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BaTi-Oxides as High-Temperature Nitrogen Oxide Sensors

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Abstract:
NOx-detection at high temperatures is complicated due to the thermal conversion of nitrogen oxides. Moreover, multiple gas combinations in the environment where nitrogen oxides are present require high selectivity. Nobel metal incorporated BaTi-Oxides have shown good high temperature sensing ability, although the factors affecting selectivity as well as the sensing mechanism are not fully established. This work yields a systematic study using different phase and morphologies of the BaTi-oxide based sensing material.

Key words: High-Temperature Sensing, NOx, Perovskites, Barium Titanates, Rh-incorporation.

Introduction

In case of complete combustion, a hydrocarbon burns in pure oxygen yielding nitrogen oxides (NOx), carbon dioxide and water. The products of the incomplete fuel oxidation are mainly nitrogen oxides (NOx), carbon monoxide (CO), CO_2, water and unburned hydrocarbons (HC) [1]: As compared with other emission pollutants, the amount of NOx generated by combustion processes is very high in the atmosphere. NOx may react with atmospheric water resulting in the formation of acid rain and damage the upper atmospheric ozone layer [2]. Therefore, NOx must be catalytically reduced, requiring the on-line monitoring at high-temperatures by means of selective sensors.

Generally, metal oxide semiconducting (MOX) materials are widely employed for the detection of various oxidizing and reducing gases due to their simple and cheap fabrication [3]. Despite having many benefits, limited working temperature range and poor selectivity are two of the main drawbacks highlighted in the literature [4–6]. At lower temperatures (below 150 °C) and at temperatures above 400 °C, the sensing properties of the semiconducting materials are reduced drastically due to decreased conductivity and/or thermal instabilities [5–8].

The literature indicates that perovskites with different formulations give great opportunity to detect gas mixtures by means of sensor arrays. Doping elements either in the lattice of perovskite or on the surface of perovskite could help to improve sensing performance of perovskite oxide and to decrease the sensing temperature [9, 10]. La-based, Ce and Pd-doped perovskites are proven to yield good sensing behavior toward CO and CH_4, respectively.

Our previous results show that trivalent doping of TiO_2 enables sensor response towards NO_2 at temperatures up to 800 °C, although sensor response yields a change in the direction of the sensor signal above 600 °C. The use of a BaTi0.95Rh0.05O3 catalytic filter layer results in stable sensor response up to temperatures as high as 900 °C, probably due to the catalytic conversion of NO_2 to NO already above 300 °C through this catalytic layer. No other sensor study is known to date with the $BaTiRhO_3$ catalytic layer to confirm its behavior. Moreover, the roles of Rh as well as $BaTiO_3$ or other phases of BaTi-Oxides are not well understood and require some systematic studies. In this work, we compared the sensing behaviors of BaTi-Oxides with and without Rh towards nitrogen oxides under high humidity in order to clarify this phenomenon.

High-Temperature Behavior of Nitrogen Oxides

It is well known that NO_2 converts gradually to NO at temperatures above 500 °C as illustrated in Fig. 1. The thermodynamic equilibrium conditions may result in the formation of ionized oxygen species (e.g., O^{2-}-ion) taking over the control of sensing mechanism through surface adsorption (see Equation (1)):

$$NO_2\,(gas) + 2e^- \rightarrow NO\,(gas) + O^{(2-)}(ads.) \quad (1)$$

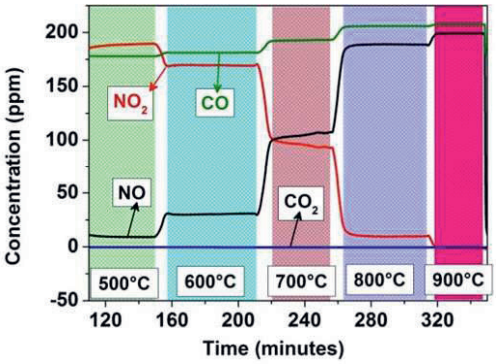

Fig. 1. Temperature-dependent conversion of NO_2 to NO without sensor or catalyst in the test chamber. Please note: there occurs visible conversion of CO to CO_2.

The tests, carried out by inserting a catalytic perovskite powder on NO_2/NO conversion at high temperatures displayed that full NO_2 to NO conversion occurs already at 300 °C (see Fig. 2).

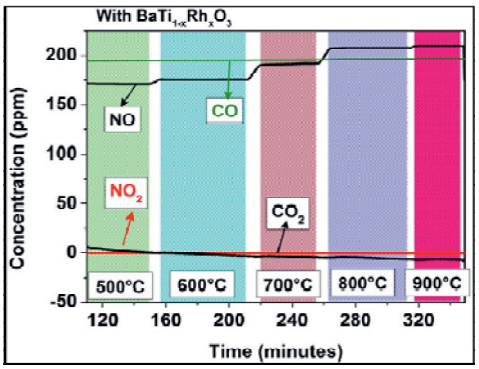

Fig. 2. Temperature-dependent conversion of NO_2 and CO in the presence of $BaTi_{0.95}Rh_{0.05}O_3$ catalytic powder in the test chamber.

Materials and Methods

In this work the sensing layers of $BaTiO_3$ and $BaTi_2O_5$ and their combinations with or without Rh incorporation are synthetized by co-precipitation and sputtering techniques (see Table 1).

Tab. 1: Test Materials and Synthesis Methods

Material	Synthesis Method
$BaTi_2O_5$	Sputter
$BaTiO_3$	Co-precipitation
$Ba_3Ti_2RhO_9$+$BaTiO_3$	Co-Precipitation
$BaTi_2RhO_5$-$BaTiO_3$	Co-precipitation

Results

Under dry argon carrier gas environment, the $BaTi_2O_5$ as well as $BaTiRhO_3$ sensor layers shows high sensitivity towards NO_2 at temperatures as high as 800°C. On addition of 5% RH, $BaTiRhO_3$ sensor layers yield stable sensitivity at 800 °C although some decrease in the response and recovery times are observed at 900 °C. In dry synthetic air environment, all sensors display some instable response towards NO_2, while the sensitivity improves towards NO.

The phase conditions and morphological effects of the sensor layers on sensing behavior will be discussed to explain the influences of targets gases.

References

[1] Glassman, I.; Yetter, R.A. Combustion, 4th ed.; Academic Press: Burlington, MA, USA, 2007.

[2] Baukal, C. Everything you need to know about NOx: Controlling and minimizing pollutant emissions is critical for meeting air quality regulations. Metal. Finish. 2005, 103, 18–24.

[3] Yamazoe, N.; Shimanoe, K. Theory of power laws for semiconductor gas sensors. Sens. Actuators B: Chem. 2008, 128, 566–573.

[4] Gardon, M.; Guilemany, J.M. A review on fabrication, sensing mechanisms and performance of metal oxide gas sensors. J. Mater. Sci.: Mater. Electron. 2013, 24, 1410–1421.

[5] Saruhan, B.; Yüce, A.; Gönüllü, Y.; Kelm, K. Effect of Al doping on NO2 gas sensing of TiO2 at elevated temperatures. Sens. Actuators B: Chem. 2013, 187, 586–597.

[6] Barsan, N.; Koziej, D.; Weimer, U. Metal oxide-based gas sensor research: How to? Sens. Actuators B: Chem. 2007, 121, 18–35.

[7] Savage, N.O.; Akbar, S.A.; Dutta, P.K. Titanium dioxide based high temperature carbon monoxide selective sensor. Sens. Actuators B: Chem. 2001, 72, 239–248.

[8] Kim, B.; Lu, Y.; Hannon, A.; Meyyappan, M.; Li, J. Low temperature Pd/SnO2 sensors for CO detection, Sens. Actuators B: Chem. 2013, 177, 770–775.

[9] Ghasdi, M.; Alamdari, H.; Royer, S.; Adnot, A. Electrical and CO gas sensing properties of nanostructured La1−xCexCoO3 perovskite prepared by activated reactive synthesis. Sens. Actuators B: Chem. 2001, 156, 147–155.

[10] Ghasdi, M.; Alamdari, H. CO sensitive nanocrystalline LaCoO3 perovskite sensor prepared by high energy ball milling. Sens. Actuators B: Chem. 2010, 148, 478–485.