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Plasma catalysis with perovskite-type catalysts for the removal of NO and CH_4 from combustion exhausts

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Abstract

The removal of NO and CH_4 from quaternary gas mixtures simulating the conditions existing in real combustion exhausts has been studied with a hybrid system integrating plasma activation and a $La_{1-x}Sr_xCoO_{3-d}$ perovskite-type catalyst. The plasma reaction produces the conversion of NO into N_2 plus O_2 and the oxidation of CH_4 into $CO + H_2O$. Incorporation of the catalyst favors the oxidation of CH_4 into CO_2 at 190 °C. At this temperature, no oxidation of CO or CH_4 is found in a conventional catalytic reactor. A similar plasma + catalyst experiment with SiO_2 found much lower CO_2 production, indicating that the perovskite is actively involved in the oxidation of CO. The efficiency of NO removal decreased with the amount of perovskite, although this efficiency could be restored by adding carbon to the reactor. Experiments using optical emission spectroscopy (OES) and in situ X-ray photoemission spectroscopy (XPS) were carried out to gain insight into the synergetic effects found with the catalyst. OES intermediate species, including NH^*, CN^*, CO^*, and CH^*, were found in the plasma. XPS experiments of samples exposed to plasmas showed the formation of $–NO_x$ and –CN species, indicating the active involvement of the catalyst in the reaction.

Keywords: Plasma catalysis; Plasma chemistry; Perovskite catalyst; In situ XPS; Optical emission spectroscopy; CO oxidation; CH_4 oxidation; NO removal; Soot particles

1. Introduction

Removal of CO, CH_x, NO, SO_x, and other compounds from exhaust combustion sources is a major challenge for environmental protection [1–3]. The most typical procedures used to remove these noxious gases are based on catalysts that can induce different selective oxidation/reduction processes [1–3]. Another possibility that has begun to be explored recently is the combination of catalysts and plasmas to induce specific reactions under mild thermal conditions. Cold plasmas have typically been studied by researchers interested in the characterization of the plasma parameters (e.g., electron temperature, concentration of different active species) [4–9] and by materials scientists for treating or preparing new materials [10–13] or even catalysts [14]. In contrast, the plasma chemistry of complex gas mixtures, alone or in the presence of catalysts, is not a well-developed subject, and much work is needed to improve the performance of these processes for practical applications [15]. Plasma catalytic processes are used mainly in various decontamination processes in which the concentration of pollutants is in the ppm range, including the abatement of volatile organic compounds [16–19], oxidation of light hydrocarbons [20,21], oxidation of CO [16,20], combustion of soot particles [22,23], and removal of NO_x or N_2O from simulated exhaust gases [15,24–33]. Nonetheless, relatively few works have focused on the simultaneous removal of these noxious gases in complex mixtures [15,25,34].

Most designs that use a mixed plasma + catalyst approach are merely the online connection of two independent processes; first, the plasma stage produces a certain reaction, and then the catalyst stage transforms these primary products into secondary final products [17,31,35]. Less frequently, plasma and catalysts are combined together in such a way that the catalyst is em-

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bedded in a plasma phase rich in radicals and other activated species [16,17]. In this latter case, despite the observation of synergetic effects, it is not clear yet whether the role of the catalyst is just to favor the combination on its surface of the active species of the plasma, or if it participates actively in the reaction. In general, in these plasma hybrid systems, the catalyst activity is typically correlated with its surface area and porosity, regardless of their chemical formulation [15,16,20].

The present work deals with the plasma catalytic removal of NO and the oxidation of CH_4 from complex mixtures consisting of NO, CH_4, and O_2 as minority components and Ar or N_2 as carrier gases. Previous plasma investigations in our laboratory with a microwave (MW) surfatron device in the absence of catalysts have revealed that for such mixtures, the NO is efficiently converted into N_2 and O_2 [36]. Simultaneously, CH_4 is oxidized to CO, a noxious gas that should be removed for practical decontamination applications.

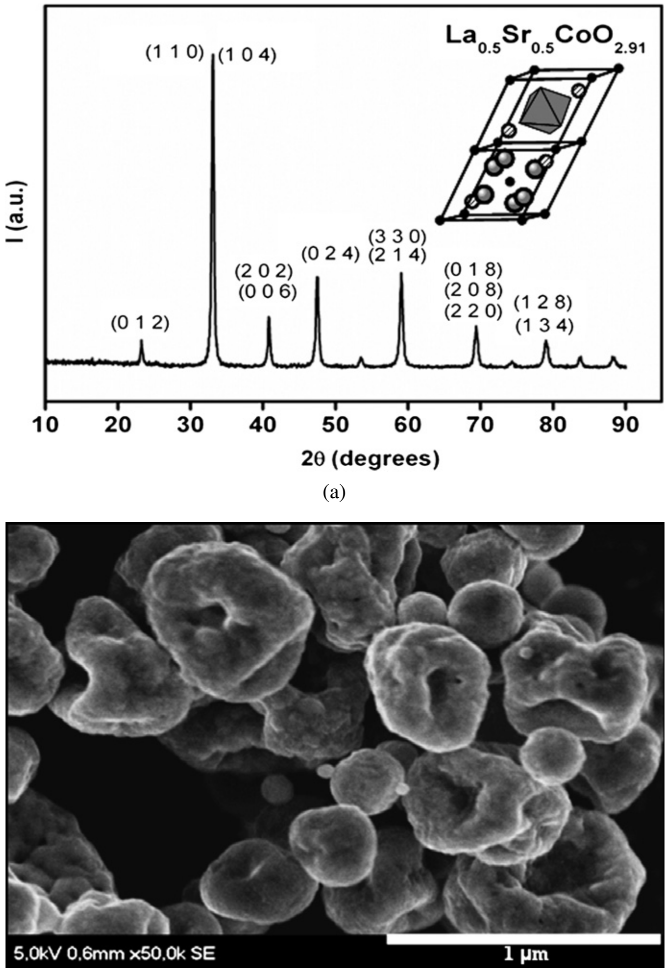
In the present investigation, we used a mixed plasma + catalyst system in an attempt to achieve the oxidation of CO into CO_2. Our results support the utility of this experimental approach and demonstrate the synergetic effects of CO plasma + catalyst oxidation at low temperatures. We used two types of catalysts, a commercial high-specific surface area SiO_2 catalyst and a perovskite-type catalyst prepared in our laboratory. The latter choice was dictated by the fact that perovskite catalysts are well-known catalysts for CO and CH_4 oxidation reactions [37,38]. We used the SiO_2 for comparative purposes to evaluate the hypothesis proposed in several papers in the sense that only the porosity of the catalyst is controlling the efficiency of the plasma + catalyst systems [16,20]. The main focus of the present investigation with complex gas mixtures containing NO, CH_4, and O_2 is to understand the chemical and plasma processes involved in the removal of NO and the conversion of CO (a primary product of the plasma reaction) into CO_2 when the plasma is used in conjunction with a perovskite catalyst. In addition, the beneficial effect of the presence of carbon together with the catalyst for the NO removal was also addressed in the context of this investigation. This carbon simulates the soot particles eventually present in most combustion outlets [15,25,37].

2. Experimental

2.1. Catalyst preparation and characterization

The two catalysts used for the present investigation are a commercial SiO_2 powder from Aldrich with a specific surface area of 270 $m^2\,g^{-1}$ and a $La_{0.5}Sr_{0.5}CoO_{3-d}$ perovskite prepared by spray pyrolysis [39] in our laboratory, with a specific surface area of 13 $m^2\,g^{-1}$. In addition, in some experiments, the perovskite was thoroughly ground with carbon nanoparticulates at a ratio of 90:10 by weight. The carbon, provided by Cabot, had a specific surface area of 190 $m^2\,g^{-1}$.

Perovskite preparation involved the uniform nebulization of nitrate solutions containing $La(NO_3)_3{\cdot}6H_2O$ (99.99%, Aldrich), $Co(NO_3)_2{\cdot}6H_2O$ (>98%, Fluka), and $Sr(NO_3)_2$ (>99%, Fluka) prepared as a 0.1 M liquid solution of precursors. Two online furnaces at 250 and 600 °C evaporated the solvent (distilled water) with the dissolved nitrates and produced an initially amorphous perovskite powder. The material was collected by a porous frit of quartz located in the outlet of the heating system. Subsequently, the powders were annealed at 600 °C for 4 h, thus obtaining a crystalline perovskite with rhombohedral symmetry [40], as evidenced by the X-ray diffractograms shown in Fig. 1a. The ultrasonic nebulization method of liquid droplets favors the formation of pseudospherical particles with a wide range of sizes, as inferred from the scanning electron microscopy (SEM) image shown in Fig. 1b. The mean diameter of particles varied from 200–500 nm to 1 µm, although smaller nanocrystalline domains of 50–60 nm were calculated by applying Scherrer's equation to the main diffraction peaks of this sample.



(a)

(b)

Fig. 1. (a) XRD pattern of the $La_{0.5}Sr_{0.5}CoO_{3-d}$ perovskite and scheme of the rhombohedral distorted geometry. (b) SEM micrograph of the perovskite catalyst.

2.2. Catalytic activity in the absence of plasma

Catalytic oxidation experiments of CO and CH_4 were carried out at atmospheric pressure in a fixed-bed stainless steel U-shaped reactor; 100 mg of perovskite particles were sustained between quartz wool in approximately the middle of the