Support information

Selective Catalytic Hydrogenation of 5-Hydroxymethylfurfural over Silica Supported FeCoNiCuRu High-Entropy Alloy Nanoparticles

Guojun Lan, Liping Zhang, Huiming Xie, Tuo Shi, Wen Luo, Yuxiang Wang, Zaizhe Cheng, Xiucheng Sun, Yiyang Qiu and Ying Li**

Institute of Industrial Catalysis, State Key Laboratory Breeding Base of Green Chemistry Synthesis Technology, Zhejiang University of Technology, Chaowang Road 18, Hangzhou, China

**Guojun Lan* − Institute of Industrial Catalysis, State Key Laboratory Breeding Base of Green Chemistry Synthesis Technology, Zhejiang University of Technology, Hangzhou 310014, PR China; Email: languojun@zjut.edu.cn

*Ying Li − Institute of Industrial Catalysis, State Key Laboratory Breeding Base of Green Chemistry Synthesis Technology, Zhejiang University of Technology, Hangzhou 310014, PR China; Email: liying@zjut.edu.cn

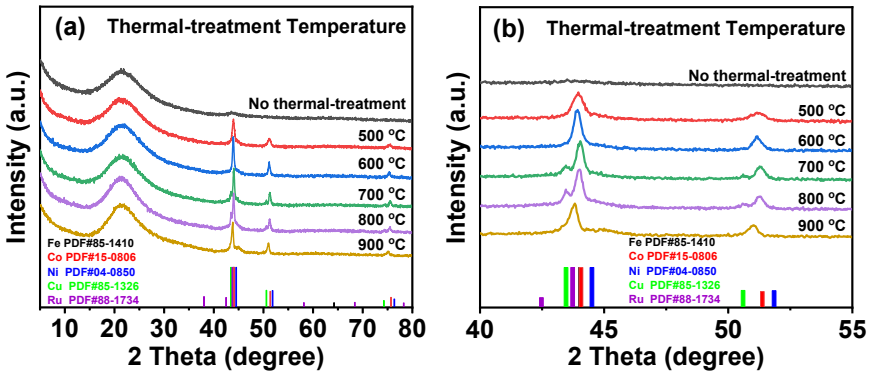


Figure S1. XRD patterns of (FeCoNiCuRu-1TA/SiO_2)-T catalysts (a), enlargement of the diffraction intensity from 40° to 55° (b).

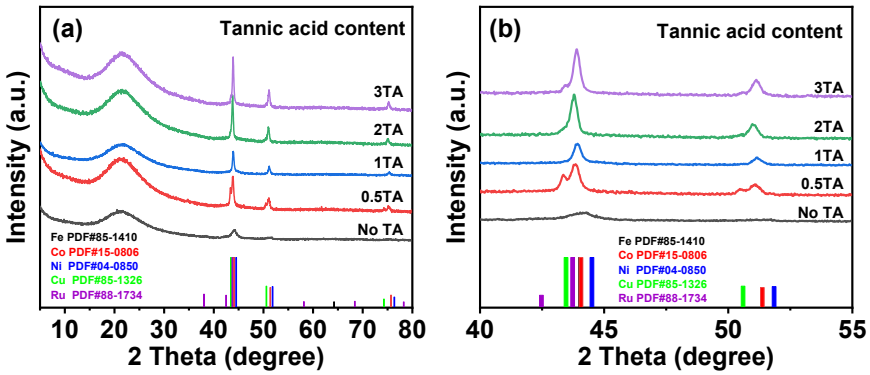


Figure S2. XRD patterns of (FeCoNiCuRu-xTA/SiO_2)-600 catalysts (a), enlargement of the diffraction intensity from 40° to 55° (b).

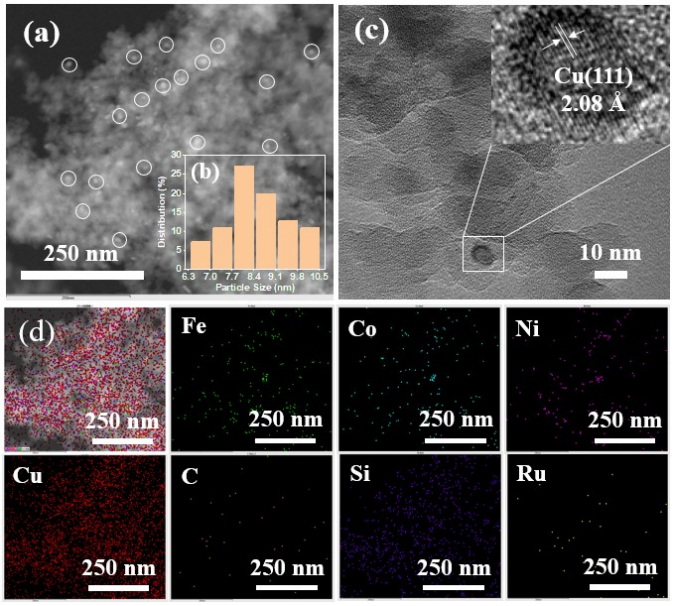


Figure S3. TEM image (a), particle size distribution (b), HAADF-STEM image (c) and EDS mapping of the various elements (d) of (FeCoNiCuRu/SiO_2)-600 catalyst.

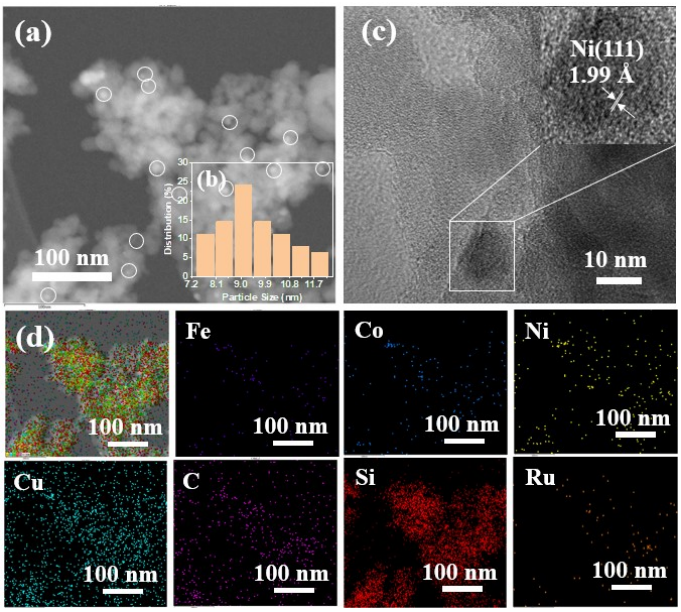


Figure S4. TEM image (a), particle size distribution (b), HAADF-STEM image (c) and EDS mapping of the various elements (d) of FeCoNiCuRu-1TA/SiO_2 catalyst.

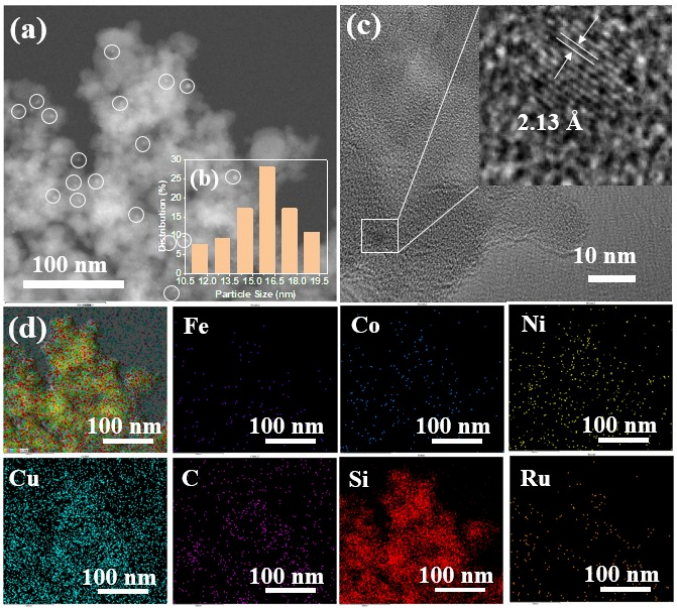


Figure S5. TEM image (a), particle size distribution (b), HAADF-STEM image (c) and EDS mapping of the various elements (d) of (FeCoNiCuRu-2TA/SiO_2)-600 catalyst.

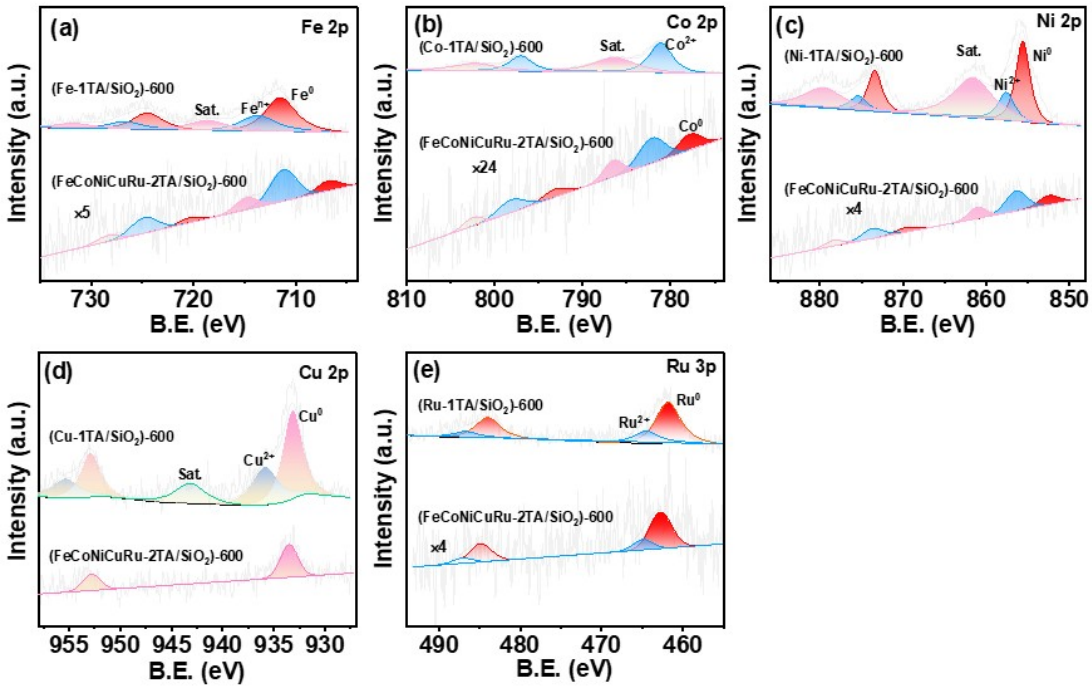


Figure S6. Fe 2p(a), Co 2p (b), Ni 2p (c), Cu 2p (d) and Ru 3p (e) spectra of (FeCoNiCuRu-2TA/SiO_2)-600, (Fe-1TA/SiO_2)-600, (Co-1TA/SiO_2)-600, (Ni-1TA/SiO_2)-600, (Cu-1TA/SiO_2)-600 and (Ru-1TA/SiO_2)-600 catalysts.

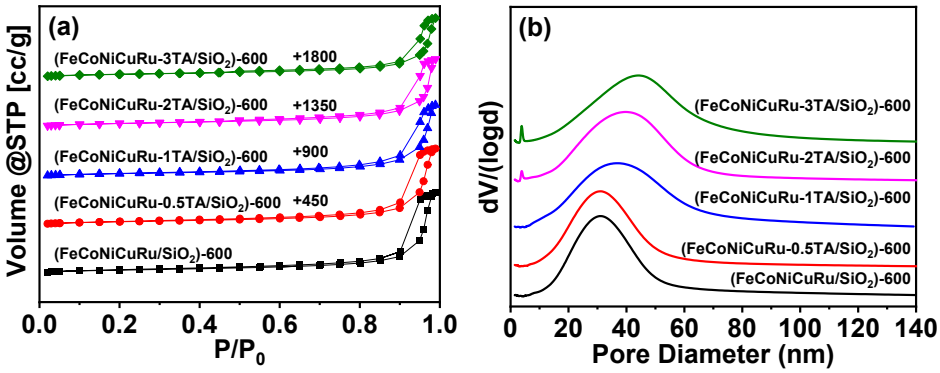
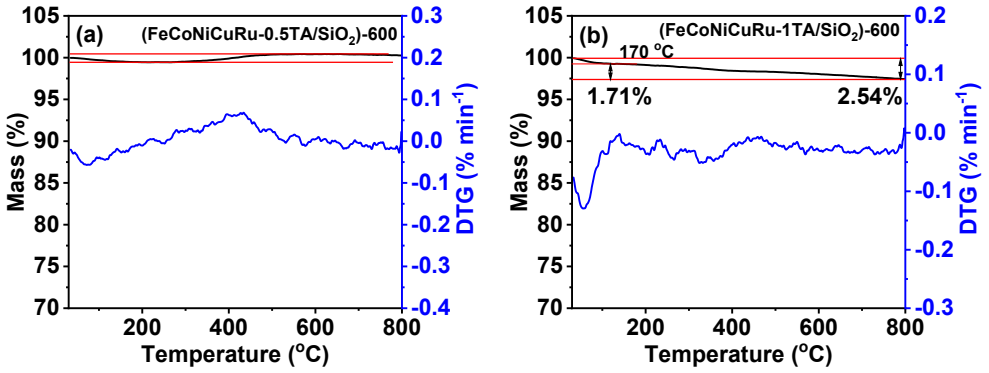


Figure S7. Nitrogen adsorption isotherms (a) and pore sizes (b) of (FeCoNiCuRu-xTA/SiO_2)-600 catalysts.



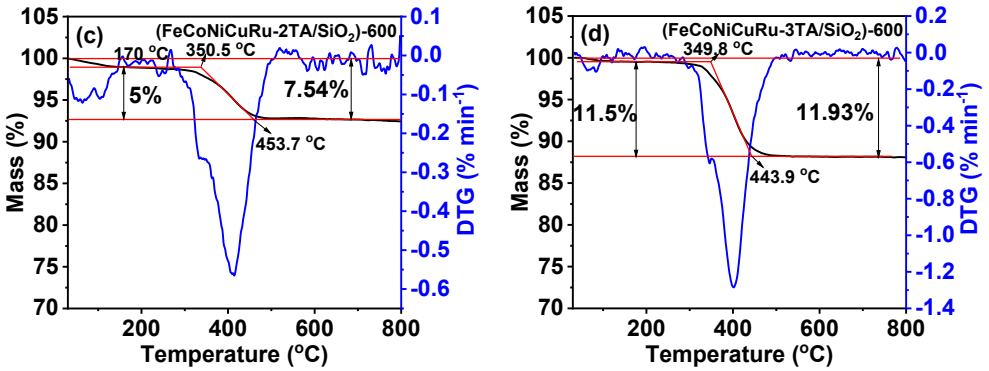


Figure S8. TG and DTG curves of (FeCoNiCuRu-0.5TA/SiO_2)-600 (a), (FeCoNiCuRu-1TA/SiO_2)-600 (b), (FeCoNiCuRu-2TA/SiO_2)-600 (c) and (FeCoNiCuRu-3TA/SiO_2)-600 (d) catalysts in air.

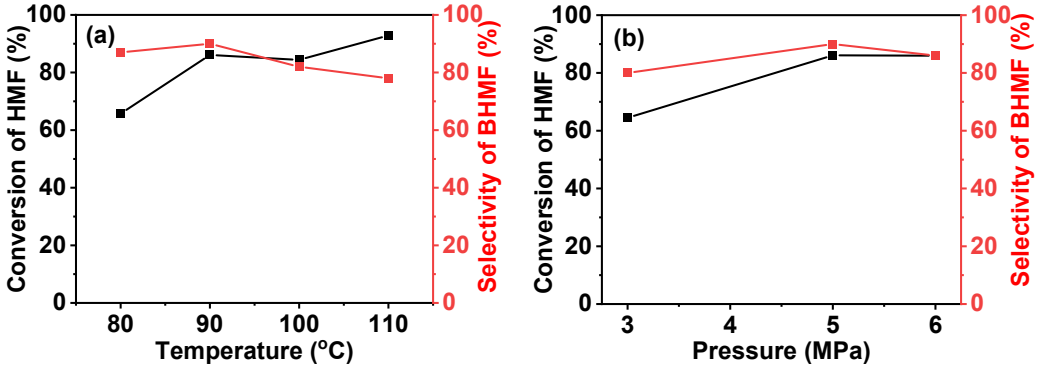


Figure S9. Hydrogenation of 5-hydroxymethylfurfural on the (FeCoNiCuRu-2TA/SiO_2)-600 in different reaction temperature (a) and different H_2 pressure (b). Reaction conditions: CH_3OH 25 mL, 0.25 g HMF, reaction time 2 h, $m_{substrate}/m_{catalyst}$= 50, 800 rpm.

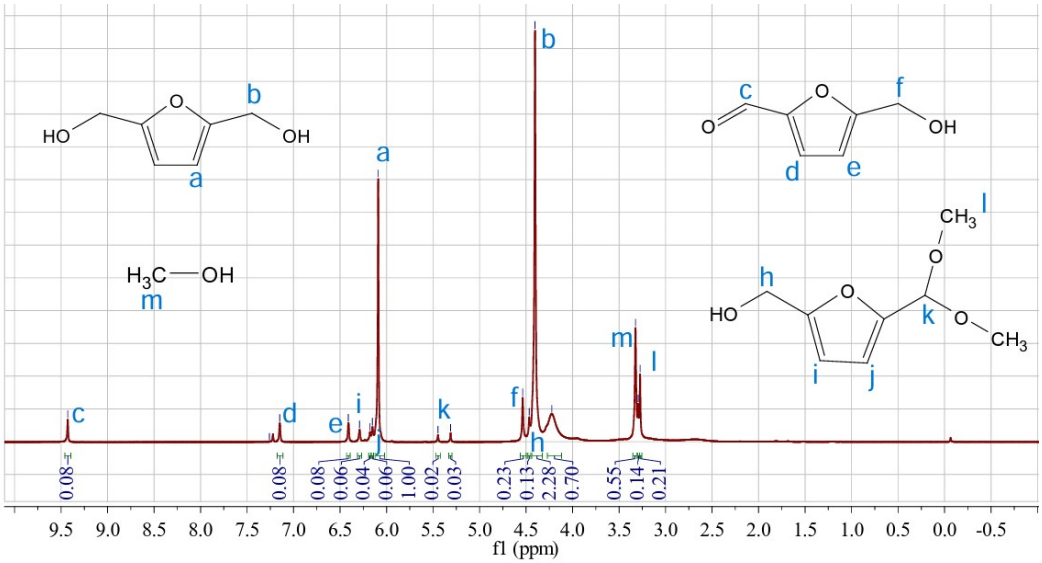


Figure S10. The NMR spectra of the HMF hydrogenation product mixture in the presence of the (FeCoNiCuRu-2TA/SiO_2)-600 catalyst (600 M, $CDCl_3$).

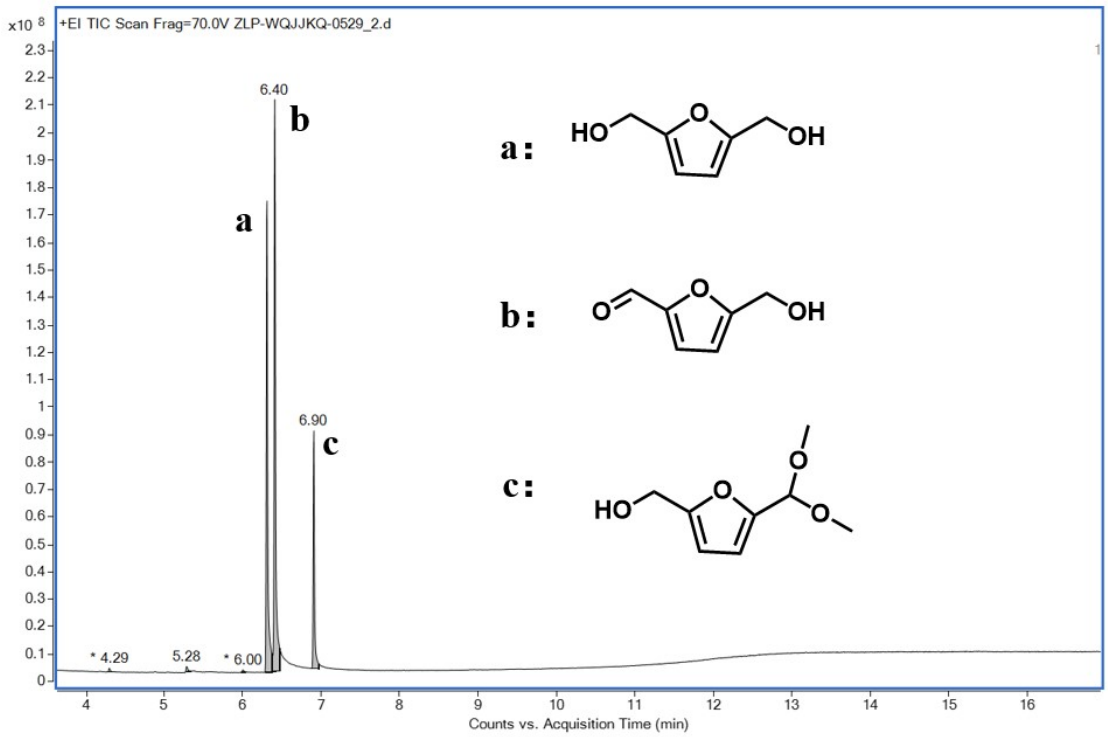


Figure S11. The TIC of the HMF hydrogenation product mixture in the presence of the (FeCoNiCuRu-3TA/SiO_2)-600 catalyst.

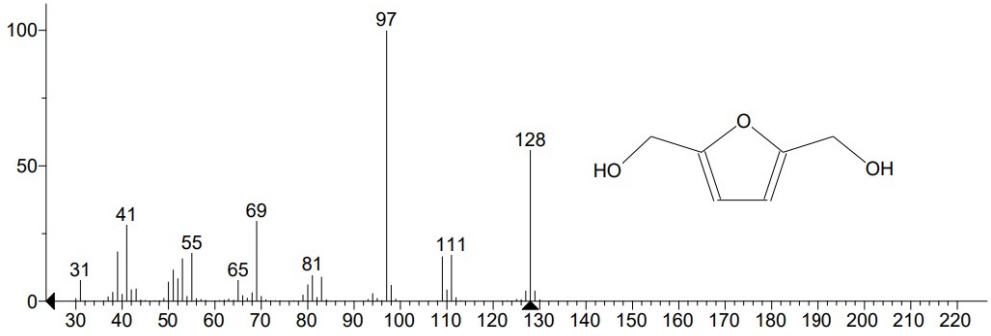


Figure S12. The mass spectrum of substance at 6.30 min in TIC .

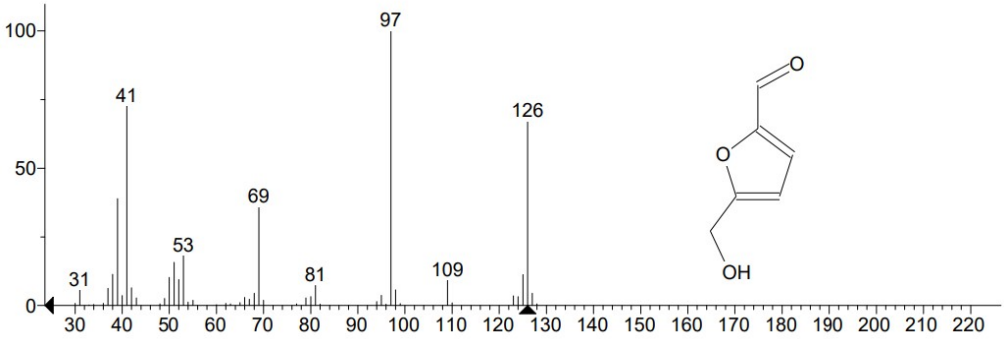


Figure S13. The mass spectrum of substance at 6.40 min in TIC.

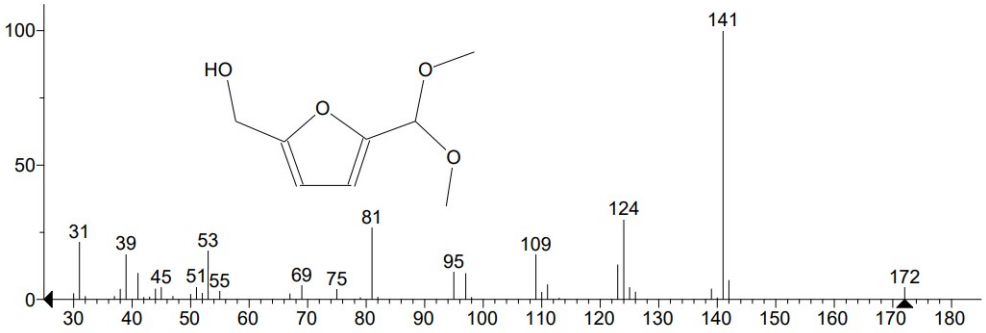


Figure S14. The mass spectrum of substance at 6.90 min in TIC.

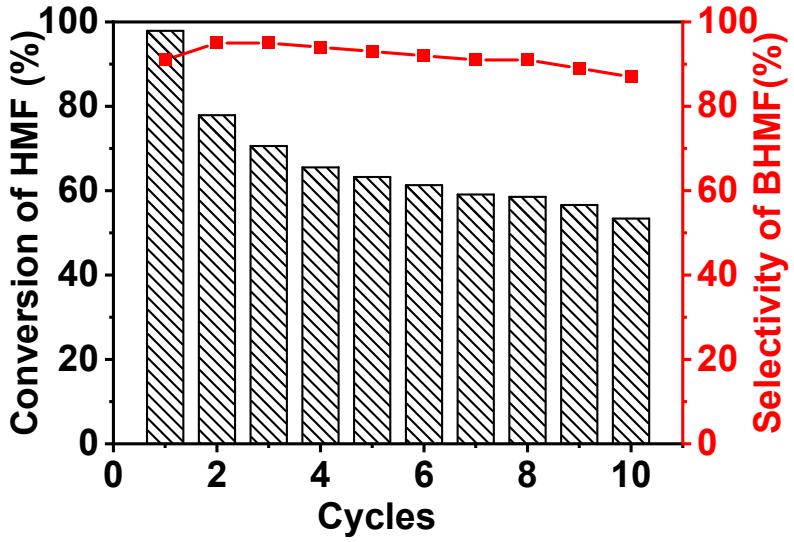


Figure S15. The cyclic stability of (FeCoNiCuRu-2TA/SiO_2)-600 in the hydrogenation of 5-hydroxymethylfurfural. Reaction conditions: 90 °C, 5 MPa H_2, CH_3OH 25 mL, 0.25 g HMF, reaction time 2 h, $m_{substrate}/m_{catalyst}$= 25, 800 rpm.

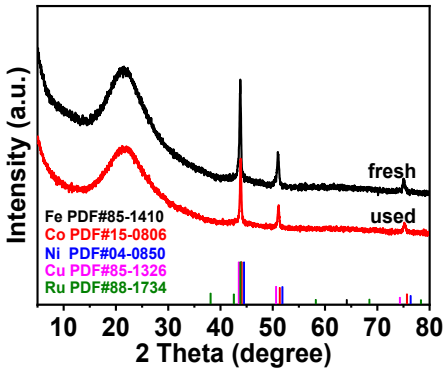


Figure S16. XRD patterns of fresh and used (FeCoNiCuRu-2TA/SiO_2)-600 catalyst.

Table S1. Thermodynamic parameters of the FeCoNiCuRu HEAs.

Parameter (unit)	Value
δ (%)	3.3
ΔS_{mix} (J/mol*K)	13.27
ΔH_{mix} (kJ/mol)	3.61
Ω	6.66
VEC_{mix}	9.34

Table S2. Binding energy of Fe, Co, Ni, Cu and Ru in (FeCoNiCuRu-2TA/SiO_2)-600, (Fe-1TA/SiO_2)-600, (Co-1TA/SiO_2)-600, (Ni-1TA/SiO_2)-600, (Cu-1TA/SiO_2)-600 and (Ru-1TA/SiO_2)-600 catalysts.

Samples	Binding energy /eV				
	Fe^0	Co^0	Ni^0	Cu^0	Ru^0
(Fe-1TA/SiO_2)-600	706.6	-	-	-	-
(Co-1TA/SiO_2)-600	-	781.5	-	-	-
(Ni-1TA/SiO_2)-600	-	-	855.6	-	-
(Cu-1TA/SiO_2)-600	-	-	-	933.0	-
(Ru-1TA/SiO_2)-600	-	-	-	-	461.8

Table S3. Physical properties of (FeCoNiCuRu-xTA/SiO_2)-600 catalysts.

Samples	S.A.(m^2/g)	P.V. (cm^3/g)	P.D. (nm) [a]
(FeCoNiCuRu/SiO_2)-600	139	1.12	31.0
(FeCoNiCuRu-0.5TA/SiO_2)-600	135	1.08	31.0
(FeCoNiCuRu-1TA/SiO_2)-600	125	0.95	45.8
(FeCoNiCuRu-2TA/SiO_2)-600	167	0.94	46.0
(FeCoNiCuRu-3TA/SiO_2)-600	186	0.79	46.2

Note: a pore diameter calculated by the desorption branches of the isotherms using the BJH method.

Table S4. Elemental analysis of fresh and used (FeCoNiCuRu-2TA/SiO_2)-600 catalyst.

Sample	Fe (wt%)	Co (wt%)	Ni (wt%)	Cu (wt%)	Ru (wt%)
(FeCoNiCuRu-2TA/SiO_2)-600-fresh	0.98	0.95	1.00	1.07	0.90

Sample	Fe (wt%)	Co (wt%)	Ni (wt%)	Cu (wt%)	Ru (wt%)
(FeCoNiCuRu-2TA/SiO_2)-600-used	0.83	0.73	0.80	0.62	0.80