Effect of Capping Ligands for the Synthesis of Gold Nanoparticles and on the Catalytic Performance for the Oxidation of 5-Hydroxymethyl-2-furfural

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Supporting Information

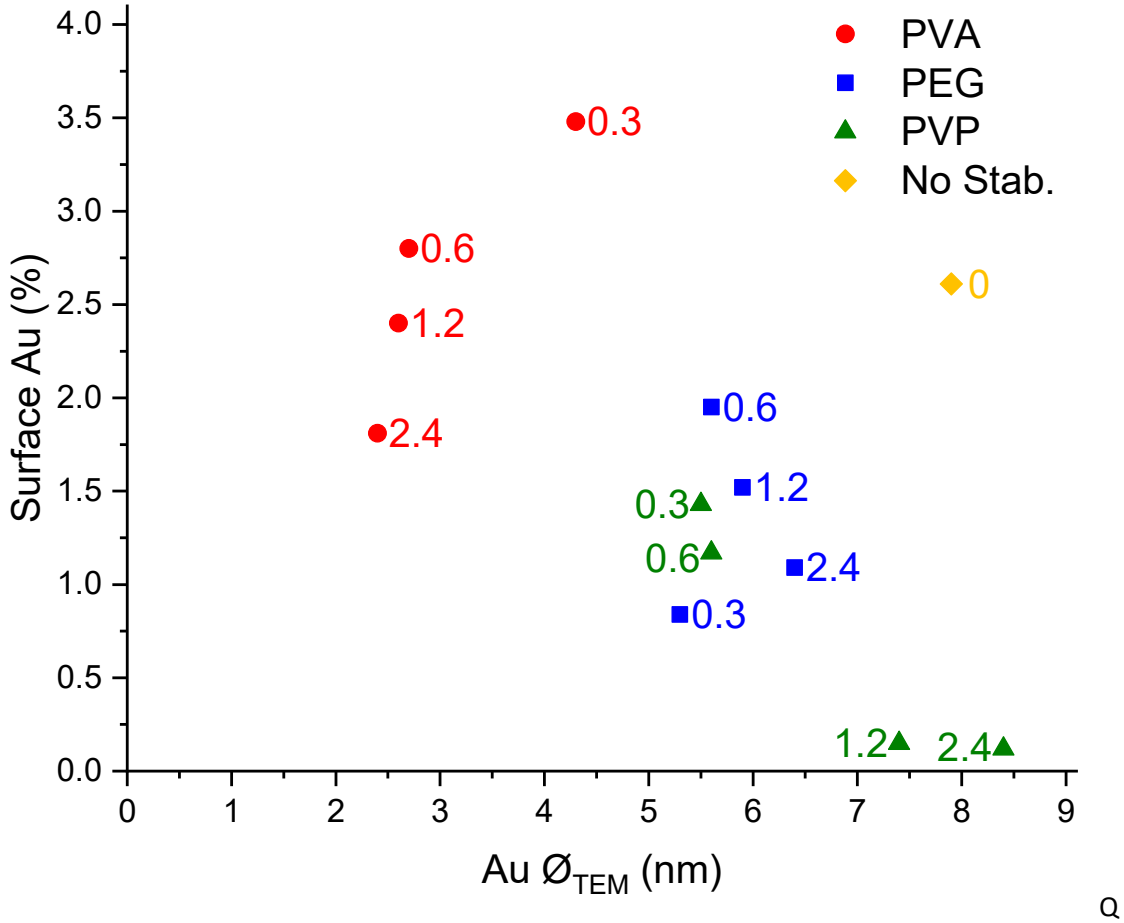

Figure S1. Correlation between mean particle size measured by TEM and percentage of Au on surface (XPS analysis).

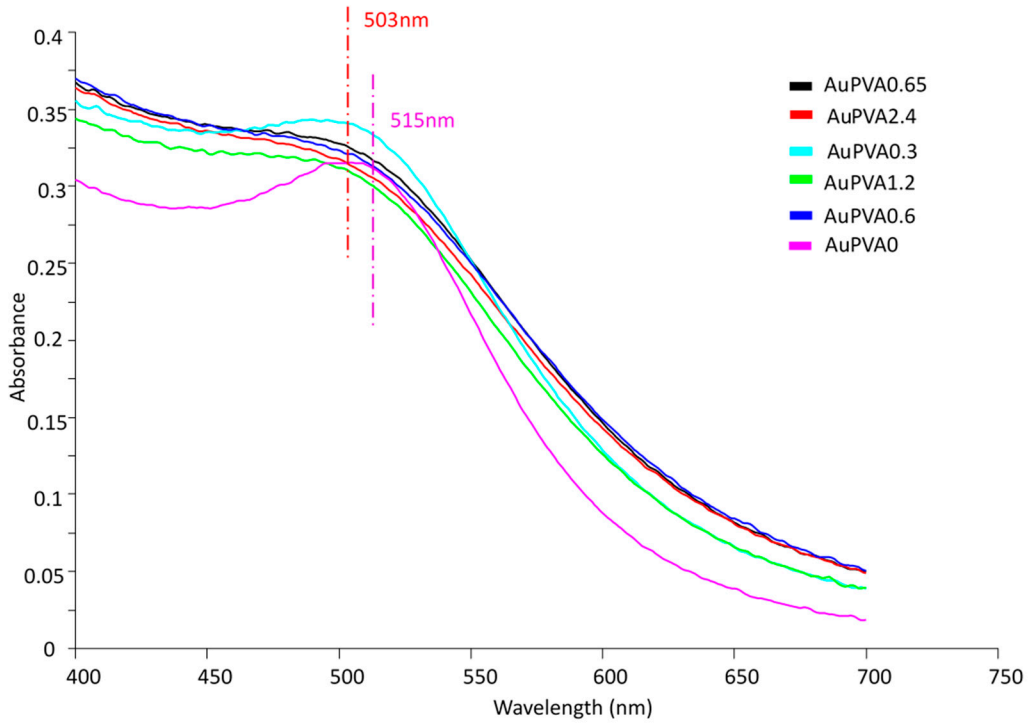

Figure S2. UV-Vis spectra of Au NPs colloidal suspension with varying amounts of PVA as stabilizer.

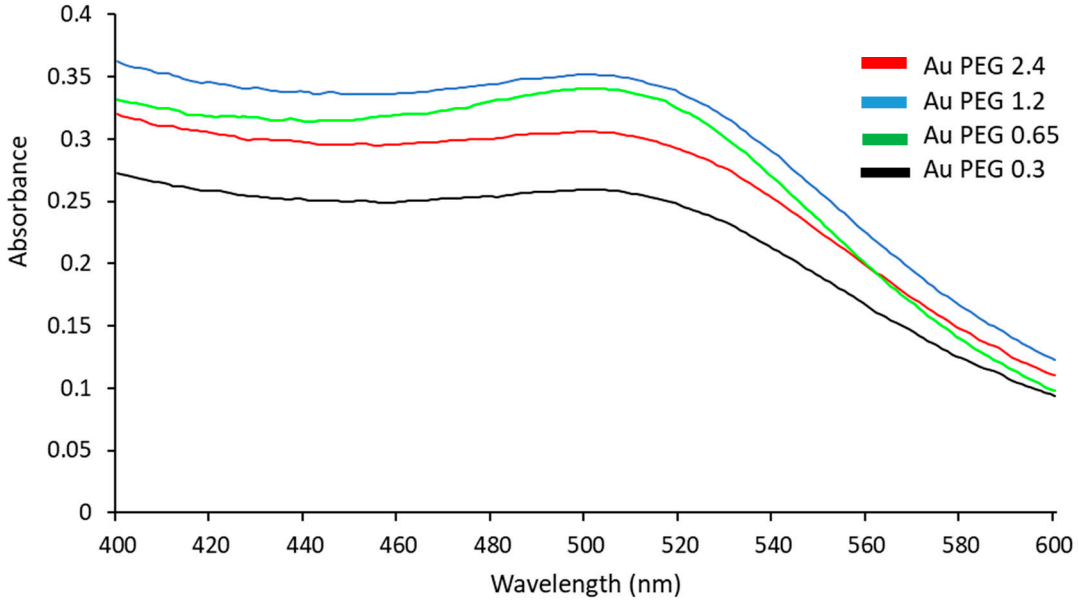

Figure S3. UV-Vis spectra of Au NPs colloidal suspension with varying amounts of PEG as stabilizer.

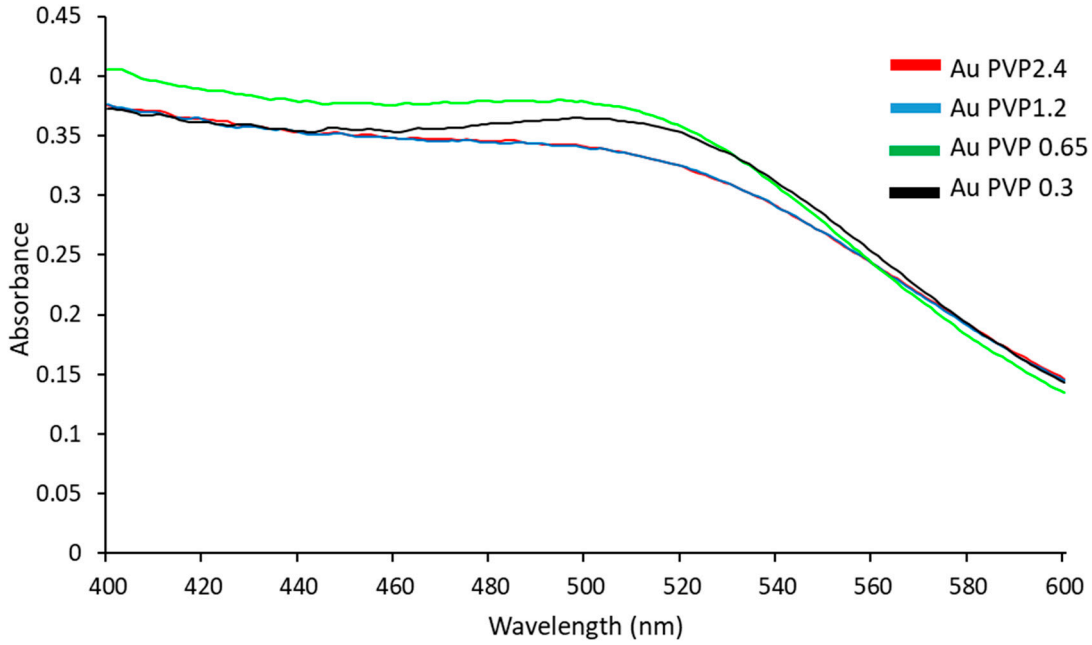

Figure S4. UV-Vis spectra of Au NPs colloidal suspension with varying amounts of PVP as stabilizer.

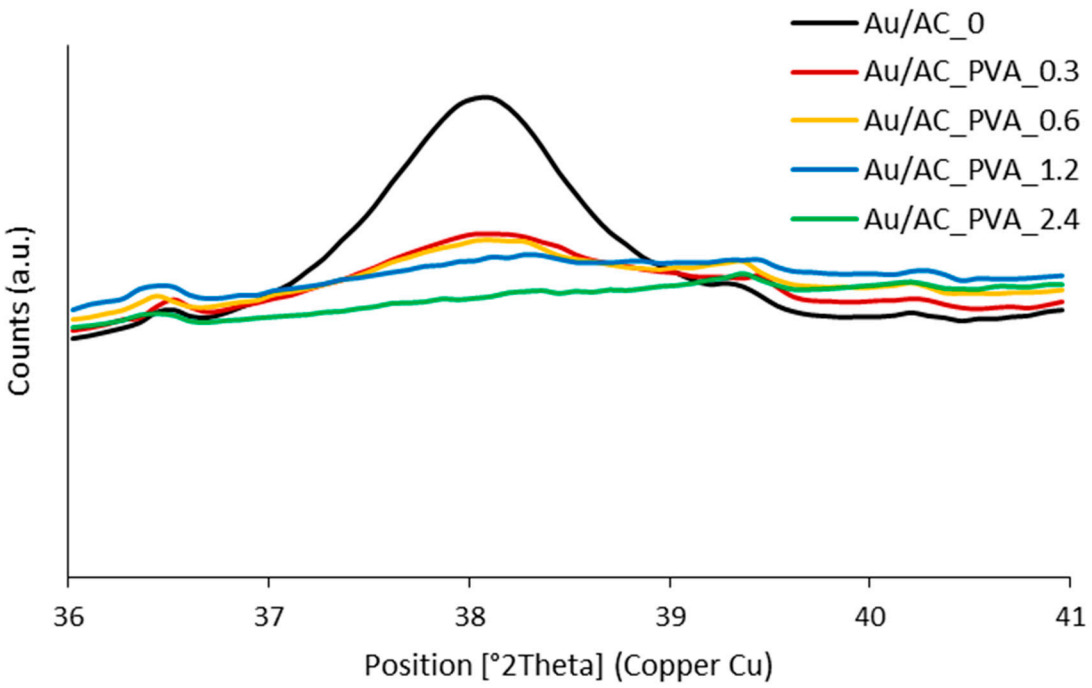

Figure S5. XRD patterns of Au/AC samples with different PVA:Au weight ratio.

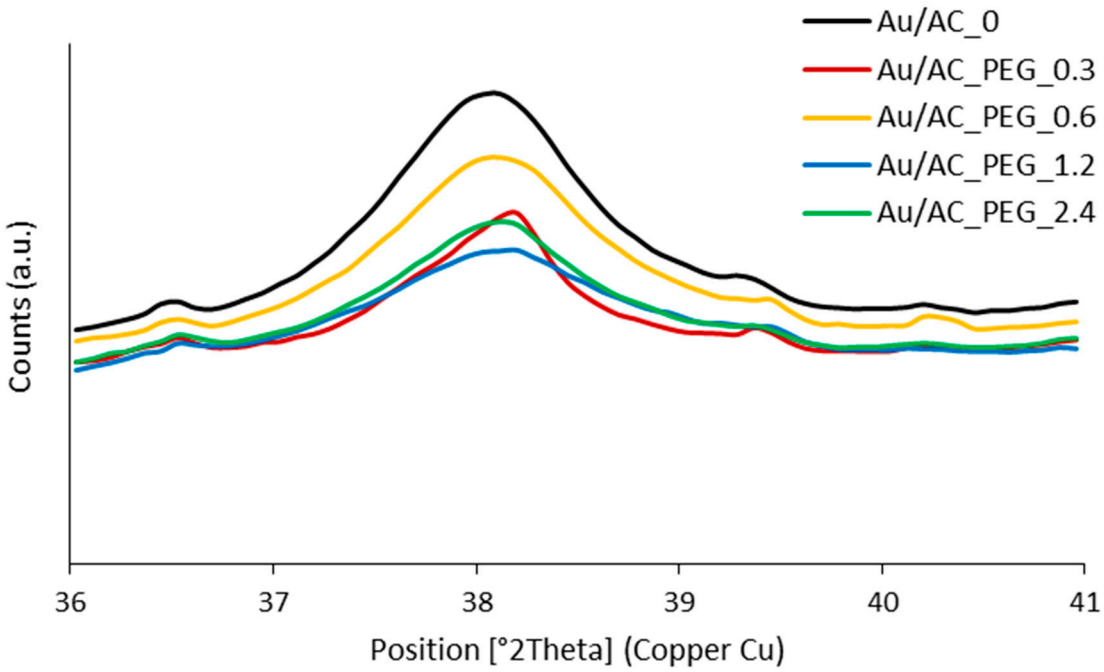

Figure S6. XRD patterns of Au/AC samples with different PEG:Au weight ratio.

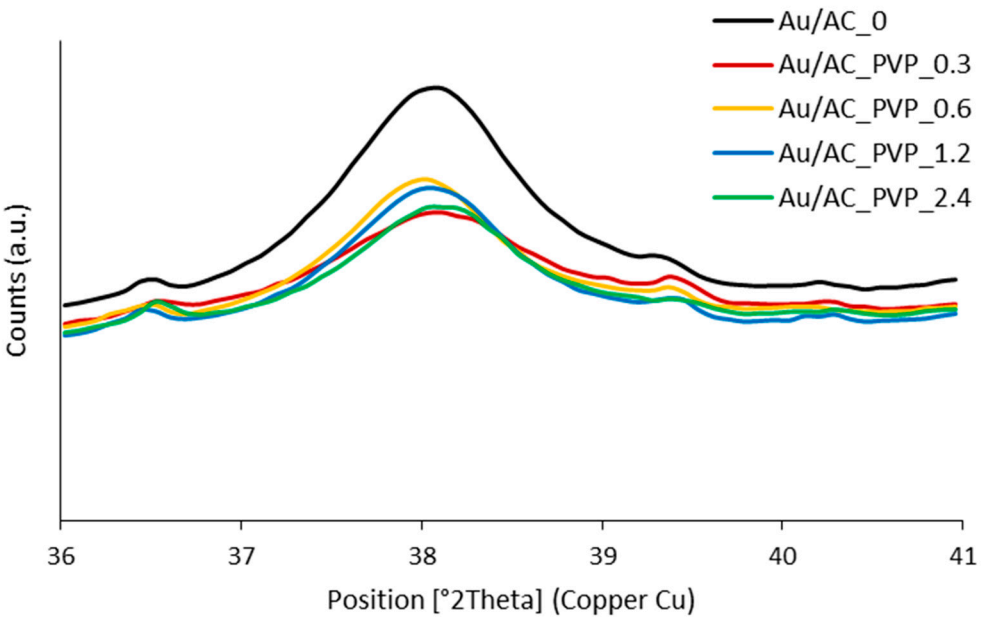

Figure S7. XRD patterns of Au/AC samples with different PVP:Au weight ratio.

Table S1. Mean crystallite size for Au/AC samples calculated from XRD analysis.

Sample	Employed polymer	Polymer:Au weight ratio	Au NPs XRD diameter (nm)
Au/AC _0	None	0	6
Au/AC_PVA_0.3	PVA	0.3	4
Au/AC_PVA_0.6	PVA	0.6	3
Au/AC_PVA_1.2	PVA	1.2	3
Au/AC _PVA_2.4	PVA	2.4	2
Au/AC _PEG_0.3	PEG	0.3	10
Au/AC _PEG_0.6	PEG	0.6	6
Au/AC _PEG_1.2	PEG	1.2	6
Au/AC _PEG_2.4	PEG	2.4	7
Au/AC _PVP_0.3	PVP	0.3	7
Au/AC _PVP_0.6	PVP	0.6	6
Au/AC _PVP_1.2	PVP	1.2	8
Au/AC _PVP_2.4	PVP	2.4	8

Table S2. XPS Analysis for the synthesised catalysts.

Samples	BE Gold [eV]	Au on surface [at%]	C on surface [at%]	N on surface [at%]	Surface atomic ratio Au/C
Au/AC_0	84	2.61	91.64	-	0.028
Au/AC_PVA_0.3	84.1	3.48	87.52	-	0.039
Au/AC_PVA_0.6	84.1	2.8	85.8	-	0.033
Au/AC_PVA_1.2	84.1	2.4	82.55	-	0.029
Au/AC_PVA_2.4	84.1	1.81	82.53	-	0.022
Au/AC_PVP_0.3	84	1.43	90.94	2.1	0.016
Au/AC_PVP_0.6	84	1.17	88.69	3.25	0.013
Au/AC_PVP_1.2	84	0.15	90.81	2.9	0.0016
Au/AC_PVP_2.4	84.1	0.12	89.53	3.6	0.0013
Au/AC_PEG_0.3	84.1	0.84	94.35	-	0.009
Au/AC_PEG_0.6	84.1	1.95	92.48	-	0.021
Au/AC_PEG_1.2	84.1	1.52	93.36	-	0.016
Au/AC_PEG_2.4	84.1	1.09	93.64	-	0.012

Table S3. XPS analysis on spent catalysts (after 3 uses).

Samples	BE Gold [eV]	Au on surface [at%]	C on surface [at%]	N on surface [at%]	Surface atomic ratio Au/C
Au/AC_PVP_0.6 3 uses	84	0.25	88.44	2.21	0.003
Au/AC_PEG_0.6 3 uses	84	0.68	88.52	0.5	0.008
Au/AC_PEG_2.4 3 uses	83.9	0.71	88.09	0.57	0.0008
Au/AC_PVA_0.6 3 uses	83.9	0.18	86.09	0.39	0.002
Au/AC_PVA_2.4 3 uses	83.9	0.24	88.87	-	0.003

- **Au/AC_PVP _0.6**

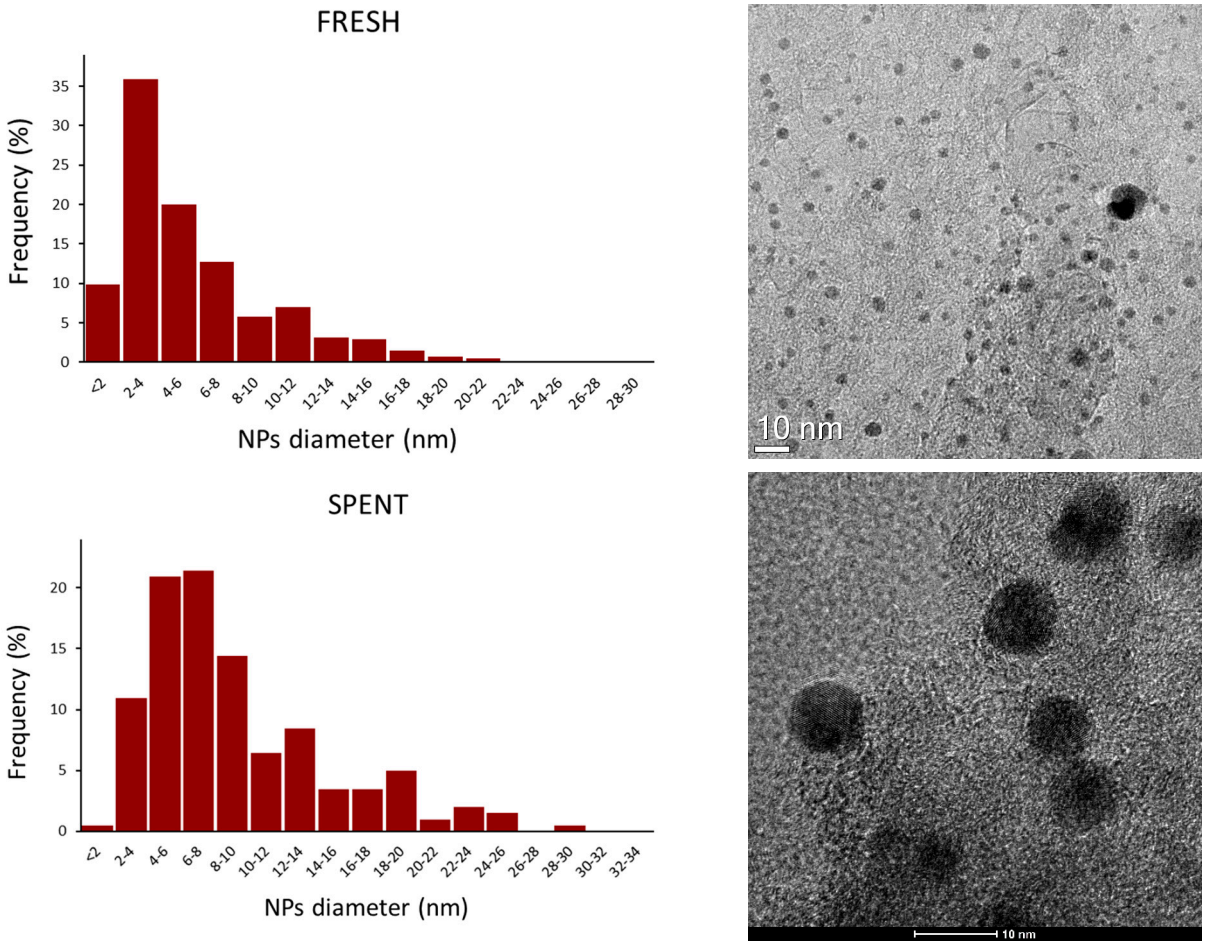

Figure S8. TEM images and particle size distributions of Au/AC_PVP_0.6 catalyst before and after two reaction cycles .

- **Au/AC_PEG_0.6**

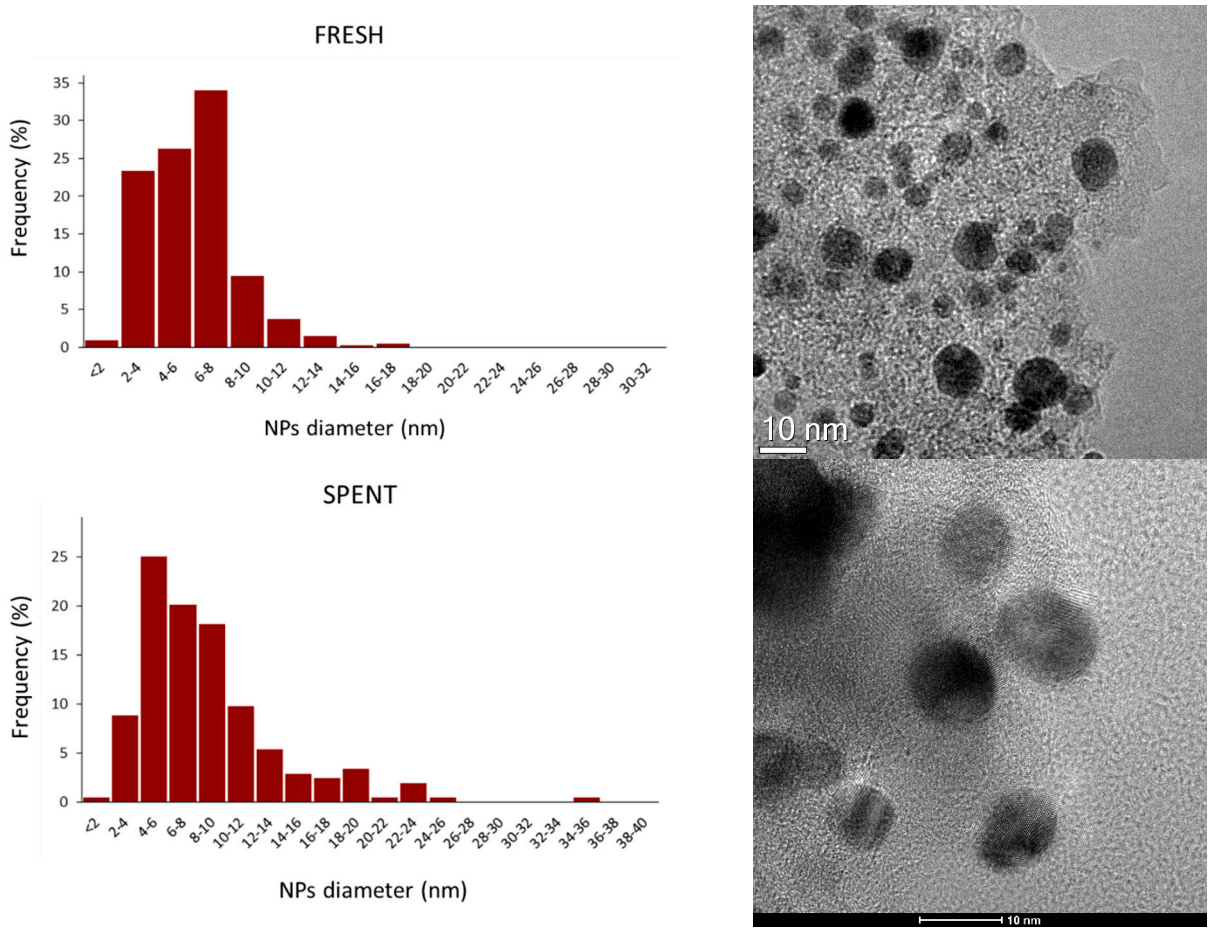

Figure S9. TEM images and particle size distributions of Au/AC_PEG_0.6 catalyst before and after three reaction cycles.

- **Au/AC_PEG_2.4**

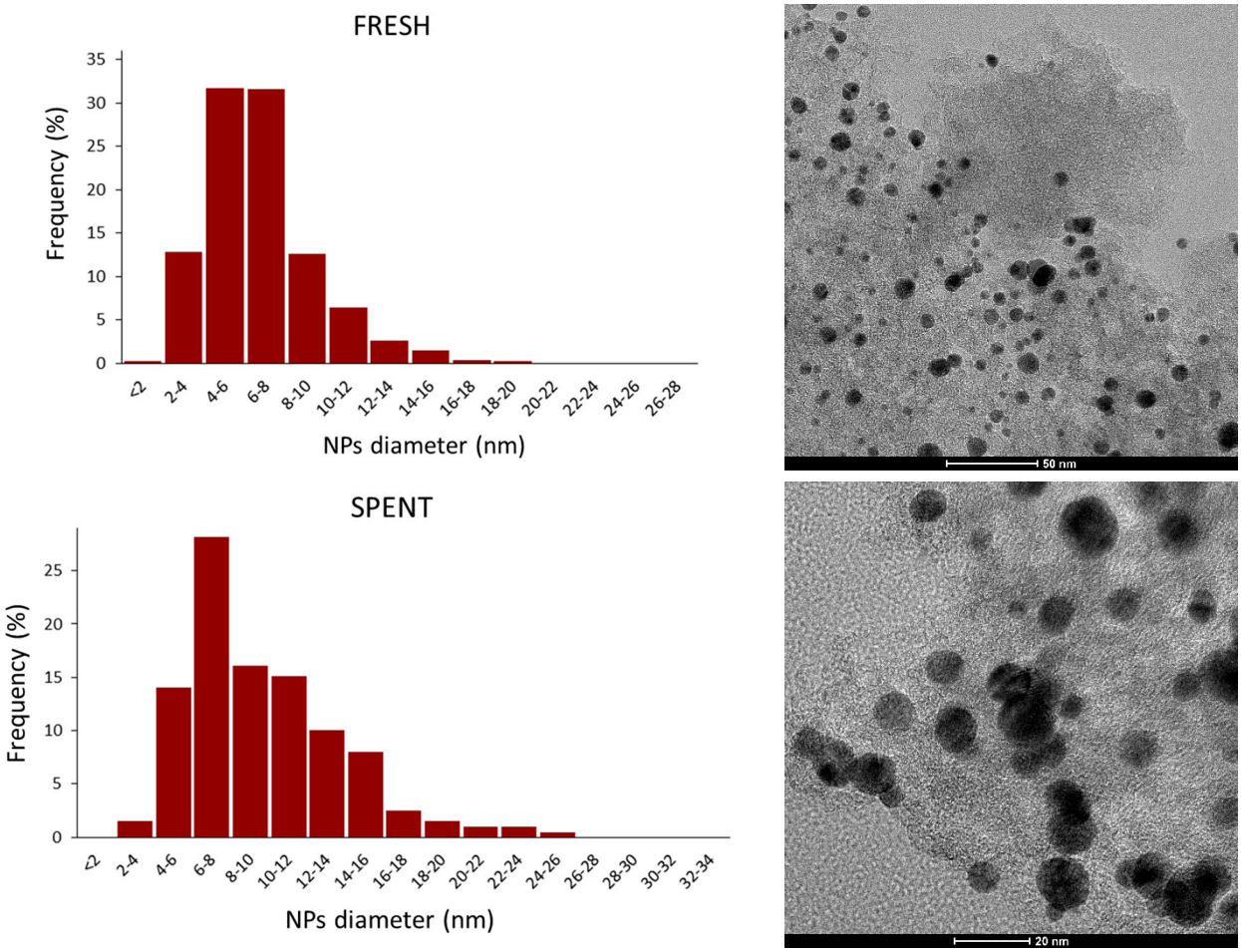

Figure S10. TEM images and particle size distributions of Au/AC_PEG_2.4 catalyst before and after three reaction cycles.

- **Au/AC_PVA_0.6**

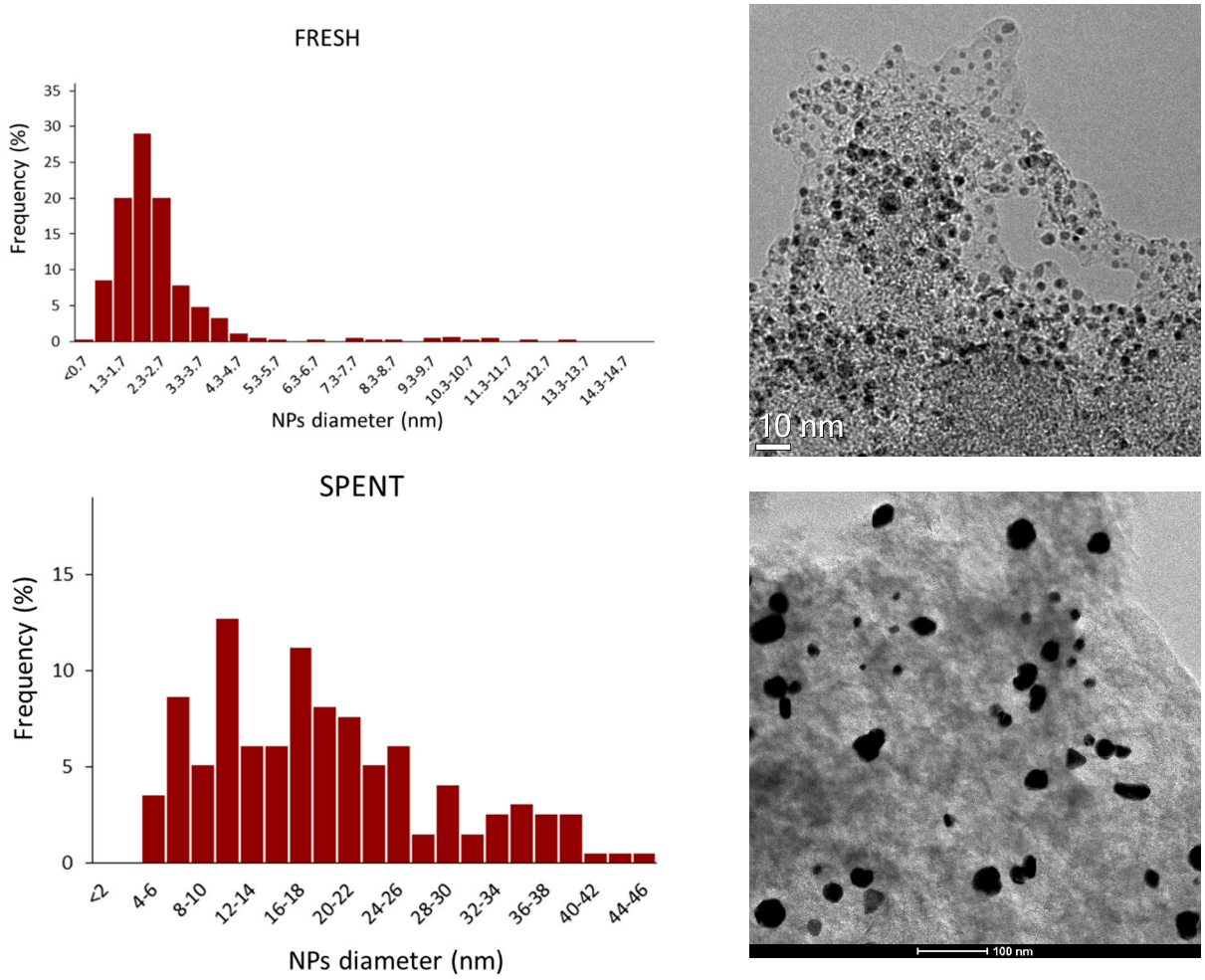

Figure S11. TEM images and particle size distributions of Au/AC_PVA_0.6 catalyst before and after three reaction cycles.

- **Au/AC_PVA_2.4**

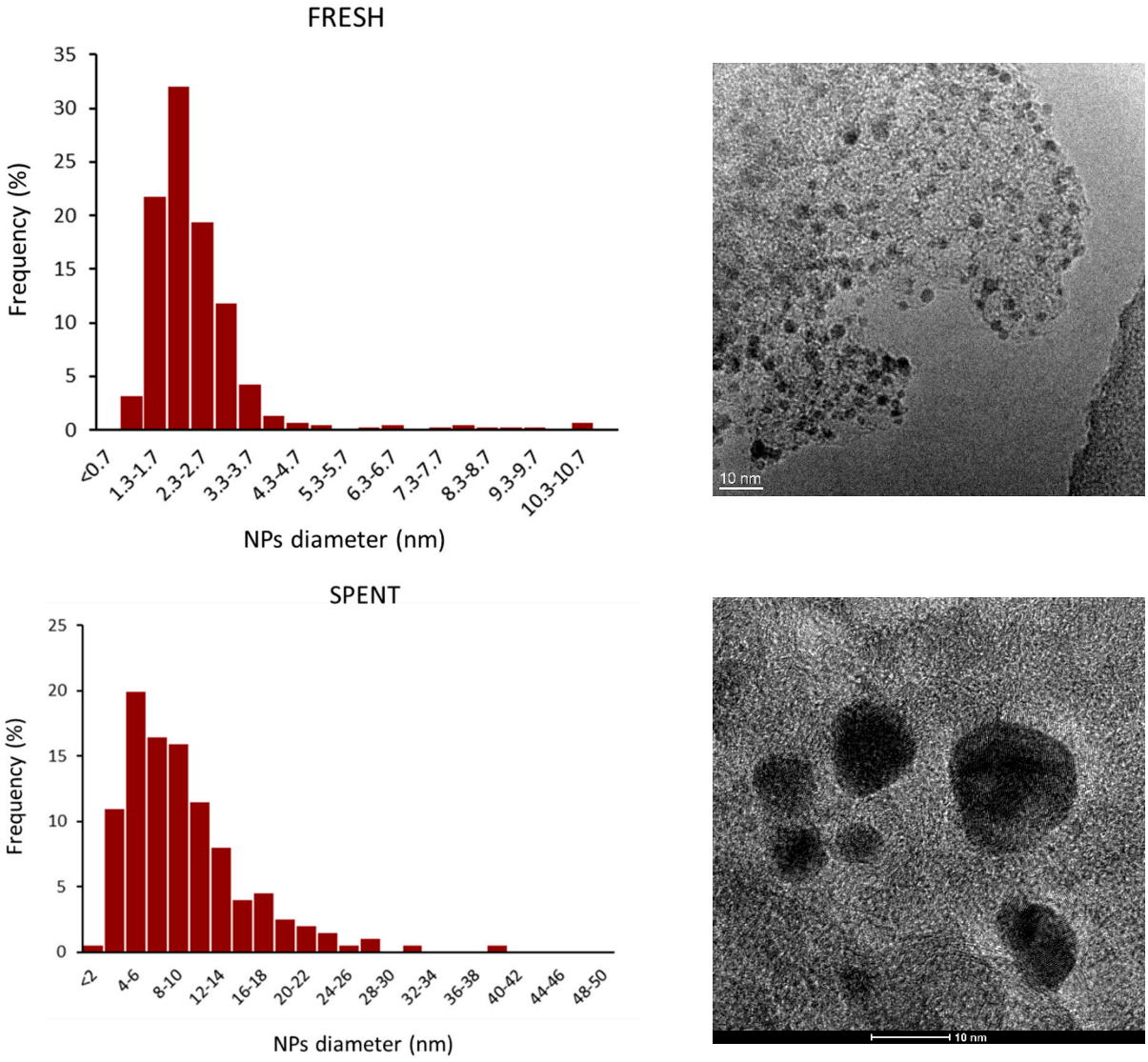

Figure S12. TEM images and particle size distributions of Au/AC_PVA_2.4 catalyst before and after three reaction cycles.

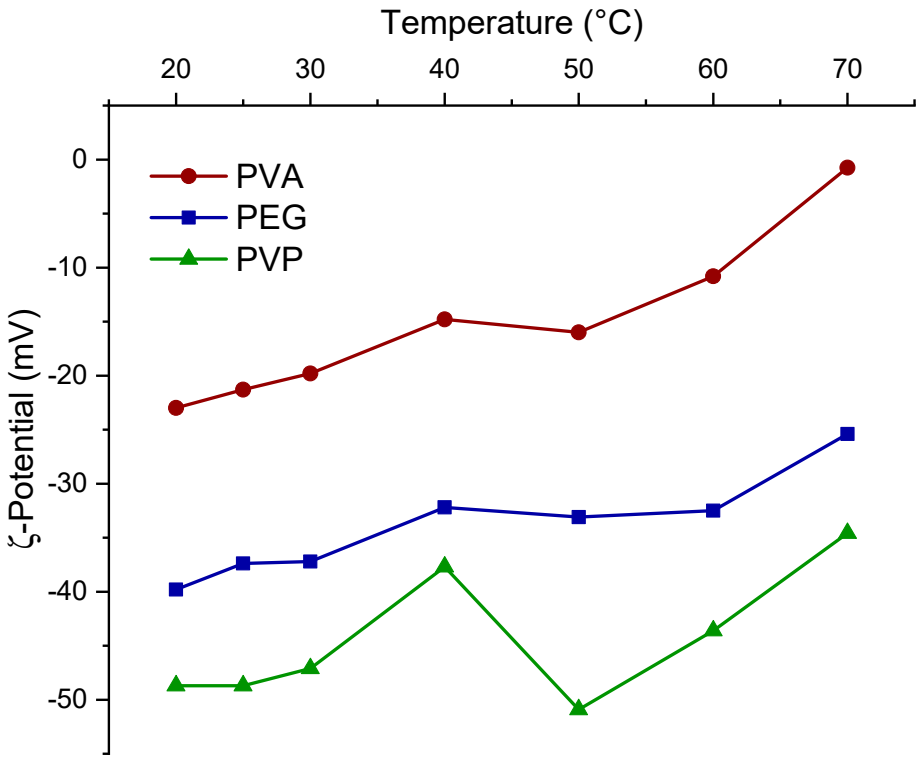

Figure S13. Temperature effect on zeta potential for the Au colloidal suspension stabilized with different polymers (PVA, PEG, PVP). Polymer:Au weight ratio of 0.6.

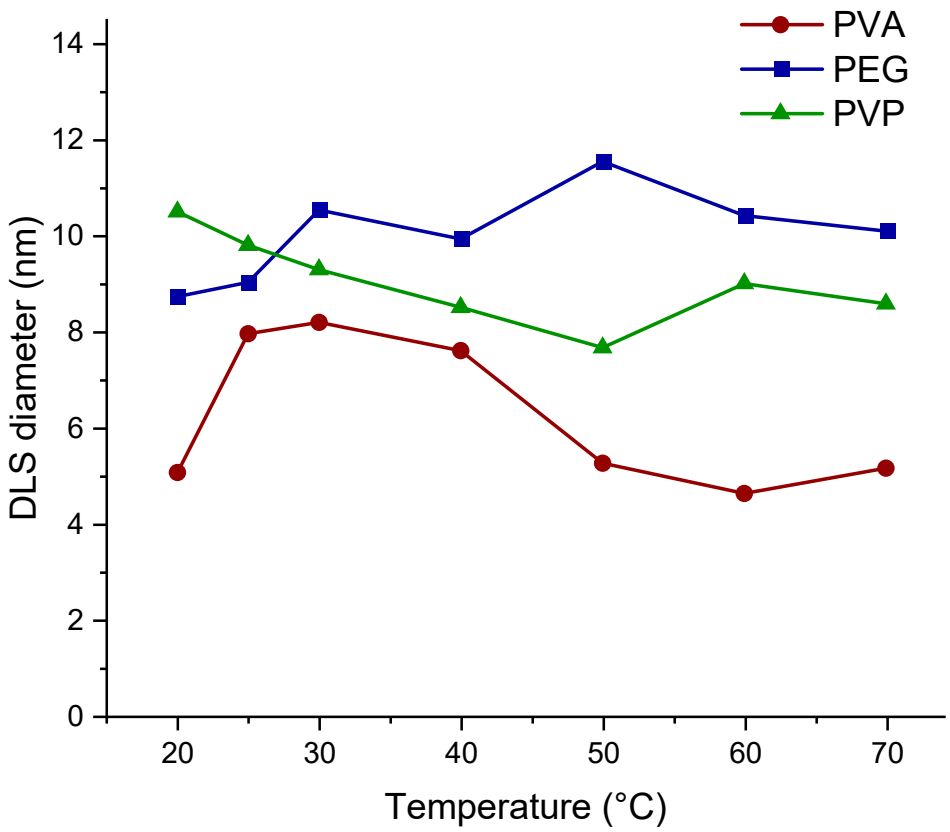

Figure S14. Temperature effect on DLS diameter for the Au colloidal suspension stabilized with different polymers (PVA, PEG, PVP). Polymer:Au weight ratio of 0.6.

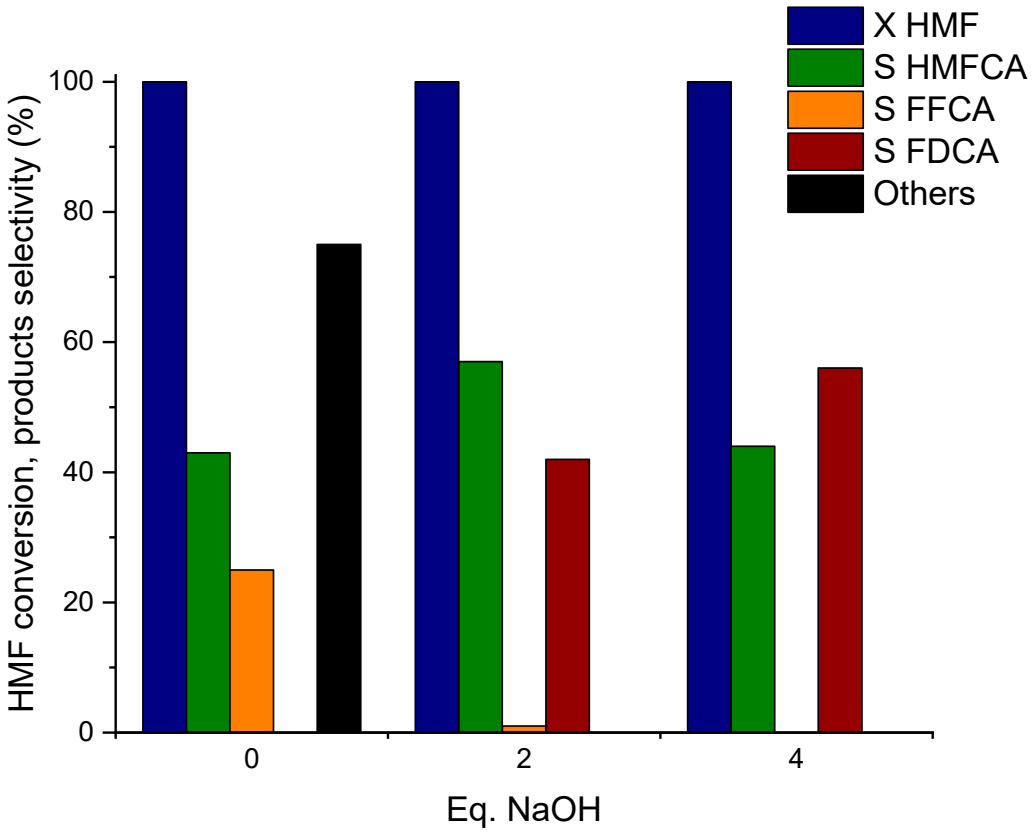

Figure S15. Effect of the NaOH equivalent on the sample Au/AC_PVA_0.6. Reaction conditions: 2 h, 70 °C, 10 bar O_2, HMF:Met:NaOH=1:0.01:4.

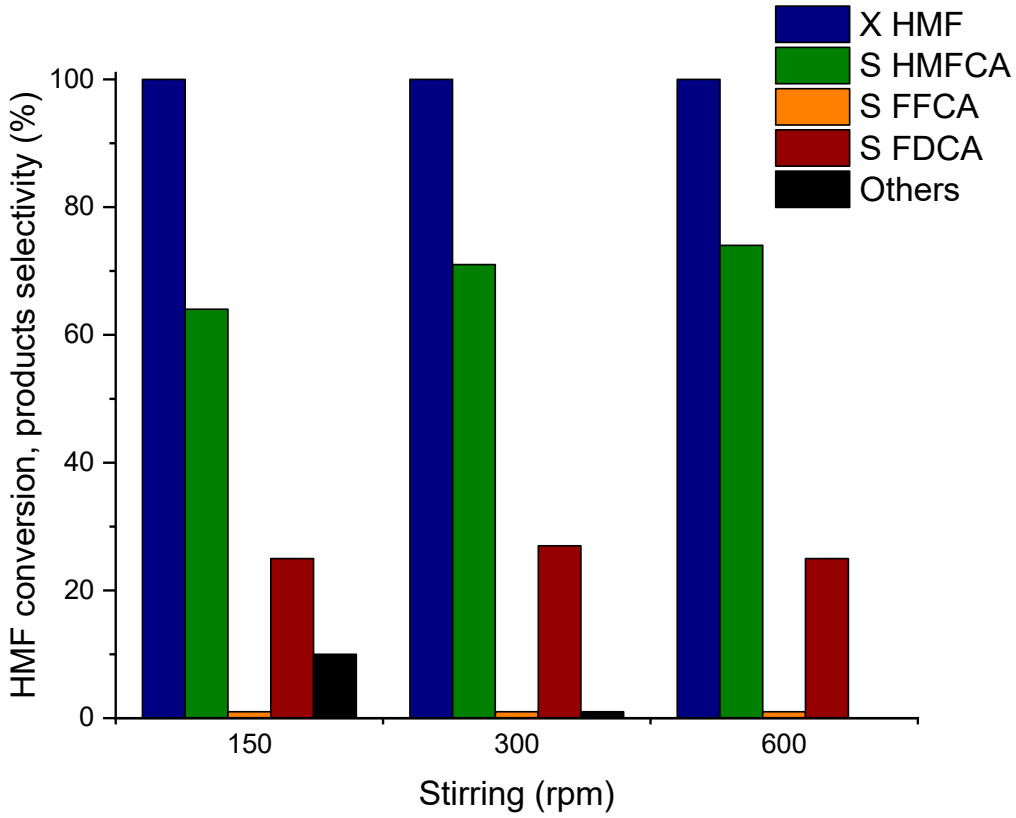

Figure S16. Effect of the stirring rate on the sample Au/AC_PVA_0.6. Reaction conditions: 1 h, 70 °C, 10 bar O_2, HMF:Met:NaOH=1:0.01:4.

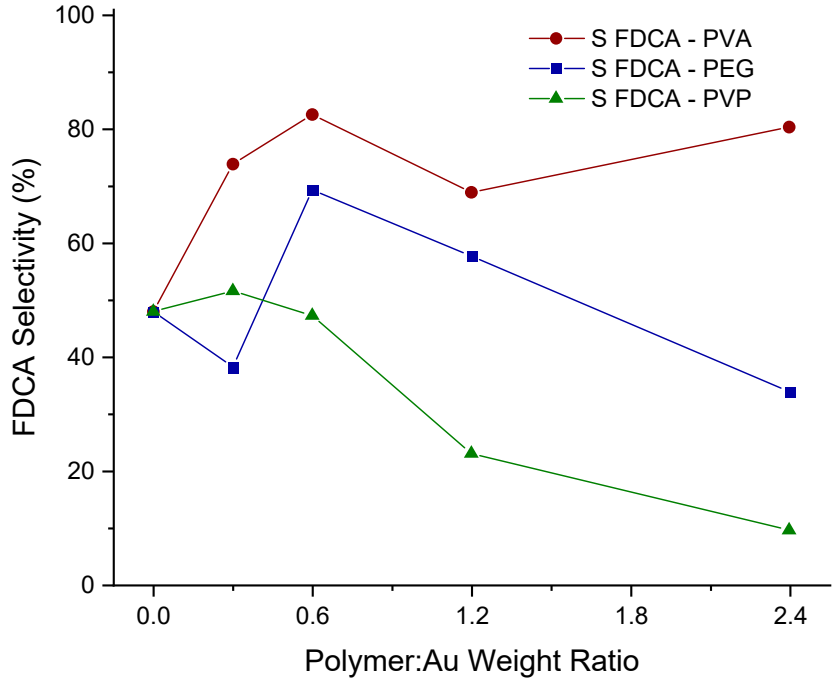

Figure S17. Correlation between catalytic performances and stabilizer to Au weight ratio for each catalyst series. Reaction conditions: 70 °C, 4 h, 10 bar O_2, HMF:Met:NaOH=1:0.01:4.

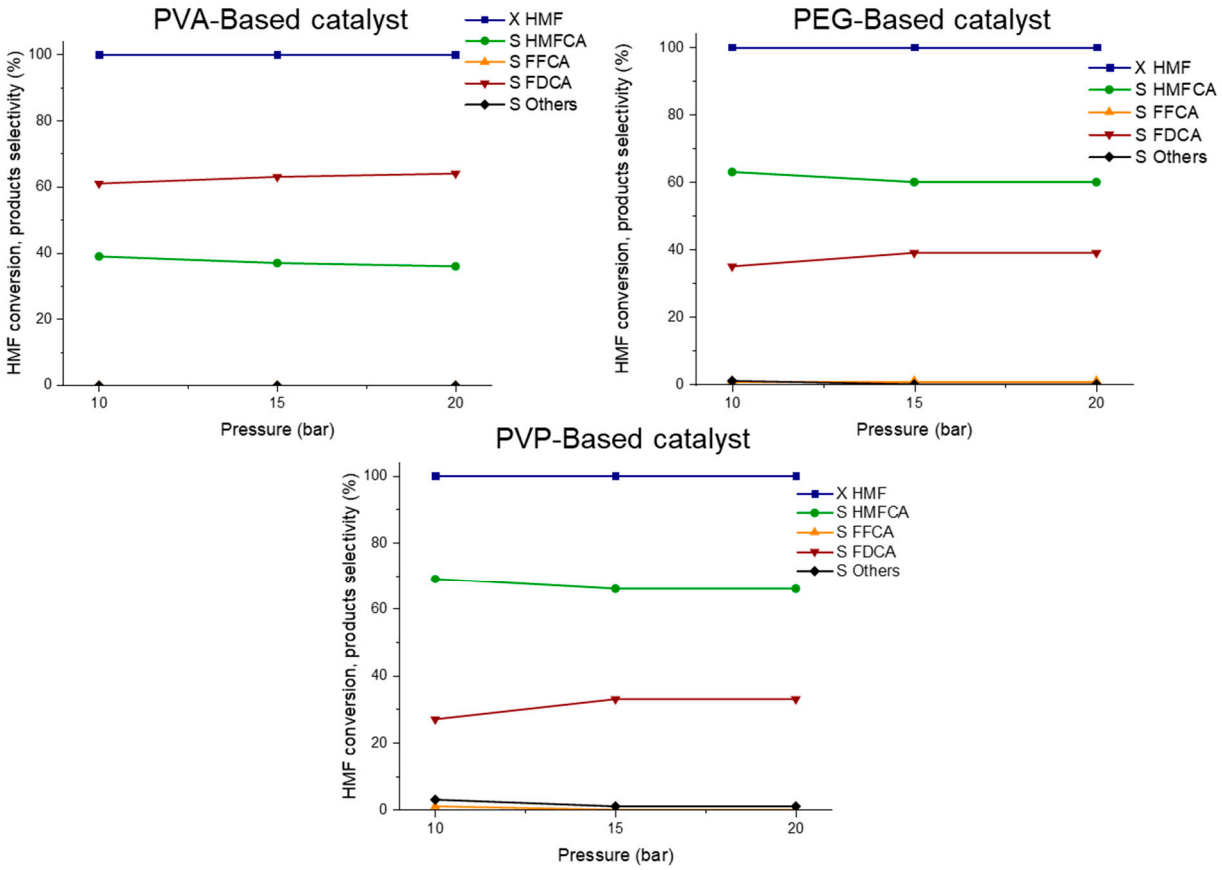

Figure S18. Effect of the oxygen pressure on the 0.6 Polymer:Au weight ratio catalysts. Reaction conditions: 2 h, 70 °C, HMF:Met:NaOH=1:0.01:4.

- **Au/AC_PEG_0.6**

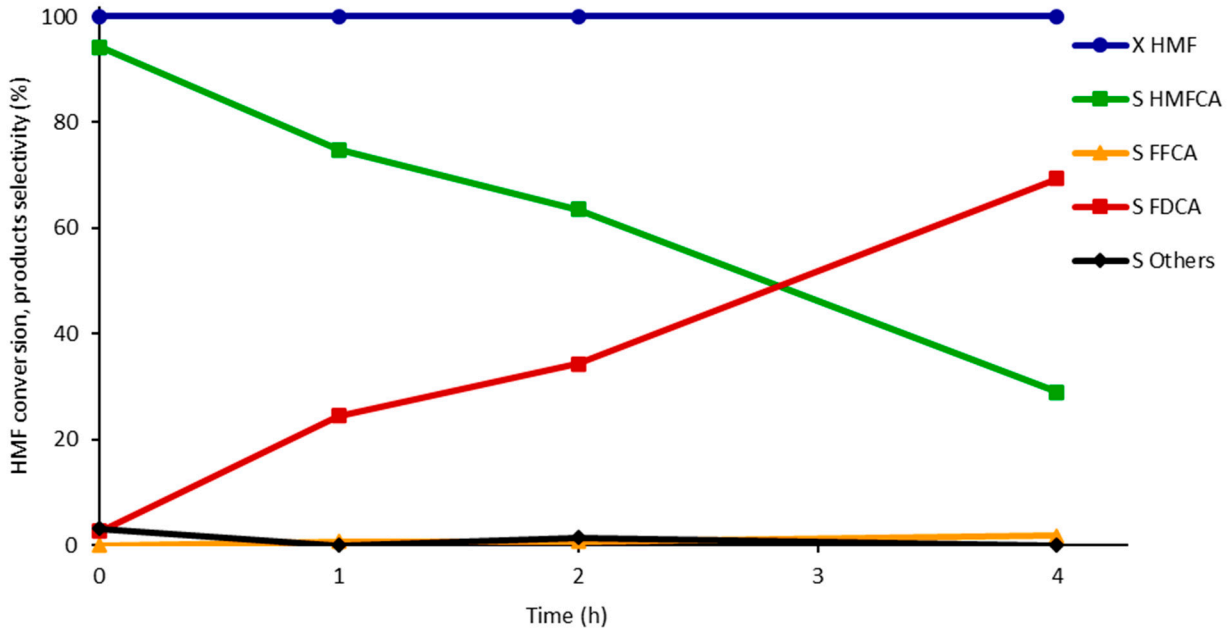

Figure S19. Study on the reaction time. Catalyst: Au/AC_PEG_0.6. Reaction conditions: 70 °C, 10 bar O_2, HMF:Met:NaOH=1:0.01:4.

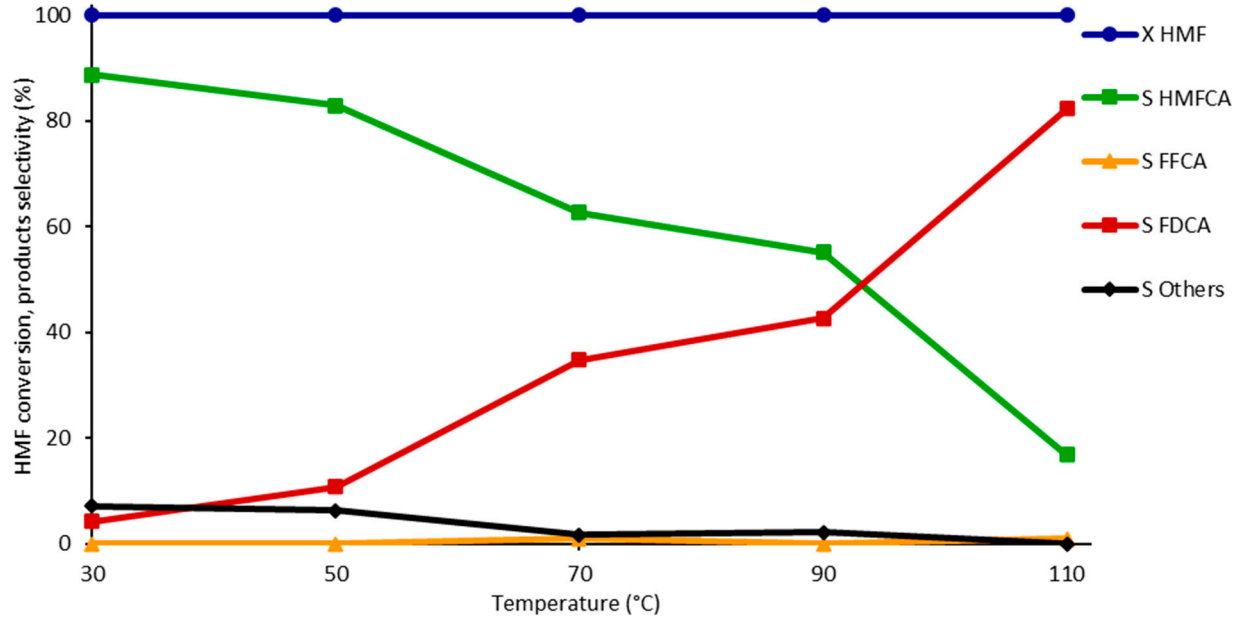

Figure S20. Study on the reaction temperature. Catalyst: Au/AC_PEG_0.6. Reaction conditions: 2 h, 10 bar O_2, HMF:Met:NaOH=1:0.01:4.

- **Au/AC_PVP_0.6**

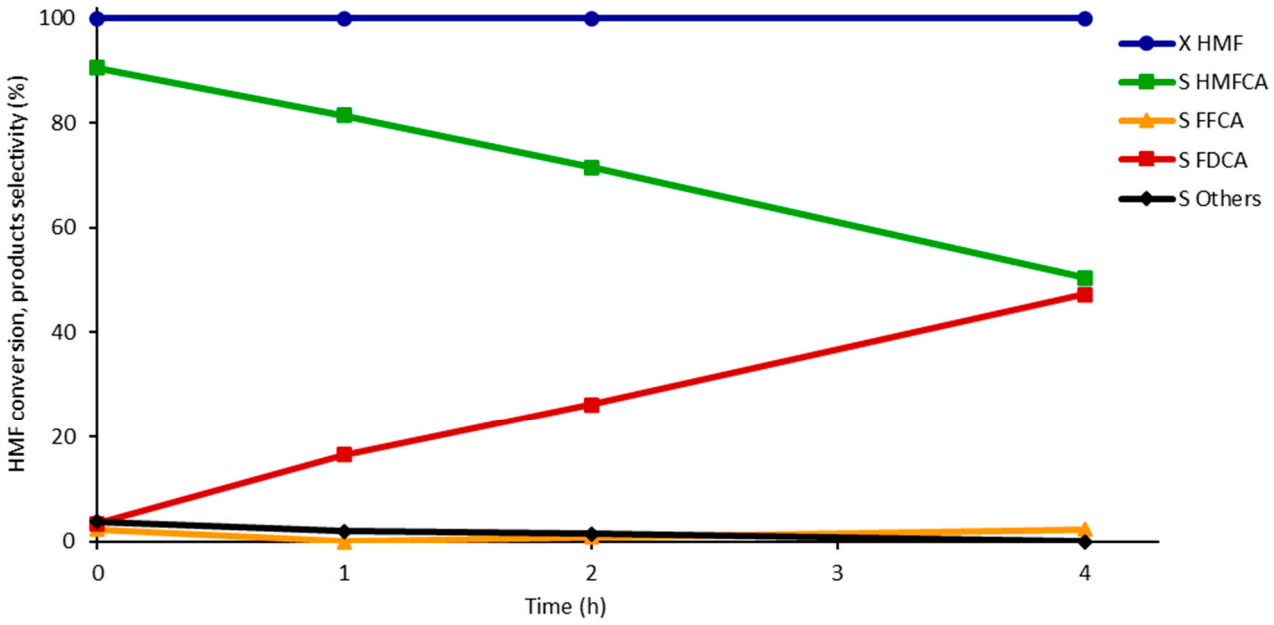

Figure S21. Study on the reaction time. Catalyst: Au/AC_PVP_0.6. Reaction conditions: 70 °C, 10 bar O_2, HMF:Met:NaOH=1:0.01:4.

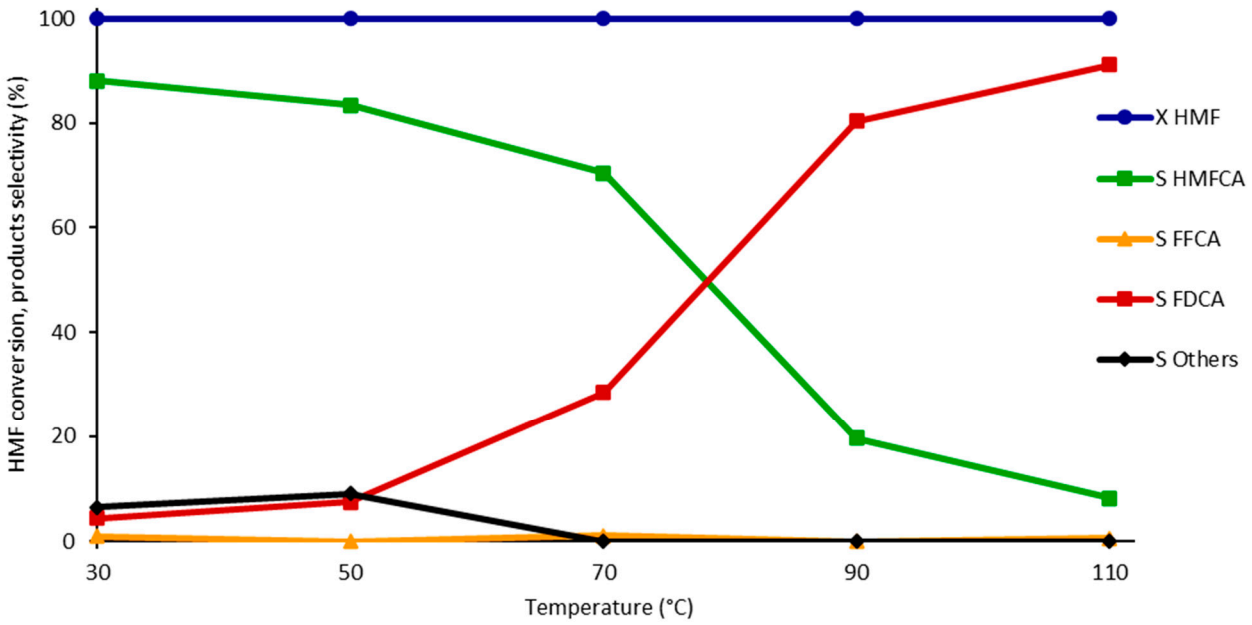

Figure S22. Study on the reaction temperature. Catalyst: Au/AC_PVP_0.6. Reaction conditions: 2 h, 10 bar O_2, HMF:Met:NaOH=1:0.01:4.

- **Au/AC_PVA_0.6**

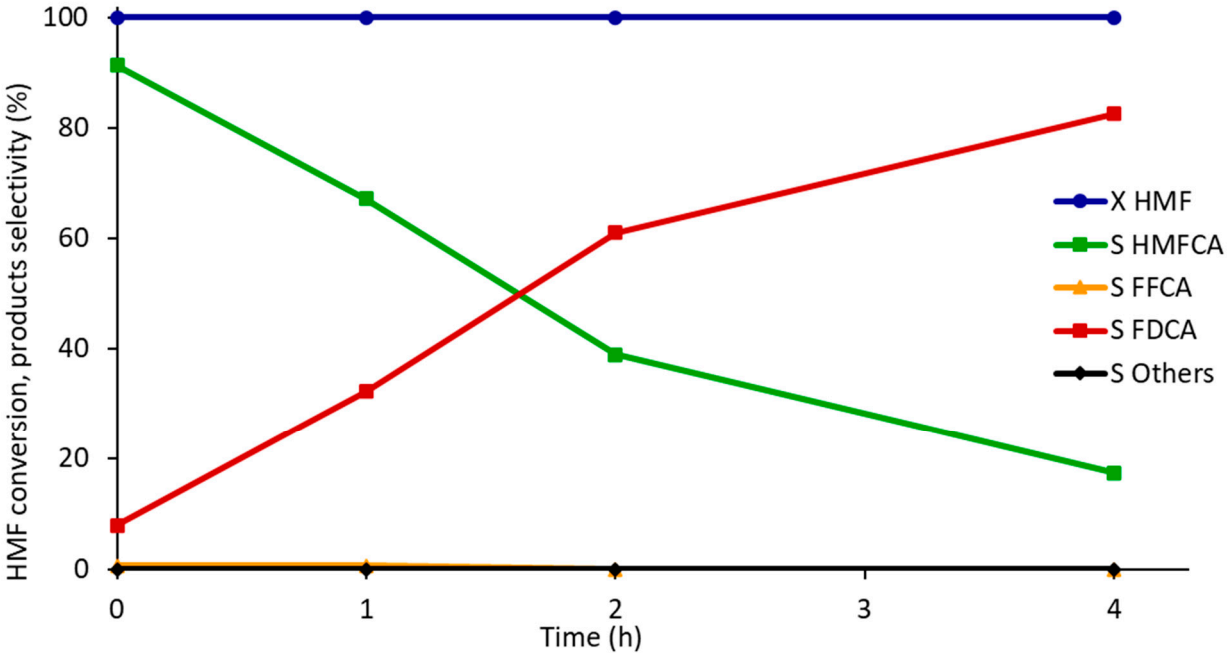

Figure S23. Study on the reaction time. Catalyst: Au/AC_PVA_0.6. Reaction conditions: 70 °C, 10 bar O_2, HMF:Met:NaOH=1:0.01:4.

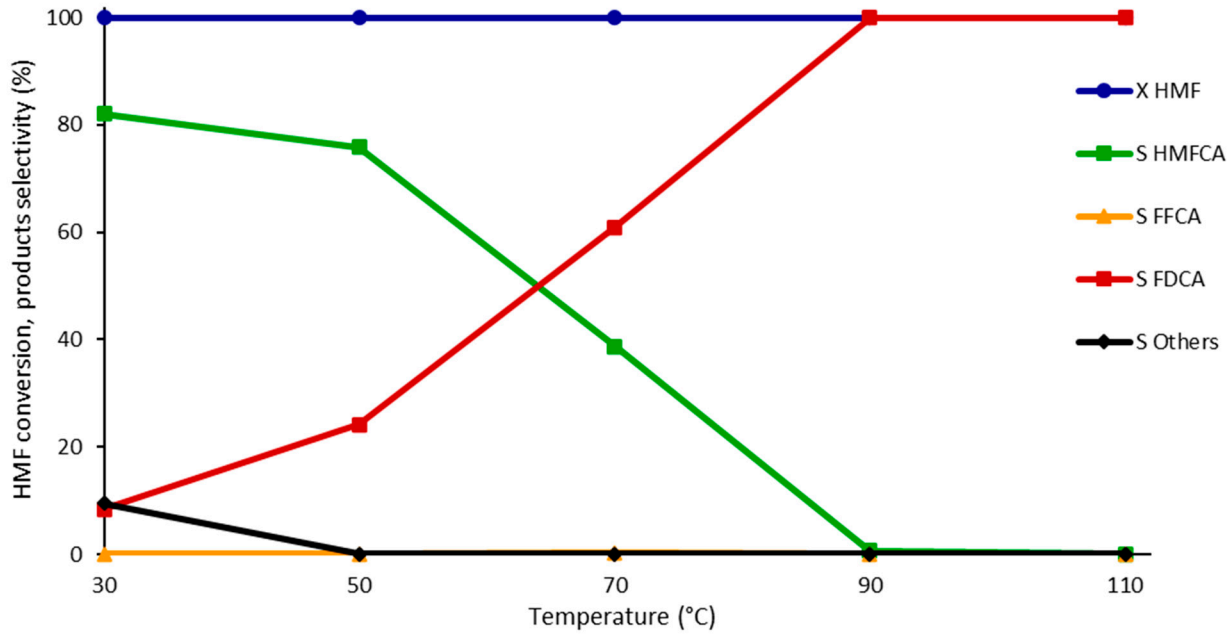

Figure S24. Study on the reaction temperature. Catalyst: Au/AC_PVA_0.6. Reaction conditions: 2 h, 10 bar O_2, HMF:Met:NaOH=1:0.01:4.

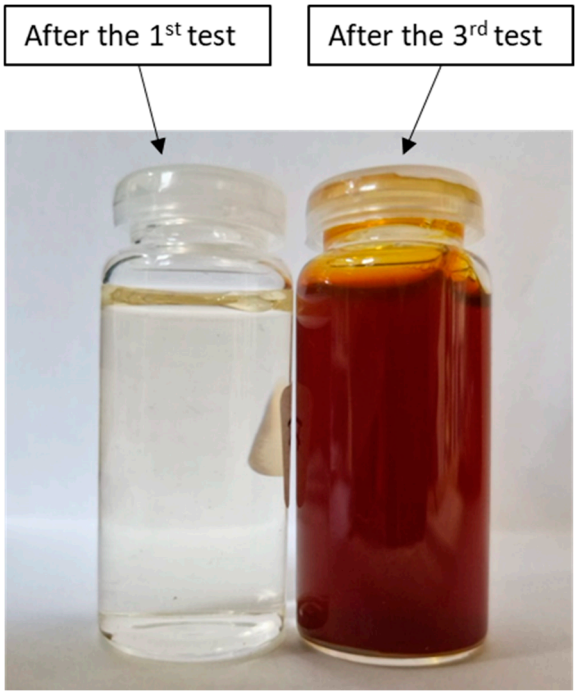

Figure S25. Comparison of reaction solution after the first test on Au/AC_PVP_0.6 and after the third test.

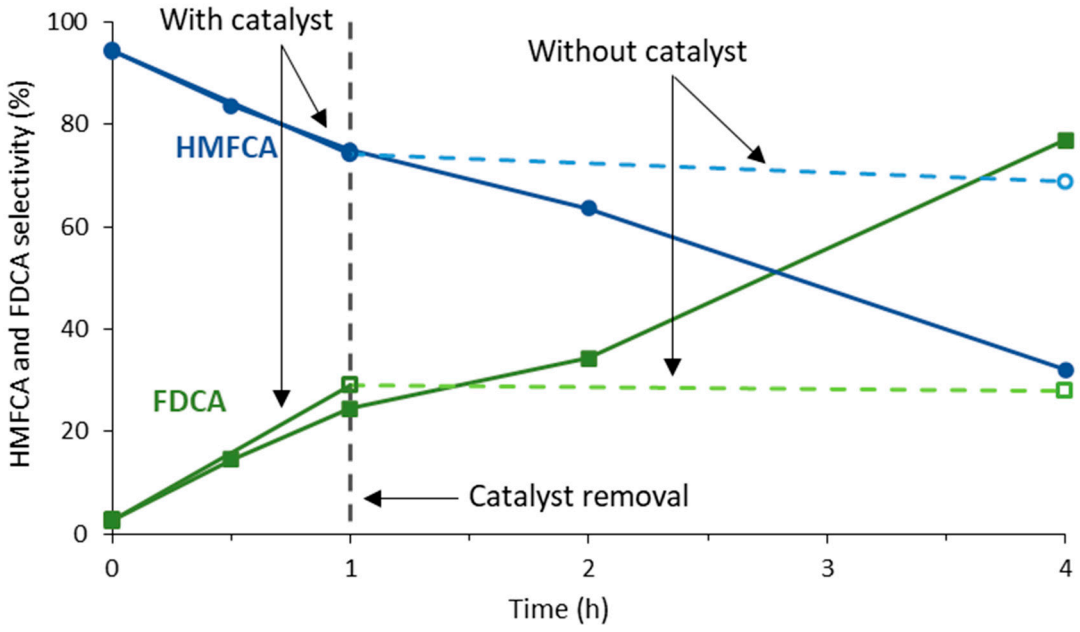

Figure S26. Leaching evaluation test. Solid lines and symbols represent the selectivity evolution during a regular catalytic test, as a reference. In the leaching test, represented by the open symbols, two steps are represented: The solid lines represent the first hour of reaction, in which the test was carried out normally; after 1h, the catalyst was removed and the liquid phase was maintained in the reaction conditions for 3 more hours, represented by the dashed lines. Reaction conditions: 4 h, 70 °C, 10 bar O_2, HMF:Met:NaOH=1:0.01:4.

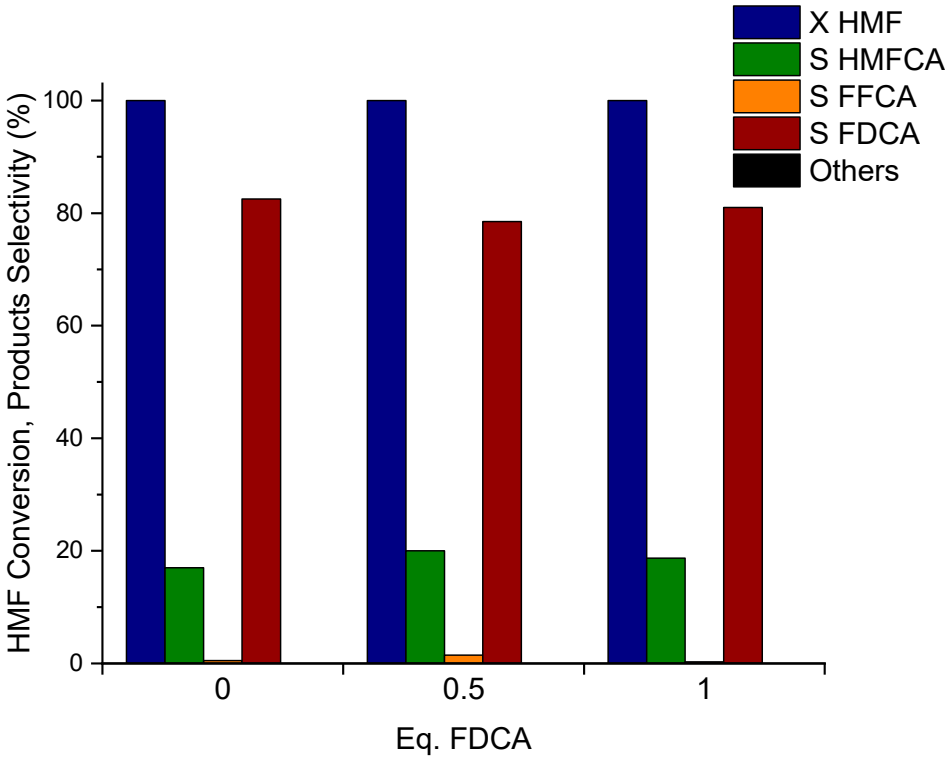

Figure S267. Effect of the FDCA in the starting reaction mixture. Reaction conditions: 4 h, 70 °C, 10 bar O_2, HMF:Met:NaOH=1:0.01:4.

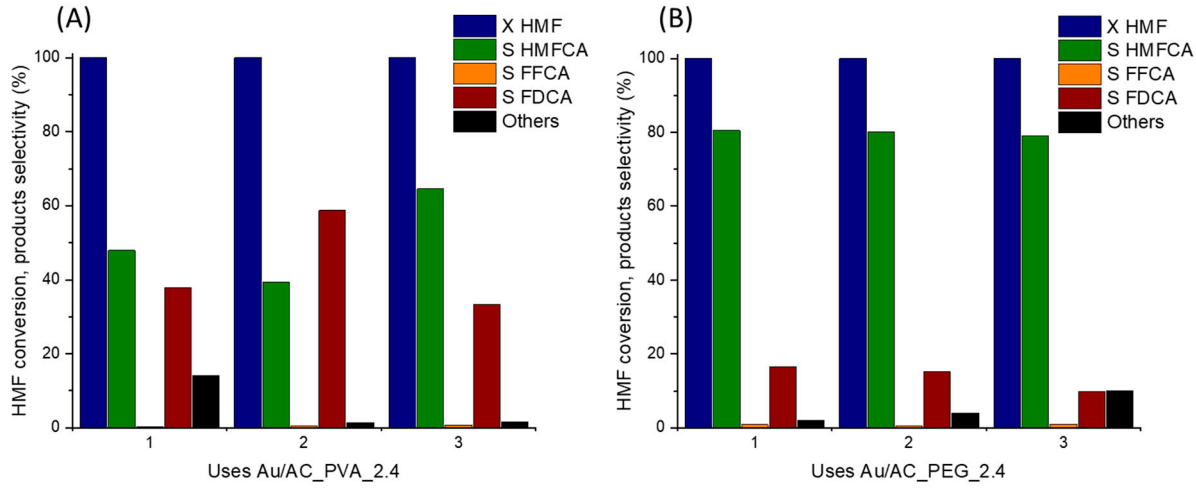

Figure S28. Reusability tests for the Au/AC_PVA_2.4 (A) and Au/AC_PEG_2.4 catalysts (B). Reaction conditions: 70°C, 2h, 10bar O_2, HMF:Met:NaOH=1:0.01:4.