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Supplementary Information

Core-shell Au/CeO_2 nanoparticles supported in UiO-66 beads exhibiting full CO conversion at 100 ˚C

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Experimental details

Materials

All reagents were purchased from Sigma-Aldrich and used without further purification. All gases were purchased from Carburos Metálicos. Deionized water, obtained with a Milli-Q system (18.2 MΩ cm), was used in all reactions.

Synthesis of PVP-Stabilized Au/CeO_2 Nanoparticles

Au/CeO_2 (Ce:Au = 1:1) NPs were synthesized in water following the simultaneous reduction/oxidation of Au and Ce precursors (N. Bastus, J. Patarroyo, J. Piella, V. Puntes, work submitted). More specifically, 400 ml of an aqueous solution containing sodium citrate (10 mM) was prepared and heated with a heating mantle in a three-neck round-bottomed flask for 15 minutes under vigorous stirring. A condenser was used to prevent the evaporation of the solvent. After boiling had commenced, $HAuCl_4$ (25 mM) and cerium (III) nitrate hexahydrate (25 mM) were sequentially injected to this solution. After cooling down to room temperature, 4 g of poly (vinylpyrrolidone) (PVP, M.W 10,000) in 200 ml of water was added dropwise to the NP solution while stirring and left overnight at room temperature. Then, 800 ml of acetone was added to the NP solution and left 24 hours at room temperature without stirring for precipitation of the NPs. After removing the supernatant, NPs were washed three times with DMF and finally, redispersed in DMF to give a colloidal solution of Au/CeO_2 NPs with a concentration of 1 mg/ml. The average size of synthesized Au/CeO_2 NPs was 12 ± 2.5 nm.

Synthesis of UiO-66@Au/CeO_2

100 mg of terephthalic acid (BDC), 3 ml of acetic acid, a volume of Au/CeO_2 NPs (concentration = 1 mg/ml; 4 ml for UiO-66@Au/CeO_2-2.8; 8.5 ml for UiO-66@Au/CeO_2-5.5; and 12.5 ml for UiO-66@Au/CeO_2-7) and 280 µl of $Zr(OPrn)_4$ were sequentially mixed in 40 ml DMF. These solutions were injected into a coil flow reactor (inner diameter: 3 mm) at a feed rate of 2.4 $ml.min^{-1}$ at 115˚ C. The resulting pre-heated solution was then spray dried at 180˚ C and a flow rate of 336 $ml.min^{-1}$ using a B-290 Mini Spray Dryer (BUCHI Labortechnik) using a spray cap with a 0.5 mm diameter hole. Then, the resulting solid was dispersed in DMF and washed twice with DMF and ethanol. The final product was calcined in the presence of air at 250˚ C for 12 hours. Encapsulation efficiency was calculated based on the initial amount of NPs in the precursors solution (4, 8.5 and 12 mg for UiO-66@Au/CeO_2-2.8, UiO-66@Au/CeO_2-5.5 and UiO-66@Au/CeO_2-7, respectively), the final mass of the

product after washing (144, 140 and 125 mg for UiO-66@Au/CeO_2-2.8, UiO-66@Au/CeO_2-5.5 and UiO-66@Au/CeO_2-7, respectively) and the Au/CeO_2 content determined by ICP-OES.

Synthesis of PVP-Stabilized Pd Nanoparticles

$NaPdCl_2$ (44 mg) was dissolved in 20 mL of ethylene glycol in the presence of 222 mg of PVP (MW = 55,000) in a three-neck round-bottomed flask. This solution was heated up to 180 °C for 10 minutes and, after cooling down to room temperature, 150 mL of acetone was added into it. Precipitated Pd NPs were then dispersed in DMF and washed twice with DMF by centrifugation. Finally, they were redispersed in 5 ml of DMF to give a colloidal solution of Pd NPs with a concentration of 0.8 mg/ml. The average size of synthesized Pd NPs was 3.3 ± 1.1 nm.

Synthesis of UiO-66@Pd

127 mg of $ZrCl_4$, 89 mg of BDC and 2 ml of PVP-stabilized Pd NPs solution with a concentration of 0.8 mg/ml were added to mixture of DMF (5 ml) and H_2O (0.4 ml). The resulting mixture was injected into a coil flow reactor (inner diameter: 3 mm) at a feed rate of 2.4 $ml.min^{-1}$ at 115˚ C. The resulting pre-heated solution was then spray dried at 180˚ C and a flow rate of 336 $ml.min^{-1}$ using a B-290 Mini Spray Dryer (BUCHI Labortechnik) using a spray cap with a 0.5 mm diameter hole. The resulting solid was dispersed in DMF and washed twice times with DMF and ethanol. Then, it was dispersed in ethanol and stirred at room temperature overnight and precipitated by centrifugation. The process was repeated one more time with ethanol. The final product was dried for 12 hours at 160˚ C under vacuum. Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) showed a Pd content of 2.3 w.t. %.

Catalytic CO Oxidation Study

The catalytic oxidation of CO was carried out in a fixed bed column reactor with dimensions of 9.0 cm in length and 0.5 cm in inner diameter set in a controlled temperature oven. 50 mg of the catalyst was packed into the column, and a mixture of gases consisting of 1 % CO, 21 % O_2 and 78 % N_2 was passed through the column reactor at a fixed flow rate of 100 ml/min. After that, the catalyst was heated up to the desired temperature and maintained until a steady state was achieved. Within this interval of time, set of samples of the outlet gas were withdrawn and analyzed to determine the CO_2 produced. A Hewlett-Packard, GC-5890, gas chromatograph equipped with TCD detector using an Agilent J&W GC column, HP-Plot Q, was used to determine the CO_2. The produced CO_2 gas was determined based on the integration area of the CO_2 peak using the relevant calibration curve. The process of the effluent gas measurements was continued until 100 %

conversion of CO. Activation energy was calculated using the rate method [M. A. Shalabi, B. H. Harji, C. N. Kenney, *J. Chem. Technol. Biotechnol.*, 1996*,* **65**, 317–324*]*, from which a value of 40.2 kJ/mol (with a R^2 value of 0.98) was determined.

Characterization

X-ray powder diffraction (XRPD) patterns were collected on an X'Pert PRO MPDP analytical diffractometer (Panalytical) at 45 kV, 40 mA using CuKa radiation (1.5419°A). Nitrogen adsorption and desorption measurements were done at 77˚ K using an Autosorb-IQ-AG analyser (Quantachrome Instruments). Field-Emission Scanning Electron Microscopy (FE-SEM) images were collected on a FEI Magellan 400L scanning electron microscope at an acceleration voltage of 1.0–2.0 kV, using aluminum as support. High-angle annular dark-field scanning transmitted electron microscopy (HAADF-STEM) images were obtained with a FEI Tecnai G2 F20 at 200 kV. A Hewlett-Packard, GC-5890, gas chromatograph equipped with TCD detector using an Agilent J&W GC column, HP-Plot Q, was used to determine CO_2. Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) measurements were performed using an ICP-OES Perkin-Elmer, model Optima 4300DV.

Figure S1. (a,b) HAADF-STEM and (c) XRPD pattern of core-shell Au/CeO_2 NPs (black) in comparison to simulate patterns of Au (red) and CeO_2 (blue). Histogram of the (d) overall diameter of Au/CeO_2, (e) Au core and (f) CeO_2 shell.

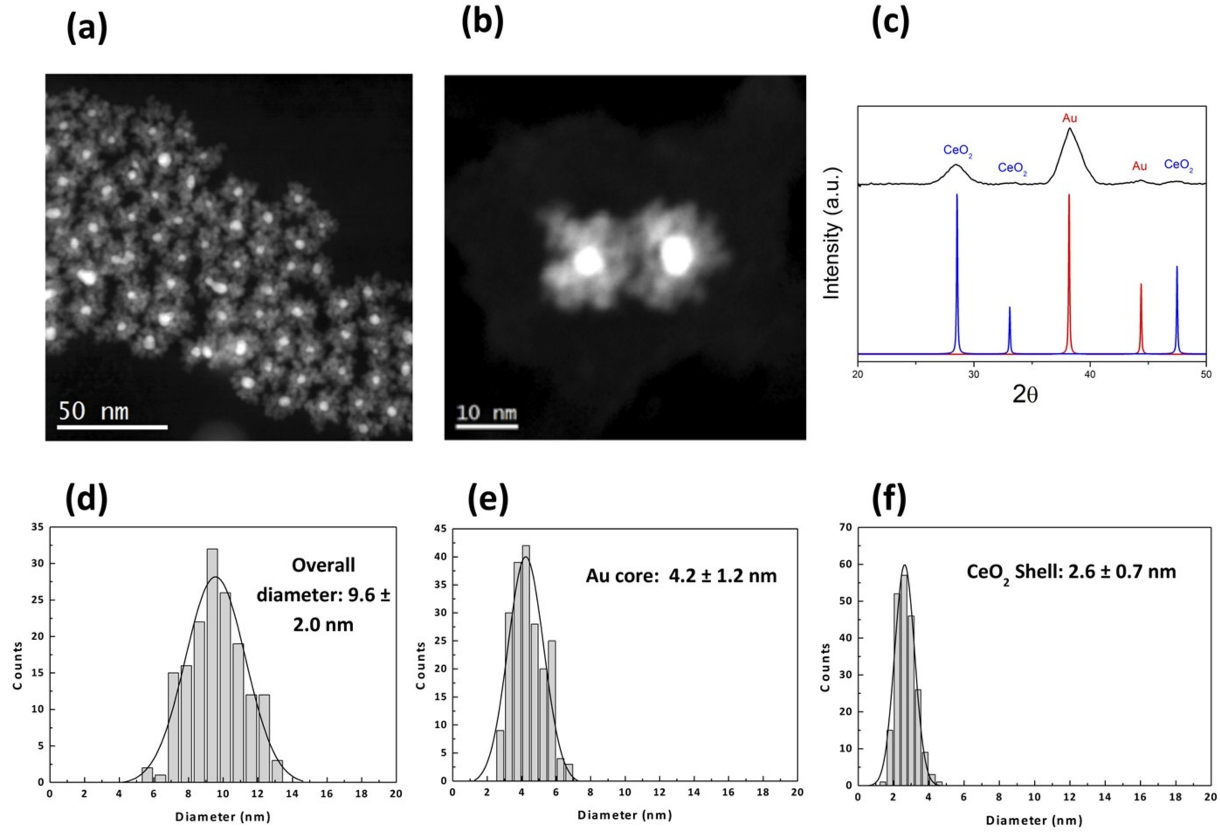


Figure S2. (a) HAADF-STEM and (b) XRPD pattern of UiO-66@Au (red) in comparison to simulated pattern of UiO-66 (black). Note here that, when we used $ZrCl_4$ as the metal salt to synthesize UiO-66@Au/CeO_2, the resulting acidic precursors solution (pH~1) at high temperature caused dissolution of CeO_2 in the process. As a result, a composite made of large Au NPs encapsulated into UiO-66 beads was produced. This phenomenon was confirmed by ICP-OES from which a Au content of 2.6 w.t. % and a Ce content of 0.02 w.t. % were found.

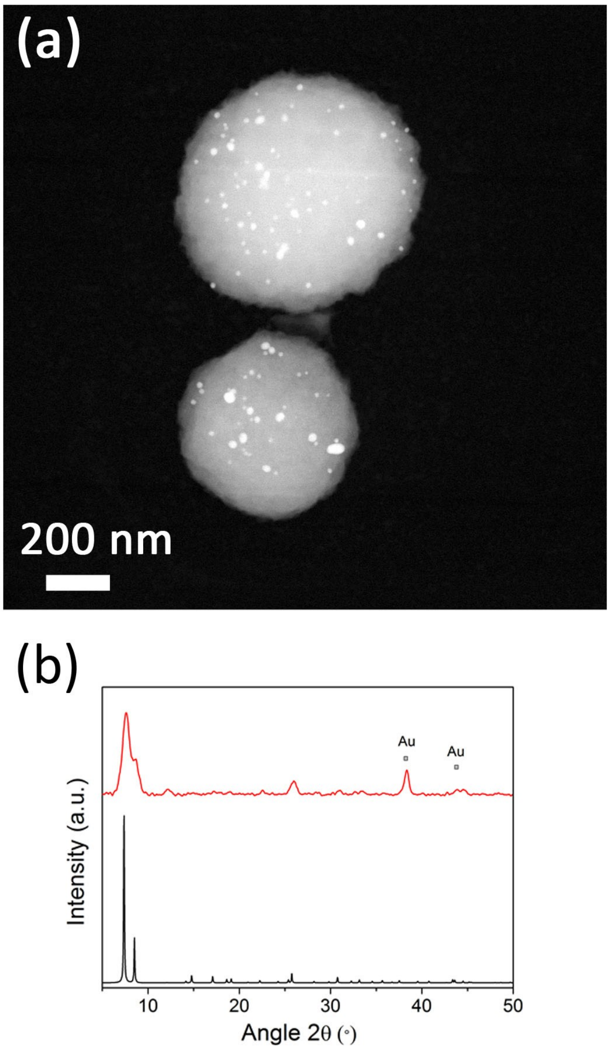
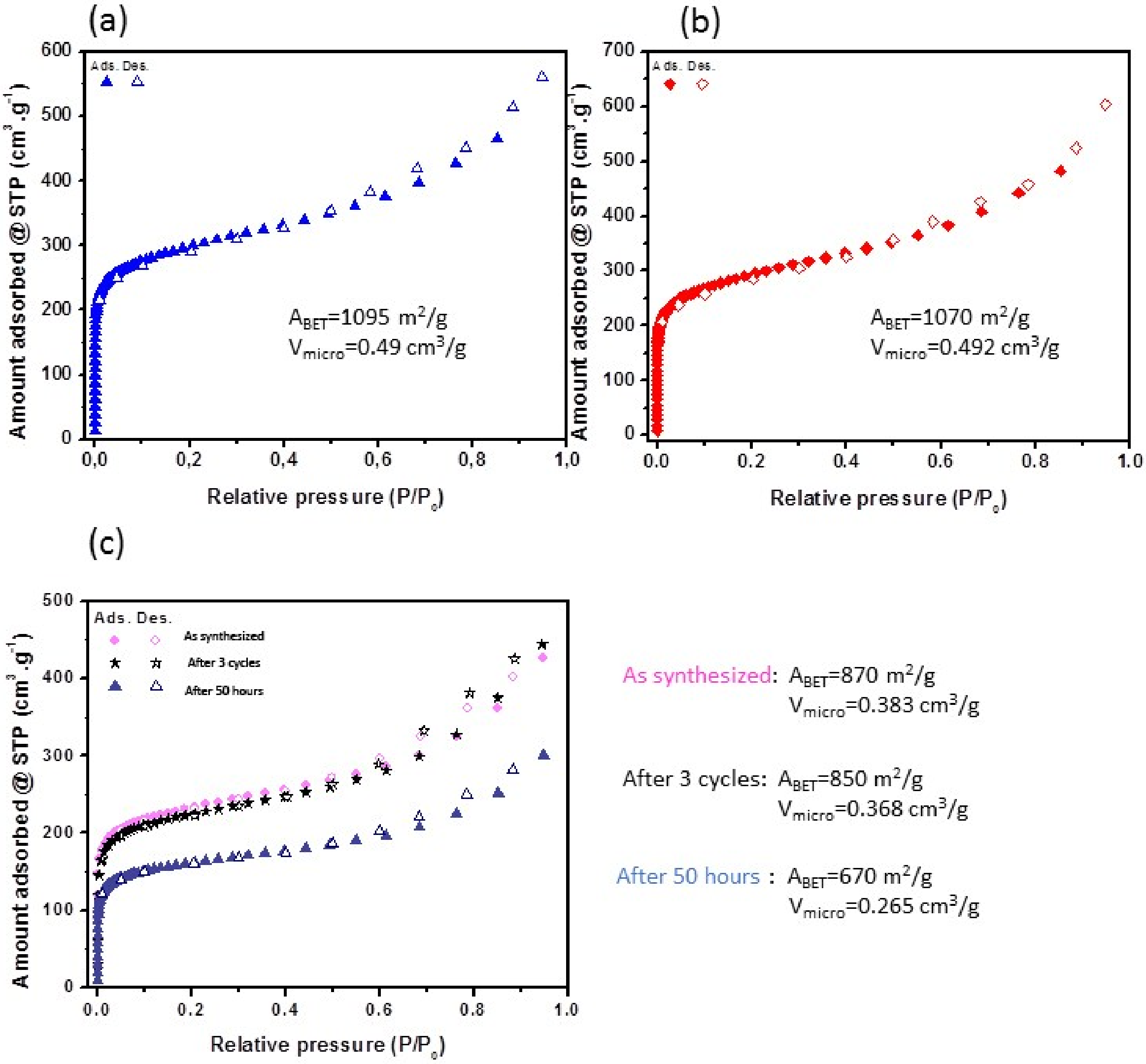


Figure S3. N_2 sorption isotherms collected at 77 K for (a) UiO-66@Au/CeO_2-2.8, (b) UiO-66@Au/CeO_2-5.5 and (c) UiO-66@Au/CeO_2-7. In this latter case, it is shown the isotherms collected before and after three temperature-programed cycles and 50 hours of continuous CO conversion.



As synthesized: A_{BET}=870 m^2/g
V_{micro}=0.383 cm^3/g

After 3 cycles: A_{BET}=850 m^2/g
V_{micro}=0.368 cm^3/g

After 50 hours : A_{BET}=670 m^2/g
V_{micro}=0.265 cm^3/g

Figure S4. CO conversion rate as a function of reaction temperature for pristine UiO-66 beads.

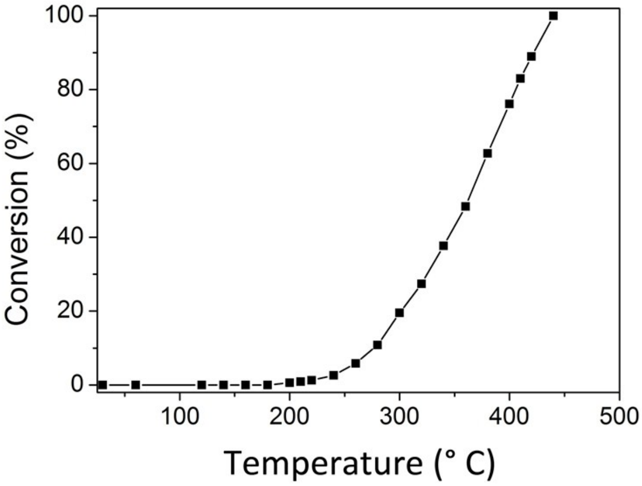


Figure S5. XRPD pattern of UiO-66@Au/CeO_2 synthesized with 16 ml of Au/CeO_2 NPs solution (red) in comparison to simulated pattern of UiO-66 (black).

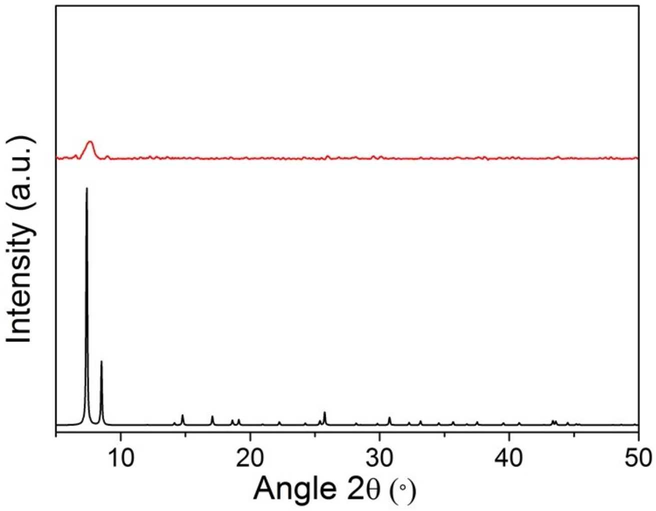


Figure S6. Stability test. (a,b) FE-SEM and (c) HAADF-STEM of UiO-66@Au/CeO_2-7 after three temperature-programed cycles. (d,e) FE-SEM and (f) HAADF-STEM of UiO-66@Au/CeO_2-7 after 50 hours of continuous CO conversion.

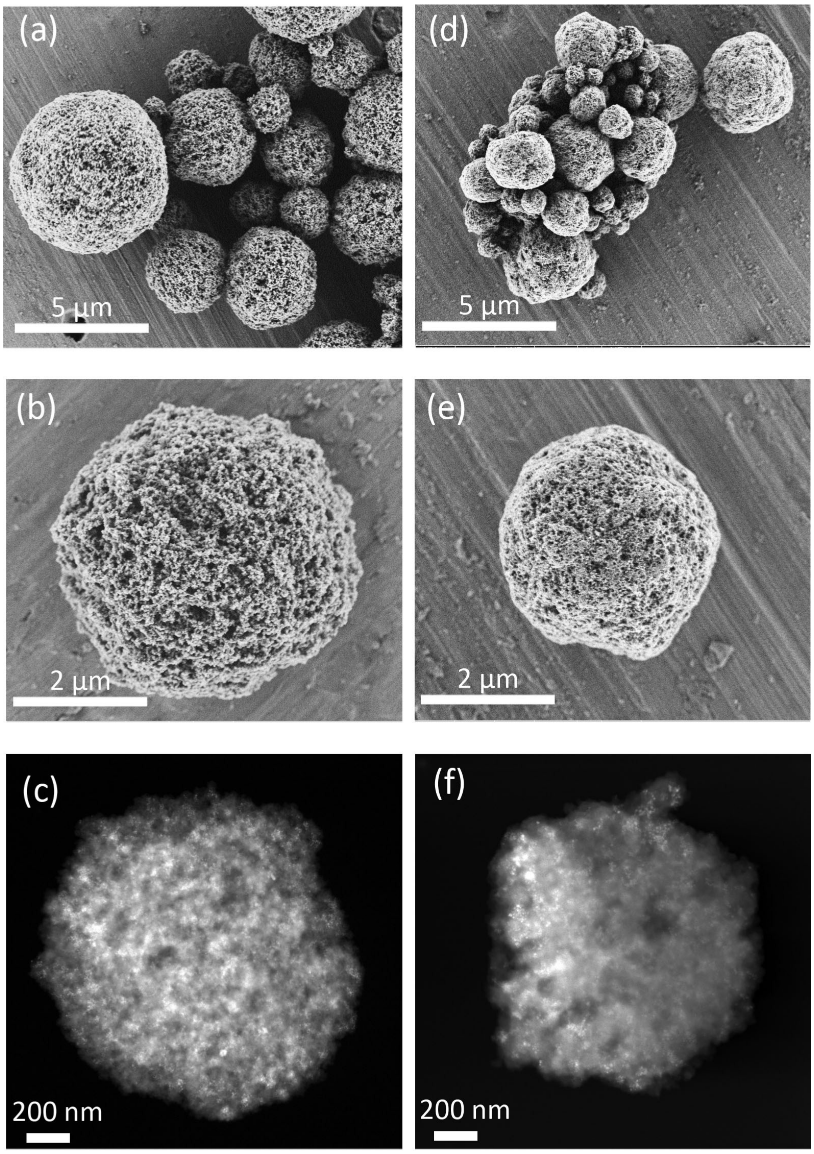


Figure S7. (a) HAADF-STEM, (b) FE-SEM and (c) XPDR pattern of UiO-66@Pd (red) in comparison to simulated pattern of UiO-66(black). (d) CO conversion rate as a function of reaction temperature for UiO-66@Pd, T_{50} = 164 ºC and T_{100} = 180 ºC.

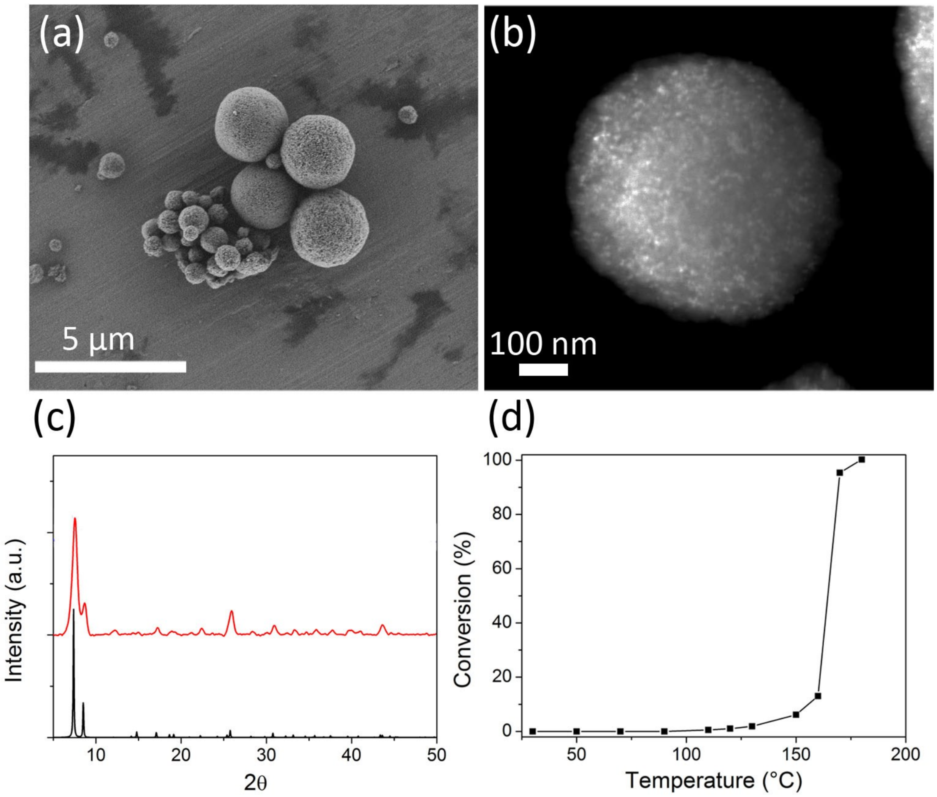


Table S1. Summary of catalysts based on Au NPs and their corresponding TOF values.

Material	T(ºC)	Au NP size (nm)	TOF (h^{-1})	Reference
UiO-66@Au/CeO_2	30	5	10	This work
	50	5	39	
	75	5	106	
	100	5	204	
2.32Au/ZnOx/CeO_2-Al_2O_3	25	5	1188	[1]
1.9Au/0.5ZnO/CeAl	25	5	1584	
1.82Au/1ZnO/Al	25	5	396	
1.7Au/1ZnO/CeAl	25	5	1836	
1.99Au/1.5ZnO/CeAl	25	5	1548	
1.57Au/0.5Fe_2O_3/CeAl	25	5.7	1152	
1.91 Au/1 Fe_2O_3/Al	25	5	72	
1.26 Au/1 Fe_2O_3/CeAl	25	18	4356	
Au/1.5 Fe_2O_3/CeAl	25	21	1368	
Pt/SiO_2	177	10	36	[2]
Al_2O_3-supported Pt	250	10	720	[3]
Al_2O_3-supported Pd	250	10	14400	
Al_2O_3-supported Rh	250	10	21600	
Au/TiO_2/Mo(100)	27	2.4	720*	[4]

*at a reaction time of 100min

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[2] N. W. Cant, *J. Catal*, 1980, **62**, 173-175.

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