

ELECTRONIC SUPPORTING INFORMATION

Chemoselective Hydrogenation of Cinnamaldehyde over Tailored Oxygen Vacancy Rich Pd@ZrO₂ Catalyst

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1. Materials

Zirconium (IV) oxynitrate hydrate (ZrO(NO₃)₂).xH₂O) (99 %), ethylene glycol (CH₂OH)₂ (99.8 %), palladium (II) nitrate dihydrate (Pd(NO₃)₂.2H₂O) (99 %) were purchased from Sigma-Aldrich, India. Authentic samples of cinnamaldehyde (CAL, 99 %), cinnamyl alcohol (COL, 95 %), hydrocinnamyl alcohol (HCOL, 98 %) and hydrocinnamaldehyde (HCAL, 99 %) were also supplied by Sigma-Aldrich, India. Solvents such as isopropanol (IPA, 99.9 %), toluene (99 %), 1,4-dioxane (99 %), ethanol (99 %) were obtained from Sigma-Aldrich, India. All the reagents and solvents were of analytical grade and were used for all the experiments without any further distillation. H₂ cylinder with 99.99 % purity was

provided by Chemix Specialty Gases and Equipment Pvt. Ltd, India. Deionized (D.I) water was used throughout the experiments.

2. Characterization Techniques

First and foremost, to confirm the successful phase formation of the as-synthesized materials, X-ray powder diffraction (XRD) patterns were obtained using X-ray diffractometer (XRD; Rigaku Japan) with Cu K α radiation source ($\lambda = 1.5406\text{\AA}$) with a scan rate of $2\text{ }^\circ\text{C min}^{-1}$ and the data was collected between the 10° and 80° (2θ range). The specific surface areas of the ZrO $_2$ support and the final Pd@ZrO $_2$ catalysts with different Pd loadings were estimated with the help of N $_2$ adsorption-desorption isotherms obtained using Brunauer-Emmett-Teller (BET) technique. The pore size distribution and pore volume were analysed using Barrett-Joyner-Halenda (BJH) method. The analysis was performed on a Belsorp MAX instrument (BEL Japan). The materials under examination were outgassed at $100\text{ }^\circ\text{C}$ for 3 h in high vacuum prior to the analysis and the final analysis was carried out at the temperature of liquid nitrogen (-77K).

In order to examine the reduction temperature and the degree of interaction between different species in all the PdO@ZrO $_2$ catalysts, the reduction profile of the PdO@ZrO $_2$ catalysts, was obtained using H $_2$ -Temperature Programmed Reduction (H $_2$ -TPR) technique using an indigenous instrument comprising of a quartz tube reactor attached to a six-port valve connected to a thermal conductivity detector (TCD) (M/s. Mayura Analyticals Pvt. Ltd, India). Prior to analysis, the samples were degassed at a $100\text{ }^\circ\text{C}$ temperature in He atmosphere. Afterwards, the temperature was lowered to room temperature by replacing He gas with 5 % H $_2$ at the flow rate of 30 mL min^{-1} . The temperature was then raised to $750\text{ }^\circ\text{C}$ at the ramping rate of $10\text{ }^\circ\text{C min}^{-1}$ and isothermal zone was attained by maintaining the temperature at $750\text{ }^\circ\text{C}$ for 0.5 h. Standard GC software was used to analyze the amount of H $_2$

being consumed for reduction by introducing a measured volume of H₂ through a loop by means of the six-port valve. In a catalyst characterization, it is equally important to determine the nature of sites (acidic or basic) present on the catalyst surface which is responsible for its activity towards the reaction. This information was obtained by analyzing the samples by temperature programmed desorption (TPD) technique using the same instrument employed for H₂-TPR analysis. Here, NH₃ (for acidic sites) and CO₂ (for basic sites) were employed as probe molecules in order to quantify the acidic and basic sites, respectively. Dispersion of active metal Pd in the catalysts along with the Pd particle size was calculated with the help of data acquired using H₂ chemisorption technique. Precisely, 100 mg of the reduced catalyst was loaded in a quartz tube. The catalyst was treated under H₂ atmosphere (20 mL/min) at 300 °C for an h followed by purging He at a flow rate of 40mL/min for 1 h. The system was then cooled to room temperature. Pulse titration method was employed to perform H₂ chemisorption and amount of H₂ in the pulses were monitored by using thermal conductivity detector (TCD)

Surface morphology and elemental analysis of as-synthesized ZrO₂ support and Pd@ZrO₂ catalysts were examined by Field Emission Scanning Electron Microscope (FE-SEM) coupled with EDAX (Energy-Dispersive X-ray spectroscopy) (JOELModel-JSM7). The sample to be analysed was evenly spread on the carbon tape which was placed on the aluminium metal stub and the stub was further subjected to sputtering for 120 sec using gold nanoparticles. The microstructure of the ZrO₂ support and the particle size of the active Pd metal on the ZrO₂ support were studied using Transmission Electron Microscopy (TEM) measurement which was carried out on a Hitachi H-8100 instrument. Precisely, the sample was dispersed in ethanol solvent by sonication and then drop casted on copper grid following which it was dried properly before analysis. In addition to this, the High Resolution Transmission Electron Microscopy (HR-TEM) was performed at an atomic scale for

investigating crystal structures and lattice imperfections. Selected Area Electron Diffraction (SAED) measurements were also carried out using the same instrument to confirm the crystalline phase of the materials. XPS technique is considered as an effective tool for surface analysis of the material to obtain detail information on its elemental composition, chemical state as well as electronic state. X-ray photoelectron spectra (XPS) were recorded on a X-ray photoelectron spectrometer (Perkin Elmer PHI1257) at a pressure of about 4×10^{-10} Torr. using Al K α X-ray as the excitation source (1486.7 eV). FT-IR spectroscopy was used as a qualitative tool for material identification to quantify specific functional groups present in ZrO₂ support and all Pd@ZrO₂ catalysts. The FT-IR spectra were recorded with the help of Perkin Elmer FT-IR spectrophotometer (Spectrum Two) by employing KBr disc method.

Adsorption mode of CAL on the Pd@ZrO₂ catalyst was also verified by FTIR spectroscopy. The FTIR spectra were recorded on a Bruker Vector 22 spectrometer in the range 4000–400 cm⁻¹. The CAL reactant was drop casted on the catalyst surface (prepared of same concentration as used in catalytic activity). The sample was treated at the reaction temperature (120 °C) in nitrogen inert atmosphere to reach adsorption equilibrium and then blow-dried under same atmosphere. For FTIR analysis, a pellet was prepared by using a pellet press machine and analyzed on the FT-IR spectrometer.

The percentage conversion of CAL and selectivity of HCAL was calculated using formula;

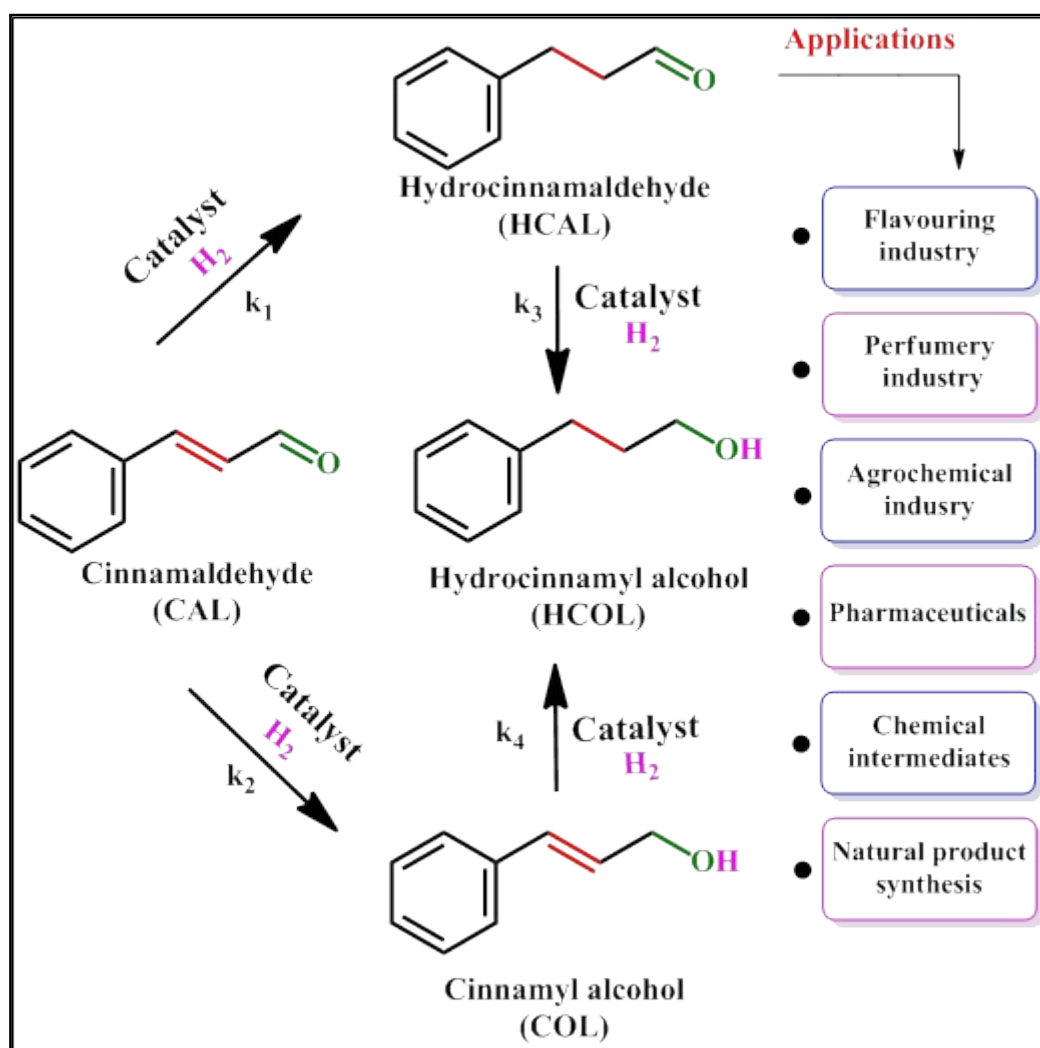
$$\text{Conversion (\%)} = (1 - C_{\text{CAL}}/C_0) \times 100, \text{ Selectivity (\%)} = (C_{\text{HCAL}}/(1 - C_{\text{CAL}}/C_0)) \times 100,$$

$$\text{Yield (\%)} = (C_{\text{HCAL}}/C_0) \times 100$$

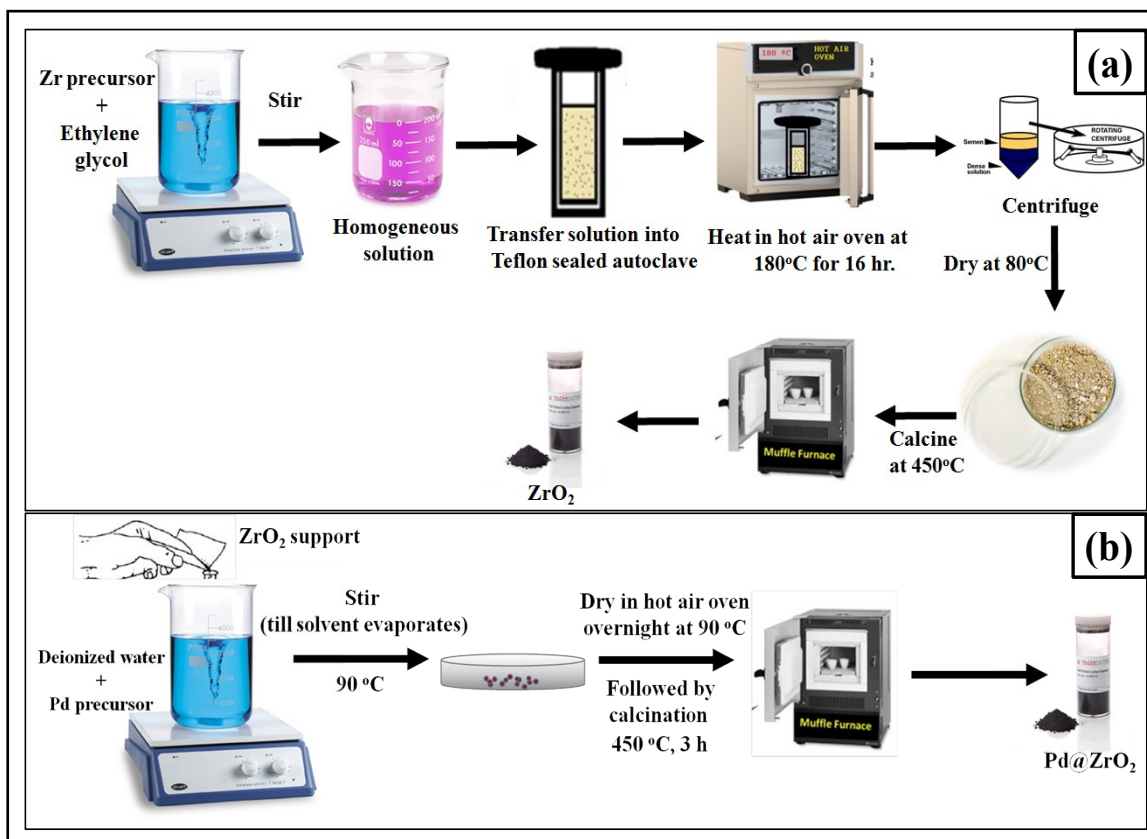
Where, C_{CAL} = Conversion of CAL, C₀ = initial concentration of CAL, C_{CAL} and C_{HCAL} = concentrations of CAL and HCAL at a certain reaction time after the Pd@ZrO₂ catalytic reaction, respectively.

(GC-7820 A; M/S Agilent, USA) equipped with a flame ionization detector (FID) having a capillary column (HP-5, 19091J-413) of 30 m length, 0.32 mm inner diameter and 0.25 mm film thickness. The products from the reaction mixture were separated by HPLC technique and the obtained products, HCAL (major) and HCOL (minor) were confirmed by ^1H NMR, ^{13}C NMR spectroscopic techniques and GC-MS as well as elemental analysis.

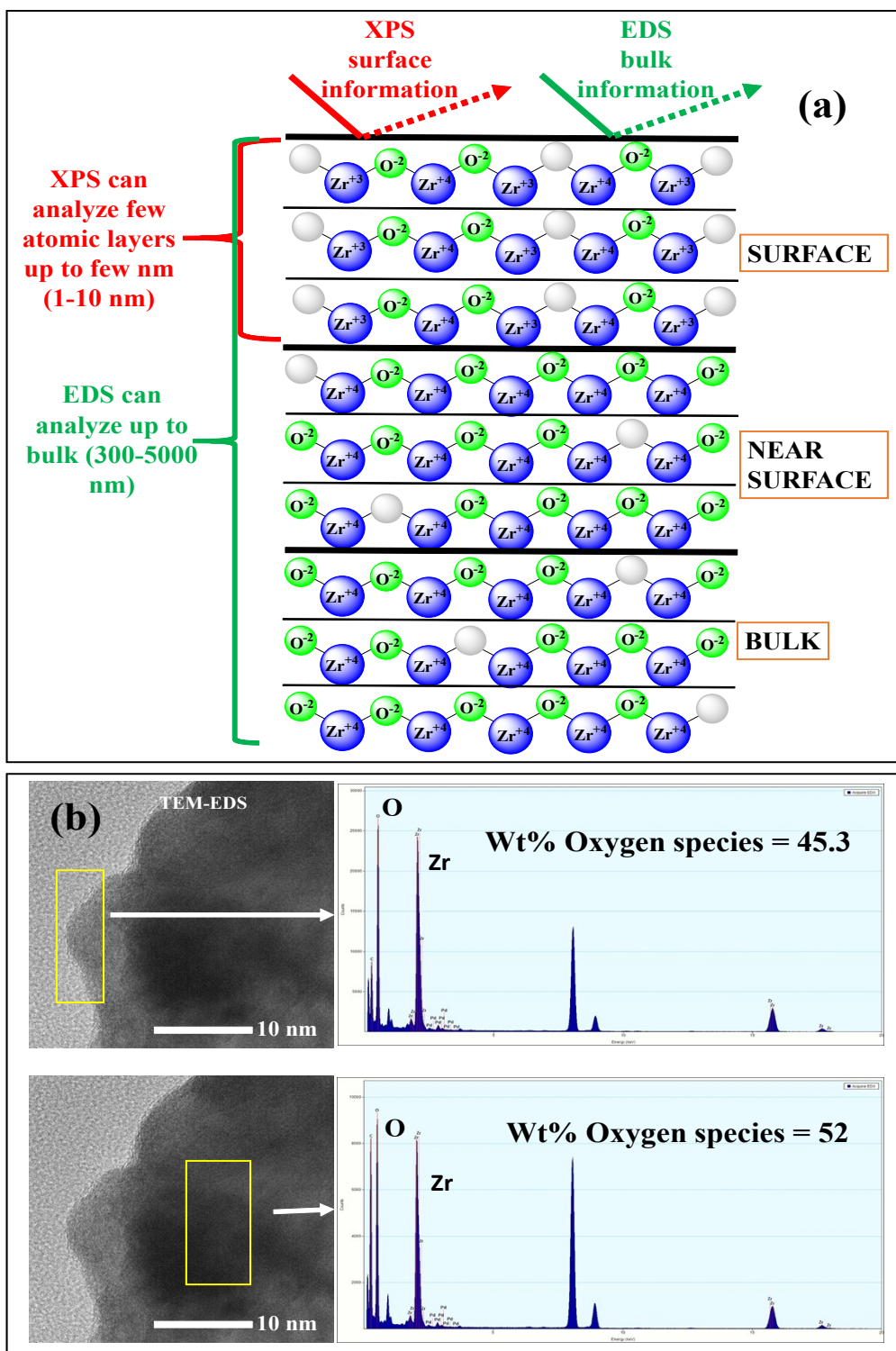
SCHEMES



Scheme S1. General reaction pathway for typical hydrogenation of cinnamaldehyde and applications of HCAL in different engineering aspects.



Scheme S2. (a) Synthesis of ZrO_2 support by hydrothermal synthesis method and (b) synthesis of $Pd@ZrO_2$ catalysts by wet-impregnation method.



Scheme S3. (a) General illustration of depth analysis of XPS and TEM/EDX for elemental analysis and (b) TEM/EDX results obtained at the center of particle and at the edge of particle of 4-Pd@ZrO₂ catalyst.

TABLES

Table S1. Comparative study of catalytic hydrogenation of cinnamaldehyde over 4-Pd@ZrO₂ with the literature.

Entry	Catalysts	Reactant/ Solvent	Temp/ Pressure	Time (h)	Con. (%)	Sel.		Ref
						(HCAL)	(COL)	
1.	5 wt % Pd/C	5 mmol/5 mL pyridine or THF	50°C/ 11 bar	0.5	60	60	-	[68]
2.	1 wt % Pt/BN	5 mmol/16 mL +4 mL (IPA+water)	25°C/ 40 bar	2	95	-	85	[66]
3.	0.2 % Pd-1.2 % Ni/SBA- 15	250 mg/15 mL cyclohexane	80°C/12 bar	2	96	88	-	[12]
4.	3 wt %Pt 0.05 wt % Sn/HPZSM- 5	3.75 mmol/9 mL +1 mL (IPA+water)	90°C/ 20 bar	1	100	-	82	[69]
5.	1.5 wt % Au/ZnO	0.1 mL/-	110°C/ 20 bar	40 min	95	-	100	[70]
6.	Au-Cu/CeO ₂	4x10 ² mol/ 100mL ethanol	70°C/60mL min ⁻¹	7	40	80	-	[11]
7.	Au/Mg-Al- CeO ₂	0.8 mmol/ 60 mL ethanol	120°C/ 10 bar	6	83	91	-	[13]
8.	Ni-TiO ₂	1.2 g/16 mL	120°C/	1	91	-	61	[71]

		methanol	20 bar					
9.	4-Pd@ZrO ₂	1 g/ 10 mL IPA	120°C/10 bar	9	100	86	-	Present work
