Supporting Information

$MnCo_2O_4$ Spinels Supported Ruthenium Catalyst for Air-Oxidation of HMF to FDCA under Aqueous Phase and Base-Free Conditions

Dinesh Kumar Mishra,[a] Hye Jin Lee,[b] Jinsung Kim,[c] Hong-Shik Lee,[a] Jin Ku Cho,[a,b] Young-Woong Suh[c] and Yong Jin Kim[a,b,*]

[a]Green Process Material Research Group, Korea Institute of Industrial Technology (KITECH), 89, Yangdaegiro-gil, Ipjang myeon, Cheonan-si 331-822, Republic of Korea.

[b]University of Science and Technology (UST), 176 Gajeong-dong, 305-350, Yuseong-gu, Daejeon, Republic of Korea.

[c]Department of Chemical Engineering, Hanyang University, Seoul 133-791, Republic of Korea

[*]Corresponding author- E-mail (Yong Jin Kim): yjkim@kitech.re.kr,

Phone: +82 41 5898469; Fax: +82 41 5898580

Experimental Section

Materials

All chemical reagents were used as received without any further purification. Commercially available cobalt(II) acetate tetrahydrate $(CH_3COO)_2Co.4H_2O$, manganese(II) acetate tetrahydrate $(CH_3COO)_2Mn.4H_2O$, ammonium sulphate $(NH_4)_2SO_4$, ammonium bicarbonate (NH_4HCO_3), and sodium borohydride ($NaBH_4$) were purchased from Sigma Aldrich. During the preparation of support and its corresponding ruthenium catalyst, deionized water was used.

Synthesis of manganese-cobalt oxides spinels supports

In a typical synthesis of $MnCo_2O_4$ spinels microsphere,[1] $(CH_3COO)_2Mn.4H_2O$ (32.6 mmol) and $(CH_3COO)_2Co.4H_2O$ (65.3 mmol) (Mn:Co= 1:2) were dissolved in water (400 mL) and allowed to homogenize by vigorous stirring for 30 min. Separately, ammonium sulfate (50 g) was dissolved in water (400 mL). These solutions were mixed slowly and stirred for 4 h. Then, an aqueous solution of ammonium bicarbonate (~50g) was added slowly to above mixture and stirred for 6 h. The light pink precipitate obtained was collected by filtration, washed thoroughly with distilled water, absolute ethanol, and dried at 60 ^oC for 12 h. The obtained carbonate precursor was calcined in a furnace at 425 ^oC (2 ^oC min^{-1}) in air for 8 h and kept for an additional 8 h, followed by cooling naturally to room temperature. For the synthesis of $CoMn_2O_4$, the procedures were performed in a similar way with molar ratio (Mn:Co= 2:1) of Mn and Co.

Synthesis of manganese-cobalt oxides spinels supported ruthenium nanoparticles catalyst

Spinels manganese-cobalt oxides spinels supported ruthenium nanoparticles catalyst, Ru/$MnCo_2O_4$, is prepared by using simple impregnation–reduction method as reported in the literatures.[2] To support Ru (4% by weight) on manganese-cobalt based spinels, 5.0 g of manganese-cobalt based spinels ($MnCo_2O_4$) and $RuCl_3 \cdot 3H_2O$ (0.429g) were placed together in a two neck 100 mL round bottom flask containing ~20 mL water, which was submerged in cooling bath. The resulting mixture was stirred under an N_2 atmosphere for a period of 12 h. Then, aqueous solution of $NaBH_4$ (10 times higher than $RuCl_3 \cdot 3H_2O$) was added drop wise to reaction mixture with constant stirring, and entire reaction mass was stirred (500 rpm) under N_2 atmosphere for a day at room temperature. Ru(III) was reduced and the Ru(0) nanoparticles were formed. Finally, catalyst was separated by filtration, washed with ethanol and dried under vacuum to give dark black manganese-cobalt oxides spinels supported ruthenium nanoparticles. Aforementioned method was used to load ruthenium (4% by weight) on different supports in preparation of different supported ruthenium catalysts.

Characterization

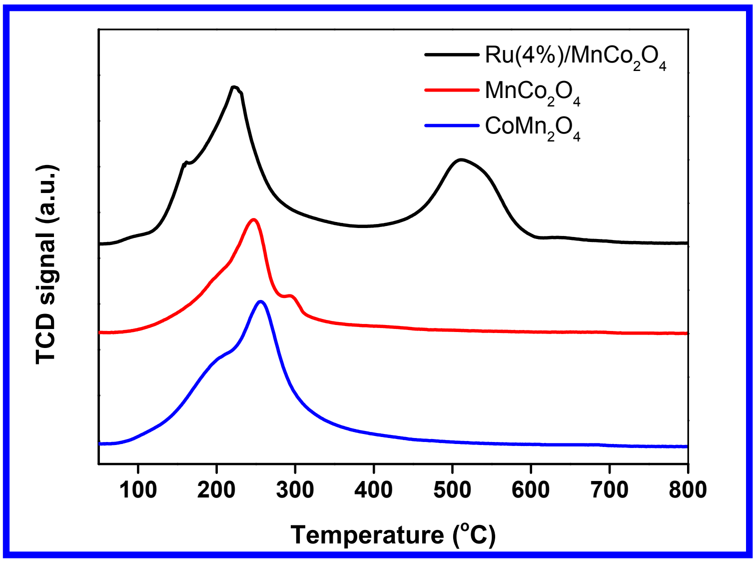

Figure S1:

NH_3-TPD of $CoMn_2O_4$, $MnCo_2O_4$ and Ru(4%)/$MnCo_2O_4$.

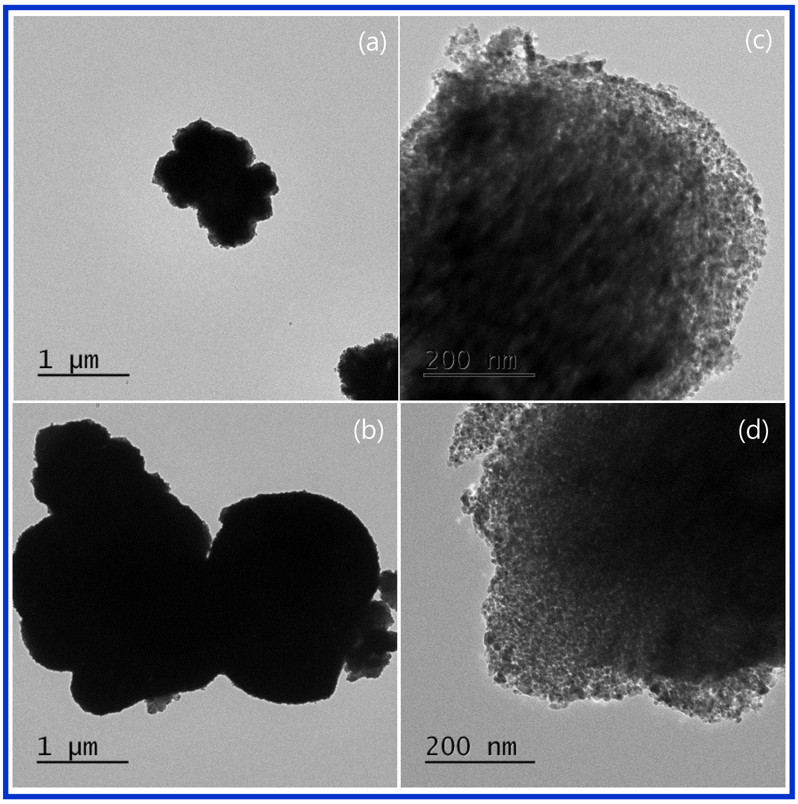

Figure S2:

TEM images of $CoMn_2O_4$ microspheres-(a), $MnCoO_4$ microspheres-(b), high magnification TEM images of $CoMn_2O_4$ microspheres-(c), and $MnCo_2O_4$ microspheres -(d).

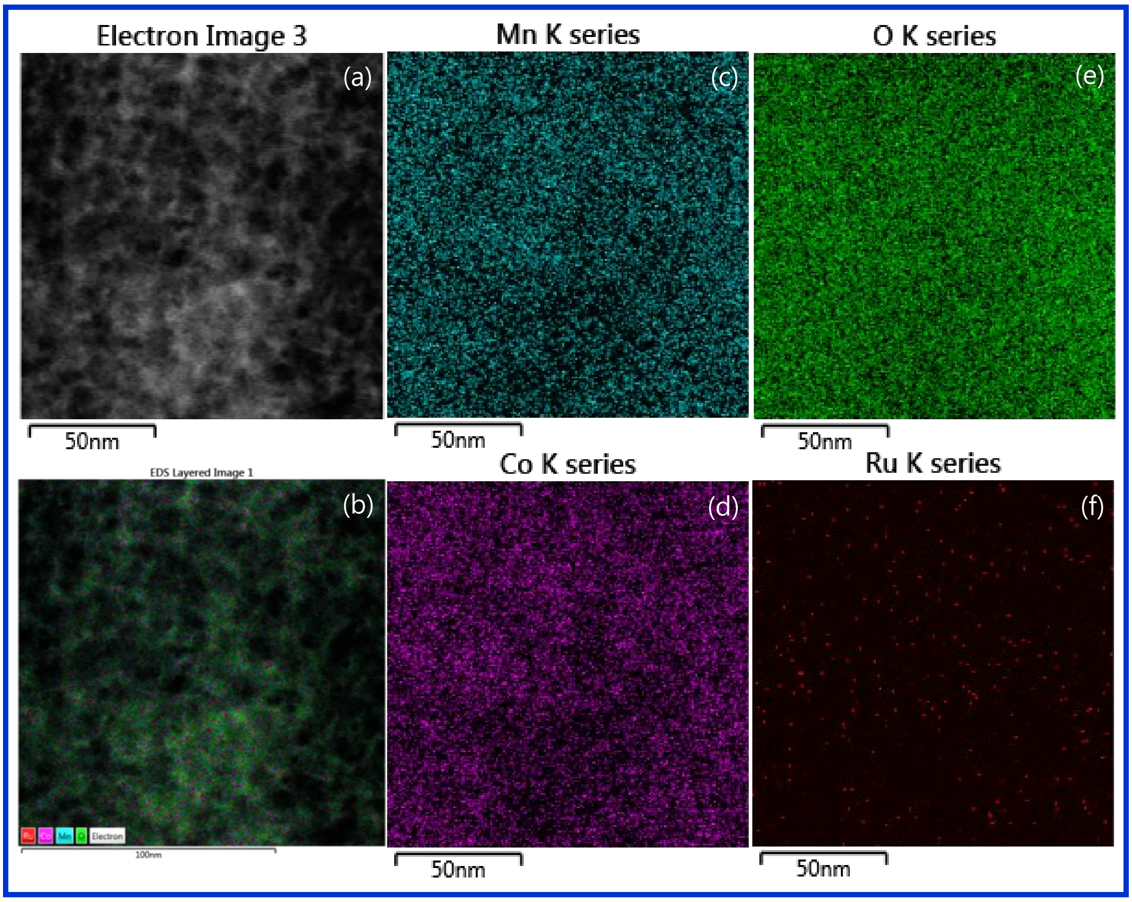

Figure S3:

TEM image of Ru(4%)/$MnCo_2O_4$ (a), and elementals mapping layered image (b), Mn (c), Co (d), O (e), and Ru (f).

X-ray photoelectron spectroscopy

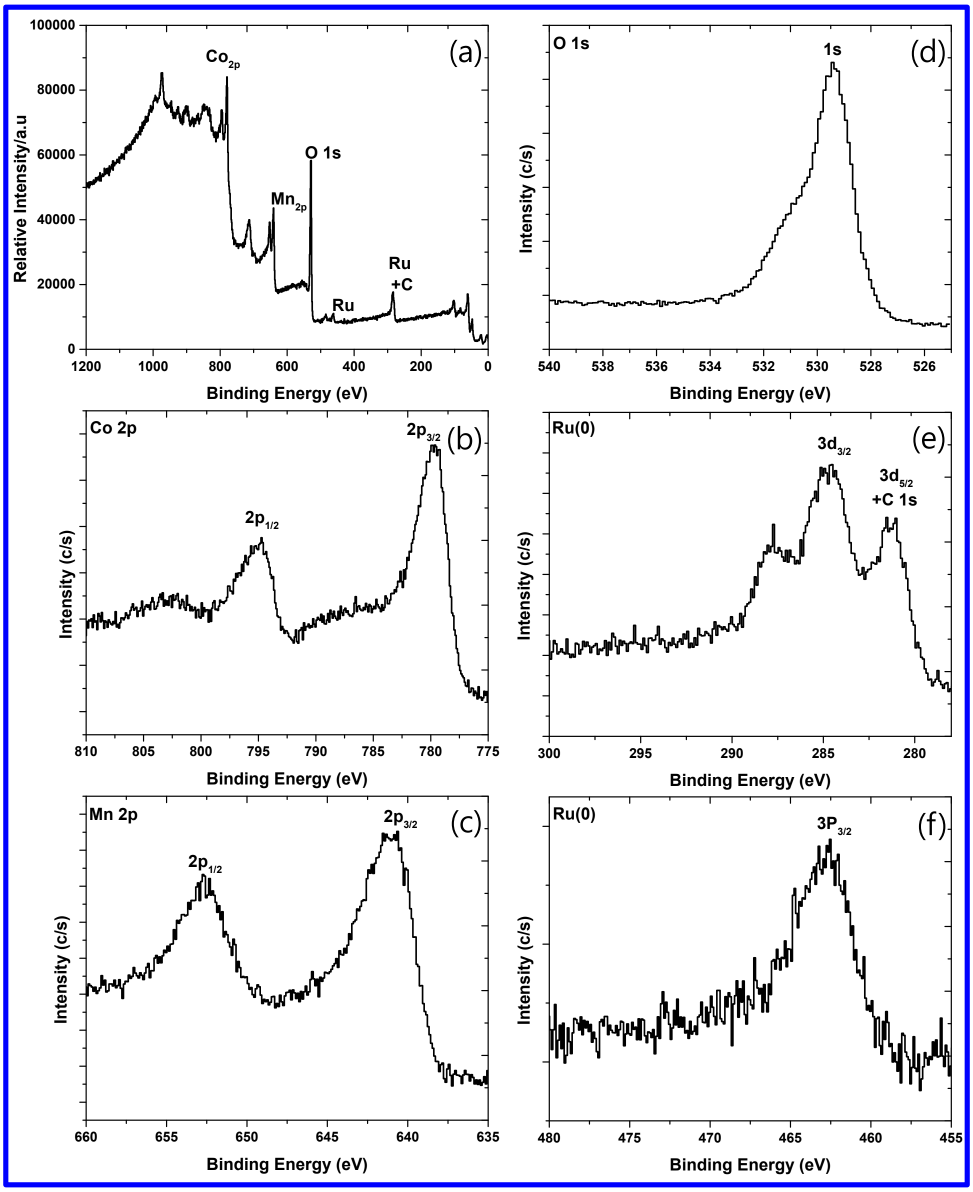

Figure S4:

XPS spectra of the Ru(4%)/MnCo$_2$O$_4$: Survey spectrum-(a), Co 2P-(b), Mn 2P-(c), O 1s-(d), Ru 3d-(e), and Ru 3p-(f).

X-ray diffraction

XRD patterns of manganese-cobalt based spinels ($MnCo_2O_4$) and its carbonate precursor ($MnCo_2CO_3$), are displayed in figure S3. It states that the diffraction peaks could be indexed to well-crystallized $MnCo_2O_4$ (JCPDS no. 23-1237) with cubic spinel structure in which manganese and cobalt are distributed over both octahedral and tetrahedral sites as well described by Menezes et al. On comparing the XRD patterns of manganese-cobalt based spinels ($MnCo_2O_4$) and its carbonate precursor ($MnCo_2CO_3$), there are additional peaks appeared in XRD pattern of carbonate precursor (as given in Figure S2) (JCPDS 11-692).[1, 3] The disappearance of those additional peaks from cobalt-manganese based spinels ($MnCo_2O_4$) indicates that its carbonate precursor is successfully converted in to the manganese-cobalt based spinels, $MnCo_2O_4$.

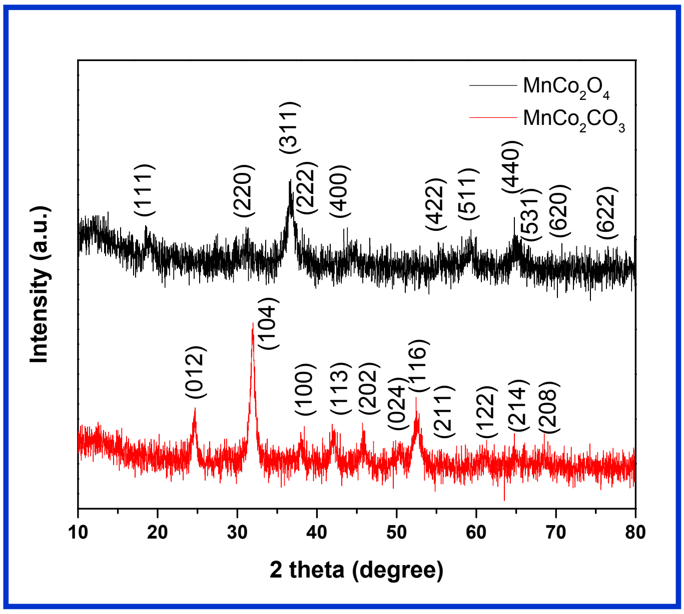

Figure-S5:

Typical XRD patterns of manganese-cobalt based spinels $MnCo_2O_4$ and its precursor $MnCo_2CO_3$.

Figure S6:

Obtained solid of $MnCo_2CO_3$ precursor (pink) and $MnCo_2O_4$ (Black).

Synthesis of $MgAl_2O_4$-manganese based spinels microspheres

In a typical synthesis, an aqueous solution (30 mL) of magnesium nitrate (4 g, 15.6 mmol) was added to another aqueous solution (60 mL) of aluminum nitrate (11.8 g, 31.2 mmol). The mixture was allowed to stir for 10 min. A stoichiometric amount of citric acid was added to above mixture under stirring conditions, and after complete mixing, a homogenous solution was achieved. These solution were slowly evaporated until a highly viscous colloid was formed, which was then heated in 140 °C under vacuum for 24 h to get a dried gel. Finally, the dried gel precursor was calcined at 600 ^{o}C temperature to obtain $MgAl_2O_4$ powder.

Purification of FDCA from product mixture

After reaction, catalyst was separated by simple filtration method. Then, the product solution was concentrated by evaporating water using rotary evaporator. To the residue of concentrated product solution, required amount of ammonia solution was added. Other solid impurities were observed with ammonium salt solution of FDCA which were separated by filtration. To the clear salt solution of FDCA, excess amount of HCl was then added slowly. FDCA was precipitated as white solid crystal when HCl was added. The solid FDCA was obtained by filtration, washed, and then dried under vacuum.

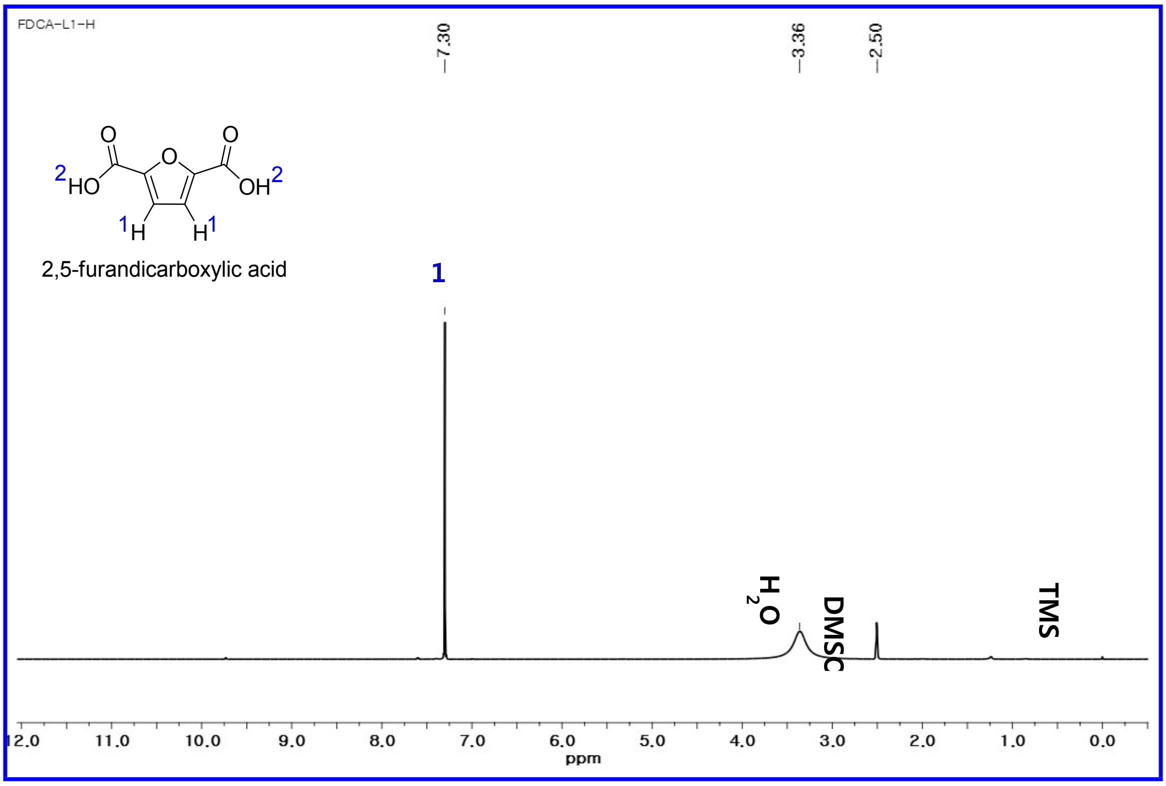

Figure-S7:

^{1}H-NMR spectrum of purified FDCA-product obtained from HMF oxidation.

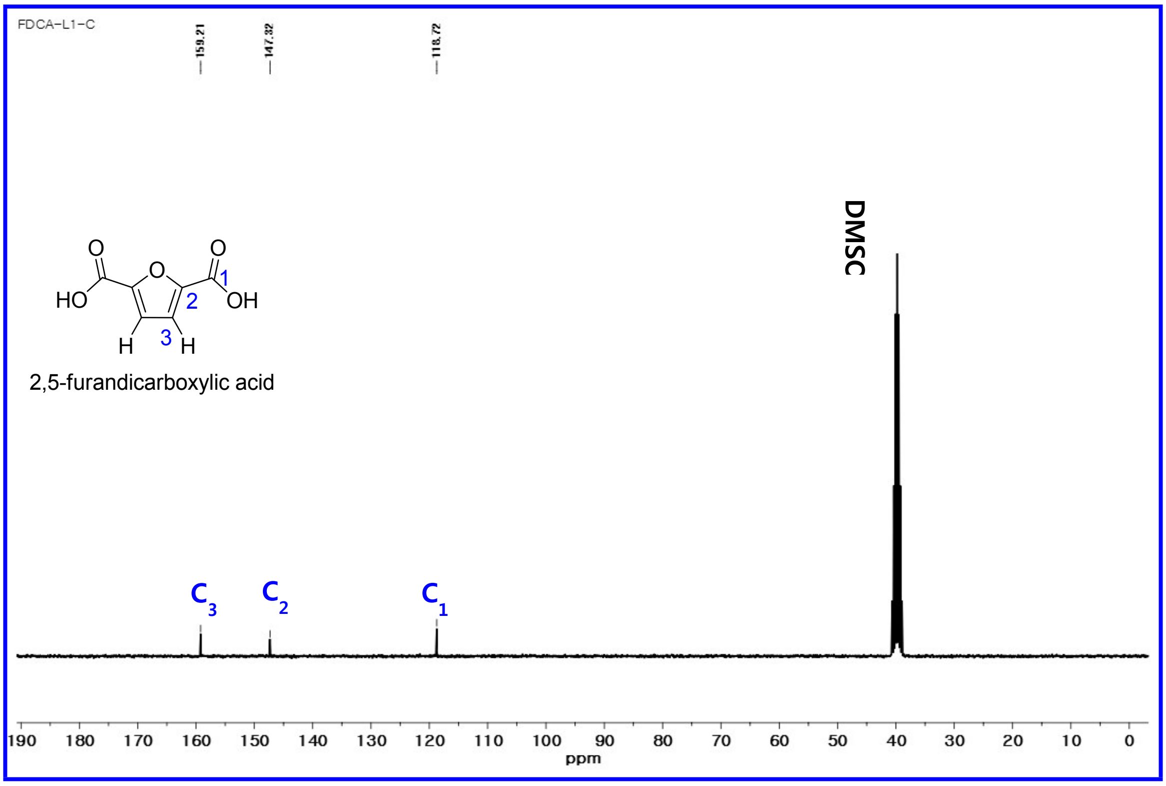

Figure-S8:

^{13}C-NMR of purified FDCA-product obtained from HMF oxidation.

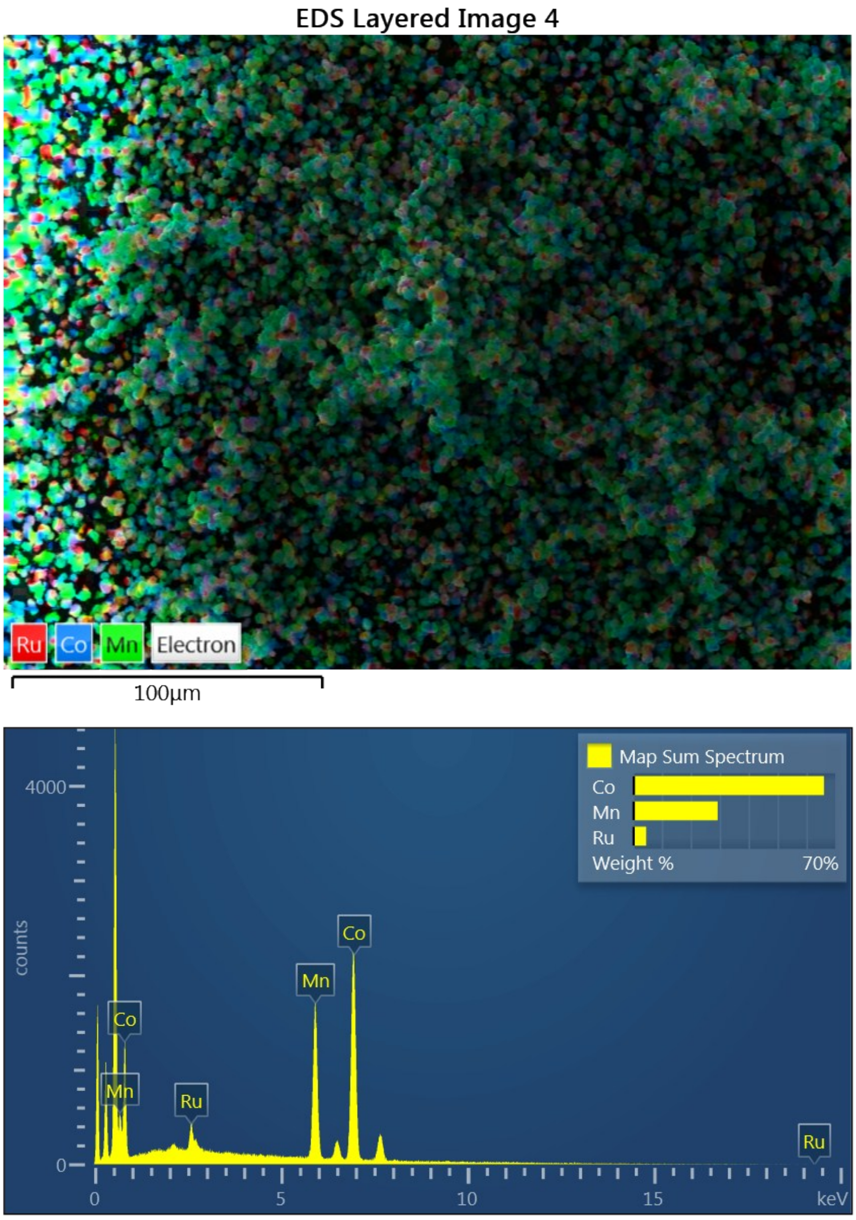

Figure S9:

SEM-EDS mapping image and EDS spectrum of Ru(4%)/MnCo$_2$O$_4$.

Table-S1:

Determination of cobalt and manganese ratio in mixed manganese-cobalt oxides with and without ruthenium.

Sample	Ru(%) **(EDS)**	Co:Mn ratio **(Theoretical)**	Co:Mn ratio **(EDS)**	Co:Mn ratio **(ICP-AES)**
Ru(4%)/$MnCo_2O_4$	3.9	2.0:1.0	2.3:1.0	-
$MnCo_2O_4$	-	2.0:1.0	2.0:1.0	2.0:1.1
$CoMn_2O_4$	-	1.0:2.0	1.0:2.1	1.0:2.1
$MnCo_2CO_3$	-	2.0:1.0	2.0:0.9	2.0:1.0
$CoMn_2CO_3$	-	1.0:2.0	1.1:2.0	1.0:2.1

Table-S2:

Summarized data obtained from NH_3-TPD.

Sample code	Lewis acid sites (mmol.g^{-1})	Brønsted acid sites (mmol.g^{-1})	Total acid sites (mmol.g^{-1})
Ru(4%)/$MnCo_2O_4$	7.3	10.7	18.0
$MnCo_2O_4$	-	8.2	8.2
$CoMn_2O_4$	-	11.7	11.7

[a] Determined by NH_3-TPD.

Table-S3:

Textural properties of different supported Ru catalysts, $MnCo_2O_4$, and $CoMn_2O_4$.

Sample	SA_{BET} [a] (m^2/g)	Total pore volume ($p/p_0=0.990$) (cm^3/g) [a]	Mean pore diameter (nm) [a]	Ru dispersion (%) [b]	Ru particle size [b] (nm)
Ru(4%)/$MnCo_2O_4$	135.4	0.3082	9.1	39.2	3.4
Ru(4%)/$CoMn_2O_4$	-	-	-	26.9	5.0
Ru(4%)/MnO_2	-	-	-	25.9	5.1
Ru(4%)/CoO	-	-	-	20.8	6.4
$MnCo_2O_4$	151.1	0.2977	7.8	-	
$CoMn_2O_4$	89.5	0.2978	13.3	-	

[a] BET method, [b]Obtained from CO-Chemisoprtion.

Table-S4:

Concentration (PPM= mg/L) of Ru element in products samples determined by ICP.

Element	Run-1 (mg/L)	Run-2 (mg/L)	Run-3 (mg/L)	Run-4 (mg/L)	Run-5 (mg/L)
Ru	0.0	0.0	0.0	0.0	0.0

References:

1. P. W. Menezes, A. Indra, N. R. Sahraie, A. Bergmann, P. Strasser and M. Driess, *ChemSusChem*, 2015, **8**, 164-171.
2. D. K. Mishra, A. A. Dabbawala and J.-S. Hwang, *Journal of Molecular Catalysis A: Chemical*, 2013, **376**, 63-70.
3. S. Ma, L. Sun, L. Cong, X. Gao, C. Yao, X. Guo, L. Tai, P. Mei, Y. Zeng, H. Xie and R. Wang, *The Journal of Physical Chemistry C*, 2013, **117**, 25890-25897.