

Highly Active and Stable Ru-(OH)-based Catalysts Supported on Ni-Manganite for the Base-free Aerobic Oxidation of 5-Hydroxymethyl Furfural to 2,5-Furan Dicarboxylic Acid in a Noble Water–organic Solvent System

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1. Experimental

1.1. Characterizations

The bulk phase and crystal structure of the synthesized catalysts were characterized by X-ray diffraction (XRD) with a scanning range of 10° – 80° and a scanning rate of $2^{\circ} \text{ min}^{-1}$. The XRD analysis was performed using a Rigaku Ultima IV X-ray diffractometer (Rigaku, Japan) with a Cu K α radiation beam ($\lambda = 0.15418 \text{ nm}$) operated at 45 kV and 200 mA. The surface areas of the catalysts were determined using an ASAP 2420 apparatus (Micromeritics, USA). The samples were degassed prior to analysis for 30 min at 90°C , followed by constant heating at 300°C for 4 h.

The surface species of the catalysts were characterized in *ex situ* condition using high-resolution X-ray photoelectron spectroscopy (XPS) (Axis Supra, Kratos Analytical Ltd, UK) equipped with a monochromatic Al K α source (1486.7 eV). The binding energy of the C_{1s} bond (284.8 eV) was used as a reference for peak assignment. The catalyst was reduced in the H₂ environment at 460°C for 4 h and sealed in a glass vial prior to analysis.

Temperature-programmed reduction (TPR) was performed to observe the reduction behavior of the metals. The analysis was performed using Micromeritics AutoChem II 2920 (USA) equipped with a thermal conductivity detector at a heating rate of $3^{\circ} \text{C min}^{-1}$ in a 10% H₂/Ar atmosphere (flow rate = 50 mL min^{-1}).

The CO-chemisorption analysis was performed using Micromeritics AutoChem II 2920 (USA). Before the CO adsorption, catalysts were reduced under H₂/Ar flow at 200°C (473 K) for 60 min. followed by purging with helium for 30 min. The stoichiometry for adsorption of CO on surface metal atoms was assumed to be 1:1. For CO chemisorption experiment, the sample (~100 mg) was pretreated with hydrogen at 200°C (473 K) for 60 min, followed by purging with high-

purity helium for 30 min. After the sample was cooled down to 50 °C, a 5% CO/He mixture was injected into the reactor repeatedly until CO adsorption was saturated.

The dispersion of Ru was calculated from the amount of CO adsorbed by assuming the CO: Ru adsorption stoichiometry to be 1:1.

An O₂-TPD process was performed on a Micromeritics Autochem II Chemisorption analyzer. Before analysis, the sample was pretreated for 30 minutes with helium at 200 °C. Then the sample was introduced to 5% O₂/He mixture for 1 hour at 50 °C. The gas-phase O₂ was then purged with helium at 50 °C. Then the O₂ desorption was carried to 800 °C at the rate of 10 °C per minute in He flow.

X-ray absorption near-edge spectra (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were measured on the 7D beamline located at the Pohang Accelerator Laboratory (PLS-II, 3 GeV, Korea). The Ru K-edge spectra (22.117 keV) of the reduced catalyst samples were recorded at 25–27 °C in transmission mode. The energy was calibrated using a standard metal foil. The data were analyzed using the Athena and Artemis programs. The Fourier transforms of the background-subtracted data were obtained using a Hanning window in the k range of 3–12 Å with a dk of 1 Å⁻¹.

The particle distribution of the catalysts was analyzed by scanning transmission electron microscopy (STEM) coupled with energy-dispersive X-ray spectroscopy (EDS). Images were collected using a Talos F200X microscope (Talos, USA) operated at 200 keV¹⁻³.

The Bruker ALPHA-T Infrared Spectrometer (IR) and the Attenuated Total Reflectance (ATR) method of the Bruker ALPHA-P Infrared Spectrometer were used to analyze the sample. The ALPHA-T instrument had a resolution of 8 cm⁻¹, a scan time of 64 scans, and a range of 4000

cm^{-1} to 400 cm^{-1} . Similarly, the ALPHA-P instrument also had a resolution of 8 cm^{-1} , a scan time of 64 scans, and a range of 4000 cm^{-1} to 400 cm^{-1} .

2. Results & Discussion

2.1. Characterization Results

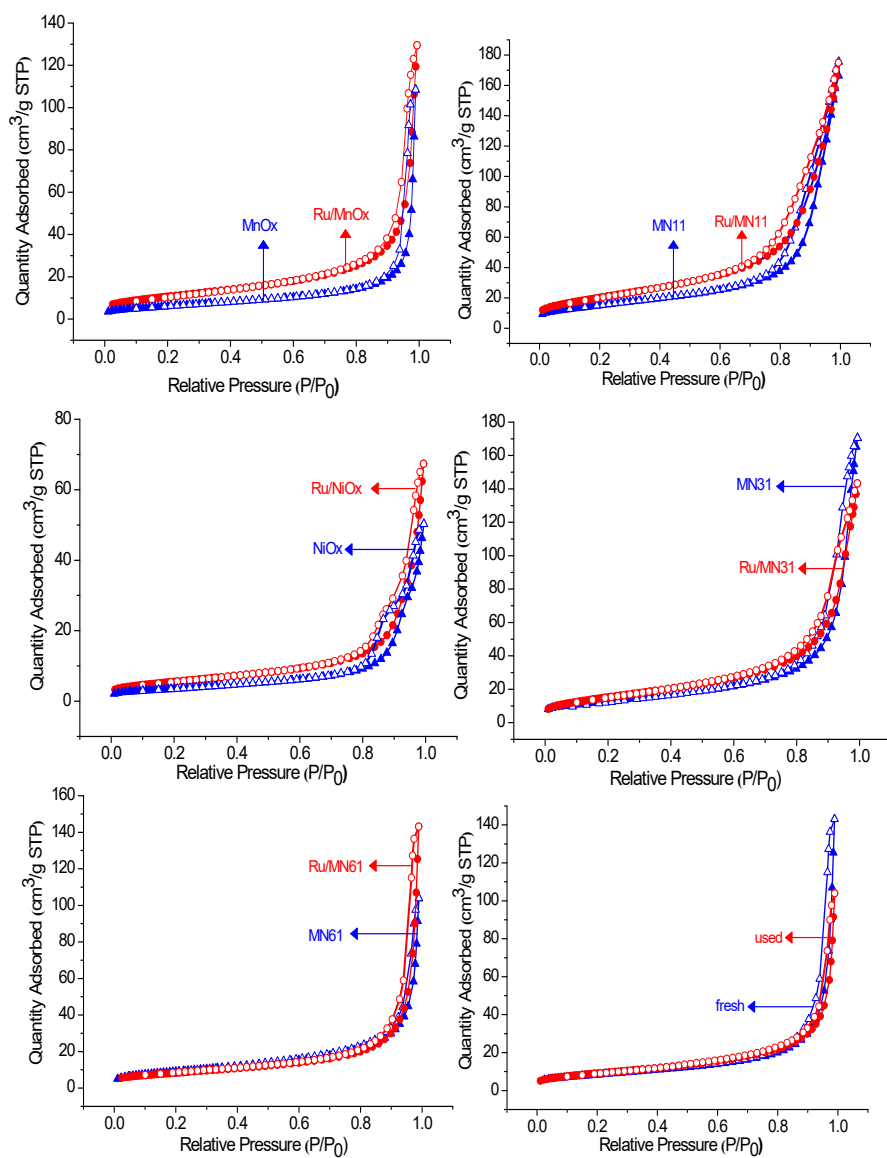
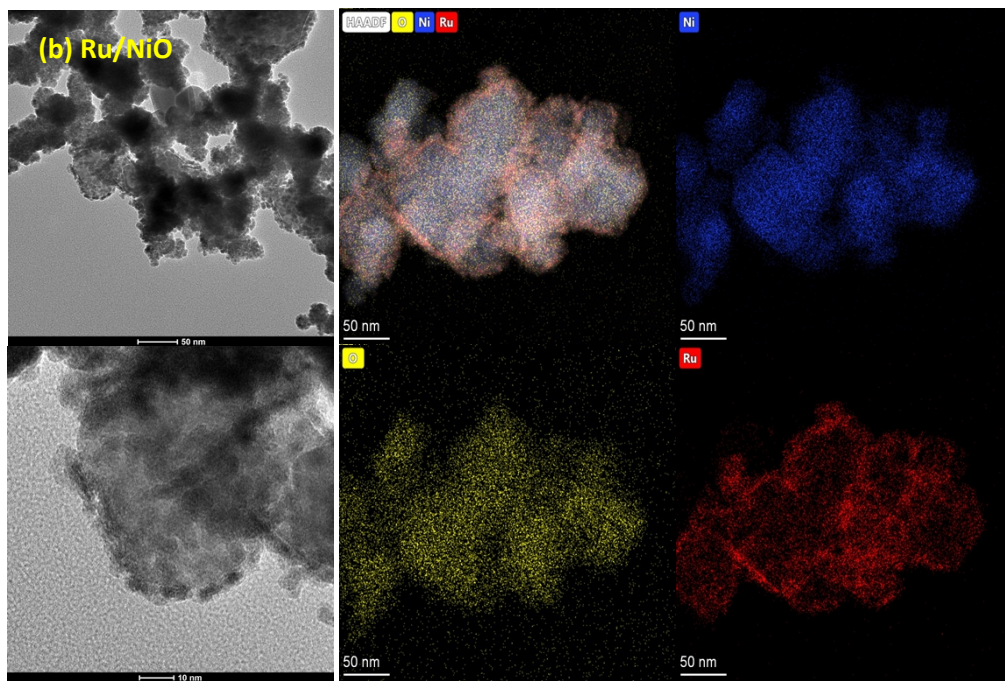
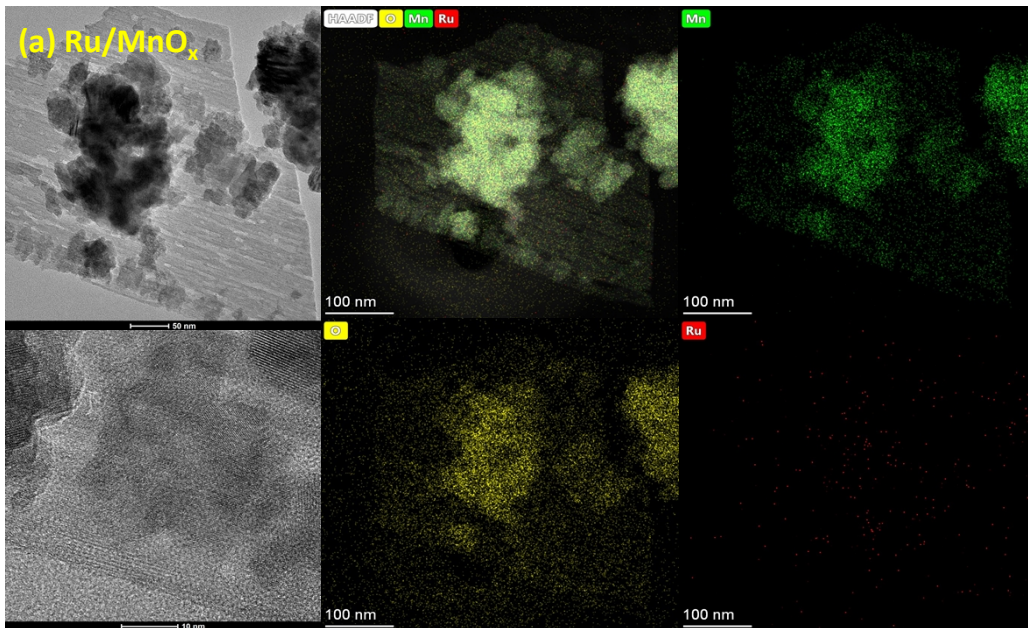


Fig. S1. N_2 -isotherms of the catalysts



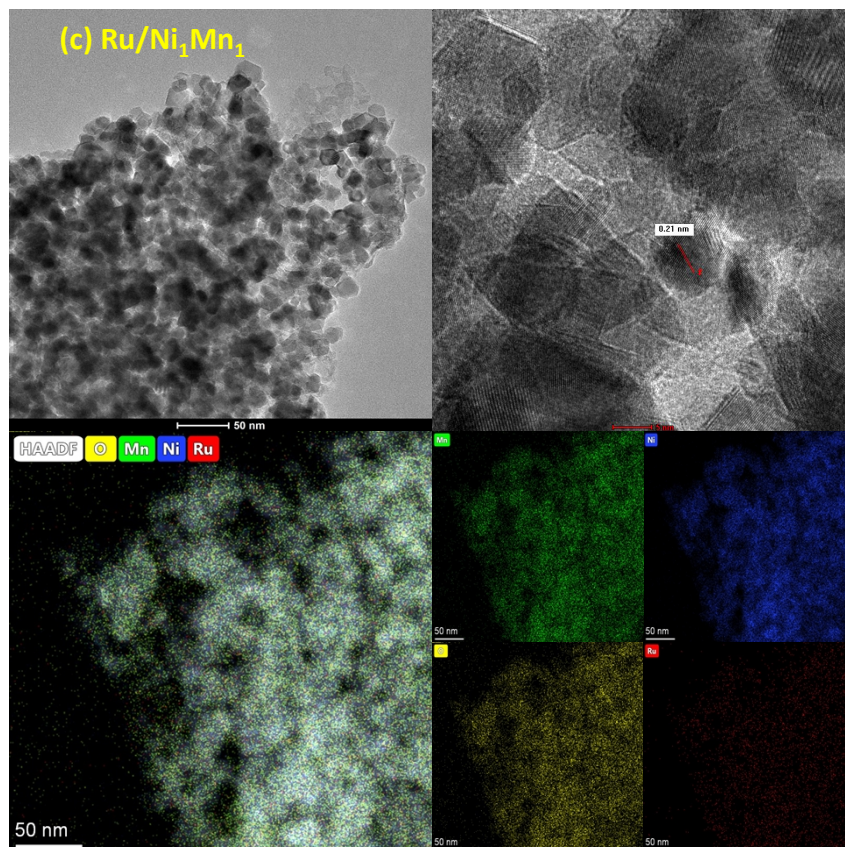


Fig. S2. TEM images and elemental distribution of (a) Ru/MnO_x, (b) Ru/NiO, and (c) Ru/Ni₁Mn₁

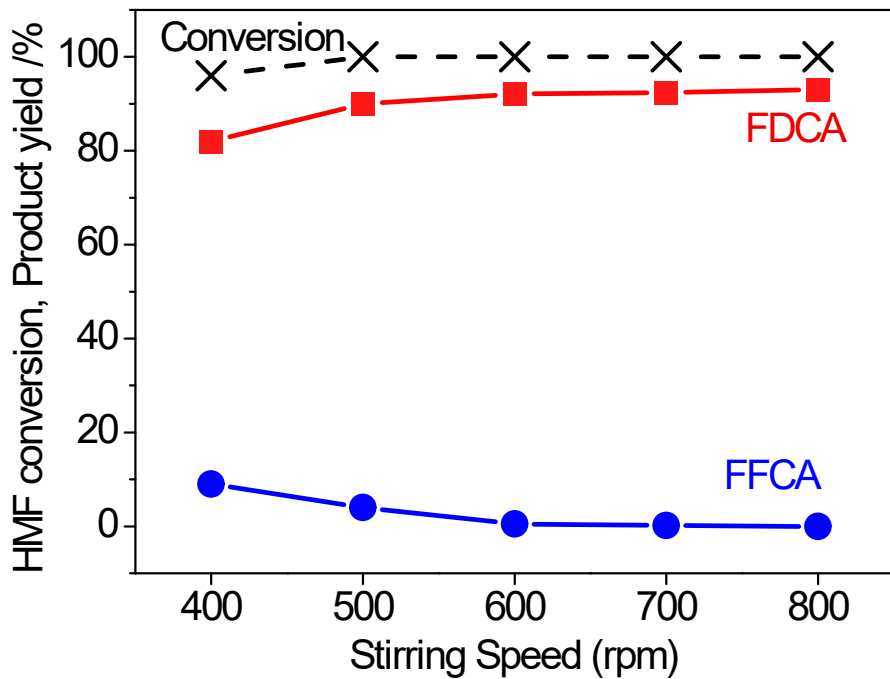


Fig. S3. Effect of stirring speed on FDCA formation. Reaction conditions: 5 wt.% HMF; water: acetone (10 g) ratio, 70:30; catalyst/HMF wt. ratio, 1.43; O₂ pressure, 10 bar; temperature, 110 °C; reaction time, 12 h.

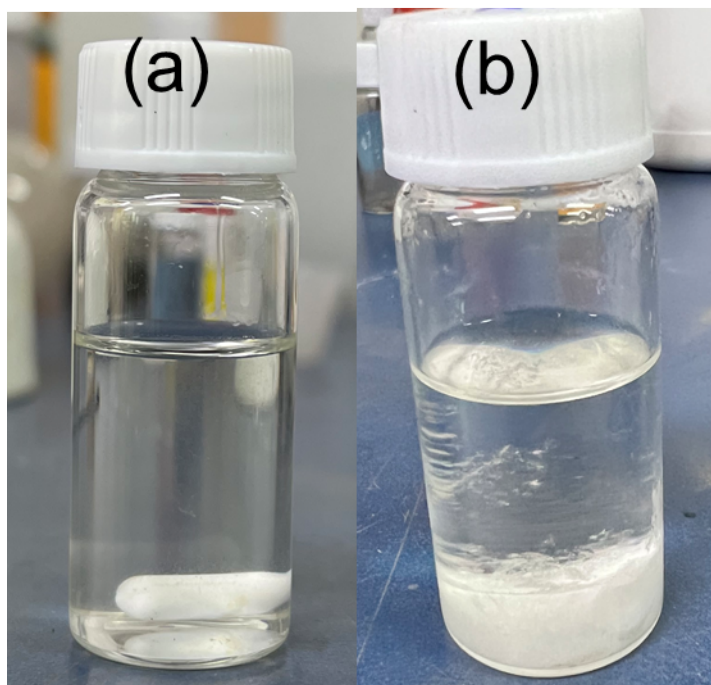


Fig. S4. (a) FDCA solubility at 110 °C, (b) Recrystallization of FDCA at 20 °C.

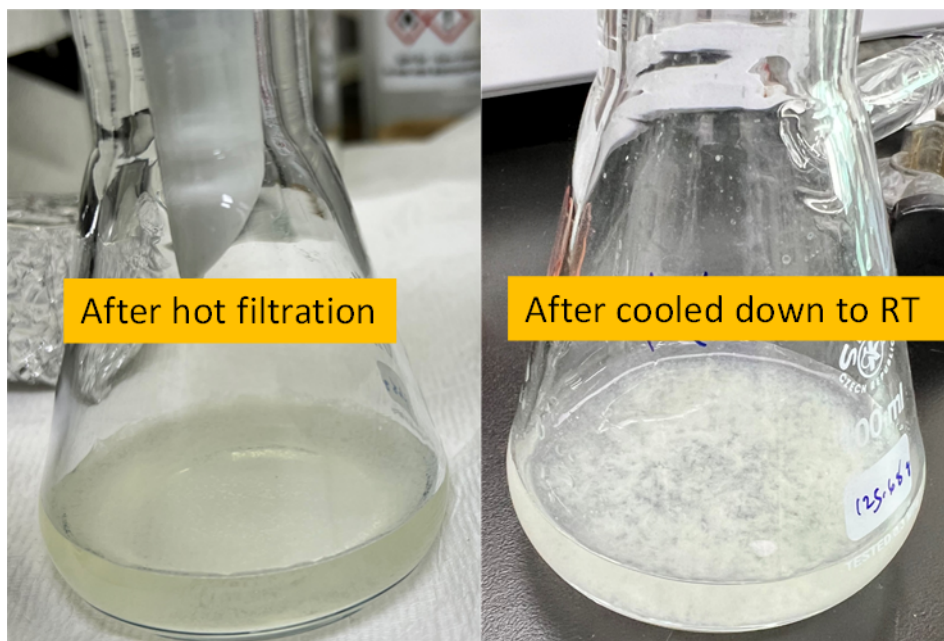


Fig. S5. Hot filtration of reaction mixture and cooled filtrate.

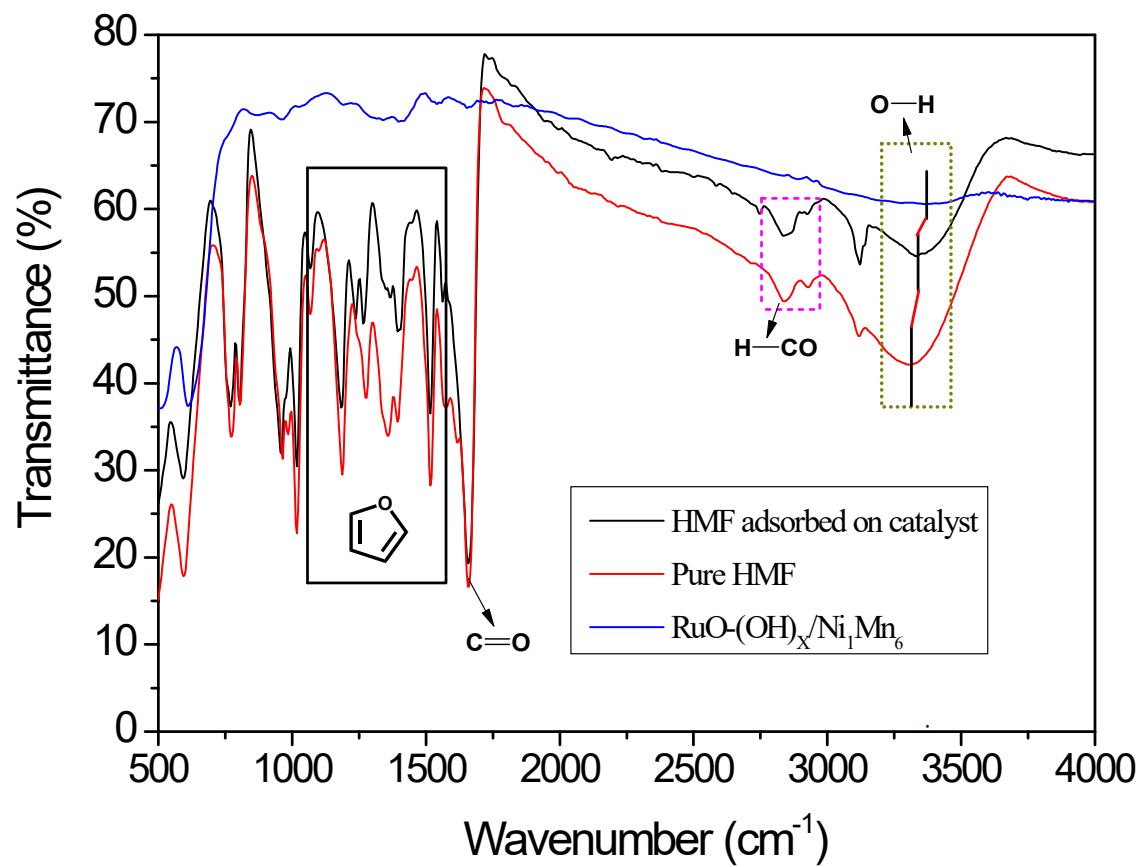


Fig. S6. FT-IR spectra of Catalyst, HMF and after adsorption on catalyst.

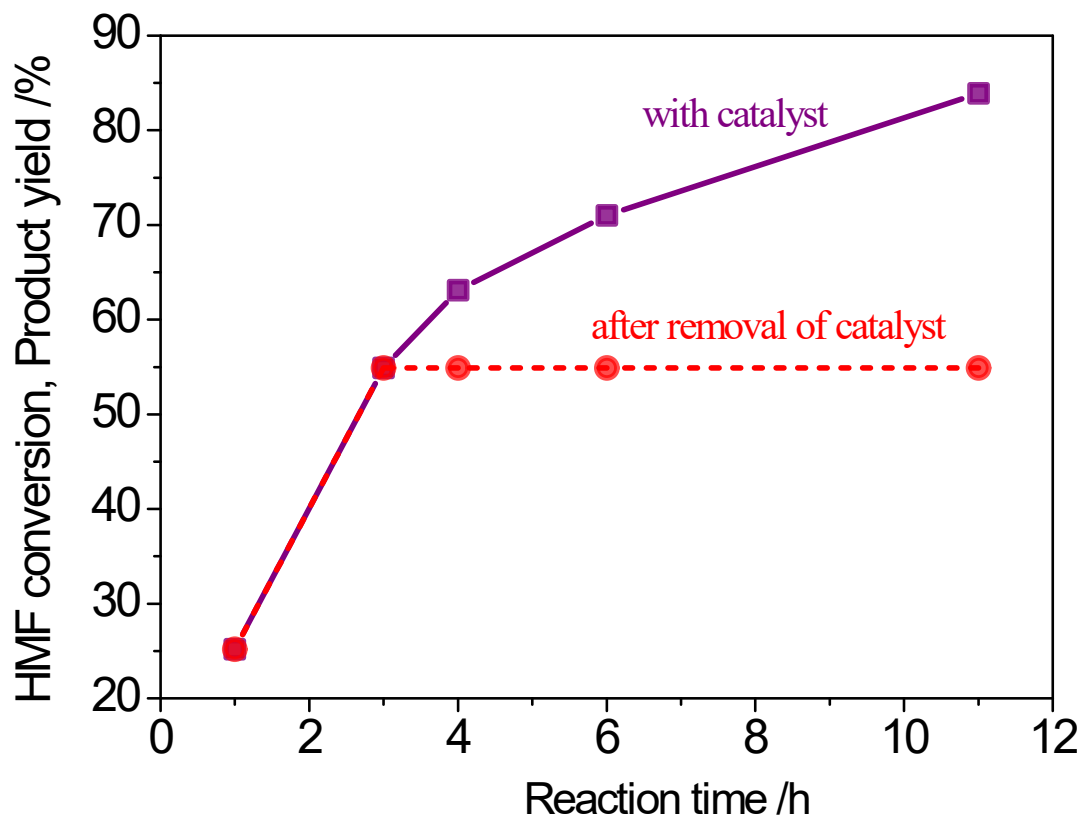


Fig. S7. Hot filtration test. Fig. S3. Effect of stirring speed on FDCA formation. Reaction conditions: 5 wt.% HMF; water: acetone (10 g) ratio, 70:30; catalyst/HMF wt. ratio, 1.43; O₂ pressure, 10 bar; temperature, 110 °C.

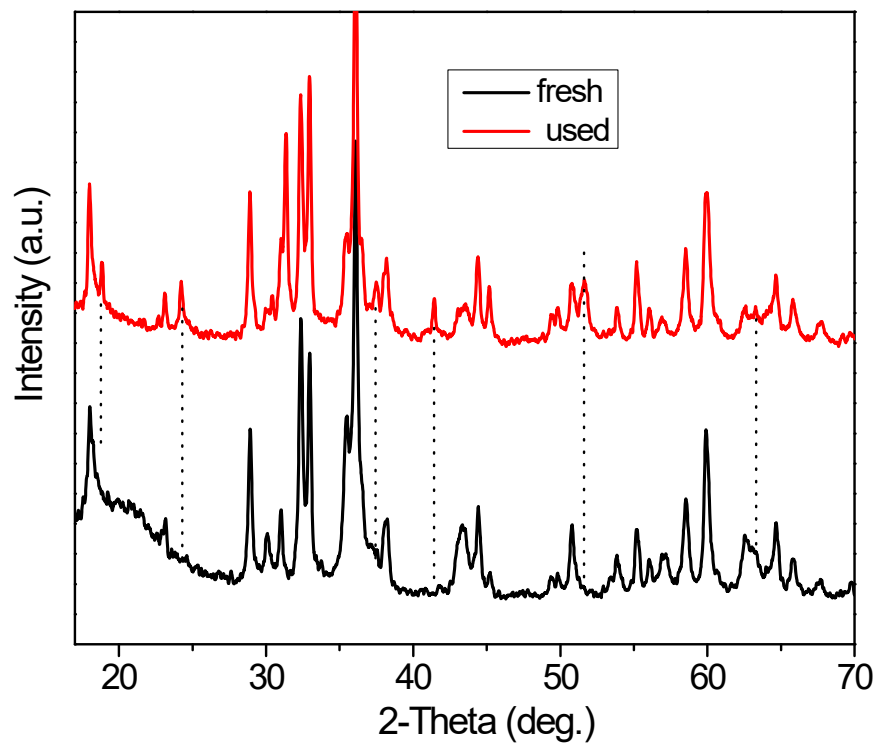


Fig. S8. XRD patterns of Ru/Ni₁Mn₆ catalysts.

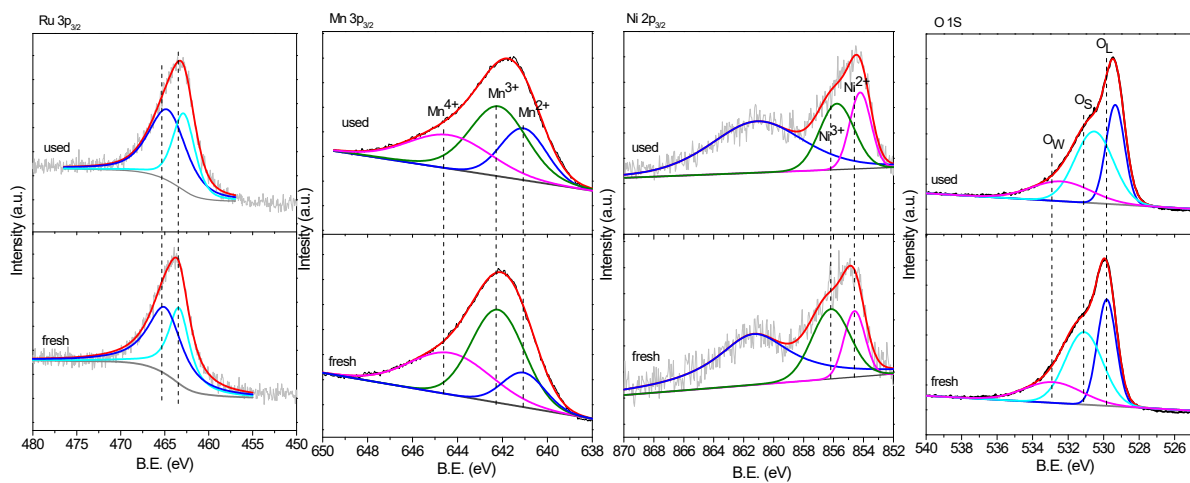


Fig. S9. XPS curves of fresh and used Ru/Ni₁Mn₆ catalysts.

Table S1. N₂-sorption results of the catalysts

Catalyst	S.A. (m ² /g)	VP (cm ³ /g)	Pore Diameter (nm)
MnO _x	22.43	0.167	292.55
MN11	54.43	0.27	183.8
MN31	46.62	0.262	205.34
MN61	30.10	0.220	283.61
MN81	23.49	0.173	298.06
NiO	12.53	0.077	199.77

Table S2. Quantity of O₂-desorbed over different catalysts by O₂-TPD

Catalyst	O _C (mmol/g)	O _L (mmol/g)	O _{bulk} (mmol/g)
NiO	0.26	0.21	0
Ni ₁ Mn ₁	0.65	2.83	1.67
Ni ₁ Mn ₁	0.47	6.04	0
Ni ₁ Mn ₁	0.14	3.49	2.06
MnOx	0.14	3.30	2.11
Ru/NiO	0.54	0.09	0
Ru/Ni ₁ Mn ₁	2.40	1.14	2.21
Ru/Ni ₁ Mn ₃	2.98	1.55	0.03
Ru/Ni ₁ Mn ₆	0.63	3.96	1.66
Ru/MnOx	0.67	3.44	1.11

Table S3. Ru 3P_{3/2} XPS B.Es of the catalysts

Catalyst	B.E. (eV)			
	Ru ⁰	RuO ₂	Ru(OH) ₃	Ru(OH) ₃ (%)
Ru/NiO	462.35	463.81	465.59	45.31
Ru/NM11	461.92	463.62	465.56	24.78
Ru/NM13	461.51	462.89	465.01	29.52
Ru/NM16	-	462.77	464.74	53.27
Ru/MnOx	-	462.65	465.20	51.32
Ru/NM16-used	-	462.71	464.65	52.76

Table S4. Mn 3P_{3/2} XPS B.Es of the catalysts

Catalyst	Mn ²⁺		Mn ³⁺		Mn ⁴⁺	
	B.E. (eV)	%	B.E. (eV)	%	B.E. (eV)	%
Ru/NM11	640.35	28.07	642	44.02	644.45	27.90
Ru/NM13	641.15	24.27	642.23	41.02	644.44	32.7
Ru/NM16	641.06	14.95	642.2	50.30	644.32	34.74
Ru/MnOx	641.05	16.72	642.23	44.78	644.25	38.49
Ru/NM16-used	641.06	25.43	642.18	45.78	644.36	29.17

Table S5. Ni 2P_{3/2} XPS B.Es of the catalysts

Catalyst	Ni ²⁺		Ni ³⁺	
	B.E. (eV)	%	B.E. (eV)	%
Ru/NiO	854.95	52.50	856.65	47.5
Ru/NM11	854.43	47.61	856.21	52.39
Ru/NM13	854.46	34.00	856.06	66
Ru/NM16	854.60	33.63	856.18	66.27
Ru/NM16-used	854.21	41.42	855.77	58.58

Table S6. O1S XPS B.Es of the catalysts

Catalyst	B.E. (eV)			
	O _L	O _S	O _{H2O}	O _L (%)
RuNiO	529.81	531.10	532.68	39.31
Ru/NM11	529.56	530.92	532.74	24.78
Ru/NM13	529.44	530.75	532.48	29.52
Ru/NM16	529.82	531.10	532.85	43.27
Ru/MnOx	529.51	530.72	532.59	41.32
Ru/NM16-used	529.35	530.53	532.38	43.09

Table S7. Catalytic activity of the NaBH₄ untreated RuO-(OH) catalysts

Catalyst	HMF Conv. (%)	FDCA Yield (%)	FFCA Yield (%)	DFF Yield (%)	HMFCFA Yield (%)
Ru/MnO _x	100	71	12	8	1
Ru/Mn-Ni11	100	61	13	14	2
Ru/Mn-Ni-31	100	72	8	6	1
Ru/Mn-Ni61	100	81	6	3	0
Ru/NiO	74	56	9	3	0

Reaction Conditions: Oxidation of HMF over different Ni-manganite catalysts. Reaction conditions: 5 wt.% HMF; water: acetone (10 g) ratio, 70:30; catalyst/HMF wt. ratio, 1.43; O₂ pressure, 10 bar; temperature, 110 °C; reaction time, 12 h.

Table S8. ICP analysis of the fresh and used catalyst

Catalyst	Condition	Mn (ppm)	Ni (ppm)	Ru (ppm)
Ru/Ni ₁ Mn ₆	fresh	10.74	1.88	0.656
Ru/Ni ₁ Mn ₆	spent	9.96	1.80	0.650

20 mg/L sample used for the analysis

References

1. M. J. Hidajat, I. T. Ghampson, G. N. Yun, D. W. Hwang, *Chem. Eng. J.*, 2023, **1**, 141912
2. M. J. Hidajat, O. Kwon, H. Park, J. Han, G. N. Yun, D. W. Hwang, *Green Chem.*, 2022, **24**, 7556-7573.
3. P. Manjunathan, P. P. Upare, Maeum Lee, D. W. Hwang, *Catal. Sci. Technol.*, 2021, **11**, 5816-5826.