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Supporting information for

Selective Carbon Dioxide Adsorption of ε-Keggin-type Zincomolybdate-based Purely-Inorganic 3D Frameworks

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The structure of Na–Mo–Zn oxide was determined in our previous paper. The structure of NH_4–Mo–Zn oxide was determined by powder X-ray diffraction (XRD). Powder XRD patterns were recorded on RINT2200 (Rigaku) with Cu Kα radiation (tube voltage: 40 kV, tube current: 40 mA, scan speed: 1 degree/min, step: 0.01 degree). First, the powder XRD pattern was indexed by programs, such as DICVOL06 and X-cell, which gave the same result. After performing Pawley refinement, the most reasonable space group was obtained. Then, Le Bail method was applied for intensity extraction with the EdPCR program. The initial structure was solved by a charge-flipping algorithm. The positions and types of heavy metal atoms (Mo and Zn) were obtained by analyzing the generated electron density maps. Most of the oxygen atoms and cations were assigned according to the residual peaks, which were indicated by the charge-flipping algorithm.

The initial structure of NH_4–Mo–Zn oxide was refined by Rietveld refinement. The lattice parameters and pattern parameters of the material were refined by Pawley refinement first. Then isotropical temperature factors were given for every atom in the initial structure. Rietveld analysis was started with the initial model of the material and lattice parameters and pattern parameters from Pawley refinement. Every atom position was refined. Occupancy of atoms in framework was fixed without further refinement and occupancies of atoms in micropores were refined with consideration of elemental analysis results. Finally, the pattern parameters were refined again for obtaining the lowest R_{wp} value. Atom positions were listed in Table S 11 and Table S 12.

The oxidation states of metal elements in NH_4–Mo–Zn oxide were investigated with XPS, the results of which indicated that Mo in the materials was mostly reduced. The ratio of Mo^{VI}/Mo^{V} was determined by curve fitting, indicating that Mo^{VI}/Mo^{V} was 0.5 in NH_4–Mo–Zn oxide and 0.1 in Na–Mo–Mn oxide. Zinc ion of both oxides was Zn^{II}.

Table S 1. The R^2 values of several model fits for the isotherms of CO_2 and CH_4 at 298 K.

Models	Materials	numbers of parameters	$R^2(CO_2)$	$R^2(CH_4)$
Langmuir	Na–Mo–Zn oxide	2	0.74973	0.99831
Langmuir-Freundlich	Na–Mo–Zn oxide	3	0.98533	0.99962
Dual site Langmuir	Na–Mo–Zn oxide	4	0.98852	0.99991
Dual site Langmuir-Freundlich	Na–Mo–Zn oxide	6	0.99975	0.99991
Langmuir	NH_4–Mo–Zn oxide	2	0.94227	0.99975
Langmuir-Freundlich	NH_4–Mo–Zn oxide	3	0.99518	0.99989
Dual site Langmuir	NH_4–Mo–Zn oxide	4	0.99949	0.99994
Dual site Langmuir-Freundlich	NH_4–Mo–Zn oxide	6	0.99997	0.99994

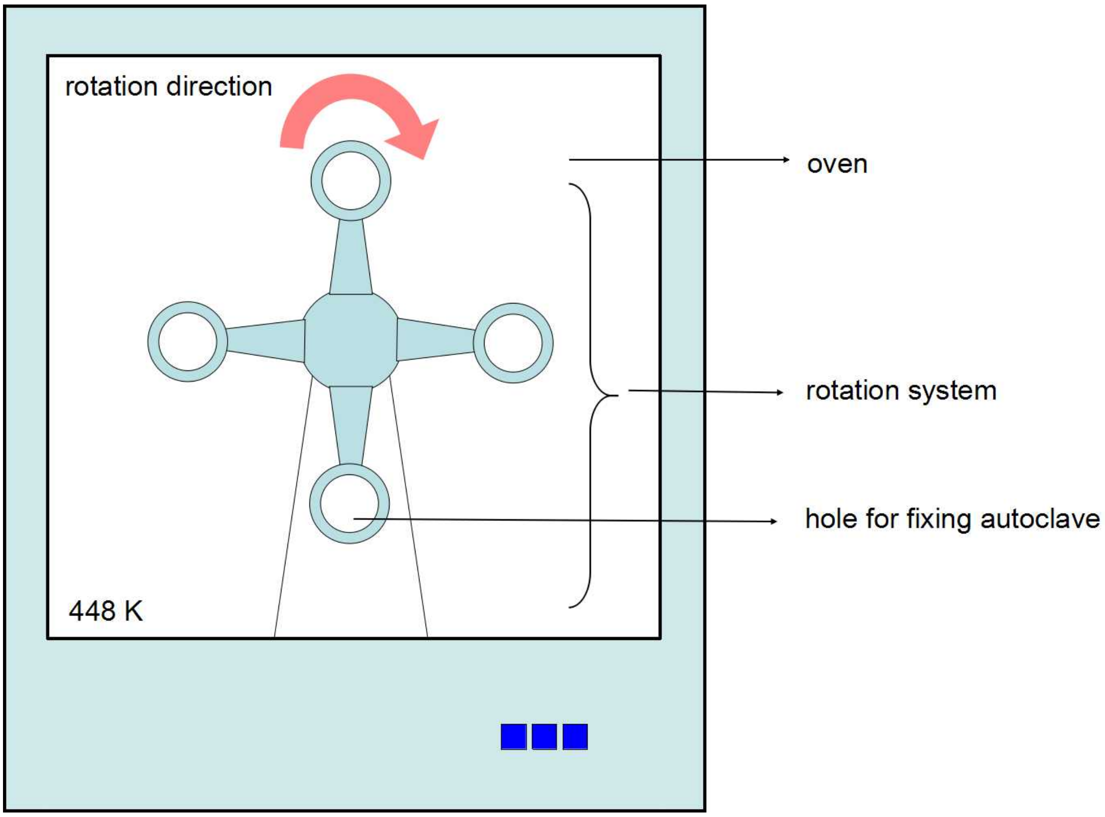

Figure S 1. The experimental apparatus to synthesize Na–Mo–Zn oxide and NH_4–Mo–Zn oxide by using dynamic method.

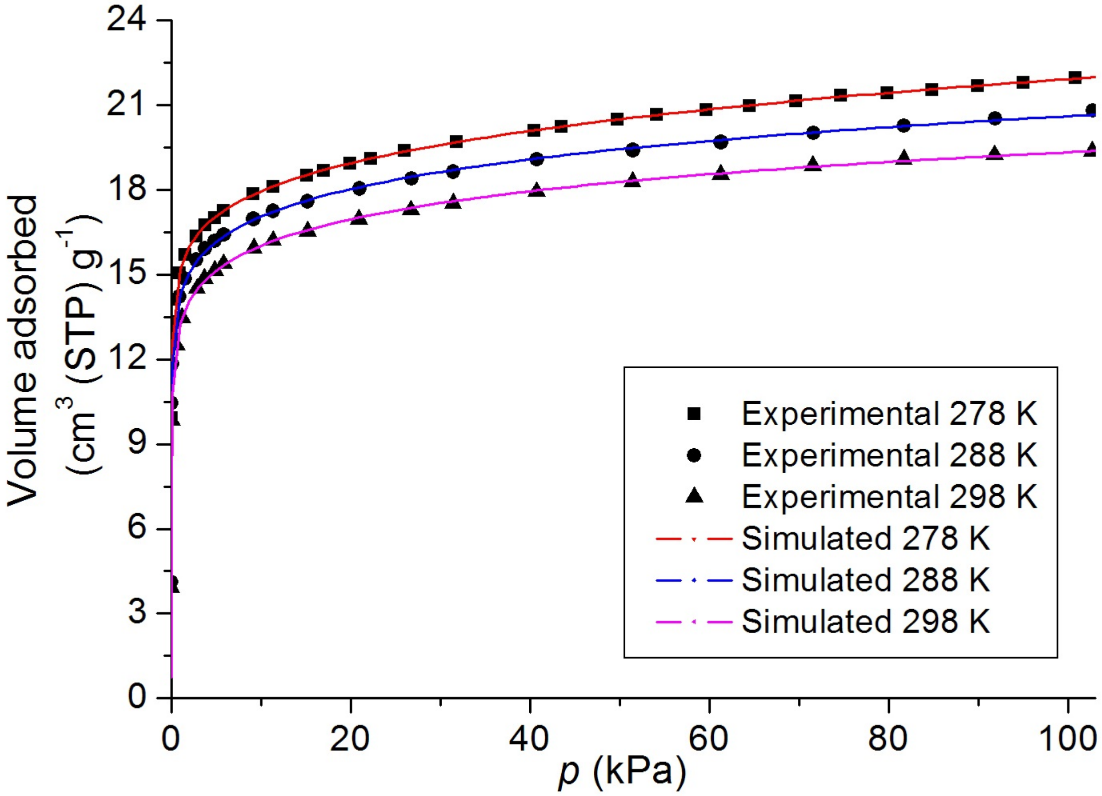

Figure S 2. CO_2 adsorption isotherms of Cal–Na–Mo–Zn oxide at different temperature.

Table S 2. Curve fitting parameters of CO_2 adsorption isotherms of Cal–Na–Mo–Zn oxide using the dual-site Langmuir-Freundlich equation at different temperature.

	278 K	288 K	298K
q1	20.80056	8.68786	7.07908
b1	2.51436	61.15111	107.04572
n1	0.22578	0.7852	1
q2	18.5472	53.50337	32.73628
b2	0.01685	0.12043	0.23647
n2	0.58338	0.18823	0.20134
R^2	0.99997	0.99958	0.99975

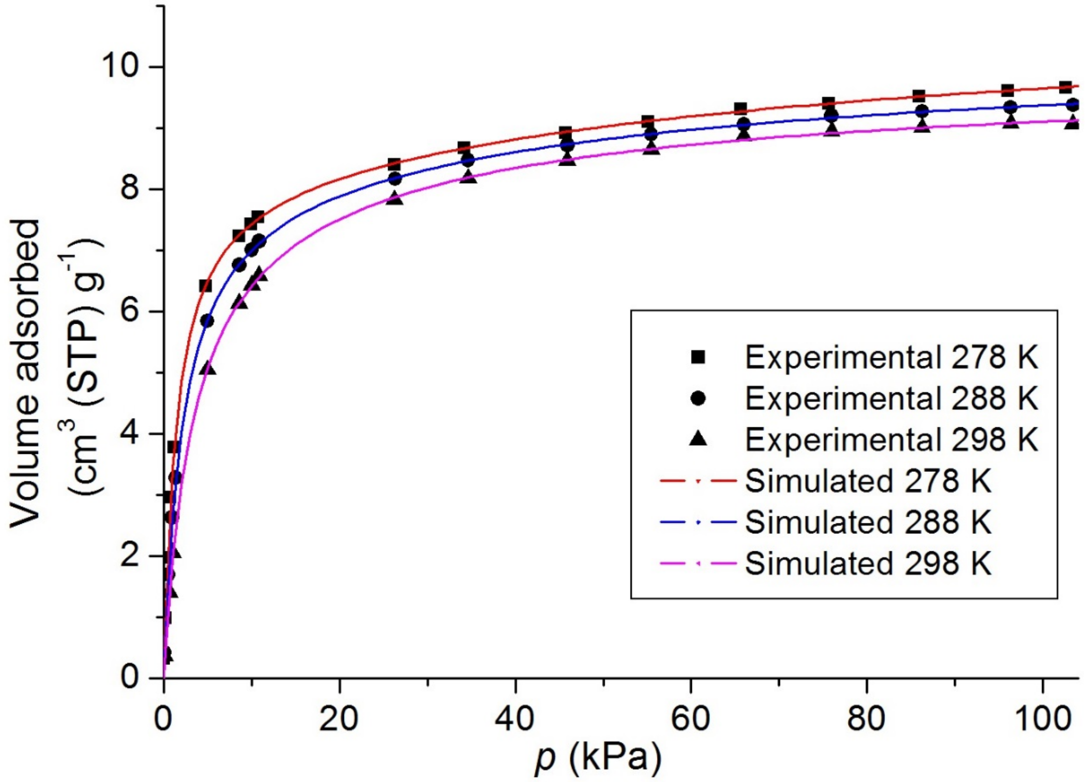

Figure S 3. CH_4 adsorption isotherms of Cal–Na–Mo–Zn oxide at different temperature.

Table S 3. Curve fitting parameters of CH_4 adsorption isotherms of Cal–Na–Mo–Zn oxide using the dual-site Langmuir-Freundlich equation at different temperature.

	278 K	288 K	298K
q1	8.15089	8.00455	7.85594
b1	0.71534	0.48415	0.31888
n1	0.98438	1	1
q2	2.99718	2.38219	2.02925
b2	0.01172	0.01794	0.02742
n2	0.99998	1	1
R^2	0.99998	0.99997	0.99991

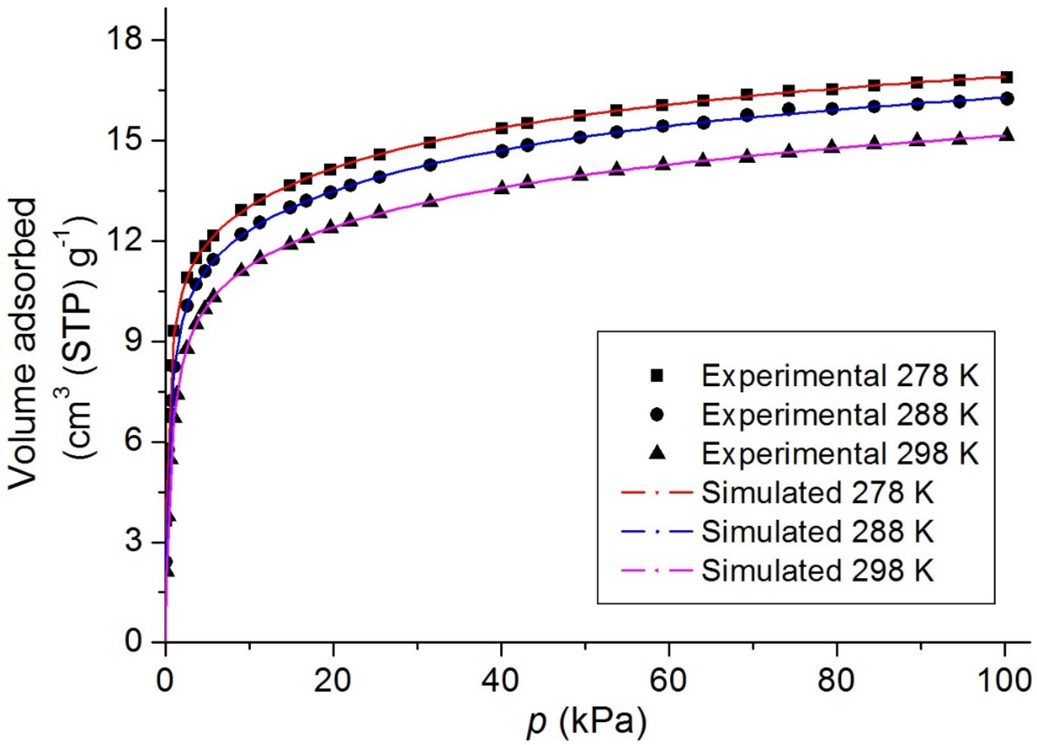

Figure S 4. CO_2 adsorption isotherms of Cal–NH_4–Mo–Zn oxide at different temperature.

Table S 4. Curve fitting parameters of CO_2 adsorption isotherms of Cal–NH_4–Mo–Zn oxide using the dual-site Langmuir-Freundlich equation at different temperature.

	278 K	288 K	298K
q1	11.69525	11.4436	8.87547
b1	3.01139	2.16161	0.0501
n1	0.76212	0.82124	0.70284
q2	8.32908	7.72081	10.29691
b2	0.05374	0.03957	1.56268
n2	0.76015	0.82922	0.86657
R^2	0.99994	0.99988	0.99997

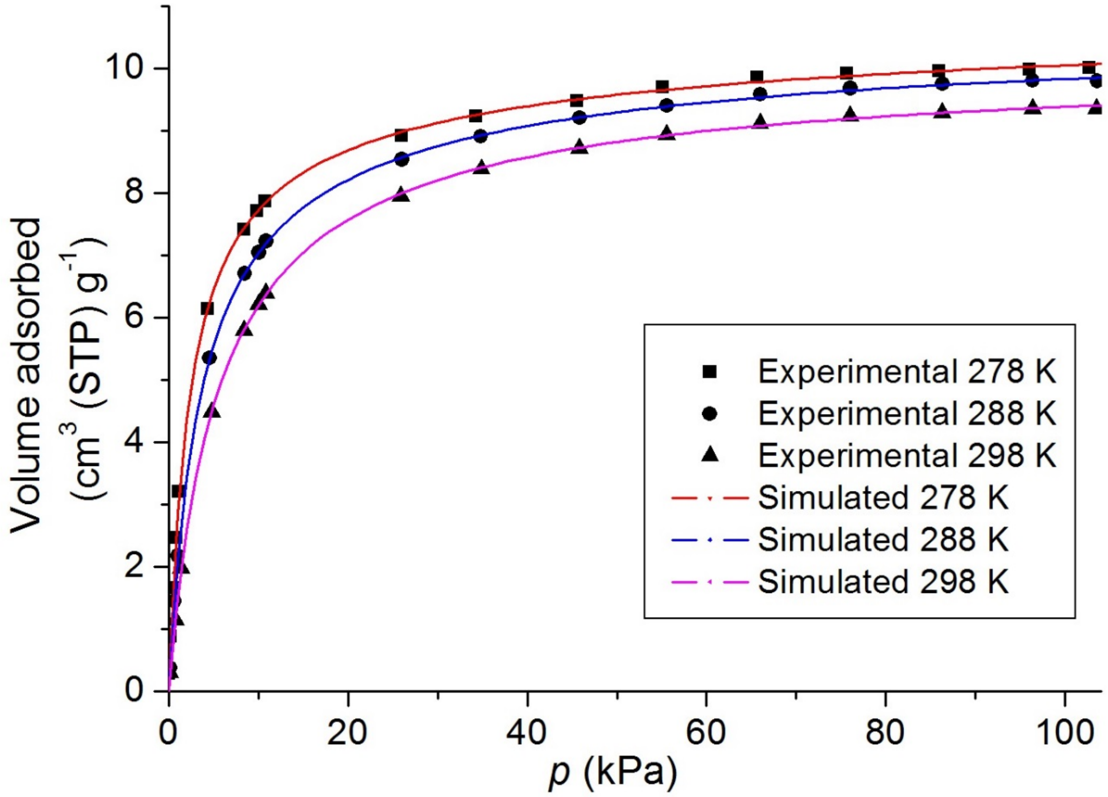

Figure S 5. CH_4 adsorption isotherms of Cal–NH_4–Mo–Zn oxide at different temperature.

Table S 5. Curve fitting parameters of CH_4 adsorption isotherms of Cal–NH_4–Mo–Zn oxide using the dual-site Langmuir-Freundlich equation at different temperature.

	278 K	288 K	298K
q1	1.29993	1.62354	8.69241
b1	0.04517	0.02378	0.45642
n1	0.92089	0.99907	1
q2	8.82744	8.97993	2.36074
b2	0.19609	0.29819	0.06047
n2	0.99951	1	0.74746
R^2	0.99989	0.99993	0.99994

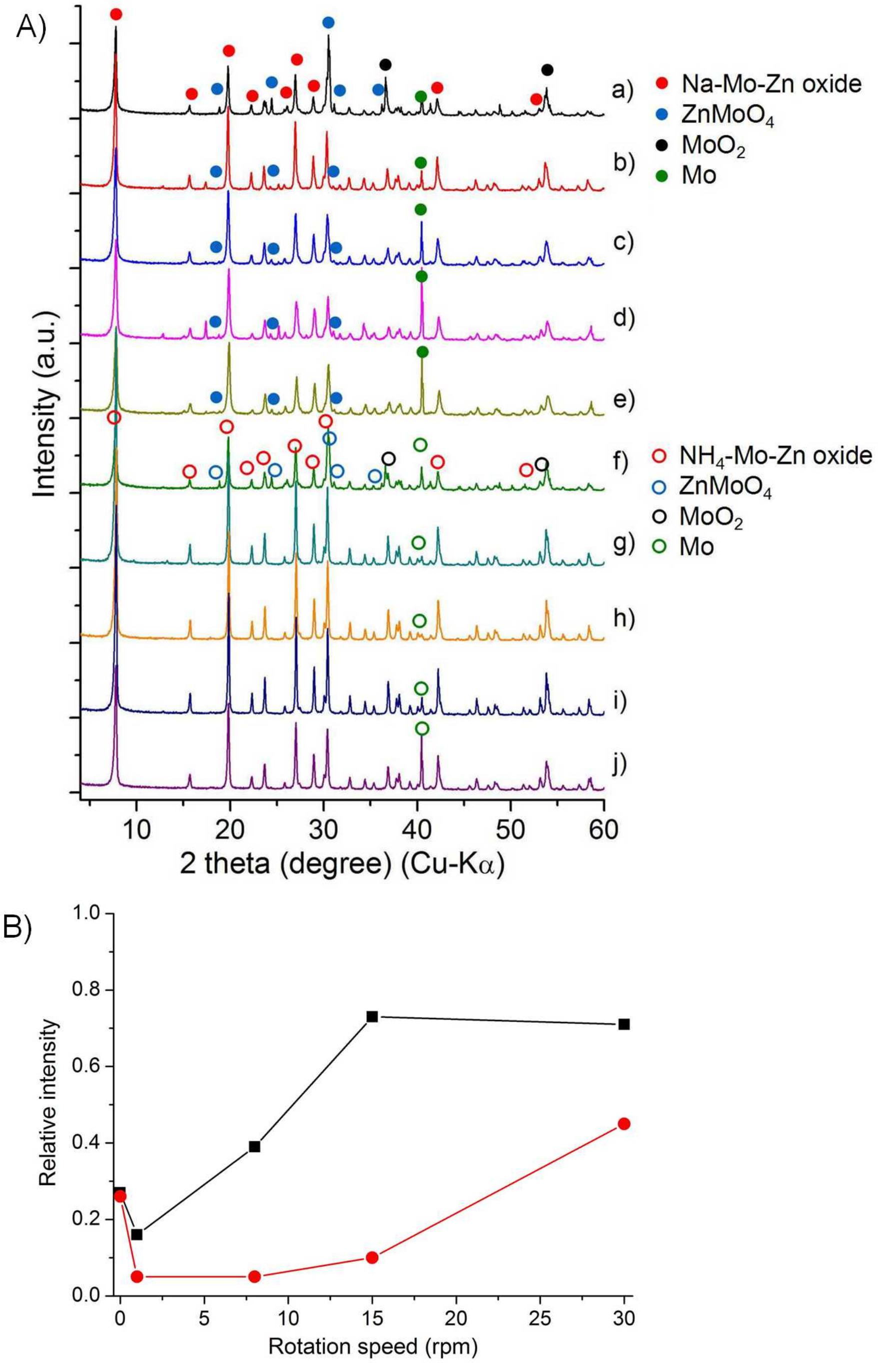

Figure S 6. A) XRD patterns of crude solids of Na–Mo–Zn oxide by a) using non-dynamic method, b) rotation (1 rpm), c) rotation (8 rpm), d) rotation (15 rpm), e) rotation (30 rpm), NH_4–Mo–Zn oxide by f) using non-dynamic method (1 rpm), g) rotation (1 rpm), h) rotation (8 rpm), i) rotation (15 rpm), and j) rotation (30 rpm), B) relative diffraction peak intensity of Mo to Na–Mo–Zn oxide (black) or NH_4–Mo–Zn oxide (red) from the synthesis with different rotation speeds, Mo–Zn oxides (7.8 degree) and Mo (41 degree).

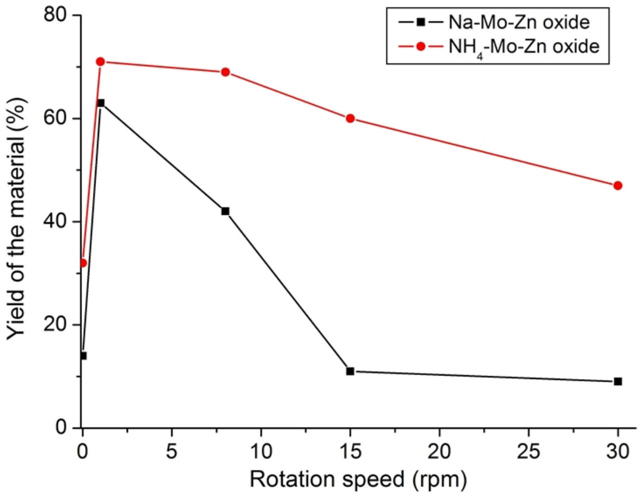

Figure S 7. Relationship between rotation speed and yields of the isolated materials.

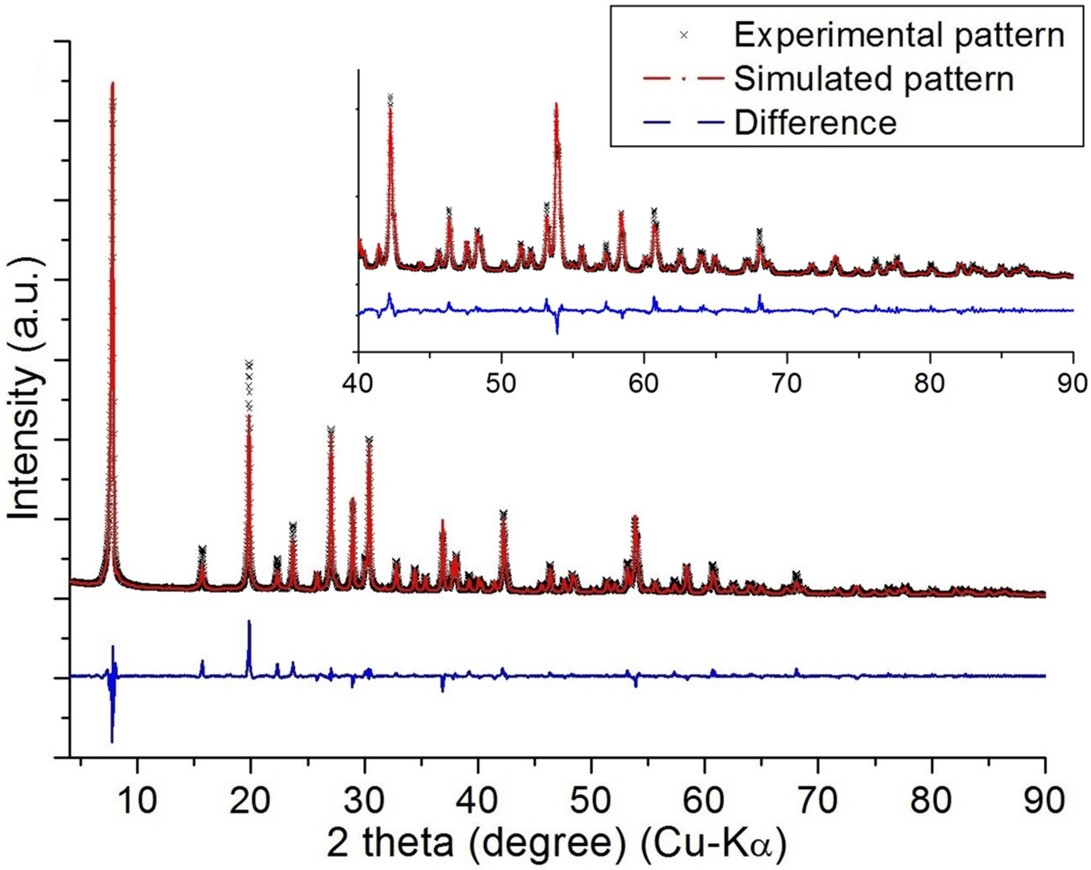

Figure S 8. Comparison of simulated pattern from Rietveld analysis with experimental pattern of NH_4–Mo–Zn oxide, insert: magnification of high angle data.

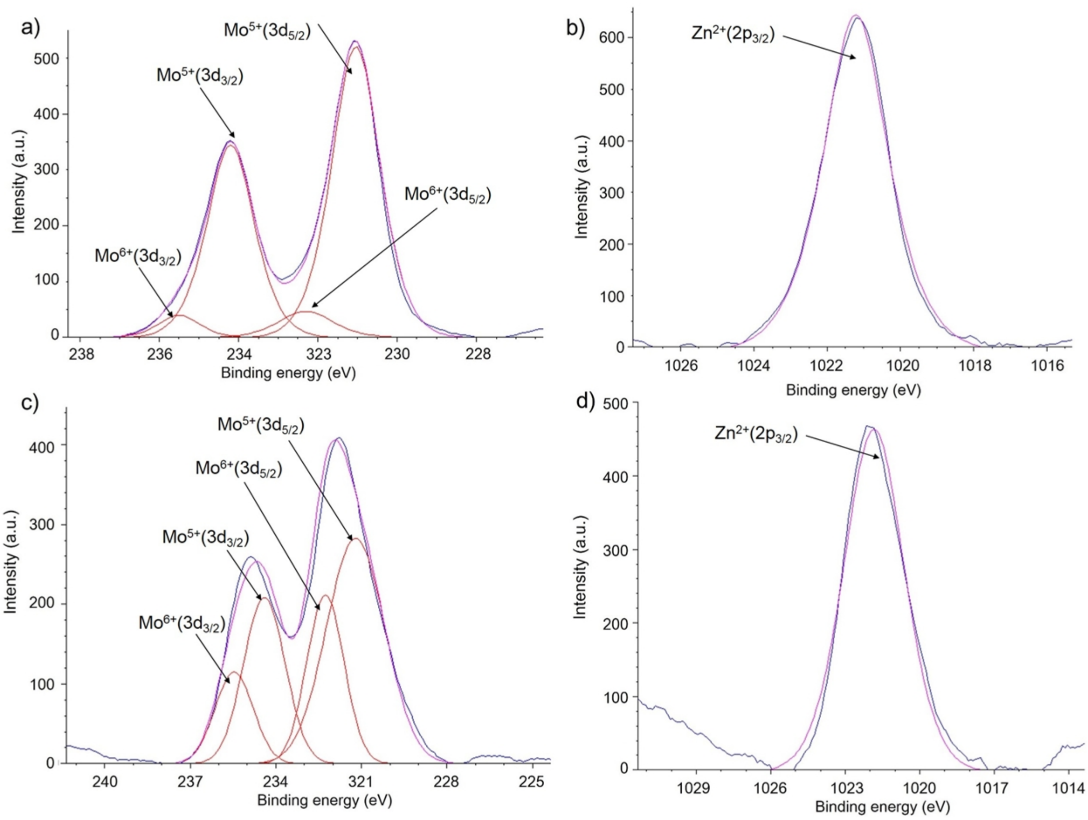

Figure S 9. XPS spectra of a) Mo of Na–Mo–Zn oxide, Mo^{VI}/Mo^{V} was 0.1, b) Zn of Na–Mo–Zn oxide, c) Mo of NH_4–Mo–Zn oxide, Mo^{VI}/Mo^{V} was 0.5, d) Zn of NH_4–Mo–Zn oxide.

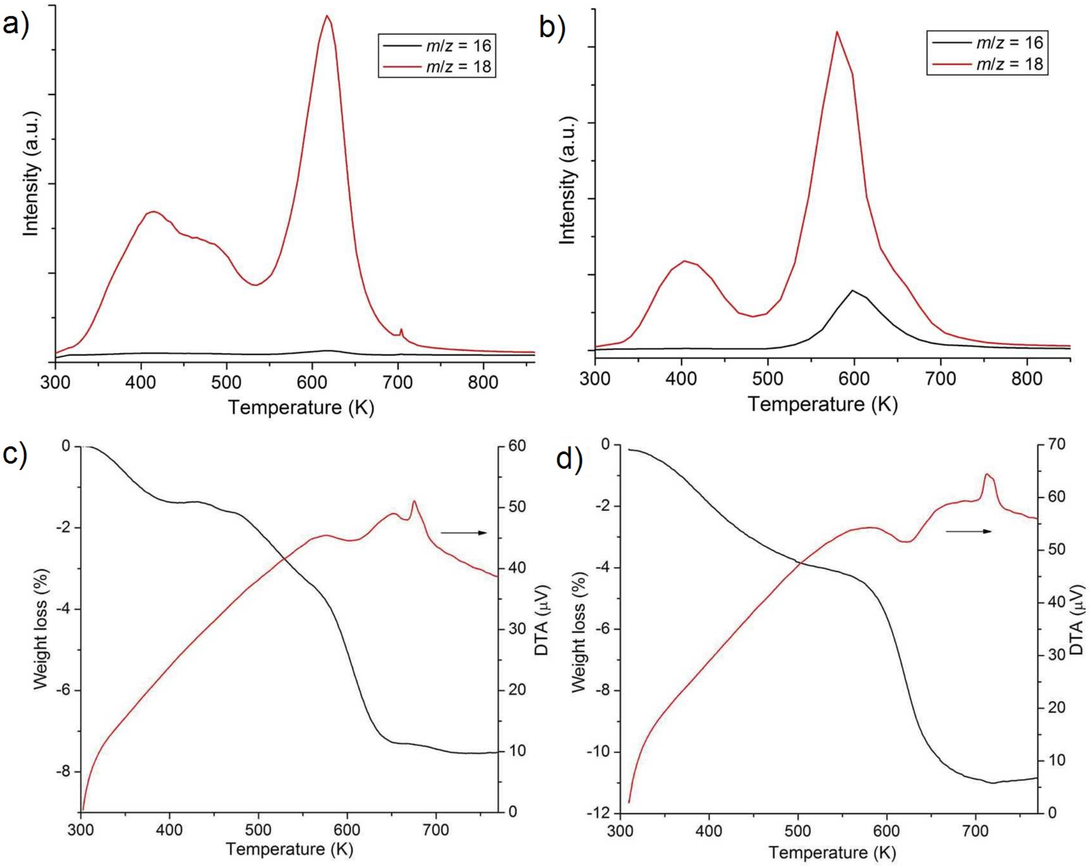

Figure S 10. TPD profiles of the materials, a) Na–Mo–Zn oxide and b) NH_4–Mo–Zn oxide, TG-DTA profiles of c) Na–Mo–Zn oxide and d) NH_4–Mo–Zn oxide.

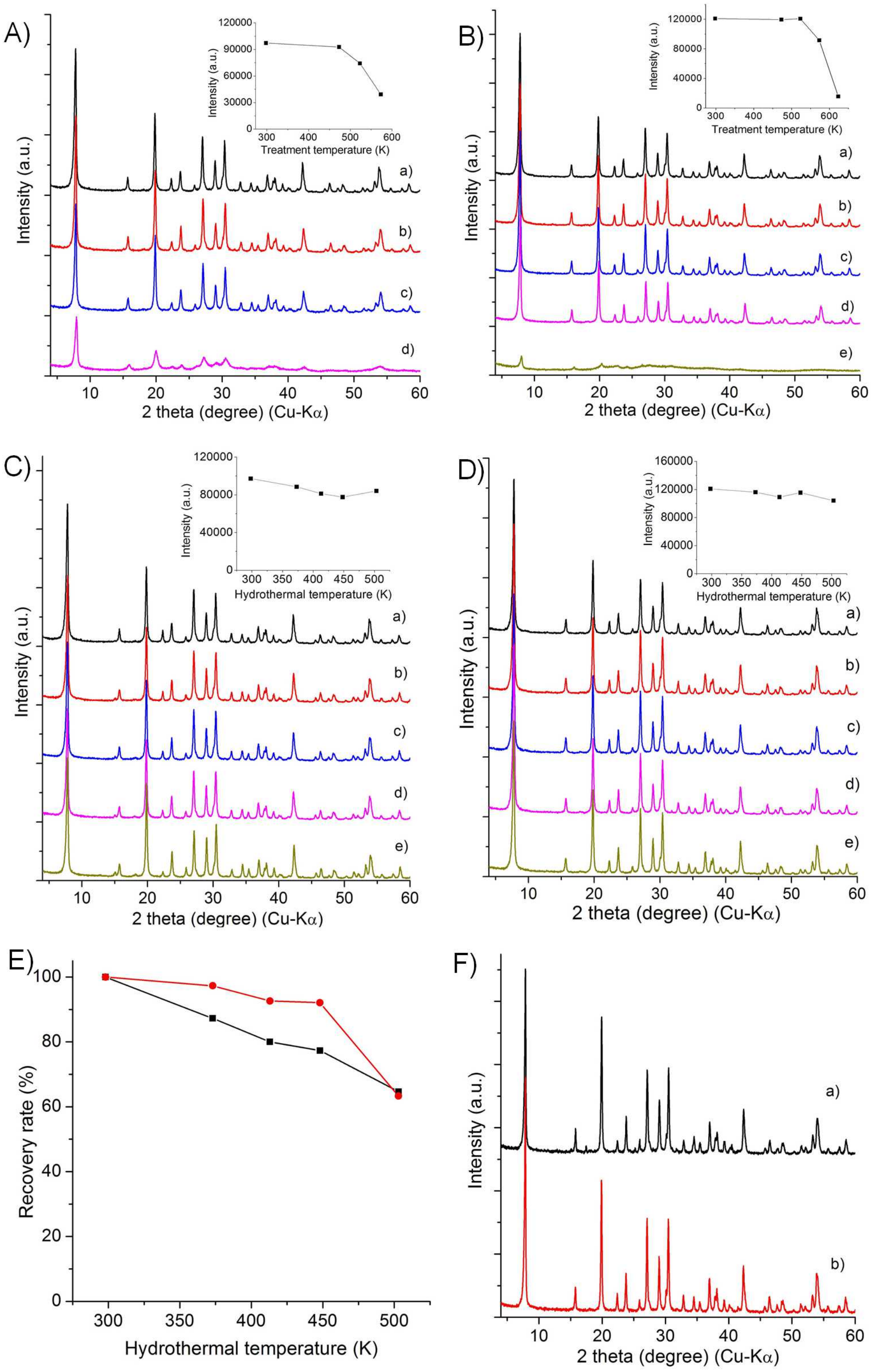

Figure S 11. XRD patterns of A) Na–Mo–Zn oxide and B) NH_4–Mo–Zn oxide a) without heat treatment, heat treatment under N_2 at b) 473 K, c) 523 K, d) 573 K, and e) 623 K (NH_4–Mo–Zn oxide only); XRD patterns of C) Na–Mo–Zn oxide and D) NH_4–Mo–Zn oxide a) without hydrothermal treatment, b) hydrothermal treatment at b) 373 K, c) 413 K, d) 448 K, and e) 503 K; insert: intensity of diffraction peak of (111) (peak at 7.8 degree); E) recovery rate of Na–Mo–Zn oxide (black) and NH_4–Mo–Zn oxide (red) after hydrothermal treatment; F) XRD patterns of a) Na–Mo–Zn oxide and b) NH_4–Mo–Zn oxide after CO_2 adsorption.

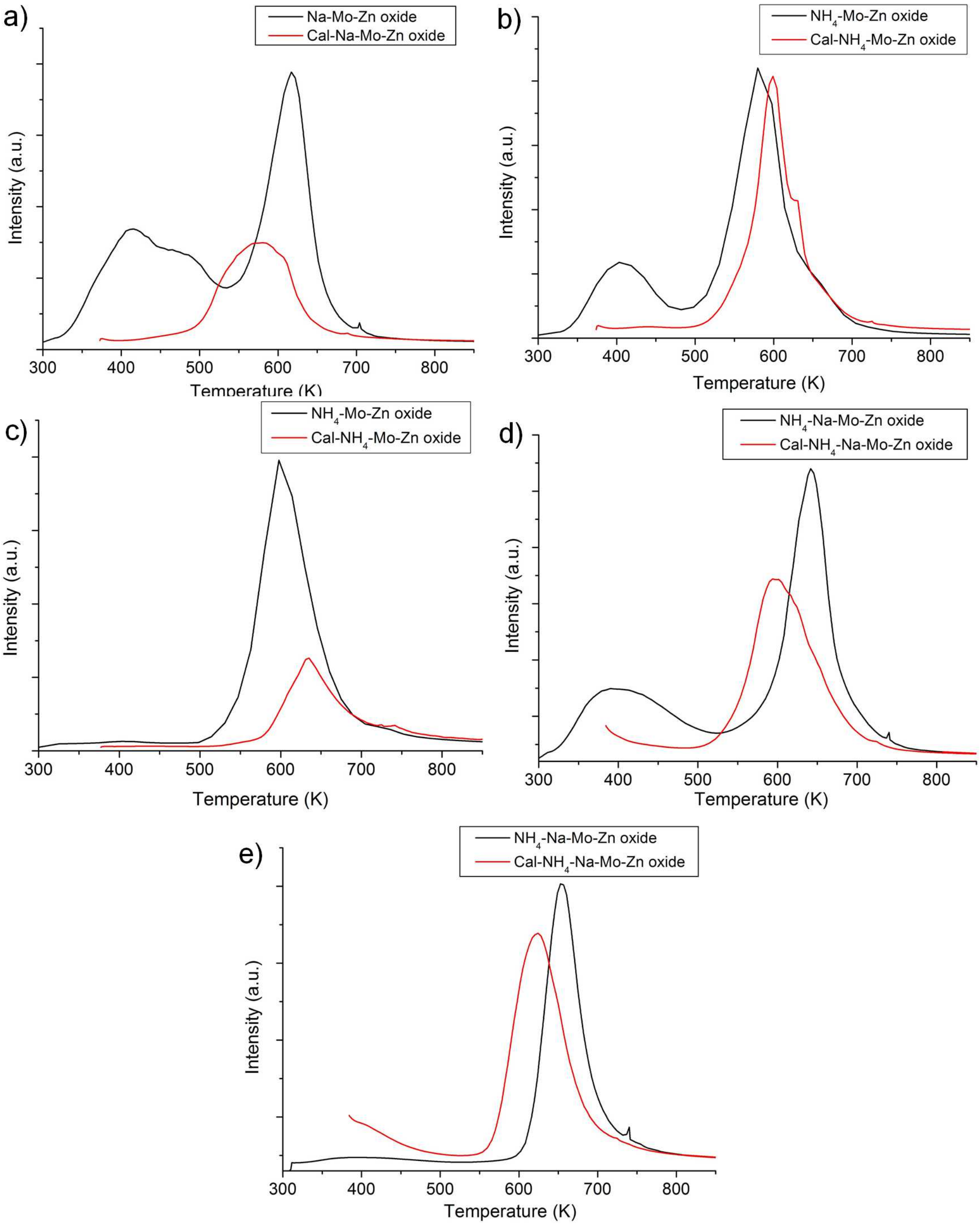

Figure S 12. TPD profiles of a) *m*/*z* = 18, Na–Mo–Zn oxide, area (as synthesized Na–Mo–Zn oxide): area (calcined Na–Mo–Zn oxide) = 1: 0.37, b) *m*/*z* = 18, NH$_4$–Mo–Zn oxide, area (as synthesized NH$_4$–Mo–Zn oxide): area (calcined NH$_4$–Mo–Zn oxide) = 1: 0.59, c) *m*/*z* = 16, NH$_4$–Mo–Zn oxide, area (as synthesized NH$_4$–Mo–Zn oxide): area (calcined NH$_4$–Mo–Zn oxide) = 1: 0.35, d) *m*/*z* = 18, NH$_4$–Na–Mo–Zn oxide, area (as synthesized NH$_4$–Na–Mo–Zn oxide): area (calcined NH$_4$–Na–Mo–Zn oxide) = 1: 0.54, and e) *m*/*z* = 16, NH$_4$–Na–Mo–Zn oxide, area (as synthesized NH$_4$–Na–Mo–Zn oxide): area (calcined NH$_4$–Na–Mo–Zn oxide) = 1: 0.98. For TPD of calcined sample, the material was heated under high vacuum at 473 K for 2.5 h in TPD instrument. Then TPD measurement carried out from 373 K to 873 K.

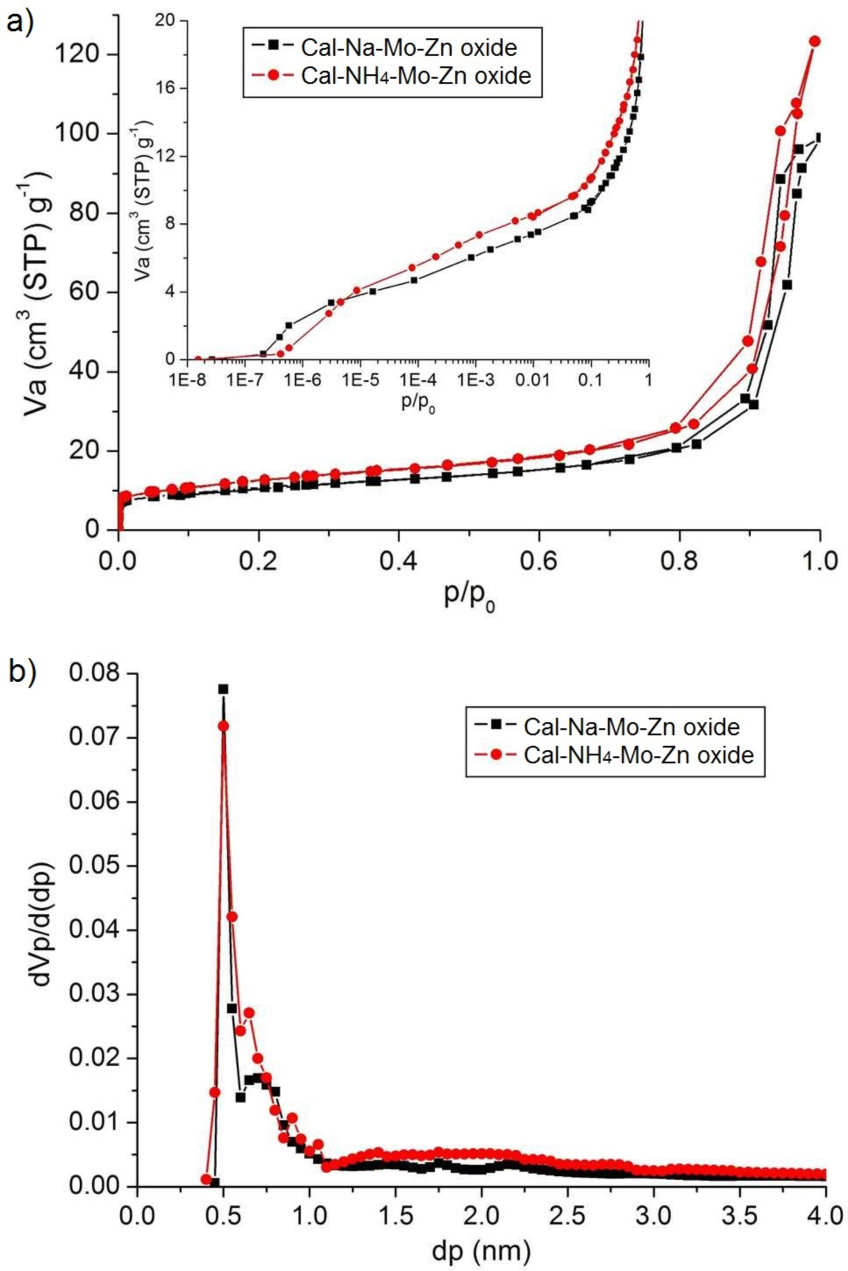

Figure S 13. a) N_2 adsorption-desorption isotherms of the POM-based porous materials, insert: low pressure range and b) pore size distribution by the SF method.

Table S 6. The amount of water and ammonium estimated by elemental analysis and TPD-MS.

	Formula	amount of guest molecules per one POM			
		Na^+	NH_4^+	H_2O	total
Na–Mo–Zn oxide	$Na_{1.5}H_{11.4}[Zn^{II}Mo^{VI}_{1.1}Mo^{V}_{10.9}O_{40}\{Zn^{II}_{2}\}]\cdot 5.5H_2O$	1.5	-	5.5	7
Cal–Na–Mo–Zn oxide	$Na_{1.5}H_{11.4}[Zn^{II}Mo^{VI}_{1.1}Mo^{V}_{10.9}O_{40}\{Zn^{II}_{2}\}]\cdot 2H_2O$	1.5	-	2	3.5
NH_4–Mo–Zn oxide	$(NH_4)_{1.5}H_{8.5}[Zn^{II}Mo^{VI}_{4}Mo^{V}_{8}O_{40}\{Zn^{II}_{2}\}]\cdot 6H_2O$	-	1.5	6	7.5
Cal–NH_4–Mo–Zn oxide	$(NH_4)_{0.4}H_{9.6}[Zn^{II}Mo^{VI}_{4}Mo^{V}_{8}O_{40}\{Zn^{II}_{2}\}]\cdot 3.6H_2O$	-	0.5	3.5	4
NH_4–Na–Mo–Zn oxide	$(NH_4)_{1.4}Na_{0.1}H_{11.4}[Zn^{II}Mo^{VI}_{1.1}Mo^{V}_{10.9}O_{40}\{Zn^{II}_{2}\}]\cdot 5.5H_2O$	0.1	1.4	5.5	7
Cal–NH_4–Na–Mo–Zn oxide	$(NH_4)_{1.4}Na_{0.1}H_{11.4}[Zn^{II}Mo^{VI}_{1.1}Mo^{V}_{10.9}O_{40}\{Zn^{II}_{2}\}]\cdot 3H_2O$	0.1	1.4	3	4.5

Table S 7. Surface area and pore volume calculated from nitrogen sorption isotherms.

	BET surface area (m^2/g)	external surface area [a] (m^2/g)	micropore volume [a] (cm^3/g)
Cal–Na–Mo–Zn oxide	37	27	0.0075
Cal–NH_4–Mo–Zn oxide	45	35	0.0044

[a] calculated by the t-plot method.

Table S 8. Calculated atomic charge for every atom in primitive cell of Na–Mo–Zn oxide.

Atom	charge	Atom	charge	atom	charge	atom	charge
Zn	0.874	Mo	1.562	O	-0.733	O	-0.762
Zn	0.875	Mo	1.542	O	-0.709	O	-0.591
Zn	0.869	Mo	1.521	O	-0.86	O	-0.701
Zn	0.784	Mo	1.433	O	-0.703	O	-0.673
Zn	0.862	Mo	1.487	O	-0.931	O	-0.621
Zn	0.803	Mo	1.491	O	-0.877	O	-0.665
Na	0.919	Mo	1.52	O	-0.871	O	-0.679
Na	0.913	Mo	1.466	O	-0.755	O	-0.631
Na	0.923	Mo	1.439	O	-0.834	O	-0.642
H	0.535	Mo	1.447	O	-0.831	O	-0.617
H	0.549	Mo	1.474	O	-0.853	O	-0.635
H	0.558	Mo	1.515	O	-0.835	O	-0.661
H	0.544	Mo	1.533	O	-0.628	O	-0.663
H	0.529	Mo	1.461	O	-0.706	O	-0.629
H	0.548	Mo	1.51	O	-0.63	O	-0.638
H	0.522	Mo	1.504	O	-0.714	O	-0.688
H	0.515	Mo	1.547	O	-0.562	O	-0.695
H	0.538	Mo	1.515	O	-0.668	O	-0.632
H	0.539	Mo	1.5	O	-0.603	O	-0.649
H	0.532	Mo	1.458	O	-0.572	O	-0.665
H	0.545	Mo	1.487	O	-0.562	O	-0.691
H	0.541	Mo	1.479	O	-0.679	O	-0.707
H	0.556	O	-0.697	O	-0.702	O	-0.629
H	0.546	O	-0.736	O	-0.671	O	-0.651
H	0.53	O	-0.71	O	-0.589	O	-0.627
H	0.514	O	-0.873	O	-0.614	O	-0.636
H	0.561	O	-0.896	O	-0.594	O	-0.75
H	0.534	O	-0.737	O	-0.545	O	-0.757
H	0.56	O	-0.845	O	-0.564	O	-0.747
H	0.559	O	-0.928	O	-0.637	O	-0.749
H	0.561	O	-0.719	O	-0.586	O	-0.755
H	0.536	O	-0.949	O	-0.601	O	-0.744
Mo	1.548	O	-0.761	O	-0.711	O	-0.74
Mo	1.501	O	-0.734	O	-0.627	O	-0.75

Table S 9. Calculated atomic charge for every atom in primitive cell of NH_4–Mo–Zn oxide.

atom	charge	atom	charge	atom	charge	atom	charge
Zn	0.886	Mo	1.49	O	-0.536	O	-0.699
Zn	0.901	Mo	1.536	O	-0.663	O	-0.678
Zn	0.914	Mo	1.55	O	-0.871	O	-0.681
Zn	0.876	Mo	1.456	O	-0.901	O	-0.688
Zn	0.903	Mo	1.463	O	-0.872	O	-0.677
Zn	0.86	Mo	1.573	O	-0.68	O	-0.65
H	0.535	Mo	1.578	O	-0.386	O	-0.644
H	0.527	Mo	1.558	O	-0.55	O	-0.691
H	0.536	Mo	1.575	O	-0.531	O	-0.645
H	0.546	Mo	1.574	O	-0.585	O	-0.658
H	0.52	Mo	1.504	O	-0.551	O	-0.654
H	0.54	Mo	1.511	O	-0.596	O	-0.645
H	0.553	Mo	1.556	O	-0.56	O	-0.695
H	0.538	Mo	1.523	O	-0.574	O	-0.631
H	0.542	Mo	1.486	O	-0.663	O	-0.675
H	0.553	Mo	1.537	O	-0.588	O	-0.678
H	0.529	Mo	1.509	O	-0.663	O	-0.672
H	0.552	O	-0.894	O	-0.553	O	-0.659
H	0.534	O	-0.696	O	-0.608	O	-0.652
H	0.534	O	-0.668	O	-0.553	O	-0.646
H	0.549	O	-0.684	O	-0.535	O	-0.655
H	0.563	O	-0.943	O	-0.585	O	-0.658
H	0.549	O	-0.724	O	-0.574	O	-0.668
H	0.543	O	-0.464	O	-0.588	O	-0.664
H	0.529	O	-0.929	O	-0.598	O	-0.725
H	0.542	O	-0.812	O	-0.573	O	-0.76
Mo	1.555	O	-0.68	O	-0.574	O	-0.72
Mo	1.557	O	-0.413	O	-0.592	O	-0.728
Mo	1.595	O	-0.674	O	-0.575	O	-0.748
Mo	1.554	O	-0.87	O	-0.553	O	-0.723
Mo	1.481	O	-0.833	O	-0.548	O	-0.743
Mo	1.514	O	-0.848	O	-0.54	O	-0.729
Mo	1.44			O	-0.543		

Table S 10. Adsorption properties and CO_2/CH_4 separation selectivities of various materials.

material	adsorbed CO_2 (cm^3/g) [a]	adsorbed CH_4 (cm^3/g)	E (CO_2) (kJ/mol)	E (CH_4) (kJ/mol)	surface area (m^2/g)	pore volume (cm^3/g)	CO_2/CH_4 mixed gas adsorption conditions	CO_2 sel. [b]
present work								
Cal─Na─Mo─Zn oxide	19	10	65~46	30~18	88	0.039	CO_2/CH_4=2/3, 298K, 125 kPa	75 [c]
Cal─NH_4─Mo─Zn oxide	15	10	45~35	30~25	68	0.033	CO_2/CH_4=2/3, 298K, 127 kPa	9 [c]
MOF materials								
$Cu_2(HBTB)_2$ [1]	26	7	NA [d]	NA	600	NA	CO_2/CH_4=1, 298K, 10~2500 kPa	35~5 [e]
Cu-BTC [2]	110	8	22~16	4	2137	NA	CO_2/CH_4=1, 298 K, 1~100 kPa	7.5 [e]
$Zn_2(NDC)_2(DPNI)$ [3]	31	29	NA	NA	1761	0.68	CO_2/CH_4=1, 296 K, 10 kPa~1500 kPa	30~7 [e]
C_{168} Schwarzite [4]	139	122	36	27	NA	NA	CO_2/CH_4=1, 300 K, 100 kPa	6 [e]
IRMOF-1 [4]	25	12	14	10	2833	NA	CO_2/CH_4=1, 300 K, 100 kPa	1.4 [e]
$Zn_3(OH)(CDC)_{2.5}(DEF)_4$ [5]	20	4	NA	NA	248	NA	CO_2/CH_4=1, 298 K, 100 kPa	9 [e]
$Cu_2(IMTA)(DMSO)_2$ [6]	40	6	NA	NA	520	NA	CO_2/CH_4=1, 298 K, 100 kPa	20 [e]
zeolites								
13X [7]	100	13	37	15	NA	NA	298 K, 100 kPa	20 [e]
MFI [4]	29	14	23	19	NA	NA	CO_2/CH_4=1, 300 K, 100 kPa	2 [e]
other material								
Macrocation-POM [8]	14	NA	40~25	NA	48	NA	CO_2/CH_4=1, 298 K, 100 kPa	27 [c]

[a] Adsorbed amount at 100 kPa.

[b] The selectivity of CO_2 over CH_4 was calculated by the following equation.
$S_{CO2} = (x_{CO2}/y_{CO2})/(x_{CH4}/y_{CH4})$
y_{CO2}: mole fraction of component CO_2 in gas phase;
y_{CH4}: mole fraction of component CH_4 in gas phase;
x_{CO2}: mole fraction of component CO_2 in adsorbed phase;
x_{CH4}: mole fraction of component CH_4 in adsorbed phase.

[c] Experimental mixed gas adsorption data.

[d] NA: not available in the paper.

[e] Selectivity of CO_2 was predicted by the ideal adsorbed solution theory (IAST) [9]
$S_{CO2} = (x_{CO2}/y_{CO2})/(x_{CH4}/y_{CH4})$

y_{CO2}: mole fraction of component CO_2 in gas phase;
y_{CH4}: mole fraction of component CH_4 in gas phase;
x_{CO2}: mole fraction of component CO_2 in adsorbed phase;
x_{CH4}: mole fraction of component CH_4 in adsorbed phase.

References:

1. B. Mu, F. Li, K. S. Walton *Chem. Commun.* **2009**, 2493–2495.

2. A. Ö. Yazaydın, A. I. Benin, S. A. Faheem, P. Jakubczak, J. J. Low, R. R. Willis, R. Q. Snurr, *Chem. Mater.* **2009**, *21*, 1425–1430.

3. Y.-S. Bae, K. L. Mulfort, H. Frost, P. Ryan, S. Punnathanam, L. J. Broadbelt, J. T. Hupp, R. Q. Snurr, *Langmuir* **2008**, *24*, 8592–8598.

4. R. Babarao, Z. Hu, J. Jiang *Langmuir* **2007**, *23*, 659–666.

5. Y.-S. Bae, O. K. Farha, A. M. Spokoyny, C. A. Mirkin, J. T. Hupp, R. Q. Snurr *Chem. Commun.* **2008**, 4135–4137, O. K. Farha, A. M. Spokoyny, K. L. Mulfort, M. F. Hawthorne, C. A. Mirkin, J. T. Hupp, *J. Am. Chem. Soc.* **2007**, *129*, 12680–12681.

6. J. Y. Lee, J. M. Roberts, O. K. Farha, A. A. Sarjeant, K. A. Scheidt, J. T. Hupp *Inorg. Chem.* **2009**, *48*, 9971–9973.

7. S. Cavenati, C. A. Grande, A. E. Rodrigues *J. Chem. Eng. Data* **2004**, *49*, 1095–1101.

8. R. Eguchi, S. Uchida, N. Mizuno *J. Phys. Chem. C* **2012**, *116*, 16105−16110.

9. A. L. Myers; J. M. Prausnitz, *A.I.Ch.E. J.* **1965**, *11*, 121–127.

Table S 11. Atom position, temperature factor, and occupancy of NH_4–Mo–Zn oxide obtained from Rietveld refinement.

Atom	X	Y	Z	Uiso	occupancy
Mo1	0.07792	0.45326	0.17208	0.005	1
O2	0.06176	0.37181	0.18824	0.06	1
O3	0.06513	0.47659	0.27341	0.06	1
O4	0.28564	0.57039	0.17961	0.06	1
O5	0.18455	0.56545	0.06545	0.06	1
Zn6	0.125	0.625	0.125	0.02	1
Zn7	0.25	0.5	0.25	0.02	1
O8	0.06523	0.18477	0.11175	0.06	0.35
O9	0.01196	0.01196	0.01196	0.06	0.75

Table S 12. Bond length of NH_4–Mo–Zn oxide obtained from Rietveld refinement.

bond	length (Å)
Mo1-O2	1.646
Mo1-O3	2.038
Mo1-O4	1.995
Mo1-O5	2.209
Zn6-O5	2.005
Zn7-O4	2.057