

Supporting information:

Constructing Pd/CeO₂/C to Achieve Highly Leaching-resistance and Active for Catalytic Wet Air Oxidation of Aqueous Amide

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1. Experimental details

Synthesis of CeO₂/C

CeO₂ was located on carbon (Cabot Corporation, BP2000) through incipient impregnation method, using CeNO₃·6H₂O (Sinopharm) as precursor. After dried in 100 °C oven for 8 h, it was then calcined in N₂ at 450 °C for 1 h. The obtained powder is donated as xCeO₂/C, while x represents the loading of CeO₂ by mass.

Synthesis of CeO₂

CeO₂ was synthesized by precipitation method. 5 g CeNO₃·6H₂O (Sinopharm) was added into 140 ml deionized water under stirring. 10 min later, NaOH solution (2 mol/L) was added to adjust the pH to 11. After 1 h, the slurry was filtered and wash with deionized water until the pH of the filtrate decreased to 7. The solid obtained was then dried (110 °C, 6 h) and calcined (250 °C, 4 h).

Synthesis of Pd/CeO₂/C

The method is similar with our previous work.¹ PdCl₂ (Sinopharm) and pre-synthesized CeO₂/C were used as precursor and support. CeO₂/C (0.5 g) was added into the solution of PdCl₂ (150 ml, containing the desired Pd). Then, ammonia solution (25 wt%, Sinopharm) was added to increase the pH to be higher than 10, and the mixture was stirred for 3.5 h at room temperature. Then 1 ml hydrazine (80 wt%, Sinopharm) was added to reduce Pd complex. Two hours later, the mixture was filtered and washed by deionized water. The resultant solid was dried at 60 °C for 24 h. The loading of Pd is 3 wt%.

Synthesis of Pd/C, Pd/CeO₂, Pd/Al₂O₃ and Pd/TiO₂

The procedure is similar with that of Pd/CeO₂/C. Support (0.5 g) was added into the solution of PdCl₂ (150 ml, containing the desired Pd) and adjusted the pH by ammonia. After the mixture was stirred for 3.5 h at room temperature, the 1 ml hydrazine (80 wt%, Sinopharm) was added to reduce Pd complex. Two hours later, the mixture was filtered and washed by deionized water. The resultant solid was dried at 60 °C for 24 h. The loading of Pd is 3 wt%. TiO₂ (Degussa P25) was purchased from Evonik and Al₂O₃ was purchased from Sinopharm.

Synthesis of Pd-CeO₂/C

The PdCl₂ solution was prepared with 1g PdCl₂, 4 ml HCl solution (38 wt%, Sinopharm) and 100 ml water. Pd was located on CeO₂/C through incipient impregnation method, using PdCl₂ as precursor. After dried in 100 °C oven for 8 h, it was calcined in Ar at 400 °C for 2 h, then in H₂ at 400 °C for 2 h. The loading of Pd is 3 wt%.

Surface area

Surface area of the materials were measured by the BET N₂ adsorption method using an ASAP2010 instrument.

Quasi-in situ XPS

Quasi in situ X-ray photoelectron spectroscopy (quasi-in situ XPS) analysis was carried out with a VG MultiLab 2000 spectrometer with an Omicron Sphera II hemispherical electron energy analyser and a home-made reaction chamber. Monochromatic Al K α X-ray source (1486.6 eV, anode operating at 15 kV and 300 W) was used to excite XPS spectra. The constant pass energy is 40 eV, and the base pressure of the system was 5.0×10^{-9} mbar. The binding energies in the spectras of

Pd/C, Pd/CeO₂/C, Pd/CeO₂, CeO₂/C, CeO₂ were calibrated according to Si 2p peak at 103.3 eV, as SiO₂ was mixed with sample before analysis. For Pd/TiO₂ and Pd/Al₂O₃, the binding energies were calibrated according to Ti 2p 459 eV and Al 2p 74.7 eV. In our study, The catalysts were firstly treated under hydrogen at 180 °C for 2 h, and then under air at 180 °C for 2 h in the reaction chamber. After that, they were transferred to the XPS analysis chamber through a load-lock gate without exposure to air. It can be known that treated catalysts are similar with those in the reaction condition.

CO-TPR analysis

CO-TPR was operated in quartz microreactor. The samples were first pretreated under H₂ flow at 180 °C for 2 h, followed by purging with Ar at the same temperature for 1 h and air for 1 h. The flow of Ar (30 ml min⁻¹) was then switched into the system, cooling down to 50 °C and purging for 1 h. CO-TPR was then conducted from 50 °C to 750 °C at a heating rate of 10 °C min⁻¹. CO, CO₂, and H₂ in the outlet gas were measured by a mass spectrometer OmniStar equipped with the software Quadstar 32-bit.

TEM

TEM images and energy dispersive X-ray spectroscopy (EDS) for elemental mapping and line-scan analysis of the samples were obtained on Tecnai F30 with an accelerating voltage of 300 KV.

Metal dispersion

The metal dispersion and crystallite size were measured using chemisorption (Auto-Chem 2920, Micromeritics). The catalyst sample

was reduced in a H₂ flow at 150 °C for 2 h, purging with He for 1 h and cooling to 50 °C. Then, it was saturated with pulses of carbon monoxide (CO/He = 10/90 as vol.%). The amount of CO uptake during the chemisorption was measured by a thermal conductivity detector (TCD).

X-ray powder diffraction

XRD patterns were obtained with a Panalytical X'pert Pro diffractometer operated at 40 kV and 30 mV, using Cu K α radiation.

Zeta-potential

The zeta-potential was measured using a Nano-ZS zetasizer (Malvern Instruments, UK). NaOH (or HCl) is used to adjust the pH of the solutions. Then, 10 mg of each materials was added into the 10 ml prepared solution. The measurements were conducted at least 3 times to give an average value.

Reaction experiments

All reactions were carried out in a stainless steel reactor equipped with a Teflon liner 2 mm thick to avoid corrosion. The volume capacity of the reactor is 100 mL and a magnetic spin bar was used for stirring. In a typical experiment, catalyst (50 mg) was added with N, N-dimethylformamide (DMF) or methylamine (MA) solution (15 ml), the TOC of which are 2500 ppm and 1000 ppm respectively. Then, air in the reactor was purged with O₂ 3 times. The initial pressure at room temperature was adjusted to be 1.5 MPa, and the stirring rate of magnetic spin bar is 1000 rpm. Then the temperature was increased to 180 °C. After reaction, reactor was quenched in ice and then liquid sample was filtered by syringe filter. After that, the TOC of liquid sample was

measured by TOC analyzer. For recycle experiments, catalysts were collected by centrifugation and washed by 500 ml deionized water. After dried in 100 °C oven for 8 h, their weight was measured and the corresponding volume of MA and DMF solution was calculated to keep the same substrate/catalyst ratio.

The Total Organic Carbon (TOC) values were measured using a total organic analyzer (Shimadzu LCPH/CPN). The DMF, formic acid, nitrate was measured by HPLC. The ammonia, DMA and MA were measured by colorimetric method. Leached Pd was measured by the atomic absorption spectroscopy (AAS).

2. Supplementary figures and tables

Table S1. Surface areas of different materials.

| Material | BET surface areas / m ² /g |
|--------------------------|---------------------------------------|
| C (BP2000) | 1372 |
| CeO ₂ | 86 |
| 20CeO ₂ /C | 1030 |
| Pd-20CeO ₂ /C | 1001 |
| Pd/20CeO ₂ /C | 1010 |

Table S2: Peak fitting results of Pd 3d spectra for different catalysts

| Catalyst | Relative contents (%) | | |
|-----------------------------------|-----------------------|------------------|------------------|
| | Pd ⁰ | Pd ²⁺ | Pd ⁴⁺ |
| Pd/C | 94 | 6 | 0 |
| Pd/CeO ₂ | 59 | 31 | 10 |
| Pd/TiO ₂ | 44 | 38 | 18 |
| Pd/Al ₂ O ₃ | 63 | 30 | 7 |
| Pd/10CeO ₂ /C | 91 | 9 | 0 |
| Pd/20CeO ₂ /C | 87 | 13 | 0 |
| Pd/30CeO ₂ /C | 73 | 21 | 6 |
| Pd/50CeO ₂ /C | 61 | 28 | 11 |

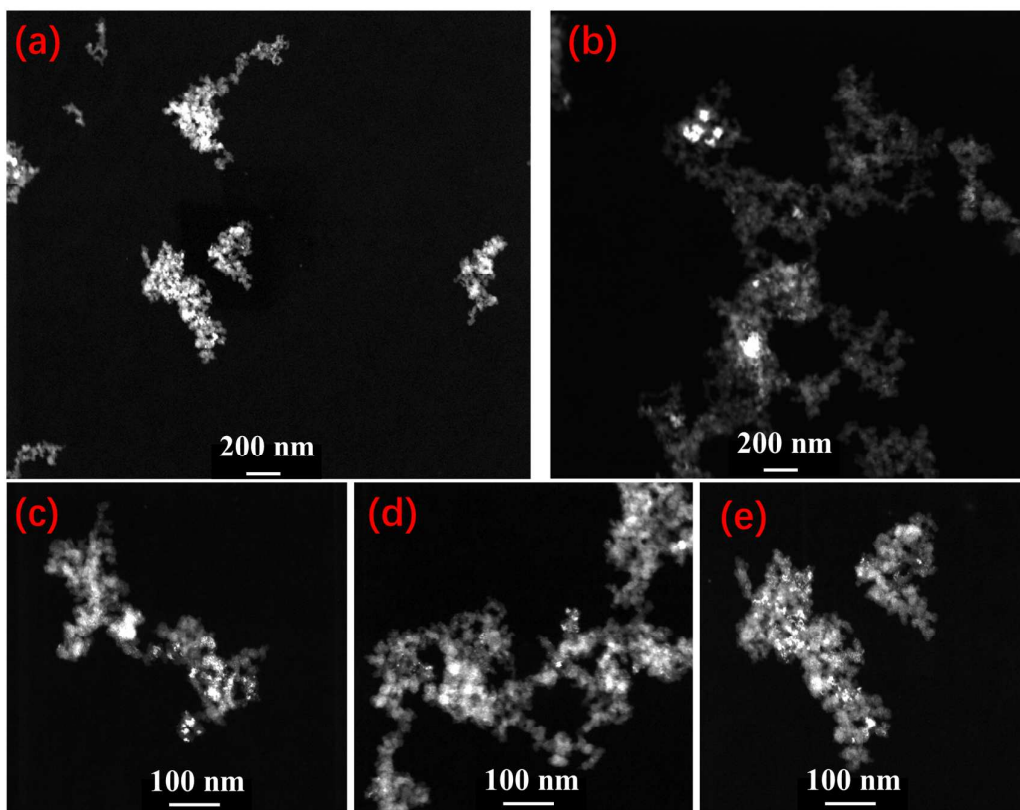


Figure S1. (a)-(e) HADDF-STEM images of 20CeO₂/C.

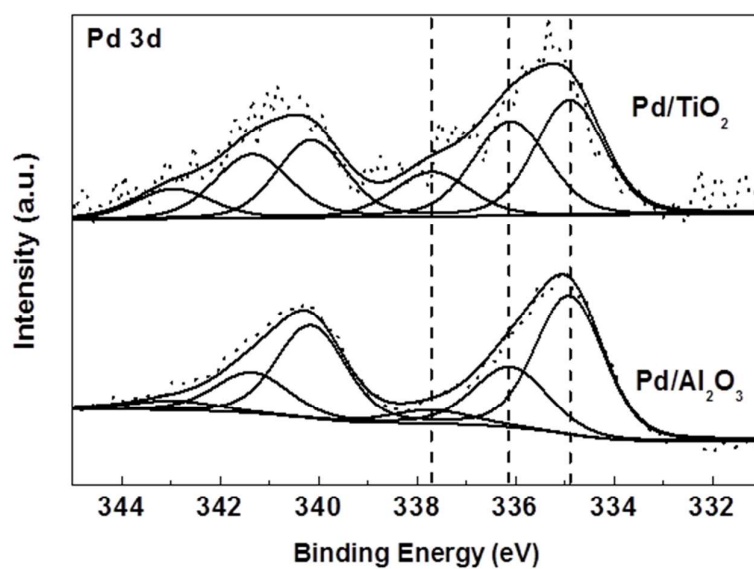


Figure S2. Quasi-in situ XPS spectra of Pd/TiO₂ and Pd/Al₂O₃.

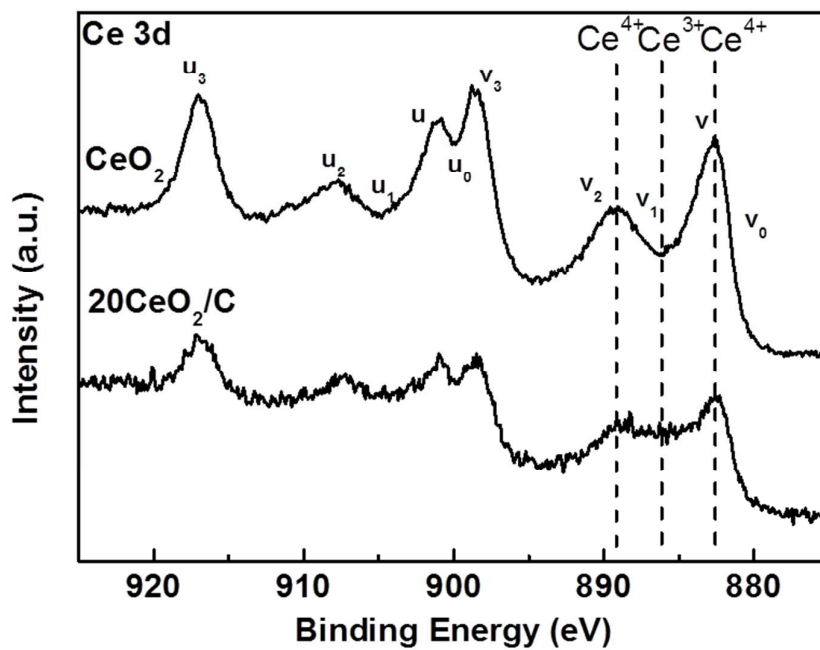


Figure S3. Quasi-in situ XPS spectra of the CeO₂ and 20CeO₂/C.

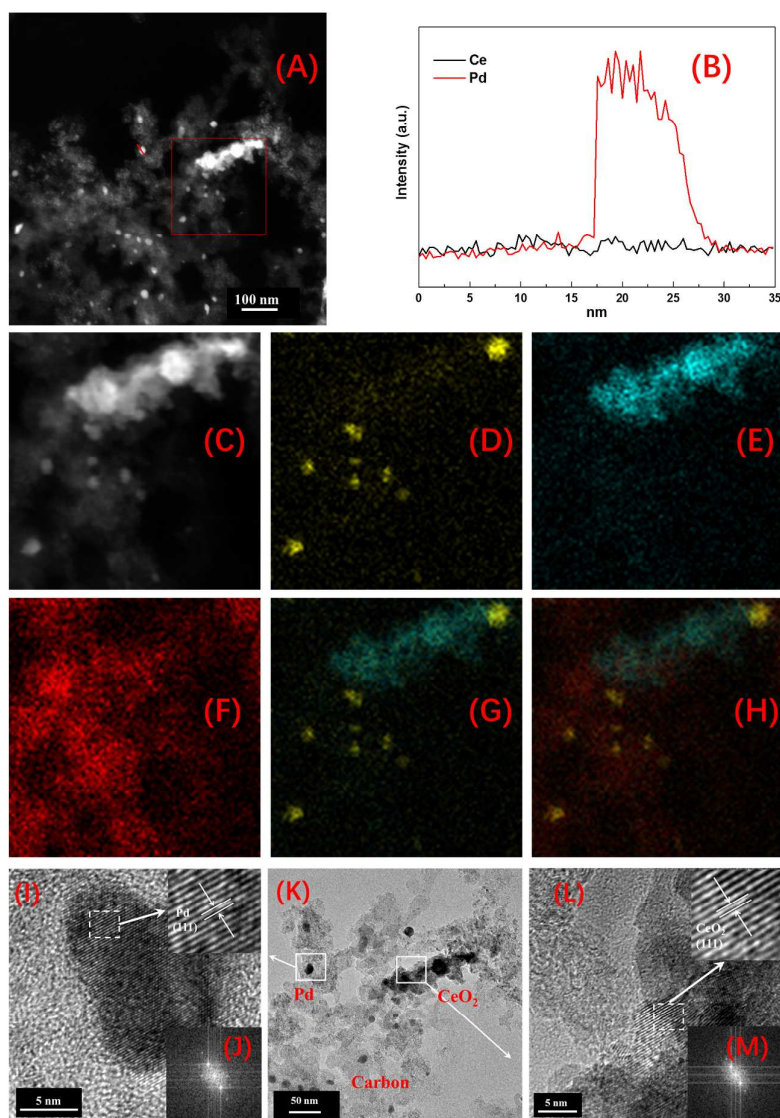


Figure S4. (A) HADDF-STEM image of Pd-20CeO₂/C with the trace of line scan. (B) line-scan analysis of Pd-20CeO₂/C. (C) HADDF-STEM image of Pd/20CeO₂/C for the elemental mapping. (D)-(F) The elemental mapping results of Pd, Ce, and C. (G) Overlay of Ce and Pd. (H) Overlay of Ce, Pd and C. (I) HRTEM of Pd in Pd-20CeO₂/C. (J) FFT pattens. (K) TEM image of Pd-20CeO₂/C. (L) HRTEM of CeO₂ in Pd-20CeO₂/C. (M) FFT pattens.

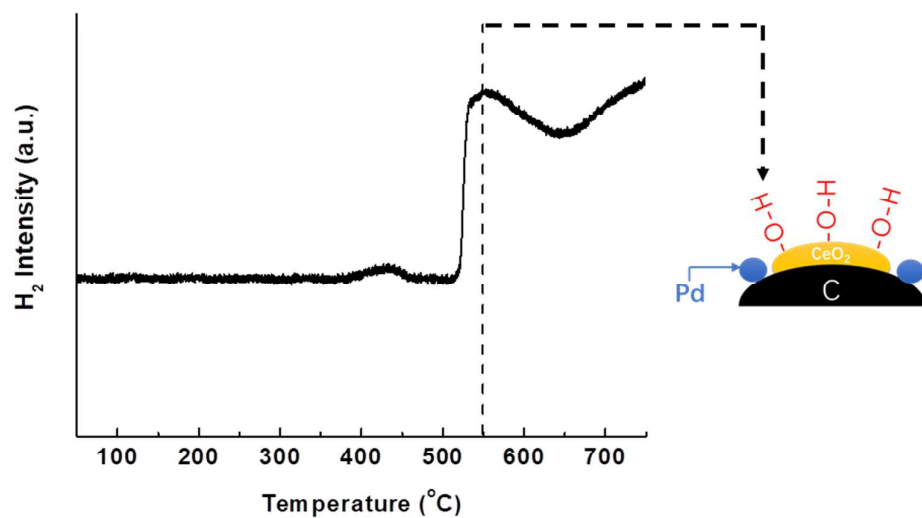


Figure S5. H₂ signal of the water shift reaction with the surface hydroxy of Pd-20CeO₂/C. The peak at 425 °C which is proof of Pd-CeO₂ interactions is negligible.

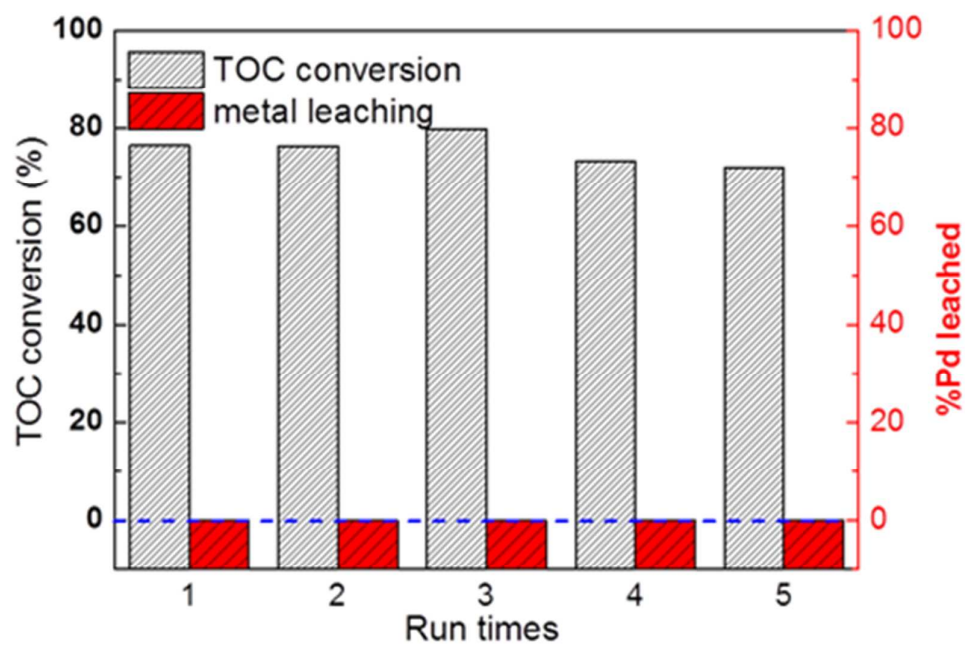


Figure S6. The stability of the Pd/20CeO₂/C catalyst for the CWAO of DMF.

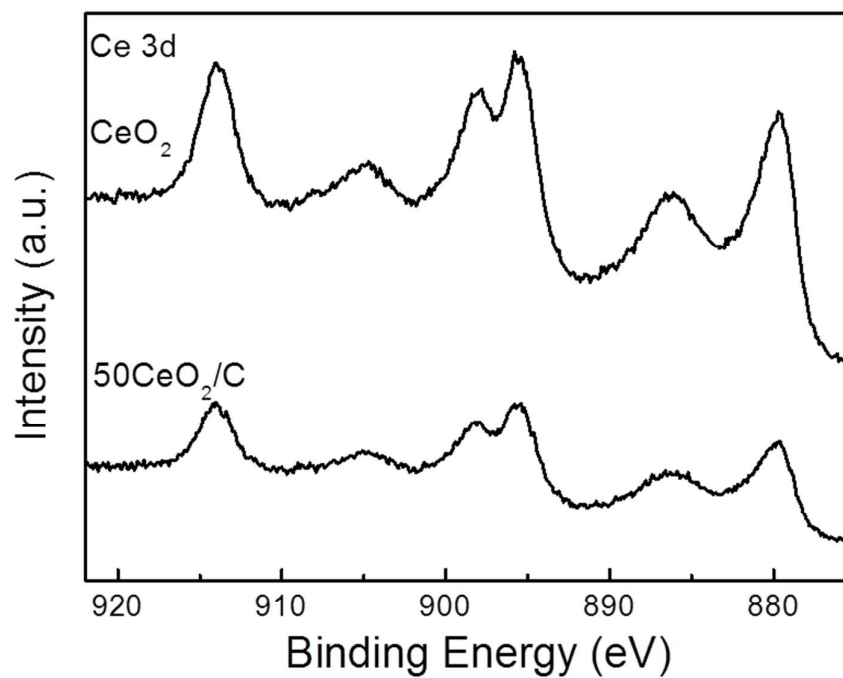


Figure S7. Quasi-in situ XPS spectra of the CeO₂ and 50CeO₂/C.

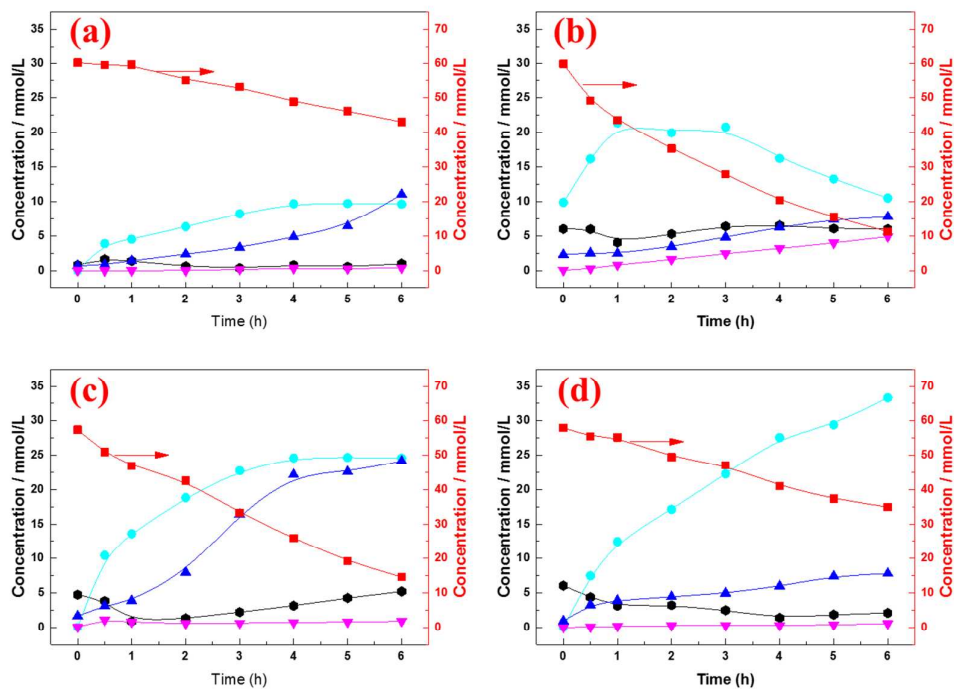


Figure S8. Products distribution vs time in the catalytic wet air oxidation of DMF with different catalysts: (a) Pd/C. (b) Pd/CeO₂. (c) Pd/20CeO₂/C. (d) Pd-20CeO₂/C.
 (■) DMF, (●) DMA+MA, (▲) NH₃, (▼) NO₃⁻, (●) formic acid.

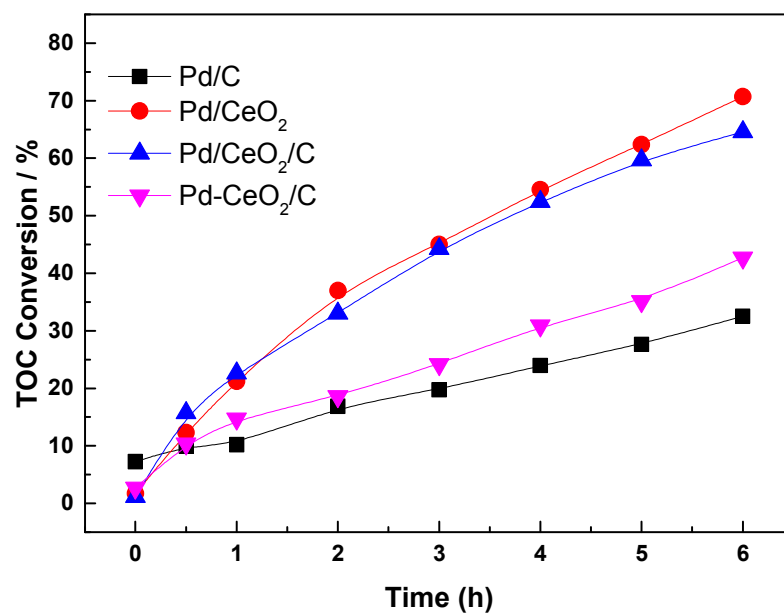


Figure S9. TOC conversion vs time in the catalytic wet air oxidation of DMF with different catalysts.

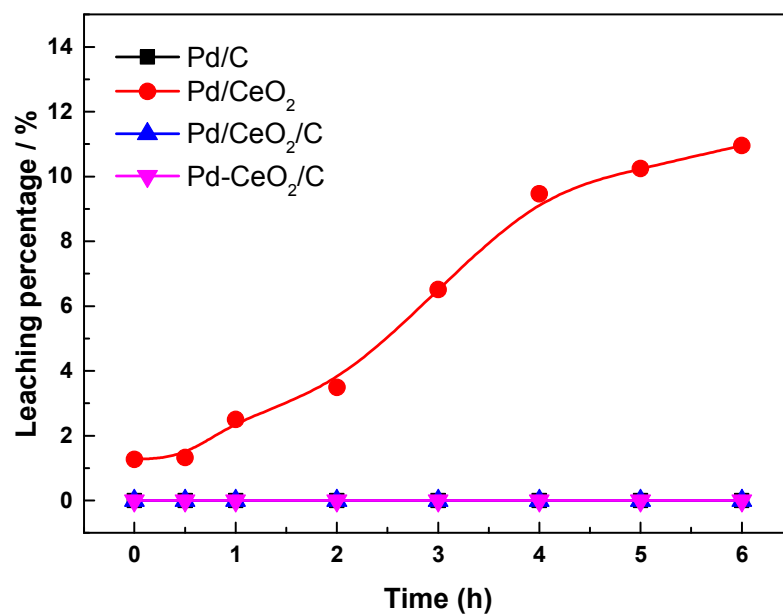


Figure S10. Pd leaching vs time in the catalytic wet air oxidation of DMF with different catalysts.

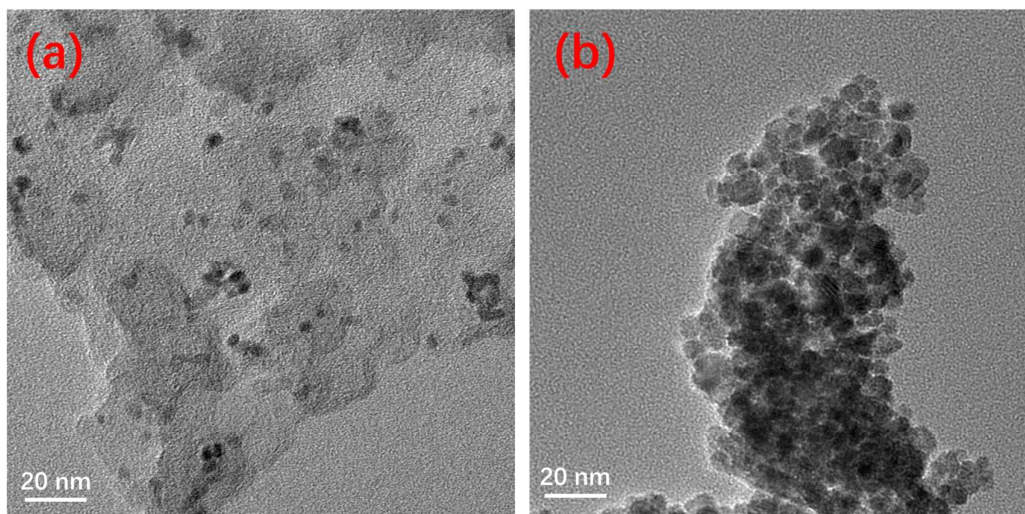


Figure S11. TEM images: (a) Pd/C, (b) Pd/CeO₂.

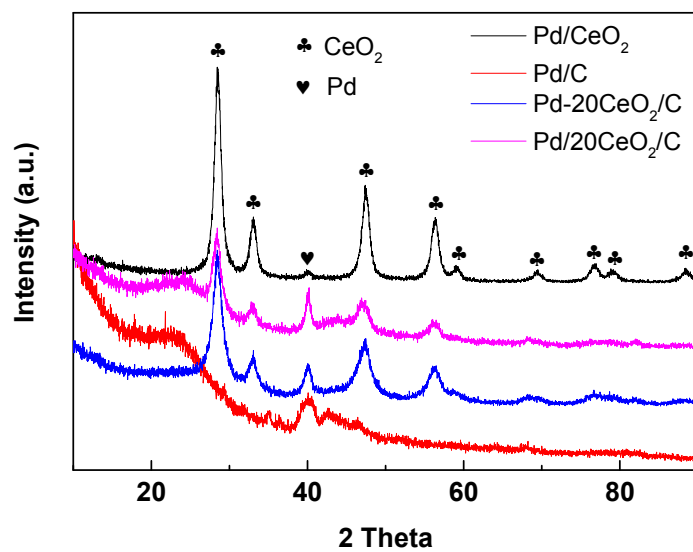


Figure S12. XRD patterns of different samples.

REFERENCES

- (1) Fu, J.; Yang, K.; Ma, C.; Zhang, N.; Gai, H.; Zheng, J.; Chen, B. H. Bimetallic Ru–Cu as a Highly Active, Selective and Stable Catalyst for Catalytic Wet Oxidation of Aqueous Ammonia to Nitrogen. *Appl. Catal., B* **2016**, *184*, 216-222.

