Supporting information

Superior catalytic performance of $Ce_{1-x}Bi_xO_{2-\delta}$ solid solution and $Au/Ce_{1-x}Bi_xO_{2-\delta}$ for 5-hydroxymethylfurfural conversion in alkaline aqueous solution

Zhenzhen Miao,[a,b] Yibo Zhang,*[a,c] Xiqiang Pan,[d] Tianxiao Wu,[a] Bin Zhang,[a] Jingwei Li,[a,b] Ting Yi,[a,b] Zhengdong Zhang,[a] and Xiangguang Yang*[a,c]

[a] *State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, China. E-mail: xgyang@ciac.ac.cn, yibozhang@ciac.ac.cn; Tel: 86-431-8526-2228*
[b] *University of Chinese Academy of Sciences, Beijing, 100039,China.*
[c] *Laboratory of Green Chemistry and Process, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, China.*
[d] *The Northwest Research Institute of Chemistry Industry, Xi'an, Shaanxi, 710061, China.*

Fig. S1 CeO_2, $Ce_{0.95}Bi_{0.05}O_{2-\delta}$, $Ce_{0.9}Bi_{0.1}O_{2-\delta}$, $Ce_{0.8}Bi_{0.2}O_{2-\delta}$ and $Ce_{0.5}Bi_{0.5}O_{2-\delta}$ powder from left to right.

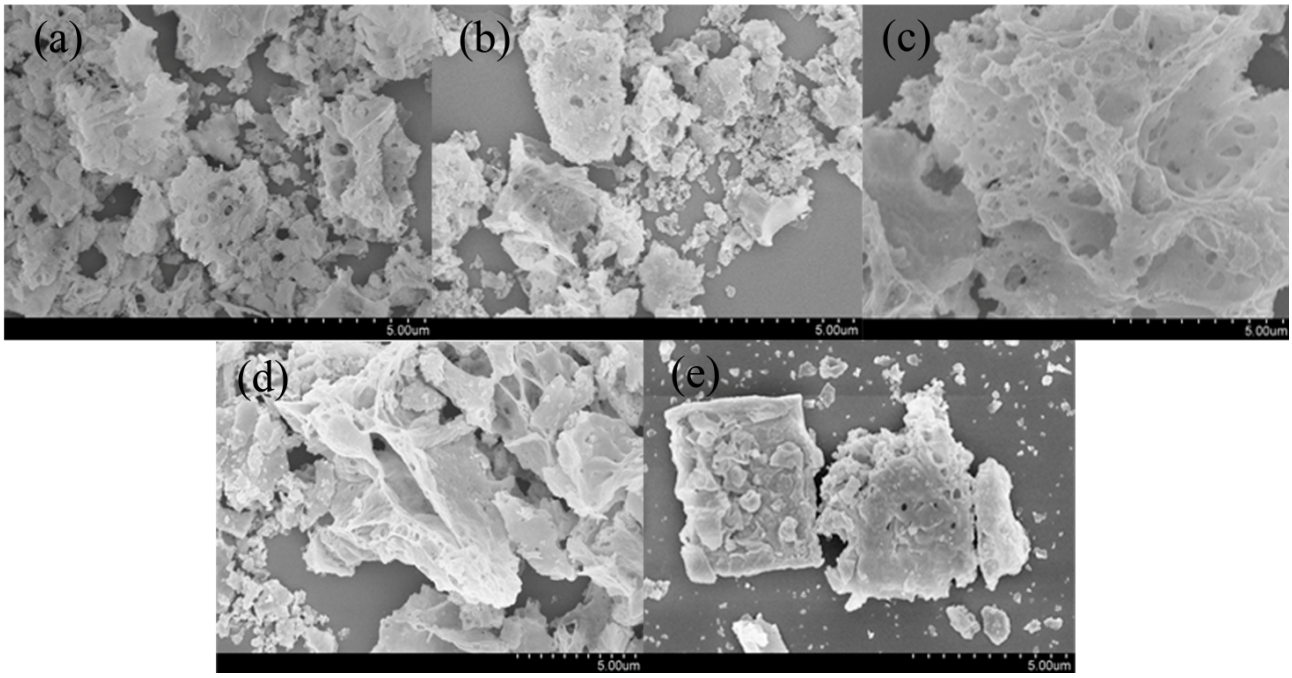

Fig. S2 SEM images of (a) CeO_2, (b) $Ce_{0.95}Bi_{0.05}O_{2-\delta}$, (c) $Ce_{0.9}Bi_{0.1}O_{2-\delta}$, (d) $Ce_{0.8}Bi_{0.2}O_{2-\delta}$ and (e) $Ce_{0.5}Bi_{0.5}O_{2-\delta}$.

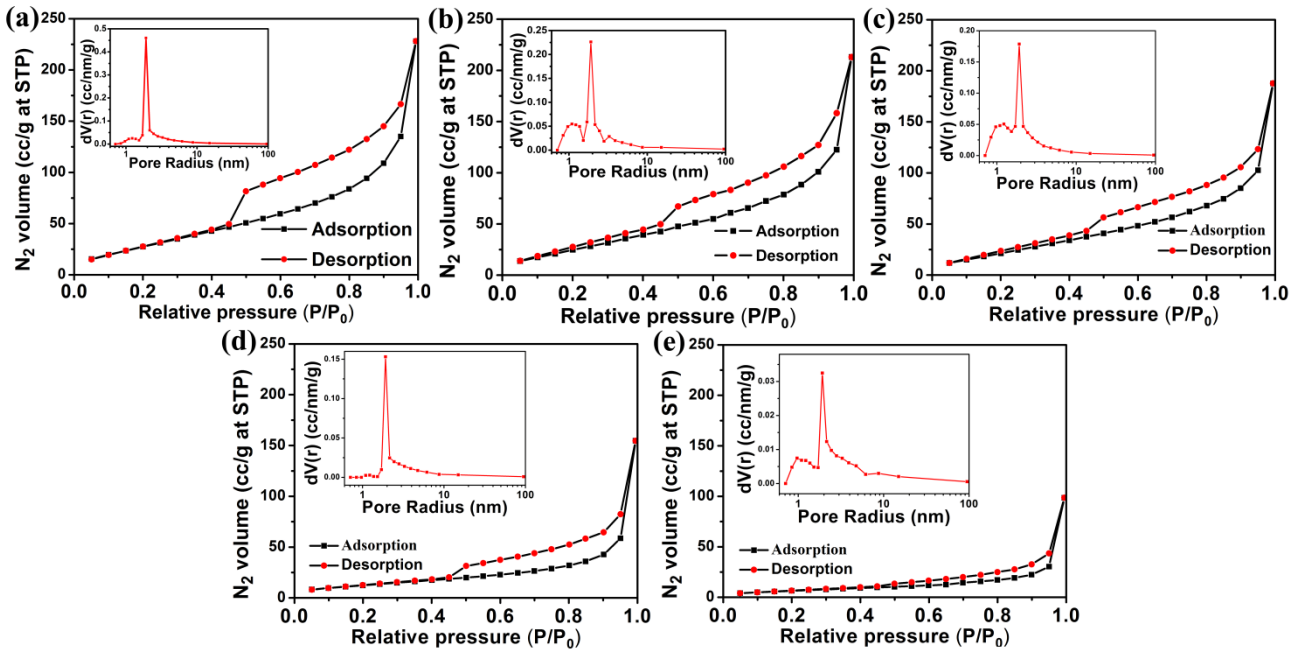

Fig. S3 N_2 adsorption isotherms and pore size distribution curves of (a) CeO_2, (b) $Ce_{0.95}Bi_{0.05}O_{2-\delta}$, (c) $Ce_{0.9}Bi_{0.1}O_{2-\delta}$, (d) $Ce_{0.8}Bi_{0.2}O_{2-\delta}$ and (e) $Ce_{0.5}Bi_{0.5}O_{2-\delta}$.

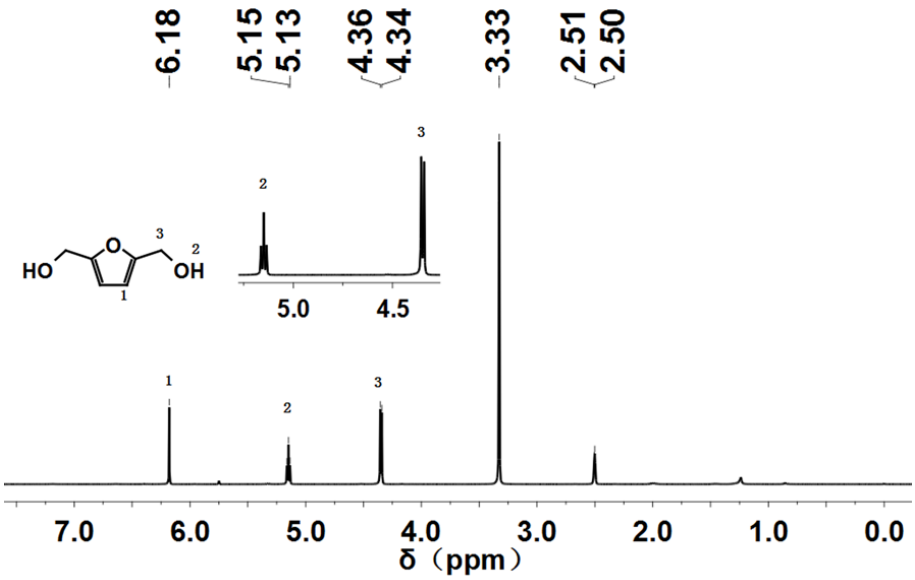

Fig. S4 ^1H NMR spectra (DMSO, 300 MHz): δ 6.18, 5.15, 4.35 belong to 2,5-bishydroxymethylfuran (BHMF), δ 3.33, 2.50 belong to DMSO solvent. (After reacted for 1 h with the presence of $Ce_{0.875}Bi_{0.125}O_{2-\delta}$, the resulted reaction solution was extracted by ethyl ether. The solid obtained after evaporating the ethyl ether was solved in deuterated DMSO and detected by ^1H NMR.)

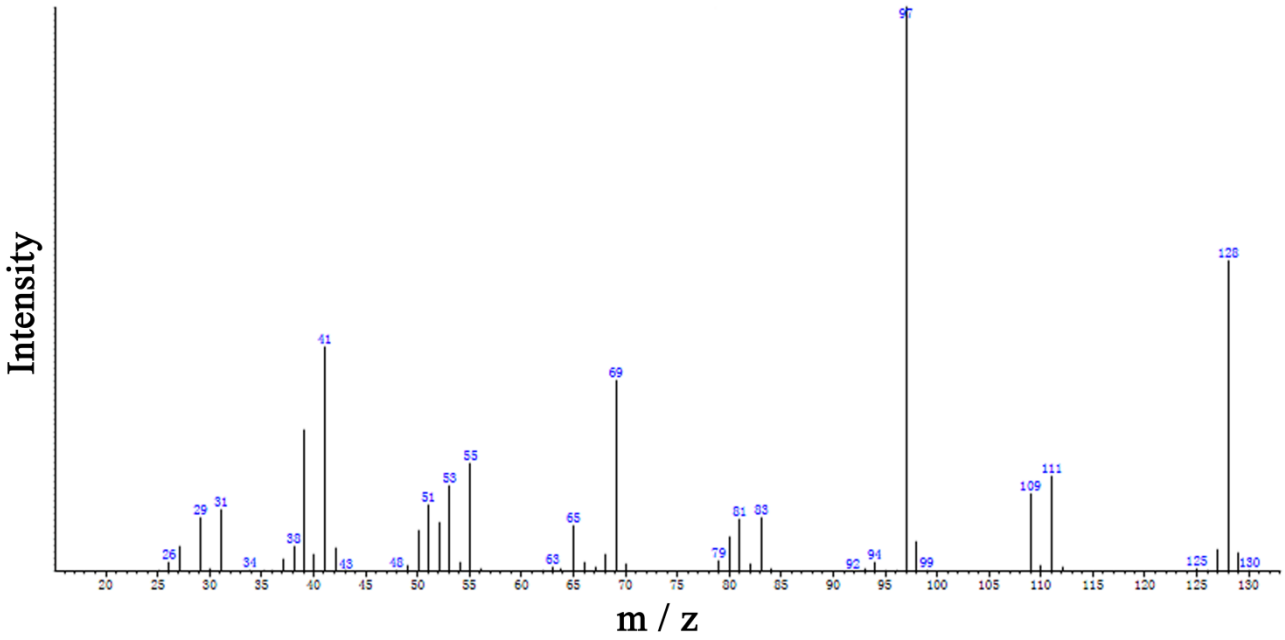

Fig. S5 Mass spectra of BHMF obtained from gas chromatography-quadrupole mass spectrometry (GC-qMS).

After extracting the resulted reaction solution by ethyl ether, BHMF was quantitative analyzed by a Shimadzu GCMS-QP2010 Plus gas chromatograph with a quadrupole mass spectrometric detector (Shimadzu, Kyoto, Japan). An Agilent WAX capillary column (60 m × 0.25 mm, 0.25 μm) and helium as carrier gas flowing at 1.0 ml/min were used for the separation. The GC injector port temperature was 250 °C. The oven temperature was programmed from 60 °C (3 min) to 250 °C at 10 °C /min, and then held at 250 °C for 30 min. The total analysis time was 52 min. The mass detector operated in full-scan mode with the mass/charge ratio ranging from m/z 20 to 800.

Table S1 Screening with other M-doped $Ce_{0.9}M_{0.1}O_{2-\delta}$

Entry	Sample	HMF Conversion (%)	Y_{FDCA}[b] (%)	Y_{HFCA}[b] (%)
1	$Ce_{0.9}Y_{0.1}O_{2-\delta}$	93	2	13
2	$Ce_{0.9}La_{0.1}O_{2-\delta}$	93	2	15
3	$Ce_{0.9}Mn_{0.1}O_{2-\delta}$	91	-	7
4	$Ce_{0.9}Fe_{0.1}O_{2-\delta}$	90	2	10

[a] General conditions: 0.15 M HMF solution in 0.6 M NaOH (6 ml), 0.1 g catalyst, 65 °C, 1.0 MPa O_2. [b] Yield determined by HPLC after reacted for 1 h.

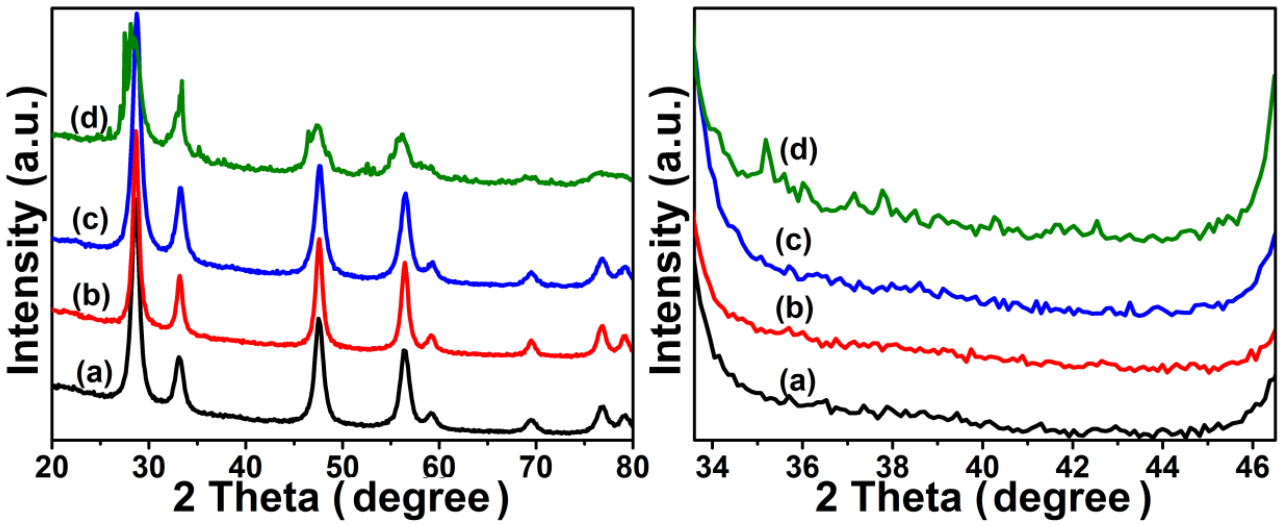

Fig. S6 XRD patterns of samples after reacted for 1h, (a) Au/CeO_2, (b) $Au/Ce_{0.9}Bi_{0.1}O_{2-\delta}$, (c) $Au/Ce_{0.8}Bi_{0.2}O_{2-\delta}$ and (d) $Au/Ce_{0.5}Bi_{0.5}O_{2-\delta}$. Right: partial enlarged view of the left.

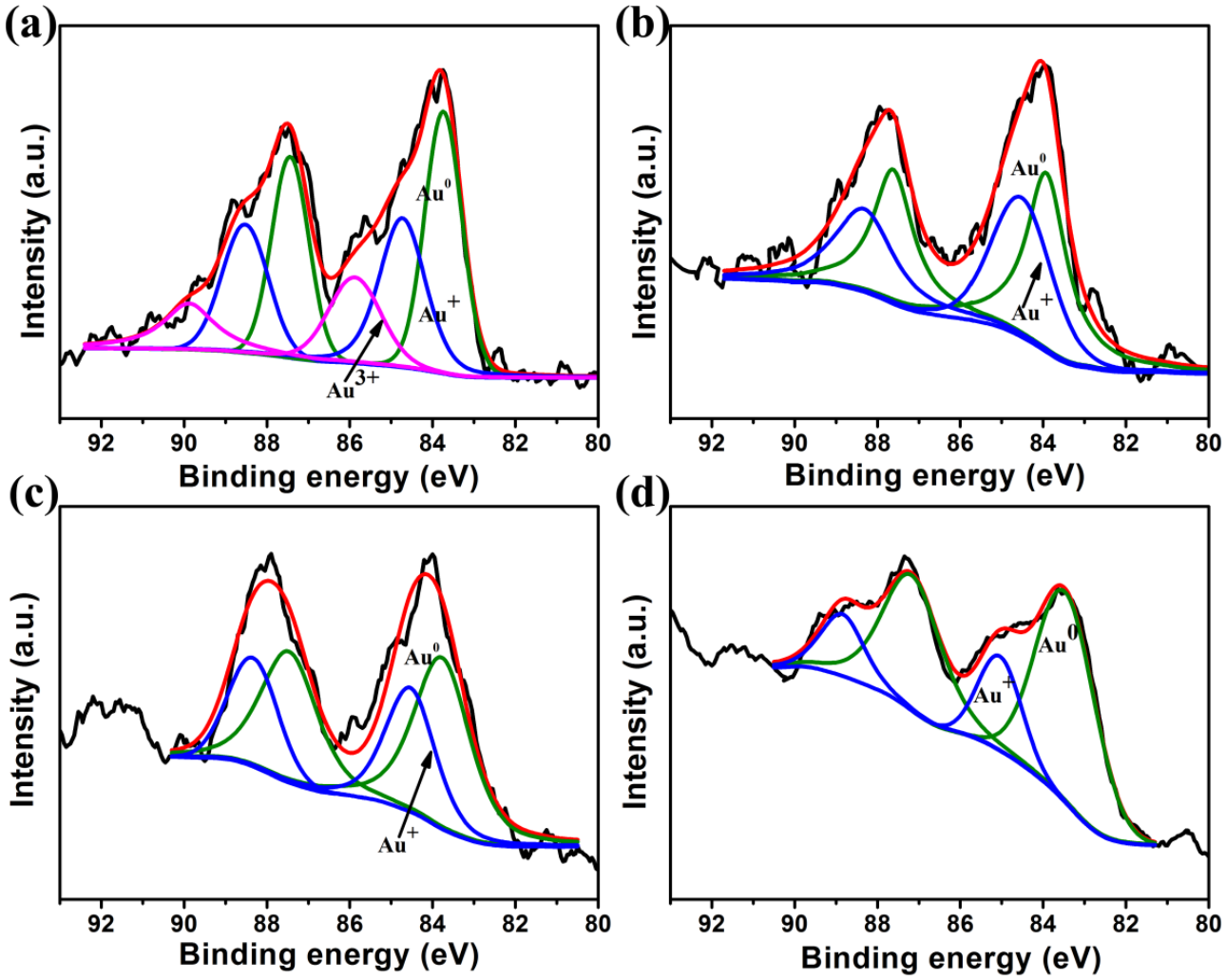

Fig. S7 XPS Au 4f peak of (a) Au/CeO_2, (b) $Au/Ce_{0.9}Bi_{0.1}O_{2-\delta}$, (c) $Au/Ce_{0.8}Bi_{0.2}O_{2-\delta}$ and (d) $Au/Ce_{0.5}Bi_{0.5}O_{2-\delta}$ after reacted for 1h.

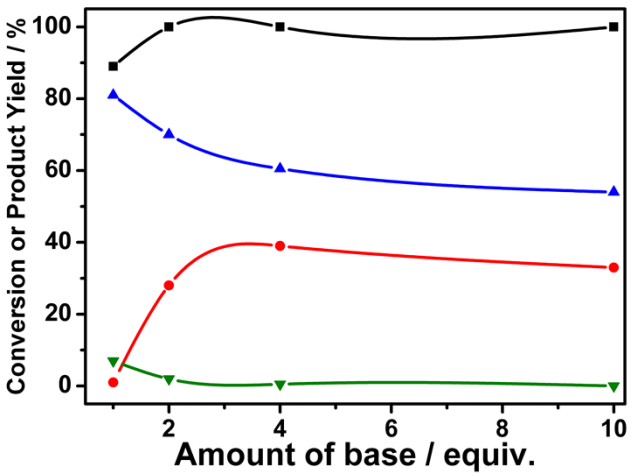

Fig. S8 HMF conversion and product yields as a function of amount of base in the oxidation of HMF in aqueous solution over $Au/Ce_{0.9}Bi_{0.1}O_{2-\delta}$ catalyst (Au : HMF = 3.33×10^{-3} mol/mol, 1.0 MPa O_2, 65 °C, 1 h; HMF: ■, FDCA: ●, HFCA: ▲, FFCA: ▼).

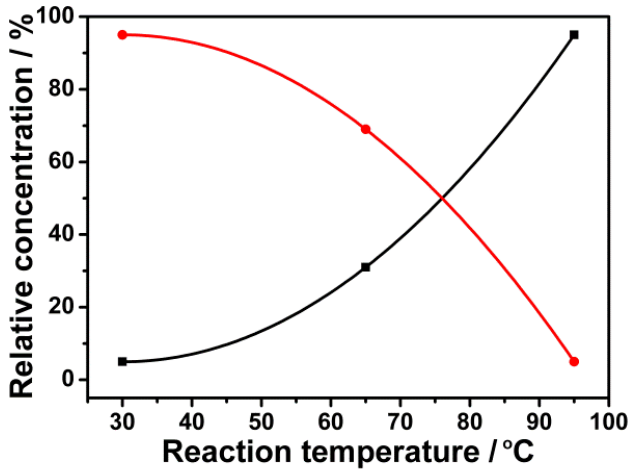

Fig. S9 Product yields as a function of reaction temperature in the oxidation of HMF in aqueous solution over $Au/Ce_{0.9}Bi_{0.1}O_{2-\delta}$ catalyst (Au : HMF = 6.67×10^{-3} mol/mol, 4 equiv. NaOH, 1.0 MPa O_2, 0.5 h; FDCA: ■, HFCA: ●).

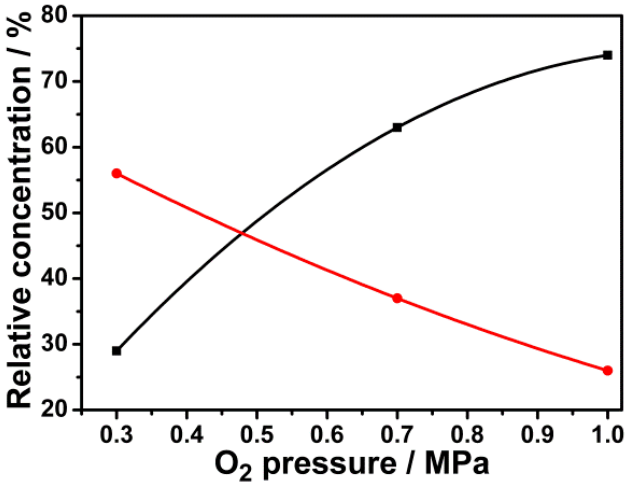

Fig. S10 Product yields as a function of O_2 pressure in the oxidation of HMF in aqueous solution over $Au/Ce_{0.9}Bi_{0.1}O_{2-\delta}$ catalyst (Au : HMF = 6.67×10^{-3} mol/mol, 4 equiv. NaOH, 65 °C, 1 h; FDCA: ■, HFCA: ●).

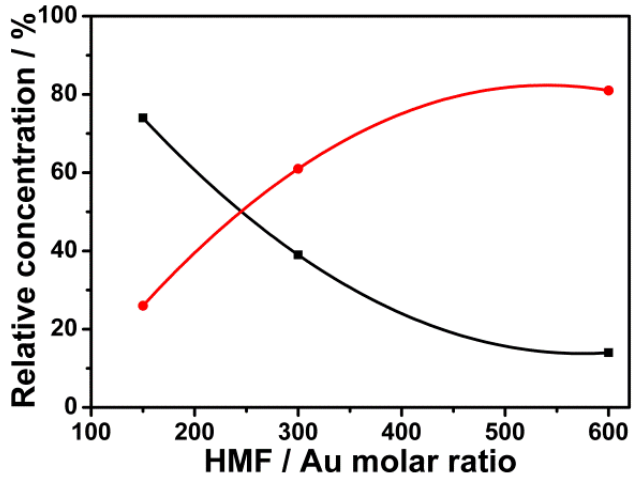

Fig. S11 Product yields as a function of the relative amounts of HMF and Au in the oxidation of HMF in aqueous solution over $Au/Ce_{0.9}Bi_{0.1}O_{2-\delta}$ catalyst (4 equiv. NaOH, 1.0 MPa O_2, 65 °C, 1 h; FDCA: ■, HFCA: ●).