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$_3$)$_3$·6H$_2$O 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 synthesized by a wet-impregnation method. In brief, the desired quantity of Co(NO$_3$)$_3$·6H$_2$O 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. H₂-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 H₂ 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% H₂ 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°. 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. 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 m² 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$_3$O$_4$/CeO$_2$ cubes, conventional CeO$_2$, Co$_3$O$_4$/conventional CeO$_2$, and with-out the catalyst are performed under identical conditions.

References

**Fig. S1** $\text{N}_2$ 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 H₂-TPR profiles of CeO₂ nanocubes and CoOₓ promoted CeO₂ 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$_3$O$_4$ 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 ($S_{\text{BET}}$), CeO$_2$ lattice parameter (LP), pore size (P), and pore volume (V) of the CeO$_2$ and Co$_3$O$_4$/CeO$_2$ samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{BET}}$ ($\text{m}^2\text{g}^{-1}$)$^a$</th>
<th>LP (nm)$^b$</th>
<th>P (nm)$^c$</th>
<th>V (cm$^3$g)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>30</td>
<td>0.547</td>
<td>14.04</td>
<td>0.165</td>
</tr>
<tr>
<td>Co$_3$O$_4$/CeO$_2$</td>
<td>27</td>
<td>0.551</td>
<td>16.28</td>
<td>0.170</td>
</tr>
</tbody>
</table>

$^a$ 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$_6$O$_{11}$-Bi$_2$O$_3$) from ambient temperature to desired temperatures (473 K to 873 K for Co$_3$O$_4$-CeO$_2$, entry 4).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Soot : catalyst (soot + catalyst, mg)</th>
<th>Limitations</th>
<th>Air flow mL/min</th>
<th>Activity $T_{50}$ (K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$_3$O$_4$/CeO$_2$ cubes</td>
<td>1 : 4 (18 ± 2)</td>
<td>10% Co</td>
<td>100</td>
<td>606</td>
<td>This work</td>
</tr>
<tr>
<td>Cu/CeO$_2$-ZrO$_2$</td>
<td>1 : 4 (8–12)</td>
<td>10% Cu, 50% Zr</td>
<td>60</td>
<td>611</td>
<td>1</td>
</tr>
<tr>
<td>CeO$_2$-Pr$<em>6$O$</em>{11}$-Bi$_2$O$_3$</td>
<td>2 : 98 (30)</td>
<td>21% Pr, 32% Bi &amp; polyvinylpyrrolidone</td>
<td>20</td>
<td>622</td>
<td>2</td>
</tr>
<tr>
<td>Co$_3$O$_4$-CeO$_2$</td>
<td>1 : 19 (20 ± 2)</td>
<td>93% Co</td>
<td>50</td>
<td>643</td>
<td>3</td>
</tr>
<tr>
<td>CeO$_2$-Mn$_2$O$_3$</td>
<td>1 : 4 (10–12)</td>
<td>30% Mn</td>
<td>100</td>
<td>665</td>
<td>4</td>
</tr>
<tr>
<td>CeO$_2$-Sm$_2$O$_3$</td>
<td>1 : 4 (18 ± 2)</td>
<td>40% Sm</td>
<td>100</td>
<td>690</td>
<td>5</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Pr$</em>{0.2}$O$_{2.5}$</td>
<td>1 : 4 (10–12)</td>
<td>20% Pr</td>
<td>100</td>
<td>711</td>
<td>6</td>
</tr>
<tr>
<td>CeO$_2$-Gd$_2$O$_3$/TiO$_2$</td>
<td>1 : 4 (8–12)</td>
<td>20% Gd, 50% Ti</td>
<td>100</td>
<td>735</td>
<td>7</td>
</tr>
<tr>
<td>CeO$_2$-La$_2$O$_3$</td>
<td>1 : 4 (18 ± 2)</td>
<td>40% La</td>
<td>100</td>
<td>740</td>
<td>8</td>
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</table>

References