

Enhanced Catalytic Activity of $Ce_{1-x}M_xO_2$ ($M = Ti, Zr, \text{ and Hf}$) Solid Solution with Controlled Morphologies

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Experimental Section

Synthesis of CeO_2 , $Ce_{1-x}M_xO_2$ ($M = Ti, Zr, \text{ Hf}$) nanomaterials and catalysts

- 1) CeO_2 nanocrystals of cubic, rod and tube shapes were synthesized under hydrothermal conditions. In general, $Ce(NO_3)_3 \cdot 6H_2O$ (99.9%, Alfa Aesar) was dissolved in deionized water (10mL) to produce a transparent orange solution, to which was added NaOH (99%, J.T. Baker, $[OH^-]=15M$) solution in a fixed amount with rigorous stirring for 10 min. The concentration of OH^- was controlled on adding deionized water. The solution contained some white precipitate, which was transferred to a Teflon-lined stainless-steel autoclave, followed by different heating profiles depending on the desired crystal shape. After that reaction, the solid products were filtered and rinsed with first deionized water and then ethanol. The nanoparticles of all CeO_2 products have a characteristic light yellow color. The yield of the product was estimated to be ~90 %, based on the initial mass of the $Ce(NO_3)_3 \cdot 6H_2O$. CeO_2 nanocubes were obtained by heating at 150 °C for 48 hr. CeO_2 nanorods were prepared at $T=100$ °C and reaction duration of 10 h, followed by calcination at 300 °C. CeO_2 nanotubes were obtained by reaction with trace amount of ZrO_2 powder (mole ratio $Ce:Zr = 92:8$), followed by heating at 150 °C for 48 h. The crystallinity, purity, crystal morphology and size of CeO_2 products were analyzed with powder X-ray diffraction and scanning electron microscopy (SEM, Figure S1, A, B, C). All CeO_2 products were obtained as pure phases in a high yield.
- 2) $Ce_{1-x}M_xO_2$ nanomaterials were synthesized under hydrothermal conditions using the as-synthesized ceria nanocrystals using precursors TiO_2 , $ZrO(NO_3)_2$, or $HfO(NO_3)_2$. The reactions were carried out under hydrothermal conditions similar to the synthesis of CeO_2 nanomaterials as described in 1). Reactions with various doped metal precursors and reaction conditions were performed and the results are summarized in Table S1.
- 3) Catalyst with $Ce_{1-x}M_xO_2$ nanocrystals was prepared on impregnating granulated alumina (Al_2O_3 , 300 m^2/g , average diameter 1.2 mm) with an aqueous solution of $RuCl_3$ (0.032 g, 99.9 %, STREM) and $Ce_{1-x}M_xO_2$ nanocrystals (0.2 g), followed by ultrasonic irradiation for 1 h, oven drying at 50 °C for 6 h and finally

calcination at 600 °C for 1 h. Catalysts with irregular CeO₂ nanoparticles were prepared on impregnating an alumina support with a known amount of Ce(NO₃)₃•6H₂O, followed by oven drying at 50 °C for 6 h and finally calcination in air at 400 °C for 6 h. The resulting material was subsequently impregnated with RuCl₃. The Ru content of all catalysts was 5-wt% and the loading of each catalyst was ~0.13 g per 2 g of alumina support. EDS analyses on Ru/CeO₂ catalysts revealed all constituent elements.¹

Characterization

- 1) X-ray powder diffraction analysis of the products was performed using a Bragg–Brentano-type powder diffractometer (Bruker D8 Advance, operated at 40 kV and 40 mA, Cu K α , $\lambda = 1.5418 \text{ \AA}$). For phase identification, XRD data were collected over a 2θ range from 20° to 80° with a step interval of 0.05°.
- 2) Scanning electron microscopy (SEM) was performed on Hitachi S4700 instrument equipped with an energy-dispersive spectroscopy (EDS) detector. Transmission electron microscopy (TEM) and high-resolution TEM analyses were performed on JEOL JEM-2010 instruments. Samples were generally prepared on depositing a drop of dilute nanoparticle solution in toluene onto carbon-coated Cu grids.
- 3) Elemental analyses were carried out by using inductively coupled plasma mass spectroscopy (Perkin Elmer SCIEX ELAN 5000) and energy dispersive X-ray spectroscopy equipped in SEM/TEM instruments. Element maps were performed on Philips TECNAI 20. ICP-MS (Perkin Elmer SCIEX ELAN 5000) analysis was obtained with Ce_{1-x}M_xO₂ powder (0.01 g) dissolved in sulfuric acid (3 mL). Semi-quantitative analysis was measured on choosing two elements of cerium and zirconium. The analytical results have been transferred from mass fraction (ppm) to atomic per cent.
- 4) The specific surface area (BET) and pore volume of the sample as synthesized were determined with N₂ adsorption/desorption isotherms at 77 K by means of an instrument (Autosorb-1C, Quantachrome).

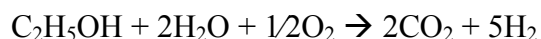
Apparatus and Product Analysis

- 1) Temperature-programmed-reduction (TPR) experiments were performed with a purpose-built system equipped with a thermal-conductivity detector. Before the initial TPR experiment, all samples were pretreated in O₂ atmosphere (0.2 SLPM) at 473 K for 1 h. The reduction was performed in a flow of H₂ (10 %) in Ar (30 mL/min) with a heating rate 10 K/min. The temperature was raised to 1273 K and the sample (0.2 g) was held at this temperature for 1 h. The amount of H₂ uptake in the TPR was estimated from integrated peak areas on comparison with those

obtained with CuO as a standard.

- 2) Tests of catalytic performance were performed with an apparatus similar to that described elsewhere¹⁻⁷. The system was equipped with mass-flow controllers and an HPLC pump (JASCO PU-2080 PLUS) for the carrier gas; the fed liquid contained a water/ethanol mixture of molar ratio 3 mol/mol (H₂O/C₂H₅OH). Reaction gases, supplied from high-pressure gas cylinders, had ultrahigh purity. Ethanol was analytic grade (Merck). The liquid was pumped to a steel chamber in which it was evaporated and in which it could be mixed (when desired) with an air stream from the mass-flow controllers. The gaseous mixture was fed to the reactor through silica tubing (inner diameter 4 mm, length ~15 cm). The temperature of the resulting gaseous mixture was maintained at 180 °C inside a furnace. The reactor was loaded with catalytic specimens of length up to 1.5 cm (~0.1 g), and having a silica glass-wool seal between the catalyst and the reactor walls. Two thermocouples were placed inside the vaporizer and on top of the catalyst to monitor the temperature profiles. A six-port valve (Valco) served to direct samples of the effluent to the injection port of a GC-MS system (Trace Ultra DSQ) equipped with a PLOT capillary column (30 m × 0.53 mm ID; Carboxeⁿ™ 1010, TCD detector, carrier gas = Ar, internal standard = N₂) to GC and a PLOT column (30 mm × ID 0.53 mm, Supel-Q, carrier gas = He) to a mass spectrometer. A condenser was placed before the latter column to condense and to remove H₂O, unreacted ethanol and other hydrocarbons from the gaseous stream.

The response factors of the TCD and MS detectors were determined by means of gaseous streams of known composition. The H₂ peak was integrated and compared against a calibration line produced from pure H₂ gas (>99.999% purity) before the experiments. The column oven was set at 50 °C and the TCD temperature was set at 200 °C. Argon or helium (>99.999% purity) served as carrier gas at a flow rate 72 mL/min with a split ratio 24. For the MS measurement, the mode of ionization was electron impact; data were collected in the full-scan mode. All experiments were performed at atmospheric pressure. In a typical experiment, after a fresh catalyst was placed in the reactor, the reactant stream with a water/ethanol molar ratio 3/1 was introduced into the reactor (T = 180 °C), in which it was heated, vaporized, mixed with Ar carrier gas and air, and finally passed through the catalyst. The rate of injection of ethanol was adjusted to control the C/O ratio. The temperature of the catalyst was increased rapidly to ~700 °C, and the product streams were fed into the GC-MS system. Freshly made catalysts were used to test the hydrogen selectivity at various C/O ratios. The overall reaction is described as follows:



The catalytic activity was evaluated in terms of hydrogen selectivity (S_{H_2}), which is defined as the molar ratio of the product H_2 (5 mol expected from the above reactions per mol ethanol) to the hydrogen production per mole of ethanol (3 mol H_2 /mol ethanol). The ideal value of S_{H_2} is 166%. Ethanol and other hydrocarbon products were condensed in water and analyzed with a mass spectrometer. In all cases the major products were H_2 and CO_2 . Small amount of CH_4 (~ 0.5 mol%), CH_3CHO (~1 mol%) and unreacted C_2H_5OH (~4 mol%) have been detected. For each catalyst, the reforming experiments were repeated several times and their results were reproducible.

References

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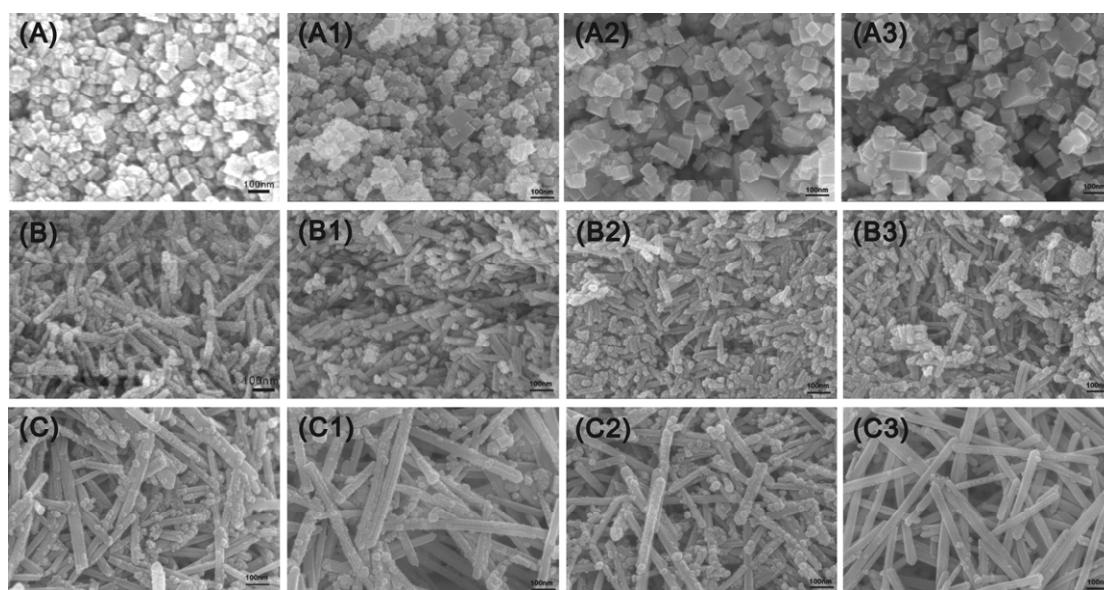


Figure S1. SEM images showing the morphology of CeO_2 and $\text{Ce}_{1-x}\text{M}_x\text{O}_2$ ($\text{M} = \text{Ti}, \text{Zr},$ and Hf) nanomaterials. (A) CeO_2 nanocube; (B) CeO_2 nanorod; (C) CeO_2 nanotube; (A1, B1, and C1) $\text{Ce}_{1-x}\text{Ti}_x\text{O}_2$ nanocube, nanorod, and nanotube, respectively; (A2, B2, and C2) $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ nanocube, nanorod, and nanotube, respectively; and (A3, B3, and C3) $\text{Ce}_{1-x}\text{Hf}_x\text{O}_2$ nanocube, nanorod, and nanotube, respectively.

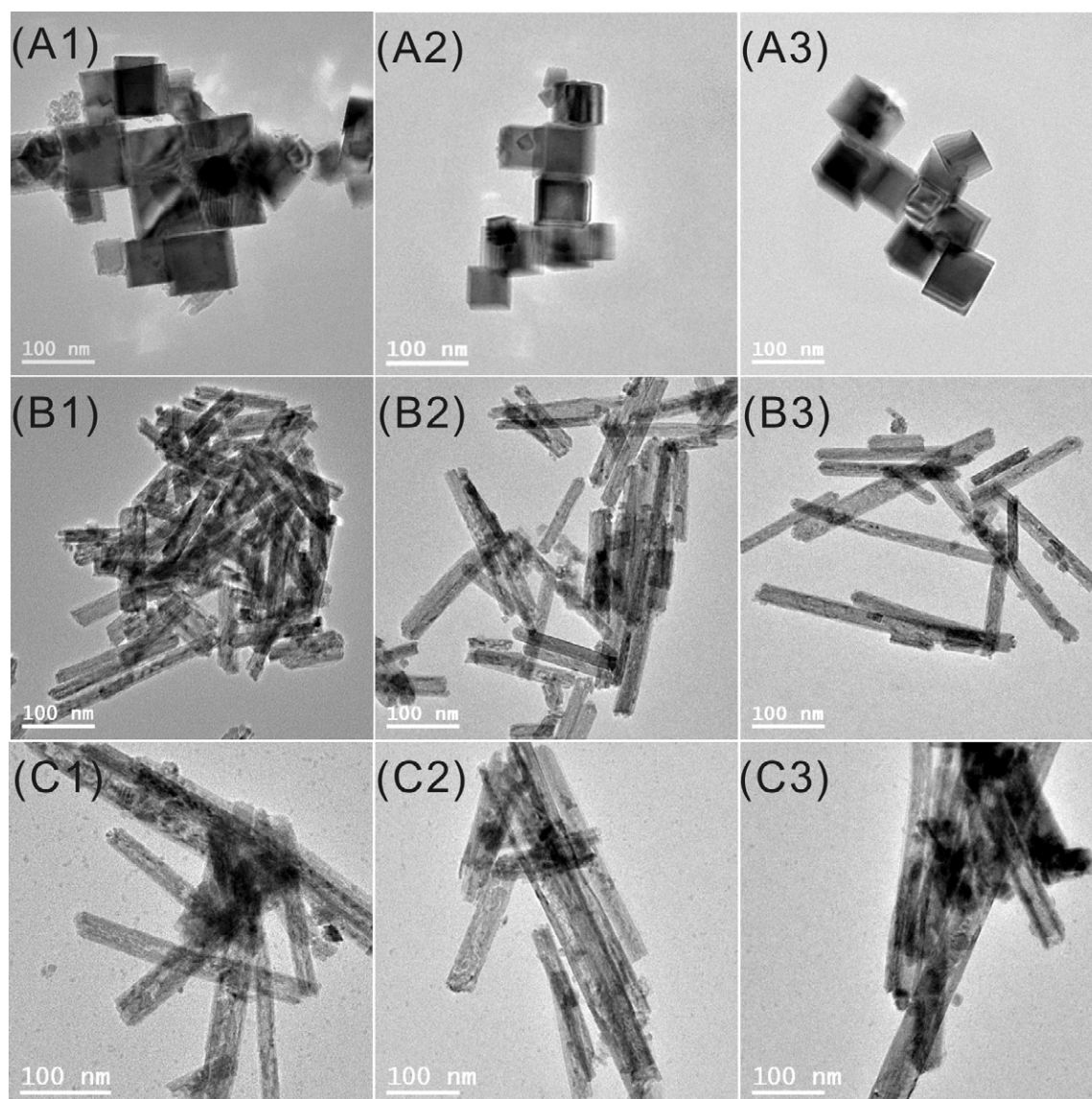


Figure S2. Magnified TEM images of $\text{Ce}_{1-x}\text{M}_x\text{O}_2$ ($\text{M} = \text{Ti}, \text{Zr}, \text{and Hf}$) nanomaterials.

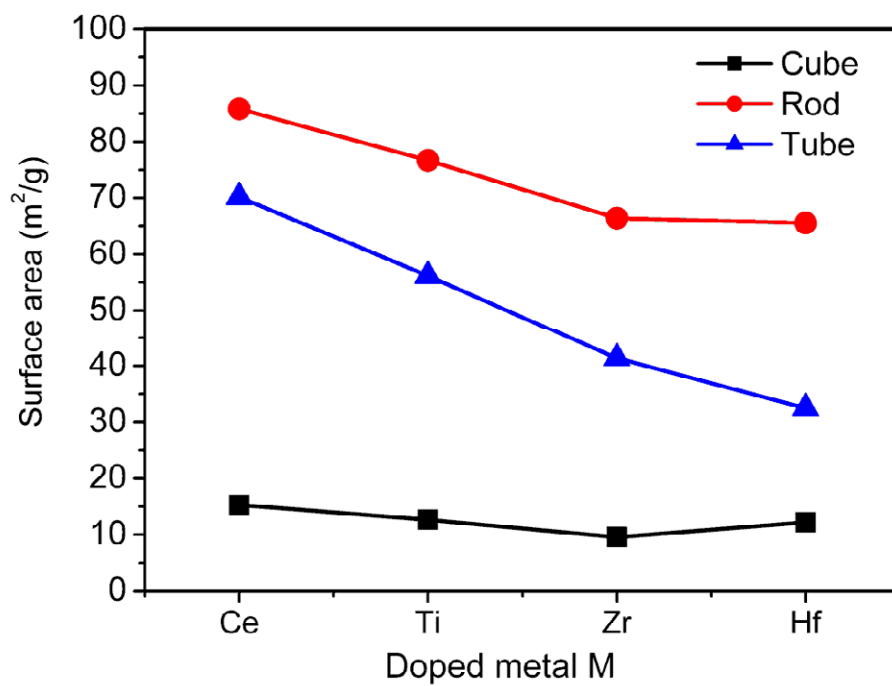


Figure S3. BET surface areas of CeO₂ and Ce_{1-x}M_xO₂ (M = Ti, Zr, and Hf) nanomaterials.

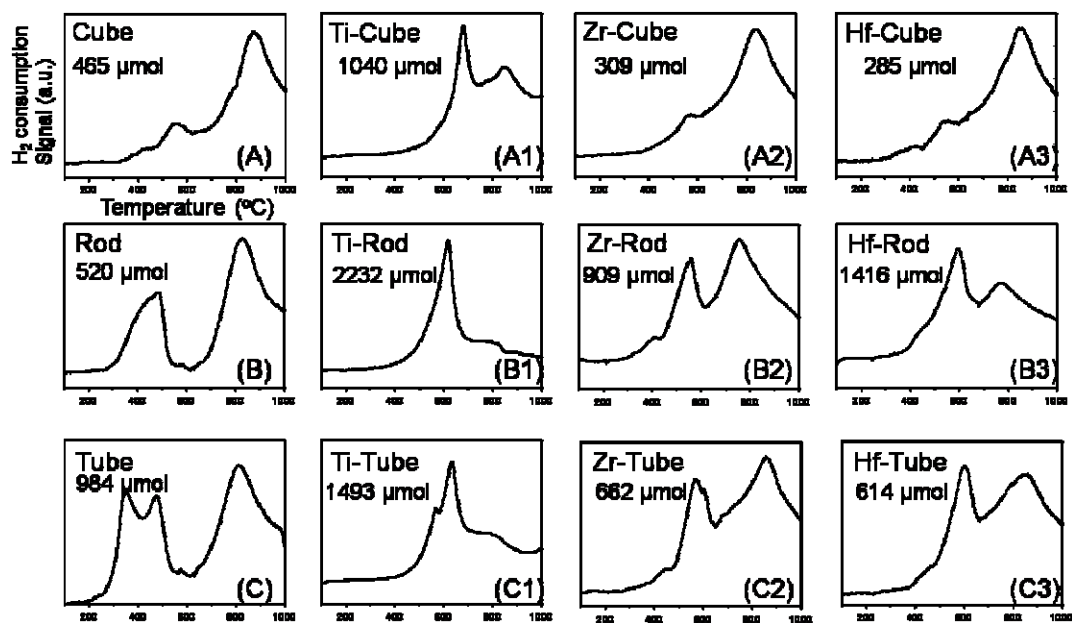


Figure S4. TPR profiles of CeO₂ and Ce_{1-x}M_xO₂ (M = Ti, Zr, and Hf) nanomaterials. The hydrogen consumption rate for the first stage of the reduction process is labeled.

Table S1. Summary of Reactions for Production of $Ce_{1-x}M_xO_2$ Nanocrystals

Morphology	Precursor	M/Ce ratio	Time	Temperature
Cube	TiO ₂	1/2	24h	180°C
	ZrO(NO ₃) ₂	1/3	24h	180°C
	HfO(NO ₃) ₂	2/3	24h	180°C
Morphology	precursor	M/Ce ratio	Time	Temp.
Rod	TiO ₂	1/2	10h	180°C
	ZrO(NO ₃) ₂	2/3	10h	180°C
	HfO(NO ₃) ₂	2/3	10h	180°C
Morphology	precursor	M/Ce ratio	Time	Temp.
Tube	TiO ₂	1/2	24h	180°C
	ZrO(NO ₃) ₂	2/3	24h	180°C
	HfO(NO ₃) ₂	2/3	24h	180°C

Table S2. Summary of elemental analysis for $M_xCe_{1-x}O_2$ (M = Ti, Zr, Hf).

M	Ti-cube	Zr-cube	Hf-cube	Ti-rod	Zr-rod	Hf-rod	Ti-tube	Zr-tube	Hf-tube
SEM-EDS	16.2%	22.0%	4.7%	29.9%	34.5%	20.1%	21.8%	32.7%	21.5%
TEM-EDS	13.3%	19.1%	4.1%	27.2%	34.6%	18.9%	19.3%	31.2%	19.4%
ICP-MS	20.7%	20.8%	4.1%	27.6%	29.4%	21.7%	24.2%	29.4%	22.3%

Table S3. Summary of hydrogen selectivity as a function of C/O ratio obtained over catalysts with $M_xCe_{1-x}O_2$ (M = Ti, Zr, Hf).

M	cube	Ti-cube	Zr-cube	Hf-cube	rod	Ti-rod	Zr-rod	Hf-rod	tube	Ti-tube	Zr-tube	Hf-tube
C/O : 0.4	74%	51%	93%	83%	70%	74%	71%	76%	68%	84%	83%	94%
C/O : 0.5	88%	90%	105%	95%	84%	113%	112%	103%	79%	103%	103%	110%
C/O : 0.6	82%	109%	94%	69%	93%	111%	109%	106%	81%	113%	89%	95%
C/O : 0.7	113%	95%	89%	55%	106%	101%	98%	96%	110%	106%	74%	84%
C/O : 0.8	73%	77%	61%	35%	99%	63%	62%	66%	83%	85%	37%	63%