Electronic Supplementary Material (ESI) for Faraday Discussions.

New crystalline complex metal oxides created by unit-synthesis and their catalysis based on porous and redox properties

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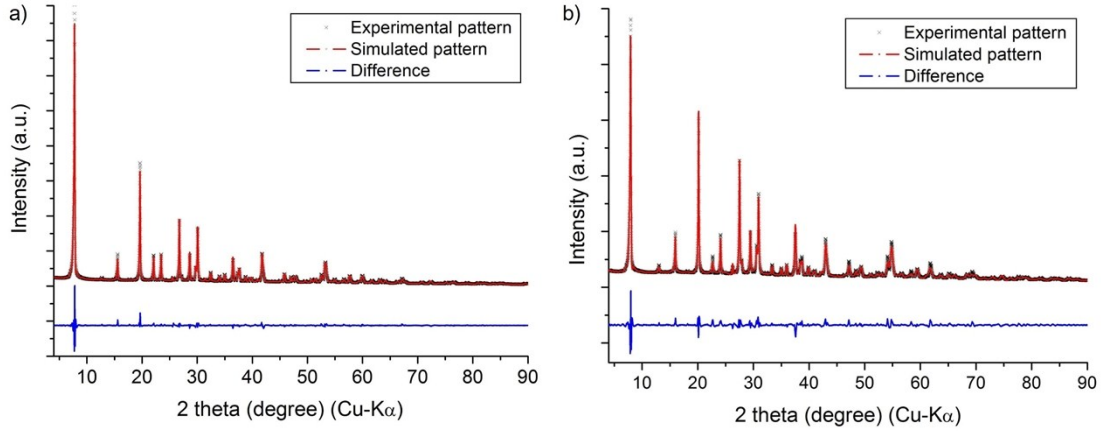

Figure S 1. Comparison of the simulated powder XRD patterns using the Rietveld method with the observed patterns, a) Na-Mo-Mn oxide and b) NH_4-Mo-Fe oxide.

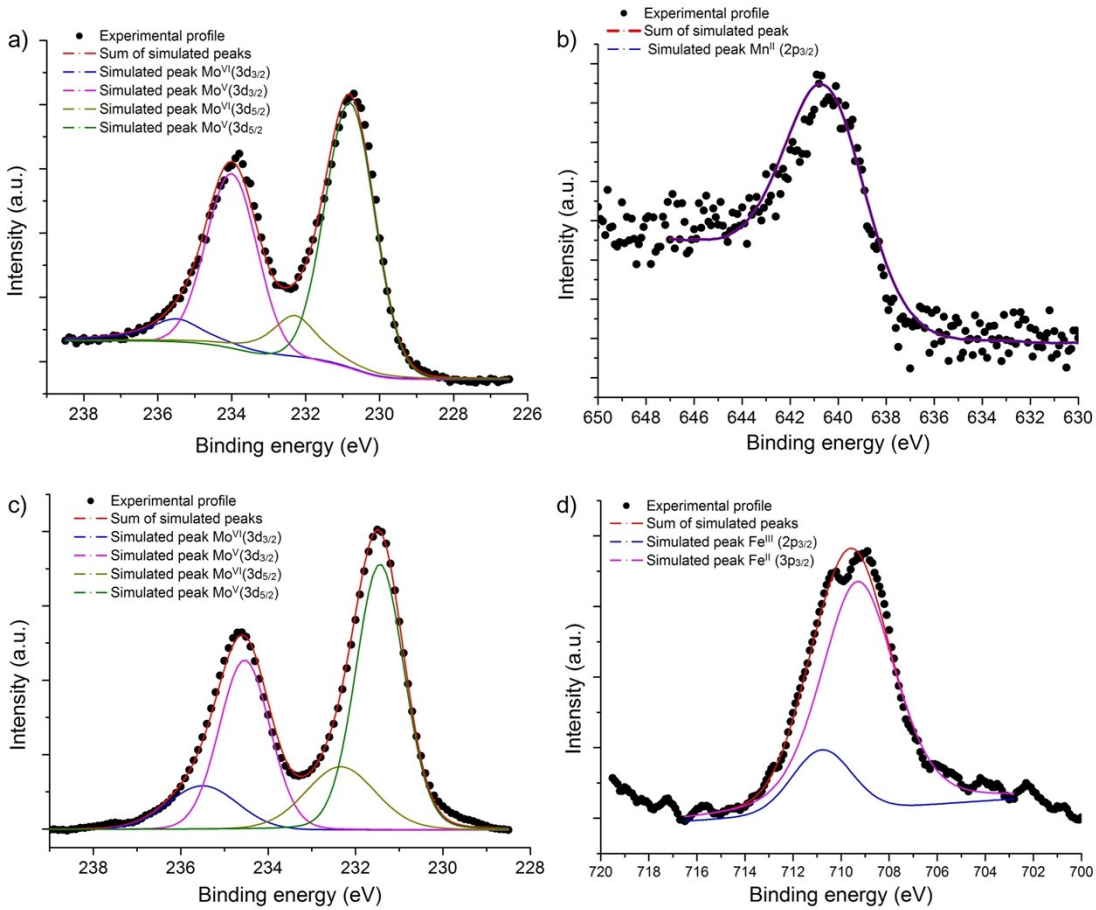

Figure S 2. XPS spectra and curve fitting of a) Mo ion in Na-Mo-Mn oxide, b) Mn ion in Na-Mo-Mn oxide, c) Mo ion in NH_4-Mo-Fe oxide and d) Fe ion in NH_4-Mo-Fe oxide.

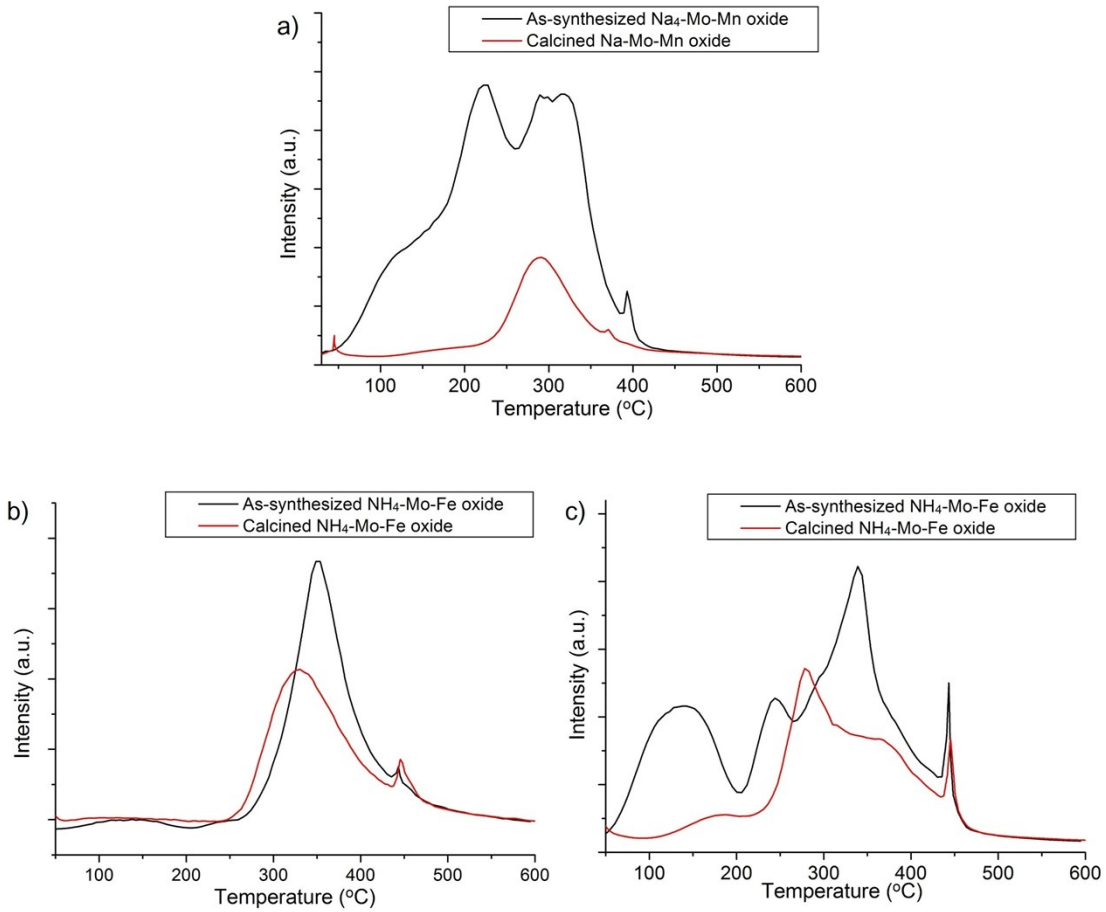

Figure S 3. TPD-MS profiles of a) Na-Mn-Mn oxide (*m/z* = 18) for water, b) NH_4-Mn-Fe oxide (*m/z* = 18) for water, and c) NH_4-Mn-Fe oxide (*m/z* = 16) for NH_3.

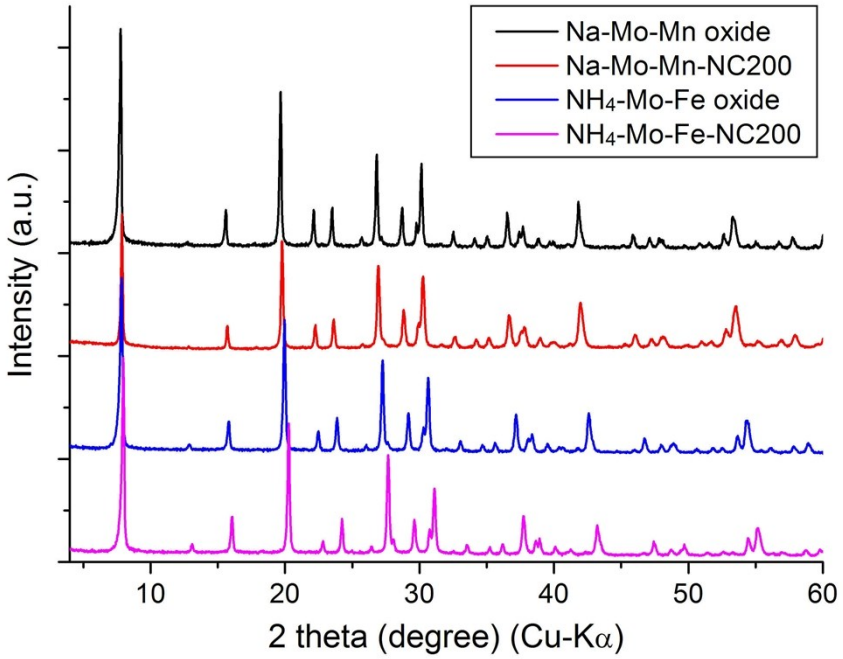

Figure S 4. XRD patterns of the materials before and after calcination.

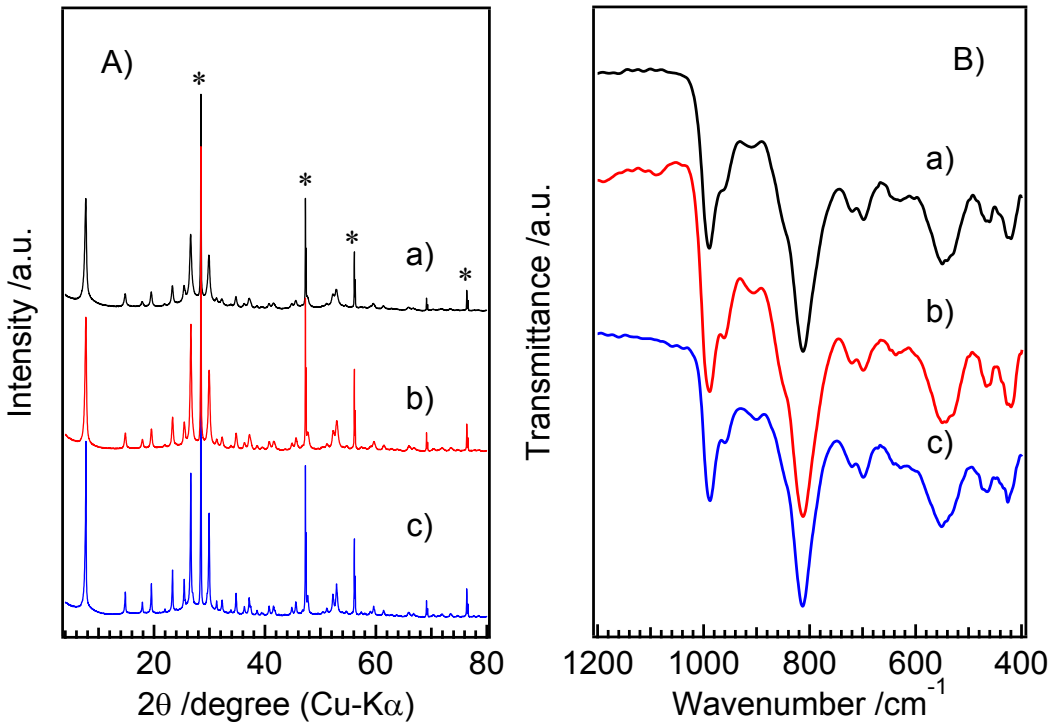

Figure S 5. A) XRD patterns and B) IR spectra of a) Mo-V-Bi-NC350(nano) before the methacrolein oxidation, b) Mo-V-Bi-NC350(nano) after the reaction, and c) well-crystallized Mo-V-Bi-NC350 before the reaction. Si internal standard (*)

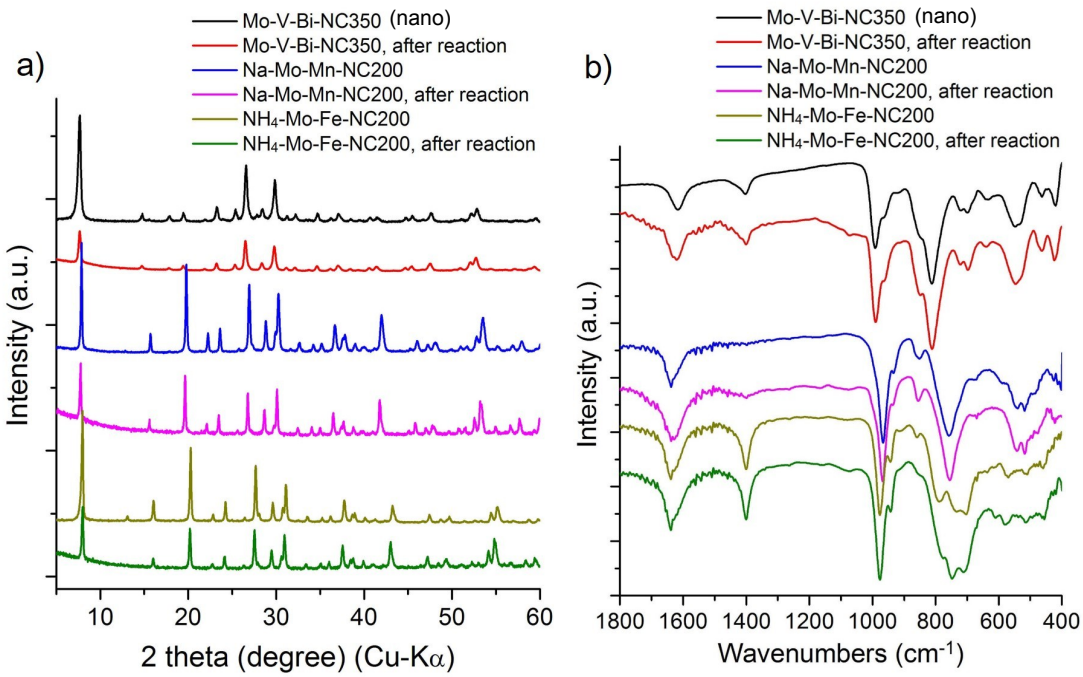

Figure S 6. a) XRD patterns and b) FT-IR spectra of porous POMs before and after hydrolysis of cellobiose.

Table S 1. Crystallographic information and Rietveld refinement parameters of Na-Mo-Mn oxide and NH_4-Mo-Fe oxide from Rietveld analysis.

	Na-Mo-Mn oxide	NH_4-Mo-Fe oxide
crystal system	cubic	cubic
space group	*F d -3 m*	*F d -3 m*
$a = b = c$ (Å)	19.7047	19.4012
V (Å^3)	7650.82	7302.73
agreement factors		
R_{wp}	6.14%	6.30%
$R_{wp(w/o\ bck)}$	11.59%	15.24%
R_p	4.43%	4.51%
pattern parameter		
peak shape		
function	Pseudo-Voigt	Pseudo-Voigt
FWHM	U = 0.69907, V = -0.29698, W = 0.05328	U = 2.33109, V = -0.88222, W = 0.10675
profile parameter	N_A = 0.86010, N_B = -0.00264	N_A = 0.86976, N_B = -0.00550
line shift		
instrument geometry	Bragg-Brentano	Bragg-Brentano
zero point	-0.74894	0.14627
shift#1	0.67997	-0.26718
shift#2	0.15176	0.87465
correction:		
method	Berar-Baldinozzi	Berar-Baldinozzi
parameter	P1 = 0.55455, P2 = -0.05288, P3 = -1.30706, P4 = 0.06146	P1 = -0.09418, P2 = -0.28598, P3 = 0.02880, P4 = 0.53677
background coefficients	polynomial = 100	polynomial = 100
R0 (preferred orientation)	1.29910	1.62976

Table S 2.Structural information of Na-Mo-Mn oxide from structural analysis.

atom	X	Y	Z	Uiso	Occupancy
O1	0.06803	0.36571	0.18197	0.06	1
Mo2	0.07721	0.45349	0.17279	0.018	1
Mn3	0	0.5	0	0.02	1
Mn4	0.125	0.625	0.125	0.02	0.6
O5	0.09848	0.22402	0.09848	0.06	0.55
O6	0.07549	0.46927	0.07549	0.06	1
O7	0.06657	0.47817	0.27183	0.06	1
O8	0.06684	0.56684	0.18316	0.06	1
O9	0.02514	0.02514	0.02514	0.06	0.87

Table S 3. Structural information of NH_4-Mo-Fe oxide from structural analysis.

Atom	X	Y	Z	Uiso	Occupancy
Mo1	0.0736	0.44972	0.1764	0.005	1
O2	0.06952	0.36923	0.18048	0.06	1
O3	0.06598	0.48145	0.26855	0.06	1
O4	0.06545	0.68455	0.06545	0.06	1
O5	0.07547	0.46965	0.07547	0.06	1
O6	0.07211	0.12172	0.07211	0.06	0.35
O7	0.03057	0.11464	0.03057	0.06	0.12
Fe8	0	0.25	0.75	0.02	1
Fe9	0.125	0.125	0.625	0.02	0.7
O10	0	0.25	0.25	0.06	0.39

Table S 4. Surface area of the POM-based microporous materials.

Material	Surface area (m^2/g)	Reference
Mo-V-Bi-NC350	75	1
Na-Mo-Zn-NC200	37	2,3
NH_4-Mo-Zn-NC200	45	3
Na-Mo-Mn-NC200	22	This work
NH_4-Mo-Fe-NC200	20	This work

Reference

1. Z. Zhang, M. Sadakane, T. Murayama, and W. Ueda, *Dalt. Trans.*, 2014, **43**, 13584–13590.

2. Z. Zhang, M. Sadakane, T. Murayama, N. Sakaguchi, and W. Ueda, *Inorg. Chem.*, 2014, **53**, 7309–7318.

3. Z. Zhang, M. Sadakane, S. Noro, T. Murayama, T. Kamachi, K. Yoshizawa, and W. Ueda, *J. Mater. Chem. A*, 2015, **3**, 746–755.