

Support Information

Ligand-Assisted Mechanochemical Synthesis of Ceria-Based Catalysts for the Selective Catalytic Reduction of NO by NH₃

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Experimental Sections

Catalyst preparation

All chemicals were of analytical grade and used as received without further purification. The CeO₂/TiO₂ catalysts were prepared by dry ball-milling using cerium (III) nitrate hexahydrate or ceria as the cerium precursor in the presence or absence of organic ligand. Cerium precursor, commercial anatase TiO₂ (Chongqing Chemical & Pharmaceutical holding (Group) Company), and adipic acid (when used), based on 20 wt% ceria, were placed into a 500 cm³ sintered zirconium oxide grinding jar with agate balls (20, 15 and 10 mm in diameter). The ball-to-powder mass ratio was 10:1, and the cerium precursor-to-ligand mass ratio was 2:1. Milling was performed in a QM-QX planetary ball mill (Nanjing NanDa Instrument Plant) at a rotation speed of 500 rpm for 1 h. The milled mixture was calcined in air at 250 °C for 2 h firstly, and then calcined in air at 450 °C for 2 h, giving the expected CeO₂/TiO₂ catalyst. The catalyst prepared by dry ball milling using cerium (III) nitrate hexahydrate as the cerium precursor without organic ligand was denoted as “CeTi-BM”, and the one prepared by ligand-assisted ball milling was denoted as “CeTi-BMA”. “CeO₂Ti-BM” and “CeO₂Ti-BMA” referred to the catalysts prepared by using commercial ceria as the cerium precursor in the absence or presence of adipic acid, respectively. For comparison, a CeO₂/TiO₂ catalyst was also prepared by incipient wetness impregnation, denoted as CeTi-IM. Briefly, TiO₂ (16.0 g) was added to the solution of cerium (III) nitrate hexahydrate (10.1 g) in 10 ml H₂O, then followed by stirring at room temperature for 2 h and drying at 80 °C for 12 h, calcining at 250 °C for 2 h and 450 °C for 2 h in air, giving the CeTi-IM sample with the CeO₂ loading of 20 wt%. When terephthalic acid or oxalic acid was used, the experimental procedure was similar to the above statement.

Catalyst characterization

Textural characteristics of TiO₂ and CeO₂/TiO₂ catalyst samples were measured by physical nitrogen adsorption at -196°C on a Micrometrics, ASAP 2020 analyzer. The specific surface area was determined using the Brunauer-Emmett-Teller (BET) method. The average pore size and the pore volume were analyzed by using the Barrett-Joyner-Halenda (BJH) model. Before each analysis, the sample (about 100 mg) was degassed under vacuum at 250 °C for 4 h. The crystal structures of the catalysts were determined by an X-ray diffractometer (Bruker/AXS D8 Advance) operating at 50 kV and 35 mA using Cu K α radiation ($\lambda=1.5406$ Å). The samples were scanned from 10 ° to 80° (2 θ) with a step size of 0.02 ° and a scanning speed of 3.5 °/min. The temperature-programmed reduction (TPR) by H₂ was performed on a chemisorption analyzer (Micromeritics, AutoChem II 2920). First, the 50 mg of the catalyst was pretreated in pure O₂ at 300 °C for 30 minutes and then cooled to room temperature. The sample was purged by He for 15 min. When the baseline remained unchanged, the TPR profile of the catalyst was obtained by heating the above sample from 30 to 850 °C in a flow of 10 % H₂/He (50 mLmin⁻¹) with a temperature ramp of 10 °C/min. The reducing gas was cooled in a bath of mixture of isopropanol and liquid nitrogen to condense the water generated from reduction of sample. The hydrogen consumption was monitored by a TCD detector. The FT-IR data were recorded on a Thermo Nicolet 6700 instrument using KBr pellets. Transmission electron microscopy (TEM) images were recorded over a JEM 2100 (JEOL) microscope, operated at an acceleration voltage of 200 KV and electric current of 20 mA. X-ray photoelectron spectra (XPS) were performed on an X-ray photoelectron spectrometer (Thermo Fisher, ESCALAB 250 Xi), using monochromatic Al K radiation (1486.6 eV) operating at an accelerating power of 15 kW. Before the measurement, the sample was outgassed at room temperature in a UHV chamber (<5 \times 10⁻⁷ Pa). The sample charging effects were compensated by calibrating all binding energies (BE) with the adventitious C 1s peak at 284.6 eV. The surface atomic concentration, atomic ratios of Ce³⁺/(Ce³⁺+Ce⁴⁺) and different oxygen species obtained by Gaussian-Lorentz fitting.

Catalytic performance evaluation

Measurements of the activity of selective catalytic reduction of NO by NH₃ over the catalysts were carried out in a fixed-bed quartz reactor (id = 10 mm) at atmospheric pressure. The catalyst (1.0 ml) with 40-60 mesh was packed in the middle of the reactor between two quartz wool plugs. The reaction temperature was monitored by a thermocouple located at the bed of the catalyst and regulated from 80 to 450 °C. The flow rate of reactant mixture of 1000 ppm NO, 1000 ppm NH₃, 6 % O₂, and 5 % H₂O

with N₂ as balance gas was controlled by mass flow regulators (Beijing Seven Star Electronics Co., Ltd, D07-7B). The total flow rate was 500 ml/min, and the space velocity (SV) was 30,000 h⁻¹. To increase the space velocity to 60,000 h⁻¹, half amount of catalyst was replaced by the same volume of quartz sand with similar size to the catalyst particles. The concentrations of NO, NO₂, N₂O, and N₂ in the outlet of the reactor were determined by an FT-IR spectrometer (Tensor 27, Bruker) and a gas chromatography (Shimadzu GC 2014C) equipped with a TCD detector. The NO conversion and N₂ selectivity were calculated according to the following equations:

$$NO_{conversion}(\%) = \frac{[NO]_{in} - \{[NO]_{out} + 2[N_2O]_{out} + [NO_2]_{out}\}}{[NO]_{in}} \times 100\% \quad (1)$$

$$N_{2selectivity}(\%) = \frac{[N_2]_{out}}{[N_2]_{out} + [N_2O]_{out} + \frac{1}{2}[NO_2]_{out}} \times 100\% \quad (2)$$

The effects of H₂O and SO₂ on the NH₃-SCR activity of the catalysts were evaluated in a fixed-bed quartz reactor (id = 10 mm) at atmospheric pressure. The reactant gas composition was as follows: 1000 ppm of NO, 1000 ppm of NH₃, 6 % of O₂, 300 ppm of SO₂, 5 % of H₂O and balance of N₂. The total flow rate was 500 ml/min, and the volume of catalyst with 40-60 mesh was 1.0 ml. The corresponding gas hourly space velocity (GHSV) was 30000 h⁻¹. The concentrations of NO were continually monitored by an SIGNAL 4000VM NO_x chemiluminescence analyzer.

Additional Figures and Data

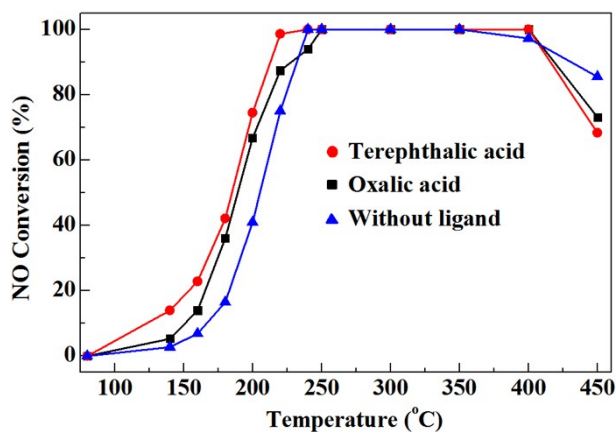


Figure S1 NO conversions over the $\text{CeO}_2/\text{TiO}_2$ catalysts prepared by dry ball milling method in the presence or absence of organic ligand using cerium (III) nitrate hexahydrate as the cerium precursor. Reaction conditions: $[\text{NO}] = [\text{NH}_3] = 1000$ ppm, $[\text{O}_2] = 6$ vol%, balance N_2 , total flow rate = 100 ml/min, GHSV = 30,000 h^{-1} .

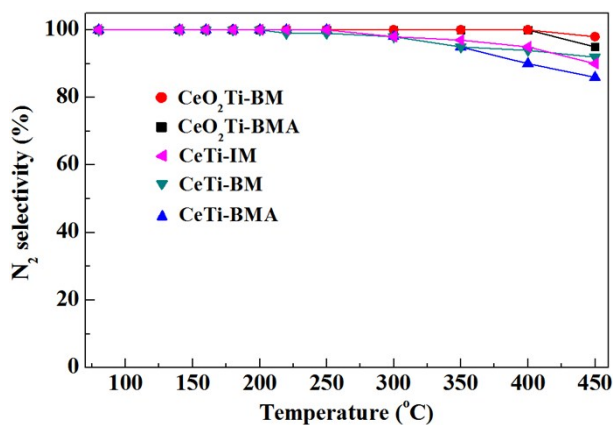


Figure S2 N_2 selectivity as a function of temperature for the NH_3 -SCR reaction over the $\text{CeO}_2/\text{TiO}_2$ catalysts. Reaction conditions: $[\text{NO}] = [\text{NH}_3] = 1000$ ppm, $[\text{O}_2] = 6$ vol%, $[\text{H}_2\text{O}] = 5$ %, balance N_2 , total flow rate = 500 ml/min, GHSV = 30,000 h^{-1} .

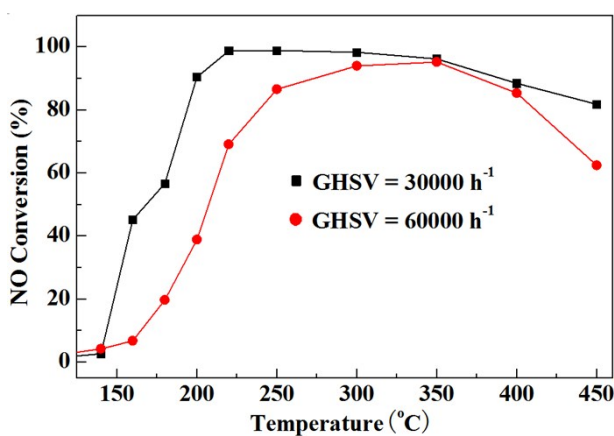


Figure S3 NO conversions over the CeTi-BMA catalyst. Reaction conditions: $[\text{NO}] = [\text{NH}_3] = 1000$ ppm, $[\text{O}_2] = 6$ vol%, $[\text{H}_2\text{O}] = 5$ %, balance N_2 , total flow rate = 500 ml/min, GHSV = 30,000 and 60,000 h^{-1} , respectively.

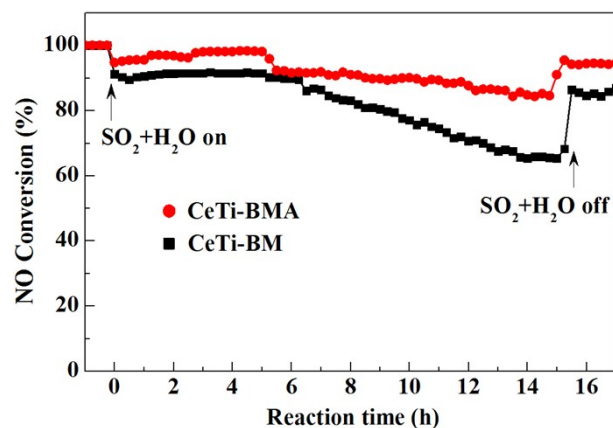
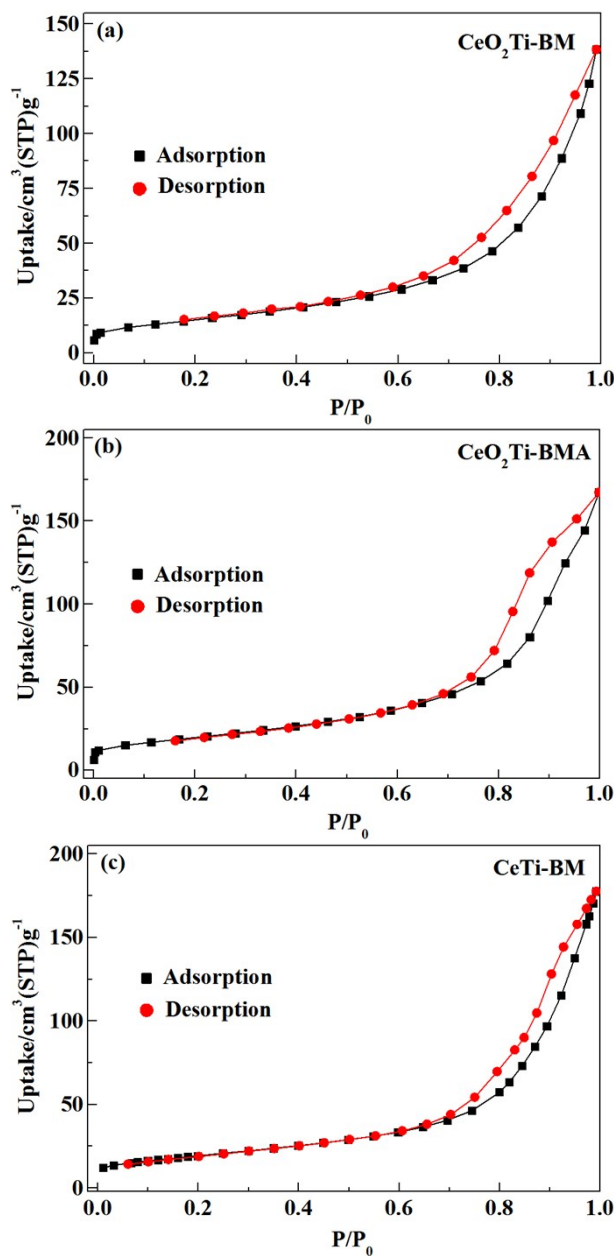


Figure S4 NO conversions over CeTi-BMA and CeTi-BM catalysts in the presence of SO₂ and H₂O at 300 °C. Reaction conditions: [NO] = [NH₃] = 1000 ppm, [O₂] = 6 vol%, 300 ppm SO₂, 5 vol% H₂O, N₂ balance, total flow rate = 500 ml/min and GHSV = 30,000 h⁻¹.



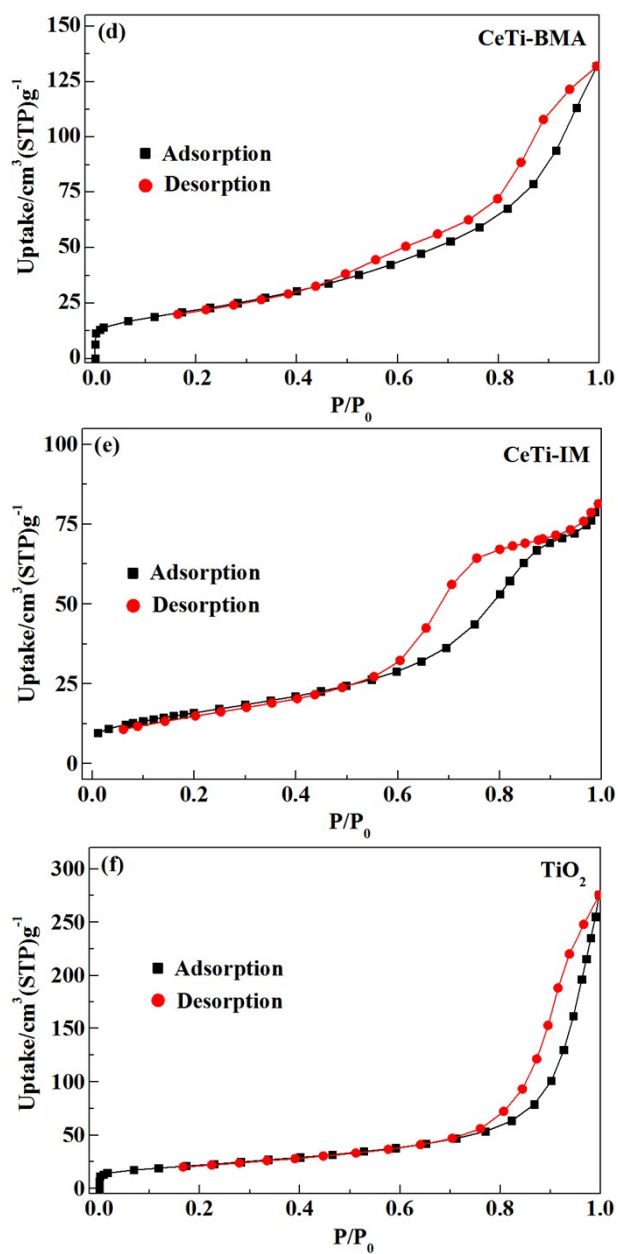


Figure S5 Nitrogen sorption isotherms of CeO₂Ti-BM (a), CeO₂Ti-BMA (b), CeTi-BM (c), CeTi-BMA (d), CeTi-IM (e) and TiO₂ (f) samples at 77K.

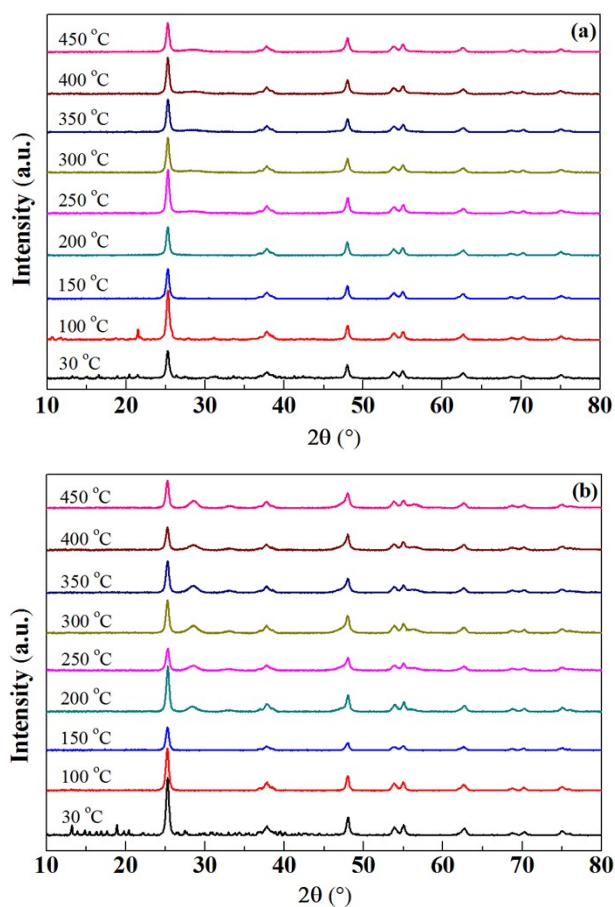


Figure S6 X-ray diffraction patterns of the ball milled mixtures of cerium nitrate and TiO_2 in the presence (a) or absence (b) of adipic acid after calcining at different temperatures for 2 h.

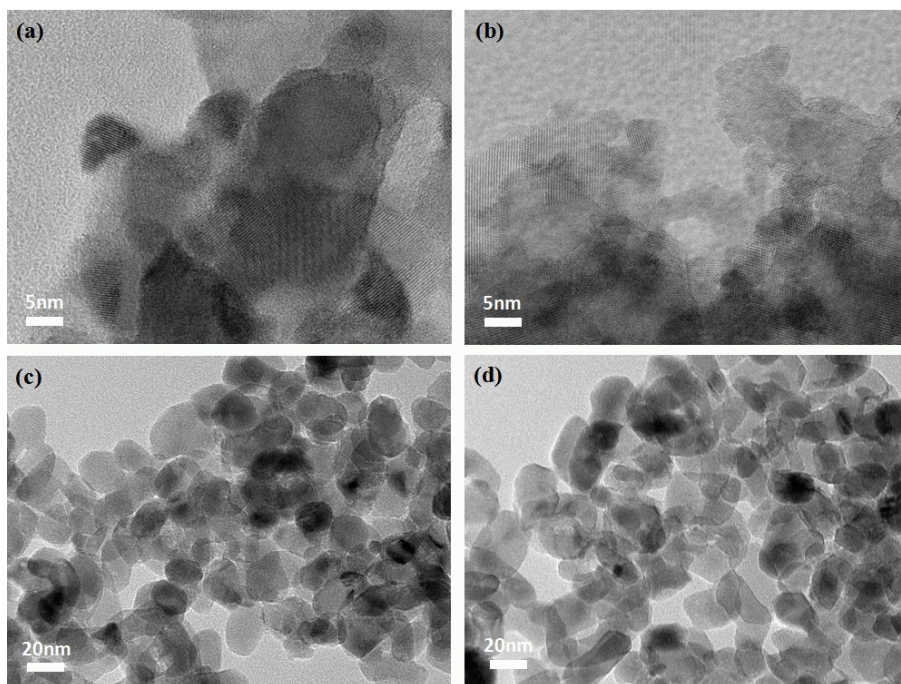


Figure S7 TEM images of CeTi-BM (a), CeTi-BMA (b), $\text{CeO}_2\text{Ti-BM}$ (c) and $\text{CeO}_2\text{Ti-BMA}$ (d) samples.

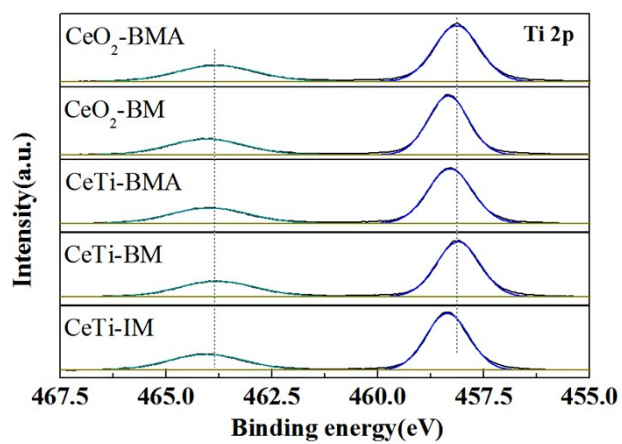


Figure S8 XPS results of Ti 2p of the CeO₂/TiO₂ catalysts.

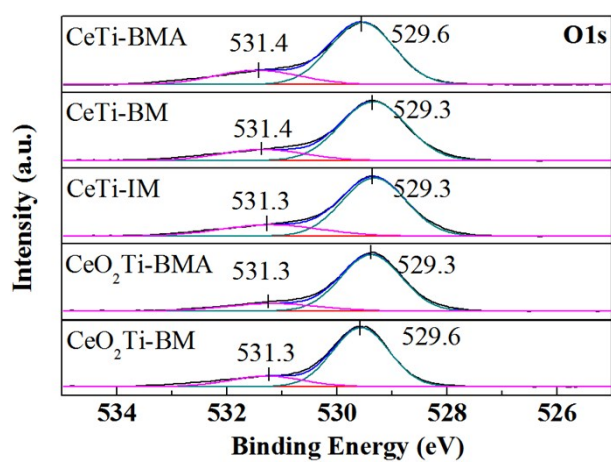


Figure S9 XPS results of O 1s of the CeO₂/TiO₂ catalysts.

Table S1 Textural properties of the CeO₂/TiO₂ catalysts and the TiO₂ support.

Samples	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)
TiO ₂	77	0.434	16.1
CeTi-BMA	82	0.217	7.5
CeTi-BM	70	0.275	13.7
CeTi-IM	60	0.127	6.9
CeO ₂ Ti-BMA	72	0.278	10.5
CeO ₂ Ti-BM	56	0.226	11.2

Table S2 Chemical composition of the CeO₂/TiO₂ catalysts, all units in wt%.

	TiO ₂	CeO ₂	SO ₃
CeO ₂ Ti-BM	79.6	19.8	0.6
CeO ₂ Ti-BMA	80.3	19.0	0.7
CeTi-BM	79.6	19.9	0.5
CeTi-BMA	80.1	19.4	0.5
CeTi-IM	80	19.5	0.5

Table S3 XPS binding energies (eV) of the CeO₂Ti-BMA, CeO₂Ti-BM, CeTi-BMA, CeTi-BM and CeTi-IM samples.

	Ce 3d _{3/2}		Ce 3d _{5/2}		O 1S			
	BE(eV)	Area(%)	BE(eV)	Area(%)	BE(eV)	Area(%)	BE(eV)	Area(%)
CeO ₂ Ti-BMA	916.4	8.9	898.1	11.2	529.3	16.3	531.3	83.7
	907.0	7.5	887.9	11.2				
	903.8	12.3	885.4	13.7				
	900.8	12.5	882.2	22.7				
CeO ₂ Ti-BM	916.3	15.0	898.1	16.9	529.6	18.3	531.3	81.7
	907.6	8.2	888.8	8.2				
	903.4	6.4	885.7	11.4				
	900.8	14.1	882.0	19.8				
CeTi-BMA	916.6	5.4	898.6	10.5	529.6	23.6	531.4	76.4
	906.9	7.6	888.4	5.2				
	904.1	12.4	885.7	22.8				
	901.1	11.8	882.0	24.3				
CeTi-BM	916.1	6.8	898.0	11.8	529.3	19.9	531.3	80.1
	906.6	8.6	888.3	8.8				
	903.2	13.3	885.2	20.3				
	900.3	9.6	881.7	20.8				
CeTi-IM	916.2	6.7	897.8	10.6	529.3	23.1	531.3	76.9
	906.3	9.3	888.2	8.9				
	903.3	11.3	885.1	20.9				
	900.3	12.0	881.6	20.3				

Table S4 Surface atomic concentrations and atomic ratios of the CeO₂Ti-BMA, CeO₂Ti-BM, CeTi-BMA, CeTi-BM and CeTi-IM samples.

	Surface atomic concentration (mol %)			Atomic ratio (mol %)	
	Ce	Ti	O	Ce ³⁺ /(Ce ³⁺ +Ce ⁴⁺)	O _{ads} /(O _{ads} +O _{latt})
CeO ₂ Ti-BMA	2.6	28.5	68.9	26.0	16.3
CeO ₂ Ti-BM	0.8	30.3	68.9	17.8	18.3
CeTi-BMA	8.1	23.9	68.0	35.2	23.6
CeTi-BM	5.9	23.4	70.7	33.6	19.9
CeTi-IM	5.5	25.4	69.1	32.2	23.1