



Isotopic transient analysis of oxygen exchange over oxides

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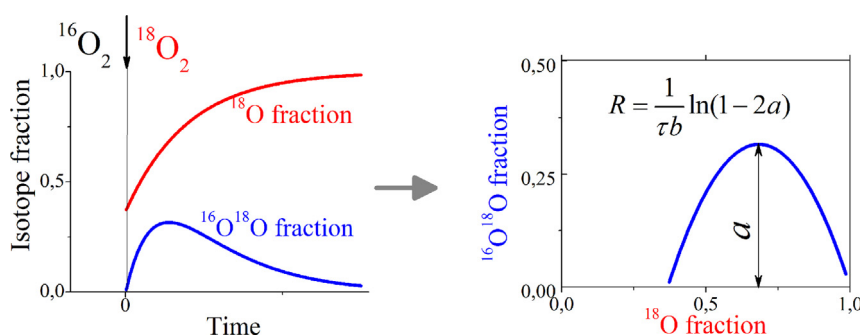
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HIGHLIGHTS

- Algorithm of isotopic transient analysis without use of numerical methods was developed.
- Criterion to discriminate between the types of isotopic exchanges was proposed.
- Formulas for estimation of exchange rate and diffusion coefficient of oxygen in oxides were derived.

GRAPHICAL ABSTRACT



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ABSTRACT

We investigated the model of oxygen isotopic exchange on solid oxides in flow reactor using numerical and analytical approaches. The study concerns the effect of the exchange mechanism (mono- or diatomic) and of the rate of exchange as well as the oxygen diffusion rate in the bulk on the isotopic response after $^{16}\text{O}/^{18}\text{O}$ switch. Ratio of $^{16}\text{O}^{18}\text{O}$ molecular fraction to ^{18}O atomic fraction is shown to depend on the kinetics of gas-surface exchange, and does not depend on the oxygen diffusion in the oxide bulk. Algorithm of isotopic transient analysis without use of numerical methods was developed. Criterion to discriminate between the types of isotopic exchanges was proposed. Formulas for estimation of exchange rate and diffusion coefficient of oxygen in oxides were derived. The estimates of the surface exchange rate and of the bulk diffusion coefficient of the complex oxide $\text{La}_{0.3}\text{Bi}_{0.7}\text{MnO}_3$ were calculated applying proposed algorithm. The comparison with the results of numerical modelling verified the reliability and sufficiently high accuracy of obtained estimates.

1. Introduction

Isotopic oxygen exchange in gas-solid systems is widely used in heterogeneous catalysis for studying oxygen activation and its state characterization on the catalyst surface. Theoretic postulates of oxygen isotopic exchange were suggested by Winter [1,2], Borekov et al. [3,4], Novákova [5,6], Ozaki [7] and Duprez [8]. Basic theory is based on classification of exchange types, depending on the number of surface

oxygen atoms, participating in exchange with O_2 (zero-atom, single-atom or two-atom exchange). Regarding the exchange type, one may reveal the most probable mechanisms of oxygen activation on the surface. Isotopic hetero-exchange rate, being one of the most important parameters, is determined by the energy of oxygen bonding to the surface. In the case of oxides, not only the surface but also the bulk oxide oxygen atoms take part in the exchange process. That is why many recent studies focus on the estimation of the rate of bulk oxygen

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Nomenclature

b	ratio of total oxide oxygen to the number of oxygen atoms in the gas phase
b_1	fraction of surface oxygen in the oxide
b_2	fraction of bulk oxygen in the oxide
C_{O_2}	mole fraction of oxygen in the gas flow
	diffusion coefficient (cm^2s^{-1})
$D_{\text{eff}} = D/h^2$	apparent diffusion coefficient (s^{-1})
h	characteristic particle size (cm)
f_{34}	fraction of $^{16}\text{O}^{18}\text{O}$ molecules
f_{34}^{input}	fraction of $^{16}\text{O}^{18}\text{O}$ molecules in the reactor inlet
L_{OX}	number of oxygen atom per catalyst gram ($\text{mol}\cdot\text{g}^{-1}$)
N_A	number of gas molecules per unit volume ($\text{mol}\cdot\text{cm}^{-3}$)
R	rate of heteroexchange (s^{-1})
U	flow rate ($\text{cm}^3\cdot\text{s}^{-1}$)
V	gas phase volume (cm^3)

W catalyst sample weight (g)

Greek letters

α	^{18}O atomic fraction in the gas phase
α^{input}	^{18}O atomic fraction in the gas phase in the reactor inlet
α_τ	jump value α in the reactor outlet after isotopic switch
α_{OX}	^{18}O fraction in the oxide
α_S	^{18}O atomic fraction in the surface layer
α_{BULK}	^{18}O atomic fraction in the oxide bulk
$\tilde{\alpha}, \tilde{\alpha}_S, \tilde{\alpha}_{BULK}$	average ^{18}O fractions over reactor length
β	coefficient of exchange between the surface and bulk oxygen, s^{-1}
τ	contact time, s
η	dimensionless particle radius
ξ	dimensionless reactor length

substitution, which may be used for characterizing the mobility of lattice oxygen [9–13].

The idea of isotopic-kinetic experiment is the following: as adsorption-desorption equilibrium between gas phase and surface is attained for the studied sample, gas is substituted. In our case $^{16}\text{O}_2$ is substituted by $^{18}\text{O}_2$, and concentrations of various isotopes $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$ and $^{18}\text{O}_2$ are followed in time. Experiments are performed in either closed or flow reactors. For the closed reactors one may use a well derived algorithm for experimental data processing, allowing the exchange type determining as well as the analytic estimate of total hetero-exchange rate and exchangeable oxygen amount in the solid. However, in the closed reactors experiments are performed under conditions close to vacuum. This obstacle reduces data availability with respect to adsorbed oxygen activity in the real catalytic process.

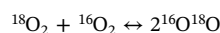
In the flow reactor there are no restrictions towards the gas pressure, and isotopic exchange may be studied under conditions similar to real catalysis. Moreover, exchange may continue till the complete oxygen substitution in the sample, which allows obtaining more reliable estimates for the rate of oxygen diffusion in the sample bulk as compared to the closed reactor. The latter is especially important for the oxides used in the solid fuel cells. Experimental procedure is similar to that of SSITKA [14–17]. At first gas flow with definite oxygen concentration in inert is supplied through the sample. After adsorption-desorption equilibrium attainment the gas flow is switched: $^{16}\text{O}_2$ in the mixture is substituted by $^{18}\text{O}_2$, and oxygen isotopic composition is analyzed at reactor outlet. Technically flow experiment is easier. However, data analysis is far more complicated. All known analysis methods are numerical and include experimental data fitting according to various mathematical models. For example Kan and Wachsmann in [18,19] applied approximated differential reactor model for hetero-exchange rate estimation. Model application correctness was not discussed, but authors used standard software MATLAB to solve the direct and reverse problem. Nibelke et al. [20] used a uni-dimensional dynamic model to follow isotopic oxygen composition in both gas and catalyst, changing in time and along plug flow reactor. In above described models oxide bulk oxygen atoms were supposed to be substituted simultaneously (independently of their remoteness from the catalyst surface). Seemingly the strictest model was considered by Sadovskaya et al. [21] and further on was used in [22–26]. According to this model isotopes concentration was followed in time, along reactor and over oxide particle radius. Oxygen substitution in the oxide bulk was described by diffusion equation. Reverse problem solution allowed authors to determine exchange mechanism and rate on the surface as well oxygen self-diffusion coefficient in the bulk of several oxide catalyst samples. However, special software was designed to solve this two-dimensional problem including hyperbolic and parabolic differential equations.

Despite the fact that flow reactor experiments are simpler and at the same time more informative, if compared to the closed reactor ones (especially regarding oxygen mobility in the oxide bulk), only few research groups perform them. On one hand, it is caused by the large consumption of isotope, on the other hand, experimental data interpreting is rather complicated and requires the application of numerical methods, including minimization procedure. In the present study we suggest experimental data analysis algorithm, which allows one to determine the exchange type and also to estimate oxygen hetero-exchange rate on the surface as well as the coefficient of oxygen atoms diffusion in the catalyst bulk not using numerical approaches.

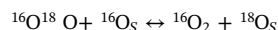
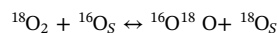
2. Isotopic exchange theory basics

Basic theory, considering the exchange types, has been formulated by Klier, Nováková and Jiru [5] as well as by Muzykantov, Popovskii and Boreskov [4]. Three kinetically resolvable types of isotope exchange were found to be possible, namely:

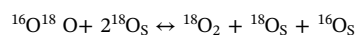
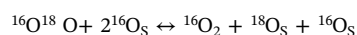
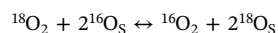
- i) zero-atom exchange with no participation of oxygen atoms from the solid. It may be represented by the following reaction:



- ii) single-atom exchange between one oxygen atom from the gas phase oxygen molecule and one oxygen atom from the solid. It involves surface atoms O_s and may be presented as follows:



- iii) two-atom exchange between molecule O_2 and two oxygen atoms from the solid



Zero-atom exchange happens on several oxides at very low temperatures ($< 100\text{ K}$) after their pretreatment in vacuum. At elevated

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