Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information for New Journal of Chemistry

Preparation of zeolitic bismuth vanadomolybdate using a ball-shaped giant polyoxometalate for olefin epoxidation

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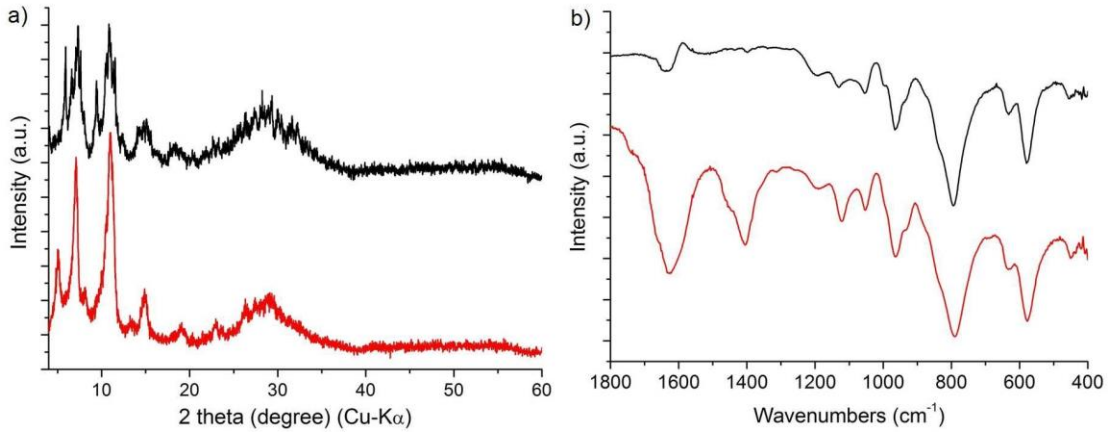

Figure S1. a) XRD patterns of K-{$Mo_{72}V_{30}$} (black) and NH_4-{$Mo_{72}V_{30}$} (red) and b) FTIR spectra of K-{$Mo_{72}V_{30}$} (black) and NH_4-{$Mo_{72}V_{30}$} (red).

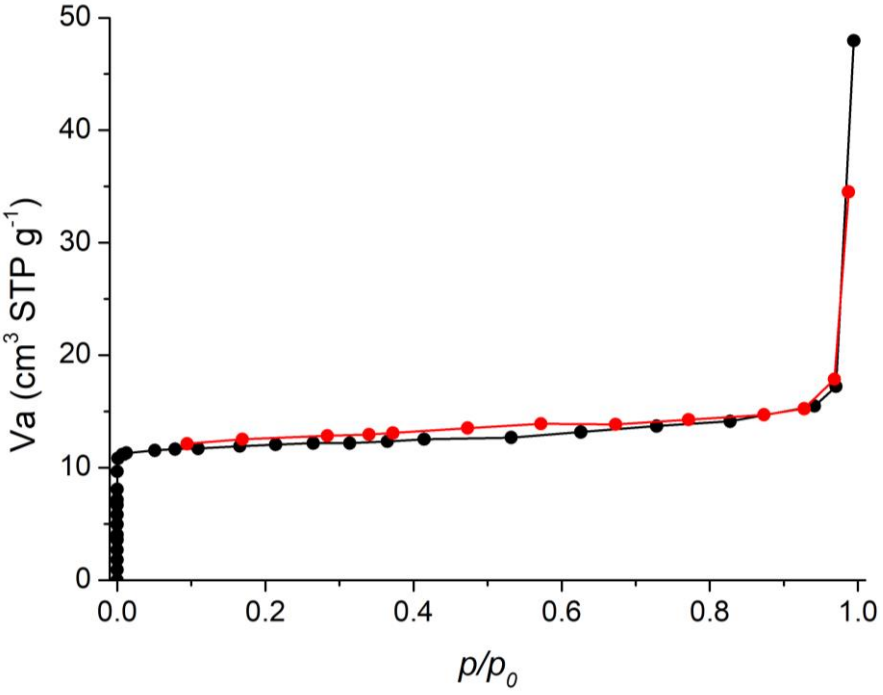

Figure S2. N_2 adsorption-desorption isotherms of **BVM**, adsorption branch (black) and desorption branch (red).

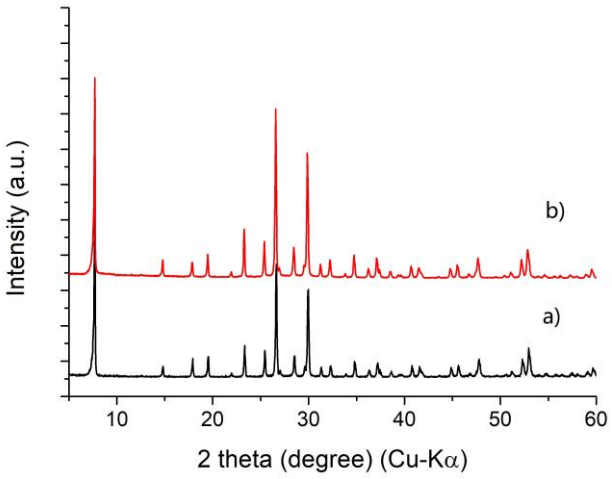

Figure S3. XRD patterns of a) **BVM** and b) **BVM-TBHP.**

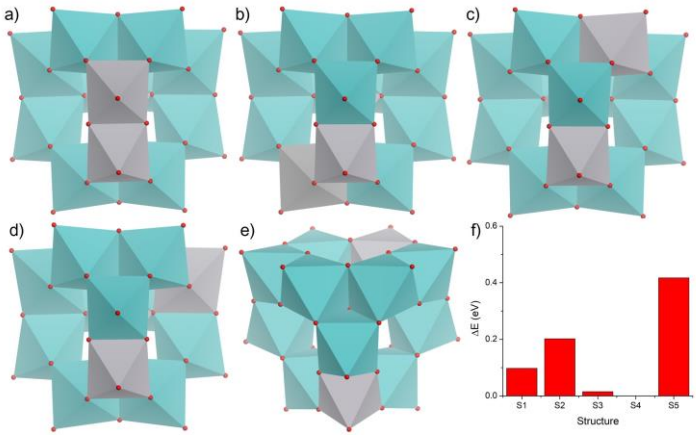

Figure S4. The relative V site in the material and the corresponding energies, a) position S1, b) position S2, c) position S3, d) position S4, e) position S5, and f) relative energy of the structures with different V sites, Mo (blue), V (gray), O (red).

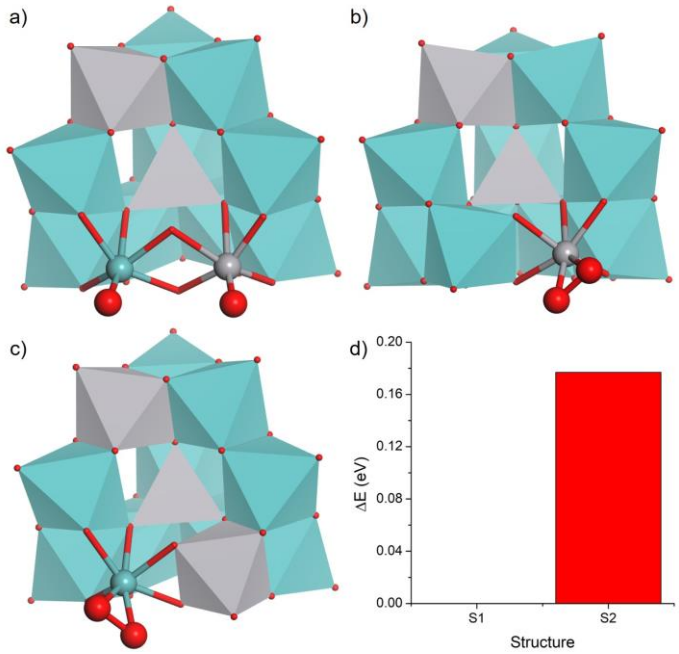

Figure S5. The structures of the material with peroxo bond in different sites and the corresponding energies, a) ε-Keggin unit, b) position S1 with peroxo bond in V site, c) position S2 with peroxo bond in Mo site, and d) relative energy of the structures with peroxo bond in different V sites, Mo (blue), V (gray), O (red).

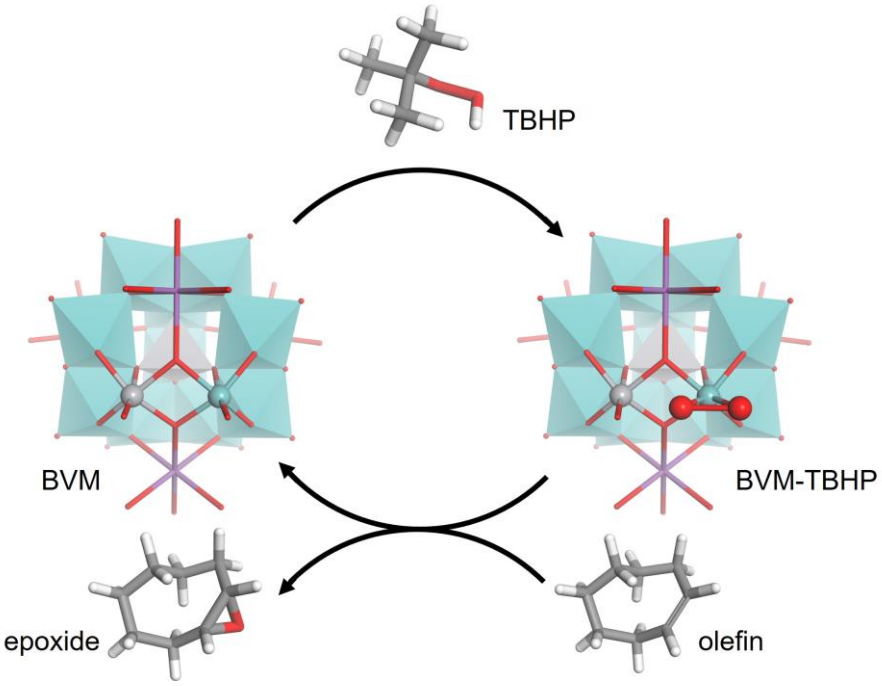

Figure S6. Reaction pathway of olefin epoxidation by **BVM**, Mo (blue), V (gray), Bi (purple), O (red), C (black), H (white).

Table S1. Comparing the reaction condition of the reported $\{Mo_{72}V_{30}\}$ with the current work.

Entry	Mo	V	Reductant	pH	Other additives	H_2O	Ref.
1	$Na_2MoO_4·2H_2O$ (10 mmol)	$VOSO_4·5H_2O$ (10 mmol)	-	-	KCl (0.65 g, 8.72 mmol	43 mL	[1]
2	$Na_2MoO_4·2H_2O$ (24.8 mmol)	$NaVO_3$ (21.3 mmol	$N_2H_6SO_4$ (0.9 g, 6.9 mmol).	2.8	KCl (3 g, 40.2 mmol)	164 mL	[2]
3	$Na_2MoO_4·2H_2O$ (2.4 mmol)	$NaVO_3$ (3.2 mmol)	Na_2SO_3 (74.0 mmol)	2.5-4.5	Triethanolamine (8.7 mmol) KCl (8.72 mmol)	25 mL	[3]
4	$(NH_4)_6Mo_7O_{24}·4H_2O$ (Mo: 24.8 mmol)	NH_4VO_3 (21.3 mmol)	$N_2H_6SO_4$ (6.9 mmol)	2	-	130 mL	This work

Table S2. Solvent effect of **BVM** for epoxidation of cyclooctene using TBHP.

Entry	Solvent	Yield (%)	Selectivity (%)
1	Acetonitrile	99	99
2	Ethanol	0	-
3	DMSO	0	-
4	Ethyl acetate	0	-
5	Toluene	3	3
6	Decane	7	7
7	Chloroform	0	-
8	1,2-dichloroethane	0	-

[a] Reaction conditions: **BVM** 40 mg, solvent 1.5 mL, cyclooctene 2.5 mmol, TBHP (5.5 M in decane) 0.5 mmol, chlorobenzene 0.5 mmol, reaction temperature 60 ^{o}C, reaction time 24 h, yield based on TBHP..

Reference

1. M. Achim, A. M. Todea, J. Van Slageren, M. Dressel, B. Hartmut, M. Schmidtmann, M. Luban, L. Engelhardt, and M. Rusu, *Angew. Chem. Int. Ed.*, 2005, **44**, 3857–3860.
2. B. Botar, P. Ko, and C. L. Hill, *Chem. Commun.*, 2005, **21**, 3138–3140.
3. H. N. Miras, M. N. C. Ochoa, D. Long, and L. Cronin, *Chem. Commun.*, 2010, **46**, 8148–8150.