# Isotopic transient kinetic study of $N_2O$ decomposition on $LaMnO_{3+\delta}$

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## A R T I C L E   I N F O

## A B S T R A C T

Analysis of label oxygen transfer during the reaction of $N_2O$ decomposition ($^{18}O_2/N_2{}^{16}O$) on $LaMnO_{3+\delta}$ indicated that $^{16}O$ transfer from $N_2{}^{16}O$ to $^{16}O_2$ preceded faster compared to oxygen exchange $^{18}O_2/^{16}O_2$ and involved the interaction with two lattice oxygen of perovskite. It suggests that surface oxygen vacancies play an important role in reactivity of $LaMnO_3$ and explains why at times correlation can be found between catalytic activity and bulk oxygen diffusion ($La_{1-x}Sr_xMnO_{3\pm\delta}$) and at other time catalytic properties correlate with surface oxygen exchange constant ($La_{1-x}Sr_xFeO_{3-\theta}$). The former can be due to general correspondence between surface oxygen exchange kinetics and bulk oxygen diffusion.

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## 1. Introduction

Catalytic decomposition of $N_2O$ is generally described by the following scheme [1,2]:

$$N_2O + S \rightarrow N_2O–S \tag{1}$$

$$N_2O–S \rightarrow N_2 + O–S \tag{2}$$

$$O–S + N_2O \rightarrow N_2 + O_2 + S (Eley–Riddell mechanism) \tag{3}$$

$$2O–S \leftrightarrow O_2 + 2S (Langmuir–Hinshelwood mechanism) \tag{4}$$
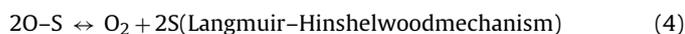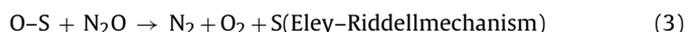
where S is surface active site, $N_2O$–S adsorbed or chemisorbed $N_2O$, O–S adsorbed or chemisorbed O.

For many oxides, it is known that at the temperature range 300–600 °C $N_2O$ conversion decreased in the presence of oxygen in the reaction mixture, which can be due to the competitive adsorption of $N_2O$ and oxygen on the same active sites [3,4] being oxygen vacancies or metal cations. Having studied activity of manganites in $N_2O$ decomposition at 400–600 °C vs lattice parameters, Raj and Srinivasan [5] came to the conclusion that oxygen desorption (stage 4) appeared to be the rate-controlling step of the reaction. Isotopic oxygen exchange carried out by Sazonov et al. on perovskites [6] and by Winter on a number of oxides [7] at 400–600 °C confirmed this assumption. Thus, it is believed that at medium temperatures (300–600 °C) catalytic activity of perovskites in $N_2O$ decomposition is determined by the binding strength of adsorbed or chemisorbed oxygen. However, at 900 °C it was found that the rate of $N_2O$ decom-

position on $La_{1-x}Sr_xMnO_{3\pm\delta}$ ($x = 0$, 0.3, 0.5) correlated with the coefficient of bulk oxygen diffusion [8], which gives us reason to suppose that reactivity of perovskites at high temperatures can depend on lattice oxygen mobility. To understand what this correlation can mean in respect to the mechanism of $N_2O$ decomposition, we aimed at studying the dynamics of oxygen transfer from $N_2O$ to $O_2$ on $LaMnO_{3+\delta}$ using label oxygen.

## 2. Experimental

The samples of $LaMnO_{3+\delta}$ and $La_{0.7}Sr_{0.3}MnO_{3\pm\delta}$ stoichiometric composition were prepared by Pechini method (calcined in air at 900 °C) [9].

Transient isotopic experiment $^{18}O_2/N_2{}^{16}O$ was performed at atmospheric pressure in a fixed-bed reactor system. A reactor was a quartz U-shaped tube (i.d. 3 mm, $L = 250$ mm) situated in a furnace, with a catalyst (0.025 g, 0.25–0.5 mm fraction) placed on a bed of non-porous quartz. Temperature of the catalyst was monitored using a thermocouple located outside the catalyst bed. Before every experiment, the sample was heated to 900 °C in 0.5% vol. $^{16}O_2$ + He flow, then replaced by the same mixture but containing $^{18}O_2$ and kept for 30 min for complete substitution of $^{16}O$ by $^{18}O$ in the bulk of the sample. Finally, flow containing 1% $N_2{}^{16}O$ + 1% Ar in He was fed to reactor. Gas flow rate for mixtures amounted to 16.7 cm³/s. Steady state $N_2{}^{16}O$ conversion value in these conditions was close to 75% and resulted in $^{16}O_2$ content in the outlet mixture 0.38%. The effluent gas composition ($^{18}O_2$, $^{16}O^{18}O$, $^{16}O_2$, $N_2{}^{18}O$, $N_2{}^{16}O$, $N_2$, Ar) was analyzed online by SRS RGA 200 mass spectrometer and GC.

Catalytic activity in $N_2O$ decomposition at the temperature range 600–900 °C was studied in the same reactor system used for the isotope experiments. Gas mixtures contained 1% $N_2O$ (+0.5%

$CH_4$) in He passed through the reactor charged by $0.0325\,cm^3$ of $LaMnO_3$ or $La_{0.7}Sr_{0.3}MnO_3$ with a flow rate $16.7\,cm^3/s$, corresponding to the contact time in normal conditions $\tau = 0.002\,s$.

## 3. Results

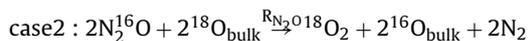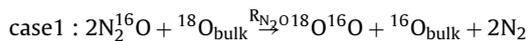### 3.1. Experimental isotopic transient curves in the switch $^{18}O_2/N_2{}^{16}O$ for $LaMnO_3$

Kinetic experiments showed that after the switch of $^{18}O_2$–$N_2{}^{16}O$, no $N_2{}^{18}O$ was detected in the gas phase, which indicates the absence of direct oxygen exchange between $N_2O$ and lattice oxygen or $O_2$ molecule. The relaxation of $N_2{}^{16}O$ and $N_2$ immediately achieved the steady-state, while the responses of differently labeled $O_2$ molecules ($^{18}O_2$, $^{16}O_2$ and $^{18}O^{16}O$) were more continuous. To match the rate of oxygen exchange with the rate of $N_2O$ decomposition, we calculated the responses of $^{16}O$ fraction in the gas phase oxygen as $\alpha_g = 2^{16}O_2 + {}^{16}O^{18}O/2^{16}O_2 + {}^{16}O^{18}O + 2^{18}O_2$ and the normalized concentration of $^{16}O^{18}O - f_{34} = {}^{16}O^{18}O/{}^{16}O_2 + {}^{16}O^{18}O + {}^{18}O_2$ and compared them with responses obtained after the switch $^{16}O_2/{}^{18}O_2$ (SSITKA $^{16}O_2/{}^{18}O_2$ discussed in Ref. [8]) (Fig. 1). As follows from Fig. 1b, total amount of exchanged oxygen after the switch $^{18}O_2/N_2{}^{16}O$ in a period of 250 s accounts for $5.6 \times 10^{21}$ at./g (75% of the total amount of exchangeable oxygen) and is less than during $^{16}O_2/{}^{18}O_2$ exchange ($7$–$7.5\ 10^{21}$ at./g) that is due to incomplete $N_2O$ conversion. At the same time, the dynamics of oxygen transfer is approximately the same. It means that the rate of $N_2O$ decomposition is relatively high and does not limit the dynamics of oxygen transfer from $N_2{}^{16}O$ to $^{16}O_2$ and $^{16}O^{18}O$ due to the combined processes of $N_2O$ decomposition and oxygen exchange. In addition, in the initial period of time after the switch the $\alpha_g$ response in $^{16}O_2/{}^{18}O_2$ experiment raised higher than that observed in $^{18}O_2/N_2{}^{16}O$, which points to the increased rate of label transfer from $N_2O$ to $O_2$ in comparison to the conditions of steady state oxygen exchange. More detail information about the mechanism of the oxygen transfer can be obtained by numerical analysis of isotope responses.

### 3.2. Numerical analysis of transient isotope responses

Numerical analysis of the dynamics of label oxygen transfer in the reaction of $N_2{}^{16}O$ decomposition was made using a model of oxygen exchange for plug-flow reactor (see Appendix A and Ref. [8]) based on the experimental data of normalized concentrations of $^{16}O_2 - (f_{32} = {}^{16}O_2/{}^{16}O_2 + {}^{16}O^{18}O + {}^{18}O_2)$ and $^{18}O^{16}O$ $(f_{34} = {}^{16}O^{18}O/{}^{16}O_2 + {}^{16}O^{18}O + {}^{18}O_2)$ in the gas phase. In modeling of isotope responses several parameters were estimated from independent experiments. The rate of oxygen diffusion in the bulk–$D/r^2$ ($s^{-1}$) and the rate of surface oxygen exchange–$R$ ($s^{-1}$) for $LaMnO_{3+\delta}$ were calculated independently from the SSITKA $^{16}O_2/{}^{18}O_2$ experiments [8], while the rate of $N_2O$ decomposition ($R_{N_2O}$) under these conditions was estimated from catalytic experiments measured value $N_2O$ conversion.

At first, when analyzing the dynamics of oxygen transfer, we considered the simplest scheme of oxygen exchange (Fig 2b) by which oxygen generated from decomposition of $N_2O$ immediately desorbs into the gas phase (as $O_2$) and then exchanges with the lattice oxygen of perovskite. However, in this case in the initial period of time after the switch (5–10 s) the concentration $^{16}O_2$ ($f_{32}$) should rise steeply, while its continuous increase was observed in the experiment (Fig. 2a). Even by increasing the rate of surface oxygen exchange $R$ we also failed to describe the kinetics of $^{16}O$ transfer. It indicates that there is direct labeled oxygen transfer to the oxide bulk from $N_2O$ molecule.

Thus, we examined two cases of $^{16}O$ transfer from $N_2O$ to $O_2$, namely,

$$\text{case 1} : 2N_2{}^{16}O + {}^{18}O_{bulk} \xrightarrow{R_{N_2O}} {}^{18}O^{16}O + {}^{16}O_{bulk} + 2N_2$$

$$\text{case 2} : 2N_2{}^{16}O + 2^{18}O_{bulk} \xrightarrow{R_{N_2O}} {}^{18}O_2 + 2^{16}O_{bulk} + 2N_2$$

Both of them assume that labeled oxygen is transferred to the oxide bulk as a result of $N_2O$ decomposition followed by recombination with one (case 1, Fig. 3b) or two (case 2, Fig. 4b) lattice oxygen atoms giving rise to the formation of $^{18}O^{16}O$ or $^{18}O_2$. As illustrated in Fig 4a, if one lattice oxygen participates in label oxygen transfer (case 1), the concentration of $^{16}O^{18}O$ ($f_{34}$) in the initial period of time (5–25 s) considerably exceeds the experimental data signifying that the calculated rate of oxygen transfer in the bulk is understated. The best correspondence between the calculated and experimental isotopic responses was observed in case 2, assuming that two lattice oxygen of perovskite take part in label oxygen transfer from $N_2O$ molecule to $O_2$ (Fig. 4a). Thus, transient isotopic experiment $^{18}O_2/N_2{}^{16}O$ allowed us to make a conclusion that $O_2$ formed at $N_2O$ decomposition on manganites at high-temperature (900 °C) involves lattice oxygen of perovskite.

## 4. Discussion

In our previous work it was noticed that catalytic activity of $La_{1-x}Sr_xMnO_{3\pm\delta}$ correlated with the rate of tracer oxygen diffusion in the bulk [8]. The question arises how can lattice oxygen mobility influence catalytic properties at steady state. Let us consider the following scheme of $N_2O$ decomposition, taking into account that at high temperatures surface lattice oxygen vacancies are the active sites for both $N_2O$ and molecular $O_2$ adsorption and dissociation:

$$N_2O + S \leftrightarrow N_2 + O\text{–}S \tag{5}$$

$$O\text{–}S + [\,]_s \leftrightarrow S + [O]_s \tag{6}$$

$$[O]_s + [O]_s \leftrightarrow O_2 + 2[\,]_s \tag{7}$$

where S—surface oxygen vacancy or coordinatively unsaturated surface metal cations, $[O]_s$—surface lattice oxygen, $[\,]_s$—surface oxygen vacancy, O–S adsorbed or chemisorbed O.

If oxygen desorption is the rate-limiting step of the reaction, then the correlation should exist between the rate of $N_2O$ decomposition and the rate of the surface oxygen exchange because oxygen exchange proceeds in adsorption–desorption equilibrium. Even at high temperatures and low oxygen partial pressures $LaMnO_{3+\delta}$ contains small amount of oxygen vacancies [10,11] and exhibits lower bulk oxygen diffusion in comparison to $LaFeO_{3-\theta}$ and $LaCoO_{3-\gamma}$ [12], but possesses good electrical conductivity [12]. According to the thermodynamic analysis made by Adler et al. [13], this is the case when surface oxygen exchange may be governed by dissociative adsorption of oxygen and exchange reaction can be limited entirely by the availability of the surface oxygen vacancies. Then surface oxygen exchange constant may correlate with bulk oxygen diffusion coefficient. Earlier, De Souza and Kilner [14] demonstrated a strong correspondence between the coefficient of bulk oxygen diffusion $D$ and the constant of surface oxygen exchange $R$ for $(La,Sr)(Mn,Co)O_{3-\gamma}$ systems. They ascribed the close relationship between these two parameters to oxygen vacancies playing a decisive role in the process of oxygen exchange on the surface as well. It means that surface concentration of oxygen vacancies, which are scarce on $LaMnO_{3+\delta}$, rather than energetic barrier of charge transfer $O_s \leftrightarrow O_s{}^-$ can be of critical importance for dissociative adsorption of $O_2$ molecule. Using $N_2O$ instead of molecular $O_2$ results in increased rate of label oxygen transfer

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