Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Nanostructured CeO2 Promoted Pd /α-Alumina Diethyl Oxalate Catalyst with High Activity and Stability

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1. Materials and methods

1.1 Materials

Palladium (II) chlolrid ($PdCl_2$, ReagentPlus, 99%), potassium hexachloropalladale (IV) (K_2PdCl_6), potassium chloride (KCl), L-ascorbic acid, aluminum oxide (fused, powder, α-phase, 325 mesh), ammonium cerium nitrate ($CeH_8N_8O_{18}$) and polyvinylpyrrolidone (PVP, Mw: 40 K) were purchased from Sigma-Aldrich and used as received without further purification.

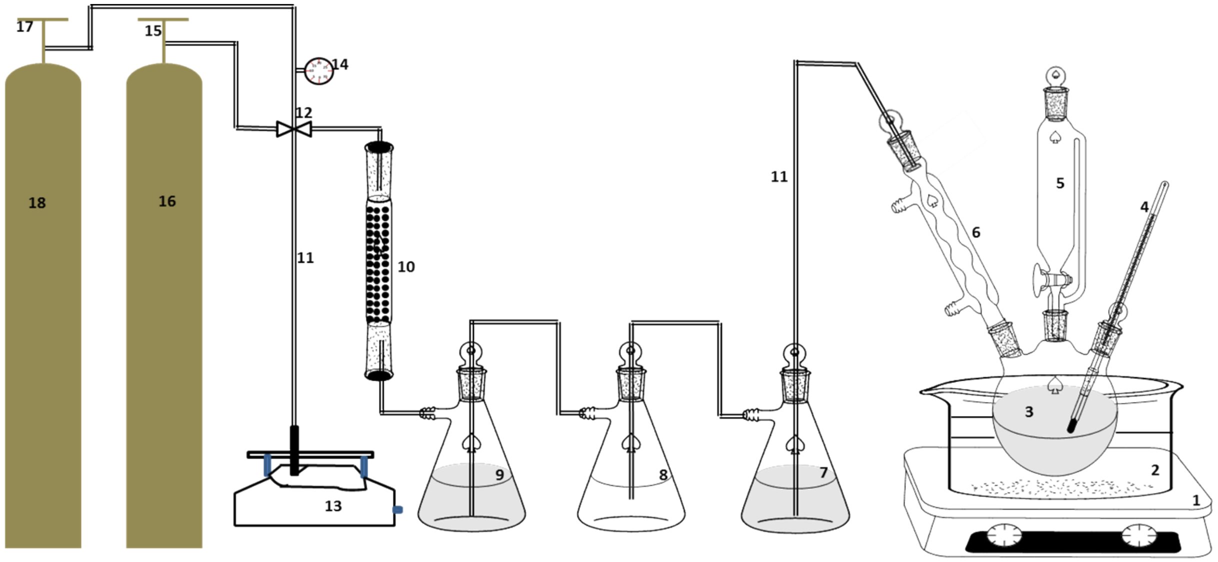
1.2 Preparation of catalysts

Pd/α-Al$_2$O$_3$: In a typical synthesis, K_2PdCl_6 (0.25 mmol), $PdCl_2$ (0.25 mmol), KCl (7.5 mmol), L-ascorbic acid (1 mmol) and PVP (10 mmol) were dissolved in 100 mL of deionized water . The mixed solution was refluxed at 100 °C for 3 h. Al_2O_3 (5 g) were added in the solution and the mixture was stirred at 60 °C until all the solvents evaporated. The product was washed with ethanol/water and ethanol for several times and vacuum dried at 60 °C overnight.

$CeO_2/\alpha\text{-}Al_2O_3$: Ammonium cerium nitrate (0.05 mmol) was dissolved into 10 mL of deionized water. Al_2O_3 (5 g) were added in the solution and the mixture was stirred at 60 °C until all the solvents evaporated. The mixture was dried at 100 °C overnight and then calcined at 500 °C for 5 h to get $CeO_2/\alpha\text{-}Al_2O_3$.

$Pd\text{-}CeO_2/\alpha\text{-}Al_2O_3$ catalysts: 0.25 mmol K_2PdCl_6, 0.25 mmol $PdCl_2$, KCl (7.5 mmol), L-ascorbic acid (1 mmol), and PVP (10 mmol) were dissolved in 100 mL of deionized water, followed by refluxing at 100 °C for 3 hrs. Then $CeO_2/\alpha\text{-}Al_2O_3$ (5 g) was added to the solution and the mixture was stirred at 60 °C until the complete evaporation of all the solvents. The resulting mixture was washed with ethanol/water and then ethanol for several times, and vacuum dried at 60 °C for 12 h.

2.3 Synthesis of ethyl nitrite (EN)



S1. The experimental set-up of ethyl nitrite production. 1. Stirrer; 2. Water bath container; 3. Three-necked bottle; 4.Thermometer; 5. Constant pressure funnel; 6. Condenser; 7. Filtering flask; 8. Buffer flask; 9. Filtering flask; 10. Drying tube; 11. Vacuum tubing; 12. Three-way connector; 13. Oil pump; 14. Vacuum Gauge; 15. Nitrogen regulator; 16. Nitrogen cylinder; 17. ethyl nitrite regulator; 18.ethyl nitrite cylinder.

The experimental set-up used for synthesis of EN was built and its schematic drawing is shown in Figure 1. Three-necked bottled was fixed on an iron stand with a flask clamp. Water bath container and stirrer were put under the bottle. Thermometer, constant pressure funnel and condenser were connected with the bottle. All the connectors were sealed with wax followed by Parafilm. Vacuum tubing was used to connect the condenser with the filtering flask (#7) which was filled with DI water to remove the methanol from the gas. Flask (#7) was then connected with the buffer flask (#8) by vacuum tubing and flask (#9) was connected orderly. Flask (#9) was filled with concentrated sulfuric acid (98%) to remove the moisture from the gas. All the flasks were fixed with clamps and sealed with rubber stoppers. Rubber stops were further sealed with wax followed by Parafilm. Flask (#9) was then connected with two drying tubes (#10) which were filled with anhydrous calcium sulfate to further remove the moisture from the gas. The heads of drying tube were further sealed with wax followed by Parafilm. Drying tubes (#11) were then connected the regulator (#17) of ethyl nitrite cylinder via vacuum tubing and a three-way valve (#12). One head of the valve was connected to either oil pump (#13) or the regulator (#14) of the nitrogen cylinder. Oil pump (#13) and the regulator of nitrogen (#14) cylinder were connected with the three-way valve (#12).

The reaction can be carried out after all the leak tests completed. At room temperature, 600 mL of sodium nitrite solution in DI water (4 mol/L) and 120 mL of ethanol (200 pf) were added into the three-necked bottle (#2, Fig. 1). A stirring bar was put in the bottle and the thermometer was put into the solution. Sulfuric acid (250 mL, 50 vol%) was added into the constant pressure funnel (#5, Fig. 1). The funnel is sealed with a glass stopper. Vacuum grease, wax and Parafilm are used to make the seal better. The EN cylinder is vacuumed thoroughly with the oil pump (#13, Fig. 1). Adjust the valve to connect the regulator (#17, Fig. 1) of the EN cylinder and the oil pump. Turn on the oil pump to vacuum the cylinder until the pressure is less than 0.1 bar from the vacuum gauge. Close the regulator valve (#19, Fig. 1) and turn off the pump. Before the reaction, the whole set-up was vacuumed and refilled with UHP nitrogen for three times. The three-way valve (#12, Fig. 1) was connected with the nitrogen cylinder, oil pump and the drying tube (#11, Fig. 1) respectively. Adjust the valve (#12, Fig. 1) to connect oil pump with the drying tube and turn on the pump to vacuum the set-up.

Sulfuric acid is added in the sodium nitrite solution dropwise [one drop every 3 seconds, adjust the valve (#3, Fig. 1) of the constant pressure funnel] while temperature is controlled at around room temperature (22 ± 5 °C) via the water both (#1, Fig. 1). The temperature of the

condenser is kept at -5 °C (chiller is used here) to cool down water and methanol. Once the gas comes out, the vacuumed EN cylinder is connected with the set up via the three-way valve. The EN gas will go into the cylinder due to the pressure difference while the water and ethanol will be removed by the condenser and the gas-washing bottles. When the pressure of the EN cylinder got to 1 atmosphere pressure, the reaction was stopped by closing the valve (#3, Fig. 1). The cylinder was refilled with UHP N_2 until the final pressure got to 5 bars. Figure 2 shows the EN characterized with GC. The concentration of EN in the N_2 + EN can be calculated by using the standard curve.

S 2. The pure EN characterized with GC.

1.4 Characterization of catalysts

The surface areas of the catalysts were measured using nitrogen physisorptionby standard Brunauer–Emmet–Teller (BET) analysis (MicromeriticsTriStar 3000 V 6.04 A). The surface areas were calculated with TriStar II 3000 software.

X-ray photoelectron spectroscopy (XPS) was measured with a Physical Electronics ESCA 5800 spectrometer which is equipped with a monochromatic Al Kα X-ray source (E = 1486.6 eV). The scanning step and working pressure were 0.1 eV and 2×10^{-9} mbar, respectively. Binding energies were calibrated to C1s peak at 284.5 eV.

X-ray diffraction (XRD) analyses were performed on a Rigaku Smartlab X-ray diffraction system. A Cu Kβ radiation source (λ = 1.392 Å) working at 40 kV and 40 mA was used in the tests. The range of 2θ measurements was between 20°to 80° with 0.02° steps.

The morphology and the particle size as well as the dispersion of the catalysts were studied by a scanning electron microscope (SEM-EDS, FEI, Quanta FEG MK2; Oxford Instruments America, Model #51-XMX0005) and a transmission electron microscopy. (TEM, FEI, Tecnai G2 F20 S-Twin 200 kV). Samples for TEM observations were prepared by dispersing the catalysts in ethanol and drying one drop of the solution on copper grids. The particle size distribution was calculated by using Image J software.

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were performed on a Nicolet iS50 FT-IR spectrometer (Thermo Scientific, Waltham, MA, USA) equipped with a DRIFTS system with reaction chamber (Praying Mantis model, Harrick Scientific Products, Pleasantville, NY, USA) employing ZnSe windows. After loading 20 μL of powder samples, the cell temperature was raised to 140 °C and allowed to thermally equilibrate for ten minutes, after which the gaseous reactants were introduced at constant flow with pressure inside the reaction chamber maintained at 2 atm. The spectra are a composite of 16 scans recorded at a resolution of 4 cm^{-1}.

1.5 Evaluation of catalysts

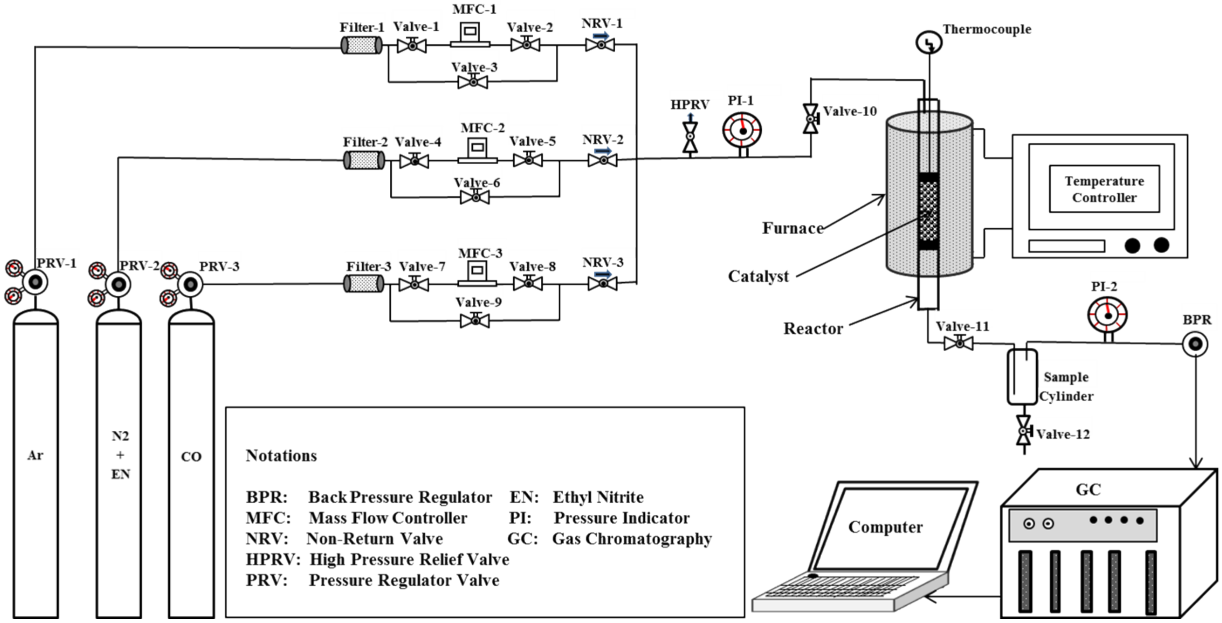


Figure 1. Schematic diagram of the EN to DEO installation.

The measurement of catalytic activity was performed in a fix-bed continuous flow reactor. The reactor configuration is shown schematically in Figure 1. The catalyst (3.5 g, 2 mL) was sandwiched with sands in as stainless steel tube reactor with an inner diameter of 1.2 cm. The reactant gases (18% CO, 15% CH_3CH_2ONO, and N_2 balance) were passed through the reactor at a gas hourly space velocity (GHSV) of 600-3000 h^{-1}. The DEO production was carried out at a temperature of 100–160 °C and under a pressure of 0.1 MPa. A thermocouple was inserted into the catalyst bed to detect the reaction temperature. Therefore, the temperature reported here is the catalyst bed temperature. A SRI 8610C gas chromatography (GC) fitted with a capillary column (Restek MXT-1 60 m × 0.53 mm × 5 μm) and a molecular sieves column (MS 13×) was used to analyze the tail gases. Gas chromatography/mass spectroscopy (GC–MS) for liquid products were performed with an Agilent Technology 7890A GC system with a split-splitless injector (model 7863 Auto-sampler Injector) fitted with a 5957C VLMSD MS system using a capillary column (HP-5MS, 30m × 0.250 mm × 0.25 μm). When the GC analysis results show that the reaction is in steady state, the sample cylinder vessel is emptied and the start time of the reaction is recorded. Samples from the sample cylinder vessel are collected in every 6 hours and the liquid products were collected and analyzed by offline GC-MS.

The conversion of CO, the selectivity of DEO and the space-time yield (STY) of the DEO were calculated using the following formulas:[9]

$$\text{Conversion of EN } (\%) = (1-([N2]_{in}/[N2]_{out})/([EN]_{in}/[EN]_{out})) \times 100\%$$

$$\text{Conversion of CO } (\%) = (1-([N2]_{in}/[N2]_{out})/([CO]_{in}/[CO]_{out})) \times 100\%$$

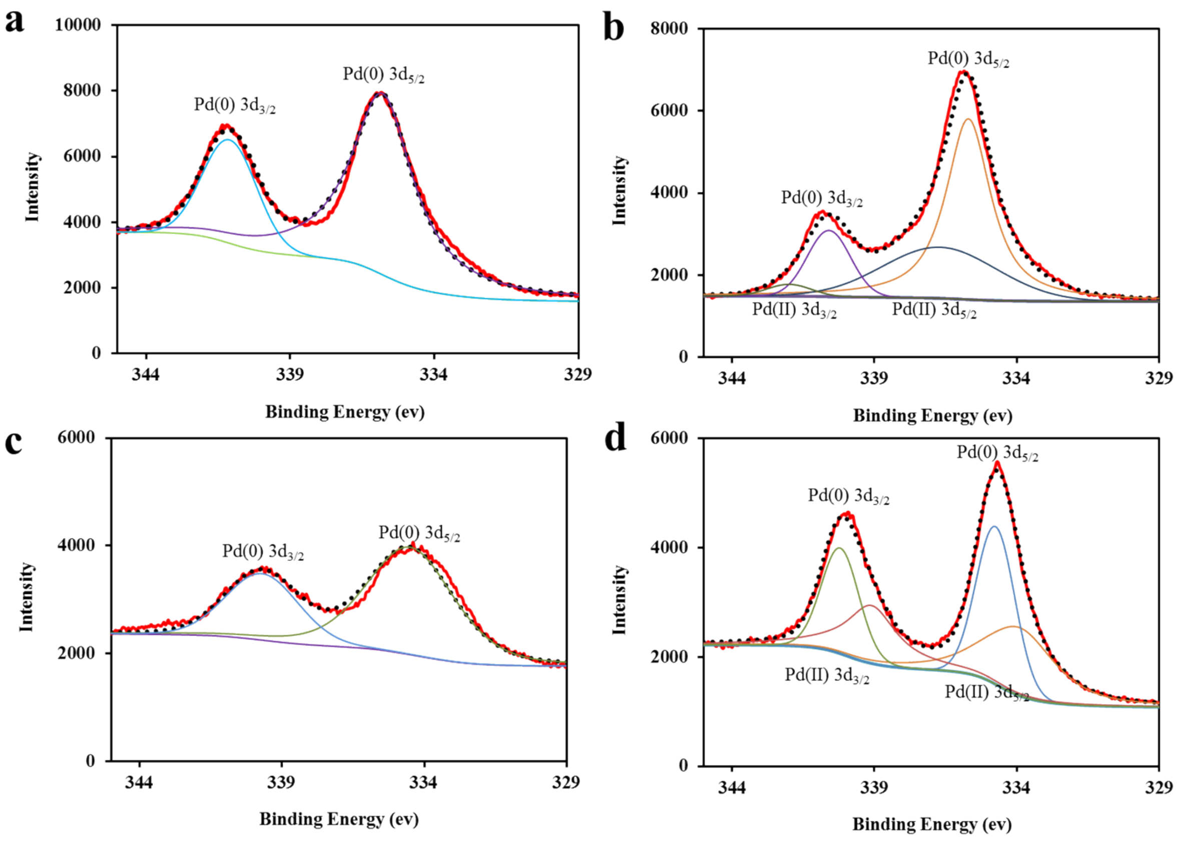
$$\text{Selectivity to DEO } (\%) = (\text{SDEO} \times \text{R-FDEO})/(\text{SDEO} \times \text{R-FDEO} + \text{SDEC} \times \text{R-FDEC}) \times 100\%$$

$$\text{STY of DEO } (\text{gL}^{-1}\text{h}^{-1}) = \text{Conversion of CO} \times \text{Selectivity of DEO} \times \text{GHSV of CO} \times 146.14\ \text{g}\cdot\text{mol}^{-1}/(2 \times 22.4\ \text{L}\cdot\text{mol}^{-1})$$

While $[N2]_{in}$ and $[N2]_{out}$ are the concentration of N_2 at the inlet and outlet, $[CO]_{in}$ and $[CO]_{out}$ are the concentration of CO at the inlet and outlet, respectively. SDMO and SDMC are the peak area of diethyl oxalate and diethyl carbonate, R-FDMO and R-FDMC are the relative correction factor of diethyl oxalate and diethyl carbonate, respectively.

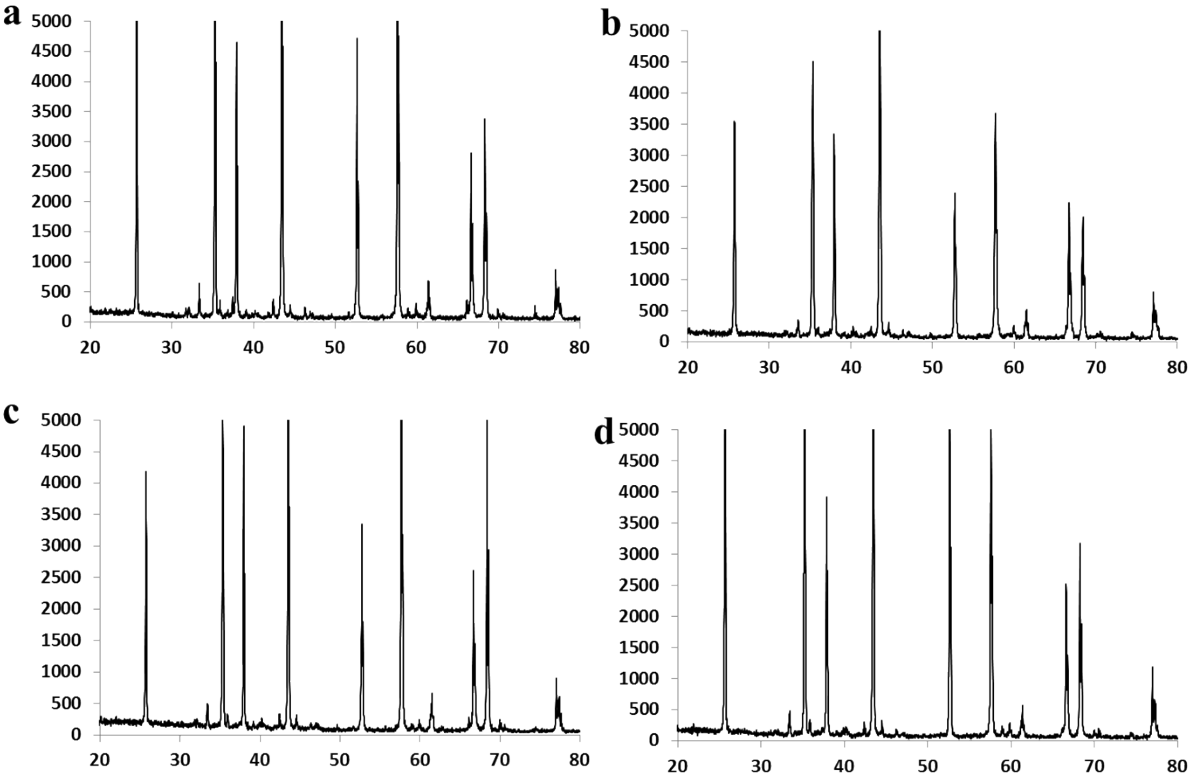
2. Results and discussion

2.1 XPS



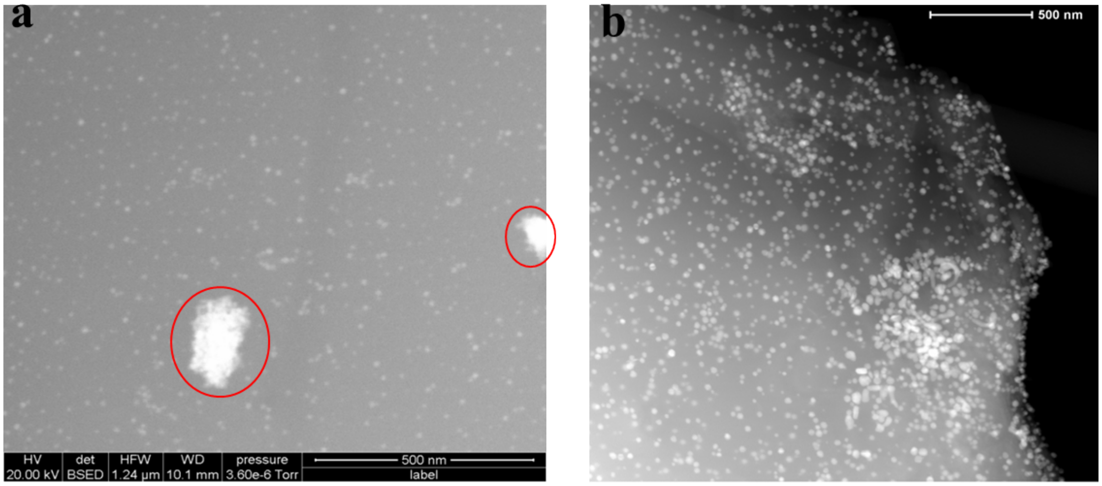
S 3. Pd 3d XPS spectra of catalysts Pd/α-Al2O3 (a before reaction and b after reaction) and Pd-CeO$_2$/α-Al$_2$O$_3$ (c before reaction and d after reaction).

2.2 XRD



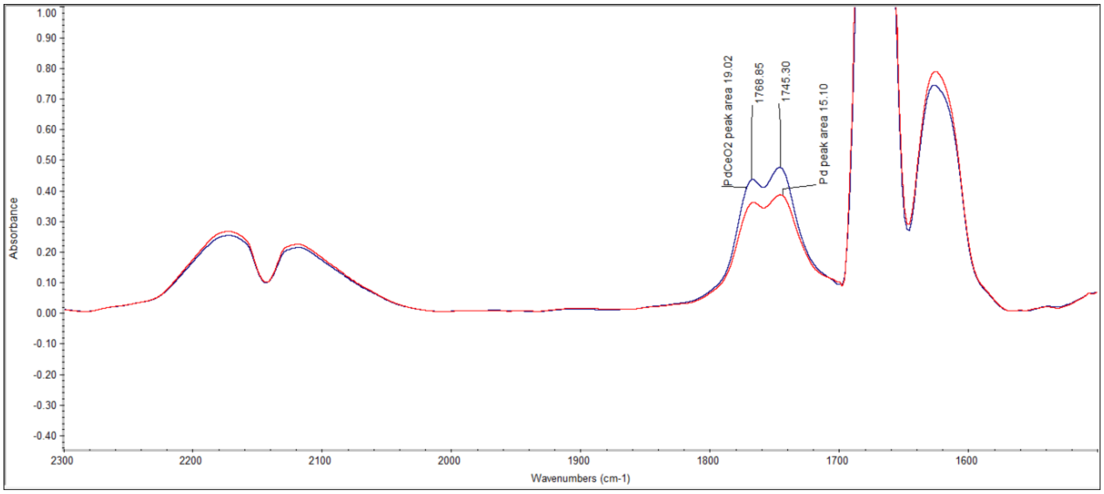
S 4. X-ray powder diffraction of catalysts and support: (a) α-Al_2O_3; (b) CeO_2/α-Al_2O_3; (c) Pd/α-Al_2O_3; (d) Pd-CeO_2/α-Al_2O_3.

2.3 SEM/TEM/STEM

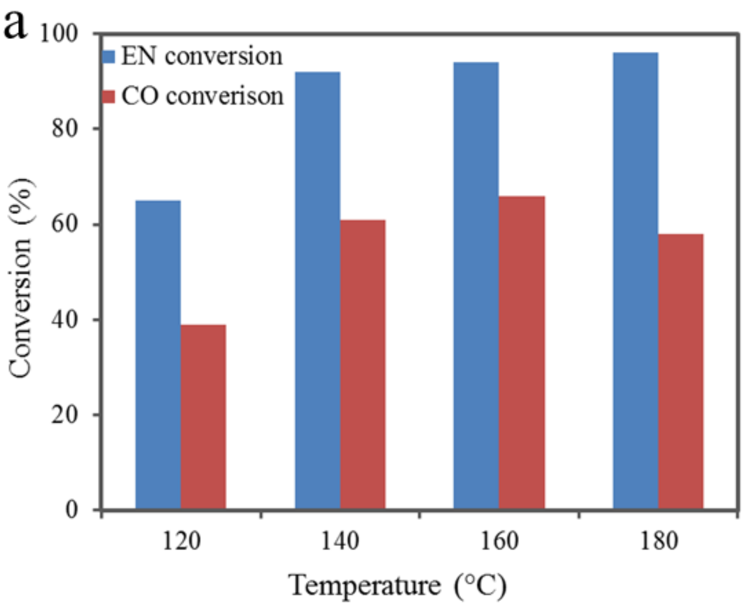


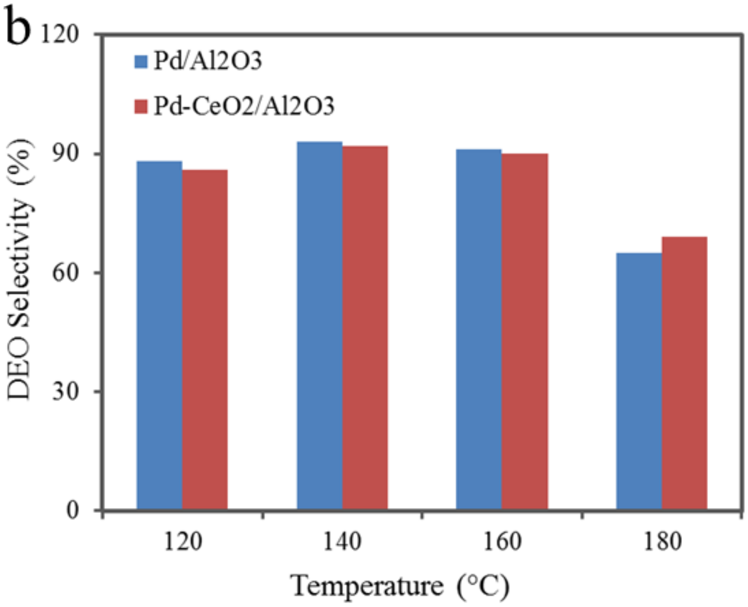
S 5. SEM (a) and STEM (b) images of catalyst Pd-CeO_2/α-Al_2O_3. The red circles in image a indicate CeO2.

2.4 In *situ FTIR*

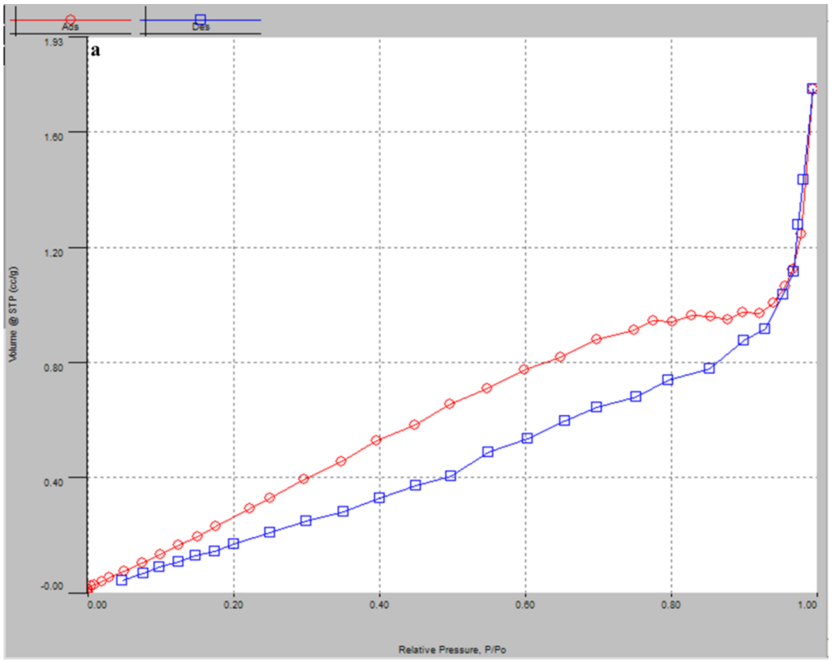


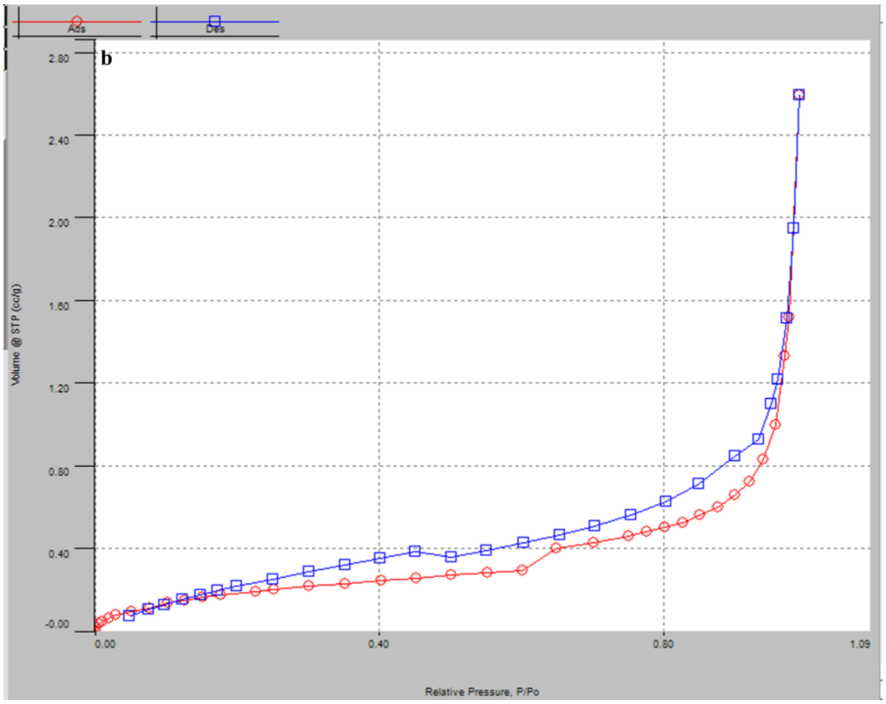
S 6. *In situ* FTIR sepctra for the CO oxidative coupling to DEO reaction.

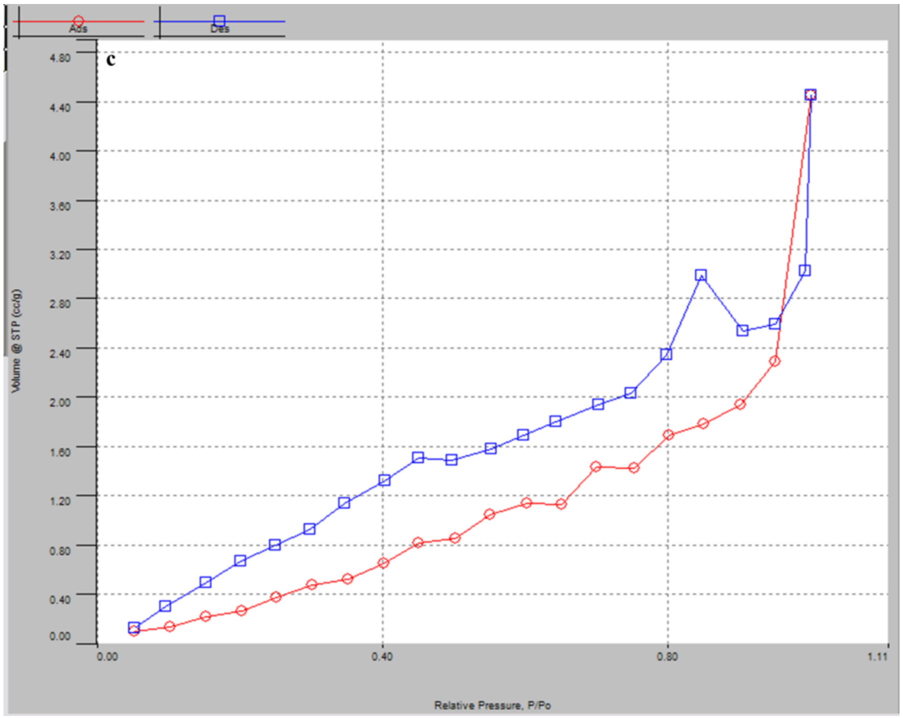




S 7. (a) Conversion of CO (blue lines) and EN (red lines) of CO oxidative coupling to DEO with different reaction temperatures. Reaction condition: 3.5 g of Pd-CeO_2/Al_2O_3 catalyst, 1200 h^{-1} of gas hourly space velocity (GHSV), reactants volume ratio CO/EN is 1.2, 0.1 Mpa. (b) DEO selectivity of CO oxidative coupling to DEO with different reaction temperatures.







S 8. BET spectra of α-Al_2O_3 (a), Pd /α-Al_2O_3 (b) and Pd-CeO_2/α-Al_2O_3 (c). The surface areas of sample a, b and c are 2.32 m^2/g, 2.28 32 m^2/g and 2.33 32 m^2/g, respectively.