

# Simultaneous removal of $\text{NO}_x$ and diesel soot over nanometer Ln-Na-Cu-O perovskite-like complex oxide catalysts

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## Abstract

The nanometric Ln-Na-Cu-O (Ln = La, Pr, Nd, Sm, Gd) perovskite-like complex oxide catalysts were prepared by sol-gel auto-combustion method using citric acid as a ligand and an adjusting agent of particle-size and morphology. Their structures and physico-chemical properties were examined by chemical analysis, XRD, SEM, FT-IR,  $\text{H}_2$ -TPR and MS-NO-TPD. The catalytic performances of these perovskite-like oxides for the simultaneous removal of soot and  $\text{NO}_x$  were investigated by a technique of the temperature-programmed reaction (TPR). In the Ln-Na-Cu-O catalysts, the partial substitution of Na for La at A-site led to the formation of  $\text{Cu}^{3+}$  and/or oxygen vacancy, thus the catalytic activity was remarkably enhanced. The optimal substitution amount of Na ( $x$ ) is equal to 0.3 for the reduction of  $\text{NO}_x$ , and  $x$  is equal to 0.7 for soot combustion. Moreover, attributing to the effects of very small surface particle sizes of the catalysts and the strong oxidizing ability of  $\text{NO}_2$  which was produced from NO and  $\text{O}_2$  in the reactant gases on these catalysts, the nanometric Ln-Na-Cu-O perovskite-like oxides exhibit very high catalytic activities for soot combustion even under loose contact conditions between soot and the catalyst.

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## 1. Introduction

Diesel-powered vehicles, because of their high thermal efficiency, emit less CO and unburned hydrocarbons than gasoline-fueled vehicles, but the emission of soot particulates and  $\text{NO}_x$  are still high. Since the reduction of both soot and  $\text{NO}_x$  emissions to the regulated level cannot be accomplished by engine modifications alone, after-treatment techniques for the simultaneous reduction of their emissions from diesel exhaust should be developed [1–3]. As one possible process, Yoshida et al. proposed the simultaneously catalytic conversion of soot and  $\text{NO}_x$  into  $\text{CO}_2$  and  $\text{N}_2$  in an oxidizing atmosphere by using catalyzed soot traps [4]. Although this method involves many technological difficulties to be overcome (the development of efficient and thermally stable traps, the contact between

catalyst and trapped soot, etc.), the active catalysts are considered to be the most important one [5].

For the simultaneous removal of soot and  $\text{NO}_x$  reaction, Teraoka et al. and other researches have done many explorative and pioneering works using perovskite and spinel oxides [5–12]. In addition, the substitutional incorporation of alkali metal into A-sites of perovskite-type ( $\text{ABO}_3$ ) oxides was quite effective in enhancing the activity and selectivity for the  $\text{NO}_x$ - $\text{O}_2$ -soot reaction [8–10]. Teraoka et al. found that La-K-Mn-O perovskite-type oxides were good candidate catalysts for diesel soot combustion [11], and Fino et al. reported that  $\text{La}_{2-x}\text{K}_x\text{Cu}_{1-y}\text{V}_y\text{O}_4$  layered oxides had good catalytic performances for the combined removal of diesel particulates and  $\text{NO}_x$  [9], but they reported the relevant catalytic activities under tight contact conditions between catalysts and soot particles. However, it is a loose contact between the catalysts on the surface of filter and soot particles under practical conditions [13,14]. Thus, it is rather significant to study and design the active catalysts for soot particulate oxidation under loose contact conditions. In recent years, Oi-Uchisawa et al. reported that a platinum catalyst oxidized NO to  $\text{NO}_2$ , which subsequently oxidized soot to CO and  $\text{CO}_2$ . So,  $\text{NO}_2$  is used as intermediate to facilitate an

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indirect contact between the platinum catalyst and soot. The catalyst system is the best one so far reported for soot combustion under loose contact conditions [15,16]. The high oxidation rate of soot is due to the strong oxidizing ability of  $\text{NO}_2$ . In the present study, we found that a similar mechanism existed on the  $\text{La}_{2-x}\text{Na}_x\text{CuO}_4$  perovskite-like complex oxide catalysts, i.e.,  $\text{NO}_2$  indirectly catalyzed soot combustion. Therefore, this series of catalysts hold good catalytic activities for soot combustion under loose contact conditions between soot and the catalysts.

Catalytic materials exist in various forms and their preparation involves different protocols with a multitude of possible preparation schemes. Moreover, preparation of any catalyst involves a sequence of several complex processes, and many of them are not completely understood. As a result, subtle changes in the preparative details may result in dramatic alteration of the final catalyst properties. Applications of catalyst materials depend on their sizes and morphology. Therefore, much emphasis has been laid on the shape control and the size control recently [17,18]. The surface particle sizes of nanometer material are small. Surface atoms on nanometer catalysts have extra and high surface energies and they are good at mobility, therefore the contact is still very good between catalysts and soot even under loose contact conditions. The development of adequate synthetic methods for the preparation of nanometric powders at low temperatures and atmospheric pressure is a task of great interest. The preparation of such materials may vary in different methods and conditions. Sol-gel technique is one of the most efficient methods, since it permits a better control of stoichiometry, high reactivity, controlled dimensions and nanoparticles. Auto-combustion is a novel way and a unique combination of the combustion process and the chemical gelation process. The process exploits the advantages of cheap precursors, a simple preparation method, and a resulted ultrafine, homogeneous, highly reactive powder [18,19]. In this study, the nanometer Ln-Na-Cu-O perovskite-like complex oxides were prepared by the sol-gel auto-combustion method using additive agent of citric acid. The substitution amounts of A-site cation affect on the catalyst structure and catalytic performances for the simultaneous removal of  $\text{NO}_x$  and soot under loose contact conditions. The probable reasons which can lead to the activity enhancement for the Na substitution samples compared to the unsubstitution sample were discussed.

## 2. Experimental

### 2.1. Catalyst preparation

Two series of  $\text{Ln}_2\text{CuO}_4$  ( $\text{Ln} = \text{La, Pr, Nd, Sm, Gd}$ ) and  $\text{La}_{2-x}\text{Na}_x\text{CuO}_4$  ( $x = 0, 0.1, 0.3, 0.5, 0.7, 0.9$ ) perovskite-like complex oxides were prepared by the sol-gel auto-combustion method. The nitrates of Ln, Na and Cu were used as starting materials for obtaining an aqueous solution of  $\text{Ln}^{3+}$ ,  $\text{Na}^+$  and  $\text{Cu}^{2+}$  with appropriate stoichiometry. A solution of citric acid 100% in excess was chosen as a ligand and an adjusting agent of particle-size and morphology. The resulting solution was

heated by constant stirring at temperatures of 80–90 °C. After about 50% of water evaporated, the solution was placed in the static air at 90 °C. The clear solution gradually turned milky sol and finally transformed into gel. The gel was translucent with a honey-like color and viscosity. Then, the wet gel was dried homogeneously in a stream of air at 120 °C for 4 h. The resulting loosened and foamy solid auto burnt or exploded by heating with an electric furnace. Finally, the precursor was calcinated at 800 °C for 4 h in static air. This technique is particularly suitable to producing nanometric particle samples. For comparison, the two catalysts among the above samples, i.e.,  $\text{La}_{1.7}\text{Na}_{0.3}\text{CuO}_4$  and  $\text{La}_{1.3}\text{Na}_{0.7}\text{CuO}_4$  were further treated. They were compressed at 10 MPa, followed by grinding and sieving at 40–80 meshes. Then, the two samples were calcinated at 900 °C for 10 h in static air. As a result, two non-nanometric catalysts were also prepared, and they were named as La7-9 and La3-9, respectively.

### 2.2. Catalyst characterization

The crystal structures of the fresh catalysts were determined by a powder X-ray diffractometer (Shimadzu XRD 6000), using  $\text{Cu K}\alpha$  ( $\lambda = 1.54184 \text{ \AA}$ ) radiation combined with Nickel filter operating at 40 kV and 10 mA. The diffractometer data were recorded for  $2\theta$  values between 15° and 80° with a scanning rate of 4°/min. The patterns were compared with JCPDS reference data for phase identification. The Scherrer equation was used to calculate the crystal size of the studied samples. The morphology of the catalysts was observed by SEM (S-4300, Japan).

FT-IR absorbance spectra were obtained in the wave number ranging between 6000 and 400  $\text{cm}^{-1}$  via a FTS-3000 spectrophotometer manufactured by American Digilab company. The measured wafer was prepared as KBr pellet with the weight ratio of sample to KBr, 1/100. The resolution was set at 2  $\text{cm}^{-1}$  during measurements.

$\text{H}_2$ -TPR measurements were performed in a conventional flow apparatus. Two hundred milligrams sample was pretreated in an air atmosphere by calcination at 600 °C for 1 h and subsequently cooled to 100 °C with helium flowing. Afterwards, the  $\text{H}_2$ -TPR was carried out using 10% hydrogen in helium at constant flow rate of 30  $\text{cm}^3/\text{min}$ , from 100 to 900 °C, at a heating rate of 10 °C/min. The hydrogen consumption signal was monitored by a thermal conductivity detector (TCD) in an on-line gas chromatograph (GC). For eliminating the effect of the outlet reactor gas containing other components which mainly consisted of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  on the TCD for  $\text{H}_2$ -TPR measurements, it was set a filter that contained 5A molecular sieve (60–80 meshes) for adsorption of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  before the reaction gases entering the TCD.

MS-NO-TPD detected by mass spectrometry was carried out on Quantachrome autosorb-1C mass spectroscopy. The samples were first heated from room temperature to 800 °C at a rate of 20 °C/min and kept at 800 °C for 1 h in helium. The pretreated sample was first cooled to 200 °C at the same atmosphere, then swept with 4000 ppm NO (helium balanced) for the adsorption of NO for 1 h, and cooled to 100 °C in the NO stream for 0.5 h again. Hereafter, swept with helium at a rate of

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