Electronic Supplementary Information

An efficient noble metal-free Ce-Sm/SiO$_2$ nano-oxide catalyst for oxidation of benzylamines under ecofriendly conditions

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1. Catalyst Preparation

The SiO$_2$-supported CeO$_2$-Sm$_2$O$_3$ nano-oxides with CeO$_2$:Sm$_2$O$_3$:SiO$_2$ = 80:20:100 were synthesized by a facile and economical deposition coprecipitation method. In a typical procedure, colloidal SiO$_2$ (Ludox, 40 wt%, Aldrich) was dispersed in deionized water and stirred for 2 h. The desired amounts of Ce(NO$_3$)$_3$·6H$_2$O (Aldrich, AR grade) and Sm(NO$_3$)$_3$·6H$_2$O (Aldrich, AR grade) were dissolved in deionised water under mild stirring conditions and then the resultant Ce–Sm nitrate solution was added to the aforesaid SiO$_2$ support solution under mild stirring conditions. Subsequently, aq. NH$_3$ solution was added drop-wise to the above mixture solution until it reaches an appropriate pH (~8.5) and the resulting slurry was filtered off. The obtained cake was oven dried at 383 K for 12 h and finally calcined at 773 K for 5 h at a heating rate of 5 K min^{-1} in dry air. For comparison, CeO$_2$-Sm$_2$O$_3$ (80:20 mole ratio based on oxides) and pristine CeO$_2$ were also prepared following the same procedure under identical conditions.

2. Catalyst Characterization

The powder XRD patterns were recorded on a Rigaku diffractometer using Cu Kα radiation (1.540 Å), operated at 40 kV and 40 mA. The diffractograms were recorded in the 2θ range of 10-80º with a 2θ step size of 0.02º and a step time of 2.4 s. The XRD phases present in the solid solution were identified with the help of a Powder Diffraction File-International Center for Diffraction Data (PDF-ICDD). The average crystallite size of the ceria samples were calculated by means of Scherrer equation and the lattice parameter was estimated by a standard cubic indexation method using the intensity of the most prominent peak (111).

$$\text{Scherrer equation:} \quad D = k\lambda/\beta \cos\theta$$

D = average crystallite size; k = constant value various from 0.98 to 1.39; λ = wavelength of X-rays; β = FWHM of a particular hkl plane; θ = angle (radians)

The BET surface area of the ceria-based 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 and flushed with Argon gas for 2 h to remove any surface adsorbed residues. Surface area was calculated by utilizing the desorption data. A Horiba Jobin-Yvon HR800 Raman spectrometer equipped with a liquid-nitrogen cooled charge coupled device (CCD) detector and a confocal microscope was used for obtaining the Raman spectra of the

samples. The emission line at 638-nm from Ar^+ laser (Spectra Physics) was focused on the sample under the microscope with the diameter of the analyzed spot being ~1 μm, under the ambient conditions. The time of acquisition was adjusted according to the intensity of Raman scattering. The wavenumber values reported from the spectra are accurate to within 2 cm^{-1}. The FT-IR spectra were recorded on a Nicolet 740 FT-IR spectrometer at ambient conditions using KBr discs with a nominal resolution of 4 cm^{-1} and averaging 100 spectra.

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 200 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. XPS measurements were performed on a PHI 5400 instrument with a 200 W Mg Kα probe beam. The analysis was done at room temperature and pressures were maintained in the order of less than 10^{-8} Pa. Survey and multi-region spectra were recorded at C 1s XPS peaks.

The NH_3-temperature programmed desorption experiments were carried out by using Auto-Chem 2910 instrument of Micromeritics. Approximately 30 mg of the sample was placed in a quartz tube and degassed up to 573 K under the He flow. Then the NH_3 gas was passed through the sample surface for 30 min followed by flushing with He gas to remove the physisorbed gas. Then, the chemisorbed amount of NH_3 was estimated in flowing He gas with a flow rate of 20mL min^{-1} from 323 to 1073 K at a heating rate of 10 K min^{-1}.

3. Activity Measurements

The liquid-phase oxidation of various benzylamines was carried out using O_2 as the green oxidant under solvent-free conditions. Typically, 0.2 g of catalyst and 0.2 mmol of benzylamine were taken into a 10 ml three-necked flask equipped with a gas inlet and outlet, a reflux condenser, and a thermometer. Then, the reaction mixture was heated to the required temperature and O_2 was bubbled at a rate of 20 ml/min under 800 rpm stirring conditions. After completion of the reaction, the liquid products and the catalyst were separated by centrifugation. The products were confirmed by GC–MS equipped with a DB-5 capillary column and a flame ionization detector (FID). Samples were taken periodically during the reaction and analyzed by GC equipped with a BP-20 (wax) capillary column and a FID.

The conversion of benzylamine and selectivity of the products were calculated based on the following equations:

$$Conversion\ (\%) = \frac{Amount\ of\ benzylamine\ converted\ (moles)}{Total\ amount\ of\ benzylamine\ taken\ (moles)} x100$$

$$Selectivity\ (\%) = \frac{Amount\ of\ benzylamine\ converted\ to\ a\ product\ (moles)}{Total\ amount\ of\ benzylamine\ converted\ (moles)} x100$$

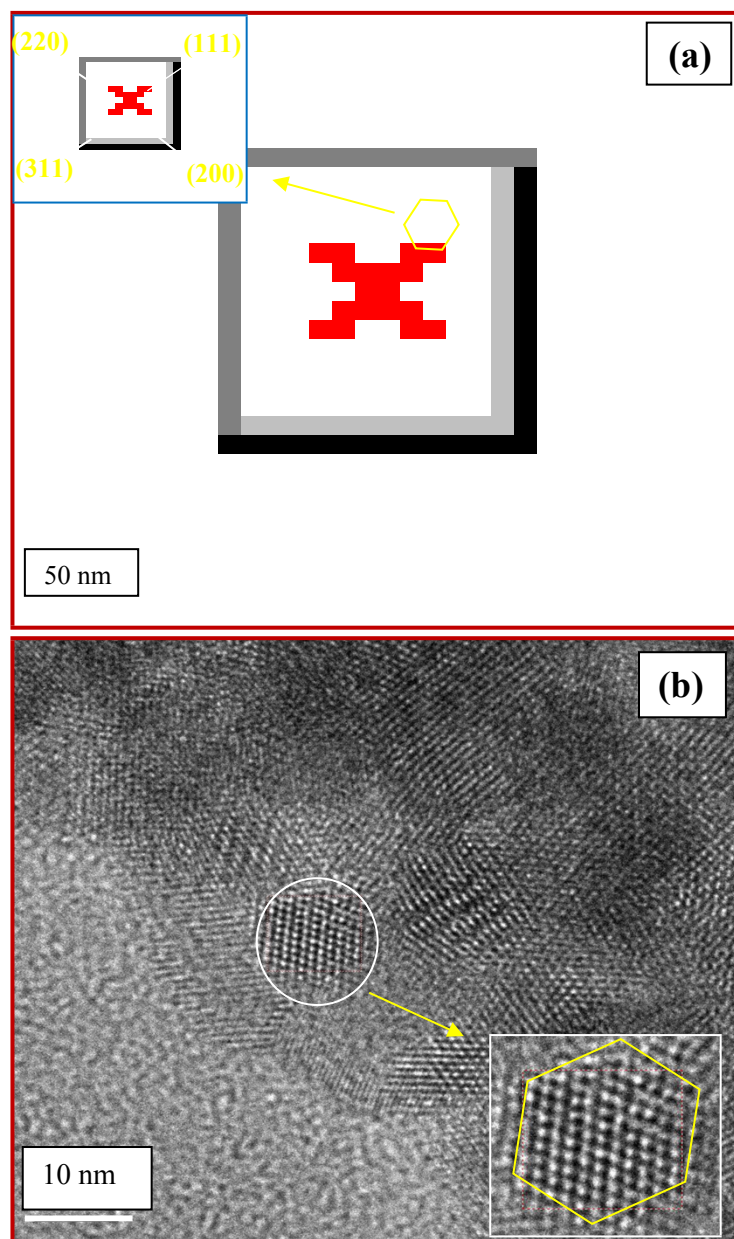**Fig. S1** (a) TEM picture with corresponding selected–area electron diffraction (SAED) pattern and (b) HRTEM picture of CeO_2-Sm_2O_3 sample (inset: enlarged views of selected areas).

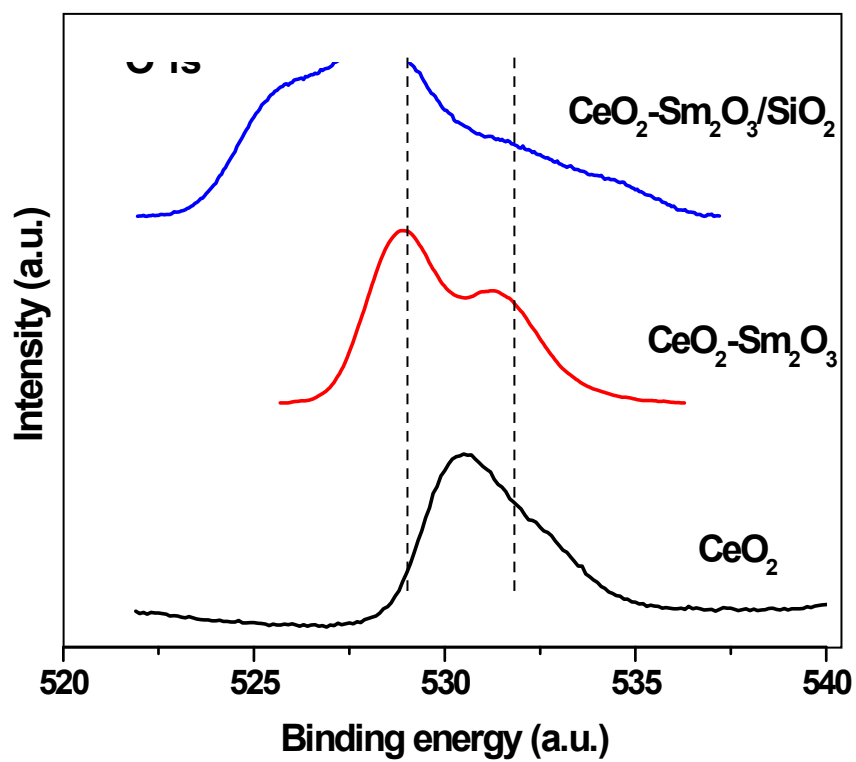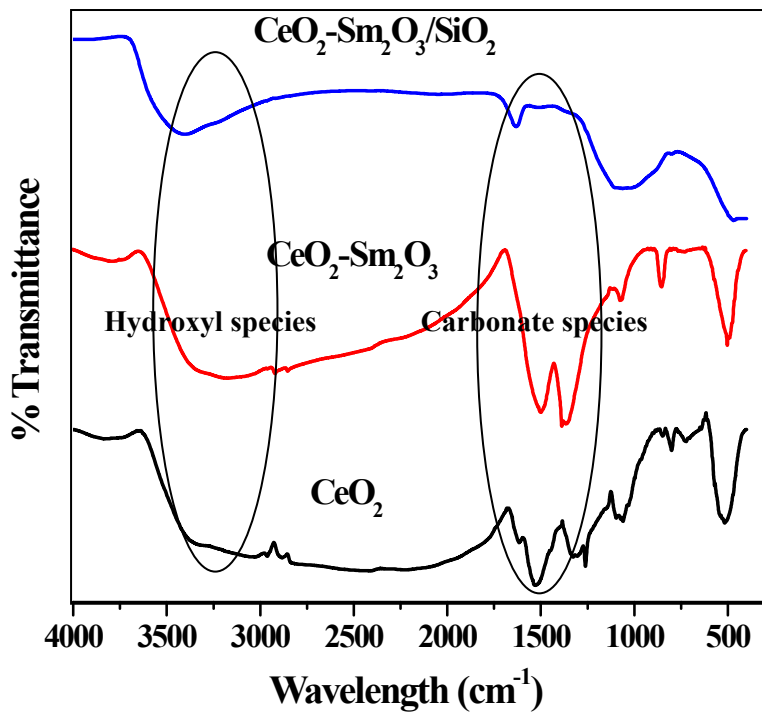**Fig. S2** O 1s XPS spectra of CeO$_2$-based samples calcined at 773 K.

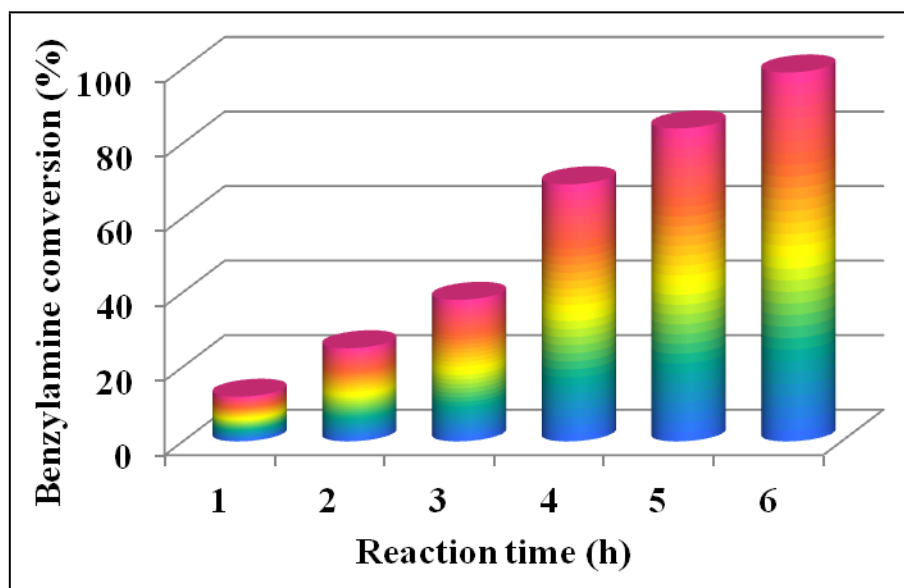**Fig. S3** FT-IR spectra of CeO$_2$-based samples calcined at 773 K.

Fig. S4 Effect of reaction time on the aerobic oxidation of benzylamine over Ce-Sm/SiO$_2$ nano-oxide catalyst.
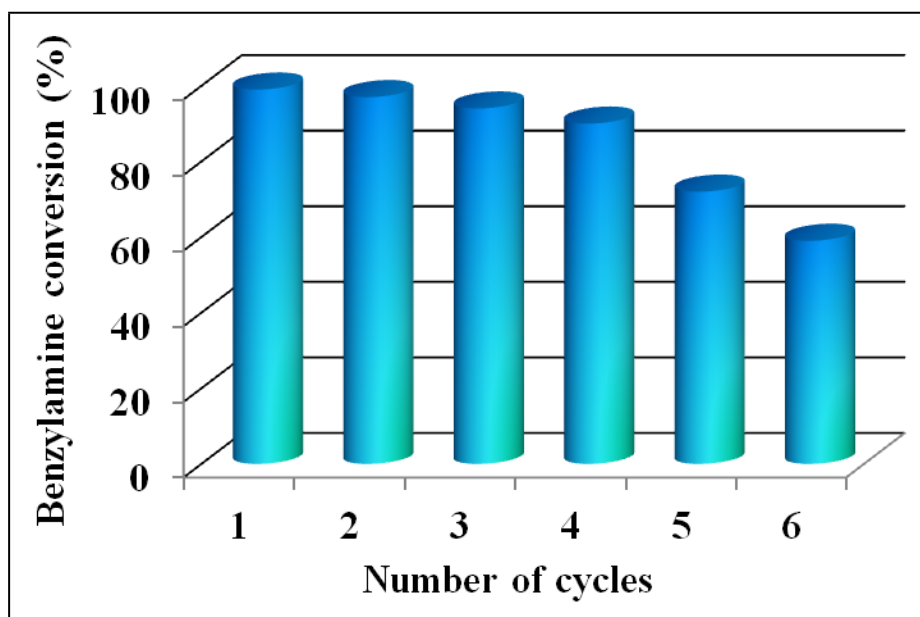
Fig. S5 Reusability analysis of the Ce-Sm/SiO$_2$ nano-oxide catalyst for solvent-free aerobic oxidation of benzylamine.