



# N<sub>2</sub>O decomposition over CuO/CeO<sub>2</sub> catalyst: New insights into reaction mechanism and inhibiting action of H<sub>2</sub>O and NO by *operando* techniques



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## ABSTRACT

In this work, a combination of *ex situ* (STEM-EELS, STEM-EDX, H<sub>2</sub>-TPR and XPS), *in situ* (CO-DRIFTS) and *operando* (DR UV–vis and DRIFTS) approaches was used to probe the active sites and determine the mechanism of N<sub>2</sub>O decomposition over highly active 4 wt.% Cu/CeO<sub>2</sub> catalyst. In addition, reaction pathways of catalyst deactivation in the presence of NO and H<sub>2</sub>O were identified. The results of *operando* DR UV–vis spectroscopic tests suggest that [Cu–O–Cu]<sup>2+</sup> sites play a crucial role in catalytic N<sub>2</sub>O decomposition pathway. Due to exposure of {100} and {110} high-energy surface planes, nanorod-shaped CeO<sub>2</sub> support simultaneously exhibits enhancement of CuO/CeO<sub>2</sub> redox properties through the presence of Ce<sup>3+</sup>/Ce<sup>4+</sup> redox pair. Its dominant role of binuclear Cu<sup>+</sup> site regeneration through the recombination and desorption of molecular oxygen is accompanied by its minor active participation in direct N<sub>2</sub>O decomposition. NO and H<sub>2</sub>O have completely different inhibiting action on the N<sub>2</sub>O decomposition reaction. Water molecules strongly and dissociatively bind to oxygen vacancy sites of CeO<sub>2</sub> and block further oxygen transfer as well as regeneration of catalyst active sites. On the other hand, the effect of NO is expressed through competitive oxidation to NO<sub>2</sub>, which consumes labile oxygen from CeO<sub>2</sub> and decelerates [Cu<sup>+</sup> Cu<sup>+</sup>] active site regeneration.

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## 1. Introduction

Nitrous oxide (N<sub>2</sub>O) is due to its high global warming potential, atmospheric stability (lifetime approximately 120 years) and contribution to ozone layer depletion considered to be one of the strongest greenhouse gases [1,2]. The total anthropogenic emissions of nitrous oxide (including nitric acid, adipic acid and caprolactam production) are estimated to be about 5.3 Tg N<sub>2</sub>O–N yr<sup>−1</sup> (teragrams of N<sub>2</sub>O in equivalent nitrogen units per year) [3]. Thus, development of an efficient technology for catalytic N<sub>2</sub>O decomposition from industrial exhaust gases is highly required. Different catalyst formulations (involving supported noble metals [4–6], metal oxides [7,8], mixed metal oxides [9,10], perovskites [11,12], spinels [13–15] and zeolite based materials [16–19]) have been studied in order to decompose N<sub>2</sub>O to environmentally benign O<sub>2</sub> and N<sub>2</sub>. Despite many scientific efforts, development of a proper catalyst which could decompose N<sub>2</sub>O even

in the presence of inhibiting gases (e.g. water, oxygen and NO) is still of great importance.

Among investigated catalytic systems, CuO/CeO<sub>2</sub> materials show very promising results and combine superior activity under moderate temperatures, long-term stability and economically favourable price (compared to highly expensive noble metals) [10,20–23]. It was previously discovered that CuO clusters measuring less than 5 nm in size exhibit the highest activity and achieve 50% of N<sub>2</sub>O conversion at around 380 °C (N<sub>2</sub>O concentration = 2500 ppm; WHSV = 60 L/(g<sub>cat</sub> h)) [21]. Exceptional catalytic properties of CuO/CeO<sub>2</sub> system have been attributed to the so-called “synergetic effect”. This originates from electronic interactions between the two oxide phases, which weakens the metal-oxygen bond and enables easier oxygen desorption and regeneration of catalyst active sites [24,25]. It was observed that nanoshaped CeO<sub>2</sub> (rods and cubes), predominantly terminated with {100} and {110} surface planes and enriched with Ce<sup>3+</sup> showed superior activity in N<sub>2</sub>O decomposition reaction compared to polycrystalline CeO<sub>2</sub> nanoparticles, terminated with {111} surface planes with lower Ce<sup>3+</sup> content [20]. This leads to an assumption that CeO<sub>2</sub> acts not only as a support material for CuO,

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but also plays an active role (through  $\text{Ce}^{3+}/\text{Ce}^{4+}$  redox pair) in  $\text{N}_2\text{O}$  decomposition pathway. Systematic fundamental research which would help to identify reaction steps occurring on the catalyst surface during  $\text{N}_2\text{O}$  decomposition, is required in order to establish a credible mechanism for catalytic  $\text{N}_2\text{O}$  decomposition over  $\text{CuO}/\text{CeO}_2$  solids. Furthermore, the inhibiting action of  $\text{H}_2\text{O}$  and  $\text{NO}$ , which are usually present in tail gases subjected to  $\text{N}_2\text{O}$  decomposition, is not completely clear.

As a result, understanding of  $\text{N}_2\text{O}$  decomposition mechanism and deactivation by  $\text{H}_2\text{O}$  and  $\text{NO}$  will allow catalyst improvement for efficient  $\text{N}_2\text{O}$  destruction. Therefore, this study was aimed to fulfil this missing knowledge gap. For this purpose, a catalyst containing 4 wt.% of  $\text{Cu}$  supported on  $\text{CeO}_2$  nanorods was thoroughly characterized by a variety of techniques (HRTEM, STEM-HAADF, STEM-EDX,  $\text{N}_2$  physisorption, XRD,  $\text{H}_2$ -TPR, XPS and dissociative  $\text{N}_2\text{O}$  adsorption) and examined in catalytic  $\text{N}_2\text{O}$  decomposition. *Operando* DRIFT and UV–vis techniques hyphenated with gas chromatography were used to investigate the mechanism of  $\text{N}_2\text{O}$  decomposition over  $\text{CuO}/\text{CeO}_2$  as well as inhibiting action of  $\text{H}_2\text{O}$  and  $\text{NO}$  on the catalyst. By bringing together results obtained from these surface sensitive techniques, comprehensive information about the reaction under consideration was obtained and mechanism of catalytic  $\text{N}_2\text{O}$  decomposition was proposed.

## 2. Experimental

### 2.1. Catalyst preparation

Catalyst containing 4 wt.% of  $\text{Cu}$  supported on  $\text{CeO}_2$  nanorods ( $\text{CuO}/\text{CeO}_2$ ) was prepared accordingly to the following synthesis protocol: Nanoshaped  $\text{CeO}_2$  support was synthesized by hydrothermal method. Briefly, 53.8 g of  $\text{NaOH}$  (99% purity, Merck) was dissolved in 140 mL of deionized water. To the obtained solution, 4.9 g of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99% purity, Sigma-Aldrich) dissolved in 84 mL of deionized water was added under vigorous stirring. Then, suspension was stirred for 30 min and transferred into a Teflon<sup>®</sup>-lined stainless steel autoclave and aged for 24 h at 100 °C. The derived suspensions were centrifuged at 5000 rpm and thoroughly washed with hot deionized water in order to remove undesired sodium ions. The obtained precipitate was re-dispersed in 10 mL of deionized water, frozen by quench-freezing with  $\text{LN}_2$  and dried for 24 h using a freeze-dryer (Christ, model Alpha 1–2 LDplus). Finally, the material was calcined in air at 400 °C for 3 h (heating ramp of 2 °C/min).  $\text{CuO}$  was deposited by means of precipitation. 400 mg of  $\text{CeO}_2$  nanorods was dispersed in 10 mL of deionized water using an ultrasonic homogenizer (Cole-Parmer) and 63.6 mg of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (99.5% purity, Sigma-Aldrich) was added to reach the 4 wt.% nominal loading. After 10 min of stirring, 5 mL of aqueous solution containing 250 mg of  $\text{Na}_2\text{CO}_3$  (99.999% purity, Merck) was added. The obtained suspension was additionally stirred at room temperature for 2 h, filtered, thoroughly washed with hot deionized water, dried in the freeze drier for 24 h and finally calcined in air at 400 °C for 3 h (heating ramp of 2 °C/min).

### 2.2. Catalyst characterization

Measurements of BET specific surface area, total pore volume and pore size distribution were performed at –196 °C using a TriStar II 3020 instrument from Micromeritics. Temperature programmed reduction ( $\text{H}_2$ -TPR) experiments were performed using a Micromeritics AutoChem II 2920 apparatus. Before analysis, a catalyst was pre-treated at 400 °C in synthetic air (20.5 vol.%  $\text{O}_2/\text{N}_2$ ). TPR analysis was performed in a 25 mL/min stream of 5 vol.%  $\text{H}_2/\text{Ar}$  mixture as a reducing agent. The samples were heated from –20 to 400 °C with a 5 °C/min ramp during analysis. A liquid

nitrogen–isopropyl alcohol cold trap was mounted on exhaust in order to condense water vapour and remove it from the effluent gas mixture before entering the TCD detector. After  $\text{H}_2$ -TPR examination, dissociative  $\text{N}_2\text{O}$  adsorption experiment was done in order to determine  $\text{Cu}$  dispersion and cluster size.  $\text{N}_2\text{O}$  pulsing (10 vol.%  $\text{N}_2\text{O}/\text{He}$ ) was performed at 35 °C (a  $\text{LN}_2$  cold trap was mounted on exhaust in order to condense unreacted  $\text{N}_2\text{O}$ ). X-ray photoelectron spectra were measured with ES-2403 modified spectrometer equipped with a PHOIBOS 100 MCD analyzer (Specs GmbH), using  $\text{MgK}\alpha$  excitation (1253.6 eV, 10 kV and 25 mA). The spectrometer was calibrated by binding energy (BE) of  $\text{Au } 4f_{7/2} = 84.0$  eV and  $\text{Ni } 2p_{3/2} = 852.7$  eV. Detailed spectra were recorded for the regions of  $\text{Cu } 2p$ ,  $\text{Ce } 3d$  photoelectrons and  $\text{Cu } L3VV$  Auger electrons with a 0.1 eV step at a pressure below  $3 \times 10^{-6}$  Pa. The binding energy of XPS peaks was further corrected by referencing to the  $\text{Ce } 3d_{5/2}$  peak at 882.0 eV (internal standards). Particle size and morphology were studied by means of high-resolution transmission electron microscopy (HRTEM) and scanning TEM high-angle annular dark field imaging (STEM-HAADF). Copper distribution was assessed by energy-dispersive X-ray spectroscopy in STEM mode (STEM-EDX). For these analyses, a probe aberration-corrected JEM-ARM200CF equipped with the JEOL Centurio 100 mm<sup>2</sup> EDXS detector and JEOL STEM detectors (JEOL, Tokyo, Japan) was employed.

### 2.3. In situ and operando experiments

All experiments were carried out at ambient pressure. Prior to catalytic runs, the  $\text{CuO}/\text{CeO}_2$  catalyst was activated *in situ* in 20 mL/min  $\text{Ar}$  flow (purity 5.0, Messer) at 400 °C for 1 h. Decomposition of  $\text{N}_2\text{O}$  was performed in reaction chambers (see details below) in the temperature range of 300–450 °C.  $\text{N}_2\text{O}$  feed concentration was 2500 ppm balanced by argon (Linde), while the total feed flow rate was equal to 30 mL/min. At each examined temperature (increments of 50 °C) the reaction was carried out for 30 min before measurements were initiated. For catalytic experiments conducted in the inhibiting atmospheres, gas mixtures containing 2500 ppm of  $\text{N}_2\text{O}$  and either 1.5 vol.% of  $\text{H}_2\text{O}$  or  $\text{NO}$  balanced by argon were used.

The *operando* diffuse reflectance Fourier transform infrared (DRIFT) spectra were recorded in the range of 900–4000  $\text{cm}^{-1}$  using a FTIR analyzer (Perkin Elmer, model Frontier) equipped with a MCT detector. High temperature reaction chamber (Pike Technologies, model DiffusIR) was used in order to monitor the catalyst surface under reaction conditions. Experiments were conducted using 10 mg of  $\text{CuO}/\text{CeO}_2$  sample placed into a sample holder made from sintered ceramics (5 mm I.D.) and finely smoothed to create a flat surface. Spectra were collected with the resolution of 4  $\text{cm}^{-1}$  and accumulation of 32 scans. The analysis of outlet gas was performed by means of a hyphenated gas chromatograph 490 Micro GC (Agilent Technologies) equipped with 10 m MS5A and 10 m Porabond Q columns. *In situ* spectra of adsorbed  $\text{CO}$  were recorded at –70 °C. The catalyst was pre-treated *in situ* either in inert gas ( $\text{He}$ ) or in 2500 ppm  $\text{N}_2\text{O}/\text{Ar}$  atmospheres at 400 °C. After cooling to –70 °C, the solid was exposed to 1 vol.%  $\text{CO}/\text{Ar}$  mixture. Spectra were collected with the resolution of 4  $\text{cm}^{-1}$  and accumulation of 16 scans.

The *operando* UV–vis diffuse reflectance spectra (DR UV–vis) were acquired using a Perkin-Elmer Lambda 650 UV–vis spectrophotometer equipped with a high-temperature reaction chamber (HVC-VUV-4, Harrick). The Spectralon<sup>®</sup> white reflectance standard or  $\text{CuO}/\text{CeO}_2$  catalyst were utilized to perform the instrument background correction in the range of 200–850 nm. The scans were acquired with the speed of 120  $\text{nm min}^{-1}$  and slit set to 4 nm. 10 mg of  $\text{CuO}/\text{CeO}_2$  catalyst was placed into a stainless steel sample holder (4.5 mm I.D.) inside the reaction chamber.  $\text{N}_2\text{O}$  conversion

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