

Isotopic transient kinetic study of N₂O decomposition on LaMnO_{3+δ}D.V. Ivanov^{a,*}, L.G. Pinaeva^a, E.M. Sadovskaya^{a,b}, L.A. Isupova^a^a Borekov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Pr. Acad. Lavrentieva 5, Novosibirsk 630090, Russia^b Novosibirsk State University, Str. Pirogova 2, Novosibirsk 630090, Russia

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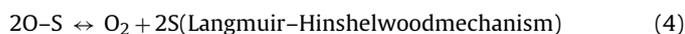
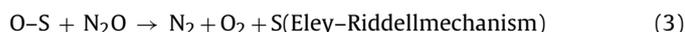
ABSTRACT

Analysis of label oxygen transfer during the reaction of N₂O decomposition (¹⁸O₂/N₂¹⁶O) on LaMnO_{3+δ} indicated that ¹⁶O transfer from N₂¹⁶O to ¹⁶O₂ preceded faster compared to oxygen exchange ¹⁸O₂/¹⁶O₂ and involved the interaction with two lattice oxygen of perovskite. It suggests that surface oxygen vacancies play an important role in reactivity of LaMnO₃ and explains why at times correlation can be found between catalytic activity and bulk oxygen diffusion (La_{1-x}Sr_xMnO_{3±δ}) and at other time catalytic properties correlate with surface oxygen exchange constant (La_{1-x}Sr_xFeO_{3-δ}). 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 N₂O is generally described by the following scheme [1,2]:



where S is surface active site, N₂O–S adsorbed or chemisorbed N₂O, O–S adsorbed or chemisorbed O.

For many oxides, it is known that at the temperature range 300–600 °C N₂O conversion decreased in the presence of oxygen in the reaction mixture, which can be due to the competitive adsorption of N₂O and oxygen on the same active sites [3,4] being oxygen vacancies or metal cations. Having studied activity of manganites in N₂O 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 N₂O decomposition is determined by the binding strength of adsorbed or chemisorbed oxygen. However, at 900 °C it was found that the rate of N₂O decom-

position on La_{1-x}Sr_xMnO_{3±δ} (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 N₂O decomposition, we aimed at studying the dynamics of oxygen transfer from N₂O to O₂ on LaMnO_{3+δ} using label oxygen.

2. Experimental

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

Transient isotopic experiment ¹⁸O₂/N₂¹⁶O 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. ¹⁶O₂ + He flow, then replaced by the same mixture but containing ¹⁸O₂ and kept for 30 min for complete substitution of ¹⁶O by ¹⁸O in the bulk of the sample. Finally, flow containing 1% N₂¹⁶O + 1% Ar in He was fed to reactor. Gas flow rate for mixtures amounted to 16.7 cm³/s. Steady state N₂¹⁶O conversion value in these conditions was close to 75% and resulted in ¹⁶O₂ content in the outlet mixture 0.38%. The effluent gas composition (¹⁸O₂, ¹⁶O¹⁸O, ¹⁶O₂, N₂¹⁸O, N₂¹⁶O, N₂, Ar) was analyzed online by SRS RGA 200 mass spectrometer and GC.

Catalytic activity in N₂O decomposition at the temperature range 600–900 °C was studied in the same reactor system used for the isotope experiments. Gas mixtures contained 1% N₂O (+0.5%

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CH₄) in He passed through the reactor charged by 0.0325 cm³ of LaMnO₃ or La_{0.7}Sr_{0.3}MnO₃ with a flow rate 16.7 cm³/s, corresponding to the contact time in normal conditions $\tau = 0.002$ s.

3. Results

3.1. Experimental isotopic transient curves in the switch ¹⁸O₂/¹⁶O for LaMnO₃

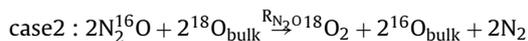
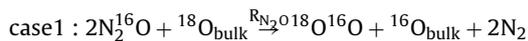
Kinetic experiments showed that after the switch of ¹⁸O₂-N₂¹⁶O, no N₂¹⁸O was detected in the gas phase, which indicates the absence of direct oxygen exchange between N₂O and lattice oxygen or O₂ molecule. The relaxation of N₂¹⁶O and N₂ immediately achieved the steady-state, while the responses of differently labeled O₂ molecules (¹⁸O₂, ¹⁶O₂ and ¹⁸O¹⁶O) were more continuous. To match the rate of oxygen exchange with the rate of N₂O decomposition, we calculated the responses of ¹⁶O fraction in the gas phase oxygen as $\alpha_g = 2^{16}\text{O}_2 + {}^{16}\text{O}^{18}\text{O}/2^{16}\text{O}_2 + {}^{16}\text{O}^{18}\text{O} + 2^{18}\text{O}_2$ and the normalized concentration of ¹⁶O¹⁸O- $f_{34} = {}^{16}\text{O}^{18}\text{O}/{}^{16}\text{O}_2 + {}^{16}\text{O}^{18}\text{O} + {}^{18}\text{O}_2$ and compared them with responses obtained after the switch ¹⁶O₂/¹⁸O₂ (SSITKA ¹⁶O₂/¹⁸O₂ discussed in Ref. [8]) (Fig. 1). As follows from Fig. 1b, total amount of exchanged oxygen after the switch ¹⁸O₂/¹⁶O in a period of 250 s accounts for 5.6×10^{21} at./g (75% of the total amount of exchangeable oxygen) and is less than during ¹⁶O₂/¹⁸O₂ exchange ($7\text{--}7.5 \times 10^{21}$ at./g) that is due to incomplete N₂O conversion. At the same time, the dynamics of oxygen transfer is approximately the same. It means that the rate of N₂O decomposition is relatively high and does not limit the dynamics of oxygen transfer from N₂¹⁶O to ¹⁶O₂ and ¹⁶O¹⁸O due to the combined processes of N₂O decomposition and oxygen exchange. In addition, in the initial period of time after the switch the α_g response in ¹⁶O₂/¹⁸O₂ experiment raised higher than that observed in ¹⁸O₂/¹⁶O, which points to the increased rate of label transfer from N₂O to O₂ 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 N₂¹⁶O 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 ¹⁶O₂-($f_{32} = {}^{16}\text{O}_2/{}^{16}\text{O}_2 + {}^{16}\text{O}^{18}\text{O} + {}^{18}\text{O}_2$) and ¹⁸O¹⁶O ($f_{34} = {}^{16}\text{O}^{18}\text{O}/{}^{16}\text{O}_2 + {}^{16}\text{O}^{18}\text{O} + {}^{18}\text{O}_2$) 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+ δ} were calculated independently from the SSITKA ¹⁶O₂/¹⁸O₂ experiments [8], while the rate of N₂O decomposition ($R_{\text{N}_2\text{O}}$) under these conditions was estimated from catalytic experiments measured value N₂O 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 N₂O immediately desorbs into the gas phase (as O₂) 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 ¹⁶O₂ (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 ¹⁶O transfer. It indicates that there is direct labeled oxygen transfer to the oxide bulk from N₂O molecule.

Thus, we examined two cases of ¹⁶O transfer from N₂O to O₂, namely,



Both of them assume that labeled oxygen is transferred to the oxide bulk as a result of N₂O 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 ¹⁸O¹⁶O or ¹⁸O₂. As illustrated in Fig 4a, if one lattice oxygen participates in label oxygen transfer (case 1), the concentration of ¹⁶O¹⁸O (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 N₂O molecule to O₂ (Fig. 4a). Thus, transient isotopic experiment ¹⁸O₂/¹⁶O allowed us to make a conclusion that O₂ formed at N₂O 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+ δ} 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 N₂O decomposition, taking into account that at high temperatures surface lattice oxygen vacancies are the active sites for both N₂O and molecular O₂ adsorption and dissociation:



where S—surface oxygen vacancy or coordinatively unsaturated surface metal cations, [O]_s—surface lattice oxygen, [O]_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 N₂O 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+ δ} contains small amount of oxygen vacancies [10,11] and exhibits lower bulk oxygen diffusion in comparison to LaFeO_{3- θ} and LaCoO_{3- γ} [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- γ} 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+ δ} , rather than energetic barrier of charge transfer O_s ↔ O_s⁻ can be of critical importance for dissociative adsorption of O₂ molecule. Using N₂O instead of molecular O₂ results in increased rate of label oxygen transfer

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