential factor, T is the temperature (K) and R is the universal gas constant.

4.2. Surface diffusion

Oxygen atoms adsorbed on the metal particles may “jump” onto the oxide surface and further diffuse. To keep the mass balance, it is assumed that the jump of one oxygen atom from the metal to the oxide is balanced by another atomic jump from the oxide to the metal particle. In fact, oxygen atoms do not accumulate on the oxide surface. Initially, there is no ^{18}O atoms in the oxide and the concentration gradient in oxygen-18 is very high. As follows from the first Fick’s law, ^{18}O atoms move from the nanoclusters to the oxide and this flux is compensated by the flux of ^{16}O atoms from the oxide to the metal surface. Then, the ^{16}O atoms arriving at the metal surface might react with other oxygen atoms and leave the surface as dioxygen molecules.

In order to calculate the gradient of ^{18}O atoms diffusing on the oxide, the surface around the metal particles was virtually divided into square-shaped rings as schematized in Fig. 2. The surface area of these layers weakly depends on

the shape of the metal particles. For example, the area of one layer around a cubic or a semispherical nanocluster would only differ by a factor of $4/\pi$. In our case, cubic metal particles were considered. The surface area of L th square-shaped layer is obtained from the following expression:

$$S^{(L)} = 4N(d + (L - 1)a)a \quad (12)$$

where: a is the thickness of one layer, $N = S_m/5d^2$ is the total number of metal nanoclusters on the catalyst, d is the size of one metal nanocluster.

Taking into account (i) the variation the area of the layers as a function of the distance from the metal particle and (ii) the different directions of the oxygen atoms fluxes, the time variation of the i th type of atom in the L th surface ($K=1$) layer (Fig. 3) is obtained from the second Fick’s law:

$$(\partial c / \partial t) = D(\partial^2 c / \partial x^2)$$

Considering finite increments:

$$\left(\frac{dc_i^{(1,L)}}{dt} \right)_{\text{SD}} = \frac{D_s}{a^2} (A^{(L-1)} (c_i^{(1,L-1)} - c_i^{(1,L)}) - A^{(L)} (c_i^{(1,L)} + c_i^{(1,L+1)})),$$

$$i = 16, 18$$

where:

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

Eq. (13) is also valid for oxygen jumps from/to the metal particles ($L=0$). This term is added to Eq. (5) when surface diffusion is included into the calculations.

Fig. 2. Square-shaped layers around the metal nanoclusters on the oxide surface.

Fig. 3. Schematic of the layers introduced for surface and bulk diffusion calculations.

The number of rings (L) around the metal particle is not infinite but limited either by the mean distance between metal particles or by the oxide grain size. The mean distance (x_L) between metal particles is obtained from the expression:

$$x_m = (S_{ox}/N)^{1/2}$$

and the number of layers is given by:

$$L = 0.5x_m/a$$

where S_{ox} is the total surface of the oxide.

However, for some catalysts, x_m can be higher than the oxide grain size (d_{ox}) and in this case:

$$L_{max} = 0.5d_{ox}/a$$

4.3. Bulk diffusion

Oxygen atoms diffusing on the surface of the oxide may also diffuse into the bulk of the oxide grain (Fig. 4). To determine the concentration gradients in the bulk of the oxide, oxide layers (K) with a thickness a were introduced. However, considering 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 (Fig. 5). So, these areas were calculated according to the following expression:

$$S_B^{(K)} = S_{ox}(1 - 2(K - 1)a/d_{ox})^2 \quad (14)$$

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, in a similar way to surface diffusion.

Taking into account the different fluxes, the variation of the concentration of the i th type of oxygen atom in the K th bulk layer and in the L th surface ring takes the following form:

$$\left(\frac{dc_i^{(L,K)}}{dt}\right)_{SD} = \frac{D_b}{a^2} (B^{(K-1)} (c_i^{(L,K-1)} - c_i^{(L,K)}) - B^{(K)} (c_i^{(L,K)} + c_i^{(L,K+1)})) \quad (15)$$

where

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

Fig. 4. Arrangement of the monolayers in a cubic oxide grain of a powder catalyst.

Fig. 5. Experimental and fitted ($R = \text{const.}$, $D = \text{const.}$) results of the kinetic curves upon heteroexchange at $T = 311$ °C on a Rh/CeO₂ catalyst.

4.4. Direct exchange between the gas phase and binuclear species present on the oxide surface

To take into account such an exchange mechanism, the following reactions, occurring at the interface between the gas phase and the oxide surface, were considered [4]:

The corresponding rate equations for the variation of the $^{16}\text{O}_2$ and $^{18}\text{O}_2$ surface molecular concentrations upon direct exchange are:

$$\left(\frac{dc_i}{dt}\right)_{\text{sup}} = k_{\text{sup}} \frac{V}{S_{\text{ox}}} (n_i c_j - n_j c_i), \quad i, j = 32, 36 \quad (17)$$

where: k_{sup} is the reaction rate constant and c_i , obtained from Eq. (18), is the average concentration in $^{16}\text{O}_2$ and $^{18}\text{O}_2$ species at the surface of the catalyst.

$$c_i = f_{\text{ox}} \frac{1}{2x_N} \sum_{L=1}^{L_{\text{max}}} c_p^{(L,1)}, \quad p = 16, 18, \quad i = 32, 36 \quad (18)$$

where f_{ox} is the fraction of binuclear oxygen species at the oxide surface.

The corresponding rate equation term for the variation of the oxygen concentration in the gas phase is:

$$\left(\frac{dn_i}{dt}\right)_{\text{sup}} = k_{\text{sup}} (n_i c_j - n_j c_i), \quad i, j = 32, 36 \quad (19)$$

Upon simulation, this term might be added to Eq. (5) whenever direct exchange should be included. If such a

process occurs, the oxygen composition at the surface is changed and surface and bulk diffusion is influenced. Then, it is necessary to recalculate the oxygen isotopes distribution in each surface layer L . The time variation of the concentration in oxygen ^{16}O and ^{18}O atoms in the surface layer L , following direct exchange, is obtained from the following expression:

$$\left(\frac{dc_i^{(L)}}{dt}\right)_{\text{sup}} = 2k_{\text{sup}} \frac{V}{x_N S_{\text{ox}}} (n_i c_j - n_j c_i), \quad i, j = 32, 36, \quad r = 16, 18 \quad (20)$$

5. Results and discussion

This newly developed model may include at the same time all the four processes described above (exchange on the metal particles, surface diffusion, bulk diffusion, direct exchange) or several of them. Exchange on metal nanoclusters always takes place. The decision about whether or not the other processes should be included can be made depending of the quality of the experimental curves fitting. Then, one should start with the simplest model and make it more and more complex to get the best fit.

In Figs. 5–7, the experimental results, obtained upon heteroexchange on a Rh/CeO₂ sample, are presented. At the beginning of the reaction, only dioxygen $^{18}\text{O}_2$ is introduced in the gas phase. Experimental results show that, upon exchange, dioxygen molecules $^{16}\text{O}_2$ and $^{16}\text{O}^{18}\text{O}$ also appear in the gas phase. It clearly indicates that ^{16}O atoms from the oxide do participate in the reaction. In fact, at the same time as exchange on metal nanoclusters occurs, surface diffusion and/or direct exchange also takes place. The first process is much more likely to occur, while the second one should take place at higher temperatures [13]. However, the correct

Fig. 6. Experimental and fitted ($R \neq \text{const.}$, $D \neq \text{const.}$) results of the kinetic curves upon heteroexchange on a Rh/CeO₂ catalyst at $T=278$ °C.

answer is obtained only after several tries to fit the experimental curves, looking for the best result. Finally, one may observe that bulk diffusion takes place only after surface diffusion occurred, when a significant part of the surface oxygen atoms has been exchanged [11].

In Fig. 5, experimental results were tentatively fitted, including only two processes: (1) exchange on the metal nanoclusters and (2) surface diffusion. One can observe that the fitting is quite good at the beginning, but some deviations appear later on. Calculations showed that this deviation could not be overcome by including bulk diffusion or

direct exchange. Theoretical curves showed higher exchange yield than the experimental results. This means that, during the reaction, the exchange is getting slower and slower. Furthermore, we observed that this deviation increases monotonously with time. This indicates that the exchange rate is not constant but decreases with time. This could be explained if the properties of the catalyst (oxidation state of the metal nanoparticles, stoichiometry of the oxide, etc.) change with time on stream, which is some kind of deactivation. It follows that the reaction rate constants and the surface diffusion coefficient also change with time.

Fig. 7. Experimental and fitted ($R \neq \text{const.}$, $D \neq \text{const.}$) results of the kinetic curves upon heteroexchange on a Rh/CeO₂ catalyst at $T=311$ °C.

Assuming an exponential time dependence for the deactivation process, the following expressions for the reaction rate constant and the surface diffusion coefficient were considered:

$$R = R_o(n + m \exp(t/\tau_1)), \quad n + m = 1; \quad (21)$$

$$D_s = D_{s0} \exp(t/\tau_2),$$

The fitted results, introducing Eq. (21), are presented in Figs. 6 and 7 for heteroexchange reactions, respectively, carried out at 311 and 270 °C on a Rh/CeO₂ sample. In that case, both fittings are optimum over whole reaction time. As good fittings were also obtained for experimental curves registered for heteroexchange reactions carried out on the same catalyst at 256, 279 and 327 °C.

Evolutions as a function of temperature of the calculated values for the reaction rate constants and the surface diffusion coefficients are displayed (Arrhenius plot) in Figs. 8 and 9, respectively. Fitting the experimental points to a line gives access to the activation energies for the different processes. Activation energies are $Q = 75.4 \text{ kJ mol}^{-1}$ for the exchange on the metal particles and $Q_s = 27.0 \text{ kJ mol}^{-1}$ for the surface diffusion. These values are in good agreement with the data available in the literature [13–15].

One can notice that the fittings of the experimental curves were good enough, even without including bulk diffusion. This was not surprising if one consider what is known about oxygen diffusion on ceria. In fact, oxygen was shown to be poorly mobile in the bulk of ceria compared to ceria–zirconia mixed oxides.

Furthermore, from the experimental results one can only state that ¹⁶O atoms diffuse from the oxide to the metal nanoparticles and then desorb as dioxygen molecules. Unfortunately, it is impossible to say from which oxide layer (L,K) ¹⁶O atoms come. Only in the case where all surface oxygen atoms would be exchanged (50% ¹⁶O–50% ¹⁸O), the kinetic curves would show qualitative differences.

Fig. 8. Arrhenius plot for the reaction rate constant on the metal particles.

Fig. 9. Arrhenius plot for the surface diffusion coefficient.

In our case in fact, the surface area of the catalyst is so high that such a surface exchange level is never reached.

From the modeling point of view, if the surface diffusion would be small, it could be compensated by bulk diffusion and vice versa. The fitted results would be the same in both cases. In fact, the fitting only depends on the total amount of exchanged oxygen atoms. Furthermore, it is known that—in most cases—bulk diffusion coefficients are about four orders of magnitude lower than surface diffusion coefficients [4,14].

To solve this problem, other experimental methods are needed to examine the bulk of the oxide after the exchange reaction. Real catalysts have a very complex structure and the characterization of such systems is very difficult. In fact, fundamental studies in heterogeneous catalysis are more easily performed on model catalysts [1]. Then, surface analytical techniques, such as SIMS, AES, etc. [16–18], might be used to look at the distribution of oxygen species in deeper layers.

6. Conclusions

1. The main processes taking place upon oxygen heteroexchange on a Rh/CeO₂ catalyst are the dissociative adsorption–desorption of dioxygen on the metal nanoparticles and the surface diffusion on the oxide. Surface ¹⁶O atoms are exchanged with diffusing ¹⁸O atoms coming from the surrounding gas phase. The formation of new dioxygen molecules and the desorption only take place on the metal nanoparticles.
2. On ceria-supported catalysts, bulk diffusion and direct exchange are not dominating processes at temperatures lower than 330 °C.
3. The physico-chemical characteristics of the catalyst change upon heteroexchange. The adsorption–desorption rate and the surface diffusion coefficient decrease with time on stream.
4. In the interval between 250 and 330 °C, the activation energy for the dioxygen activation on the metal nanoparticles is $Q = 75.4 \text{ kJ mol}^{-1}$ and the activation energy

for oxygen atoms surface diffusion is $Q_s = 27.0 \text{ kJ mol}^{-1}$. At the same time, surface diffusion coefficient varies from 2.7×10^{-19} to $5.7 \times 10^{-19} \text{ m}^2 \text{ s}^{-1}$.

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