Supporting information

CeO_2 nanorods anchored on mesoporous carbon as an efficient catalyst for imine synthesis

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Experimental Section

Materials. All chemicals were of analytical grade and were used without further purification. Double-distilled water was used in all of the experiments.

Catalyst preparation. The mesoporous carbon support was prepared using a modified hard-template method.[1,2] The procedure is as following: 48 g aluminium nitrate nonahydrate, 13.5 g citric acid and 15.6 g sucrose were solved in 200 mL water. After stirring for 30 min, 8.7 mL phosphoric acid (85%) was dropped into above aqueous solution. A 10 % ammonia solution was used to adjust the pH value of the solution to 5.1. Then, the mixture was heated at 80 ºC to remove water and other volatiles. The obtained solid was first pretreated at 300 ºC in muffle for 10 minutes, and then calcined at 800 ºC under argon atmosphere for 6 h. Finally, the composite was treated with 4 M HNO_3 at 80 ºC for 6 h to remove all the AlPO component. The left species was determined by TG, which is about 1.6 wt%. The resulting products were filtered, washed with deionized water, and dried at 100 ºC overnight. The resultant carbon was denoted as MC.

Anchored CeO_2 nanorods catalyst was prepared by a wet impregnation method with MC as a support. The procedure is as following: 0.145 g $Ce(NO_3)_3 \cdot 6H_2O$ was solved in 10 mL water, and then 0.5 g MC was added into above solution. The resultant mixture was stirred for about 3 h at room temperature, and then heated at 80 ºC to remove the water. The obtained solid was thermal-treated at 350 ºC for 4 h under an argon flow with a heating rate of 5 $ºC \cdot min^{-1}$. The resultant catalyst was denoted as CeO_2/MC. The loading amount is 10 wt%, which is calculated with CeO_2.

For comparison, bulk CeO_2 and CeO_2 morphologies（rod, cube and octahedron）were also prepared. Bulk CeO_2 was obtained with a conventional precipitation method using $Ce(NO_3)_3 \cdot 6H_2O$ and ammonia as ceria precursor and precipitation agent, respectively. 10 % ammonia was added into an $Ce(NO_3)_3$ solution to obtain a pH value of 9.0. The obtained solid was dried overnight and calcined at 350 ºC for 3 h. The resultant material was denoted as CeO_2.

CeO_2 morphologies were synthesized using a modified hydrothermal method reported by Gao and Mai et al.[3,4] Briefly, $Ce(NO_3)_3 \cdot 6H_2O$ (0.868 g) and the requisite amount of NaOH (0.016-15 g) were dissolved in 5 and 35 mL of deionized water, respectively, after which these two solutions were mixed and the suspension was aged at room temperature under continuous stirring for 0.5 h. Subsequently, the mixtures were hydrothermal treated at 100-180 ºC for 24 h in a 100 mL Teflon-lined autoclave. After cooling to room temperature, the mixture was centrifuged, and the obtained precipitates were washed with distilled water for several times. Then the solid was dried at 80 ºC overnight and further thermal-treated at 350 ºC for 3 h to obtain the resultant CeO_2 catalyst.

Catalyst characterizations. Transmission electron microscopy (TEM) analyses were performed with a FEI Tecnai F20 EM operated at 200 kV. Scanning electron microscopy (SEM) images were taken on a Hitachi-SU8020 with an accelerating voltage of 30 kV. X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray diffractometer equipped with a CuKα radiation source (λ=0.1543 nm). The data was collected from 10 ° to 70 ° at a scanning speed of 5 °/min. N_2 adsorption-desorption isotherms were measured at 77 K, using a Micromeritics ASAP 2010N analyzer. Samples were degassed at 200 ºC for 20 h before measurements. Specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) model. Pore size distributions were evaluated from desorption branches of nitrogen isotherms using the Barret-Joyner-Halenda (BJH) model. The surface composition and the elemental valence of the catalysts were determined by X-ray photoelectron spectra (XPS) on a Thermo ESCA LAB 250 system with MgKα source (1254.6 eV). Binding energies were obtained by referencing to the C (1s) binding energy of carbon (peak at 284.6 eV) and a mixed Gaussian-Lorentzian curve-fitting procedure was used to fit the spectra in order to get the relative amount of Ce with different elemental valence. The P and Al species left on the MC support was estimated using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Perkin-Elmer emission spectrometer). Raman spectra were collected on a Bruker RFS 100 Raman spectrometer with an argon laser (532 nm) as an excitation source. Temperature-programmed reduction (H_2-TPR) and temperature-programmed desorption (TPD) experiments were performed on a TP-5079 apparatus (Tianjinxianquan Company, China) equipped with TCD detector. In the H_2-TPR experiment, the sample (30 mg) was first treated under Ar at 350 ºC for 30 min and then cooled to room temperature. Then 5 vol% H_2/Ar mixture was switched with a flow rate of 30 $mL\cdot min^{-1}$. After a stabilized baseline was reached, the sample was heated from room temperature to 800 ºC, at a rate of 10 $ºC\cdot min^{-1}$. As for the CO_2-, NH_3- and O_2-TPD experiments, the sample (30 mg) was also pre-treated under Ar at 350 ºC for 30 min. After cooling to 50 ºC and being flushed in Ar flow for 30 min, the sample was exposed to repeated 10% CO_2/Ar, 10% NH_3/Ar or 20% O_2/Ar pluses until saturation. Subsequently, the sample was purged at 50 ºC with He for 1 h to remove the physical adsorbed CO_2, NH_3 or O_2 species, and then the temperature was brought up to 500-600 ºC at a ramping rate of 10 $ºC\cdot min^{-1}$. The final TPD profile were obtained by applying subtraction treatment between the adsorbed curve (CO_2, NH_3 or O_2 species) with blank curve without adsorbing any probe molecular. Solid-state NMR experiments were performed on a Bruker Avance III spectrometer at an external magnetic field of 9.4 T with a 4 mm double-tuned MAS probe at a spinning rate of 14 kHz. ^1H MAS NMR spectra were acquired with a recycle day of 0.5

s. $^{1}H \rightarrow ^{13}C$ cross polarization (CP) MAS NMR spectra were recorded with high-power ^{1}H decoupling using a contact time of 1 ms and a recycle delay of 0.5 s. Both ^{1}H and ^{13}C shifts were referenced to tetramethylsilane (TMS) at 0 ppm.

Catalytic performance test. The catalytic activity for aerobic oxidation coupling of alcohol and amine was carried out in a 50 mL two-neck flask at atmospheric pressure. For each test, 0.3 g of catalyst sample was added to the reactor containing 1.0 mmol alcohol, 2.0 mmol amine and 10 mL toluene. The mixture was contacted with air balloon and the reaction temperature was kept at 80 ºC. The products were taken via a sampling pipe and the products were analyzed by gas chromatography fitted with a HP-5 capillary column (25 m × 0.32 mm) and flame ionization detector. A gas chromatography-mass spectroscopy (GC-MS) method was applied for the identification product mixtures. The conversion of the imine product were calculated using normalization method based on the alcohol to imine ratio. The yield of imine was calculate based on the alcohol conversion and imine selectivity. In the recycle experiment, the solid catalyst was separated by filtration after 2 h reaction and further treated at 350 °C for 1 h before next cycle test. The hot filtration test was carried out as following: after 15 min reaction, the solid catalysts were separated by a Buchner funnel. The mixture of filtrate was put into the reactor and continuously reacted under the same condition (80 °C, air 1 atm) without a solid catalyst. For the kinetics test, a stiring rate of 1000 r/min was carried out to decrease the influence of diffusion in the reaction process.

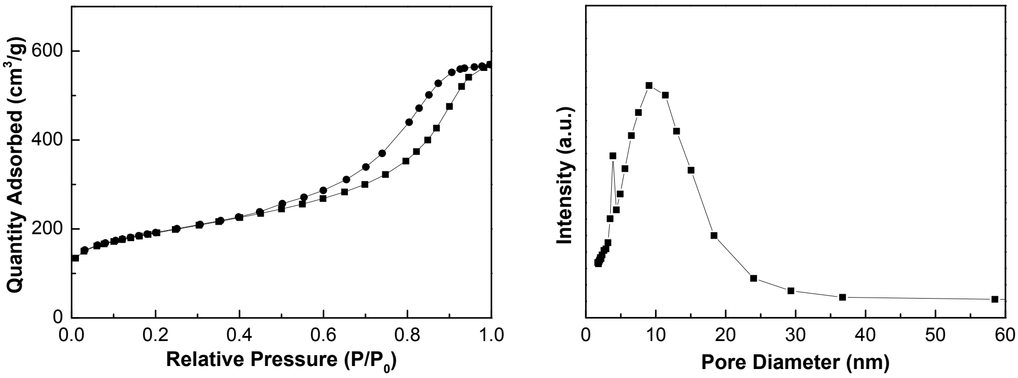


Fig. S1 N_2 adsorption profiles and the corrsponding pore size distribution of CeO_2/MC.

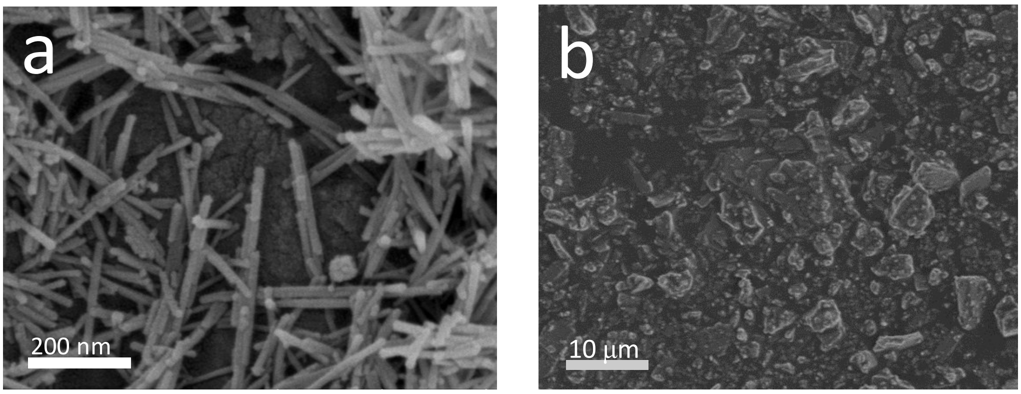


Fig. S2 SEM images of CeO_2 nanorod (a) and bulk CeO_2 (b).

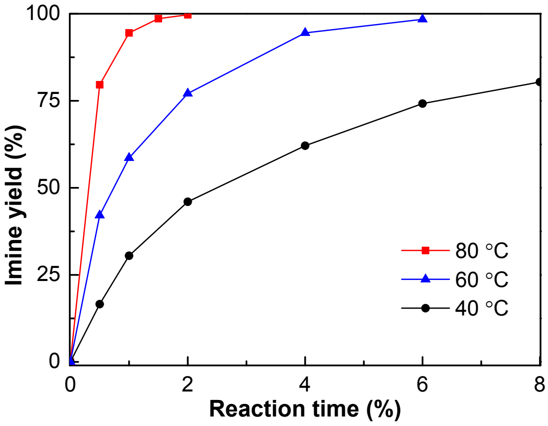


Fig. S3 Effect of reaction temperature on the catalytic performance of CeO_2/MC in imine synthesize from oxidative coupling of alcohol and aniline. Reaction conditions: benzyl alcohol (1 mmol), aniline (2 mmol), catalyst (0.3 g), solvent (toluene 10 mL), air (1 bar).

Table S1 Catalytic performance of imine synthesis from oxidative coupling of alcohol and aniline over different catalysts.[a]

Entry	Catalyst	Time (h)	Conv.	Select.	TOF (h^{-1}) [b]	Reuse	Ref
1	CeO_2/MC	2	99%	98%	5.4	4	This work
2	CeO_2/MC	6 [c]	79%	98%	3.5	-	This work
3	CeO_2/MC	8 [d]	47%	98%	1.8	-	This work
4	CeO_2-Rod	12 [c]	99%	94%	0.4	4	5
5	CeO_2	24 [c]	98%	99%	0.4	2	6
6	MnO_x/HAP	24	99%	98%	1.1	9	7
7	FeO_x/HCMK-3	6	98%	98%	2.9	5	8
8	Fe_2O_3	8	13%	98%	0.07	-	8

[a] Substrates: benzyl alcohol and aniline, temperature: 80 ºC. [b] TOF was calculated based on the 60 min conversion. [c] Reaction temperature: 60 ºC. [d] Reaction temperature: 40 ºC.

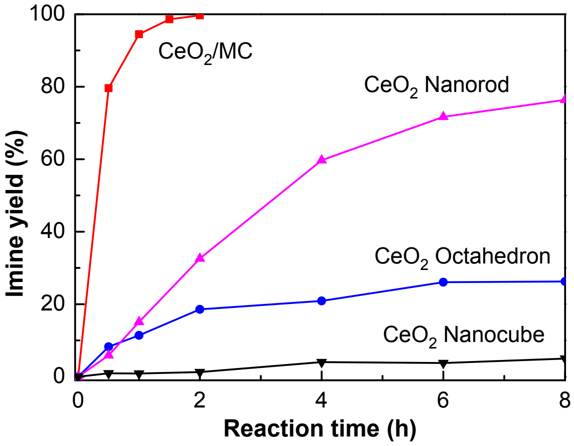


Fig. S4 The synthesis of imine from benzyl alcohol and aniline over CeO_2 catalysts with different morphologies. Reaction conditions: benzyl alcohol (1 mmol), aniline (2 mmol), catalyst (0.3 g), solvent (toluene 10 mL), 80 ºC, 2 h, air (1 bar).

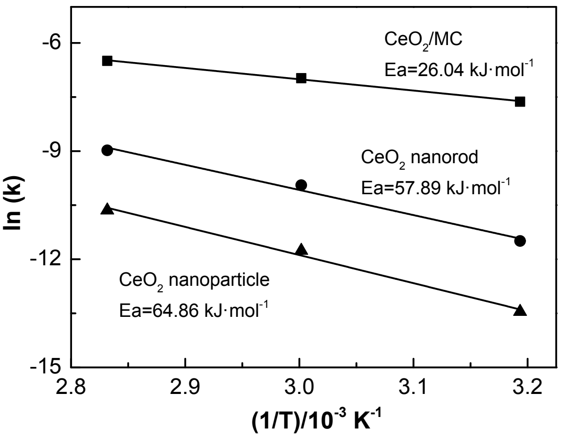


Fig. S5 Arrhenius plot of imine synthesis over CeO_2/MC, CeO_2 nanorod and bulk CeO_2 catalysts.

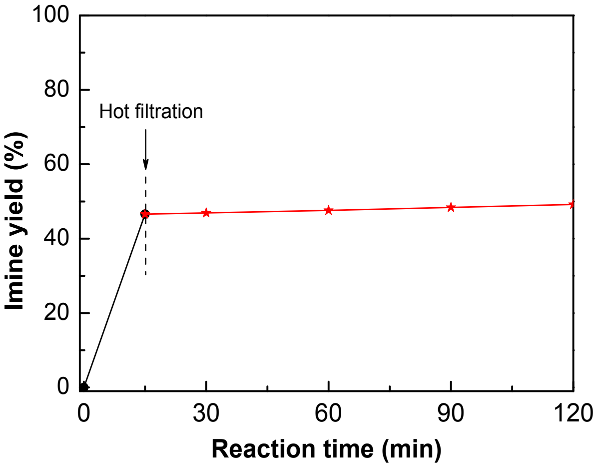


Fig. S6 Leaching experiment of CeO_2/MC by continuing the reaction after filtration of the catalyst. The red line indicate the imine yield after removing the solid catalysts. Reaction conditions: benzyl alcohol (1 mmol), aniline (2 mmol), catalyst (0.3 g), solvent (toluene 10 mL), 80 ºC, air (1 bar).

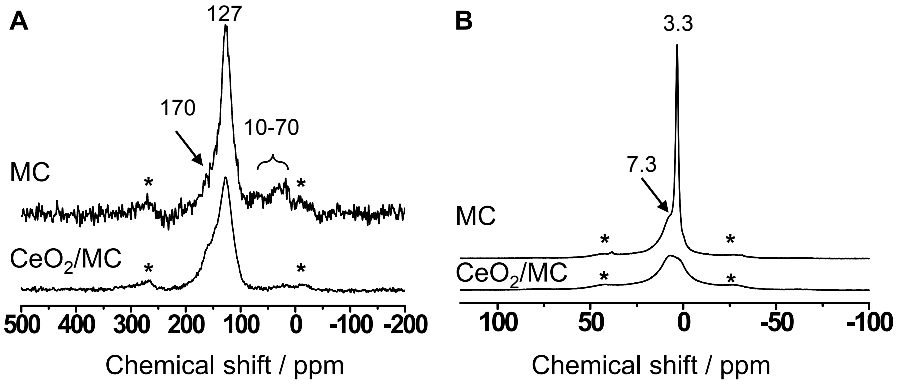


Fig. S7 (A) ^{13}C CP MAS NMR and (B) ^{1}H MAS NMR spectra of CeO$_2$/MC and MC samples. Asterisks denote spinning sidebands.

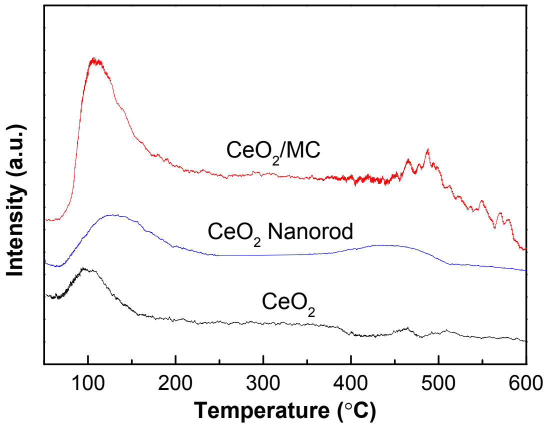


Fig. S8 O_2-TPD profiles of CeO_2/MC, CeO_2 nanorod and bulk CeO_2 catalysts.

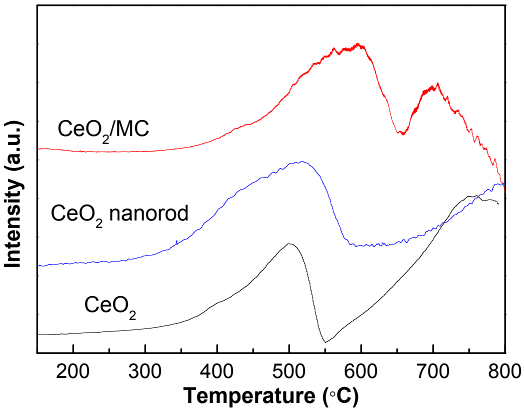
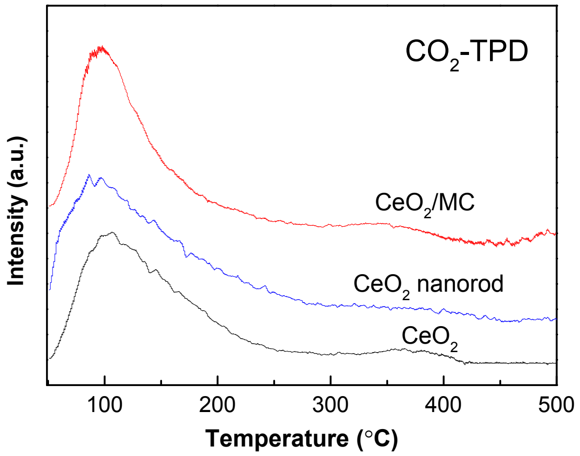


Fig. S9 H_2-TPR profiles of CeO_2/MC, CeO_2 nanorod and bulk CeO_2 catalysts.



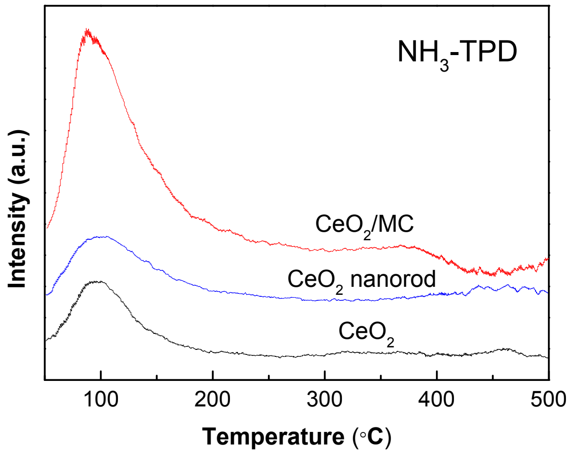


Fig. S10 CO_2-TPD and NH_3-TPD profiles of CeO_2/MC, CeO_2 nanorod and bulk CeO_2 catalysts.

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