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High-porosity Pt–CeO₂ nanosponges as oxidation catalyst†

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Pt–CeO₂ nanosponges (1 wt% Pt) with high surface area (113 m² g⁻¹), high pore volume (0.08 cm³ g⁻¹) and small-sized Pt nanoparticles (1.8 ± 0.4 nm) are prepared by thermal decomposition of a cerium oxalate precursor and examined for catalytic oxidation of CO, volatile organic compounds (VOCs), and NH₃. The cerium oxalate precursor Ce₂(C₂O₄)₃·10H₂O is prepared by aqueous precipitation from Ce(NO₃)₃·6H₂O and K₂C₂O₄·H₂O and thermally converted to CeO₂ nanosponges by heating in air. Optimal conditions for decomposition in terms of surface area and porosity are observed at 350 °C for 20 min. Finally, the CeO₂ nanosponges are decorated with small-sized Pt nanoparticles, using a wet-chemical impregnation with Pt(ac)₂ in methanol. Electron microscopy with tomography, electron spectroscopy and further methods (TG, XRD, FT-IR, sorption analysis) are used to characterize the catalyst composition and especially the structure and porosity of the Pt–CeO₂ nanosponges as well as the uniform distribution of the Pt nanoparticles. The Pt–CeO₂ nanosponges show good thermal stability (up to 400 °C) and, already as a new, non-optimized catalyst, promising activity for catalytic oxidation of CO, VOCs, NH₃ as indicated by high activities in terms of low and stable light-out and light-off temperatures as well as a high selectivity to N₂ (for NH₃ oxidation) with >80% at 170–250 °C.

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Introduction

Ceria, in combination with a precious metal, is specifically interesting for oxidation catalysis as it combines several beneficial properties.¹ Thus, the oxidation states Ce³⁺ and Ce⁴⁺ – specifically in the solid phases Ce₂O₃ and CeO₂ – are of comparable stability,² which promotes reversible redox reactions. Moreover, the structures of Ce₂O₃ (defect CaF₂ type)³ and CeO₂ (CaF₂ type)⁴ are in close relation so that oxygen can be reversibly stored and released. With a Mars–van-Krevelen-like mechanism,⁵ oxygen at the interface of ceria and a noble metal (e.g., Pt, Pd, Ru) can be provided for a catalytic oxidation of species (e.g., CO, volatile organic compounds/VOCs, NH₃) adsorbed on the precious metal.⁶ As a result, ceria is widely

applied as a metal-oxide support in heterogeneous catalysis.¹ Particularly important are emission control,⁷ reverse water–gas shift, electrocatalysis and fuel cells,⁷ direct synthesis of H₂O₂,⁸ or the detection of combustible gases.⁹

To promote heterogeneous catalytic reactions with high activity at low temperatures, ceria with high surface area and high porosity is required.¹⁰ On the one hand, this guarantees a sufficient contact between the solid metal-oxide support and the gaseous reactants. On the other hand, a uniform distribution of small-sized noble metal particles is possible over the large surface of the metal-oxide support. Due to its high oxidation conductivity, specifically at elevated temperature (>200 °C), however, ceria is also known for limited thermal stability. Thus, sintering due to the high oxide-ion mobility can result in a rapid decrease of surface area and porosity.¹¹ Currently, the highest surface areas for ceria are reported with about 100 m² g⁻¹ for mesoporous mixtures of ceria and zirconia, using the latter to stabilize ceria.¹² Higher surface areas of 170 m² g⁻¹ and 250 m² g⁻¹ were yet only reported for very small (1–5 nm) massive CeO₂ nanoparticles.¹³ Despite a high surface area as such, ceria nanoparticles are not suitable for establishing porous 3D-networks and tend to form close-packed particle arrays. Furthermore, the respective high-surface-area CeO₂ materials are not stable at higher temperature or were not even examined in regard of sintering and/or thermal shrinkage of the surface area.

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Aiming at ceria metal-oxide supports with high surface area and porosity, we previously focused on ceria hollow nanospheres using either water droplets¹⁴ or sodium-chloride templates.¹⁵ The resulting ceria hollow nanospheres exhibited surface areas up to $210 \text{ m}^2 \text{ g}^{-1}$ and pore volumes up to $0.08 \text{ cm}^3 \text{ g}^{-1}$.^{14,15} The preparation and removal of the respective template, however, resulted in additional process steps for synthesis and purification. To facilitate the synthesis and specifically to reproducibly realize higher quantities, we here suggest a novel concept to obtain high-porosity ceria based on a cerium-oxalate precursor, which is thermally decomposed to ceria at low temperature ($350 \text{ }^\circ\text{C}$). After wet-chemical impregnation with $\text{Pt}(\text{ac})_2$, Pt-CeO₂ nanosponges with high surface area ($113 \text{ m}^2 \text{ g}^{-1}$), high pore volume ($0.08 \text{ cm}^3 \text{ g}^{-1}$), small-sized Pt nanoparticles ($1.8 \pm 0.4 \text{ nm}$) and good temperature stability (up to $400 \text{ }^\circ\text{C}$) were obtained and examined in regard to the catalytic oxidation of CO, VOCs (volatile organic compounds), and NH₃.

Results and discussion

Synthesis of Ce₂(C₂O₄)₃ precursor particles

The need of high surface area and high porosity of CeO₂ for catalysis was most often addressed either by hydrothermal, solvothermal or sol-gel processes,¹⁶ template-based techniques,^{16,17} or the preparation of nanostructured ceria with certain size and shape (*e.g.*, hollow spheres, nanorods, nanotubes).¹⁸ These approaches, on the one hand, require the presence of the respective porous host lattices and templates as well as a deep infiltration with CeO₂ and/or a complete removal of the template. On the other hand, a sufficient thermal and chemical stability of the resulting material structure at the transient conditions occurring for catalysis (*e.g.*, variable temperature and pressure, presence of moisture and/or catalyst poisons) is mandatory. Concepts to transfer a suitable ceria precursor into high-surface porous ceria are rare by now. Most comparable is the so-called Pechini method^{16,19} with, for instance, Ce(NO₃)₃ converted to CeO₂ *via* combustion, with *e.g.*, glucose acting as a gelation agent.²⁰ The temperature of reaction and the resulting surface area and porosity, however, are difficult to control *via* this approach.

Aiming at a suitable ceria precursor, which can be thermally transferred to CeO₂ at moderate temperature, we here use cerium oxalate (Fig. 1a). Metal oxalates are generally well-known for low-temperature decomposition to metal oxides with release of CO/CO₂. In this regard, cerium oxalate was yet only described to obtain nanocrystalline ceria with rod-type shape.²¹ Since Ce₂(C₂O₄)₃ is insoluble in water, the precursor particles can be obtained by simple aqueous precipitation. Accordingly, a solution of Ce(NO₃)₃·6H₂O in ethanol was injected with a solution of K₂C₂O₄·H₂O in water. Thereafter, the formation of Ce₂(C₂O₄)₃ is indicated by the instantaneous nucleation of particles and the formation of a suspension. The resulting colourless solid was then separated by centrifugation and purified by repeated redispersion/centrifugation in/from water.

The as-prepared Ce₂(C₂O₄)₃ precursor particles were characterized by Fourier-transform infrared (FT-IR) spectroscopy, X-ray powder diffraction (XRD), scanning transmission electron microscopy (STEM), and sorption analysis. FT-IR spectra of the Ce₂(C₂O₄)₃ precursor particles clearly evidences the presence of the characteristic vibrations of [C₂O₄]²⁻ ($\nu_{\text{as}}(\text{C}=\text{O})$: 1630 cm^{-1} , $\nu_{\text{s}}(\text{C}=\text{O})$: 1315 cm^{-1} , $\delta_{\text{as}}(\text{COO})$: 790 cm^{-1} , $\delta_{\text{s}}(\text{COO})$: 495 cm^{-1}), which are also in accordance with K₂C₂O₄·H₂O as the starting material (Fig. 2a). In addition, $\nu(\text{O}-\text{H})$ ($3600\text{--}3000 \text{ cm}^{-1}$) indicates the presence of water. After drying at room temperature in vacuum, XRD only shows non-specific, broad reflexes of a predominately amorphous compound (Fig. 2b). Subsequent to heating ($70 \text{ }^\circ\text{C}$, 8 h), the precursor particles become crystalline and can be clearly identified as Ce₂(C₂O₄)₃·10H₂O. Scanning transmission electron microscopy (STEM) shows rod- to platelet-shaped particles with a length of $0.5\text{--}3.5 \text{ }\mu\text{m}$ and a diameter of $200\text{--}650 \text{ nm}$ (Fig. 2c). Detail STEM images indicate the precursor particles to be non-porous (Fig. 2d). Finally, sorption analysis with nitrogen as the sorbent and an analysis *via* the Brunauer-Emmett-Teller (BET) approach confirms the presence of a dense material with a surface area of $14 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of $0.015 \text{ cm}^3 \text{ g}^{-1}$ only (Table 1, Fig. 3c and S1†).

Thermal decomposition to CeO₂ nanosponges

For the thermal conversion of the Ce₂(C₂O₄)₃ precursor particles to porous CeO₂ nanosponges (Fig. 1b), first of all, suitable

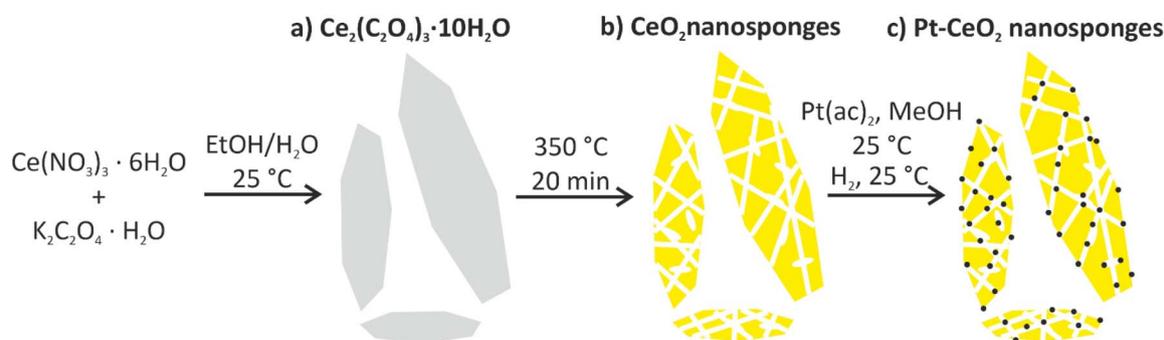


Fig. 1 Scheme illustrating the synthesis of Pt-CeO₂ nanosponges: (a) formation of rod- to platelet-shaped Ce₂(C₂O₄)₃·10H₂O precursor particles, (b) thermal conversion of Ce₂(C₂O₄)₃·10H₂O precursor particles to CeO₂ nanosponges, (c) wet-chemical impregnation of the CeO₂ nanosponges with a solution of Pt(ac)₂ in methanol followed by Pt nanoparticle formation (at $25 \text{ }^\circ\text{C}$).



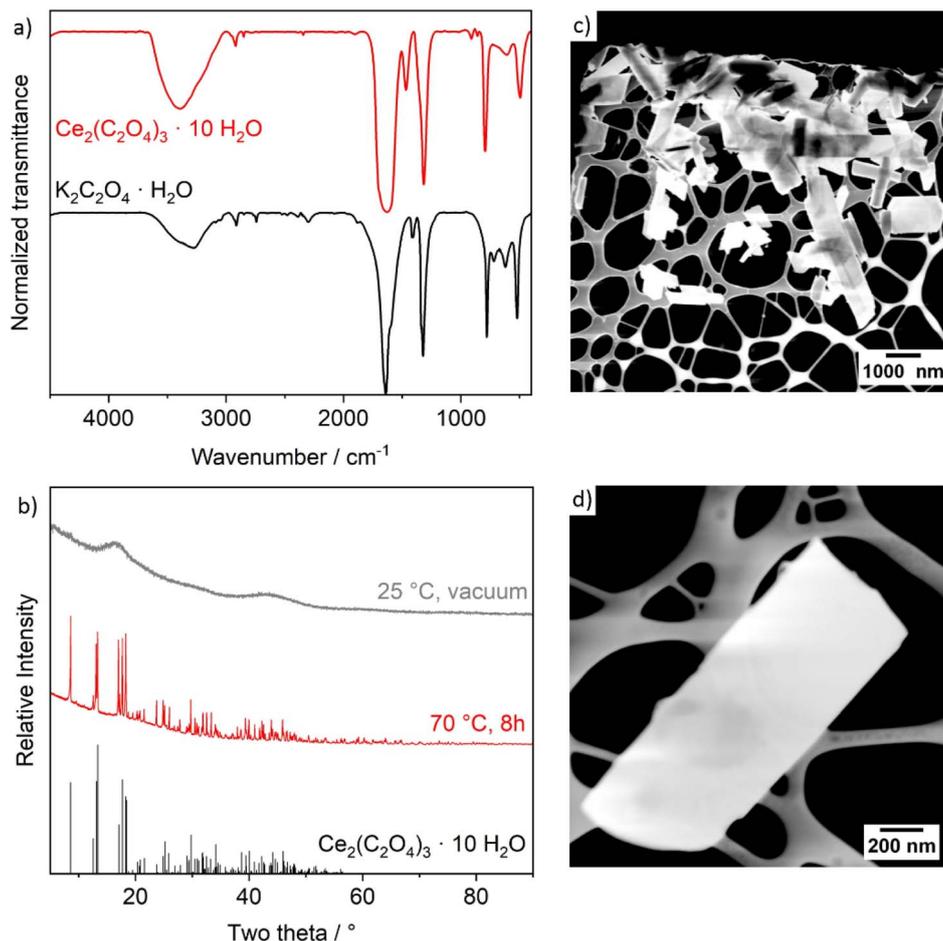


Fig. 2 Characterization of the $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ precursor particles: (a) FT-IR spectrum ($\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ as a reference), (b) XRD ($\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ as a reference, ICDD-No. C01-075-7101), (c) STEM overview image, (d) STEM detail image of a single precursor particle.

Table 1 Surface area and pore volume of the $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ precursor particles as well as of the CeO_2 nanosponges depending on the conditions of thermal decomposition

Conditions for thermal decomposition	Surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)
$\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ (as-prepared)	14	0.015
300 °C (2 h, 1 K min^{-1})	86	0.057
350 °C (20 min)	113	0.082
400 °C (20 min)	93	0.100

conditions for the thermal decomposition need to be identified. Accordingly, thermogravimetry (TG) was conducted (Fig. 3a). Here, thermal decomposition is observed in two steps. First, a mass loss of 22% is observed at 30–210 °C, which is followed by a second mass loss at 210–400 °C with 28%. Hereof, the first step can be related to the evaporation of water (calculated: 24.9%). The second step relates to the loss of CO and CO_2 (calculated: 27.6%) according to the following reaction: $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \rightarrow 2\text{CeO}_2 + 4\text{CO} + 2\text{CO}_2$. Based on this thermal behaviour, in principle, there are several options for decomposition: (i) a fast decomposition putting a powder sample into

the already hot oven at the upper temperature limit (≥ 350 °C) or (ii) a slow decomposition with a ramp (1 K min^{-1}) from room temperature to the lower temperature limit of decomposition (≤ 300 °C). Aiming at high surface area and porosity, both measures may have disadvantages. Fast heating may lead to a gas evolution being too fast and, thereby, destroying the thin walls of the intended nanosponges. Slow heating may cause extensive sintering due to the significantly longer time of the decomposition reaction. Therefore, we have examined different conditions (Table 1, Fig. 3c). With a surface area of $113 \text{ m}^2 \text{g}^{-1}$ and a pore volume of $0.082 \text{ cm}^3 \text{g}^{-1}$, fast heating (350 °C, 20 min) and fast decomposition turn out to be optimal (Table 1, Fig. 3c and S2a†). When exceeding 350 °C, the pore volume increases due to the formation of larger pores but with the surface area decreasing at the same time (Table 1, Fig. 3c). In regard of the pore diameter, predominately mesopores (≥ 25 Å and ≤ 45 Å) were observed (ESI Fig. S2b†). With these values, the CeO_2 nanosponges are among the highest surface areas reported for CeO_2 . The highest specific surface area was yet reported with $100 \text{ m}^2 \text{g}^{-1}$ for mesoporous zirconia-ceria mixtures¹² or with $170 \text{ m}^2 \text{g}^{-1}$ for very small (3–5 nm) massive CeO_2 nanoparticles.¹³ Higher values of $250 \text{ m}^2 \text{g}^{-1}$ were – to the best of our knowledge – only reported for microemulsion-made



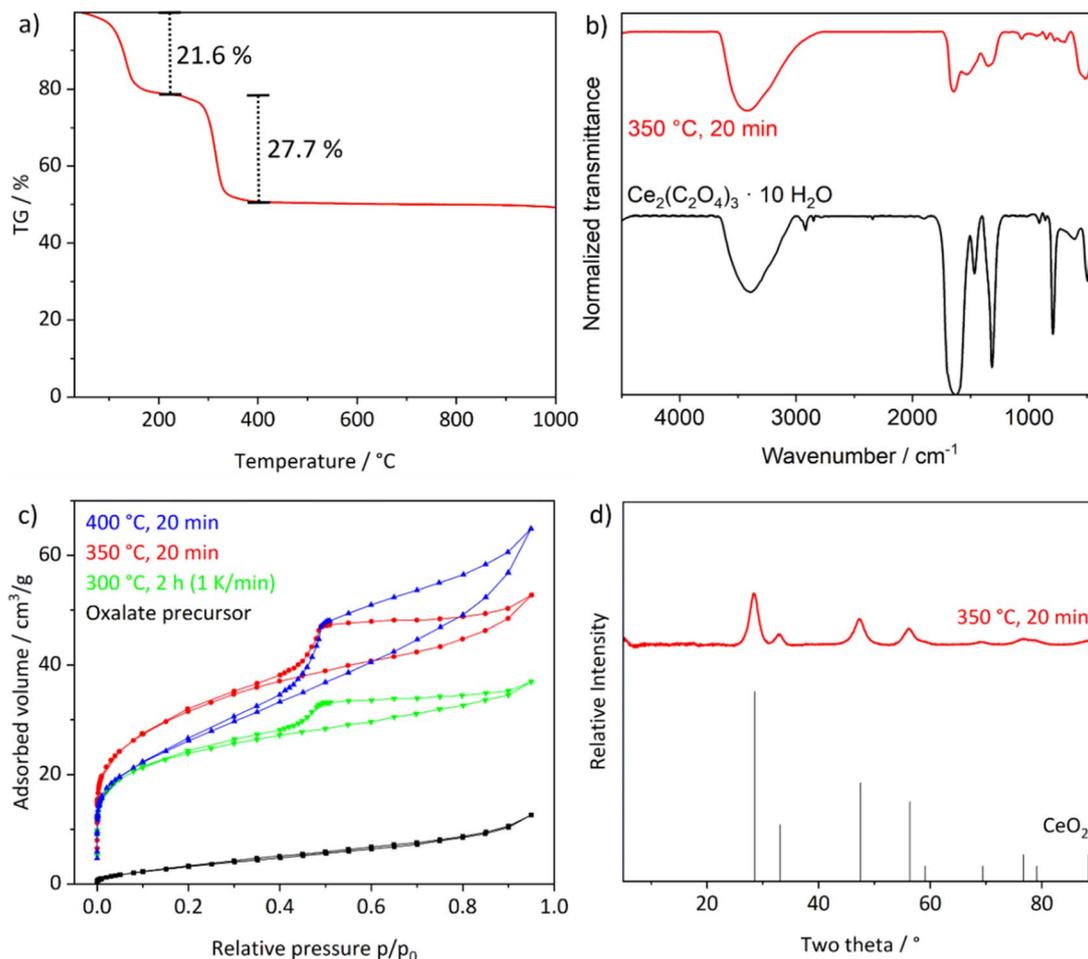


Fig. 3 Characterization of the CeO_2 nanosponges: (a) thermogravimetric analysis, (b) FT-IR spectra before and after thermal conversion, (c) volumetric sorption analysis after different thermal treatments, (d) XRD (CeO_2 as a reference, ICDD-No. C00-034-0394).

CeO_2 nanoparticles, which, however, results in very small amounts of material.¹³

The conversion of the $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ precursor particles is validated by XRD, which only shows the Bragg reflexes of CeO_2 (Fig. 3d). FT-IR spectra only exhibit very weak vibrations related to remains of oxalate (Fig. 3b). The width of the Bragg reflexes already points to the presence of small crystallite sizes (Fig. 3d). Based on the Scherrer approach, a mean crystallite size of 4.5 nm can be deduced. In fact, this is in good agreement with the mean wall thickness of 3.5 ± 0.5 nm observed for the CeO_2 nanosponges on TEM images (Fig. 4, 5 and 6). On a larger scale, STEM images still show a rod- to platelet-type shape with a length of 0.5–3.5 μm and a diameter of 200–650 nm of the $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ precursor particles (Fig. 4). High-resolution STEM images and electron diffraction confirm the conversion of the dense precursor nanoparticles to high-surface-area and highly porous CeO_2 nanosponges (Fig. 4b–g). STEM-based tomography reconstructions of the 3D structure further confirm the high porosity with a bimodal 3-dimensional network of interconnected large (up to 300 nm) and small pores (starting at 1–3 nm) (Fig. 4; for volume rendering and reconstruction of Z-slices see ESI Videos S1–S4†). Aiming at a catalyst

material, such an interconnected fractal porous structure is beneficial as a fast gas-phase transport is possible *via* larger pores to reactive sites in smaller pores without the need of high pressure gradients.

Decoration of CeO_2 nanosponges with Pt nanoparticles

After the formation of the CeO_2 nanosponges, the highly porous structure was impregnated with Pt precursors (1 wt% Pt) *via* a wet-chemical deposition process (Fig. 1c). To this concern, a solution of $\text{Pt}(\text{ac})_2$ in methanol was slowly dropped on a powder sample of the CeO_2 nanosponges. Due to the low surface tension of methanol, the $\text{Pt}(\text{ac})_2$ solution was instantaneously distributed over the support surface due to capillary forces. Thereafter, the as-deposited $\text{Pt}(\text{ac})_2$ was reduced by reducing gas ($\text{N}_2 : \text{H}_2 = 10 : 90$) already at room temperature (25 °C). Due to the fine dispersion of $\text{Pt}(\text{ac})_2$ over the nanosponge surface prior to the reduction, a homogeneous distribution of small Pt nanoparticles is achieved. Accordingly, a uniform distribution of small Pt particles occurs with 1 wt% of Pt and a particle size of 1.0–2.5 nm (Fig. 5) and a mean size of 1.8 ± 0.4 nm (ESI Fig. S3 and S6†). This wet-chemical process with $\text{Pt}(\text{ac})_2$ is preferred here over the more often used aqueous



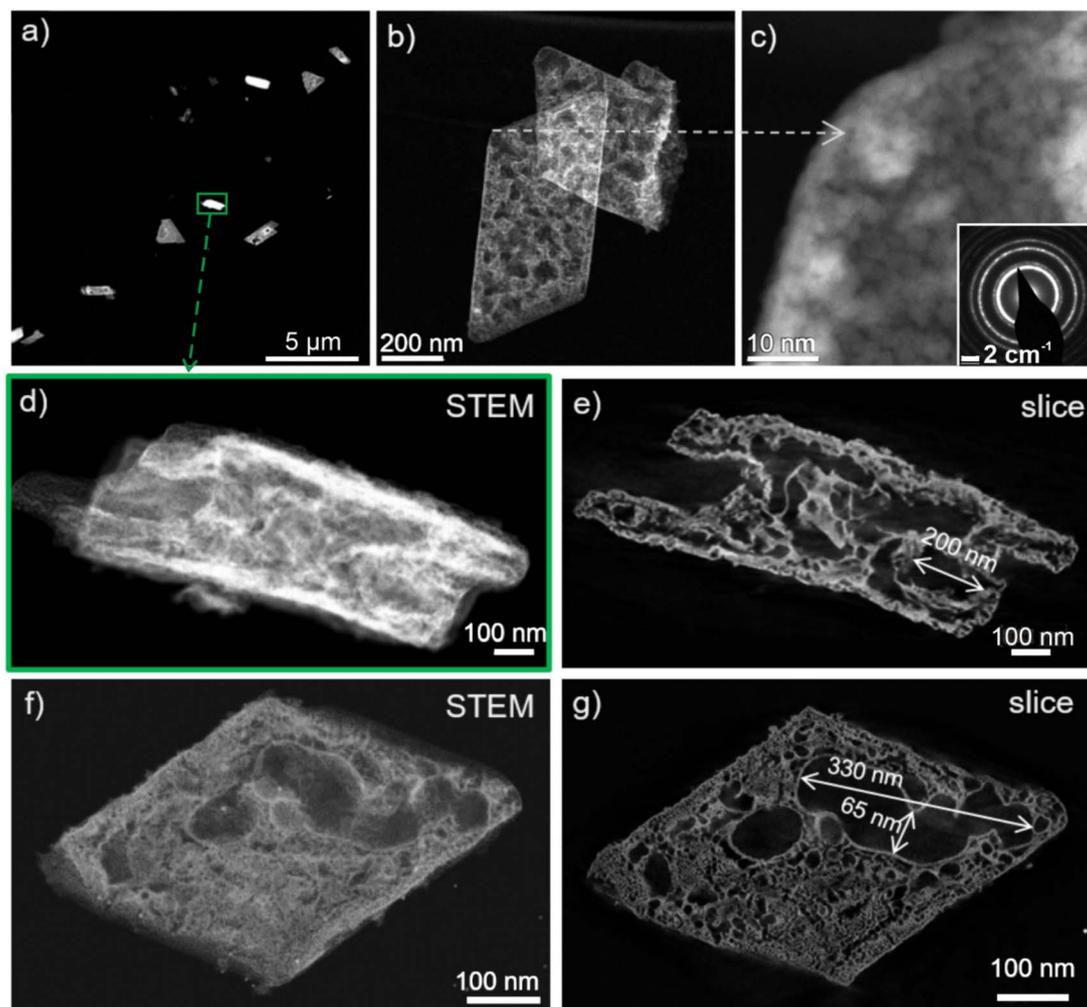


Fig. 4 Electron microscopy and tomography of CeO₂ nanosponges: (a–d and f) HAADF-STEM images at different magnification (inset in (c) showing the crystallinity, ESI Fig. S4†), (e and g) examples of Z-slices obtained from 3D electron tomographic reconstructions of nanosponges shown in (d) and (f) (for volume rendering and reconstruction of Z-slices see ESI Fig. S5 and Videos S1–S4†).

solutions of platinum chloride or platinum nitrate²² as the latter require certain heating for reduction (100–300 °C), which promotes particle growth and leads to larger Pt nanoparticles than obtained here by reduction at room temperature.

STEM images display the uniform size distribution of the Pt nanoparticles all over the inner surface of the Pt–CeO₂ nanosponges with the bright spots indicating the presence of high-density Pt nanoparticles (Fig. 5a), which was confirmed by energy-dispersive X-ray spectroscopy (EDXS) elemental mapping (Fig. 5b). Beside high surface area and porosity of the CeO₂ nanosponges and a small size of the Pt nanoparticles, a sufficient thermal stability of the Pt–CeO₂ catalyst system is required for catalytic application. This includes the sintering stability of the cerium-oxide support as well as the size stability of the Pt nanoparticles. As the CeO₂ nanosponges were prepared by thermal decomposition of Ce₂(C₂O₄)₃·10H₂O at 350 °C, a sufficient thermal stability at least up to this temperature can be expected.

The thermal stability of the Pt–CeO₂ nanosponges was examined by XRD, sorption analysis, and TEM up to

a temperature of 400 °C. To this regard, XRD still indicates comparably broad Bragg reflections after heating (ESI Fig. S7†). Here, it should be noticed that no Bragg reflections of the Pt nanoparticles occur due to their low concentration and small size. Sorption analysis indicates a single drop of the surface area by about 5% to 107 m² g⁻¹ while the pore volume remains constant at 0.082 cm³ g⁻¹ after heating to 400 °C for 24 h. For longer heating, both surface area and pore volume remain stable. Furthermore, STEM images of the Pt–CeO₂ nanosponges point to the stability of the inner pore structure of the nanosponges as well as the stability of the size and distribution of the Pt nanoparticles. Thus, the structure and porosity of the CeO₂ framework as well as a size and distribution of the Pt nanoparticles for the samples heated to 400 °C (Fig. 6) are quite similar to the as-prepared Pt–CeO₂ nanosponges (Fig. 5).

Oxidation catalysis with Pt–CeO₂ nanosponges

To evaluate the potential of the novel Pt–CeO₂ nanosponges for oxidation catalysis, different reactants and reactions were tested, using standard conditions (*e.g.*, applied temperature,



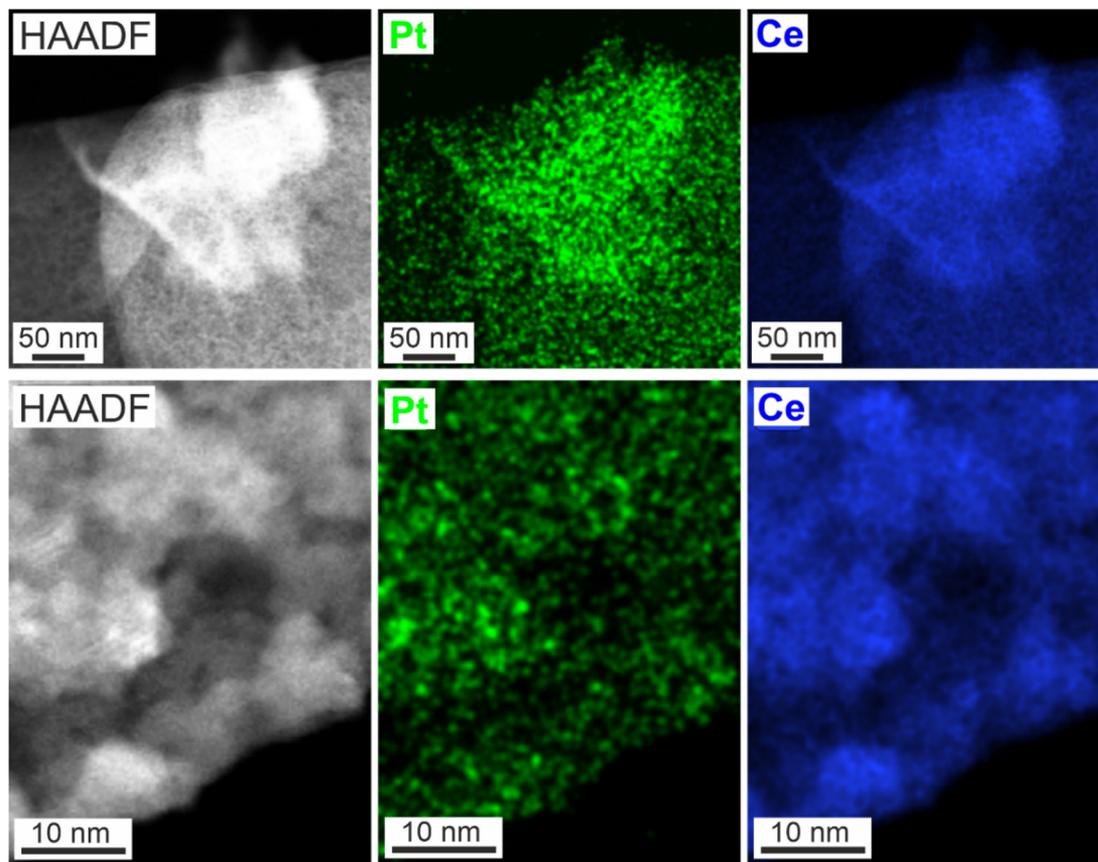


Fig. 5 EDXS elemental maps of Pt on CeO₂ nanosponges: STEM images of Pt–CeO₂ nanosponges at different magnification and corresponding Pt and Ce elemental maps.

pressure, concentration) without a further optimization of the nanosponge catalyst and/or the respective conditions of the reaction. Specifically, the catalytic oxidation of CO, volatile organic compounds (VOCs) and NH₃ were studied with regard to activity and temperature range up to 250 °C for CO oxidation and 400 °C for NH₃ oxidation. As a representative of VOCs, the oxidation of formaldehyde (HCHO) was investigated up to temperature of 250 °C.

The CO, HCHO and NH₃ conversion and the catalyst stability were monitored in three single experiments with three consecutive light-off/light-out cycles, while applying a ramp rate of 5 °C min⁻¹ for CO and HCHO oxidation as well as a ramp rate of 10 °C min⁻¹ for NH₃ oxidation (Fig. 7). In this way, not only the initial activity was determined but also the performance after catalyst degreening under reaction conditions. When considering that the Pt–CeO₂ nanosponges were exposed to ambient atmosphere prior to the catalytic tests, at least a partial oxidation of the Pt nanoparticle surface is to be expected. As a result, the CO, HCHO, and NH₃ oxidation is anticipated to occur only at temperatures sufficiently high for the reduction of Pt nanoparticles under reaction conditions.²³ A relatively high light-off temperature – the temperature at which 50% of activity were reached – of 159 °C during the heating phase, and a slow increase of the CO oxidation activity were observed for the 1st cycle (Fig. 7a). In contrast, 100% conversion was maintained

during the cooling down step even at 135 °C, followed by a sharp decrease in activity and a light-out temperature of 114 °C (the temperature at which 50% activity are reached in the cooling cycle, Table 2). Despite the reducing treatment (N₂ : H₂ = 10 : 90) applied at 25 °C for the sample, this behaviour can be ascribed to a certain catalyst degreening, including the removal of precursor traces and changes in the oxidation state during the reaction.²⁴ Additionally, the noble metal structure is expected to change under reaction conditions due to the interaction with the CeO₂ support, leading to sintering/redispersion processes depending on the temperature and CO concentration.^{5a} The improved activity and the steep CO oxidation profile is then maintained during the 2nd and 3rd reaction cycle. In comparison to the 1st cycle, the light-off and light-out temperatures are very close in values (140 °C and 118 °C, Table 2), showing a good stability of the catalyst system (Fig. 7a). The hysteresis occurring between the light-off and light-out curves points to Pt particles with a size of 1–3 nm as previously reported for alumina-supported catalysts.²⁴ This size is also in accordance with STEM images of the Pt–CeO₂ nanosponges with Pt nanoparticles, 1.8 ± 0.4 nm in size (ESI Fig. S6†). In addition, the different CO oxidation mechanism involving perimeter sites at the interface between the noble metal and the CeO₂ support can contribute as well to the variation between the heating and cooling curves.²³ Thus, Ce³⁺ sites are generated at the interface



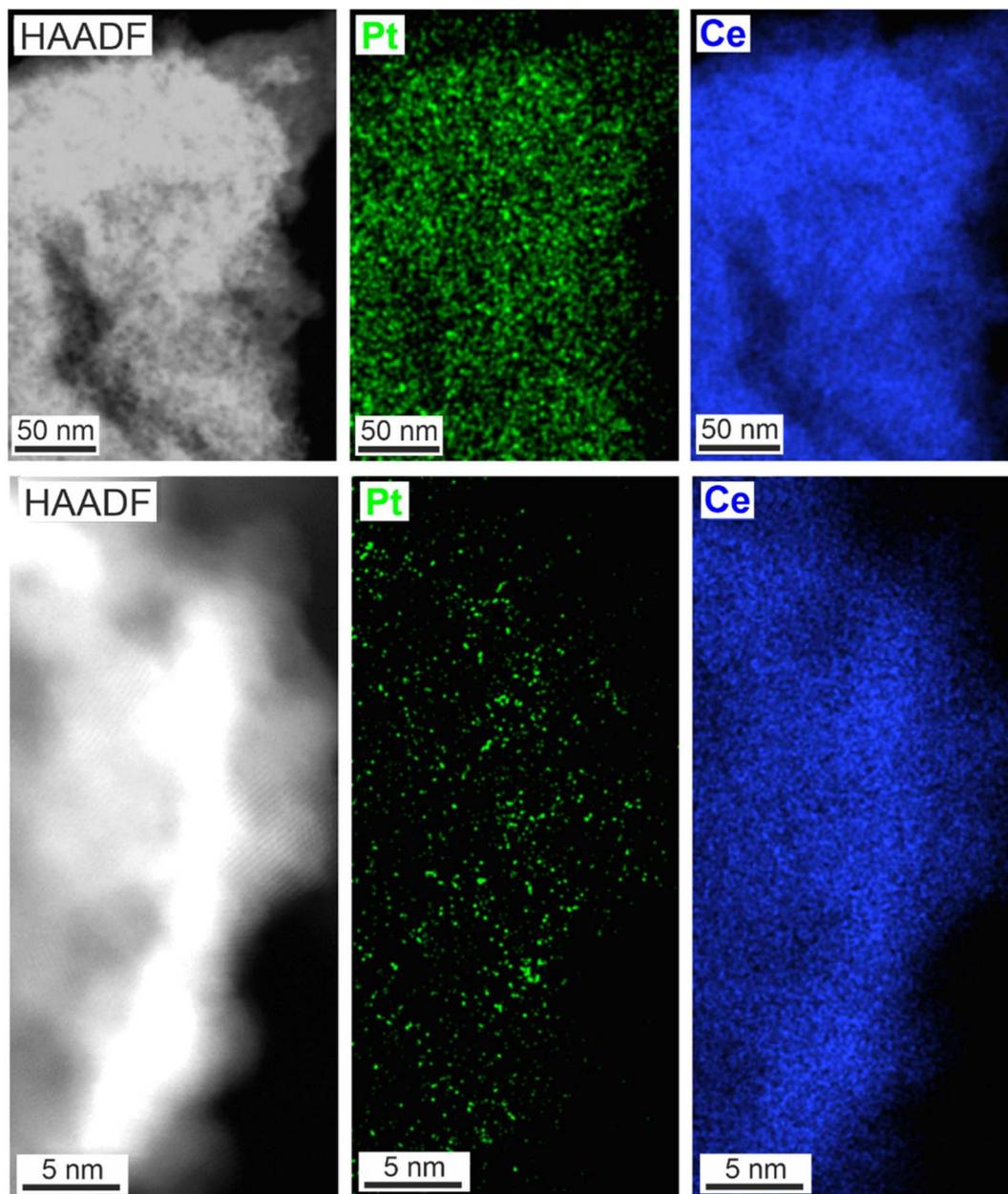


Fig. 6 Thermal stability of the Pt–CeO₂ nanosponges: STEM images of Pt–CeO₂ nanosponges at different magnification and corresponding Pt and Ce EDXS elemental maps.

between Pt and CeO₂ support and in the topmost layer of ceria during CO oxidation.²⁵ This availability of oxygen at the perimeter sites further minimizes the CO self-inhibition effect on Pt.^{24,26}

A comparable behaviour as for the catalytic CO oxidation with Pt–CeO₂ nanosponges is also observed for the 1st cycle of the catalytic HCHO oxidation with a light-off temperature of 107 °C but in combination with a very low light-out temperature of 39 °C (Fig. 7b). For the 2nd and 3rd cycle, the difference between light-off and light-out temperature becomes much smaller reaching 83 and 51 °C for the 3rd cycle (Table 2). For the catalytic NH₃ oxidation, the Pt–CeO₂ nanosponges show a light-off temperature of 241 °C and a light-out temperature of 207 °C

in the 1st cycle (Fig. 7c), which are shifted after the 1st cycle to stable values in the 2nd and 3rd catalytic cycle. Due to the lower reactivity of NH₃, both the light-off and light-out temperatures are higher compared to CO and HCHO oxidation (Table 2). Finally, the high selectivity of the Pt–CeO₂ nanosponges for catalytic NH₃ oxidation is remarkable with >80% of N₂ at 220–250 °C (light off of 3rd cycle) and 170–200 °C (light out of 3rd cycle) (Fig. 7d).²⁷ The selectivity to nitrogen is high up to 300 °C. At higher temperatures, both NO and NO₂ are formed due to over-oxidation. Compared to the activity reported in the literature for small platinum species on non-interacting support, the Pt–CeO₂ nanosponges show a high activity with comparable if not better selectivity to nitrogen and low selectivity towards



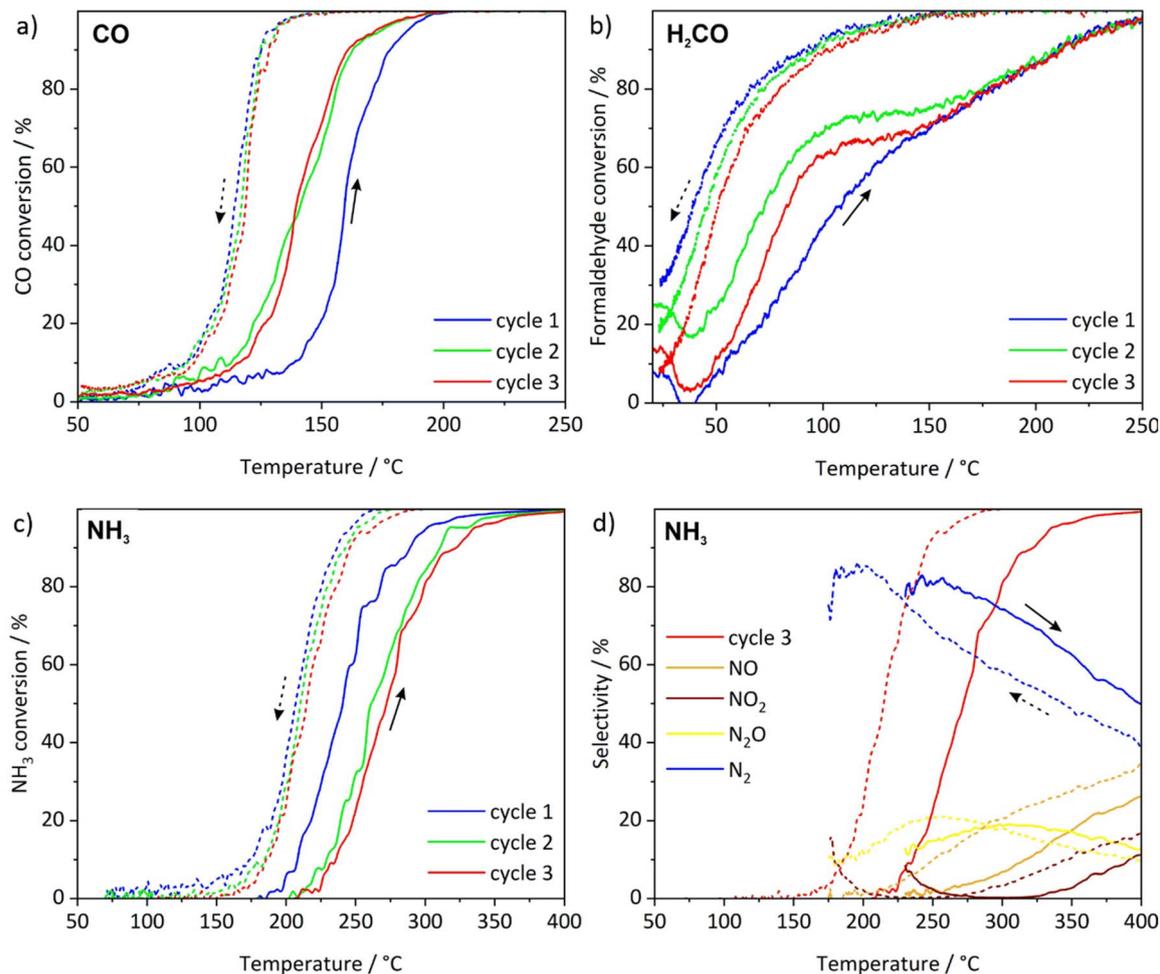


Fig. 7 Evaluation of the catalytic properties of the Pt–CeO₂ (1%) nanosponges: (a) CO oxidation (gas mixture: 50 mL min⁻¹ of 1000 ppm CO, 10% O₂ in He, temperature ramp rate: 5 °C min⁻¹), (b) VOC oxidation (gas mixture: 50 mL min⁻¹ of 260 ppm HCHO, 10% O₂ in He, temperature ramp rate: 5 °C min⁻¹), (c) NH₃ oxidation (gas mixture: 50 mL min⁻¹ of 1000 ppm CO, 10% O₂ in He, temperature ramp rate: 10 °C min⁻¹), (d) NH₃ oxidation product selectivity at cycle 3 (for conversion >10%).

Table 2 Light-off (L_{off}) and light-out (L_{out}) temperatures (indicating a level of 50% activity, T_{50} , reached during heating or cooling, respectively) for the Pt–CeO₂ (1%) nanosponges

	1st cycle $L_{off} T_{50}/^{\circ}\text{C}$	1st cycle $L_{out} T_{50}/^{\circ}\text{C}$	2nd cycle $L_{off} T_{50}/^{\circ}\text{C}$	2nd cycle $L_{out} T_{50}/^{\circ}\text{C}$	3rd cycle $L_{off} T_{50}/^{\circ}\text{C}$	3rd cycle $L_{out} T_{50}/^{\circ}\text{C}$
CO	159	114	141	117	140	119
HCHO (VOCs)	107	39	73	46	83	51
NH ₃	241	207	261	210	272	215

N₂O. The CeO₂ nanosponges appears to significantly support the reaction.²⁷

Although a reliable comparison with industrially applied catalyst systems or other Pt–CeO₂ catalysts reported in the literature is difficult due to different types of materials and conditions, the novel Pt–CeO₂ nanosponges show very promising catalytic performance regarding the oxidation of CO, HCHO, and NH₃. This holds the more as the nanosponges were not yet optimized in regard of their surface area, pore size and volume, the Pt load and particle size or the specific conditions of the catalytic reaction.

Conclusions

Pt–CeO₂ nanosponges with high surface area (113 m² g⁻¹), pore volume (0.08 cm³ g⁻¹), small-sized Pt nanoparticles (1.8 ± 0.4 nm), and good thermal stability (up to 400 °C) are obtained by an optimised thermal decomposition of Ce₂(C₂O₄)₃·10H₂O precursor particles. The latter are prepared by precipitation upon reaction of Ce(NO₃)₃·6H₂O and K₂C₂O₄·H₂O in an ethanol–water mixture. The cerium oxalate precursor is then thermally converted to CeO₂ nanosponges by heating to 350 °C in air (20 min). Finally, the CeO₂ nanosponges are decorated



with small-sized Pt nanoparticles using a wet-chemical process with Pt(ac)₂ in methanol. The resulting Pt–CeO₂ nanosponges (1 wt% Pt) show promising activity for the catalytic oxidation of CO, volatile organic compounds (VOCs), and NH₃ with low light-out and light-off temperatures, and – in the case of the NH₃ oxidation – good selectivity for N₂ formation (>80% at 170–250 °C). Although the Pt–CeO₂ nanosponges have not yet been optimized in detail, *e.g.*, with respect to pore size and volume, the Pt loading and particle size or the specific conditions of the catalytic reactions, a further increase of the performance can be expected. The synthesis strategy using metal oxalates as precursors for high-surface-area metal oxides in the low-temperature conversion regime can be transferred also to other metal oxides. New material and catalyst concepts with promising results, finally, might also be transferable to other oxides and catalysts, supplemented by further screening in catalyst composition (*e.g.*, variation in noble metal loading, testing under more realistic conditions, long-term durability tests).

Experimental section

General

Ce(NO₃)₃·6H₂O (extra pure, Merck), ethanol (99.9%, Seulberger), methanol (99.9%, Seulberger) K₂C₂O₄·H₂O (P. A., Merck) were handled as purchased. Pt(Ac)₂ was prepared according to the literature.²⁸

Ce₂(C₂O₄)₃·10 H₂O precursor particles

631 mg of Ce(NO₃)₃·6H₂O were dissolved in 150 mL of ethanol. In addition, 442 mg of K₂C₂O₄·H₂O were dissolved in 15 mL of water. This latter solution was injected with intense stirring at room temperature to the Ce(NO₃)₃·6H₂O solution. The immediate nucleation of the precursor particles was indicated by the formation of a suspension, which was stirred over night to yield crystalline Ce₂(C₂O₄)₃·10H₂O. The as-prepared Ce₂(C₂O₄)₃·10H₂O precursor particles were purified by centrifugation/resuspension twice from/in water. Finally, the Ce₂(C₂O₄)₃·10H₂O precursor particles were dried at 70 °C over night.

Thermal conversion of precursor particles to CeO₂ nanosponges

The thermal conversion of the Ce₂(C₂O₄)₃·10H₂O precursor particles to the CeO₂ nanosponges with optimal performance was performed by heating at 350 °C for 20 min. Thereafter, the CeO₂ nanosponges were redispersed/centrifuged twice in/from water to remove all remaining KNO₃. Finally, the CeO₂ nanosponges were dried at 70 °C over night.

Modification with Pt nanoparticles

The CeO₂ nanosponges were impregnated with Pt (1 wt%) by a wet-chemical process. To this concern, 4.2 mg of Pt(ac)₂ were dissolved in 0.3 mL of methanol and dropped on 200 mg of a dried powder sample of the CeO₂ nanosponges. This was conducted in two steps with addition of 0.15 mL for each and drying at 70 °C after each step. To obtain Pt nanoparticles, dried

powder samples were treated in reducing-gas atmosphere (N₂ : H₂ = 90 : 10) for 30 min at room temperature. The formation of Pt nanoparticles can be followed with the naked eye due to the color change from greenish-blue to grey.

CO oxidation

Sieved Pt–CeO₂ nanosponge powders (5 mg, 125–250 μm grain size) were placed in quartz microreactors (Ø: 1.5 mm) with quartz-wool plugs in the front and at the back of the catalyst bed. A gas mixture of 50 mL min⁻¹ with 1000 ppm CO and 10% O₂ in He was dosed over that catalyst bed at ambient pressure. This corresponds to weight hourly space velocity (WHSV) of 30 000 L g_{Pt}⁻¹ h⁻¹. The temperature was varied between 50–250 °C with a heating/cooling rate of 5 °C min⁻¹. The outlet-gas composition was analyzed with an FT-IR spectrometer (Multi-gas 2030 Analyzer™, MKS Instruments) with a focus on the CO and CO₂ concentration.

NH₃ oxidation

For ammonia oxidation similar reaction conditions were used. Analogously, sieved Pt–CeO₂ nanosponge powders (5 mg, 125–250 μm grain size) were used (quartz microreactors with Ø: 1.5 mm, WHSV of 30 000 L g_{Pt}⁻¹ h⁻¹, FT-IR analysis with same analyzer as for CO-oxidation). For the experiments, a gas mixture of 50 mL min⁻¹ with 1000 ppm NH₃ and 10% O₂ in He was dosed between 50–400 °C (heating/cooling rate of 10 °C min⁻¹). The NH₃ concentration together with that of possible reaction products (*i.e.*, NO, N₂O, NO₂) was determined.

Formaldehyde oxidation

Analogously, sieved Pt–CeO₂ nanosponge powders (5 mg, 125–250 μm grain size) were placed in the same quartz microreactors (Ø: 1.5 mm) and fixed in place using quartz-wool plugs. For the experiments, a gas mixture of 50 mL min⁻¹ with 260 ppm formaldehyde and 10% O₂ in He was dosed over that catalyst bed at ambient pressure (WHSV of 30 000 L g_{Pt}⁻¹ h⁻¹). Formaldehyde was dosed using a gas saturator containing a commercial 16% formaldehyde solution in water (Science Services). The temperature was varied between 25–250 °C with a heating/cooling rate of 5 °C min⁻¹. The outlet gas composition was analyzed by FT-IR determining the concentration of HCHO together with the possible reaction products (CO and CO₂). Further details regarding the analytical equipment can be obtained from the ESI.†

Data availability

Additional data regarding experiments and methods can be obtained from the ESI† and on request from the authors.

Conflicts of interest

The authors declare no competing financial interests.



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