

Electronic Supplementary Information (ESI) for

Highly Selective Oximation of Aldehydes Catalyzed by Recyclable Heterogeneous Sandwich-type Polyoxometalate

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Experimental section

Reagents and measurements

Analytically pure NaOH, Mg(NO₃)₂·6H₂O, Zn(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, Na₂WO₄·2H₂O, aqueous 65% HNO₃, aqueous NH₃·H₂O (25 wt.%), aqueous H₂O₂ (30 wt.%), Cyclohexanone (99%), Valeraldehyde (98%), 2-Methylvaleraldehyde (98%), Hexanal (98%), Heptanal (99%), Octanal (98%), Nonanal (99%), Decanal (96%), Cyclohexanecarboxaldehyde (98%), 9-Anthraldehyde (98%), Indole-3-carboxaldehyde (99%), Quinoline-2-carboxaldehyde (97%) and Fluorene-2-carboxaldehyde (99%) were purchased from Alfa Aesar and used without further purification.

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku XRD-6000 diffractometer under the following conditions: 40 kV, 30 mA, Cu K α radiation ($\lambda = 0.154$ nm). Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Vector 22 infrared spectrometer using KBr pellet method. Scanning electron microscopy (SEM) images and energy dispersive X-ray (EDX) analytical data were obtained using a Zeiss Supra 55 SEM equipped with an EDX detector. Transmission

electron microscopy (TEM) micrographs were recorded using a Hitachi H-800 instrument. Thermogravimetric (TG) analysis was carried out on a locally produced HCT-2 thermal analysis system in flowing N₂ with a heating rate of 10 °C·min⁻¹. Inductively coupled plasma–atomic emission spectroscopy (ICP-AES) analysis was performed using a Shimadzu ICPS-7500 spectrometer. Nitrogen absorption and desorption experiments were performed at 77 K on a Quantachrome Autosorb-1C analyzer, and the samples were degassed at 120 °C for 6 hours before the measurements. ¹H-NMR spectra was recorded on a Bruker AV400 NMR spectrometer at resonance frequency of 400 MHz, and the chemical shifts were given relative to TMS as the internal reference. The products of the catalytic reactions of cyclohexanone and aliphatic aldehydes were analyzed by Agilent 7820A gas chromatography (GC) system using a 30 m 5% phenylmethyl silicone capillary column with an ID of 0.32 mm and 0.25 μm coating (HP-5). The products were identified using reference standards. The products of the catalytic reactions of polycyclic aromatic aldehydes were analyzed by Varian Prostar High Performance Liquid Chromatography (HPLC) system. Diluted samples of filtered reaction mixtures were eluted with methanol/water (30/70 vol.-% HPLC grade, 1 ml·min⁻¹) on a ChromSpher5 C18 column, connected to a UV detector (λ = 254 nm). All above products were identified using reference standards.

Preparation of catalysts

Preparation of Na₁₂[WZn₃(H₂O)₂[ZnW₉O₃₄]₂·46H₂O (Na-Zn₅W₁₉). This POM cluster was prepared and characterized according to the literature methods.^{S1} The detailed procedure is as following: A solution of Na₂WO₄·2H₂O (127 g, 0.38 mol) in 350 ml H₂O was heated at 80~85 °C and vigorously stirred. The above solution was treated with (25 ml, 0.35 mol) aqueous 65% HNO₃ until the formed precipitate dissolved completely. A solution of Zn(NO₃)₂·6H₂O (29.8 g, 0.10 mol) in 100 ml H₂O was then added dropwise and the mixture was heated at 90~95 °C. The obtained solution was then evaporated to half volume, kept still at room temperature. After several days, the precipitate was filtered and the product was air-dried.

Preparation of the layered double hydroxides (LDHs) support of Mg₃Al–NO₃.

Mg₃Al–NO₃ was prepared using a method involving separate nucleation and aging steps (SNAS) developed by Duan et al.^{S2} In a typical experiment, a solution of Mg(NO₃)₂·6H₂O (7.7 g, 0.03 mol) and Al(NO₃)₃·9H₂O (3.8 g, 0.01 mol) in 100 ml decarbonated H₂O (Mg/Al=3/1) was mixed in a colloid mill rotating at 3000 rpm with a solution of NaOH (3.2 g, 0.08 mol) in 100 ml of decarbonated H₂O. In two minutes, the resulting slurry was transferred to autoclave for static crystallization at 100 °C. After aging for 12 hours, the slurry was separated into two equal portions. Both of the two portions were centrifuged and washed with boiling decarbonated H₂O for three times. One portion was dried at 60 °C overnight and used for characterization; the other was stored in refrigerator under N₂ for the next step. The anion exchange capacity (AEC) of the Mg₃Al–NO₃ stored in refrigerator is about 5 mmol (assuming 10 mmol Al³⁺ all incorporated into LDHs layers).

Preparation of LDHs–POM catalyst. Mg₃Al–Zn₅W₁₉ catalyst. The detailed procedure is as follows: the slurry of Mg₃Al–NO₃ was obtained by dispersing the precipitate of Mg₃Al–NO₃ (AEC = 5 mmol) in 100 ml decarbonated H₂O. A solution of Na–Zn₅W₁₉ (5.0 g, 0.84 mmol) in 40 ml of decarbonated H₂O was added dropwise to the Mg₃Al–NO₃ slurry under N₂ with rapid stirring. The amount of Na–Zn₅W₁₉ (0.84 mmol, 12 × 0.84 mmol ≈ 10 mmol of negative charge capacity) was two-fold excess of AEC of Mg₃Al–NO₃. The mixture slurry was stirred for 5 hours at 60 °C. Finally, Mg₃Al–Zn₅W₁₉ catalyst was obtained as a white solid after being washed with boiling decarbonated water for three times and dried at 60 °C overnight under vacuum.

Procedure for oximation

Procedure for oximation of cyclohexanone and aliphatic aldehydes. In a typical experiment, 1 mmol cyclohexanone or aliphatic aldehydes, aqueous H₂O₂ (30 wt.%), aqueous NH₃·H₂O (25 wt.%), 2.5 μmol Na–Zn₅W₁₉ or 24 μmol Mg₃Al–Zn₅W₁₉ as catalyst and 200 μL solvent were placed in a 20 ml glass bottle at room temperature and the reaction mixture was kept stirring vigorously. The reaction was effectively

quenched after 6 hours. The resulting oily products were extracted by dichloromethane, analyzed by GC and identified by $^1\text{H-NMR}$ to determine the conversion and selectivity. After being washed with acetone, the $\text{Mg}_3\text{Al-Zn}_5\text{W}_{19}$ catalyst was recovered by centrifugation, dried under vacuum and reused.

Procedure for oximation of polycyclic aromatic aldehydes. In a typical experiment, 1 mmol polycyclic aromatic aldehydes, aqueous H_2O_2 (30 wt.%), aqueous $\text{NH}_3\cdot\text{H}_2\text{O}$ (25 wt.%), 2.5 μmol $\text{Na-Zn}_5\text{W}_{19}$ or 24 μmol $\text{Mg}_3\text{Al-Zn}_5\text{W}_{19}$ as catalyst and 1 ml methanol were added to a 20 ml glass bottle at room temperature and vigorously stirred with a magnetic stirrer. The reaction was effectively quenched after 6 hours. The reaction mixtures were then diluted by methanol and filtered using a 0.22 μm microfilter. The filtrate was analyzed by HPLC and identified by $^1\text{H-NMR}$ to determine conversion and selectivity. After being washed with acetone, the $\text{Mg}_3\text{Al-Zn}_5\text{W}_{19}$ catalyst was recovered by centrifugation, dried under vacuum and recycled.

References

[S1] Y. Zhao, F. Li, R. Zhang, D. G. Evans and X. Duan, *Chem. Mater.*, 2002, **14**, 4286.

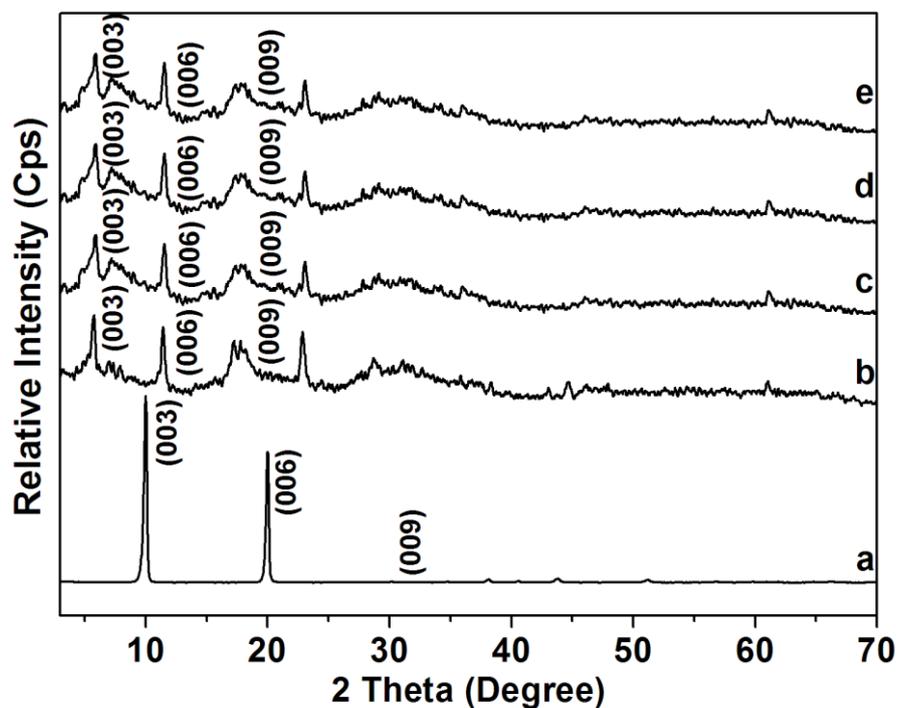


Figure S1. Powder XRD patterns of (a) Mg₃Al-NO₃, (b) Mg₃Al-Zn₅W₁₉, (c) the recycled Mg₃Al-Zn₅W₁₉ catalyst for 3 times, (d) the recycled Mg₃Al-Zn₅W₁₉ catalyst for 7 times and (e) the recycled Mg₃Al-Zn₅W₁₉ catalyst for 10 times.

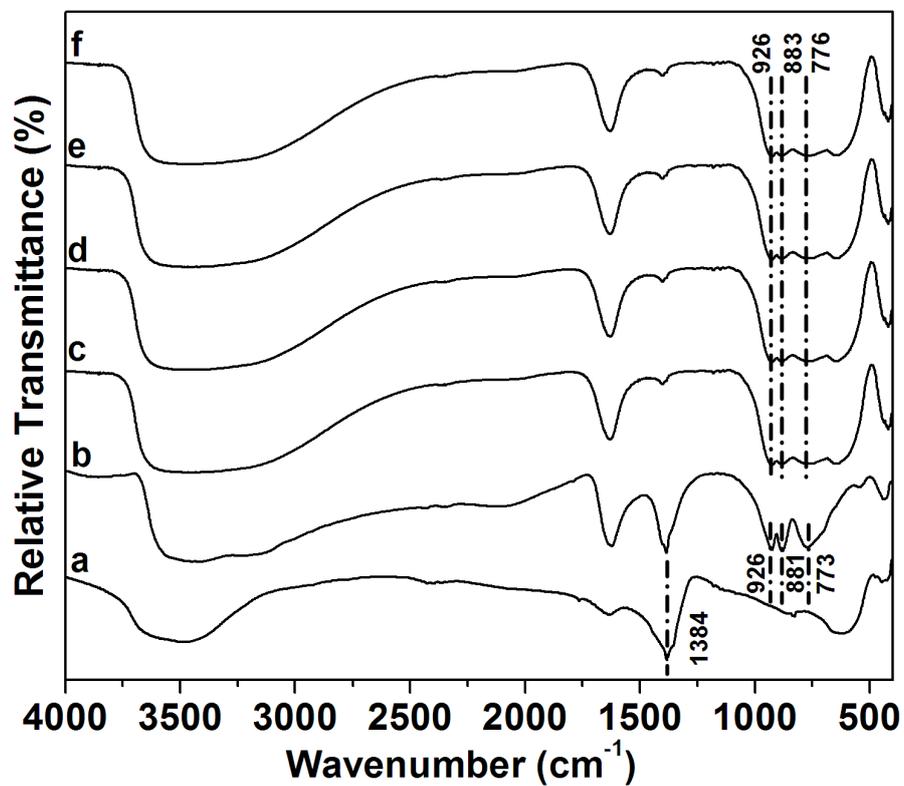


Figure S2. FT-IR spectra of (a) Mg₃Al-NO₃, (b) Na-Zn₅W₁₉, (c) Mg₃Al-Zn₅W₁₉, (d) recycled Mg₃Al-Zn₅W₁₉ for 3 times, (e) recycled Mg₃Al-Zn₅W₁₉ for 7 times and (f) recycled Mg₃Al-Zn₅W₁₉ for 10 times.

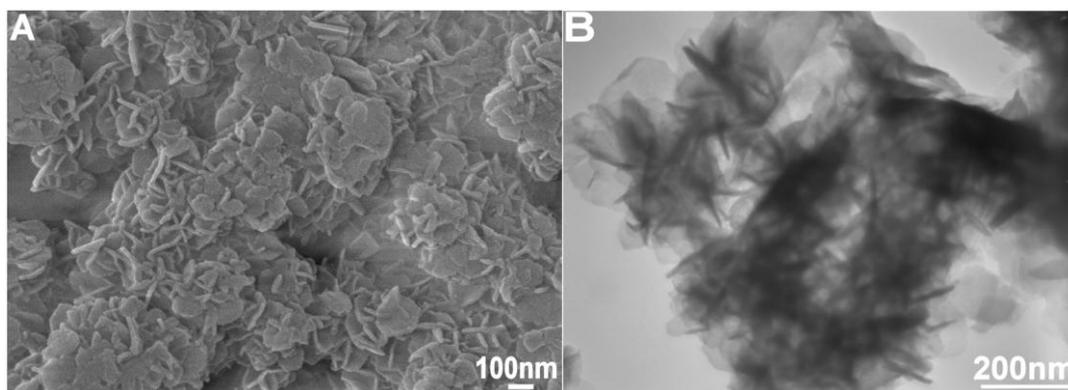


Figure S3. (A) SEM and (B) TEM images of Mg₃Al-Zn₅W₁₉.

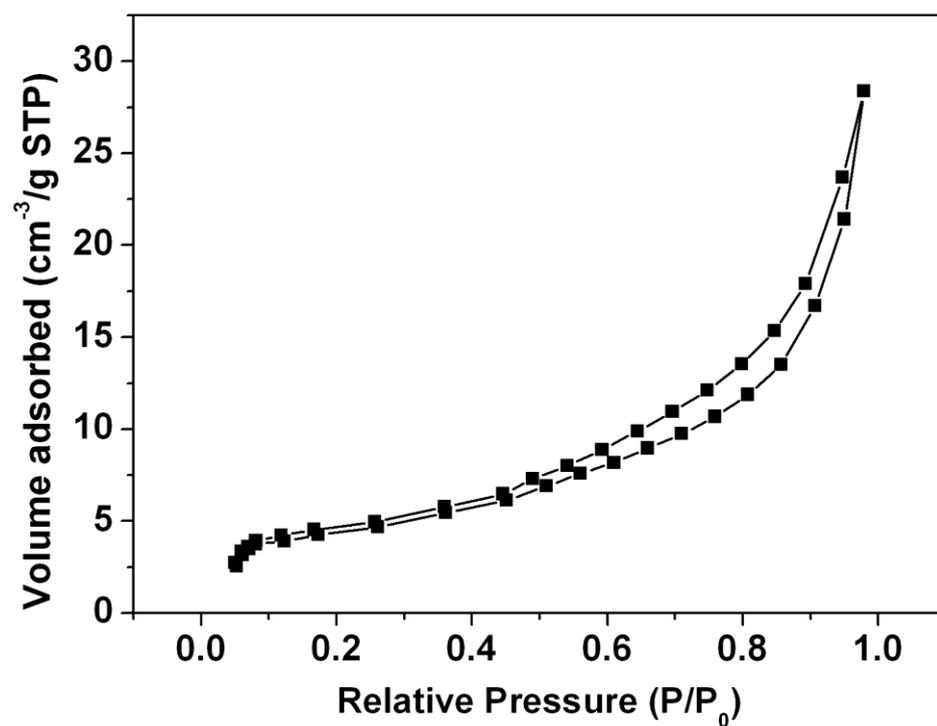


Figure S4. N₂ adsorption-desorption isotherm of Mg₃Al-Zn₅W₁₉.

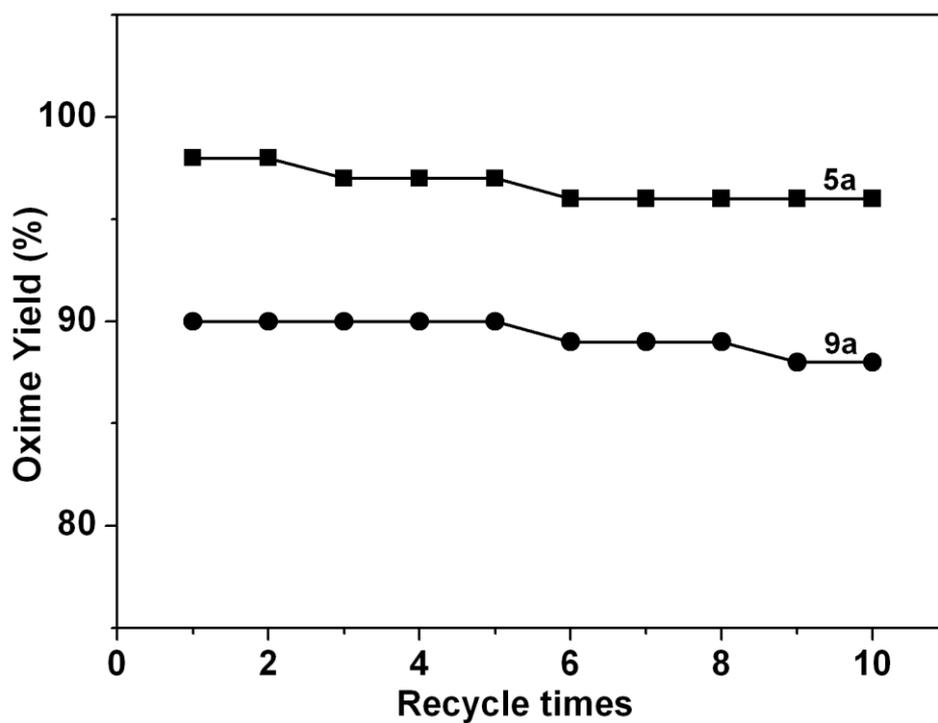


Figure S5. Oximation of **5a** and **9a** by $Mg_3Al-Zn_5W_{19}$ and the catalyst are recycled for 10 times.

Table S1. Composition of Mg₃Al-NO₃ and Mg₃Al-Zn₅W₁₉.

Sample	<i>d</i> (003) (nm)	Composition (Mg: Al: Zn: W) ^a	<i>S</i> _{BET} (m ² ·g ⁻¹)	<i>S</i> _{Microporous} (m ² ·g ⁻¹) ^b	Formula ^c
Mg ₃ Al-NO ₃	0.88	3.08 : 1.00 : 0.00 : 0.00	7	0	Mg _{0.75} Al _{0.25} (OH) ₂ (NO ₃) _{0.25} ·0.37H ₂ O
Mg ₃ Al-Zn ₅ W ₁₉	1.54	3.05 : 1.00 : 0.42 : 1.59	24	6	Mg _{0.75} Al _{0.25} (OH) ₂ (Zn ₅ W ₁₉ O ₆₈) _{0.021} ·1.26H ₂ O

a determined by ICP-AES. b determined by the t-plot method. c determined by ICP-AES and TG.

Table S2. Optimization of the cyclohexanone: H₂O₂: NH₃ ratio for oximation of cyclohexanone by Mg₃Al-Zn₅W₁₉ in water.

Entry	Cyclohexanone: H ₂ O ₂ : NH ₃	Conversion	Selectivity	Yield ^a
1	1:4:2	90	67	60
2	1:4:3	91	74	67
3	1:4:4	92	78	72
4	1:4:5	91	71	65
5	1:5:2	94	85	80
6	1:5:3	95	86	82
7	1:5:4	98	92	90
8	1:5:5	96	84	81
9	1:6:2	95	71	67
10	1:6:3	95	76	72
11	1:6:4	96	84	81
12	1:6:5	97	75	73

a: Yield = Conversion × Selectivity.

Table S3. Selection of solvents for oximation of cyclohexanone by Mg₃Al-Zn₅W₁₉ with cyclohexanone: H₂O₂: NH₃ = 1:5:4.

Entry	Solvents	Conversion	Selectivity	Yield ^a
1	Water	98	92	90
2	Methanol	98	62	61
3	Ethanol	96	78	75
4	1-Propanol	96	86	80
5	<i>iso</i> -Propanol	92	72	66
6	1-Butanol	99	99	98
7	<i>tert</i> -Butanol	91	81	74

a: Yield = Conversion × Selectivity.

Table S4. ICP measurements of the composition of the catalyst ($\text{Mg}_3\text{Al-Zn}_5\text{W}_{19}$).

Samples	Composition (Mg: Al: Zn: W) ^a
$\text{Mg}_3\text{Al-Zn}_5\text{W}_{19}$ -Fresh	3.05 : 1.00 : 0.42 : 1.59
$\text{Mg}_3\text{Al-Zn}_5\text{W}_{19}$ -Reused-3 times	3.04 : 1.00 : 0.41 : 1.58
$\text{Mg}_3\text{Al-Zn}_5\text{W}_{19}$ -Reused-7 times	3.04 : 1.00 : 0.41 : 1.58
$\text{Mg}_3\text{Al-Zn}_5\text{W}_{19}$ -Reused-10 times	3.03 : 1.00 : 0.40 : 1.57

a: Determined by ICP-AES.
