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Supporting Information

Bi Doped CeO$_2$ Oxide Supported Gold Nanoparticle Catalysts for the Aerobic Oxidation of Alcohols

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Micro kinetic analysis: The criteria below must be met for the reaction rates to be free from mass transfer limitations [a-c]:

(a) Gas-liquid mass-transfer resistance is considered insignificant if

$$\alpha_1 = \frac{R_{O_2}}{K_1 a_b C_A^*} < 0.1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

$$K_1 a_b = (1.48 \times 10^{-3})(N)^{2.18}\left(\frac{V_g}{V_l}\right)^{1.88}\left(\frac{d_i}{d_t}\right)^{2.16}\left(\frac{h_i}{h_2}\right)^{1.16} \ldots\ldots\ldots\ldots(2)$$

(b) Liquid-solid mass-transfer limitation is considered unimportant if

$$\alpha_2 = \frac{R_{O_2}}{K_s a_p C_A^*} < 0.1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

$$a_p = \frac{6w}{\rho_p d_p} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

$$\frac{K_s d_p}{D_M F_c} = 2 + 0.4\left[\frac{e(d_p)^4 \rho_1^3}{\mu_1^3}\right]^{0.25}\left[\frac{\mu_1}{\rho_1 D_M}\right]^{0.333} \ldots\ldots\ldots\ldots\ldots\ldots(5)$$

F$_C$ assumed 1 for spherical particles

$$D_M = \frac{(7.4 \times 10^{-8}) T (\chi M_w)^{\frac{1}{2}}}{\mu_l v_M^{0.6}} \ldots\ldots\ldots\ldots\ldots\ldots(6)$$

$$e = \frac{N_P N^3 d_i^5 \psi}{\rho_l V_l} \ldots\ldots\ldots\ldots\ldots\ldots(7)$$

$$\psi = 1.0 - 1.26\left[\frac{Q_g}{N d_i^3}\right] for \left[\frac{Q_g}{N d_i^3}\right] < 3.5 \times 10^{-2} \ldots\ldots\ldots\ldots\ldots(8)$$

$$\psi = 0.62 - 1.85\left[\frac{Q_g}{N d_i^3}\right] for \left[\frac{Q_g}{N d_i^3}\right] > 3.5 \times 10^{-2} \ldots\ldots\ldots\ldots\ldots(9)$$

$$Q_g = r_{max} V_L V_M \ldots\ldots\ldots\ldots\ldots\ldots\ldots(10)$$

$$V_M = \frac{V}{n} = \frac{RT}{P_{O_2}} \text{..........................}(11)$$

(c) Pore diffusion resistance can be considered to be insignificant if

$$\Phi_{exp} = \frac{d_P}{6}\left[\frac{(m+1)\rho_P R_{O_2}}{2D_e w C_A^*}\right]^{1/2} < 0.2 \text{ ....}(12)$$

$$D_e = D_M\left(\frac{\epsilon}{\tau}\right) \text{.................}(13)$$

Porosity and tortuosity can be assumed 0.40-0.50 and 3, respectively; m can be assumed to be 1, unless experimentally determined.

If gas-liquid mass-transfer limitation is significant, C_A^* is replaced by C_{AS} which is calculated by using the formula

$$C_{AS} = C_A^* - \frac{R_{O_2}}{\left[\frac{1}{K_l a_b} + \frac{1}{K_s a_P}\right]^{-1}} \text{ ....}(14)$$

List of Symbols

a_b= Gas-liquid interfacial area per unit volume of reactor, m^2/m^3
a_P= Liquid–solid interfacial area, m^{-1}
C_A^* = Saturation solubility of O_2 in liquid phase, $kmol/m^3$
C_{AS} = O_2 concentration on the catalyst surface, $kmol/m^3$
D_e = Effective diffusivity, m^2/s
d_i = Impeller diameter, m
D_M = Molecular diffusivity, m^2/s
d_p = Particle diameter, m
d_t = Reactor diameter, m
H_e = Henry's law constant, $kmol/m^3/atm$
h_1 = Height of the first impeller from the bottom, m
h_2 = Height of the liquid, m
K_l = Liquid film mass-transfer coefficient, m/s
$K_l a_b$= Overall gas-liquid mass-transfer coefficient, s^{-1}
K_s = Liquid-solid mass-transfer coefficient, m/s
m = Order of reaction with respect to oxygen
M_w = Molecular weight of solvent, g/mol
n = Moles of gas at constant pressure, kmol
N = Agitation speed, Hz
N_p = Power number
P_O= Partial pressure of oxygen, MPa
R = Universal gas constant, kJ/kmol/K
R_{O_2}= Overall rate of oxidation, $(kmol/m^3)s^{-1}$
r_{max} = Maximum rate of hydrogenation, $(kmol/m^3)s^{-1}$
T = Temperature, K
V_g = Volume of the gas in the reactor, m^3
V_l = Volume of the liquid in the reactor, m^3
W = Catalyst loading, kg/m^3

Greek Letters

α_1 = Parameter defined by Eq. 1
α_2 = Parameter defined by Eq. 3
Φ_{exp} = Parameter defined by Eq. 12
ρ_l = Density of liquid, kg/m^3
μ_l = Viscosity of liquid, centipoise
χ = Association factor
υ_M = Molar volume of the solute, cm^3/mol
ρ_P = Density of particle, kg/m^3
ϵ = Porosity of the catalyst particle
τ = Tortuosity

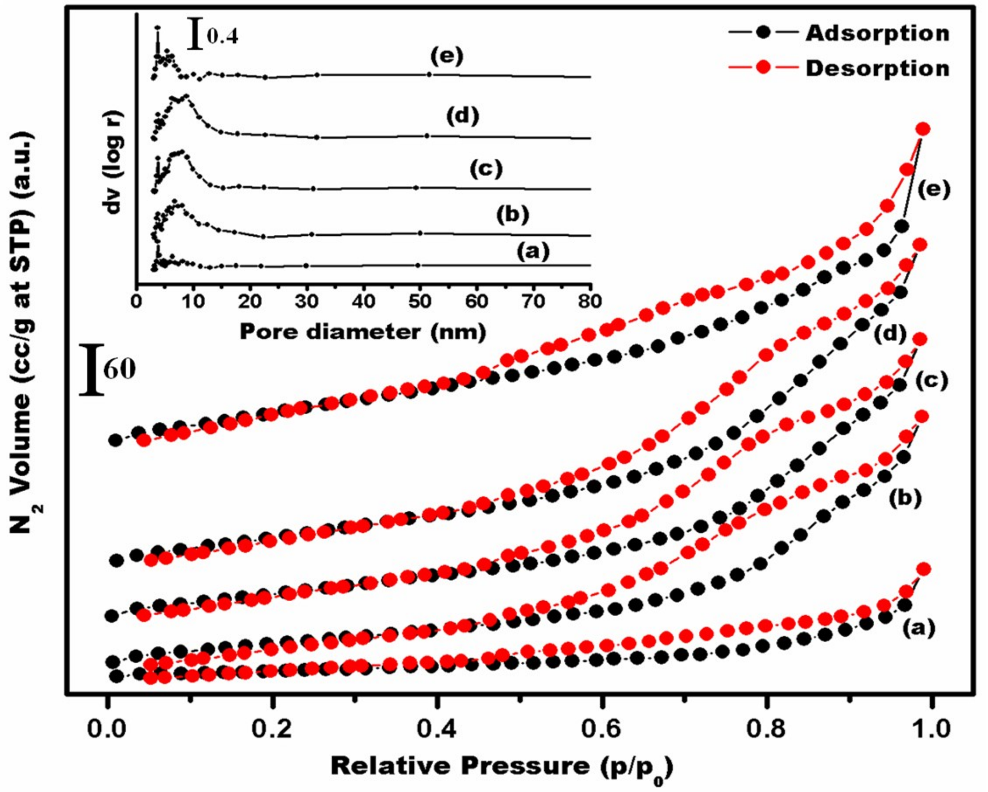

Fig. S1 Adsorption/desorption isotherms and pore size distribution of the supports: (a) CeO_2, (b) Bi(2 mol%)-CeO_2, (c) Bi(4 mol%)-CeO_2, (d) Bi(6 mol%)-CeO_2, and (e) Bi(8 mol%)-CeO_2.

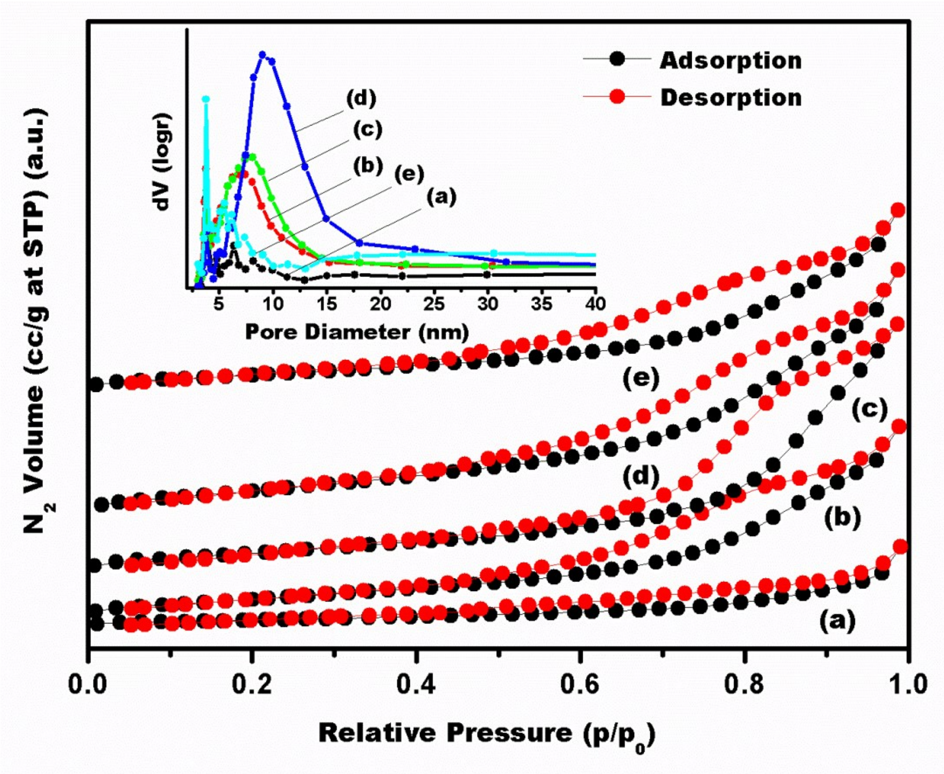

Fig. S2 Adsorption/desorption isotherms and pore size distribution for 3.5 wt% of (a) Au/CeO$_2$, (b) Au/Bi(2 mol%)-CeO$_2$, (c) Au/Bi(4 mol%)-CeO$_2$, (d) Au/Bi(6 mol%)-CeO$_2$, and (e) Au/Bi(8 mol%)-CeO$_2$.

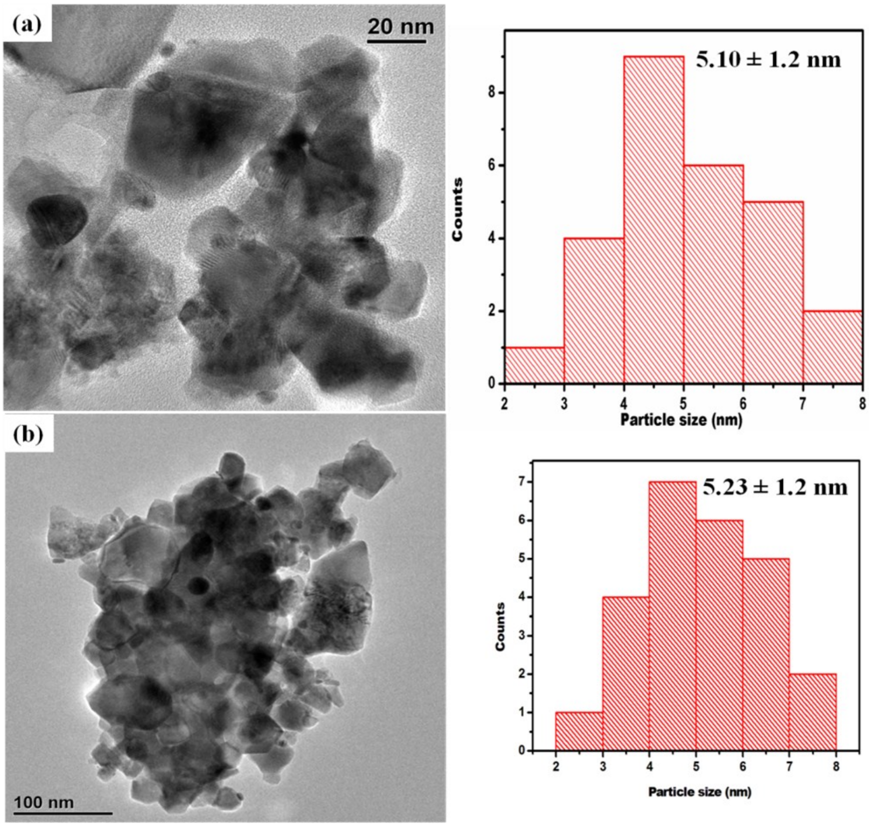

Fig. S3 HRTEM images of 3.5 wt% nominal gold loading on (a) Au/Bi(2 mol%)-CeO$_2$ and (b) Au/CeO$_2$.

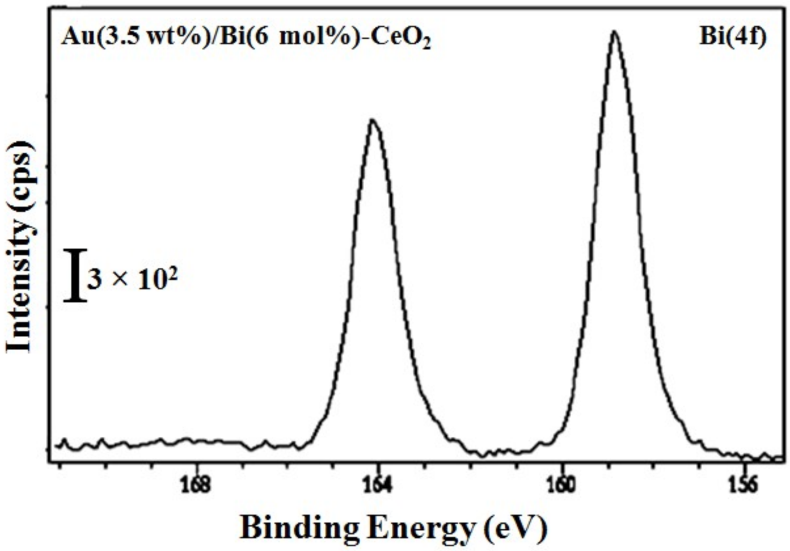

Fig. S4 Bi(4f) core level XPS spectra of Au(3.5 wt%)/Bi(6 mol%)-CeO_2 catalyst.

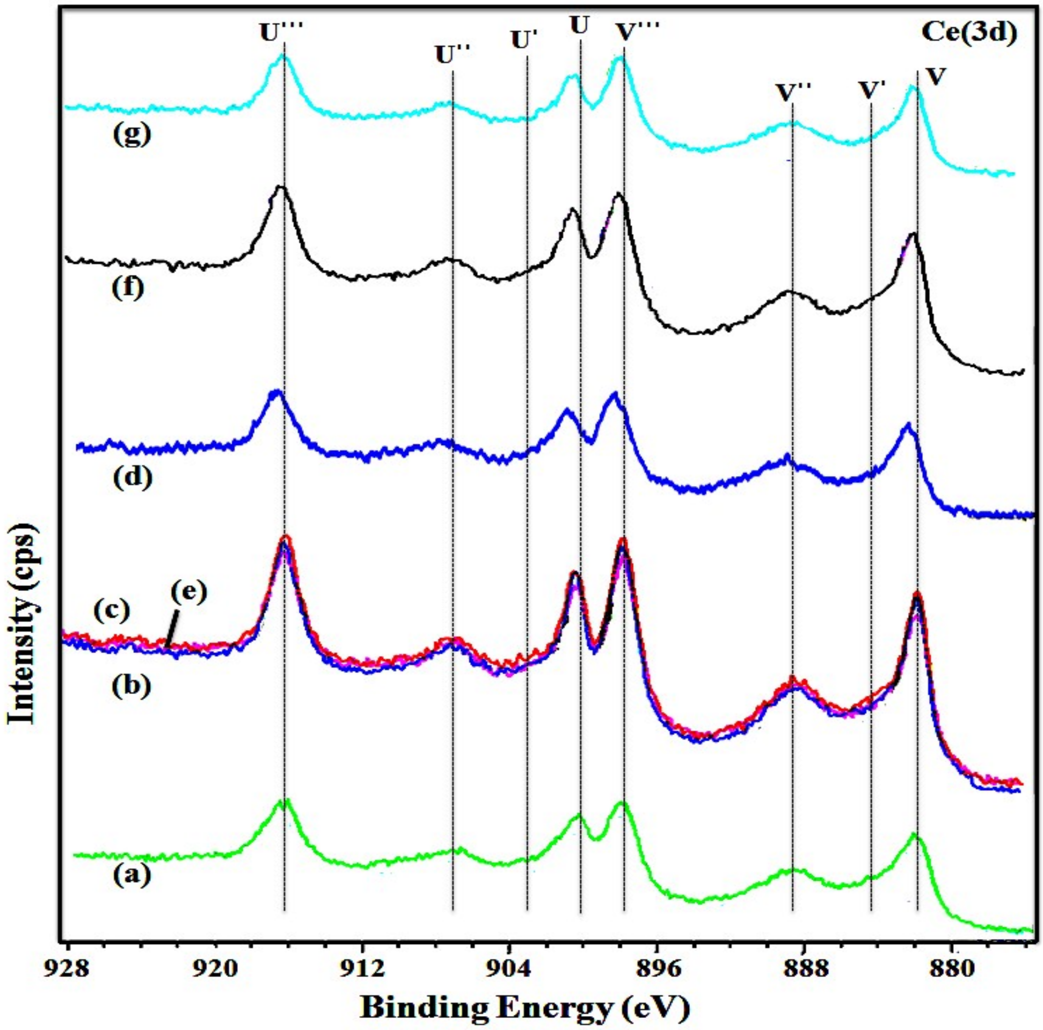

Fig. S5 Ce(3d) core level XPS spectra of (a) CeO_2, (b) Bi(2 mol%)-CeO_2, (c) Bi(4 mol%)-CeO_2, (d) Bi(6 mol%)-CeO_2, (e) Bi(8 mol%)-CeO_2, (f) Au(3.5wt%)/CeO_2, and (g) Au(3.5wt%)/Bi(6 mol%)-CeO_2.

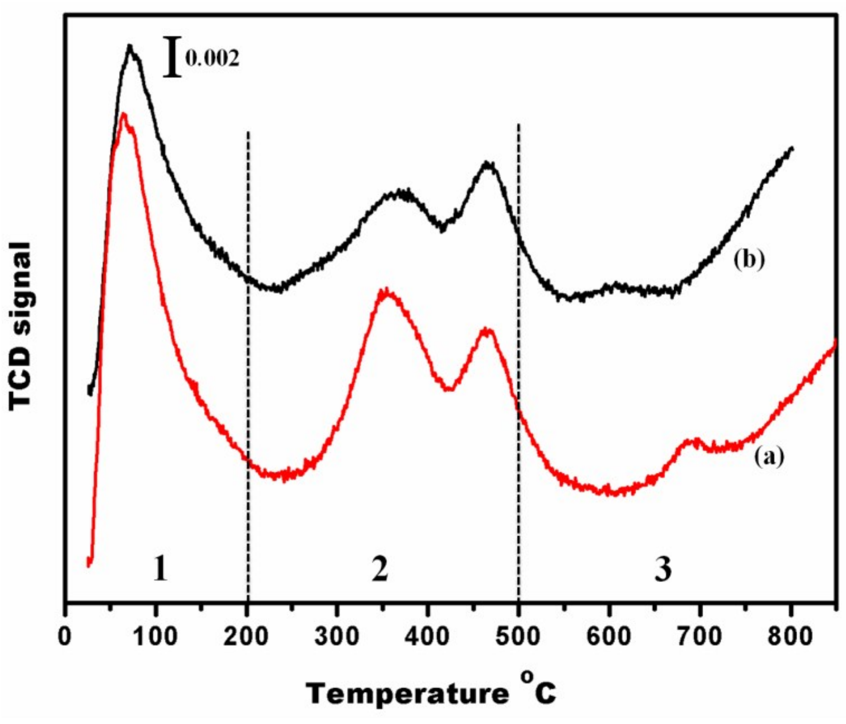

Fig. S6 CO_2-TPD traces of (a) Au(3.5 wt%)/CeO_2 and (a) Au(3.5 wt%)/Bi(4 mol%)-CeO_2 catalysts. Here regions 1, 2, and 3 represent weak, medium, and strong basic sites respectively.

Table S7 Quantitative analysis of CO_2-TPD of the following catalysts.

Sample	Volume of CO_2 (cm^3 g^{-1} STP)
Bi(4 mol%)-CeO_2	1.285
Bi(6 mol%)-CeO_2	1.150
Bi(8 mol%)-CeO_2	0.683
Au(3.5 wt%)/CeO_2	0.893
Au(3.5 wt%)/Bi(4 mol%)-CeO_2	1.300
Au(3.5 wt%)/Bi(6 mol%)-CeO_2	1.726

Table S8 Summary of BET surface area and porosity results of doped Au/Bi(6 mol%)-CeO_2 with different gold loading.

Sample	Surface area (m^2g^{-1})	Pore size (nm)	Pore volume (cc g^{-1})
1 wt% Au/Bi-CeO_2	18.53	10.80	0.050
2.33 wt% Au/Bi-CeO_2	16.90	11.21	0.047
3.5 wt% Au/Bi-CeO_2	15.53	12.98	0.050
4 wt% Au/Bi-CeO_2	15.22	10.98	0.044

Table S9 Aerobic oxidation of benzyl alcohol to benzaldehyde (selectivity >99% in each case) over Au(3.5 wt%)/Bi(6 mol %)-CeO_2 catalyst at different temperature.

Temperature (°C)	Conversion (%)
60	12.4
90	39.1
120	63.1
130	42.8

Reaction condition: Toluene solvent, 4 cm^3; alcohol, 4 mmol; catalyst, 0.1 g; O_2, 50 std cm^3 min^{-1}; temperature 110 °C; reaction time, 3 h; ambient pressure; dodecane used as an internal standard.

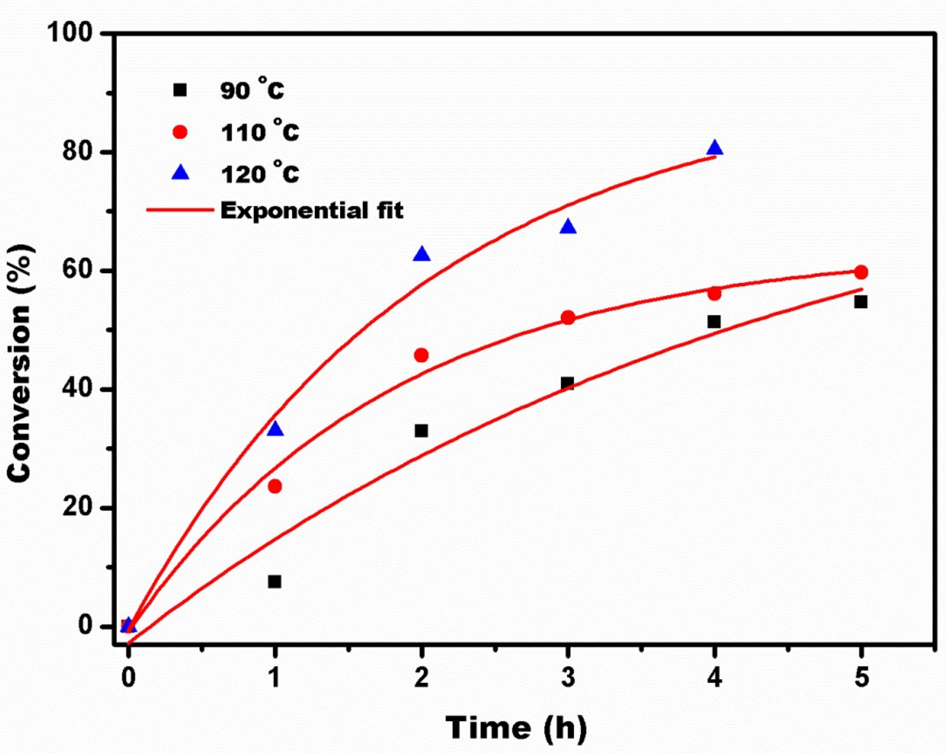

Fig. S10 Initial conversion rates dependence on reaction temperature with Au(3.5 wt%)/Bi(6 mol %)-CeO_2. Initial rates derived from transient conversion rates extrapolated to residence time zero.

Oxygen solubility calculation: Oxygen solubility in methanol, ethanol, water and toluene used as solvent for the benzyl alcohol oxidation reaction were calculated from the experimental data provided in literature.[1-4] We have calculated vapour pressure (bar) of the solvent at desired temperature by using $\log_{10} P = A - \{\frac{B}{T + C}\}$ equation, where A, B, C are Antoine equation parameters and T is temperature (K). A plot was drawn with oxygen concentration (mol/m^3) vs partial pressure of oxygen (MPa). With the help of slope and intercept of the plot, we can calculate the solubility of the oxygen in that particular solvent at that specific temperature. In case of solvent free conditions, we calculate solubility of oxygen in benzyl alcohol by Hansen's solubility parameters (HSPs). The HSPs of benzyl alcohol oxygen were taken from Hansen's 1971 parameters listed in Handbook of Solubility Parameters[4], where δd= 6.7 MPa$^{1/2}$, δp = 0.0 MPa$^{1/2}$, δh = 3.8 MPa$^{1/2}$, and δt= 7.7 MPa$^{1/2}$. The HSPs of oxygen; oxygen were taken from literature.[4] Further the distance between the HSPs of two substances in the three-dimensional (3D)-HSP diagram can be calculated as formula mentioned below.[5]

$$R_a = [4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2]^{1/2}$$

The relationship between Ra and logxG for oxygen is taken as equation below[6]

$$\log x_G = (-8.89 \times 10^{-2})R_a - 1.10$$

Further with the help Henry low, we calculate the concentration of oxygen at desired pressure.

Reference

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