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# Research on SCR of NO with CO over the $Cu_{0.1}La_{0.1}Ce_{0.8}O$ mixed-oxide catalysts: Effect of the grinding

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## ABSTRACT

In this work, the mixed oxide catalysts $Cu_{0.1}La_{0.1}Ce_{0.8}O$ with the different grinding time (denoted as x, x = 0, 1, 5, 10, 15, or 20) for low-temperature selective catalytic reduction (SCR) of NO with CO are prepared by the grinding method. XRD, SEM, BET, XPS, *in situ* DRIFTS, $H_2$-TPR, and $O_2$-TPD measurements are used to characterize the catalysts CLC xh, which is objective to illuminate the influence of the grinding on the physicochemical and catalytic properties of CLC xh composite materials and understand the reaction mechanism of the CO-SCR catalytic process. The results show that CLC 10 h exhibited the highest catalytic performance, well water-resistance capacity and excellent catalytic stability for NO reduction by CO model reaction, because more catalytic domains (SSOV, Cu-□-Ce (La) species) can generate in the reaction process due to the enhancement of redox behavior with Cu-O-Ce (La) active species, and more active sites are able to form in the grinding process. Undoubtedly, the high concentration of $Cu^+$ is beneficial to NO adsorption and the doping of La enhanced the $N_2$ selectivity of the catalysts significantly. Combined with the *in situ* DRIFTS results, a possible catalytic reaction mechanism is tentatively proposed to discuss the NO + CO model reaction.

## 1. Introduction

As is known to all, nitrogen oxides ($NO_x$) are as a major air pollutant that are produced by the combustion of fossil fuels, which is the main reason that caused a series of environment problems such as photochemical smog, acid rain, and ozone depletion in recent years [1–5]. Nowadays, catalytic technologies, especially for selective catalytic reduction (SCR) technology, has been generally regarded as one of the most efficient removal techniques in the field of the $NO_x$ removal [2,6,7]. However, the typical commercial SCR catalysts such as $V_2O_5$-$WO_3$ (or $MoO_3$)/$TiO_2$ have been widely applied in industry [8,9], they still remain some problems such as high reaction temperature, narrow active temperature window and poor thermal stability. Hence, transition metal oxides catalysts like $CeO_2$, $MnO_x$, $CuO_x$, and $LaO_x$ are attempted to replace commercial SCR catalysts for the SCR process.

Among them, ceria-based catalysts have been presenting a potential application for $NO_x$ removal. It is widely accepted that pure $CeO_2$ has the excellent oxygen storage capacity, transport capability, and redox capability, which contribute to the transformation of surface oxygen species through the $Ce^{4+} \leftrightarrow Ce^{3+}$ redox process. Moreover, pure $CeO_2$ has been studying extensively for catalytic materials in oxidizing and reducing conditions. On the other hand, $CeO_2$ owns the poor thermal stability and effortless deactivation under the high temperature, and so forth [5,10–12,15]. It is reported that the introduction of some transition metal oxides (such as Cu, La, Mn, Zr, etc.) into cerium oxide can improve some capability of the composite materials effectively, such as redox properties and thermal stability [13–17]. This may impact on the catalytic pathway by changing the physicochemical properties for Ce-based catalytic materials. Based on this purpose, many preparation methods have attracted more and more attention for improving Ce-based catalysts.

In the past few decades, many ways can be used as the preparation methods of the catalyst for NO reduction by CO, such as sol-gel method [1,18,19], hydrothermal method [4,14,20], co-precipitation method [3,10,12,16,21]. The research achievements of these preparation methods illustrate that these methods can be used to prepare

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the catalysts with the excellent SCR performances. Nevertheless, no matter what kind of method is, it always needs larger energy consumption [9] and/or has a certain negative impact on the environment. The synthetic route of the grinding method can be a promising candidate to replace those methods, probably because it owns the lower energy consumption, more convenience for the operation and/or lower influence on the environment for the comprehensive utilization of metal oxides particularly for the low-cost transition metal oxides.

Therefore, in this work, a series of multicomponent oxide catalysts CLC xh are prepared by the grinding method, moreover the influence of the grinding on catalytic performances is evaluated from some aspects. In addition, the physical properties, mechanical properties, and other properties of the CLC xh catalysts are characterized by several measurements, such as X-ray diffraction (XRD), $N_2$ adsorption/desorption (BET), Scanning electron microscope (SEM), $H_2$-Temperature programmed reduction (TPR), $O_2$-Temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), *In situ* diffuse reflectance infrared Fourier transform spectra (*In situ* DRIFTS). These measurements can provide some favorable information about the interaction among Cu and Ce (La) (Cu-O-Ce (La) species) with the extension of the grinding time and the possible catalytic reaction pathway. For instance, the possible catalytic mechanism are obtained by investigating the *in situ* DRIFTS results for CO or/and NO adsorption of catalysts. Furthermore, the low-temperature SCR activities of the samples for the reduction of NO with CO are investigated by establishing micro reactor devices with NO + CO.

## 2. Experimental

### 2.1. Sample preparations

A series of $Cu_{0.1}La_{0.1}Ce_{0.8}O$ mixed oxides are prepared by the grinding method. Firstly, $CeO_2$, CuO, and $La_2O_3$ are prepared by thermal decomposition with corresponding nitrate at 450 °C for 4 h in the flowing air, respectively. And then the CLC catalysts with the same $CuO/La_2O_3/CeO_2$ mass ratio of 1: 1: 10 are prepared by the grinding method, where the $Cu_{0.1}La_{0.1}Ce_{0.8}O$ catalysts with the different grinding time are marked as CLC 0 h, CLC 1 h, CLC 5 h, CLC 10 h, CLC 15 h, and CLC 20 h, respectively. For comparison, $La_{0.1}Ce_{0.8}O$ (labeled as LC) and $Cu_{0.1}Ce_{0.8}O$ 5 h (marked as CC 5 h) samples are also prepared by the same method.

### 2.2. Samples characterization

#### 2.2.1. BET surface area

BET specific surface area and pore structure data are measured by $N_2$ adsorption/desorption at −196 °C using a gassorption analyzer (Micrometrics TriStar II 3020 system). Prior to the measurements, about 100 mg of the fresh samples are degassed at 90 °C for 1 h and 300 °C for 2 h in flowing of high purity nitrogen. BET surface area for each sample is calculated by applying Brunauer-Emmett-Teller (BET) equation.

#### 2.2.2. Scanning electron microscope (SEM)

SEM images are measured on a Hitachi SU-8020 scanning electron microscope spectrometer, which can acquire the surface morphologies of CLC xh catalysts. Before the testing, the sample is fixed in a rotating disk with the conductive adhesive.

#### 2.2.3. X-ray diffraction (XRD)

XRD patterns are recorded on a Japan Rigaku D/MAX-2600 ray diffractometer employing Cu Kα radiation ($\lambda = 0.15418$ nm), and the X-ray tube is operated at 40 kV and 120 mA. The X-ray powder diffractogram is performed at 0.01° intervals and the scanning rate is 8° $min^{-1}$ for 2θ ranges from 10 to 80°.

#### 2.2.4. $H_2$-TPR

$H_2$-TPR experiment is performed on a Pantech instruments company's Finesorb-3010 chemisorption analyzer using a thermal conductivity detector with $H_2$/Ar mixture (7.03 vol% $H_2$ by volume) as reductant. Approximate 50 mg of the fresh samples were treated with high purity nitrogen (50 mL $min^{-1}$) at 110 °C for 1 h at the pretreatment process. Then the temperature cooled down to room temperature in $N_2$ atmosphere, and subsequently $N_2$ (50 mL $min^{-1}$) gas was switched into mixed gas ($N_2$ (50 mL $min^{-1}$), 7.03% $H_2$ (10 mL $min^{-1}$, Ar as balance gas)) and keep time for 0.5 h. After that, the reduction process was started with the temperature which was raised from 20 to 800 °C and the heating rate was 10 °C $min^{-1}$.

#### 2.2.5. $O_2$-TPD

$O_2$-TPD experiment also uses the Pantech instruments company's Finesorb-3010 chemisorption analyzer adopting a thermal conductivity detector to analyze the $O_2$ absorptive capacity of catalysts with pure $O_2$ gas as adsorbent. Approximate 100 mg of the samples were treated with He (30 mL $min^{-1}$) at 200 °C for 1 h at the pretreatment process. Then the temperature was cooled down to room temperature in He atmosphere, and He (50 mL $min^{-1}$) gas was switched into pure oxygen (10 mL $min^{-1}$) and keep time for 0.5 h at room temperature. Subsequently blowing 0.5 h in He atmosphere so as to remove oxygen gas in the samples. After that, the desorption process was started with the temperature which was raised from 20 to 800 °C and the heating rate was 10 °C $min^{-1}$.

#### 2.2.6. X-ray photoelectron spectroscopy (XPS)

XPS spectra is measured on a PHI 5000 Versa Probe X-ray photoelectron spectrometer using Al Kα radiation (1486.6 eV) at an accelerating power of 15 kW. All the binding energies are calibrated by the carbon deposit C1 s peak (284.6 eV). Before starting the measurement, all of the samples are pressed into a small and thin slice of the nail.

#### 2.2.7. In situ diffuse reflectance infrared fourier transform spectra measurement (In situ DRIFTS)

DRIFTS spectra is recorded on a Nicolet iS50 Fourier transform infrared spectrometer, working in the range of wave numbers 4000 ∼ 650 $cm^{-1}$ at a resolution of 4 $cm^{-1}$ with accumulation of 32 scans. The samples in powder form are flattened in quarts IR cell, pretreated in the flowing $N_2$ with the temperature from 25 to 350 °C at a rate of 5 °C $min^{-1}$. After which background spectra (in the flowing $N_2$) are recorded in the range of 350 ∼ 25 °C at intervals of 25 °C, NO gas (5 vol% in He, 10 mL $min^{-1}$) and/or CO gas (10 vol% in He, 10 mL $min^{-1}$) is carried out at room temperature. Then the system reaches an adsorption/desorption equilibrium (about 40 min), the spectra of adsorbed species on catalysts is collected in the range of 25 ∼ 350 °C at intervals of 25 °C. DRIFTS spectra are obtained by subtraction of the corresponding background reference.

### 2.3. NO + CO SCR activity measurements

The activities of CLC xh catalysts for NO reduction by CO are tested by building a NO + CO micro reactor device, herein the fresh sample (about 50 mg) with the particle sizes of 40 ∼ 60 meshes is loaded into a quartz tube. The reaction gas is a feed steam with a fixed composition, NO 5 vol%, CO 10 vol% and He as balance gas. The catalysts are pretreated at 110 °C for 1 h in the flowing $N_2$, and then cooled down to room temperature. Thereafter the micro reaction system are connected to the gas reactants, and the temperature increases from room temperature to 400 °C with a space velocity

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