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SCR of NO by propene over nanoscale $LaMn_{1-x}Cu_xO_3$ perovskites

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Abstract

Nanoscale $LaMn_{1-x}Cu_xO_3$ perovskites with high specific surface areas were prepared by reactive grinding and characterized by N_2 adsorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), H_2-temperature programmed reduction (TPR), O_2-, $NO + O_2$- and C_3H_6-temperature programmed desorption (TPD) and $NO + O_2$-temperature programmed surface reduction (TPSR) under C_3H_6/He flow. The samples were then submitted to activity tests in the selective catalytic reduction (SCR) of NO by C_3H_6 with or without O_2. The catalytic performances over unsubstituted $LaMnO_3$ is observed with maximum N_2 yield of 62% and a C_3H_6 conversion of 80% at 550 °C at a space velocity of 50,000 h^{-1} (3000 ppm NO, 3000 ppm C_3H_6, 1% O_2 in helium). The N_2 yield is however significantly improved by Cu incorporation into the lattice, achieving a remarkable N_2 yield of 86% at 500 °C at 20% Mn substitution by Cu. The content of α-oxygen over lanthanum manganite is enhanced by Cu substitution, but the opposite occurs for excess oxygen. The better performance of Cu-substituted samples is likely to correspond to the facility in the formation of adsorbed nitrate species via the oxidation of NO by α-oxygen in addition to the intrinsic effect of Cu in NO transformation. However, the excessive α-oxygen content observed over $LaCo_{0.8}Cu_{0.2}O_3$ accelerated the unselective hydrocarbon oxidation and suppressed the formation of organo nitrogen compounds, which led to a poor N_2 yield with respect to Mn-based perovskites. A mechanism involving the formation of an organic nitrogen intermediate, which further converts into N_2, CO_2 and H_2O via isocyanate, was proposed. The gas phase oxygen acts as a promoter when its concentration is lower than 1000 ppm because of the promotion of nitrate formation and organo nitrogen compounds transformation. O_2 acts however as an inhibitor when its concentration is higher than 5000 ppm due to the heavily unselective combustion of C_3H_6 by O_2, in the reaction of NO and C_3H_6 over $LaMn_{0.8}Cu_{0.2}O_3$ at 400 °C.

Keywords: SCR of NO; Propene; Reactive grinding; High surface area; Mn-based; Perovskite; TPR; TPD

1. Introduction

The purification of auto exhaust gases from gaseous impurities, including NO, hydrocarbons and CO is regarded as one of the main objectives of environmental catalysis. Great success has been achieved by applying three-way catalysts (TWC) in NO reduction using CO as a reducing agent [1]. These catalysts mainly consist of noble metals (platinum, palladium and rhodium) deposited on a CeO_2-γ-Al_2O_3 wash-coat. Taking into account the limited supply and high cost of noble metals and the need to eliminate hydrocarbons from the exhaust gases, the study of NO reduction using hydrocarbons as reducing agents over low cost oxide-based catalysts appears as highly necessary. In these studies, C_3H_6 is often used as a model reducing hydrocarbon gas. Recently, special attention has been paid to the perovskite-type mixed oxides due to their excellent redox properties, early pointed out by Libby [2].

Among the perovskites, lanthanum manganite has been investigated intensively because it is one of the few perovskite systems that display a wide range of deviations from stoichiometry (oxygen excess). This deviation can be modified by partial substitution of A and B cations, with significant changes in their physicochemical properties [3–5]. Moreover, Mn_2O_3 was also reported as a valuable additive to some selective catalytic reduction (SCR) catalysts such as Ce-ZSM-5 [6] and Au/Al_2O_3 [7]. Hence, $LaMnO_3$ and its derivatives can be considered as promising candidates for NO reduction.

Although the effect of the partial substitution of cation A, by elements having a valence state different from 3+, on catalytic performance in the NO reduction by C_3H_6 has been widely studied [8], the effect of the B site substitution on NO elimination has been much less investigated.

Copper containing catalysts are of special interest because they are active in various reactions for the transformation of

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nitrogen oxides, as reviewed by Centi and Perathoner [9]. Low coordination isolated Cu ions are regarded as the active sites for SCR of NO over Cu-zeolites [10]. Our recent work showing that Cu/MCM-41 was also an active catalyst [11] indicates that the surface environment of the Cu ion is of crucial importance for the catalyst activity. Introducing Cu cations into the B sites of a perovskite structure is thus likely to yield good catalytic performances.

Due to their preparation which usually involves a temperature as high as 800 °C to ensure the formation of the crystalline phase, perovskites are synthesized with the low specific surface areas of several m^2/g by the usual ceramic method which suppresses their activity and limits their application [12]. A new preparation method designated as reactive grinding was developed in our group to synthesize perovskites at room temperature via high-energy-ball milling, achieving a relatively high surface area, on the order of 100 m^2/g when grinding additives are used [13–15].

A series of $LaMn_{1-x}Cu_xO_3$ perovskites with various atomic ratios $x = 0$, 0.1 and 0.2 was prepared by reactive grinding. The aim of this work is therefore to study the influence of Cu substitution in the B site of ABO_3 solids on their physicochemical properties and their catalytic performances in NO reduction by propene. It is furthermore attempted to clarify the role of oxygen in NO reduction and propene oxidation, to determine the correlation between physicochemical properties and catalytic behavior, finally, to propose a reaction mechanism in NO-SCR over these perovskites. This work is therefore a continuation of our recently reported study of $LaCo_{1-x}Cu_xO_3$ catalysts [16].

2. Experimental

2.1. Preparation of perovskites

$LaMn_{1-x}Cu_xO_3$ perovskites were prepared by reactive grinding, by fully mixing powders of La_2O_3 (Alfa, 99.99%), Mn_3O_4 (Baker & Adamson, 98.22%) and CuO (Aldrich, 99.98%) in a high-energy-ball mill as described in ref. [14]. La_2O_3 was calcined at 600 °C for 24 h. Grinding was conducted in two steps of 8 h for synthesis and 10 h for refining with ZnO as the grinding additive.

2.2. Characterization of perovskites

BET surface areas of the materials calcined at 500 °C for 5 h were measured by nitrogen adsorption at −196 °C using an automated gas sorption system (NOVA 2000; Quantachrome) operating in continuous mode. The specific surface area was determined from the linear part of the BET curve ($P/P_0 = 0.01$–0.10). Pore volume and average diameter were obtained from the pore size distribution curve, which was calculated from the desorption branch of N_2 isotherms using the Barrett–Joyner–Halenda (BJH) formula.

The chemical composition (Mn, Cu) of the prepared samples and the impurities (Fe, Zn) were analyzed by atomic absorption spectroscopy (AAS) using a Perkin-Elmer 1100B spectrometer. The La content of the perovskites was established using an inductively coupled plasma spectrometer (ICP; Optima 4300DV; Perkin-Elmer).

Powder X-ray diffraction (XRD) patterns were recorded using a Siemens D5000 diffractometer and Cu Kα radiation ($\lambda = 1.5406$ Å) with a 0.05° step scan from 20° to 70° in 2θ angle. Crystal domain sizes (D) were evaluated by means of the Scherrer equation after Warren's correction for instrumental broadening. The identification of the crystal phases took place using the JCPDS data bank.

The solids obtained after calcination at 500 °C were observed with magnification of 100,000× by scanning electron microscopy (SEM) using a JEOL JSM 840A instrument operated at 110 kV.

Transient studies were carried out with a multifunctional catalyst testing and characterization system (RXM-100; ASDI), equipped with a quadrupole mass spectrometer (UTI 100) and a thermal conductivity detector (TCD). Prior to H_2-TPR, the samples (50 mg) were pretreated under 10% O_2/He flow at 20 cm^3/min total flow rate (STP) for 1 h at 500 °C, cooled down to room temperature under the same atmosphere, purged with 20 cm^3/min of helium for 40 min to remove the physically adsorbed O_2, and then heated under a 20 cm^3/min total flow rate of 5% H_2/Ar stream with temperature rising up to 900 °C at a constant heating rate of 5 °C/min. The water in the effluent gas of the temperature programmed reduction (TPR) process was condensed via a cold trap with a mixture of dry-ice and ethanol. H_2 consumption was monitored continuously by TCD using a 20 cm^3/min flow of 5% H_2/Ar as reference gas.

Prior to the temperature programmed desorption (TPD) of O_2, NO + O_2 and C_3H_6, 50 mg samples were treated under an atmosphere of 10% O_2, 3000 ppm NO + 1% O_2, 3000 ppm C_3H_6, respectively, with a total flow rate of 20 cm^3/min at 500 °C for 1 h and then cooled down to room temperature under the same flow, subsequently, flushed with 20 cm^3/min He for 40 min to remove the physically adsorbed molecules. The temperature was then raised up to 500 °C (800 °C for TPD of O_2) at a rate of 10 °C/min. O_2, NO, N_2O and N_2 desorbed during O_2- and NO + O_2-TPD experiments were simultaneously detected and recorded on-line by mass spectrometry (MS) with the mass numbers of 32, 30, 44 and 14, respectively. Moreover, C_3H_6, CO and CO_2 desorbing during C_3H_6-TPD experiments were monitored with the mass numbers of 41, 28 and 44, respectively.

Temperature programmed surface reduction (TPSR) of NO + O_2 under C_3H_6/He flow was performed with the same sample pre-treatment as that during TPD of NO + O_2 experiment. The thermodesorption was however performed under 1000 ppm C_3H_6/He instead of He. The desorbed C_3H_6, NO, O_2 together with generated CO_2, N_2, H_2O were monitored by MS with mass number of 41, 30, 32, 44, 14 and 18, respectively. The gas responses obtained by MS were calibrated using standard mixtures.

2.3. Activity measurements

The catalytic tests were performed in a fixed-bed quartz reactor under an atmosphere of 3000 ppm NO, 3000 ppm C_3H_6, with 1% or without O_2, balanced by He at a space velocity of