

Crystal structure, redox properties and catalytic performance of Ga-based mixed oxides for NO reduction by C₃H₆

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Abstract

A comparative study between LaGa_{1-x}Cu_xO₃ perovskites and ZnGa₂O₄ was conducted to clarify the correlation between crystal structure and redox properties as well as catalytic performance for the reduction of NO by C₃H₆. The oxidation ability of the prepared catalysts decreases following the order LaGa_{0.8}Cu_{0.2}O₃ > LaGaO₃ > ZnGa₂O₄. Perovskites, with the general composition of LaGa_{1-x}Cu_xO₃, were found to be suitable materials for NO reduction under scarce oxygen conditions, whereas excess oxygen (O₂ > 1%) led to a significant decline in N₂ yield. On the contrary, the presence of O₂ is necessary for NO conversion to N₂ over the ZnGa₂O₄ spinel, whose SCR activity was moderately enhanced at higher oxygen concentrations. The poor oxidation ability of ZnGa₂O₄ makes it as a promising candidate for lean NO reduction.

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1. Introduction

Catalytic reduction is effective to control the nitrogen oxides pollutants due to the emission of motor vehicles, which lead to serious problems of global environment and human health. Three ways catalysts (TWCs), involving metal ion-exchanged zeolites [1], supported noble and transition metals [2,3] and metal oxides [4] have been so far reported to selectively reduce NO using the emitted CO and hydrocarbons (HCs) as reductants for auto-exhaust aftertreatment. Among these Ga-based catalysts are of interest because of the high selectivity towards N₂ of Ga-ZSM-5 and the good activity of Ga₂O₃/Al₂O₃ during NO catalytic reduction by HCs. However, their application is limited either because of the possible dealumination under hydrothermal treatment and pore blockage caused by carbonaceous deposit for Ga-ZSM-5, or because of poisoning

by water vapor and thermal sintering for Ga₂O₃/Al₂O₃ [4–7].

Mixed oxides act as catalytic materials but with the advantages of high thermal and mechanical stability, structure and chemical diversity, excellent redox properties, better resistance against steam and SO₂ deactivation compared to their simple oxides [8]. ABO₃ perovskites and AB₂O₄ spinels are two kinds of mixed oxides commonly used for NO catalytic abatement [9–12]. B is in general a transition metal cation coordinated to six oxygens in octahedral symmetry and A usually stands for a rare earth metal cation coordinated to 12 oxygens for perovskites. For spinels, A generally stands for a metal cation tetrahedrally coordinated by 4 oxygens and B is octahedrally coordinated to 6 oxygens, as illustrated in Fig. 1. The potential application of perovskites as deNO_x catalysts for automobile exhaust purification was pointed by Libby as early as 1971 [9]. Recently, we prepared LaFe_{1-x}(Cu,Pd)_xO₃ perovskite-type oxides achieving satisfactory performances in NO reduction by C₃H₆ under a simulated atmosphere of the gasoline engine exhaust at

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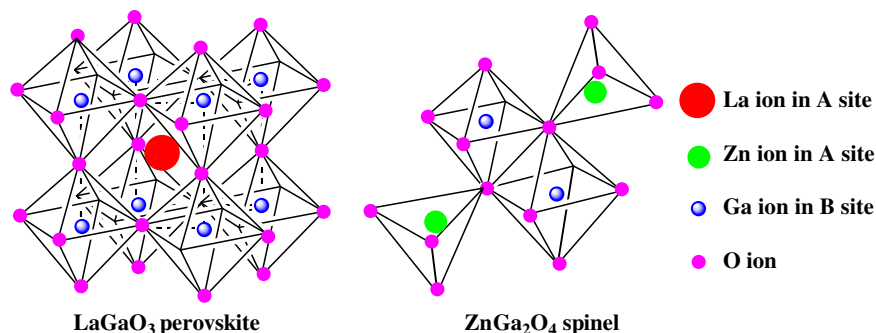


Fig. 1. Crystal structure of LaGaO₃ perovskite and ZnGa₂O₄ spinel.

approximately stoichiometric O₂ feed content [10]. Facing up the energy crisis, the use of diesel engine which achieves a more complete combustion of fuel at overstoichiometric oxygen (lean burn conditions) became a popular tendency. NO_x abatement under such oxidizing conditions is a great challenge for the conventional TWCs. The spinel-type Ga₂O₃–Al₂O₃–ZnO was announced to be able to reduce NO under an excess of oxygen [11,12]. The distinct catalytic behaviors at different oxygen contents of Ga-based oxides with perovskite and spinel structure during NO reduction attracted our attention.

In the present work, a comparative study was therefore carried out between LaGa_{1-x}Cu_xO₃ perovskites and ZnGa₂O₄ spinel, by means of X-ray diffraction (XRD), temperature-programmed desorption (TPD) of O₂, temperature-programmed reduction (TPR) by H₂, and activity test towards NO reduction by propene in the presence of oxygen. An effort was also made to correlate the crystal structure of perovskite- and spinel-type oxides with their redox properties and catalytic performance.

2. Experimental

2.1. Catalyst preparation

LaGa_{1-x}Cu_xO₃ ($x = 0, 0.2$) and ZnGa₂O₄ were synthesized by reactive grinding, as previously described in the literature [10]. Powders of La₂O₃ (Alfa, 99.99%), Ga₂O₃ (Alfa, 99.999%), CuO (Aldrich, 99%) and ZnO (Aldrich, 99.9%) in desired proportions were mixed and the solid state reaction was induced by high-energy-ball milling (SPEX 800) normally at a speed of 1100 rpm.

2.2. Catalyst characterization

The specific surface area of the mixed oxides after calcination at 500 °C for 5 h was determined from the linear part of nitrogen adsorption/desorption isotherms ($P/P_0 = 0.01–0.10$) obtained at –196 °C, using an automated gas sorption system (NOVA 2000, Quantachrome). Their crystal structures were determined by XRD using a Siemens D 5000 diffractometer and Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) with step scans from 20° to 80° in 2θ angle.

Identification of the crystal phases was achieved via the JCPDS data bank.

O₂-TPD and H₂-TPR were performed using a multifunctional characterization system (RXM-100, ASDI) equipped with a quadrupole mass spectrometer (MS) (UTI 100) and a thermal conductivity detector (TCD). Samples (50 mg) were pretreated under a 10% O₂/He stream at 500 °C for 1 h before the temperature-programmed experiments. During O₂-TPD, 20 ml/min He passed through the reactor heated at 10 °C/min up to 800 °C and the desorbed O₂ was monitored by MS at mass number of 32. The gaseous response obtained by MS was calibrated using standard gas mixtures. During H₂-TPR, 20 ml/min of 5% H₂/Ar as reductant was flowing over the sample heated at 5 °C/min up to 900 °C and H₂ consumption was recorded online using TCD. The water in effluent gas of the TPR experiments was condensed via a cold trap filled with a mixture of dry ice and ethanol.

2.3. Catalytic test

The catalytic reduction of NO by propene was carried out in a fixed-bed reactor under a mixture of NO (1000 ppm), C₃H₆ (3000 ppm), and O₂ (0–10%), balanced by He at 500 °C. Catalyst (200 mg) was used yielding a gas hourly space velocity (GHSV) of ~30,000 h⁻¹.

Nitrogen oxides (NO and NO₂) were analyzed using a chemiluminescence NO/NO₂/NO_x analyzer (Model 200AH, API). CO and N₂O gases were monitored using an IR gas analyzer (FTLA 2000, ABB). N₂ was determined using a gas chromatograph (GC) (HP 5890) fitted with columns of 13X and Silicone OV-101. The higher NO₂ value obtained from the NO_x analyzer compared to that from the IR spectrometer was ascribed to the organo nitrogen compounds (ONCs), thought as intermediates of NO reduction by hydrocarbons [13]. Yields of N₂, ONCs and NO₂ were determined as the NO fractional conversion towards these products. CO and CO₂ yields were calculated from the carbon balance as fractional conversions of C₃H₆. N₂O yields were not shown and discussed in this study due to their almost nil values under the investigated conditions. The mass balance of carbon is usually closed within 5% whereas the one of nitrogen is consistently within 3%.

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