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Electronic Supplementary Information

Monodisperse-porous cerium oxide microspheres as a new support with appreciable catalytic activity for a composite catalyst in benzyl alcohol oxidation

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1. Materials

Cerium (III) nitrate hexahydrate ($Ce(NO_3)_2.6H_2O$) and hexamethylenetetraamine (HMTA) were purchased from Sigma-Aldrich Chemical Co. (Milwaukee, WI, U.S.A.). For the derivatization of CeO_2 microspheres, 3-aminopropyltriethoxysilane (APTES), 3-glycidoxypropyltrimethoxysilane (GPTMS) and polyethylenimine (PEI) (Mw:) were obtained from Sigma-Aldrich. Polyvinyl alcohol (PVA), sodium borohydride ($NaBH_4$), concentrated sulphuric acid (H_2SO_4) and palladium (II) nitrate hydrate, used in the synthesis and immobilization of Pd NPs were obtained from Sigma Chemical Co. Benzyl alcohol (BzOH), the oxidation agent, tertiary-butylhydrogenperoxide (TBHP) and the solvent, diethyleneglycol dimethylether (DEGDME) were purchased from Sigma-Aldrich. Commercial cerium dioxide (c-CeO_2) microparticles as a reference support was also purchased from Sigma-Aldrich. All runs were performed using dDistilled-dieonized (DDI) water (Direct-Q 3 UV (Type 1), Millipore, USA) with a resistivity of 18 MΩ·cm.

2. Catalyst characterization

The size distribution and the surface morphology of catalysts were determined by scanning electron microscopy (SEM, QUANTA 400F Field Emission, USA). The pore size distribution and the specific surface areas of catalysts were determined by using the nitrogen adsorption/desorption method according to Brunauer–Emmett–Teller (BET) model (Quantachrome, Nova 2200E, UK). The means size and the size distribution of the Pd NPs were determined by transmission electron microscopy (TEM, JEM JEOL 2100F 200kV HRTEM, Japan). The crystal structures of catalysts were investigated with X-ray diffraction spectroscopy (XRD, Rigaku Ultima-IV, Japan). The surface atomic compositions of catalysts were determined by energy dispersive X-ray spectroscopy (JEOL JXA-8230 EPMA, Japan). Pd contents of all catalysts were determined by Inductively Coupled Plasma – Mass Spectrometer (ICP-MS, Thermofisher X series II, Thermo Fisher Scientific, USA).

3. Calculation of overall benzyl alcohol (BzOH) conversion, selectivity for benzaldehyde (BzCHO) and BzCHO formation yield

The equations used for the calculation of overall benzyl alcohol (BzOH) conversion, selectivity for benzaldehyde (BzCHO) and BzCHO formation yield are given below:

Overall BzOH conversion (%) = $\left(\frac{C_0 - C_{BzOH}}{C_0}\right) * 100$

Selectivity for BzCHO (%) = $\left(\frac{C_{BzCHO}}{C_0 - C_{BzOH}}\right) * 100$

BzCHO formation yield (%) = ($Selectivity\ forBzCHO(\%) * Overall\ BzOH\ conversion\ (\%))/100$

4. Characterization of the catalyst

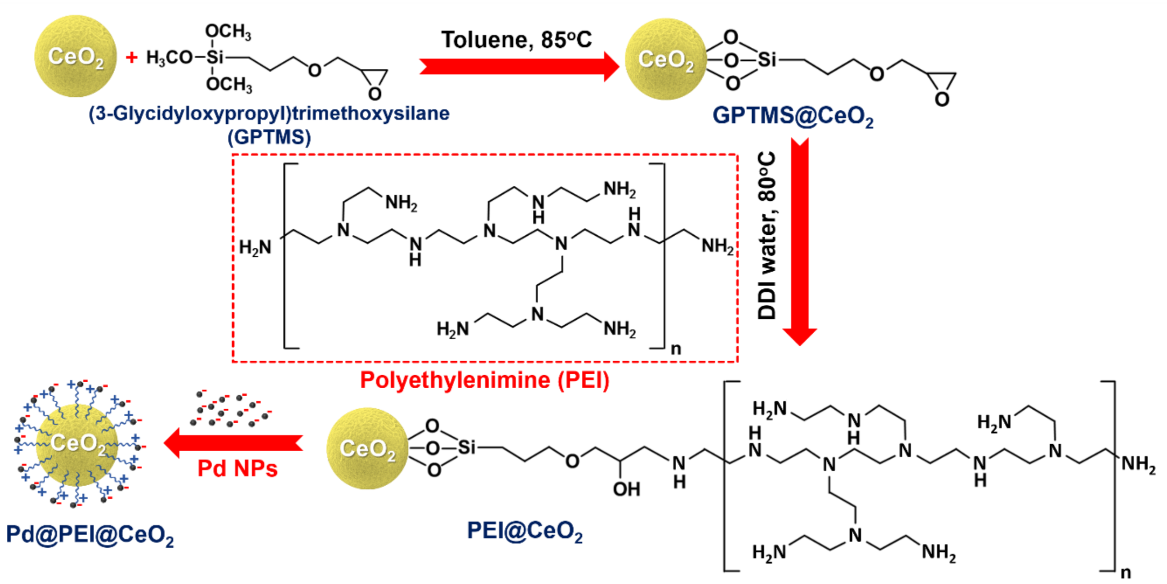

Figure S1. The chemical route used for attachment of Pd nanoparticles (Pd NPs) onto the monodisperse-porous CeO_2 microspheres using PEI as the macromolecular cationic linker.

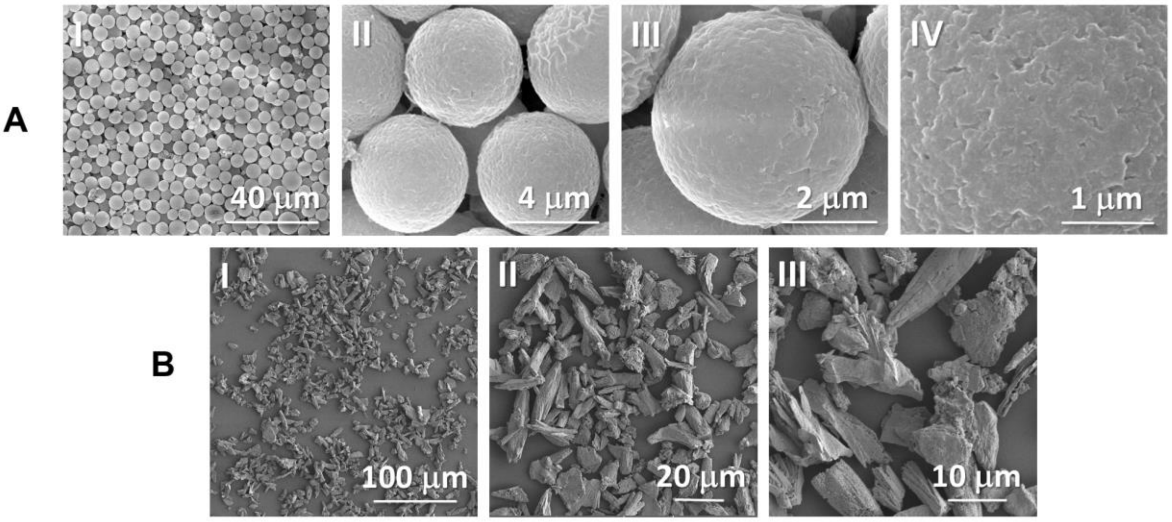

Figure S2. The SEM photographs of (A) Pd@APTES@SiO_2 microspheres. Magnification: (I) 2500X, (II) 25000X, (III) 45000X, (IV) 100000X. (B) Pd@APTES@c-CeO_2 microparticles. Magnification: (I) 650X, (II) 1900X, (III) 4500X.

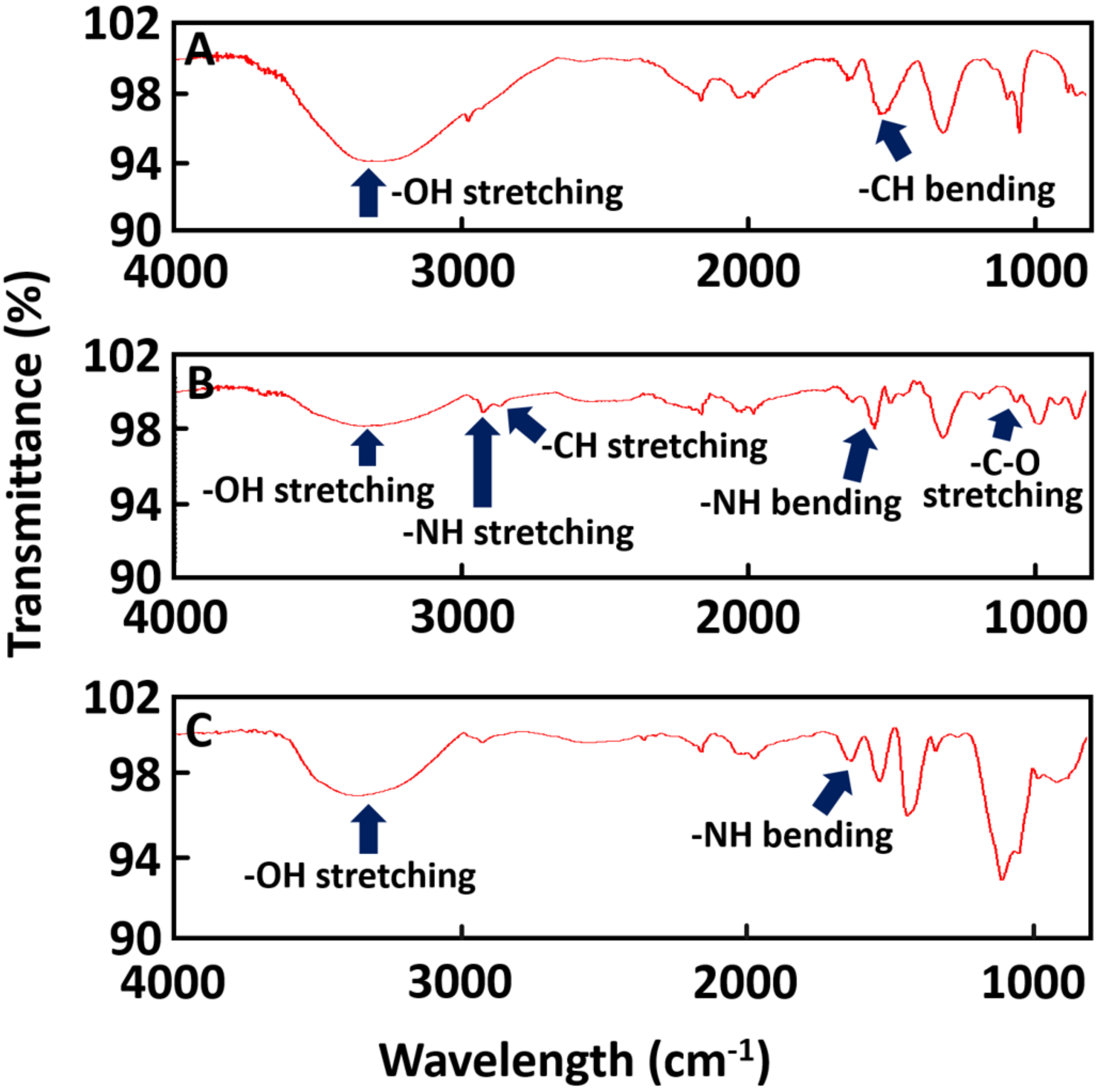

Figure S3. FTIR-ATR spectra of (A) plain CeO_2 microspheres, (B) APTES@CeO_2 and (C) Pd@APTES@CeO_2 microspheres.

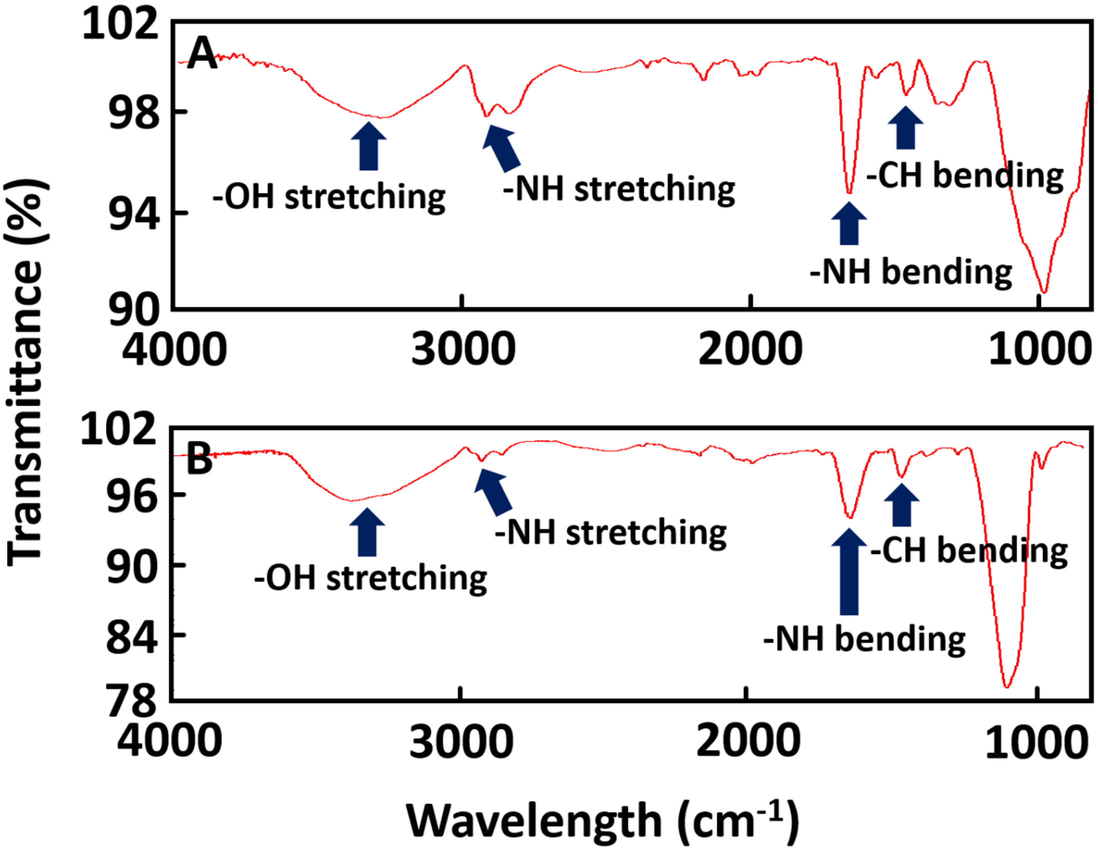

Figure S4. FTIR-ATR spectra of (A) PEI@CeO_2 and (B) Pd@PEI@CeO_2 microspheres.

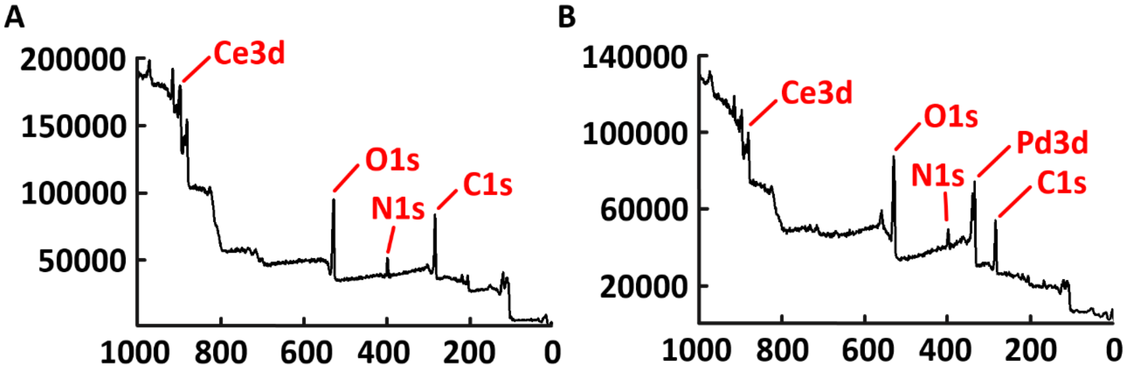

Figure S5. Survey XPS spectra of (A) PEI@CeO_2, and (B) Pd@PEI@CeO_2 microspheres.

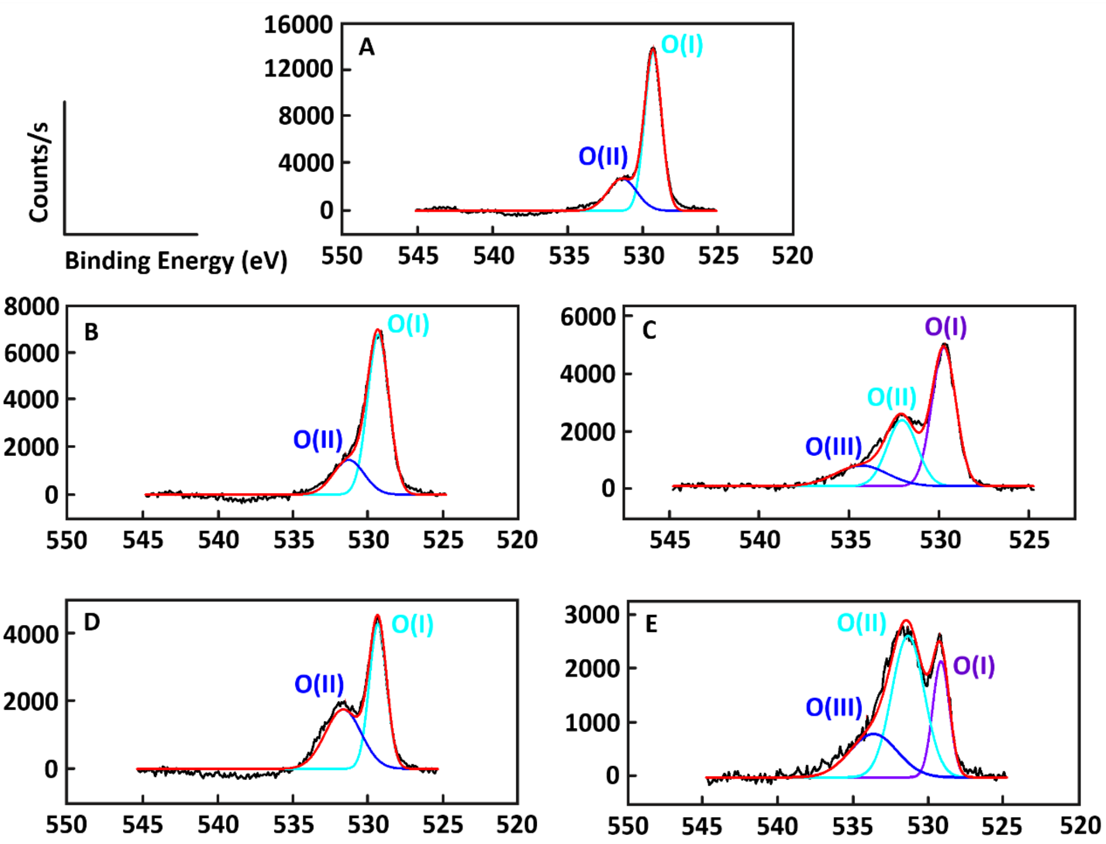

Figure S6. Core-level XPS spectra of O1s scan for (A) plain CeO_2, (B) APTES@CeO_2, (C) Pd@APTES@CeO_2, (D) PEI@CeO_2, and (E) Pd@PEI@CeO_2 microspheres.

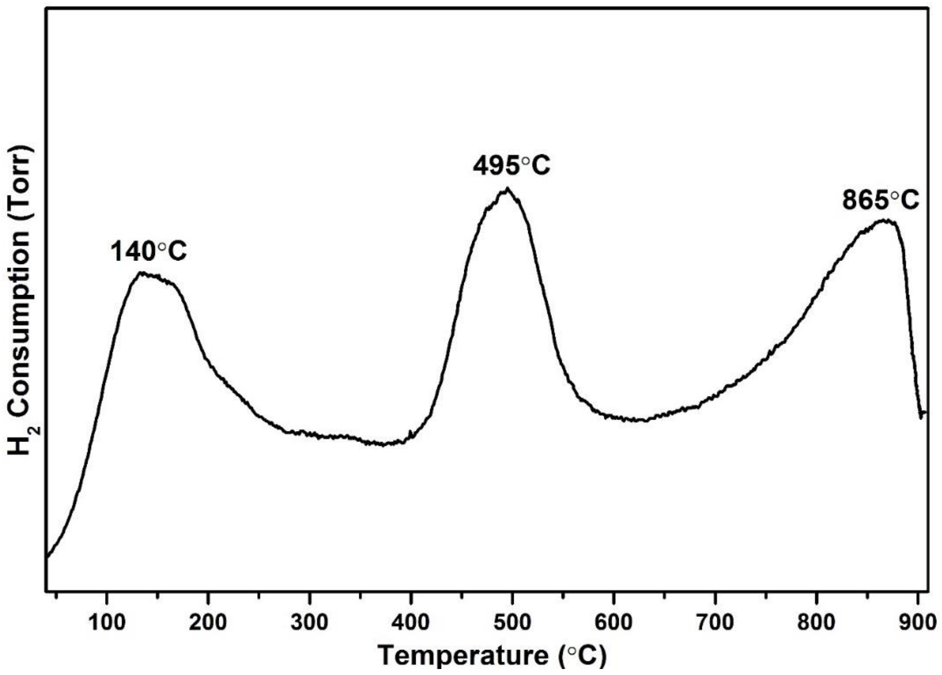

Figure S7. H2-TPR spectrum of Pd@APTES@CeO_2 microspheres.

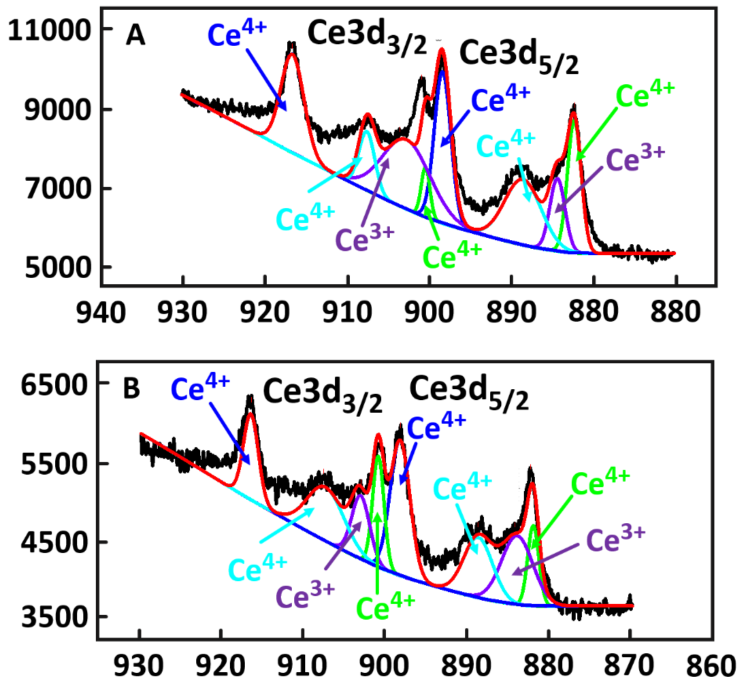

Figure S8. Core-level XPS spectra of Ce3d scan for (A) PEI@CeO_2 and (B) Pd@PEI@CeO_2 microspheres.

5. Kinetic behaviour of synthesized catalysts

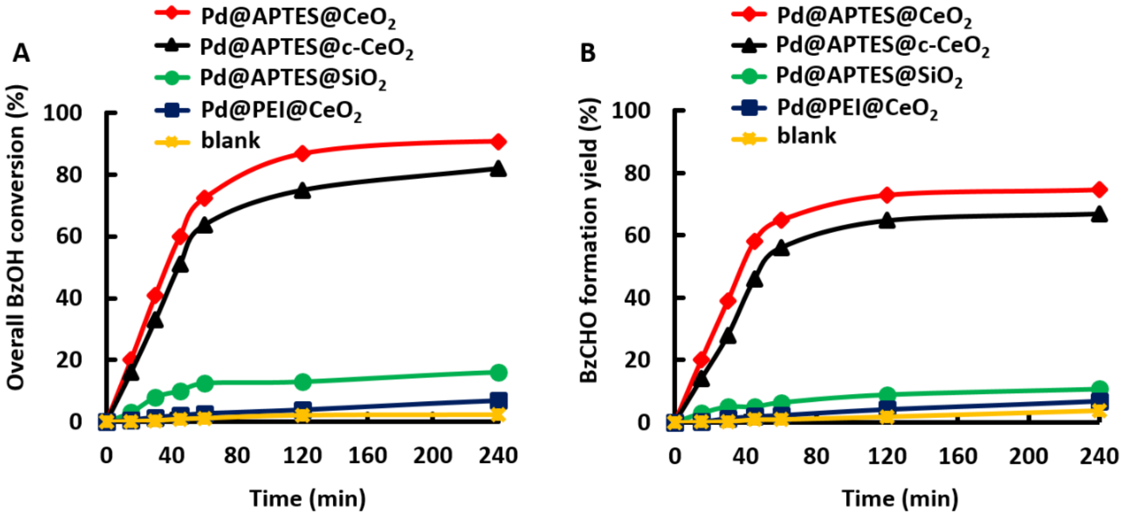

Figure S9. The variation of **(A)** overall BzOH conversion and **(B)** BzCHO formation yield with the time in the presence of Pd@APTES@CeO_2, Pd@PEI@CeO_2, Pd@APTES@SiO_2 microspheres and Pd@APTES@c-CeO_2 microparticles as the catalysts. The blank run performed without using any catalyst was also included in the plots.

6. Quantum Mechanical Protocol

The approach followed in quantum mechanical calculations is summarized below. Some simplifications were made during the modeling of system components. A CeO_2 slab which represents a small part of CeO_2 microspheres was defined. Lattice parameters are used as a=b=c=3.866 Å and α=β=γ=60° with P1 symmetry space group as provided by the VASP calculation results in the literature.[1] By using these parameters a $Ce_{50}O_{90}$ surface was constructed. A couple of unsaturated oxygen atoms were saturated by the addition of hydrogen atoms for making the complete surface neutral. The structure of Pd_{55} NP is taken from the literature and used in its neutral form.[2] Both CeO_2 surface and Pd NP were fully optimized without any constraints using

PM7 method, before preparing the reaction system. In the next step, the optimized structures of Pd NP and CeO_2 surface were linked to APTES. The obtained Pd@APTES@CeO_2 system was fully optimized with PM7 method. In the last step, isolated TBHP and BzOH structures were fully optimized by using DFT at the B3LYP/6-311+G(d,p) level of theory, and then their DFT optimized structures were implemented into the PM7 calculations to separately investigate their interactions with Pd@APTES@CeO_2 system and Pd NP. Both reaction systems were fully optimized without any constraints with PM7. Binding energies were calculated as given below:

$$\Delta E_{bind_1} = E(\mathrm{Pd@APTES@}CeO_2 + \mathrm{TBHP} + \mathrm{BzOH}) - [E(\mathrm{Pd@APTES@}CeO_2) + \mathrm{E(TBHP)} + \mathrm{E(BzOH)}]$$

$$\Delta E_{bind_2} = E(\mathrm{Pd} + \mathrm{TBHP} + \mathrm{BzOH}) - [E(\mathrm{Pd}) + \mathrm{E(TBHP)} + \mathrm{E(BzOH)}]$$

In these equations, $E(\mathrm{Pd@APTES@}CeO_2), E(\mathrm{Pd}), \mathrm{E(TBHP)}, \mathrm{E(BzOH)}$ indicate the PM7 calculated total energy of the isolated objects, while $E(\mathrm{Pd@APTES@}CeO_2 + \mathrm{TBHP} + \mathrm{BzOH})$ and $E(\mathrm{Pd} + \mathrm{TBHP} + \mathrm{BzOH})$ indicate the total energy of the interacting assembly of the objects. Both interacting assemblies are given in **Figure S10 of the Supplementary Information**.

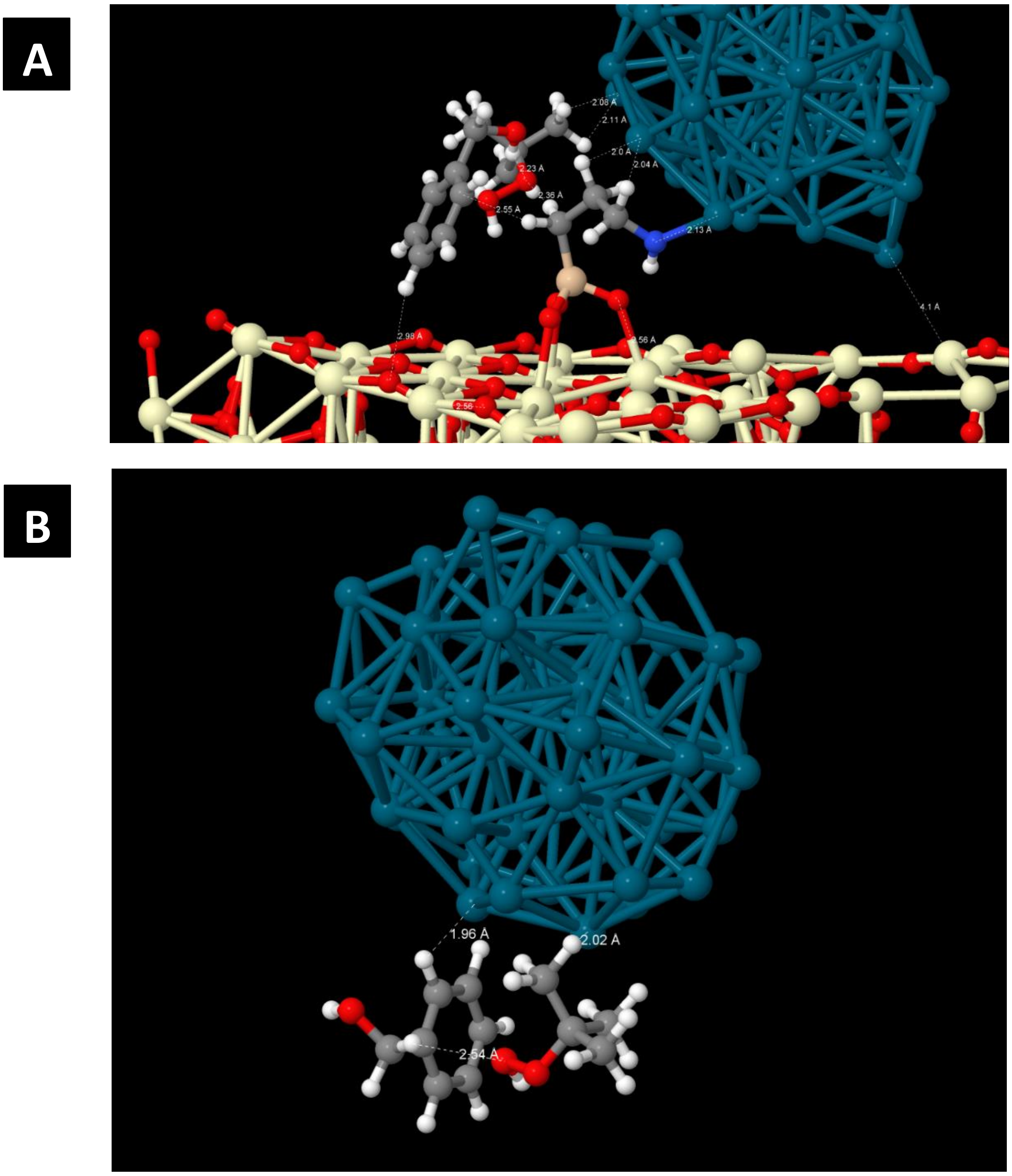

Figure S10. Interactions among **(A)** Pd@APTES@CeO$_2$, TBHP and BzOH. **(B)** Pd NP, TBHP and BzOH.

References

1. A. Jain, S.P. Ong, G. Hautier, W. Chen, W.D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, K.A. Persson, APL Materials, 2013, **1**, 011002.

2. S. Kohaut, T. Rapps, K. Fink, D. Schooss, J. Phys. Chem. A, 2013**, 123**, 10940-10946.