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Supporting Information

Highly efficient cerium dioxide nanocubes-based catalyst for low temperature diesel soot oxidation: cooperative effect of cerium- and cobalt-oxides

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1. Catalyst Preparation

The CeO_2 nanocubes were synthesized by an alkaline hydrothermal method. In a typical procedure, the required amount of $Ce(NO_3)_3{\cdot}6H_2O$ was dissolved in double distilled water under mild stirring conditions until the formation of a clear solution. An aqueous 60 mL of NaOH solution (6 M) was added drop-wise to the above solution and the stirring was continued for 30 min at room temperature. The solution was then transferred into a Teflon bottle and then sealed tightly in a stainless-steel autoclave. The hydrothermal treatment was performed at 453 K for 24 h. After cooling, the products were collected, washed with deionized water, oven-dried at 373 K for 12 h and finally calcined at 773 K for 4 h in air with a heating ramp of 1 K/min.

The promoted CeO_2 cubes containing 10 wt.% of Co were synthesised by a wet-impregnation method. In brief, the desired quantity of $Co(NO_3)_2{\cdot}6H_2O$ was dissolved in double distilled water followed by the addition of finely powdered CeO_2. The excess water was evaporated on a hot plate under vigorous stirring at 373 K. The obtained products were oven-dried at 373 K for 12 h and finally calcined at 773 K for 4 h in air atmosphere with a heating ramp of 1 K/min.

2. Catalyst Characterization

The powder XRD patterns were recorded on a Rigaku diffractometer using Cu Kα radiation (1.540 Å) source, operated at 40 kV and 40 mA. The diffractograms were recorded in the 2θ range of 10-80° with a 2θ step size of 0.02° and a step time of 2.4 s. The XRD phases present in the samples were identified with the help of a Powder Diffraction File-International Center for Diffraction Data (PDF-ICDD). The lattice parameter was estimated by a standard cubic indexation method using the intensity of the most prominent peak (111). Raman experiments were performed on Perkin Elmer-Raman Station 400F spectrometer equipped with a liquid N_2 cooled charge coupled device detector and a confocal microscope. A 350 mW near infrared 785 nm laser was used for analysis.

The BET surface area of the materials was determined by means of N_2 adsorption on a Micromeritics Gemini 2360 instrument. Prior to analysis, the samples were oven-dried at 423 K for 12 h to remove any surface adsorbed residues. Surface area was calculated by utilizing the desorption data. Pore size and pore volume were calculated by BJH method applied to the desorption leg of the isotherms. The FT-IR spectra were recorded on a Nicolet 740 FT-IR spectrometer at ambient conditions with a nominal resolution of 4 cm^{-1} and averaging 100 spectra. H_2-TPR experiments were conducted in a tubular quartz reactor coupled to a gas chromatograph (Varian, 8301) equipped with a thermal conductivity detector and performed in a conventional apparatus by monitoring the H_2 consumed. The sample (30 mg of fresh catalyst) was heated at a rate of 5 K min^{-1} from room temperature to 1100 K in 30 mL min^{-1} flow of 10% H_2 in Ar. Before the TPR run, the catalysts were pre-treated under argon flow at 573 K for 2 h.

XPS studies were performed using a Thermo K-5 Alpha XPS instrument at a pressure less than 10^{-9} torr to avoid noise in the spectra. The overall energy resolution of the XPS measurement is 1 eV. The general scan and Ce 3d, Co 2p, and O 1s core level spectra from the respective samples were recorded using Al Kα radiation (photon energy = 1486.6 eV) at a pass energy of 50 eV and electron take off angle (angle between electron emission direction and surface plane) of 90^{o}. The core level binding energies (BEs) were charge corrected with respect to the adventitious carbon (C 1s) peak at 284.6 eV.

TEM-HRTEM studies were made on a JEOL JEM-2100F instrument equipped with a slow-scan CCD camera and the accelerating voltage of the electron beam was 80 kV. The preparation of samples for TEM-HRTEM analysis involved sonication in ethanol for 2-5 min followed by deposition of a drop on a copper grid. The specimen was examined under vacuum at room temperature. The elemental analysis of the catalysts was carried out with the help of an energy dispersive X-ray spectrometer (EDX) attached to a JEOL JEM-2100F instrument operating at 80 kV. STEM-EELS analysis was carried out using a JEM-2100F equipped with a Gatan Imaging Filter (GIF) operating at 80 kV.

3. Activity Measurements

The catalytic efficiency of the samples for soot oxidation was conducted in a thermogravimetric analyzer (Mettler Toledo, TGA/SDTA851e). Oxidation experiments consisted of heating the catalyst–soot mixtures (18 ± 2 mg) at a rate of 10 K min^{-1} from ambient temperature to 1273 K under a 100 mL min^{-1} flow of air. The activity measurements were performed under both ‘tight and loose contact’ conditions with catalyst–soot mixtures in a 4:1 wt/wt ratio.[1-4] The soot used in this study was Printex-U carbon black provided by Degussa. The average particle size and specific surface area of Printex-U carbon black are 25 nm and 100 m^2 g^{-1}, respectively. This soot was proven to be an appropriate model for the soot oxidation reaction. The soot and catalyst with a weight ratio of 1:4 were ground in a mortar for 10 min to obtain so-called tight contact mixtures. Same weight ratio of soot and catalyst was mixed with spatula for 2 min to obtain loose contact mixtures. Each test was repeated three times to ensure the reproducibility of the obtained results: the maximum deviation from the mean value over the three tests was ±5 K (ca. 1% of the measured temperature). Temperatures corresponding to 50% soot conversion (denoted as T_{50}) were taken as indices of the activity of the tested catalysts. All the experiments over CeO_2 cubes, Co_3O_4/CeO_2 cubes, conventional CeO_2, Co_3O_4/conventional CeO_2, and with-out the catalyst are performed under identical conditions.

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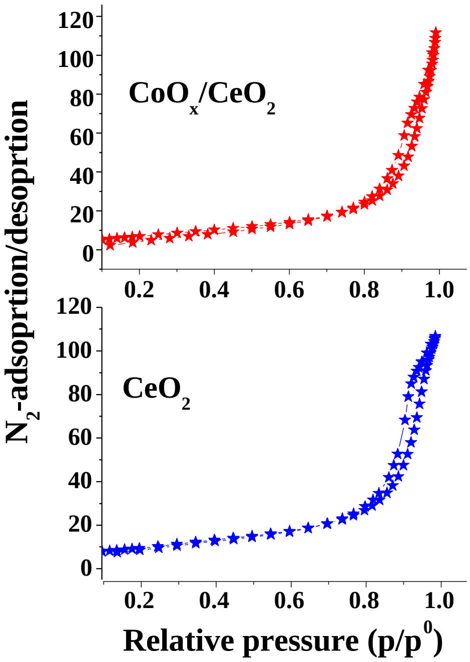

Fig. S1 N$_2$ adsorption–desorption isotherms of the catalysts.

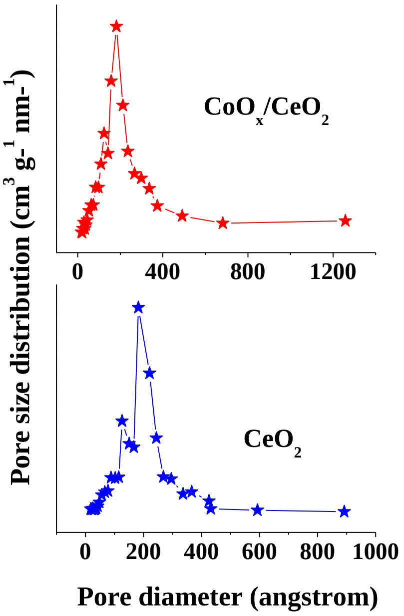

Fig. S2 Pore size distribution profiles of the samples.

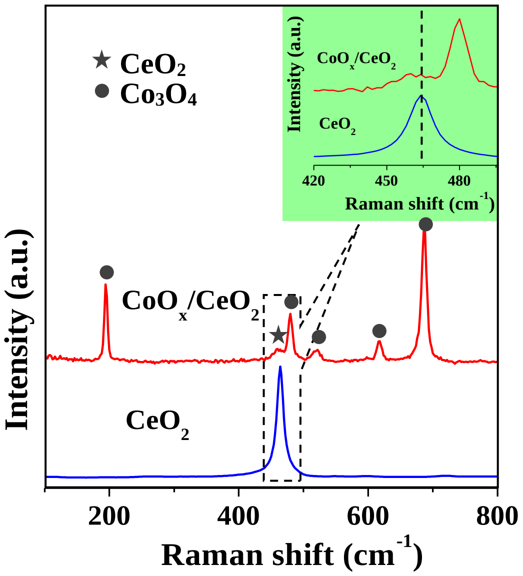

Fig. S3 Raman spectra of the CeO_2 and CoO_x/CeO_2 cubes.

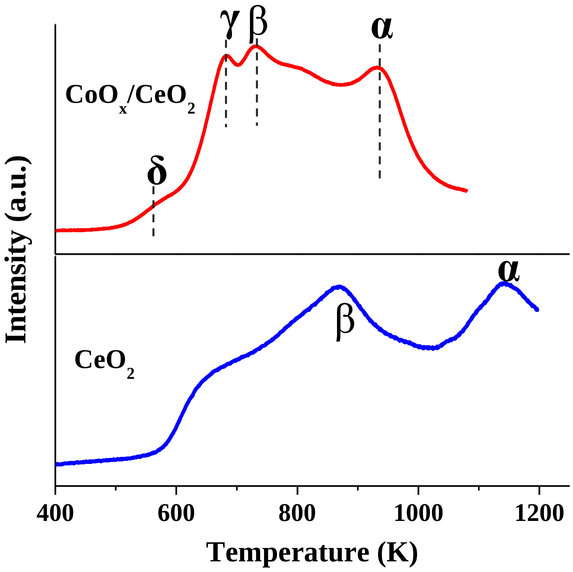

Fig. S4 H_2-TPR profiles of CeO_2 nanocubes and CoO_x promoted CeO_2 nanocubes.

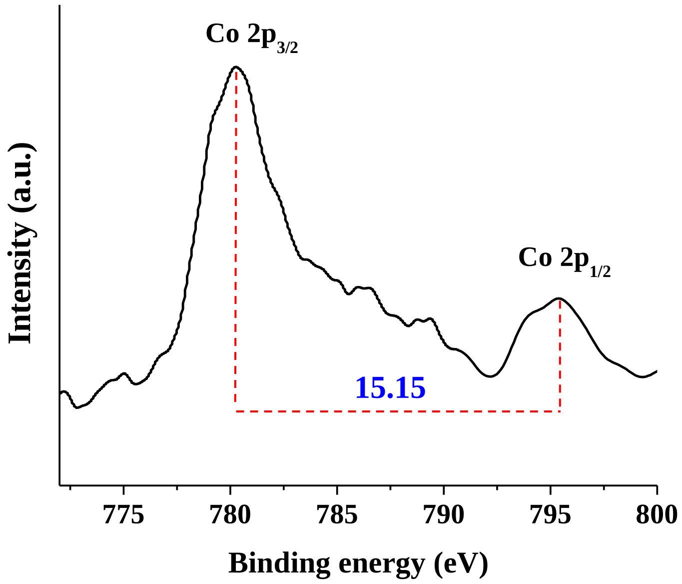

Fig. S5 Co 2p XPS spectrum of the CoO_x/CeO_2 sample.

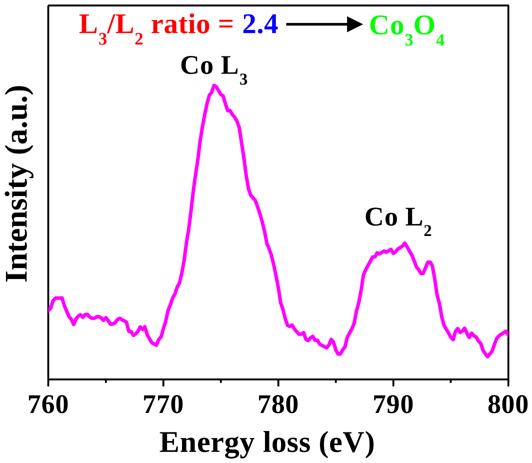

Fig. S6 Co $L_{2,3}$ EELS spectrum of the CoO_x/CeO_2 sample.

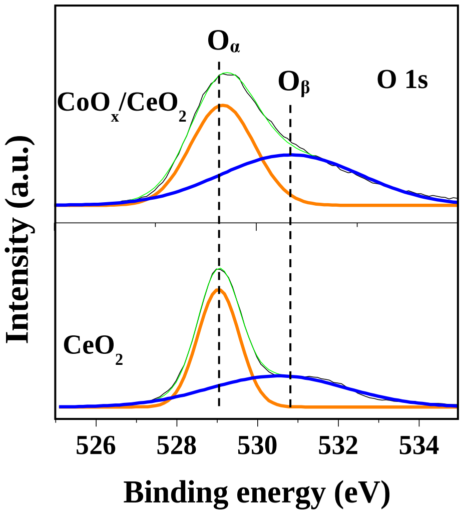

Fig. S7 O 1s XPS spectra of the CeO_2 and CoO_x/CeO_2 samples.

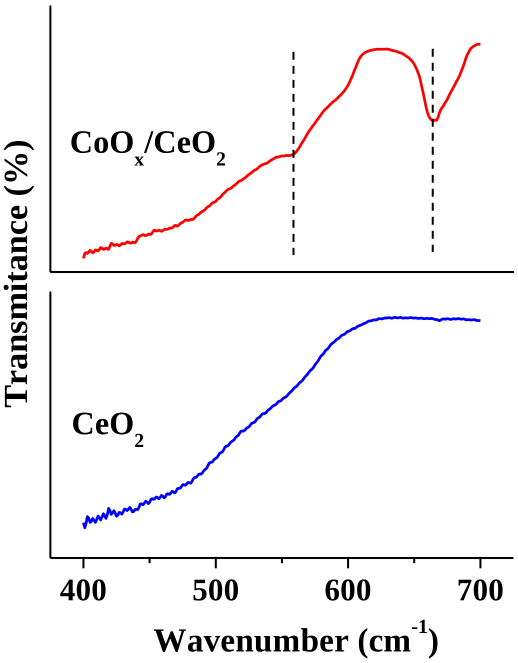

Fig. S8 FT-IR spectra of the CeO_2 cubes and CoO_x/CeO_2 cubes.

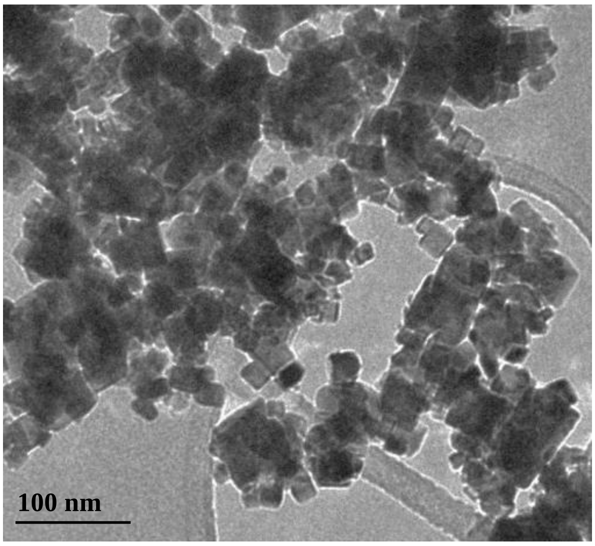

Fig. S9 TEM image of as-synthesized CeO_2 cubes.

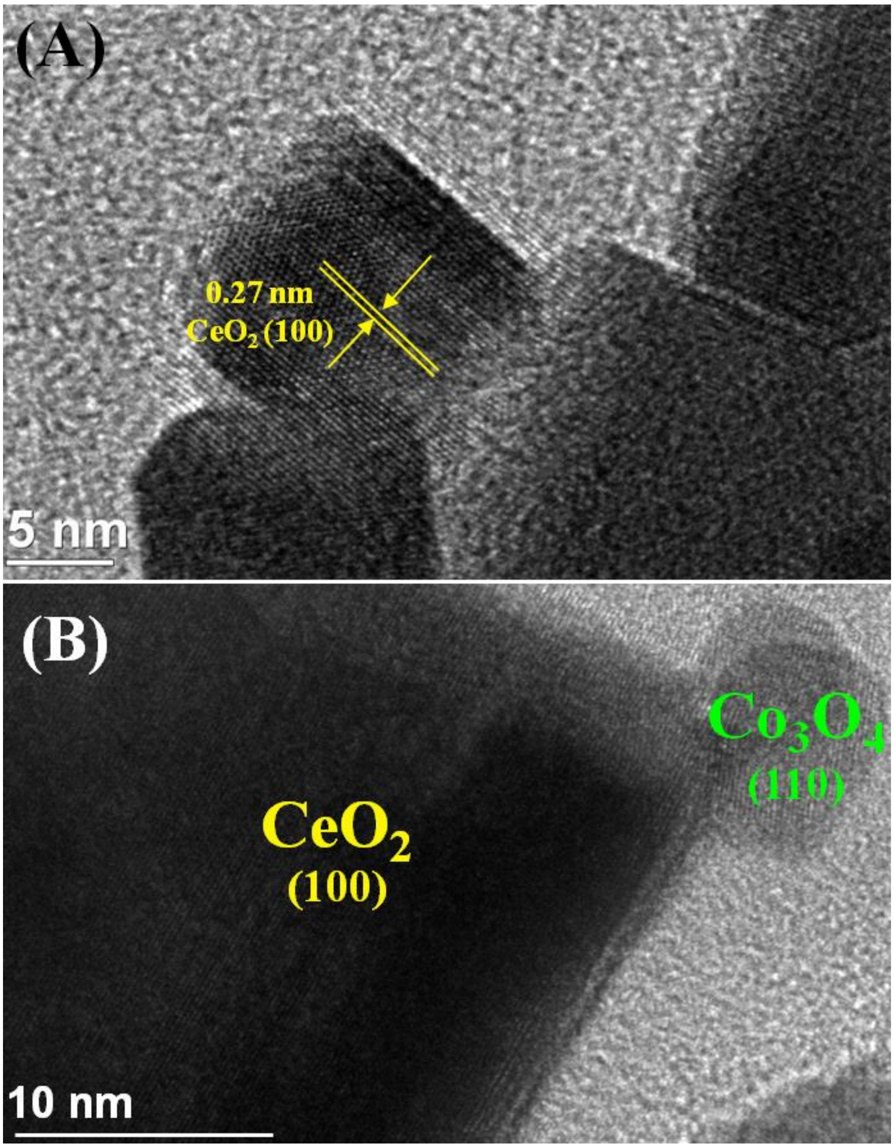

Fig. S10 HRTEM images of CeO_2 cubes (A) and Co_3O_4 promoted CeO_2 cubes (B).

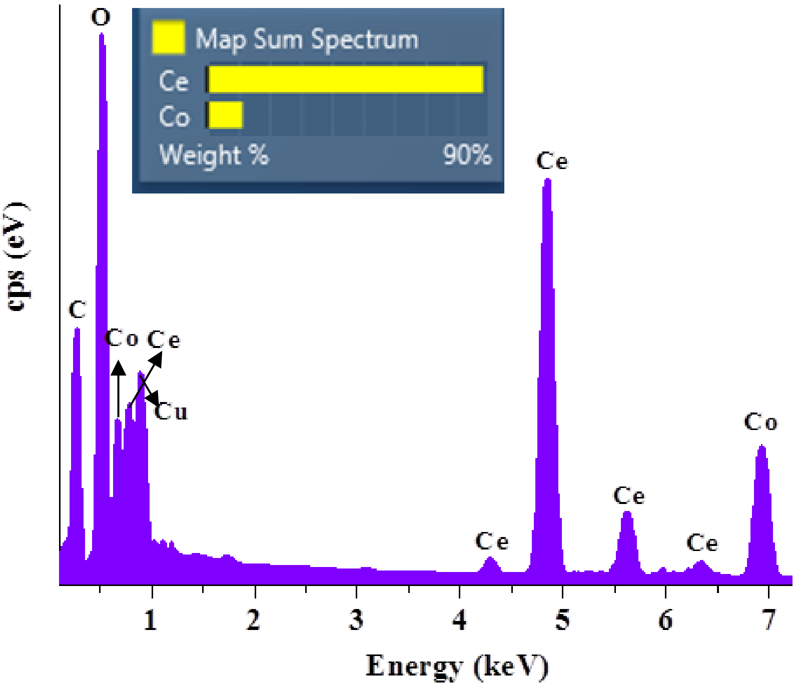

Fig. S11 TEM-EDS spectrum of the CoO_x/CeO_2 sample. Cu signal in the EDS profile is due to the grid used for the investigation.

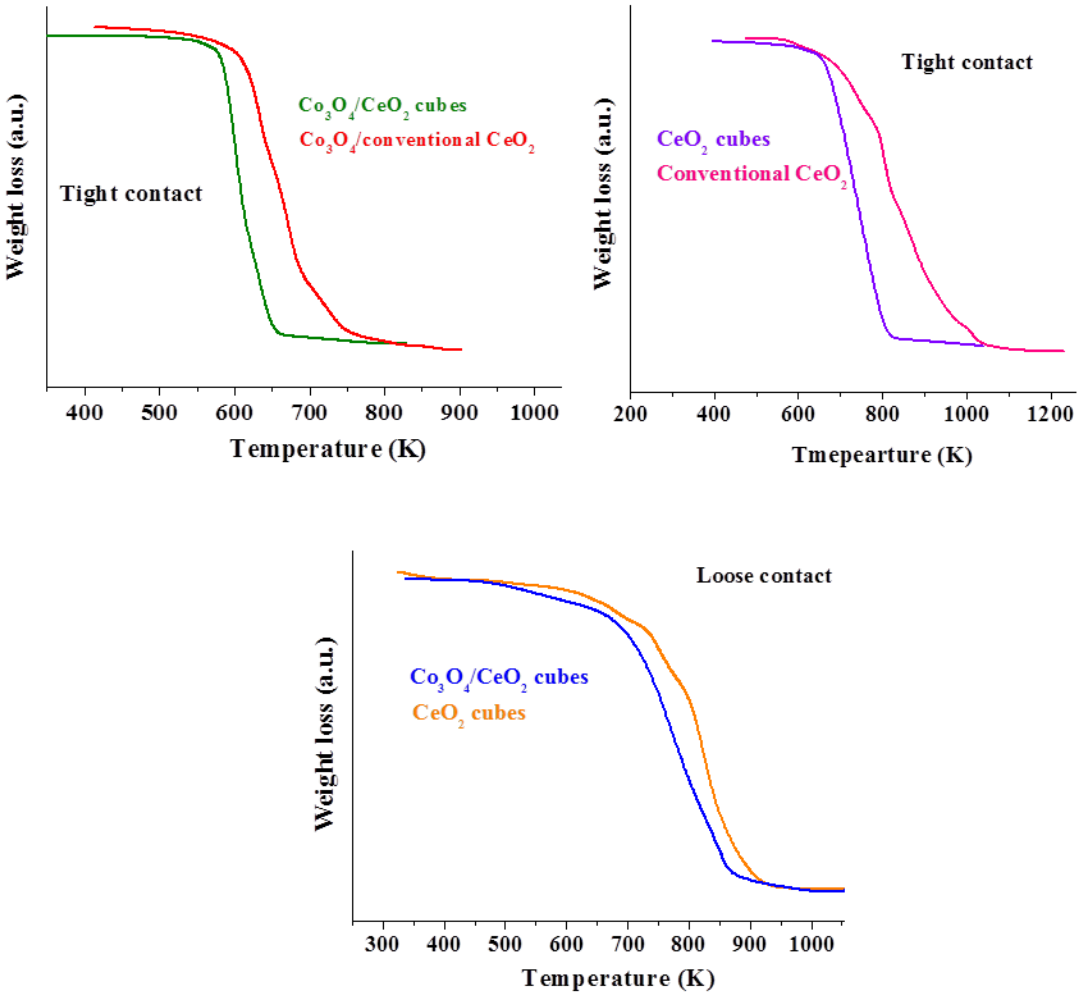

Fig. S12 TGA curves for soot oxidation over CeO_2 based catalysts under tight and loose contact conditions.

Table S1 BET surface area (S_{BET}), CeO_2 lattice parameter (LP), pore size (P), and pore volume (V) of the CeO_2 and Co_3O_4/CeO_2 samples.

Sample	S_{BET} (m^2g^{-1})[a]	LP (nm)[b]	P (nm)[c]	V ($cm^{3/}g$)[c]
CeO_2	30	0.547	14.04	0.165
Co_3O_4/CeO_2	27	0.551	16.28	0.170

[a] From BET analysis. [b] From XRD studies. [c] From BJH analysis.

Table S2 Comparative activity assessment of various CeO_2-based catalysts reported in literature for soot oxidation under tight contact conditions. For all the catalysts, Printex-U carbon black from Degussa is used as model soot for the activity studies. For all the catalysts, soot experiments were performed at a rate of 10 K min^{-1} (2 K min^{-1} for CeO_2-Pr_6O_{11}-Bi_2O_3) from ambient temperature to desired temperatures (473 K to 873 K for Co_3O_4-CeO_2, entry 4).

Catalyst	Soot : catalyst (soot + catalyst, mg)	Limitations	Air flow mL/min	Activity T_{50} (K)	Ref.
Co_3O_4/CeO_2 cubes	1 : 4 (18 ± 2)	10% Co	100	606	This work
Cu/CeO_2-ZrO_2	1 : 4 (8–12)	10% Cu, 50% Zr	60	611	1
CeO_2-Pr_6O_{11}-Bi_2O_3	2 : 98 (30)	21% Pr, 32% Bi & polyvinylpyrrolidone	20	622	2
Co_3O_4-CeO_2	1 : 19 (20 ± 2)	93% Co	50	643	3
CeO_2-Mn_2O_3	1 : 4 (10–12)	30% Mn	100	665	4
CeO_2-Sm_2O_3	1 : 4 (18 ± 2)	40% Sm	100	690	5
$Ce_{0.8}Pr_{0.2}O_{2-\delta}$	1 : 4 (10–12)	20% Pr	100	711	6
CeO_2-Gd_2O_3/TiO_2	1 : 4 (8–12)	20% Gd, 50% Ti	100	735	7
CeO_2-La_2O_3	1 : 4 (18 ± 2)	40% La	100	740	8

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