



# Isotopically labeled oxygen studies of the NO<sub>x</sub> exchange behavior of La<sub>2</sub>CuO<sub>4</sub> to determine potentiometric sensor response mechanism

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## ABSTRACT

The harmful nature of nitrogen oxides (NO<sub>x</sub>) to environmental systems necessitates sensors to detect their presence. One effective means is the use of solid state sensors. These sensors are compact, rugged, and can be inexpensively fashioned, making them a viable option for measuring gas concentration. A non-Nernstian potentiometric sensor can be used to detect low concentrations of NO<sub>x</sub> gas in multiple regions of oxygen concentration. Understanding the mechanism for this behavior can assist in optimizing the sensor couple for a given application. Previous studies using Temperature Programmed Reaction and Desorption (TPR/TPD), along with IR and XPS analysis, have identified the formation of charge-building compounds that establish voltage on the sensing electrode when exposed to NO<sub>x</sub> gas. To further elucidate the mechanism, TPR and TPD were performed using isotopically labeled oxygen with simultaneous exposure to NO<sub>x</sub>. The material was examined under multiple gas conditions of NO<sub>x</sub> and <sup>16</sup>O<sub>2</sub>/<sup>18</sup>O<sub>2</sub> atmospheres, as well as varied levels of <sup>18</sup>O enrichment in the lattice itself. Through these studies, it was determined that the formation of charged surface complexes occurs solely through the use of lattice oxygen (vs. gas phase O<sub>2</sub>) with adsorbed NO<sub>x</sub>.

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## 1. Introduction

There is a tremendous need for sensitive and selective sensors to detect pollutant gasses such as NO<sub>x</sub> in a variety of combustion exhaust streams. As such there is a tremendous body of work, with particular recent emphasis on potentiometric sensors based on a zirconia electrolyte and metal/metal oxide electrodes [1–11]. The most cited operational mechanism for these non-Nernstian potentiometric sensors is “Mixed Potential” [8–13]. However, the metal oxide electrodes are semiconducting, thus exposure to NO<sub>x</sub> and other gases can change the Fermi level in the oxide resulting in an additional potential source. Therefore, we have proposed “Differential Electrode Equilibria” as a more comprehensive mechanism to include these multiple contributions to the observed sensor potential [1–7]. One of the semiconducting oxide electrodes we have studied extensively in potentiometric NO<sub>x</sub> sensors is La<sub>2</sub>CuO<sub>4</sub> [3,4,6,7]. In this paper we focus on heterogeneous catalysis techniques to determine the sensing mechanism of this sensor.

Isotope exchange studies utilizing heavy oxygen (<sup>18</sup>O<sub>2</sub>) have proven useful in the study of catalysis, and by use on sensor materials, permit further exploration of the adsorption and reaction mechanism involved in solid-state gas sensor response. Previous research in this topic focused on diffusion, using secondary ion mass spectrometry (SIMS) [14–17] and gas-phase mass spectrometry to track exchange

with surface oxygen [18–20]. Gas phase mass spectrometry (MS) using heavy oxygen has also been used to examine reactions at the gas/solid interface through temperature programmed experiments [21–25]. Standard temperature programmed reaction (TPR) and temperature programmed desorption (TPD) experiments provide important information about the composition of reaction/desorption products, but can only inform of the presence of compounds, not necessarily their method of formation.

We demonstrated in a previous study, using infrared and X-ray photoelectron spectroscopy experiments, that a substantial amount of nitrate and nitrite complexes form on the surface of La<sub>2</sub>CuO<sub>4</sub> powder as a result of NO adsorption with additional nitro complex formation resulting from NO<sub>2</sub> exposure [26]. Through MS analysis of the TPR/TPD effluent, we determined that NO remained unconverted to either NO<sub>2</sub> or N<sub>2</sub>, but NO<sub>2</sub> will decompose to NO and O<sub>2</sub> over La<sub>2</sub>CuO<sub>4</sub> [4,27]. NO adsorption resulted in a mix of adsorbate complexes that utilize adsorbed gas-phase or lattice oxygen. These complexes decomposed on the surface to re-form and desorb the NO molecule, while desorbing the sequestered oxygen in both the TPD and TPR case. While these experiments confirmed the uncatalytic nature of La<sub>2</sub>CuO<sub>4</sub> to the NO→NO<sub>2</sub> and NO→N<sub>2</sub> reactions, the mechanism by which the NO reformed as it desorbed was still unknown.

Similarly, NO<sub>2</sub> formed nitrate, nitrite, and nitro complexes on the powder surface [26] then decomposed to NO, NO<sub>2</sub>, and O<sub>2</sub>. The products of desorption and reaction were easily characterized, but there again remained only a suggestion of the process by which these gases formed during separation from the powder surface.

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By using heavy  $^{18}\text{O}$  in place of the naturally occurring  $^{16}\text{O}$ , the origin of molecules desorbing from the surface can be determined. Mass spectra of the effluent gas from the reactor can be used to distinguish nitrogen oxides desorbed with their original oxygen atoms from those produced from labeled compounds on the surface [28]. By isolating the regions of desorption where scrambled products occur in the reactor effluent, the larger TPD desorption peaks for  $\text{NO}_x$  can be separated by Gaussian analysis into component regions, for subsequent compositional analysis.

Using  $^{18}\text{O}_2$  as the gas-phase oxygen with  $\text{N}^{16}\text{O}$  and  $\text{N}^{16}\text{O}_2$ , the possible reaction pathways can be probed experimentally. By examining the results of TPD, TPR, and isothermal reaction, the most likely methods of complex formation can be obtained. If the compounds desorbing from the surface show a large amount of  $^{18}\text{O}$ -containing products, the gas-phase adsorbates of oxygen will play a much larger role than previously considered. If the mass of the products is the same as the naturally occurring type, then the oxygen in  $\text{NO}_x$  compounds results in the same atoms during desorption, or the oxygen in the compounds is a result of exchange with the lattice. This approach allows for the separation of the relative mechanistic contributions to the  $\text{NO}_x$  sensor response.

## 2. Experimental

### 2.1. Powder preparation

$\text{La}_2\text{CuO}_4$  powder was prepared by the autoignition technique [29]. A stoichiometric mixture of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Kanto Chemical Company, 99.99%) and  $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$  (Alfa Aesar, 99.999%) was prepared in deionized water and verified by ICP analysis (Perkin-Elmer Plasma 3200). After dissolving the metal nitrates, citric acid (Alfa Aesar, 99.5%) was added to the mixture until 0.25 mol % was achieved, making this a fuel-lean solution. The solution was heated to  $\sim 60^\circ\text{C}$  with constant stirring until the solution thickened. The gel was held near  $70^\circ\text{C}$  for 7 h, until the gel hardened from water loss. Following the drying step, the crusty gel was heated  $\sim 3^\circ\text{C}/\text{min}$  until the precipitate autoignited due to heating. The powder generated by the autoignition process was calcined at  $600^\circ\text{C}$  for 10 h.

### 2.2. Isotopically labeled TPR/TPD

The procedure of the temperature-programmed desorption (TPD) and reaction (TPR) experiments was described previously [3,4,30,31]. Samples of  $\text{La}_2\text{CuO}_4$  containing nominally 12 mg of powder (BET area  $10\text{ m}^2/\text{g}$ ) were initially purged of atmospheric adsorbed species by cycling the sample to  $700^\circ\text{C}$  and back to room temperature under an atmosphere of  $1\%^{16}\text{O}_2$ . The process was repeated until spectra did not show any desorption peaks. Once clean, the sample was cooled under  $1\%^{16}\text{O}_2$  and then maintained under the helium atmosphere until further experiments were performed. Concentrations for the reactor were maintained by MKS mass flow controllers (MFC) for all standard gases, and  $^{18}\text{O}_2$  was controlled by a custom-built low-flow Alicat MFC.

For all mass spectrometry experiments, specific mass to charge ratios were examined:  $m/z=14$  (nitrogen species),  $m/z=16$  (oxygen species),  $m/z=28$  ( $\text{N}_2$ ),  $m/z=30$  ( $\text{N}^{16}\text{O}$ ),  $m/z=32$  ( $\text{N}^{18}\text{O}$  and  $^{16}\text{O}_2$ ),  $m/z=34$  ( $^{16}\text{O}^{18}\text{O}$ ),  $m/z=36$  ( $^{18}\text{O}_2$ ),  $m/z=44$  ( $\text{N}_2^{16}\text{O}$ ),  $m/z=46$  ( $\text{N}_2^{18}\text{O}$  and  $\text{N}^{16}\text{O}_2$ ) and  $m/z=48$  ( $\text{N}^{16}\text{O}^{18}\text{O}$ ). The ratios of  $m/z$  14 and  $m/z$  16 were monitored to distinguish between gases with the same  $m/z$  ratio, in particular  $m/z=32$ , corresponding to  $\text{N}^{18}\text{O}$  and  $^{16}\text{O}_2$ . To distinguish between the two gases, a matrix approach was used. The characteristic signal strength ratio of  $m/z$  14 and 16 (common for nitrogen and oxygen containing molecules) was isolated and compared to the identifying  $m/z$  of a nitrogen or oxygen containing species, for each gas present in the gas stream. Using these ratios, the contribution of every directly identifiable species was subtracted from the signal intensity at  $m/z$  14 and 16, and so the signal remainder of  $m/z$  14 and 16 after subtraction corresponded to the contribution of the undetermined species. This process allowed the

determination of each gas concentration, including the unknown species, but had the undesired effect of injecting some noise into the measurement for  $\text{N}^{18}\text{O}$  as that concentration was typically low.

For TPR experiments, the sample was exposed to 30 cubic centimeters per minute (ccm) of a reaction mixture at  $30^\circ\text{C}$ , and held until gas flow and mass spectrometer signal remained steady. The sample was heated to  $700^\circ\text{C}$  at  $30^\circ\text{C}/\text{min}$ , and the effluent spectra recorded to determine the extent of reaction and reaction products.

Experimental procedure for TPD was modified slightly to conserve isotopic oxygen. The sample was cooled to  $30^\circ\text{C}$  from  $300^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$  without a dwelling period at elevated temperature. At  $30^\circ\text{C}$ , the sample was purged with 30 ccm helium until a stable baseline for mass analysis was achieved. The sample was heated to  $700^\circ\text{C}$  at  $30^\circ\text{C}/\text{min}$  beneath 30 ccm flowing helium atmosphere. During heating, the effluent gas was analyzed to determine the quantity and nature of desorbed products. Measurements were normalized to the initial surface area of the powder sample measured following calcination step. This surface area was assumed to change during heating cycles, but samples used for the experiments were too small to accurately determine the change through BET analysis. Table 1 shows the list of experiments.

To determine the mechanism, it proved necessary to anneal the sample in order to exchange  $^{18}\text{O}$  into the lattice, and then repeat experiments in order to see whether the powder exchanges lattice oxygen by measuring for desorption products of increased mass. This mechanism allowed the separation of the relative contribution of electrochemical (i.e. Mixed Potential) reactions to the sensor response to  $\text{NO}_x$  gas compared to purely adsorptive effects.

TPR and TPD experiments were carried out on separate powder samples in order to preserve the sequence and maximize similarity between experiments. Primary experiments maintained an atmosphere of  $\text{N}^{16}\text{O}_x$  and  $^{16}\text{O}_2$ . After the initial run, the sample pretreatment consisted of annealing in  $^{16}\text{O}_2$  at  $500^\circ\text{C}$  followed by cooling to room temperature. After this pretreatment, runs were performed in  $\text{N}^{16}\text{O}_x$  and  $^{18}\text{O}_2$ . Subsequent pretreatments of the sample were performed in  $1\%^{18}\text{O}_2$  in order to exchange lattice oxygen for isotopic oxygen to produce  $\text{La}_2\text{Cu}^{18}\text{O}_4$  in lightly and heavily  $^{18}\text{O}$ -enriched forms. The “lightly enriched” sample was prepared by annealing  $\text{La}_2\text{Cu}^{16}\text{O}_4$  in  $1\%^{18}\text{O}_2$  for 1 h at  $500^\circ\text{C}$ , and the “heavily enriched” sample by annealing the sample under the same conditions for 3 h. The final two runs in the sequence contained  $\text{N}^{16}\text{O}_x$  and  $^{18}\text{O}_2$  followed by  $\text{N}^{16}\text{O}_x$  and  $^{16}\text{O}_2$  in the gas phase, respectively. Additionally, a TPR of 1000 ppm  $^{18}\text{O}_2$  was performed on a freshly prepared sample in order to examine the oxygen exchange behavior of pure  $\text{La}_2\text{Cu}^{16}\text{O}_4$ .

## 3. Results and discussion

### 3.1. $^{18}\text{O}_2$ temperature programmed reaction

A  $\text{La}_2\text{CuO}_4$  sample was exposed to 1000 ppm of  $^{18}\text{O}_2$  at room temperature and heated to examine the oxygen exchange behavior of  $\text{La}_2\text{CuO}_4$ . The mass spec data for this experiment can be seen in Fig. 1.

**Table 1**  
List of experiments performed

Gas mixture (ppm)	Type	Initial lattice oxygen
$^{18}\text{O}_2$ (1000)	TPR	$\text{La}_2\text{Cu}^{16}\text{O}_4$
$\text{NO}$ (10000) + $^{16}\text{O}_2$ (10000), $\text{NO}_2$ (10000) + $^{16}\text{O}_2$ (10000)	TPD	$\text{La}_2\text{Cu}^{16}\text{O}_4$ $^{18}\text{O}$ lightly enriched $^{18}\text{O}$ heavily enriched
$\text{NO}$ (10000) + $^{18}\text{O}_2$ (10000), $\text{NO}$ (10000) + $^{18}\text{O}_2$ (10000)	TPD	$\text{La}_2\text{Cu}^{16}\text{O}_4$ $^{18}\text{O}$ lightly enriched $^{18}\text{O}$ heavily enriched
$\text{NO}$ (700) + $^{16}\text{O}_2$ (600), $\text{NO}_2$ (700) + $^{16}\text{O}_2$ (600)	TPR	$\text{La}_2\text{Cu}^{16}\text{O}_4$ $^{18}\text{O}$ lightly enriched $^{18}\text{O}$ heavily enriched
$\text{NO}$ (700) + $^{18}\text{O}_2$ (600), $\text{NO}_2$ (700) + $^{18}\text{O}_2$ (600)	TPR	$\text{La}_2\text{Cu}^{16}\text{O}_4$ $^{18}\text{O}$ lightly enriched $^{18}\text{O}$ heavily enriched

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