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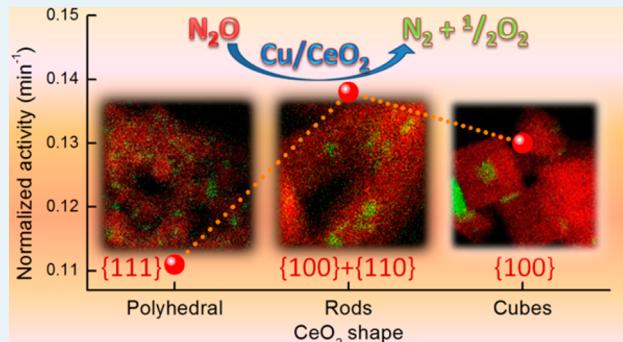
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Supporting Information

ABSTRACT: This study reports a thorough investigation of nanosized CuO/CeO₂ materials as an efficient catalyst for decomposition of N₂O, which is a strong greenhouse gas largely produced by chemical industry. Effect of terminating CeO₂ crystalline planes ($\{100\}$, $\{110\}$, and $\{111\}$) on the behavior of CuO dispersed over CeO₂ nanocubes, nanorods and polyhedral crystallites was examined in detail by using a variety of catalyst characterization techniques. The 4 wt % Cu was found as the most advantageous metal loading, whereas higher Cu content resulted in lower dispersion and formation of significantly less active, segregated bulk CuO phase. It was discovered that CuO/CeO₂ solids should enable both excessive oxygen mobility on the catalyst surface as well as formation of highly reducible Cu defect sites, in order to ensure high intrinsic activity. Detailed studies further revealed that CeO₂ morphology needs to be tailored to expose $\{100\}$ and $\{110\}$ high-energy surface planes, as present in CeO₂ nanorods. Oxygen mobility and regeneration of active Cu phase on these surface planes is easier, which in turn facilitates higher catalytic activity through the recombination of surface oxygen atoms and desorption as molecular oxygen that replenishes active sites for subsequent catalytic cycles. As a consequence, CuO supported on CeO₂ nanorods demonstrated lower activation energy (87 kJ/mol) in N₂O decomposition reaction compared to catalysts based on CeO₂ nanocubes (102 kJ/mol) or polyhedral CeO₂ (92 kJ/mol).



KEYWORDS: N₂O decomposition, CuO defect sites, structure–activity relationship, redox catalyst, nanoshaped CeO₂

1. INTRODUCTION

Cerium dioxide (CeO₂) is a versatile material in heterogeneous catalysis, solid oxide fuel cells, solar cells, and oxygen membranes.^{1–3} It is often used to support transition or noble metals and provide distinctive catalytic functionality, for example in PROX, WGS, and H₂O₂ synthesis reactions.^{4–7} Tailored CeO₂ nanomorphology such as cubes or rods can result in drastic improvement of CeO₂-mediated catalytic performance in reactions where redox property of a catalyst is crucial, compared to randomly shaped CeO₂ crystallites.^{8–11} This manifests itself through different selectivity or improved activity, which enables the catalyst to be operated at lower temperatures. Numerous theoretical^{12–14} and experimental^{8–11,15–21} investigations have revealed that nanoshaped CeO₂ (nanocubes and nanorods) with well-defined $\{100\}$ and $\{110\}$ reactive planes show higher catalytic activity than conventional and thermodynamically more stable polyhedral CeO₂ nanoparticles. This is likely connected to lower activation energy for oxygen vacancy formation over $\{110\}$ and $\{100\}$ planes, compared to $\{111\}$.²² The benefit of nanoshaping CeO₂ is dependent on particular reaction, where this catalyst is

utilized. For example, catalysts based on CeO₂ nanorods were more active and selective in NO reduction,⁸ catalytic oxidation of ethanol in air,¹⁶ oxidative dehydrogenation of methanol,⁹ catalytic combustion of chlorobenzene,¹⁷ and water–gas shift (WGS) reaction,¹⁰ while catalysts based on CeO₂ nanocubes showed superior properties in soot combustion,¹¹ hydrogen oxidation,¹⁸ and CO-PROX.¹⁹

In this work, catalytic N₂O decomposition over CuO supported on nanoshaped CeO₂ was investigated. Catalysts commercially used for N₂O abatement (CuO/Al₂O₃, La_{0.8}Ce_{0.2}CoO₃, Co₂AlO₄/CeO₂, and Fe-ZSM-5) require either high operating temperatures or addition of reducing agents.^{23,24} Among the catalysts which can decompose N₂O under moderate temperatures (300–500 °C), CuO/CeO₂ materials show very promising results.^{25–28} Interest in N₂O decomposition arises from the fact that it is a potent greenhouse gas, produced in nitric acid and fertilizer industry, which contributes

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to ozone layer depletion.^{29,30} As a result, understanding and design of the catalyst that enables its efficient destruction is of great importance. In N₂O decomposition reaction, coupling of adjacent surface oxygen atoms and desorption (as molecular oxygen) governs the overall reaction rate.³¹ Fast replenishment of the catalytically active sites through weakening the M–O bond provides the leverage for boosting the catalytic activity. This is expected to be achieved by increasing oxygen mobility in CuO/CeO₂ catalysts.

Adamski et al. have studied N₂O decomposition using 5 mol % CuO/CeO₂ catalysts.²⁵ They have supported their experimental results by quantum chemical DFT modeling, where the most stable {111} surface of CeO₂ was modified with copper by replacing Ce⁴⁺ cations with Cu²⁺ and the creation of an adjacent oxygen vacancy. Calculations have confirmed the dominating role of oxygen atom recombination and desorption steps on catalyst activity. Zhou et al., who investigated an influence of copper loading in the CuO/CeO₂ catalyst on N₂O decomposition activity, discovered that at low copper loadings stronger synergistic effect between CuO and CeO₂ takes place, which results in good catalytic performance of studied solids.²⁶ Our previous work was dedicated to the enhancement of catalytic activity by using high surface area (HSA) CeO₂ support ($S_{BET} = 190 \text{ m}^2/\text{g}$), prepared by means of glycothermal method.^{27,28} The highest activity of CuO/CeO₂ catalyst was obtained in the presence of subnanometer CuO clusters on HSA CeO₂. It should be noted that all previous studies were carried out over random, polyhedral CeO₂ nanoparticles; therefore, the role of CeO₂ morphology and exposed crystalline planes to act as a leverage to boost N₂O decomposition activity remains unknown. This was investigated in the present study. The correlation between catalytic properties of examined materials as well as their chemical state and morphology was made possible by using HRTEM, STEM-HAADF, STEM-EDX, N₂ physisorption, DR-UV-vis, in situ DRIFTS CO, XRD, XPS, H₂-TPR, and dissociative N₂O adsorption techniques.

2. EXPERIMENTAL SECTION

2.1. Catalyst Synthesis. CeO₂ nanocubes (CeO₂-C) and nanorods (CeO₂-R) were synthesized by dissolving 53.8 g of NaOH (99% purity, Merck) in 140 mL of deionized water. Then, 84 mL of aqueous solution containing 4.9 g of Ce(NO₃)₃·6H₂O (99% purity, Sigma-Aldrich) was added under vigorous stirring. The suspension was stirred for additional 30 min and transferred into a Teflon-lined stainless steel autoclave. For preparation of CeO₂-C and CeO₂-R samples, suspension was aged 24 h at 180 and 100 °C, respectively. Aged suspensions were centrifuged at 5000 rpm and washed with deionized water until reaching pH = 7. The obtained solids were dispersed in 10 mL of deionized water, frozen by quench-freezing with LN₂, and finally dried for 24 h using freeze-dryer (Christ, model Alpha 1-2 LDplus). The samples were calcined in air at 400 °C for 3 h (heating ramp 2 °C/min). For preparation of polyhedral CeO₂ nanoparticles (CeO₂-P), synthesis conditions were identical to those of CeO₂-R with one exception: 8.96 g of NaOH was utilized instead of 53.8 g.

The following method was applied for depositing 2–8 wt % Cu over CeO₂ supports: 400 mg of CeO₂ (cubes, rods, or polyhedral nanoparticles) was dispersed in 10 mL of deionized water using an ultrasonic homogenizer (Cole-Parmer) and an appropriate amount of Cu(NO₃)₂·3H₂O (99.5% purity, Sigma-Aldrich) was added to reach the nominal loading. Then, 5 mL

of aqueous solution containing 250 mg of Na₂CO₃ (99.999% purity, Merck) was added under vigorous stirring. The formed suspension was stirred at room temperature for additional 2 h, filtered, washed with 150 mL of deionized water, redispersed in 5 mL of deionized water and dried in a freeze drier for 24 h. The obtained solid was calcined in air at 400 °C for 3 h (heating ramp 2 °C/min). Prepared materials were marked as X-Cu/CeO₂-M, where X represents Cu content in weight percent accordingly to synthesis conditions and M represents morphology of utilized CeO₂ supports—cubes, rods, or polyhedra.

2.2. Catalyst Characterization. BET specific surface area, total pore volume and pore size distribution was determined at –196 °C using a TriStar II 3020 instrument from Micromeritics. Prior to measurements, samples were degassed in N₂ stream (purity 6.0, Linde) at 90 °C for 1 h, followed by 3 h soaking at 300 °C using the Micromeritics SmartPrep degasser. The Brunauer–Emmett–Teller (BET) method was applied for specific surface area calculations. The pore size distributions were derived from the desorption branch of the isotherms employing the Barrett–Joyner–Halenda (BJH) method. The total pore volume was estimated at a relative pressure of 0.989.

X-ray diffraction measurements were performed on a PANalytical X'pert PRO diffractometer equipped with the monochromator for Cu K α 1 radiation, $\lambda = 0.15406 \text{ nm}$. Materials were scanned in the 2 θ range between 10° and 85° with 0.0348° increments, respectively, and 100 s measuring time at each increment.

H₂ temperature-programmed reduction (H₂-TPR) experiments were performed using a Micromeritics AutoChem II 2920 apparatus. Examined samples (approximately 100 mg) were preoxidized at 300 °C in 5 vol % O₂/N₂ and cooled to –40 °C. TPR analysis was performed in a 25 mL/min stream of 5 vol % H₂/Ar mixture. The samples were heated from –40 to 900 °C (CeO₂ supports) or to 500 °C (CuO/CeO₂ materials) with a 5 °C/min ramp during analysis. Deconvolution of recorded TPR profiles was performed in Origin 8.1 software using Gaussian and Lorentzian functions. Immediately following H₂-TPR examination, dissociative N₂O adsorption experiment was done for selected samples in order to determine Cu dispersion and cluster size. To selectively probe only metallic copper surface sites and avoid titration of oxygen defect sites of CeO₂ support,³² N₂O pulsing (10 vol % N₂O/He) was performed at 35 °C. Decomposition of N₂O and formation of N₂ were monitored with a TCD detector (a LN₂ cold trap was mounted on exhaust in order to condense unreacted N₂O, so only N₂ formed during N₂O pulse titration was detected by the TCD detector).

UV-vis diffuse reflectance spectra of synthesized materials were recorded at room temperature (RT) using a PerkinElmer Lambda 35 UV-vis spectrophotometer equipped with the RSA-PE-19 M Praying Mantis accessory. Pure CeO₂-C, CeO₂-R, and CeO₂-P supports were utilized to perform the instrument background correction in the range of 200–1100 nm. The scans were acquired with the speed of 120 nm/min, and the slit was set to 4 nm.

The diffuse reflectance Fourier transform infrared (DRIFT) spectra were recorded in the range of 400–4000 cm^{–1} using a FT-IR analyzer (PerkinElmer, model Frontier), equipped with a DRIFT cell and high temperature reaction chamber (Pike Technologies, model DiffusIR). Prior to CO adsorption, the samples were degassed in situ at 300 °C and N₂ flow for 30 min. After degassing, the samples were cooled to 35 °C and

exposed to 10 vol % CO/N₂ mixture for 10 min, followed by N₂ purging (50 mL/min) for 30 min. Spectra were collected at 35 °C with the resolution of 4 cm⁻¹ and accumulation of 16 scans. During temperature-programmed desorption of CO, temperature was increased from 35 to 450 °C (heating rate 10 °C/min in N₂ flow) and every 15 s the FTIR spectrum was recorded. Analysis of recorded FTIR spectra was performed in Origin 8.1 software.

X-ray photoelectron spectra were measured with ES-2403 modified spectrometer (Russia) equipped with a PHOIBOS 100 MCD analyzer (Specs GmbH), using Mg K α excitation (1253.6 eV, 10 kV, and 25 mA). The spectrometer was calibrated by binding energy (BE) of Au 4f_{7/2} = 84.0 eV and Ni 2p_{3/2} = 852.7 eV. Detailed spectra were recorded for the regions of Cu 2p, Ce 3d photoelectrons and Cu L₃VV Auger electrons with a 0.1 eV step at a pressure below 3×10^{-6} Pa. Data acquisition was realized by the SpecsLab2 software and analysis was performed by the CasaXPS software. The binding energy of XPS peaks (with the accuracy of ± 0.1 eV) was corrected by referencing to the Ce 3d_{5/2} peak at 882.0 eV (internal standards).

Morphology of synthesized materials was 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 JEOL Centurio 100 mm² EDXS detector and JEOL STEM detectors (JEOL, Tokyo, Japan) was employed.

2.3. Catalytic Experiments. Catalytic N₂O decomposition activity was tested in a fixed-bed quartz reactor using 50 mg of catalyst, diluted with 200 mg of SiC. Powdered catalyst was positioned inside the 9 mm I.D. quartz tube and fixed between two quartz wool beads. Prior to tests, catalysts were *in situ* activated in Ar flow (50 mL/min) at 400 °C for 2 h (heating rate 2 °C/min). N₂O decomposition was performed at atmospheric pressure in the temperature range between 300 and 550 °C. N₂O feed concentration was 2500 ppm, balanced by Ar, while the gas flow rate was equal to 100 mL/min (WHSV = 120 L/(g_{cat} h)). At each reaction temperature, the catalyst was allowed to stabilize for 30 min before analyzing the gas stream discharged from the reactor. Analysis of reaction products and remaining N₂O at the reactor outlet was performed by gas chromatography using Agilent 490 Micro GC (Agilent Technologies) equipped with 10 m MSSA and 10 m Porabond Q columns.

3. RESULTS AND DISCUSSION

3.1. Material Characterization. N₂ physisorption revealed a considerable difference in BET specific surface of synthesized nanoshaped CeO₂ supports (Table 1). The following decreasing trend can be established: CeO₂-P > CeO₂-R > CeO₂-C. The obtained values are in good agreement with the results of other works.⁹

Reducibility of prepared CeO₂ supports (measured by using H₂-TPR technique) is provided in Table 1 and Figure 1. H₂-TPR profile of CeO₂ usually comprises two reduction peaks, which are attributed to a two-step reduction mechanism: low-temperature reduction of surface-capping Ce⁴⁺, followed by reduction of bulk CeO₂ at higher temperature.^{11,33–35} The CeO₂-P and CeO₂-R samples exhibit a low-temperature peak between 200 and 560 °C and a high temperature peak between

Table 1. Physical–Chemical Properties of Synthesized Nanoshaped CeO₂ Supports

sample	S _{BET} (m ² /g)	crystallite size ^a (nm)	H ₂ consumption ^b (cm ³ /g)	reduction of Ce ⁴⁺ to Ce ³⁺ ^c (%)
CeO ₂ -C	29	27	3.6	19.8
CeO ₂ -R	87	11	10.4	29.4
CeO ₂ -P	115	8	15.5	39.2

^aCalculated using Scherrer equation accordingly to the (111) diffraction peak of CeO₂. ^bEvaluated from H₂ consumed between –40 and 560 °C. ^cEvaluated from H₂ consumed between –40 and 900 °C.

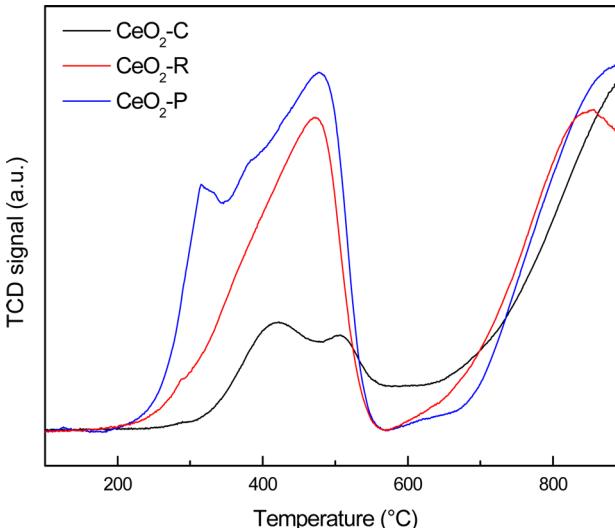


Figure 1. H₂-TPR profiles of nanoshaped CeO₂ supports.

700 and 900 °C. In the case of CeO₂-C sample, low-temperature peak is much weaker and reduction occurs predominantly at temperatures above 600 °C. This difference is related to considerably lower BET specific surface area of CeO₂-C solid compared to CeO₂-P and CeO₂-R samples, and as a result to lower fraction of reducible surface Ce⁴⁺ ions.³⁶ If we consider the average CeO₂ crystallite size, calculated from XRD analysis as representative, then the H₂ amount consumed between 200 and 560 °C suffices for 0.9, 1.8, and 1.0 monolayers of CeO₂ reduction in CeO₂-C, CeO₂-R, and CeO₂-P samples, respectively, indicating that the assigned TPR signal indeed originates from surface CeO₂ reduction.

TEM micrographs presented in Figure 2 show that the nanoshaped CeO₂ supports maintain their authentic morphology after the Cu deposition. The CeO₂-C material (Figure 2a) consists of nanoparticles exhibiting a cubic morphology with the dimensions between 13 and 55 nm with the average particle size being ~21 nm. The determined interplanar spacing of 0.27 nm (HRTEM image on the inset) corresponds to the {200} type lattice planes, which leaves {100} type planes exposed as a surface terminating plane. It should be noted that truncated nanocubes with the {110} type planes and particles with polyhedral morphology were also observed in the CeO₂-C sample, however, only in a small fraction of less than 5%.

Size of the investigated ceria nanorods (CeO₂-R, Figure 2b) is between 80 and 140 nm in length and with the average width being ~8 nm. Interplanar spacings determined from the STEM-HAADF image on the inset are 0.27 and 0.19 nm, respectively,

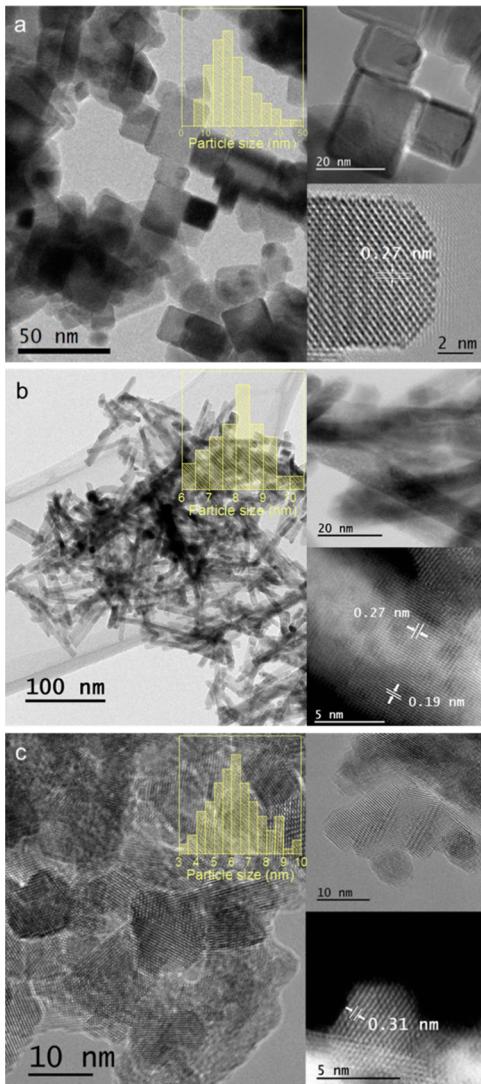


Figure 2. TEM images of 4-Cu/CeO₂-C (a), 4-Cu/CeO₂-R (b), and 4-Cu/CeO₂-P (c) catalysts.

which corresponds to {200} and {220} type lattice planes of CeO₂.

Figure 2c shows CeO₂-P sample, which is composed of nanoparticles of irregular morphologies with the average particle size being 6.5 nm. The {111} lattice fringes with interplanar spacing of 0.31 nm were identified from the STEM-HAADF micrograph shown on the inset. Based on TEM analysis, it can be concluded that synthesized nanoshaped CuO/CeO₂ materials terminate with different planes.

Diffraction patterns of materials containing 6 wt % Cu are illustrated in Figure S1. The main reflections could be assigned to FCC CeO₂ (PDF data file 03-065-5923). Only in 6-Cu/CeO₂-C sample, very small peaks belonging to most intensive (1̄11) and (111) reflections of CuO (PDF 00-048-1548) were observed as a result of its lowest BET specific surface area, which consequently results in lower CuO dispersion. For solids containing 2 and 4 wt % of Cu, no diffraction peaks belonging to ordered copper phase can be detected.

In order to determine the particle size of CuO, STEM-HAADF, STEM-EDX, and N₂O titration techniques were utilized (Table 2). Two series of materials were analyzed: catalysts containing the same copper loading on differently

Table 2. Results of N₂O Adsorption Measurements

sample	Cu dispersion (%)	d _{Cu} ^a (nm)
2-Cu/CeO ₂ -R	60.2	1.8
4-Cu/CeO ₂ -C	21.7	5.1
4-Cu/CeO ₂ -R	45.7	2.4
4-Cu/CeO ₂ -P	52.4	2.1
6-Cu/CeO ₂ -R	35	3.1
8-Cu/CeO ₂ -R	20.3	5.4

^aMeasured by means of dissociative N₂O adsorption.

shaped supports (i.e., 4-Cu/CeO₂-C, 4-Cu/CeO₂-R, and 4-Cu/CeO₂-P samples) and materials based on the same support but having different Cu contents (i.e., 2-Cu/CeO₂-R, 4-Cu/CeO₂-R, 6-Cu/CeO₂-R, and 8-Cu/CeO₂-R samples). In the first group of solids, the Cu dispersion increased with increasing BET specific surface area (21.7, 45.7, and 52.4% for 4-Cu/CeO₂-C, 4-Cu/CeO₂-R, and 4-Cu/CeO₂-P catalysts, respectively). With increasing Cu loading from 2 to 8 wt %, Cu dispersion decreased from 60.2 to 20.3% on CeO₂-R support, which corresponds to an increase of CuO cluster size from 1.8 to 5.4 nm.

The STEM-EDX analysis was performed for samples containing 4 wt % of Cu (Figure 3). The 4-Cu/CeO₂-C sample showed nonuniform size distribution of the Cu-containing particles, with the particles sizes ranging from 3 to 15 nm (Figure 3a). More homogeneous Cu distribution was observed on CeO₂-R and CeO₂-P samples. Cu-containing particles size for these two samples varied from 1.5 to 4.5 nm, with the average size being ~2 nm. Also, over CeO₂-R and CeO₂-P materials, clusters containing one or several copper atoms were also observed to densely populate the CeO₂ support. This was not the case with the CeO₂-C based catalyst. The STEM-EDX results are in good agreement with data obtained from the dissociative N₂O adsorption measurements (Table 2).

UV-vis diffuse reflectance spectra of solids containing 2 and 4 wt % of Cu are presented in Figures S2 and S3. All materials containing 2 wt % Cu have two peaks with maxima located at 450–470 nm and 750–800 nm. The first peak could be attributed to Cu¹⁺ clusters and/or bis(μ -oxo)dicopper core ([Cu₂O]²⁺), while the second peak is due to d-d Cu²⁺ transition in more or less tetragonally distorted O_h symmetry (these attributions were thoroughly discussed in our previous works^{27,28}). Increasing Cu loading to 4 wt % in the case of 4-Cu/CeO₂-C sample results in appearance of an additional absorption peak at 600 nm (Figure S3), which is most likely a consequence of segregated bulk CuO.^{28,37,38} Relatively low BET specific surface area of this sample results in poor dispersion of Cu (further confirmed by both N₂O chemisorption experiments and TEM investigation) and formation of larger CuO particles. At the same time, for high surface area CeO₂-R and CeO₂-P based materials, peak at 600 nm appears only for samples with Cu loading higher than 6 wt % (Figure S4).

Additional information on surface Cu oxidation states in Cu/CeO₂ catalysts was obtained by FTIR spectroscopy with adsorbed CO (Figure S5). Position of characteristic Cu-carbonyl peaks is very sensitive to oxidation states of Cu (Cu²⁺, Cu⁺, and Cu⁰). Vibrations belonging to CO adsorbed on Cu sites can be distinguished as (i) Cu²⁺ carbonyl species with absorption above 2140 cm⁻¹, (ii) Cu⁺ carbonyl species with absorption between 2140 and 2110 cm⁻¹, and (iii) Cu⁰

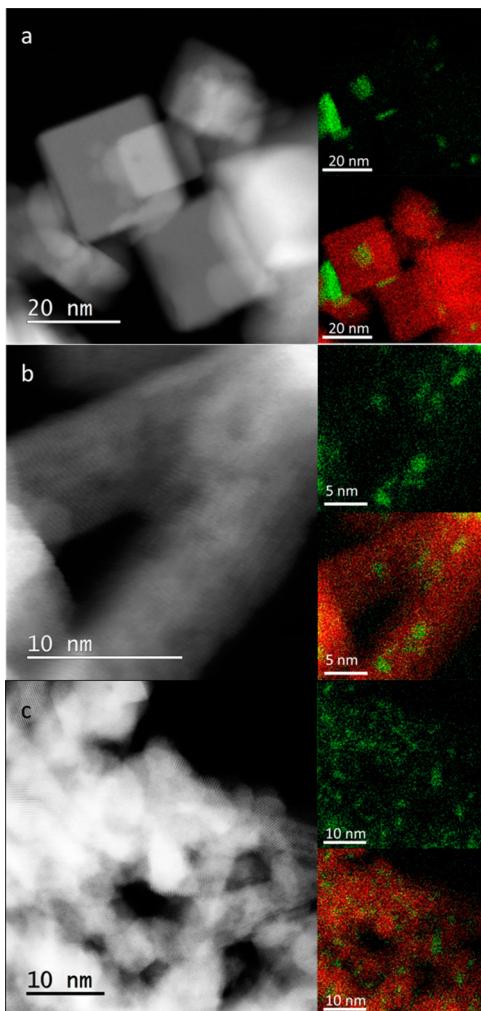


Figure 3. STEM image and EDX mapping of Cu as well as overlay of Ce and Cu distribution observed for 4-Cu/CeO₂-C (a), 4-Cu/CeO₂-R (b), and 4-Cu/CeO₂-P (c) catalysts.

carbonyl species which usually absorb at a frequency lower than 2110 cm⁻¹.^{39–44} By applying the second derivative (for resolving the actual number of overlapping peaks, Figures S6–S8) and temperature resolved in situ DRIFT spectroscopy (Figure 4), extraction of valuable information from the apparently simple spectra was possible. For detailed interpretation please refer to the Supporting Information.

Copper carbonyl spectra of CeO₂-C, CeO₂-R, and CeO₂-P based catalysts all exhibit absorption peaks at 2118, 2102, 2092, 2067, and 2056 cm⁻¹; whereas, peaks with maximum at 2140 and 2110 cm⁻¹ are characteristic only for 4-Cu/CeO₂-R and 4-Cu/CeO₂-P samples. The presence of Cu⁺ defect sites in several-atom Cu clusters, which are visualized over CeO₂-P and CeO₂-R based materials during EDX mapping (Figure 3), results in an additional peak at 2140 cm⁻¹ in 4-Cu/CeO₂-R and 4-Cu/CeO₂-P samples that causes broadening of the CO carbonyl signal. Smaller CuO clusters contain more unsaturated and highly reactive surface defect sites, which produce additional absorption bands at higher wavenumbers and broaden the overall CO carbonyl absorption band. The presence of both Cu⁰ and Cu⁺ sites in Cu/CeO₂ catalysts indicates facile reducibility and occurrence of copper in low oxidation states, which is especially important for utilizing these catalysts in N₂O decomposition reaction.²⁸

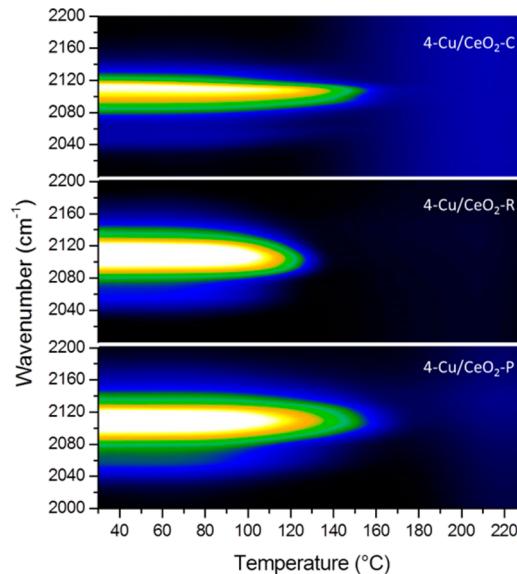


Figure 4. Results of CO-TPD experiments presented as color surfaces for CuO/CeO₂ solids containing 4 wt % of Cu.

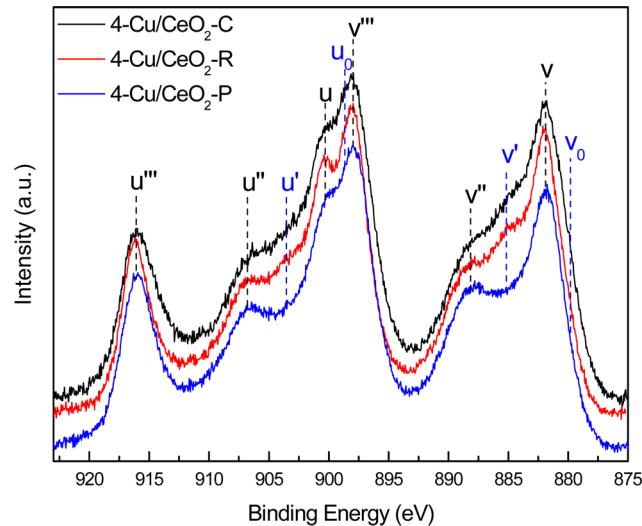
Temperature-resolved in situ DRIFTS analysis (Figure 4) revealed different thermal stability of individual Cu-carbonyls in the studied materials. Absorption in the region between 2160 and 2040 cm⁻¹ disappeared at 130 °C for 4-Cu/CeO₂-R sample, while Cu carbonyls in 4-Cu/CeO₂-P and 4-Cu/CeO₂-C samples were stable up to 160 °C. Lower stability of carbonyls on the surface of 4-Cu/CeO₂-R solid could be ascribed to easier reduction of Cu⁺ sites into Cu⁰ by adsorbed CO molecules, indicating superior redox properties of this sample compared to 4-Cu/CeO₂-P and 4-Cu/CeO₂-C materials.

In order to identify surface oxidation state of Cu, X-ray photoelectron spectroscopy was utilized. It is known that Cu electronic state (Cu⁰, Cu⁺, and Cu²⁺) can be identified from the position and shape of both photoelectron Cu 2p_{3/2} line and Auger Cu L₃VV electron line.^{45–47} The lack of shakeup satellites at higher apparent Cu 2p_{3/2} binding energy than the main core level indicates the absence of Cu²⁺ species (Figure S9). Furthermore, Cu 2p_{3/2} band is centered at 932.3–932.7 eV, which is characteristic of reduced Cu species. The Cu L₃VV Auger line and modified Auger parameter were used to identify Cu electronic state. The Auger kinetic energies for bulk Cu₂O and Cu metal are 916.6 and 918.3 eV, respectively. The Auger Cu L₃VV electron line is centered at about 916.1–917.1 eV, which can be ascribed to the presence of Cu⁺. Modified Auger parameter, which was calculated by adding binding energy of Cu 2p_{3/2} photoelectron peak and kinetic energy of Cu L₃VV Auger peak, confirms the presence of Cu⁺ species on the catalysts surface (Table 3).⁴⁶ Therefore, we can conclude that copper in all examined solids exists in Cu⁺ oxidation state, which is in line with the results of CO chemisorption experiments.

The Ce 3d core-level XPS spectra for the studied solids basically denote a mixture of both Ce⁴⁺ and Ce³⁺ oxidation states (Figure 5), indicating that catalyst surface is partially reduced due to oxygen desorption and formation of oxygen vacancies. However, degree of surface CeO₂ reduction significantly alters for different CeO₂ morphologies. XPS spectrum of 4-Cu/CeO₂-P catalyst exhibits six photoelectron peaks corresponding to three pairs of spin-orbit split doublets

Table 3. Results of XPS Analysis

sample	Cu 2p _{3/2} BE (eV)	Cu L ₃ VV KE (eV)	Cu Auger parameter α' (eV)	Ce ³⁺ content (%)
4-Cu/ CeO ₂ -C	932.7	917.1	1849.8	33
4-Cu/ CeO ₂ -R	932.6	916.1	1848.7	41
4-Cu/ CeO ₂ -P	932.3	916.7	1849.0	26

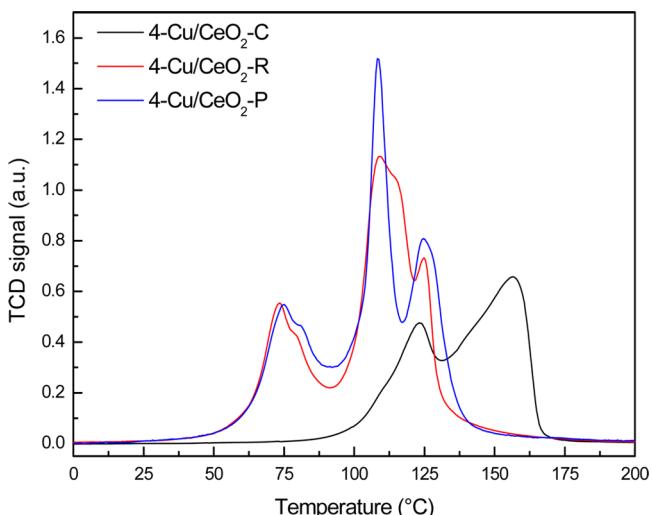
**Figure 5.** Ce 3d XPS spectra of catalysts containing 4 wt % of Cu.

(v, v'', v''', u, u'', and u'''), which can be ascribed to 4f configuration of Ce⁴⁺ ion.^{48–52} The appearance of new photoelectron peaks at 885.1 and 903.6 eV (v' and u') as well as peak broadening at 879.8 and 898.7 eV (v₀ and u₀) for 4-Cu/CeO₂-C and 4-Cu/CeO₂-R samples provides an evidence of the presence of Ce³⁺.^{51–53} The percentages of Ce⁴⁺ and Ce³⁺ in the studied solids were determined after Spline linear baseline subtraction and by fitting of Ce 3d core-level XPS spectra with symmetric Gaussian–Lorentzian functions. Results of deconvolution are presented in Figures S10–S12 and Table 3. Observed difference regarding the amount of ceria present in Ce³⁺ oxidation state (33% for 4-Cu/CeO₂-C, 41% for 4-Cu/CeO₂-R and 26% for 4-Cu/CeO₂-P) originates from the exposed surface planes of nanoshaped CeO₂ supports. CeO₂-C and CeO₂-R samples expose {100} and {110} surface planes; desorption of oxygen from these surfaces occurs more easily, which results in higher Ce³⁺ content. On the other hand, CeO₂-P material predominantly exposes the most stable {111} planes; therefore, the extent of Ce³⁺ in 4-Cu/CeO₂-P sample is lower. These results are in good agreement with the work of Sreeremya et al., where the highest concentration of Ce³⁺ (44.3%) was found in the sample containing ceria nanorods and nanocubes, while in polyhedral CeO₂ only 26.2% of Ce³⁺ was present.⁵⁴

The lability of oxygen in the structure of Cu/CeO₂-R catalysts was evaluated using H₂-TPR analysis (Figure S13). Reduction of studied catalysts occurred between 50 and 150 °C. Co-reduction of the CeO₂ support is confirmed by quantifying H₂ consumption, which greatly surpasses the theoretical values, required for complete reduction of CuO to Cu⁰ (Table S1). H₂ consumed for CeO₂ reduction is very similar for all CeO₂-R based materials, regardless of Cu loading

and equals to $13.2 \pm 1 \text{ cm}^3/\text{g}$. This value is comparable to H₂ consumed for surface reduction of bare CeO₂-R, 10.4 cm³/g (Figure 1 and Table 1). Reduction of Cu/CeO₂-R materials occurring at temperatures significantly lower than those of individual CuO and CeO₂ components is due to electronic interactions between the two oxide phases that weaken the metal–oxygen bonds (so-called “synergetic effect”).^{55,56} For samples with higher Cu loading, reduction peaks shift to higher temperatures, which is due to lower Cu dispersion and increase of CuO cluster size (confirmed by N₂O titration experiments).

Figure 6 and Table S1 provide H₂-TPR results for samples containing 4 wt % of Cu supported on differently nanoshaped

**Figure 6.** H₂-TPR profiles of CuO/CeO₂ catalysts containing 4 wt % of Cu.

CeO₂ supports (i.e., CeO₂-C, CeO₂-R, and CeO₂-P). The amount of H₂ consumed for reduction of CeO₂ support correlates with BET specific surface area of analyzed materials (CeO₂-P > CeO₂-R > CeO₂-C) and is very similar to the values obtained during reduction of pure CeO₂. Reduction profiles significantly differ among examined solids and depend on morphology of CeO₂ support. Reduction of 4-Cu/CeO₂-C sample occurs at temperatures 50 °C higher than for CeO₂-R and CeO₂-P based catalysts. This phenomenon is caused by lower CuO dispersion and formation of larger CuO particles as well as bulk CuO aggregates (up to 15 nm) on CeO₂-C support.

3.2. Catalytic N₂O Decomposition. N₂O conversions obtained over nanoshaped Cu/CeO₂ catalysts as a function of reaction temperature exhibit typical S-shaped curves (Figures S14–S16). Synthesized materials show excellent catalytic stability, which was confirmed by long-term stability tests in the period of 50 h time on stream (Figure S17). Activation energies (Table 4) vary from 87 to 102 kJ/mol for solids containing 4 wt % of Cu. Table S2 shows a comparison of E_a calculated in this work and activation energies for materials (Cu/ZSM-5, Cu/Al₂O₃, Co/ZSM-5, Fe/ZSM-5) utilized for N₂O decomposition by other research groups.^{57–59} The activation energy for 4-Cu/CeO₂-R sample is about 43–64 kJ/mol lower than E_a values for other Cu based solids.

Activity, expressed per amount of copper (Figure 7) goes through a maximum at 4 wt % Cu loading for all nanoshaped CeO₂ supports. Catalysts based on CeO₂-C support demonstrate lower activity over the whole concentration range of

Table 4. Catalytic Properties of Nanoshaped CeO₂ Supported CuO Catalysts

sample	<i>E_a</i> (kJ/mol)	activity ^a	<i>A_{norm}</i> ^b (min ⁻¹)
4-Cu/CeO ₂ -C	102	28.2	0.130
4-Cu/CeO ₂ -R	87	63.2	0.138
4-Cu/CeO ₂ -P	92	58.0	0.111

^aActivity measured in $\mu\text{mol}(\text{N}_2\text{O})/(\text{mmol}(\text{Cu}) \text{ min})$ at $T = 375^\circ\text{C}$.

^bNormalized activity measured at $T = 375^\circ\text{C}$ by counting surface Cu atoms determined by means of dissociative N₂O chemisorption.

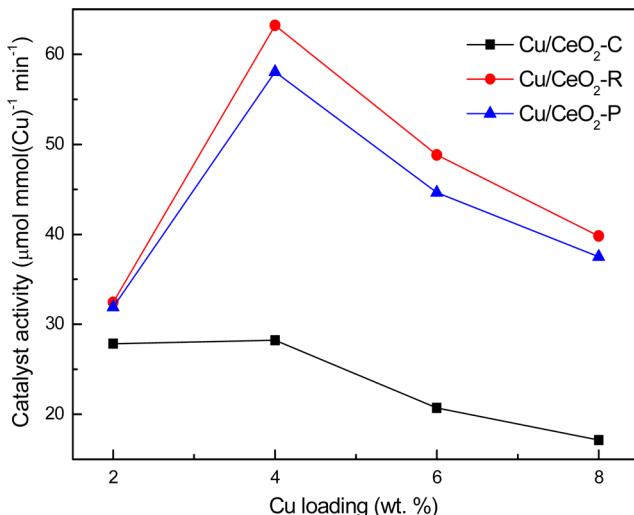
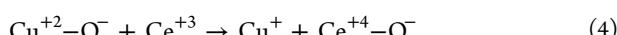


Figure 7. Activity of nanoshaped CuO/CeO₂ catalysts measured at $T = 375^\circ\text{C}$.

deposited Cu, compared to CeO₂-P and especially CeO₂-P based solids. Small CuO clusters possess the highest activity in N₂O decomposition reaction, while either atomically dispersed copper or bulk CuO phase have lower intrinsic catalytic activity.²⁸ This is due to the requirement of at least two adjacent Cu atoms to favor merging of two oxygen atoms and its desorption as molecular oxygen.²⁷ According to a tentative mechanism of nitrous oxide decomposition that we propose, N₂O molecule adsorbs on Cu⁺ active sites and, after N–O bond cleavage accompanied by N₂ molecule liberation, formation of Cu²⁺–O[−] species takes place (eqs 1 and 2). Regeneration of active Cu⁺ sites can be achieved either by a recombination step (if two oxidized copper sites are close enough to each other) or through reduction by Ce³⁺ (eqs 3 and 4). The latter step is likely to occur because of synergistic effect and high lattice oxygen mobility between CuO and CeO₂ active phases, which is confirmed by results of H₂-TPR examination. Formed Ce⁴⁺ can further desorb oxygen and regenerate oxygen vacancy and Ce³⁺ species (eq 5).



Lower intrinsic activity of copper sites in bulk CuO clusters originates from their lower surface energy as a result of higher coordination and lower number of very active defect sites.

Therefore, no improvement in catalytic activity for materials containing more than 4 wt % Cu could be attributed to lower Cu dispersion as well as formation of larger CuO clusters, which was confirmed by results of DR UV-vis and H₂-TPR experiments.

By comparing the activity of catalysts, normalized per number of surface Cu atoms ($A_{\text{norm}} = n(\text{N}_2\text{O})_{\text{decomposed}}/[n(\text{Cu})_{\text{surf}} \times \text{time}]$) (Figure 8 and Table 4), shape-dependent

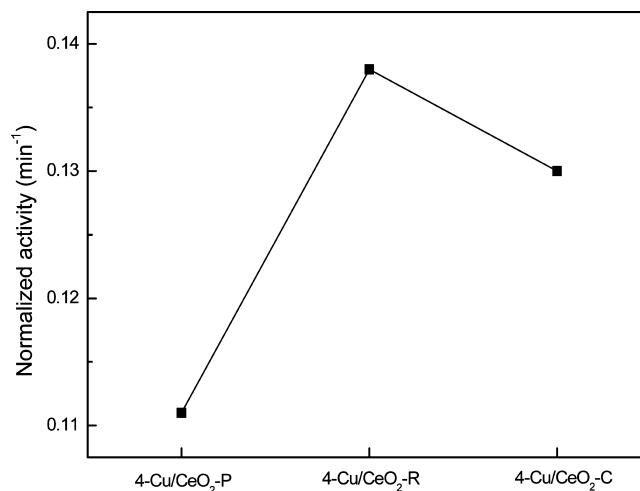


Figure 8. Normalized activity for nanoshaped CuO/CeO₂ catalysts measured at $T = 375^\circ\text{C}$.

activity of CuO/CeO₂ catalysts is revealed, indicating higher activity of copper deposited over the {100} and {110} planes of CeO₂ support. The A_{norm} value for 4-Cu/CeO₂-P sample is around 20% lower in comparison with corresponding CeO₂ nanocubes and nanorods based samples (0.130 min⁻¹ for 4-Cu/CeO₂-C, 0.138 min⁻¹ for 4-Cu/CeO₂-R, and 0.111 min⁻¹ for 4-Cu/CeO₂-P).

Above-mentioned results signify the effect of exposed surface planes of ceria support on the catalyst reactivity in N₂O decomposition. We can claim that copper clusters supported on {100} and {110} surface planes of CeO₂ are more active compared to clusters deposited on {111} planes of CeO₂-P support. It was shown by theoretical investigation that {100} and {110} surface planes possess lower activation energy for oxygen desorption and formation of anion vacancies than {111} surface plane of CeO₂ (2.26, 2.1, and 2.76 eV, respectively), which allows easier oxygen desorption and formation of oxygen vacancies.²² We have confirmed this fact by results of XPS examination, where formation of Ce³⁺ was favored on ceria nanorods and nanocubes based samples, while polyhedral ceria surface with {111} planes contains less Ce³⁺ ions. Strong interaction between CeO₂ support and active Cu phase (confirmed by H₂-TPR examination) further promotes oxygen mobility between two phases and enables easier oxygen desorption especially in the case where Cu clusters populate {100} and {110} surface planes. The above-mentioned steps are crucial in the N₂O decomposition mechanism, which implies that A_{norm} values of CuO/CeO₂ catalysts are highly sensitive to surface planes exposed by the ceria support. To sum up, combination of very reactive {100} and {110} surface planes of ceria nanorods support with high values of BET specific surface area and Cu dispersion results in superior catalytic properties of CeO₂-R based solids.

4. CONCLUSIONS

The lability of surface oxygen atoms in nanoshaped CeO₂ depends on the exposed crystalline planes and defect sites and decreases in the following order: CeO₂-R > CeO₂-C > CeO₂-P. Accordingly to DRIFTS examination, surface Cu is present as Cu⁺ and Cu⁰ oxidation states. XPS analysis shows that under high vacuum, surface of CeO₂-R and CeO₂-C solids is enriched with Ce³⁺ (41 and 33%, correspondingly), while the one in CeO₂-P sample has the lowest Ce³⁺ content (26%).

Deposition of copper decreases the initiation of CeO₂ reduction by about 150 °C, but the extent of its reduction is only negligibly influenced by copper addition. Cu clusters populating easily reducible {100} and {110} planes of CeO₂, as preferentially exposed on CeO₂-R and CeO₂-C supports, exhibit normalized activity about 20% higher, compared to copper on {111} planes of CeO₂-P. The most likely reasons for the observed catalytic performance are mainly produced from combination of more reactive {110} and {100} planes exposed on the CeO₂ nanorod surface with high BET specific surface area of this support, the latter enabling higher active metal dispersion and formation of highly reducible copper defect sites.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acscatal.5b01044](https://doi.org/10.1021/acscatal.5b01044).

Interpretation of DRIFTS results, Tables S1 and S2, and Figures S1–S17 ([PDF](#))

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Notes

The authors declare no competing financial interest.

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