Supporting Information

Aerobic Oxidation of 5-Hydroxymethylfurfural to high yield 5-hydroxymethyl-2-furancarboxylic acid by polyvinylpyrrolidone -capped Ag Nanoparticle Catalysts

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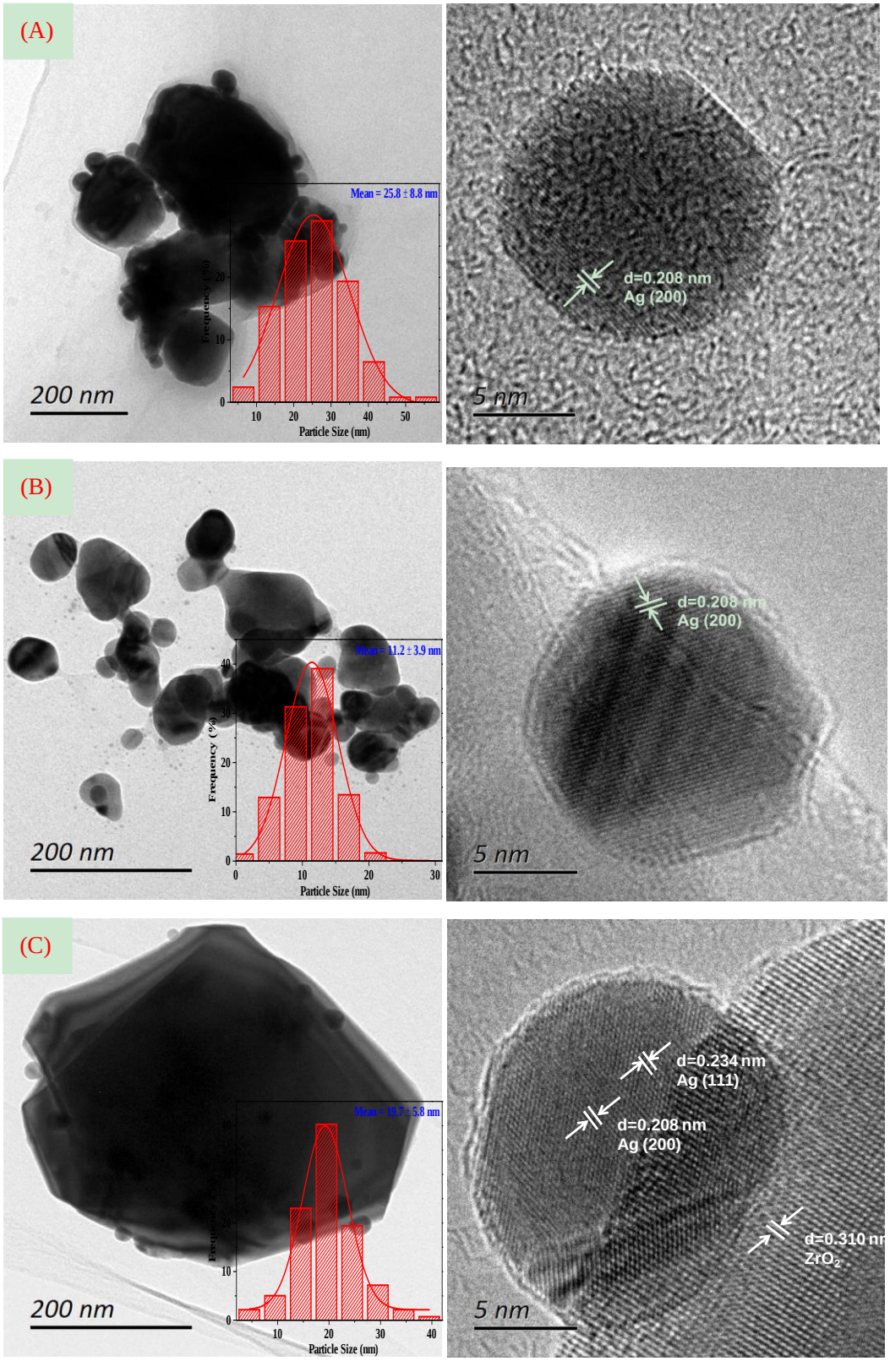
Characterization of the catalysts.

HRTEM images combined with their size distribution for Ag nanoparticle catalysts



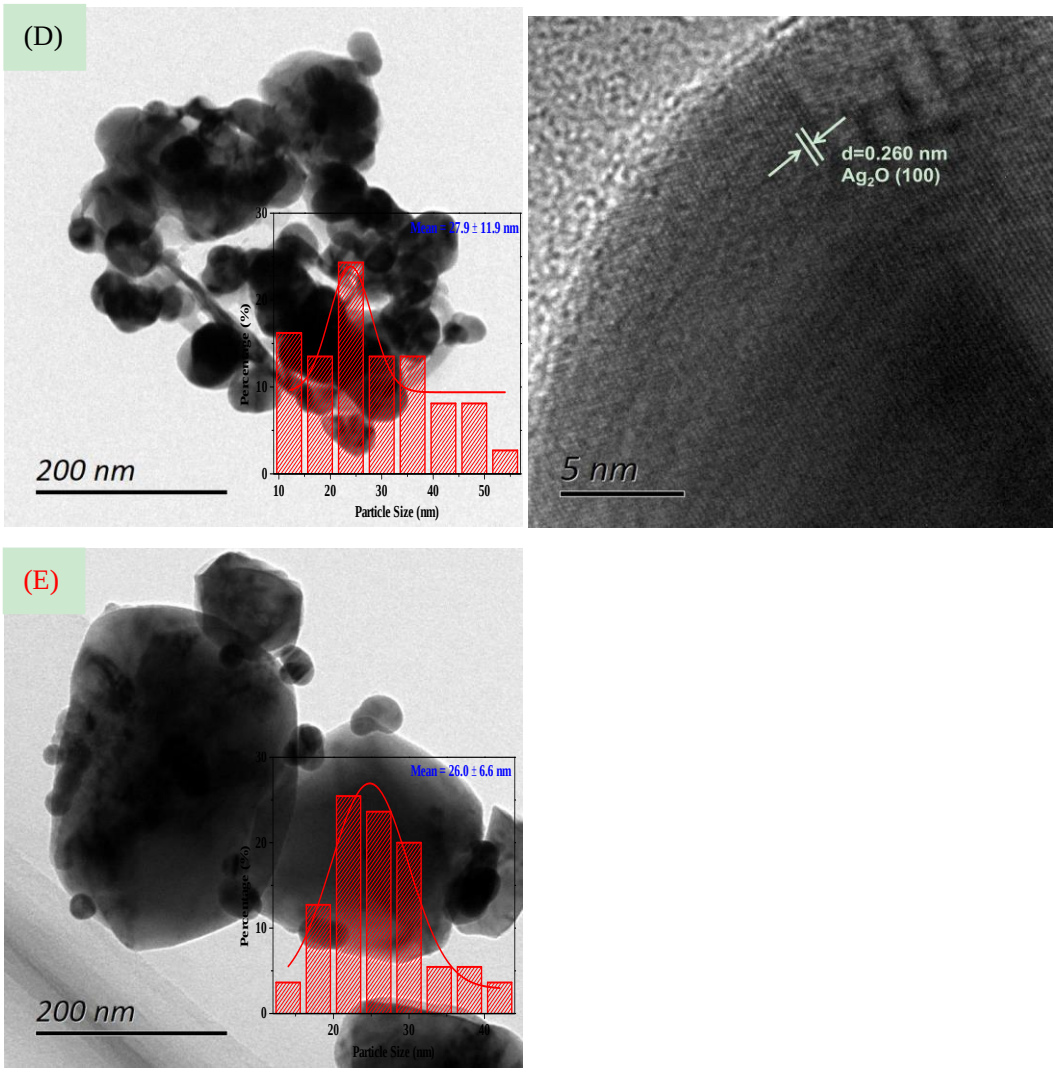


Fig. S1 HRTEM images and particle sizes distributions: (A) 2.5%Ag-PVP/ZrO_2(1:0.5); (B) 2.5%Ag-PVP/ZrO_2(1:2); (C) 1%Ag-PVP/ZrO_2(1:1); (D)5%Ag-PVP/ZrO_2 (1:1); (E) The recovered catalyst.

XPS analysis

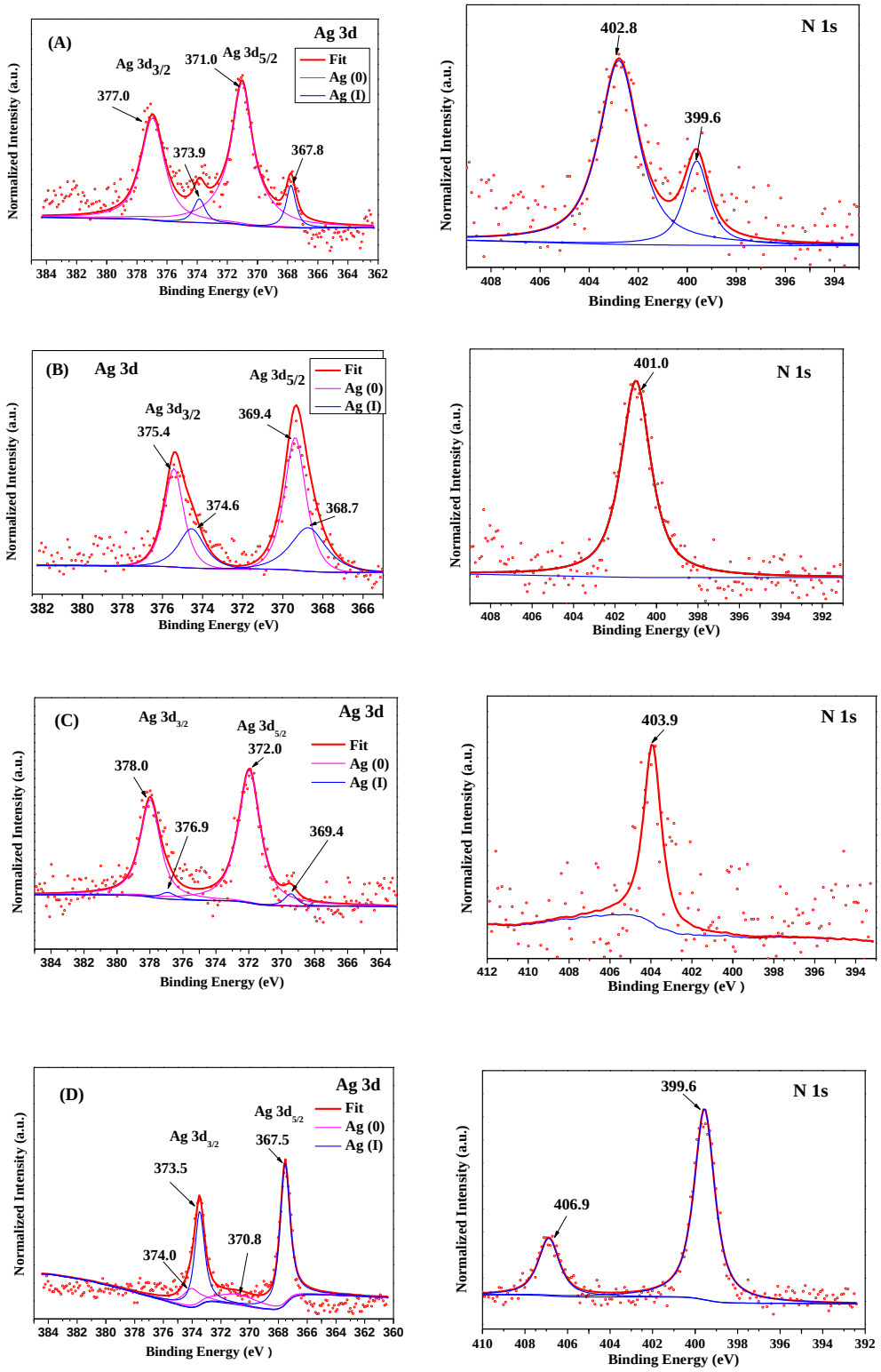
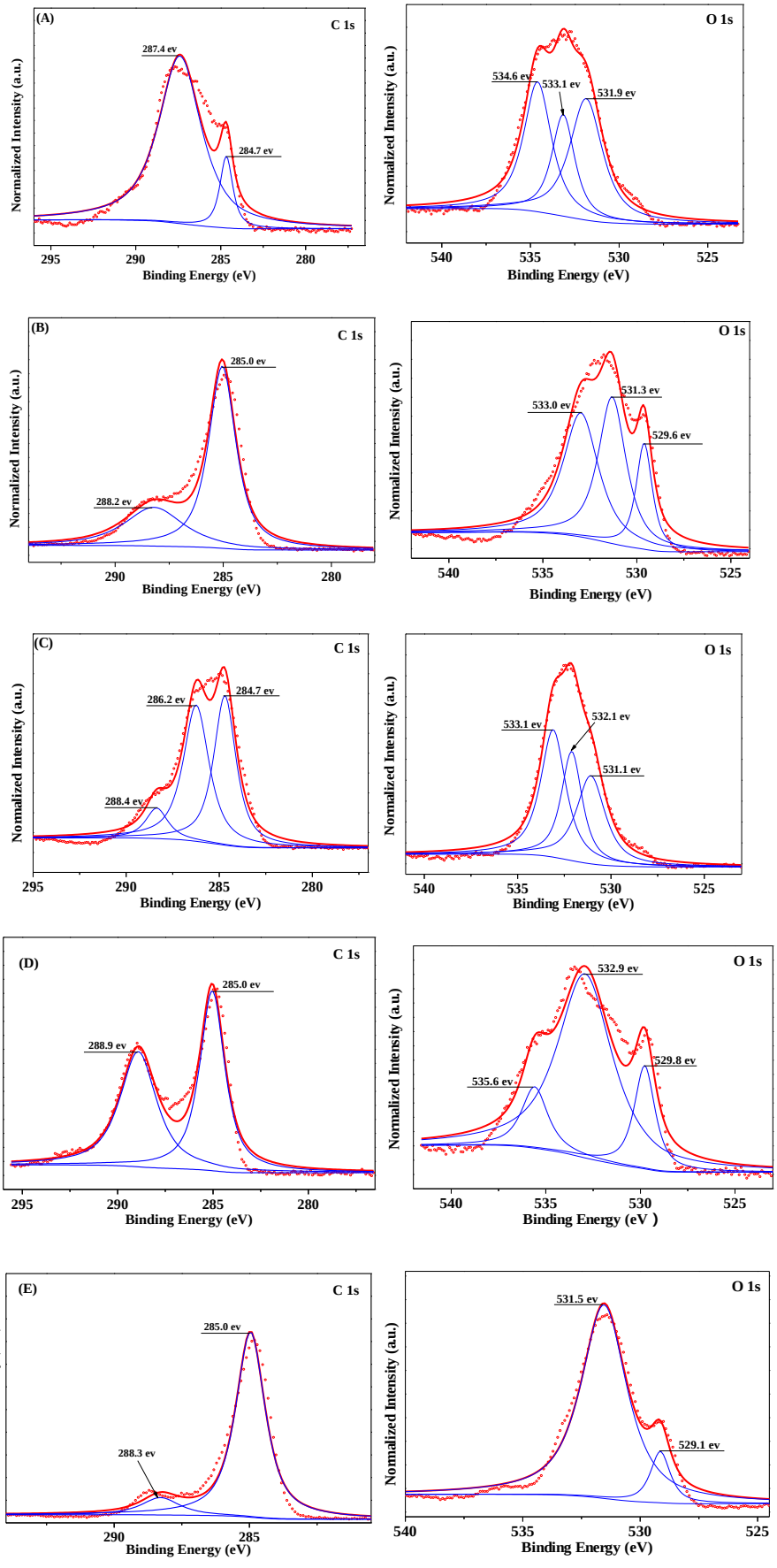


Fig. S2 X-ray photoelectron spectra for Ag (3d) and N (1s) of the catalysts: (A) 2.5%Ag-PVP/ZrO_2 (1:0.5); (B) 2.5%Ag-PVP/ZrO_2 (1:2); (C) 1%Ag-PVP/ZrO_2 (1:1); (D) 5%Ag-PVP/ZrO_2 (1:1).


(A)
C 1s
287.4 ev
284.7 ev
Normalized Intensity (a.u.)
295
290
285
280
Binding Energy (eV)
O 1s
534.6 ev
533.1 ev
531.9 ev
540
535
530
525
Binding Energy (eV)
(B)
C 1s
285.0 ev
288.2 ev
O 1s
531.3 ev
533.0 ev
529.6 ev
(C)
C 1s
286.2 ev
284.7 ev
288.4 ev
O 1s
533.1 ev
532.1 ev
531.1 ev
(D)
C 1s
285.0 ev
288.9 ev
O 1s
532.9 ev
529.8 ev
535.6 ev
Binding Energy (eV)
(E)
C 1s
285.0 ev
288.3 ev
O 1s
531.5 ev
529.1 ev

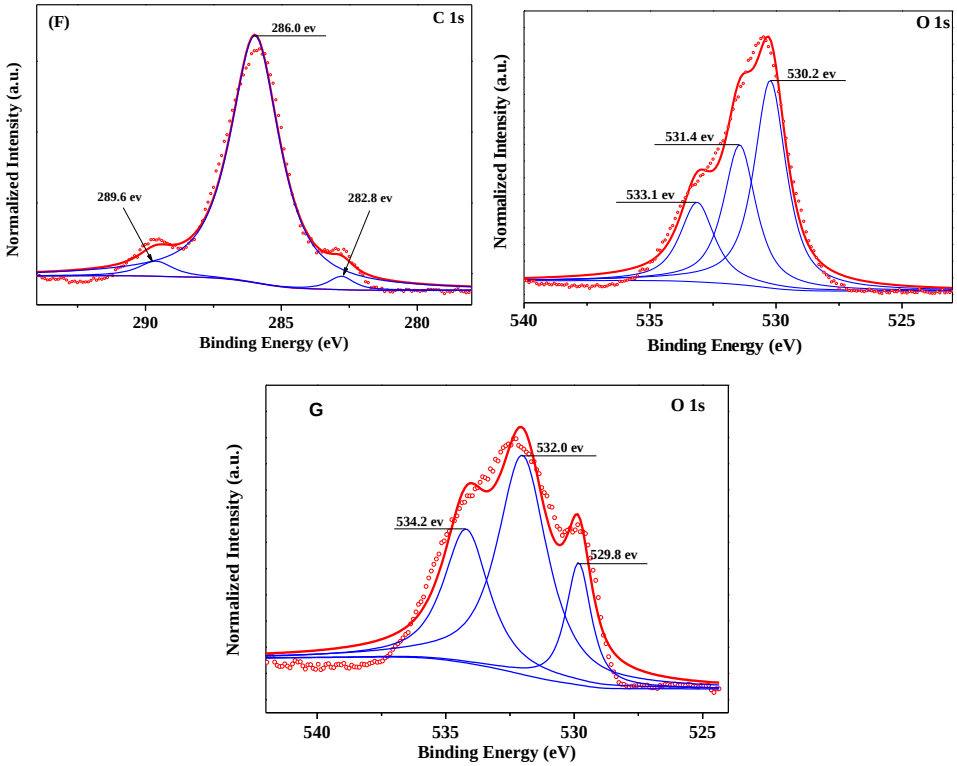


Fig. S3 X-ray photoelectron spectra for C 1s and O 1s of the catalysts: (A) 2.5%Ag-PVP/ZrO_2 (1:0.5); (B) 2.5%Ag-PVP/ZrO_2 (1:1); (C) 2.5%Ag-PVP/ZrO_2 (1:2); (D) 1%Ag-PVP/ZrO_2 (1:1); (E) 5%Ag-PVP/ZrO_2 (1:1); (F) 2.5%Ag-PVP/ZrO_2 (1:1)-II. (G) 2.5%Ag/ZrO_2;

Fig. S3 shows the C 1s XPS spectra contains two or three peaks of Ag-PVP/ZrO_2 catalysts. The peaks at 284.8, 286.0, and 287.6 eV are assigned to C-C/C=C, C-N/C-O and C=O[1], respectively. There are two peaks (C-C, C=O) for 2.5%Ag-PVP/ZrO_2 (1:0.5), 2.5%Ag-PVP/ZrO_2(1:1), 1%Ag-PVP/ZrO_2(1:1) , 2.5%Ag-PVP/ZrO_2 (1:2) and 5%Ag-PVP/ZrO_2(1:1) catalysts. In addition, a new peak around 288.5 eV are observed for some samples, which is typically ascribed to the O-C=O group. The presence of carboxyl groups, further demonstrates that some chemisorbed PVP molecules undergo breakage of the C-N bond and subsequent hydrolysis, which is in

consistence with N1s spectra.

The O 1s binding energy of C=O are located at 534.8 eV[2], but there are obvious shifts for Ag-PVP/ZrO_2 catalysts because the PVP molecules chemisorb with Ag NPs. The peak at 529.4 eV is ascribed to O-Ag, which evidently shifts to higher binding energy. It is so interesting that the peaks (~532.5 eV) of ZrO_2 shifts due to the strong Ag-ZrO_2 interaction.

FT-IR spectrum of the catalysts

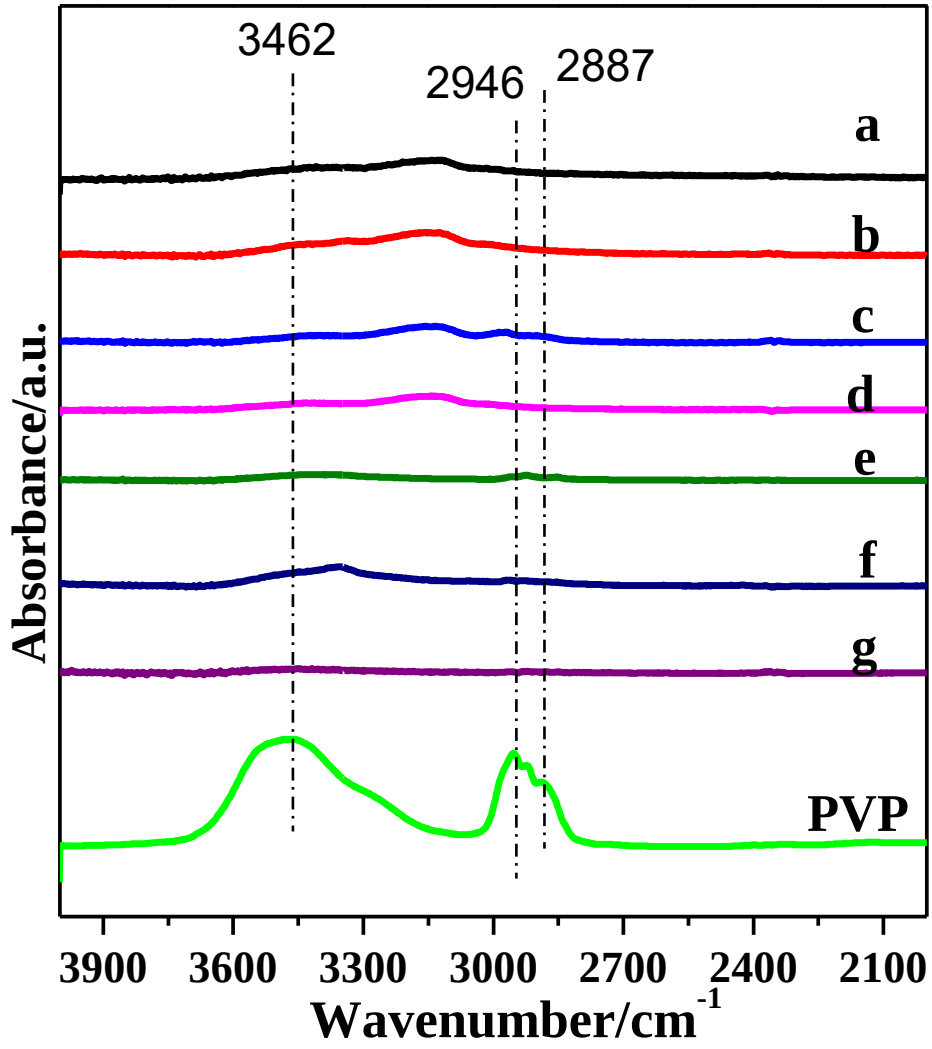


Fig. S4 FT-IR spectra of a. 2.5%Ag/ZrO_2; b. 2.5%Ag-PVP/ZrO_2 (1:0.5); c. 2.5%Ag-PVP/ZrO_2 (1:1); d. 2.5%Ag-PVP/ZrO_2 (1:2); e. 1%Ag-PVP/ZrO_2 (1:1); f. 5%Ag-PVP/ZrO_2 (1:1).g. 2.5%Ag-PVP/ZrO_2 (1:1)-*in situ*.

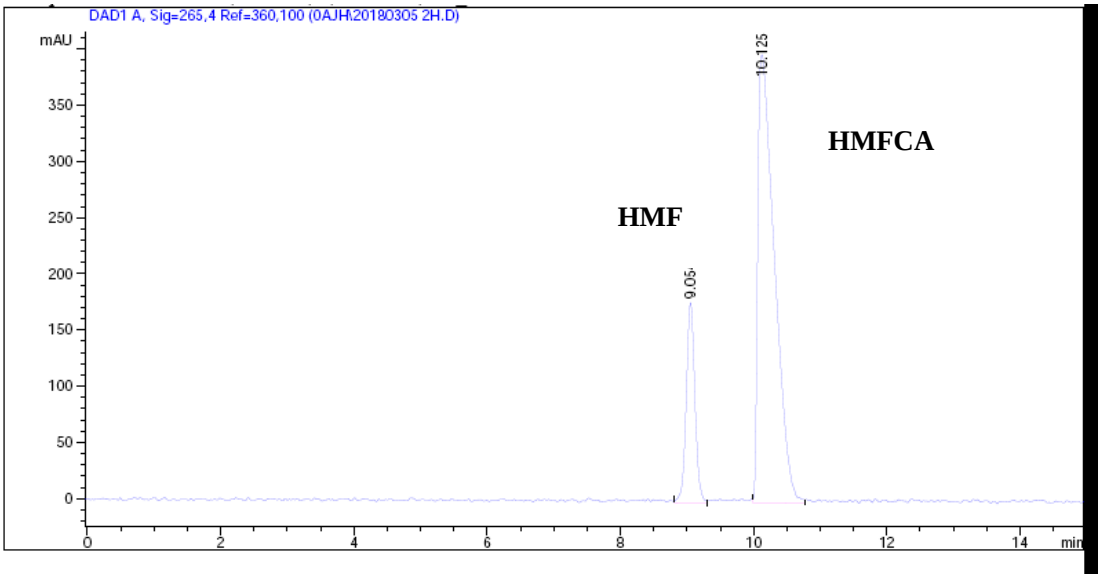


Fig. S5 HPLC result of aerobic oxidation of HMF over Ag/ZrO_2 catalyst for 2 h. Reaction condition: 0.2 g HMF, 0.126 g NaOH, 50 mL H_2O, 50 mg catalyst, 60 mL/min O_2, 20 ℃.

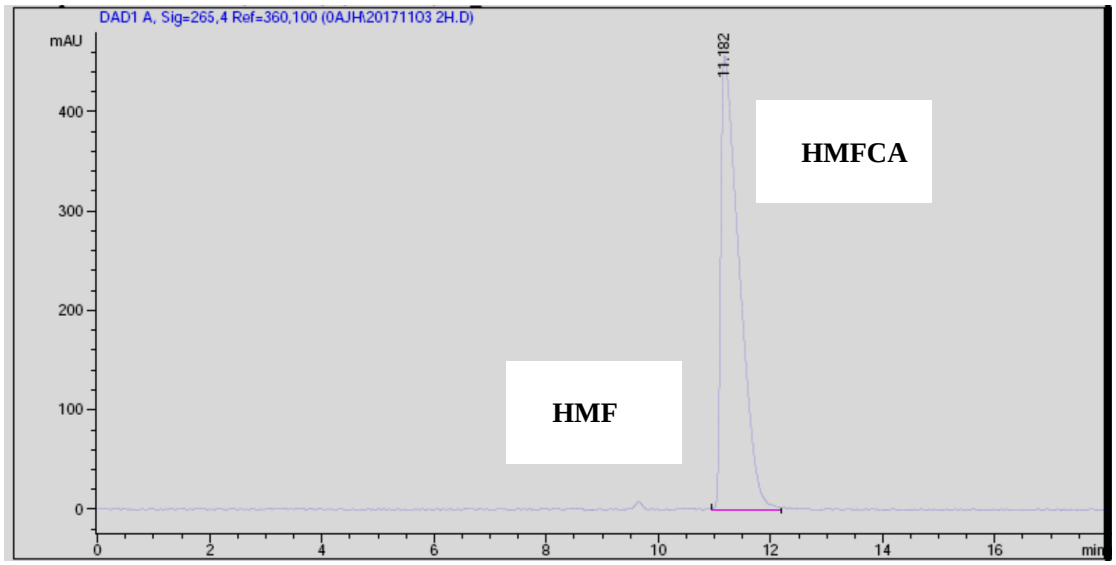


Fig. S6 HPLC result of aerobic oxidation of HMF over 2.5%Ag-PVP/ZrO_2 (1:1) catalyst for 2 h. Reaction condition: 0.2 g HMF, 0.126 g NaOH, 50 mL H_2O, 50 mg catalyst, 60 mL/min O_2, 20 ℃.

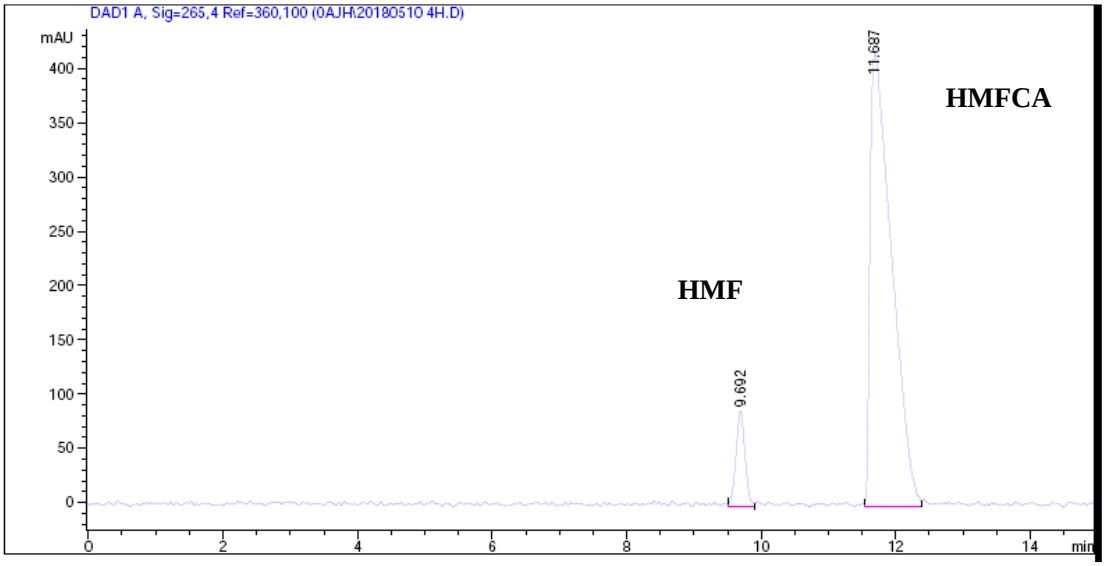


Fig. S7 HPLC result of aerobic oxidation of HMF over 2.5%Ag-PVP/ZrO_2 (1:1)-*in situ* catalyst for 2 h. Reaction condition: 0.2 g HMF, 0.126 g NaOH, 50 mL H_2O, 50 mg catalyst, 60 mL/min O_2, 20 ℃.

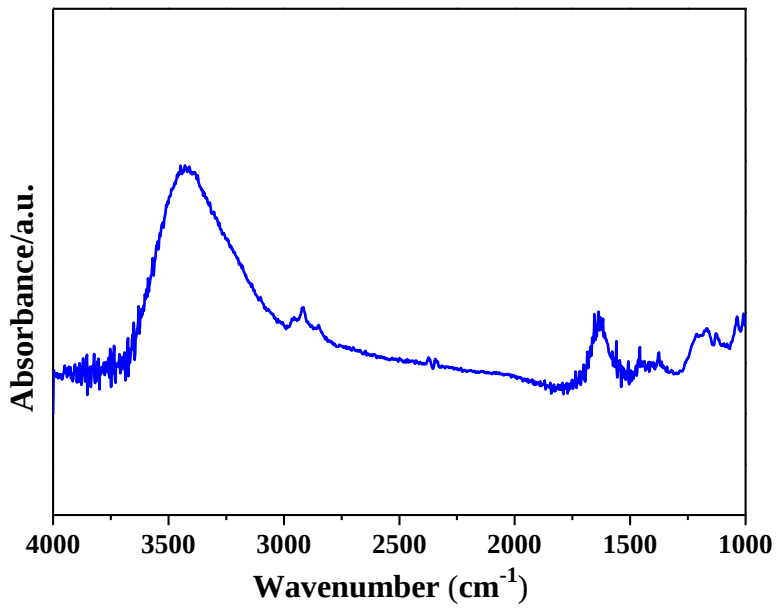


Fig. S8 FT-IR spectrum of the reused catalysts.

References

[1] G. Collins, M. Schmidt, G.P. McGlacken, C. O'Dwyer, J.D. Holmes, Stability, Oxidation, and Shape Evolution of PVP-Capped Pd Nanocrystals, The Journal of Physical Chemistry C, 118 (2014) 6522-6530.

[2] M.H. Patel, T.K. Chaudhuri, T. Shripathi, U. Deshpande, V.K. Patel, Influence of Pb+2-Thiourea complex concentration on the structural, optical, thermal and electrical properties of PbS/PVP-PVA nanocomposite films, Journal of Polymer Research, 25 (2017).