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SO_2 poisoning of $LaFe_{0.8}Cu_{0.2}O_3$ perovskite prepared by reactive grinding during NO reduction by C_3H_6

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Abstract

Nanoscale $LaFe_{0.8}Cu_{0.2}O_3$ was prepared by reactive grinding, characterized by XRD, SEM, H_2-TPR, O_2-, NO + O_2-, and C_3H_6-TPD (with and without SO_2), FTIR, tested for catalytic reduction of NO by C_3H_6 and aged in presence of SO_2 to investigate the effect of sulfurous species on its catalytic behavior. Two distinct poisoning mechanisms depending on SO_2 feed concentration were thus proposed. At low concentration SO_2 ($\leq$20 ppm) can cause a reversible poisoning due to the competitive adsorption of SO_2 and reactants as well as the coverage of active sites by surface sulfite and sulfate species. By contrast, 80 ppm SO_2 leads to a severe sulfatation with destruction of the perovskite structure and the generation of $La_2(SO_4)_3$ and Fe_2O_3 phases resulting in an irreversible loss of activity in NO reduction by C_3H_6. Partial regeneration of this spent sample can be realized by releasing sulfur from the perovskite under a 5% H_2/He atmosphere followed by reconstructing the perovskite structure under an oxygen containing atmosphere.

Keywords: Perovskite; Reactive grinding; NO reduction; Propene; SO_2 poisoning; TPD; FTIR

1. Introduction

Purification of the nitrogen oxides emissions from motor vehicles, which cause acid rain and photochemical smog, leading to ecological damages and respiratory diseases, has become one of the most important issues for environmental protection. ABO_3 perovskite oxides have been proposed as promising three-way catalysts (TWCs) for the removal of exhaust gases since 1970s [1], because of their low cost, thermal and mechanical stability at relatively high temperature, great diversity, and excellent redox properties.

One major problem of perovskites prepared by traditional ceramic method [2], which involves high temperatures to ensure the perovskite crystallization, is their poor specific surface areas (usually less than 2 m^2/g) severely limiting their practical application. A new preparation method for perovskites [3–5], recently proposed by our group, can allow to avoid the thermal treatment and the crystallization to proceed at nearly ambient temperature. This technique uses high-energy-ball milling resulting in relatively high surface areas for the prepared samples. The catalytic reduction of NO by propene in the presence of oxygen was previously performed over three series of ($LaCo_{1-x}Cu_xO_3$ [6], $LaMn_{1-x}Cu_xO_3$ [7], $LaFe_{1-x}(Cu, Pd)_xO_3$ [8]) perovskites synthesized by this reactive grinding. $LaFe_{0.8}Cu_{0.2}O_3$ was found to be the most active one among the transition metal perovskites showing both N_2 yield and C_3H_6 conversion above 80% at 450 °C under the tested conditions. In a humid (10% H_2O) atmosphere, the water vapor sensitivity to catalytic activities in C_3H_6 + NO + O_2 reaction for these three series of perovskites was further investigated [9]. The best performance was again obtained over $LaFe_{0.8}Cu_{0.2}O_3$ with a moderate loss of N_2 yield and C_3H_6 conversion to 59% and 76%, respectively, at 500 °C under a feed mixture of 3000 ppm NO, 3000 ppm C_3H_6, 1% O_2, 10% H_2O and 50,000 h^{-1} GHSV. This deactivation by water vapor was however verified to be reversible by releasing steam from the feed.

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Since fuels contain residual sulfur, the resistance to SO_2 poisoning has become one of the main issues in the development of technologies in which NO reduction is involved. Unfortunately, perovskites are expected to be sensitive to SO_2 poisoning due to the basic properties of lanthanum, iron, manganese, cobalt oxides. It is thus necessary to clarify the SO_2 poisoning mechanism during catalytic reduction of NO by C_3H_6 in order to improve our understanding of the key factors related to poisoning and propose the composition of better performing perovskite-based catalysts with relatively higher resistance to SO_2 poisoning. According to the literature different sulfur species such as SO_2, SO_3, SO_3^{2-}, SO_4^{2-} and S^{2-} can be formed over SO_2 poisoned catalysts depending on temperature, time, and SO_2 feed concentration [10–12]. A primary SO_2 poisoning mechanism during methane oxidation over $LaCo_{1-x}Fe_xO_3$ perovskites displaying two distinct stages depending on poisoning time was proposed in our early publication [13]. Surface sulfur species interact with the accessible perovskite surface in the first stage while a linear diminution of conversion with time occurs at the second stage. Nevertheless, there are still some issues such as the influence of gaseous SO_2 on the reactants adsorption, the change in physicochemical properties of mixed oxides under SO_2 gas, the identification of sulfur species over and/or in perovskites, and the regeneration of poisoned catalysts, requiring attention.

In the present work, the poisoning effect of SO_2 on the catalytic behavior in the $C_3H_6 + NO + O_2$ reaction was investigated for the best performing nanocrystalline $LaFe_{0.8}Cu_{0.2}O_3$ perovskite. The fresh and poisoned $LaFe_{0.8}Cu_{0.2}O_3$ perovskites were characterized by N_2 adsorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), temperature programmed reduction (TPR) by H_2, temperature programmed desorption (TPD) of O_2, $NO + O_2$, and C_3H_6 (with and without SO_2), Fourier transform infrared (FTIR) spectroscopy. Activity tests towards NO reduction by C_3H_6 in the absence and presence of SO_2 were performed in order to study the influence of SO_2 in gas phase on the reactants adsorption and physicochemical properties of perovskite catalyst. Attempts to propose a SO_2 poisoning mechanism as well as to regenerate the poisoned samples have also been performed in this study.

2. Experimental

2.1. Preparation

$LaFe_{0.8}Cu_{0.2}O_3$ mixed oxide was synthesized by reactive grinding in a manner similar to that previously described [3,4,8]. Desired amounts of La_2O_3 (Alfa, 99.99%), Fe_2O_3 (Baker & Adamson, 97.49%), CuO (Aldrich, 99%) were fully mixed and high-energy milled inside a tempered steel vial using three tempered steel balls under an air atmosphere. Grinding was conducted in two steps of 8 h for synthesis and 10 h for refining with leachable ZnO as a grinding additive. Efficient leaching of ZnO was obtained by repeated washing with NH_4Cl solution. The sample was then dried and calcined under air at 500 °C for 5 h.

2.2. Physicochemical characterizations

The specific surface area of solid solutions was determined by means of an automated gas sorption system (NOVA 2000, Quantachrome) through nitrogen adsorption equilibrium at −196 °C. The specific surface area and pore size distribution of mixed oxides were calculated from the linear part of the BET curve ($P/P_0 = 0.01$–0.10) and the desorption branch of N_2 isotherms using the Barrett-Joyner-Halenda (BJH) formula, respectively. The solid solutions were characterized by X-ray diffraction using a diffractometer (D5000 Siemens) employing Cu Kα radiation ($\lambda = 1.5406$ Å) in a range $10^\circ < 2\theta < 80^\circ$ with a resolution of 0.05° (2θ) each 2.4 s. Crystallite sizes were determined using Scherrer equation after considering the instrumental broadening, while the crystal phases were identified via JCPDS reference. The image of solids was recorded at 25,000× magnification by scanning electron microscopy (JSM 840A JEOL) at 110 kV.

Temperature programmed reduction by H_2 (H_2-TPR) and temperature programmed desorption of O_2, $NO + O_2$, C_3H_6 in the presence or absence of 20 ppm SO_2 in the adsorption gas were conducted in a fixed-bed reactor equipped with a thermal conductive detector (TCD) and a quadrupole mass spectrometer (MS) (UTI 100). Before performing the H_2-TPR, the fresh sample (~50 mg) was pretreated under 10% O_2/He at 500 °C for 1 h and cooled down under the same atmosphere, flushed by 5% H_2/Ar for 40 min and then heated up to 900 °C at a rate of 5 °C/min under the same atmosphere. For the 80 ppm SO_2 poisoned sample (~50 mg) and bulk $La_2(SO_4)_3$ (Alfa Aesar, 99.9%) (~5 mg), O_2 pretreatment was not performed and the tested samples were directly flushed by 5% H_2/Ar at ambient temperature until a stable baseline of TCD was achieved, and the above heating procedure was repeated. The H_2 consumption in effluent was monitored by TCD.

Prior to the TPD of O_2, $NO + O_2$, C_3H_6 in the presence or absence of SO_2, the sample (~50 mg) was, respectively, pretreated in 10% O_2, 3000 ppm NO + 1% O_2, 3000 ppm C_3H_6, accompanied with 0 or 20 ppm SO_2, balanced by He at 500 °C for 1 h, followed by cooling down to room temperature under the same atmosphere and then purged by He for 40 min to remove physisorbed molecules. The sample was subsequently flushed by 20 ml/min of He at rising temperature up to 500 °C (800 °C for O_2-TPD) and a rate of 10 °C/min in the TPD analysis. The concentrations of O_2 and NO desorbing during O_2-TPD and $NO + O_2$-TPD experiments were on-line recorded by MS using the mass numbers of 32 and 30. Moreover, C_3H_6, CO and CO_2 desorbing during C_3H_6-TPD experiments were monitored with 41, 28 and 44 mass numbers, respectively. TPD experiments for bulk $La_2(SO_4)_3$ (~5 mg) and poisoned $LaFe_{0.8}Cu_{0.2}O_3$ (~50 mg, after exposure to 20 ppm SO_2 for 3 h or 80 ppm SO_2 for 36 h) were performed to investigate the sulfur species formed over the perovskite via a similar process but without any pretreatment before starting the TPD analysis. The mass numbers of 48, 64 and 32 were, respectively, selected to monitor the desorption of sulfur species as SO, SO_2 and O_2 fragments.