Electronic Supplementary Information

$MnCo_2O_4$ and $CoMn_2O_4$ octahedral nanocrystals synthesized via a one-step co-precipitation process and their catalytic properties in benzyl alcohol oxidation

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Table S1 Synthetic details for MCo series ($MnCo_2O_4$). The "instant." is the abbreviation of "instantaneously", which means that the 1 mL NaOH solution was added quickly all together.

Metal salts	Sample No.	Reaction time/min	$n(Mn^{2+})$/ mmol	$n(Co^{2+})$/ mmol	V(NaOH)/mL; adding manner	n(NaCl)/ mmol
$Mn(OAc)_2•4H_2O$ and/or $Co(OAc)_2•4H_2O$	MCo0	30	0	0.27	1.0; instant.	0
	MCo1	30	0.09	0.18	1.0; instant.	0
	MCo1-T1	3				
	MCo1-T2	5				
	MCo1-T3	10				
	MCo1-T4	15				
	MCo1-T5	20				
	MCo1-T6	25				
	MCo2	30	0.18	0.36	1.0; instant.	0
	MCo3	30	0.045	0.09	1.0; instant.	0
	MCo4[a]	30	0.09	0.18	2.0; instant.	0
	MCo5	30	0.09	0.18	1.0; ~ 176 μL/min	0
	MCo6	30	0.09	0.18	1.0; instant.	0.54
	MCo7	30	0.09	0.18	1.0; ~ 176 μL/min	0.54
$MnCl_2•4H_2O$ $CoCl_2•6H_2O$	MCo8	30	0.09	0.18	1.0; instant.	0
	MCo9	30	0.09	0.18	1.0; ~ 176 μL/min	0

[a] The metal salts for MCo4 were dissolved in 8.0 mL UP H_2O before addition of NaOH solution to keep the total volumes of reacting mixtures same (10 mL) for all products listed here.

Table S2 Synthetic details for CMn series ($CoMn_2O_4$). The "instant." is the abbreviation of "instantaneously", which means that the 1 mL NaOH solution was added quickly all together.

Metal salts	Sample No.	Reaction time/min	$n(Mn^{2+})$/ mmol	$n(Co^{2+})$/ mmol	V(NaOH)/mL; adding manner	n(NaCl)/ mmol
$Mn(OAc)_2•4H_2O$ and/or $Co(OAc)_2•4H_2O$	CMn0	30	0.27	0	1.0; instant.	0
	CMn1	30	0.2	0.067	1.0; instant.	0
	CMn1-T1	1				
	CMn1-T2	3				
	CMn1-T3	5				
	CMn1-T4	10				
	CMn1-T5	15				
	CMn1-T6	25				
	CMn2	30	0.4	0.134	1.0; instant.	0
	CMn3	30	0.1	0.034	1.0; instant.	0
	CMn4[a]	30	0.2	0.067	2.0; instant.	0
	CMn5	30	0.2	0.067	1.0; ~ 86 μL/min	0
	CMn6	30	0.2	0.067	1.0; instant.	0.54
	CMn7	30	0.2	0.067	1.0; ~ 86 μL/min	0.54
$MnCl_2•4H_2O$ $CoCl_2•6H_2O$	CMn8	30	0.2	0.067	1.0; instant.	0
	CMn9	30	0.2	0.067	1.0; ~ 86 μL/min	0

[a] The metal salts for CMn4 were dissolved in 8.0 mL UP H_2O before addition of NaOH solution to keep the total volumes of reacting mixtures same (10 mL) for all products listed here.

Table S3 The ratios of bivalent and trivalent cations in MCo1, CMn1, 1-MCo1 and 1-CMn calculated by the Lorentzian-Gaussian method. "1- " means the catalysts were collected after 1 run of catalytic reaction. It is clearly that the proportion of bivalent cations, no matter Co^{2+} or Mn^{2+}, increased after catalysis. M represents Co or Mn.

Catalysts	Cations	Total areas of deconvolved peaks	Ratio of M^{2+}/M^{3+}	Ratio of Mn/Co
MCo1	Co^{2+}	11155.402	0.49	0.41
	Co^{3+}	22555.098		
	Mn^{2+}	8691.533	1.66	
	Mn^{3+}	5249.431		
CMn1	Co^{2+}	5098.727	1.21	2.26
	Co^{3+}	4230.411		
	Mn^{2+}	9143.936	0.77	
	Mn^{3+}	11928.372		
1-MCo1	Co^{2+}	20582.446	6.50	0.50
	Co^{3+}	3166.315		
	Mn^{2+}	8422.438	2.38	
	Mn^{3+}	3538.283		
1-CMn1	Co^{2+}	4288.505	3.31	2.88
	Co^{3+}	1294.238		
	Mn^{2+}	10157.285	1.72	
	Mn^{3+}	5901.695		

Table S4 Proportions of different surface oxygen species. The "1– " means the catalysts were collected after 1 run of catalytic reaction.

Catalysts	Proportions of oxygen species on the surface					
	Lattice oxygen		Adsorbed oxygen		Carbonate/Adsorbed water	
	BE/eV	%	BE/eV	%	BE/eV	%
MCo1	530.0	29.8	531.4	46.2	532.4/533.2	24.0
1-MCo1	529.6	25.4	531.9	63.0	533.2	11.6
CMn1	529.9	36.0	531.6	43.7	532.8	20.3
1-CMn1	529.5	17.3	531.6	47.7	532.9	35.0

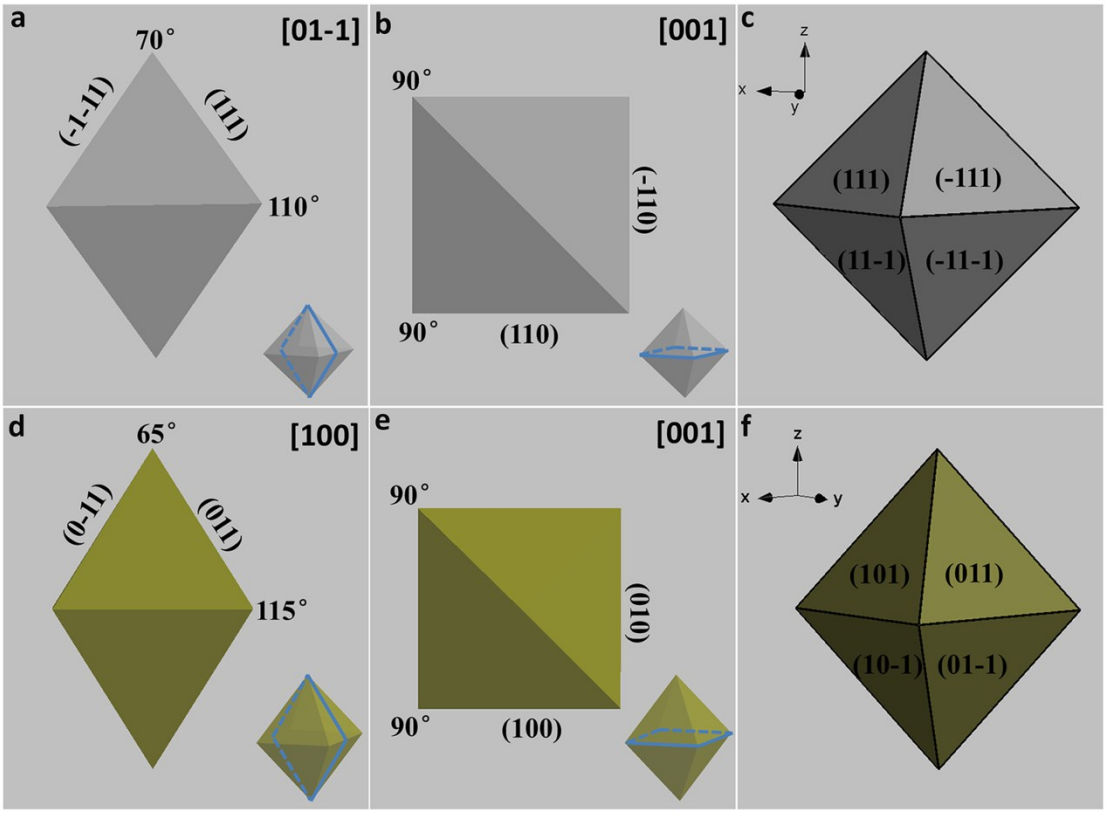

Fig. S1 (a-c) structural information of MCo1: the exterior forms of the established model along [01-1] direction (a), [001] direction (b) and the Miller indices of the exposed planes from crystal orientation (c). (d-f) structural information of CMn1: exterior forms of the model along [100] direction (d), [001] direction (e) and the Miller indices of the exposed planes from crystal orientation (f). Insets of (a), (b), (d) and (e) display the images (pattern restricted by the blue lines) of corresponding projections along the specific directions in a randomly placed octahedron. The {111} and {101} planes are finally determined for the as-prepared $MnCo_2O_4$ and $CoMn_2O_4$ octahedral crystals, respectively.

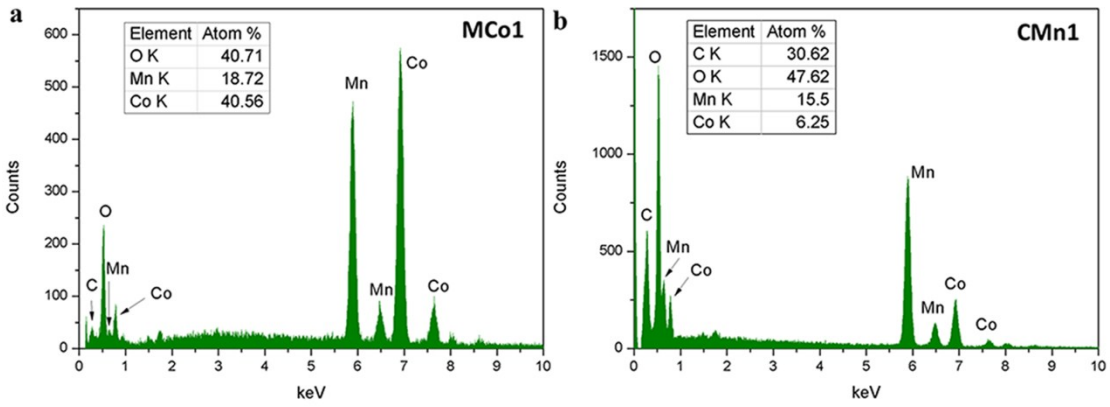

Fig. S2 EDX spectra of as-prepared MCo1 (a) and CMn1 (b).

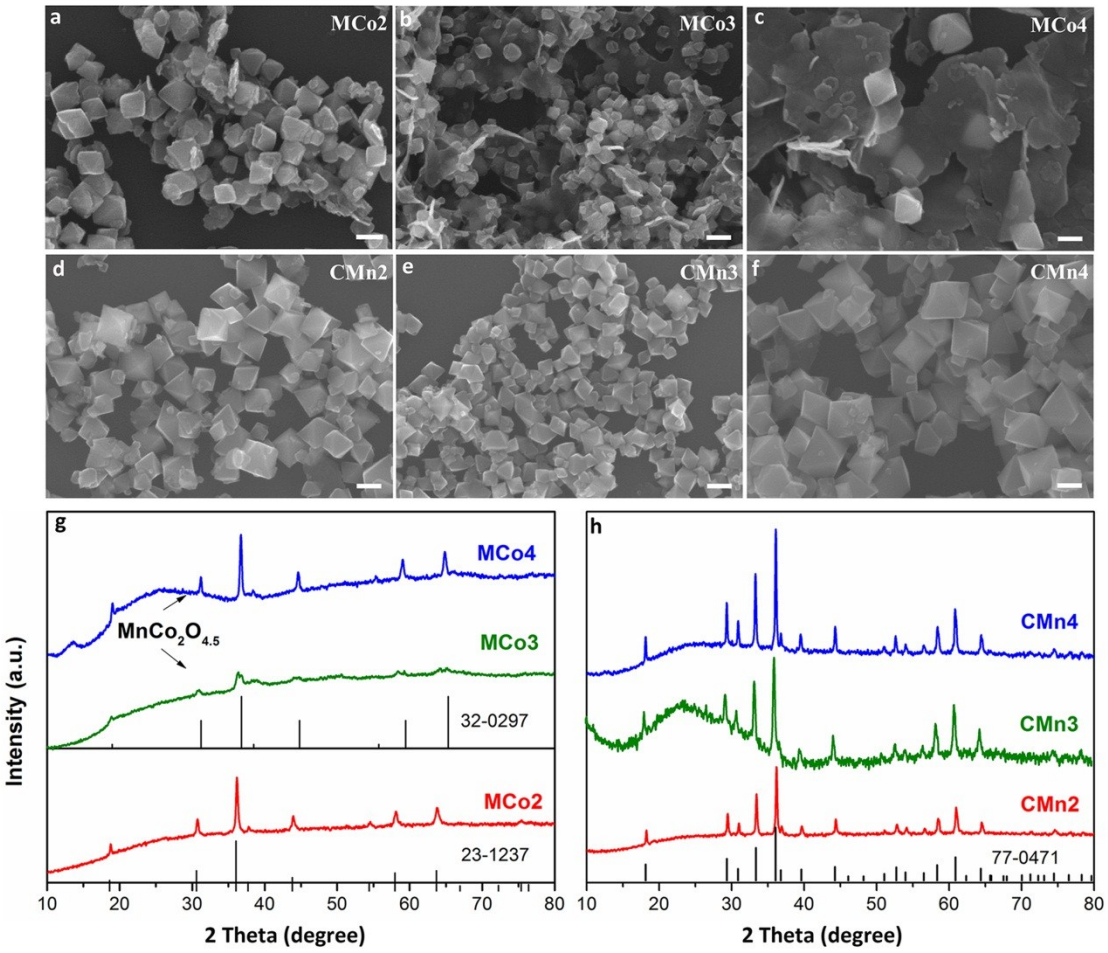

Fig. S3 SEM and XRD results of MCo2-MCo4 (a-c, g) and CMn2-CMn4 (d-f, h), respectively. The MCo3 and MCo4 are indexed to $MnCo_2O_{4.5}$ (JCPDS No. 32-0297) instead of $MnCo_2O_4$ (JCPDS No. 23-1237). The scale bar in a-f: 100 nm.

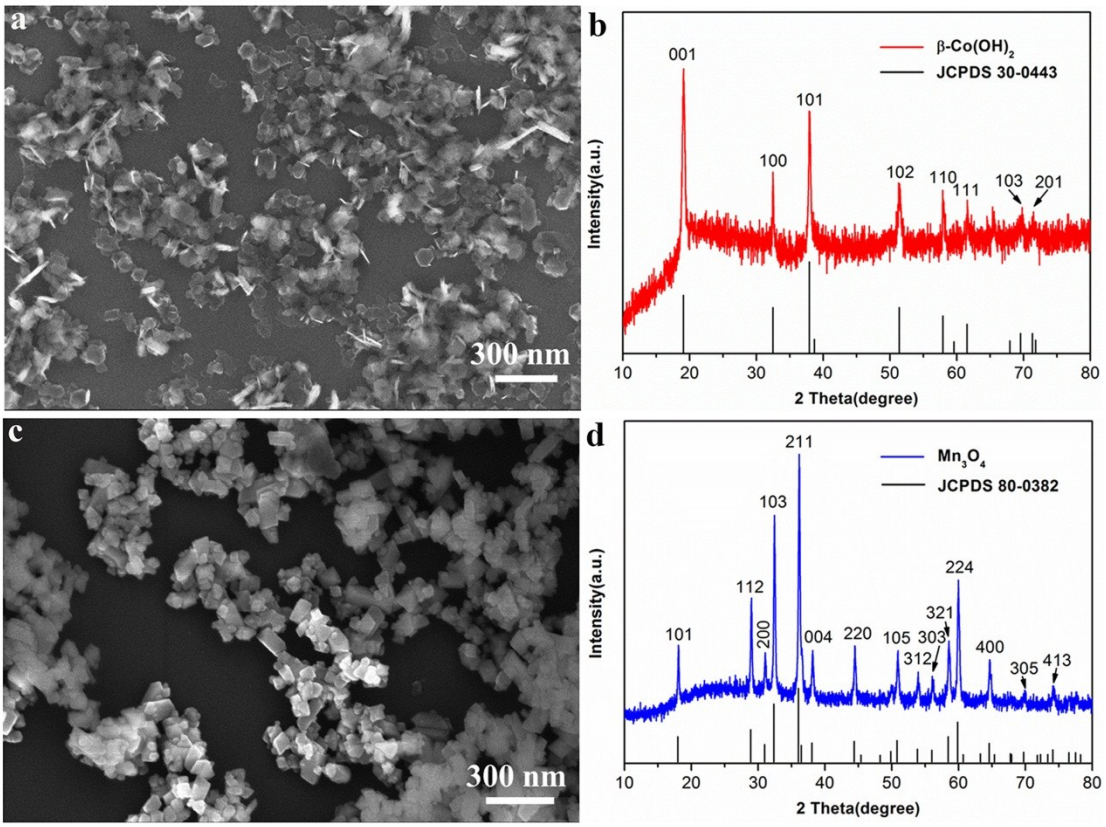

Fig. S4 SEM images and XRD patterns for the β-$Co(OH)_2$ (a and b) and Mn_3O_4 (c and d) prepared using only one kind of metal salt. It is worth noting that the (001) peak has higher intensity than the (101) peak in Fig. S4b, suggesting a preferred growth along its c-axis for β-$Co(OH)_2$ (hexagonal crystalline phase) under the present synthetic conditions. Similar phenomena have been also noticed by V. Pralong[1] and Y. L. Hou[2] *et al.*.

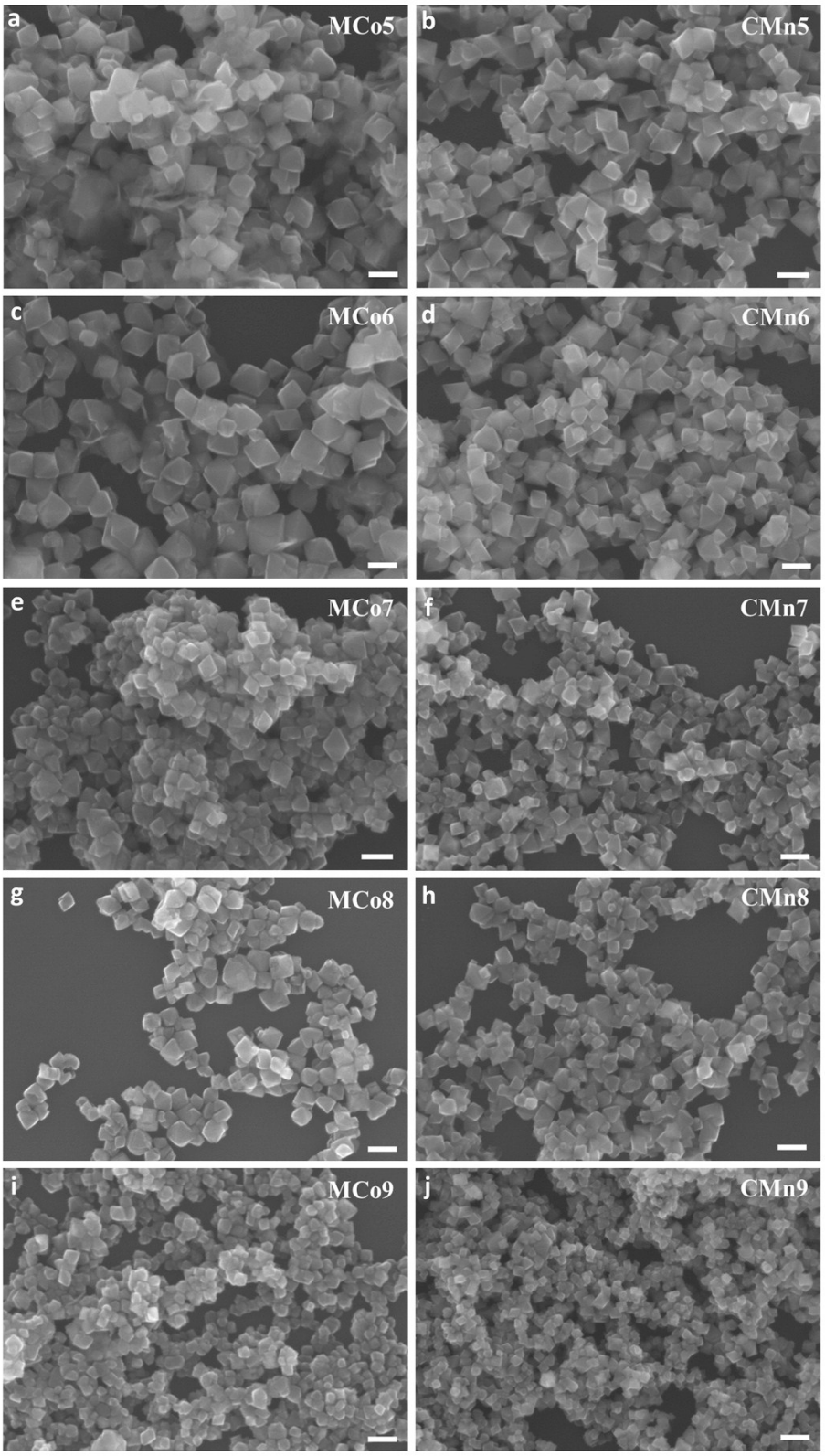

Fig. S5 SEM images of products MCo5-9 (a, c, e, g, and i) and CMn5-9 (b, d, f, h, and j). The scale bar: 100 nm.

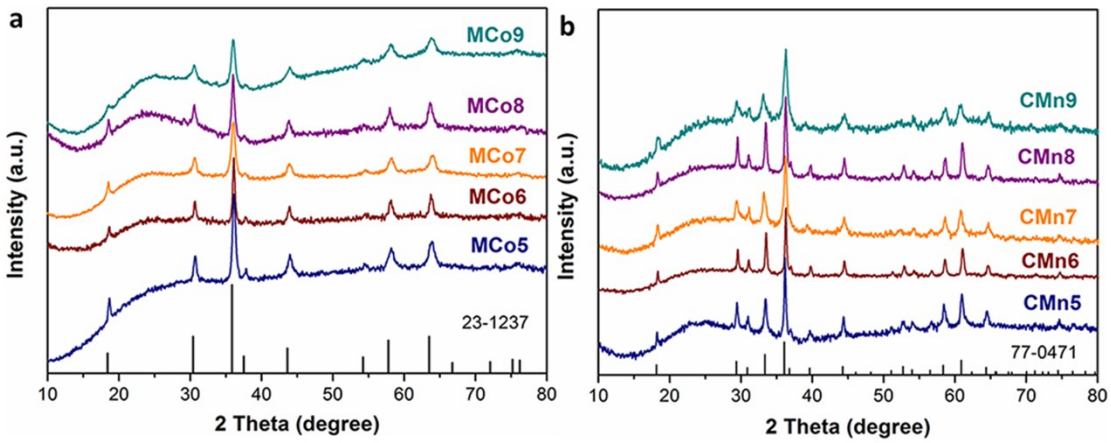

Fig. S6 XRD patterns of products MCo5-9 (a) and CMn5-9 (b). All patterns show no phase change either for MCo5-9 or for CMn5-9 compared to MCo1 and CMn1, respectively.

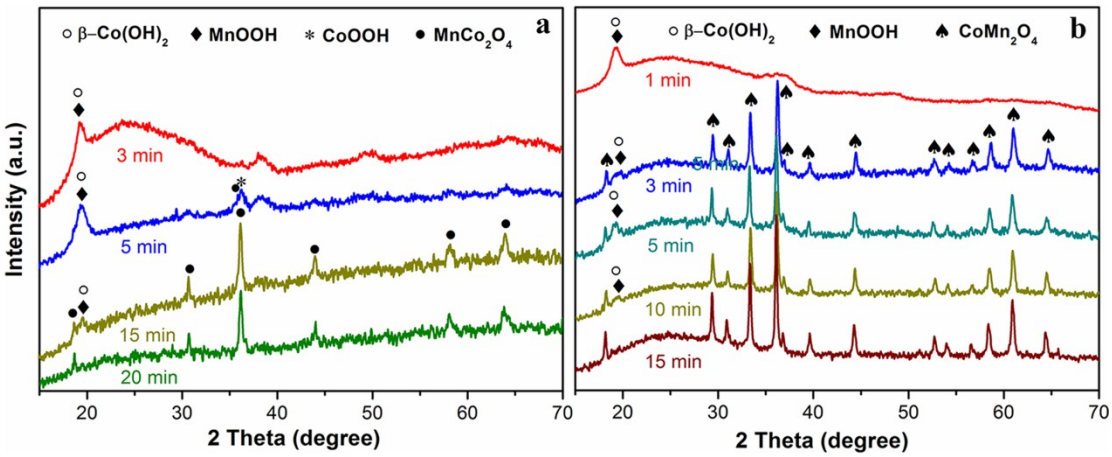

Fig. S7 XRD patterns of main samples of MCo1-Tx (a, x = 1, 2, 4, 5) and CMn1-Ty (b, y = 1-5) series to study the formation processes of MCo1 and CMn1.

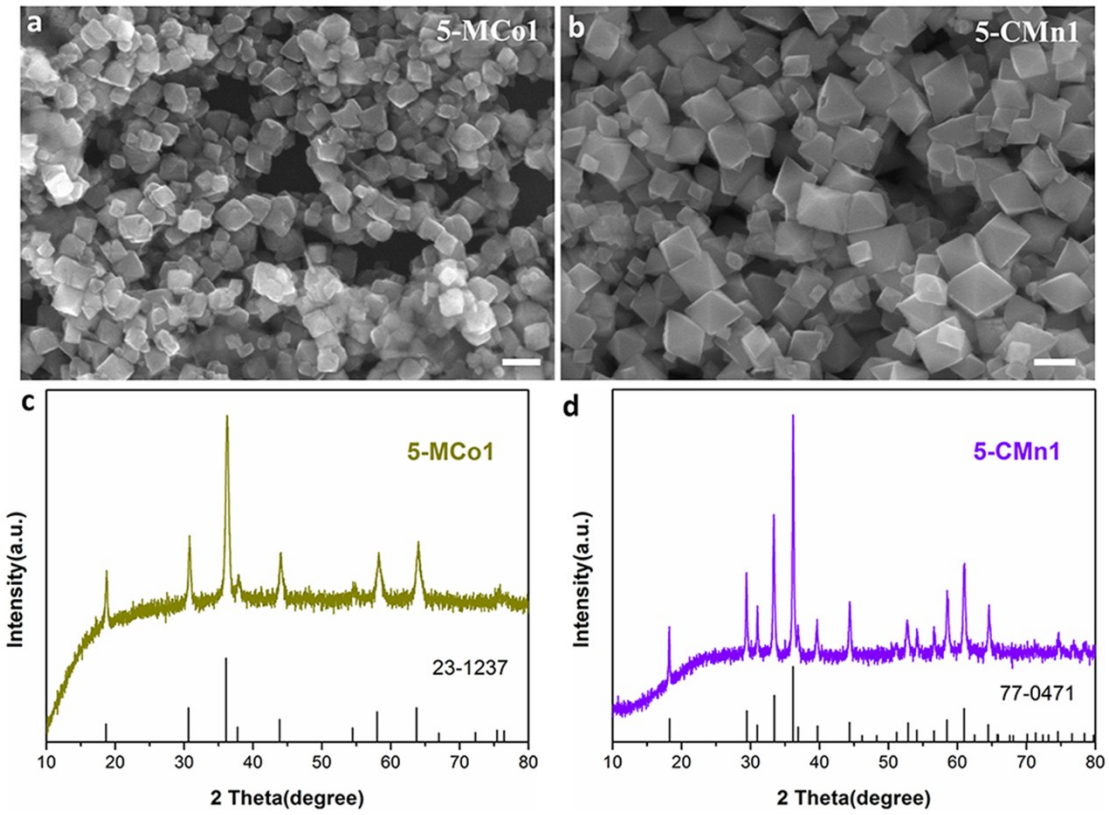

Fig. S8 SEM images and XRD patterns of 5-MCo1 (a and c) and 5-CMn1 (b and d). "5-" means the catalysts were collected after five runs of catalytic reactions. Scale bar of a and b: 100 nm. No obvious morphological or phase change are observed for these two catalysts.

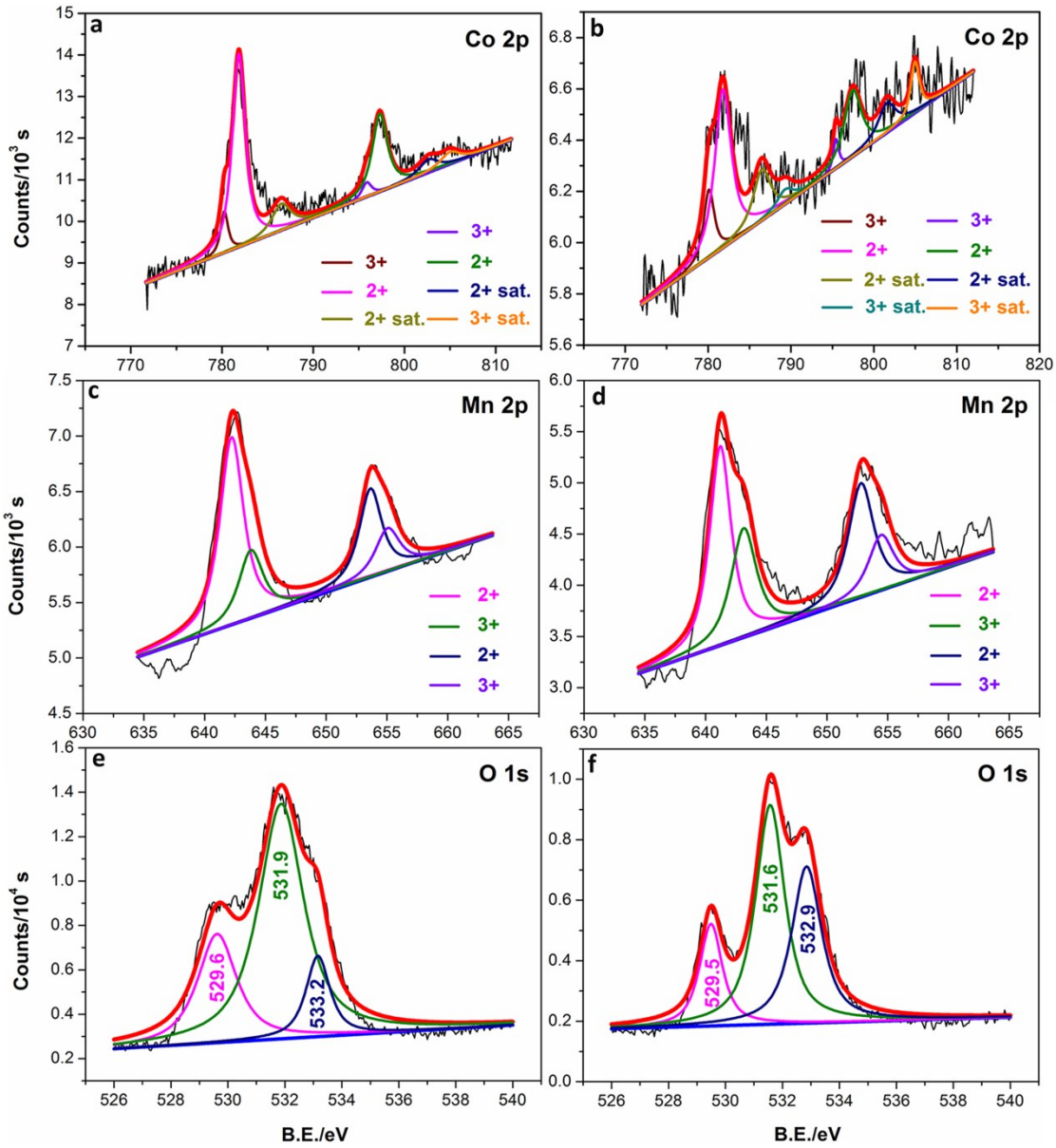

Fig. S9 XPS spectra of catalysts after 1 run of reaction of Co 2p, Mn 2p and O 1s for 1-MCo (a, c, and e, respectively), and Co 2p, Mn 2p and O 1s for 1-CMn1 (b, d, and f, respectively). "1-" represents the catalysts were collected after the first run of reaction.

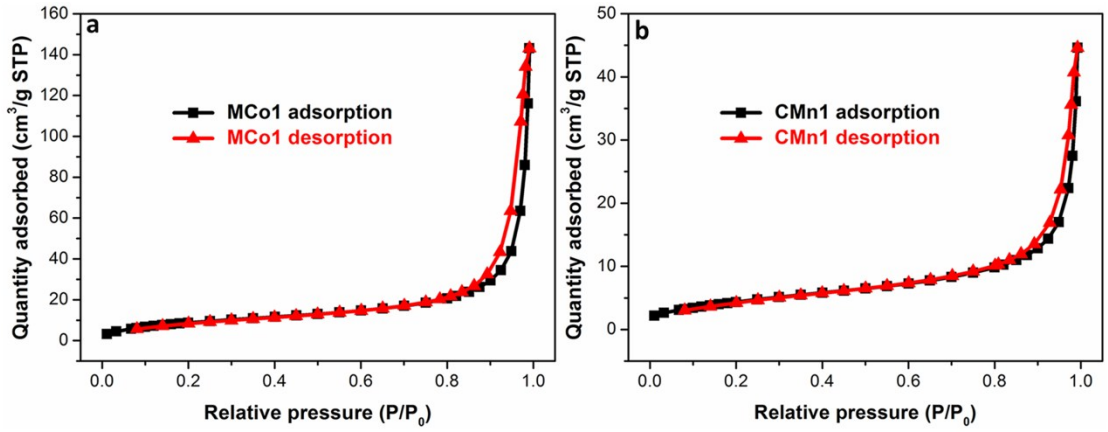

Fig. S10 N_2 adsorption-desorption isotherm of MCo1 (a) and CMn1 (b).

References

1 V. Pralong, A. Delahaye-Vidal, B. Beaudoin, B. Gerand and J. M. Tarascon, *J. Mater. Chem.*, 1999, **9**, 955.

2 Y. L. Hou, H. Kondoh, M. Shimojo, T. Kogure and T. Ohta, *J. Phys. Chem. B*, 2005, **109**, 19094.