NOx storage and reduction on a SrTiCuO$_3$ perovskite catalyst studied by *operando* DRIFTS

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ABSTRACT

The behaviour of a perovskite SrTiCuO$_3$ as NSR catalyst has been studied by simultaneous DRIFTS and activity measurement. The amount of NOx stored on the perovskite SrTiCuO$_3$ (41 μmol/m^2 at 300 °C) is much higher, when compared on a surface area basis, than on noble metal-containing reference catalysts (0.3–23 μmol/m^2). The perovskite SrTiCuO$_3$ is able to perform both the NO oxidation to NO$_2$ and the NOx storage, and copper enhances both the NO oxidation and NOx chemisorption capacities of copper-free SrTiO$_3$ perovskite. During NOx chemisorption on SrTiCuO$_3$, the following process have been identified (i) NO chemisorption and nitrite formation or NO oxidation to gas phase NO$_2$ and further chemisorption of NO$_2$ with nitrites or nitrates formation, (ii) nitrite oxidation to nitro and/or nitrates, and (iii) nitro and/or nitrate decomposition with release of NO$_2$. NOx chemisorption at 300 °C is more effective than chemisorption at 350 °C, while regeneration at 350 °C is more effective than regeneration at 300 °C because: (i) decreased NOx slip (only for CO regeneration) and (ii) maintains the same chemisorption capacity of the perovskite after regeneration. H$_2$ is a better reductant than CO, and the differences between both reducing gases are much higher at 300 °C than at 350 °C.

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1. Introduction

Soot and NOx are the main pollutants emitted by diesel engines. Filters are fitted in the exhaust pipe for soot removal [1], and the NO$_2$-assisted soot combustion allows filter regeneration at around 350–400 °C with a suitable catalyst. During this process, few NOx is reduced to N$_2$, typically less than 15–20%, and an additional NOx removal system must be located downstream the soot filter, where the temperature is usually lower than 400 °C.

NOx can be converted into innocuous gases mainly by three methodologies [2]: (i) direct decomposition, (ii) selective catalytic reduction (SCR), or (iii) NOx storage and reduction (NSR). Although direct decomposition of NO is thermodynamically favourable and occurs without any reductant, the reaction possesses relatively high activation energy and this limits the practical use of this approach. SCR consist of selectively reducing NO with a reductant added in the exhaust, like H$_2$, hydrocarbons, NH$_3$ or urea. SCR requires a selective catalyst to promote the NOx-reductant reaction in the presence of excess oxygen, and research is being carried out to develop such catalysts [3–6]. NSR, which is the approach studied in this article, works under cyclic conditions of fuel lean and fuel rich environments. Under lean conditions, when oxygen is in excess,

NOx is adsorbed on the catalyst, and under rich conditions, when the reductant is added, NOx reduction takes place. A typical NSR catalyst combines a NOx adsorption material, like alkali or alkaline earth metal compounds, with noble metals, which catalyse the oxidation of NO under lean conditions and the reduction of the stored NOx under rich conditions.

Due to the high price of noble metals, noble metal-free NSR catalysts would be desired, and in the current study a SrTiCuO$_3$ perovskite catalyst is investigated for this application. This material was first synthesised for the catalytic combustion of diesel soot [7], and it was observed that, in addition to high soot combustion activity, also presents both NOx storage and NO oxidation capacity. These features lead us to think in the potential application of this perovskite as NSR catalyst. The perovskite SrTiCuO$_3$, with copper located within the SrTiO$_3$ structure, has superior activity for soot combustion than some other materials with similar composition, like copper supported on SrTiO$_3$, or the counterpart impregnated and substituted copper catalysts with Mg instead of Sr [7,8].

The application of perovskites as NSR catalyst has been scarcely reported and articles focussed on the use of copper-containing perovskites for NSR application in the open literature are limited. However, as an example, Ueda et al. studied the perovskite with composition (La$_{0.7}$Ba$_{0.3}$)(Fe$_{0.776}$Nb$_{0.194}$Pd$_{0.03}$)O$_3$ as NSR catalyst [9], and Hodjati et al. [10] studied the NOx adsorption–desorption on ABO$_3$ perovskites with A = Ca, Sr, or Ba and B = Sn, Zr, or Ti, and reached the conclusion that, for A sites, the

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NOx adsorption–desorption order was Ba > Sr > Ca and, for B sites, Sn > Zr > Ti.

The aim of the current study is to analyse the behaviour of a perovskite $SrTiCuO_3$ as NSR catalyst by *operando* analysis, which combines activity measurement with simultaneous DRIFTS study of the NOx species detected under reaction conditions.

2. Experimental

2.1. Catalyst preparation and characterisation

The catalyst $SrTiCuO_3$, with the stoichiometric formula $SrTi_{0.89}Cu_{0.11}O_3$, and the counterpart copper-free mixed oxide $SrTiO_3$, were prepared by the sol–gel method as reported elsewhere [7]. A summary of the main physico-chemical properties of both samples is provided here although a detailed description of their characterization has been reported previously [7,8]. In brief, the BET surface areas of $SrTiCuO_3$ and $SrTiO_3$ are 6 and 11 m^2/g, respectively. XRD showed perovskite-like structure for both mixed oxides, with some surface segregation of TiO_2 (rutile) and $SrCO_3$ in the sample $SrTiCuO_3$, and full incorporation of copper within the mixed oxide framework. The incorporation of Cu (II) cations within the mixed oxide framework was confirmed by XPS, and H_2-TPR experiments showed that the copper cations of the sample $SrTiCuO_3$ can be only partially reduced at low or mild temperature (below 400 °C). O1s XPS analysis also evidenced the presence of a high population of loosely bound surface oxygen species, such as chemisorbed oxygen, surface carbonates, and/or OH^- groups on the $SrTiCuO_3$. In the previous study [7], the catalytic activity for soot combustion of $SrTiCuO_3$ under simulated diesel exhaust conditions was attributed to the NO oxidation to NO_2 capacity. Surface CuO was identified as the active component for NO oxidation on a sample $Cu/SrTiO_3$ (copper impregnated on $SrTiO_3$) while the active sites on $SrTiCuO_3$ (the perovskite selected for the current study) are not necessarily linked to the copper cations. In this case, the role of lattice copper is to modify the perovskite structure, promoting the catalytic activity.

2.2. NOx storage and reduction experiments

The NOx storage experiments have been performed in an IR reactor cell and is studied under both Temperature Programmed conditions (5 °C/min from room temperature to 550 °C) and also isothermally at 300 °C. For these experiments a gas mixture with 500 ppm NOx + 5% O_2 in N_2 was used. Some experiments were performed with the as-prepared catalyst, and in some other experiments, the catalyst was reduced in situ at 400 °C for 30 min with 30% H_2 in nitrogen before the NOx storage measurements. Consecutive NOx storage-reduction cycles were carried out at 300 and 350 °C with lean (NO + O_2 balanced with N_2) and rich (3% H_2 or 3% CO balanced with N_2) gas flows, respectively.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis of species present on the catalyst under reaction conditions was carried out using a Perkin-Elmer 100 FTIR fitted with an MCT detector. On-line analysis of the NO and NO_2 concentrations at the outlet of the IR cell were performed by chemiluminescence (Thermo Environmental Instruments 42C). Additional on-line gas analysis was performed using a Baltzers Prisma Quadrupole mass spectrometer for H_2O, NH_3, N_2O, CO and CO_2. The DRIFTS cell (Harrick DRP-series) was fitted with ZnSe windows and a heating cartridge that allowed samples to be heated to 550 °C. DRIFT spectra were recorded at 4 cm^{-1} resolution as an average of 10 scans. The gas mixtures were prepared using a computer-controlled gas-blender with 50 cm^3/min passing through the catalyst bed which equates to a GHSV = 21,000 h^{-1} using *ca.* 100 mg of sample.
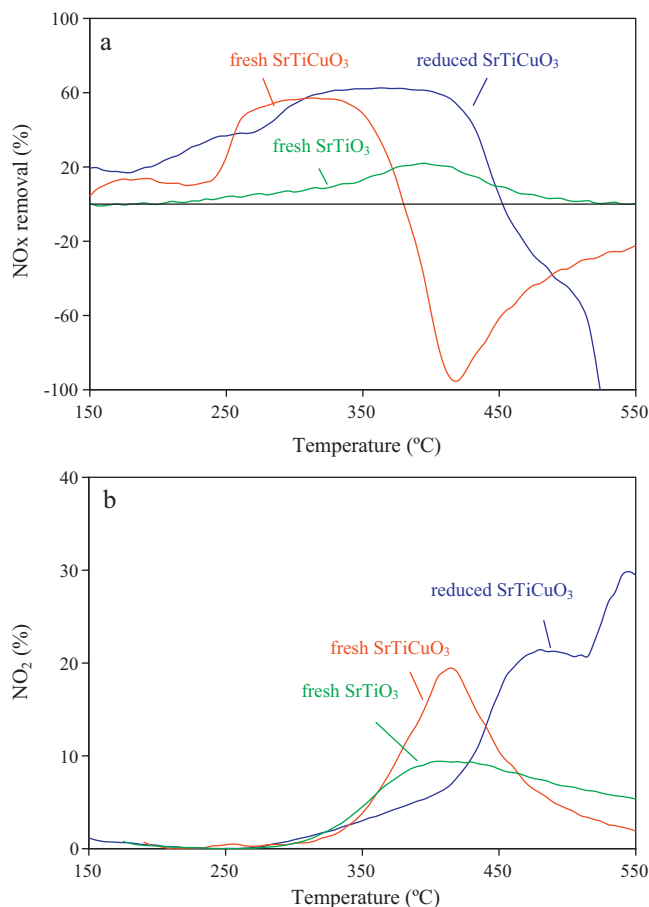

Fig. 1. Temperature programmed reactions: (a) NOx removal profiles and (b) NO_2 release profiles. (prereduced catalysts H_2/400 °C/30 min; NOx removal (%) = 100 × (NOx_{in} − NOx_{out})/NOx_{in}); NO_2 (%) = 100 × NO_2out/(NOout + NO_2out).

3. Results and discussion

3.1. NOx storage under temperature programmed conditions

The NSR mechanism is generally assumed to take place in five steps [2]: (i) NO oxidation to NO_2, (ii) NOx adsorption as nitrites or nitrates on the basic adsorption sites of the catalyst, (iii) reductant feed, (iv) NOx release from the catalyst, (v) and NOx reduction to N_2. In order to determine a suitable range of temperatures for the NOx storage to occur in the studied perovskites, experiments under temperature programmed conditions have been carried out. From these experiments the oxidation of NO to NO_2, the chemisorption of NOx on the perovskites and the thermal release of adsorbed NOx species at high temperature can be studied.

Fig. 1a and b shows NOx removal and NO_2 formation profiles, respectively, obtained with the fresh and reduced perovskite $SrTiCuO_3$ and with the fresh copper-free perovskite $SrTiO_3$. These profiles obtained in the DRIFTS cell are qualitatively similar to those previously monitored in a fix-bed reactor [7], with the expected differences in the absolute NOx levels because of the different space velocity used in each experimental set-up (GHSV = 21,000 h^{-1} and 30,000 h^{-1} for the DRIFT cell and fix-bed reactor [7], respectively).

The NOx storage capacity of the copper-free perovskite $SrTiO_3$ is the lowest (see Fig. 1a). The NOx species adsorbed on this sample are stable in the whole range of temperature screened, since negative values in the NOx removal curve are not reached. NOx chemisorption on $SrTiO_3$ takes place from 200 °C, reaching the maximum NOx removal level (20%) at 400 °C and decreasing afterwards. NO is oxidised to NO_2 (see Fig. 1b) together with NOx chemisorp-