### ELECTRONIC SUPPLEMENTARY INFORMATION

# Epoxidation vs. dehydrogenation of allylic alcohols: Heterogenization of the VO(acac)<sub>2</sub> catalyst in a metal-organic framework

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#### **Experimental Section.**

#### General.

Reagents were obtained from commercial sources and used without further purification unless otherwise indicated. Anhydrous solvents were obtained from a resin-exchanger apparatus. Reactions were performed in conventional round-bottomed flasks or sealed vials equipped with a magnetic stirrer. All the products were characterized by gas chromatography-mass spectrometry (GC-MS), proton (<sup>1</sup>H), carbon (<sup>13</sup>C) and distortionless enhancement by polarization transfer (DEPT) nuclear magnetic resonance (NMR) spectroscopy. Gas chromatographic analyses were performed in an instrument equipped with a 25 m capillary column of 1 % phenylmethylsilicone using *n*-dodecane as an external standard. GC/MS analyses were performed on a spectrometer equipped with the same column as the GC and operated under the same conditions. <sup>1</sup>H-, <sup>13</sup>C and DEPT were recorded in a 300 MHz (or 400 MHz when available) instrument using CD<sub>3</sub>CN as solvent unless otherwise indicated, containing TMS as internal standard. Infrared (IR) spectra of the compounds were recorded with a spectrophotometer by impregnating the windows with a dichloromethane solution of the compound and leaving evaporate before analysis.  $\{Ca^{II}Cu^{II}_{6}[(S,S)-methox]_{3}(OH)_{2}(H_{2}O)\} + 16H_{2}O$  (4) and  $\{Ca^{II}Cu^{II}_{6}[(S,S)-methox]_{3}(OH)_{2}(H_{2}O)\}$ serimox]<sub>3</sub>(OH)<sub>2</sub>(H<sub>2</sub>O) $\}$  · 39H<sub>2</sub>O (5) were prepared as earlier reported.<sup>1,2</sup>

Elemental (C, H, S, N), and ICP-MS analyses were performed at the Microanalytical Service of the Universitat de València. FT–IR spectra were recorded on a Perkin-Elmer 882 spectrophotometer as KBr pellets. The thermogravimetric analysis was performed on crystalline samples under a dry N<sub>2</sub> atmosphere with a Mettler Toledo TGA/STDA 851<sup>e</sup> thermobalance operating at a heating rate of 10 °C min<sup>-1</sup>.

#### Gas adsorption

The N<sub>2</sub> adsorption-desorption isotherms at 77 K, were carried out, on policrystalline samples of **4** and **VO(acac)(H<sub>2</sub>O)@4**, with a BELSORP-mini-X instrument. Samples were first activated with methanol and then evacuated at 348 K during 19 hours under  $10^{-6}$  Torr prior to their analysis.

#### **Microscopy measurements**

Scanning Electron Microscopy (SEM) elemental analysis was carried out for all compounds, using a HITACHI S-4800 electron microscope coupled with an Energy Dispersive X–ray (EDX) detector. Data was analyzed with QUANTAX 400.

#### **X-ray Powder Diffraction Measurements**

Polycrystalline samples of **4** and **VO**(acac)(H<sub>2</sub>O)@**4** were introduced into 0.5 mm borosilicate capillaries prior to being mounted and aligned on a Empyrean PANalytical powder diffractometer, using Cu K $\alpha$  radiation ( $\lambda = 1.54056$  Å). For each sample, five repeated measurements were collected at room temperature ( $2\theta = 2-60^{\circ}$ ) and merged in a single diffractogram. A polycrystalline sample of **VO**(acac)(H<sub>2</sub>O)@**4** was also measured after catalysis following the same procedure.

#### X-ray photoelectron spectroscopy (XPS) measurements

Samples of VO(acac)<sub>2</sub> and VO(acac)(H<sub>2</sub>O)@4 were prepared by sticking, without sieving, the samples onto a molybdenum plate with scotch tape film, followed by air drying. Measurements were performed on a K-Alpha<sup>TM</sup> X-ray Photoelectron Spectrometer (XPS) System using a monochromatic Al K(alpha) source (1486.6 eV). As an internal reference for the peak positions in the XPS spectra, the C1s peak has been set at 284.8 eV.

#### Procedures for the synthesis of MOF catalyst.

 $[V^{IV}O(acac)(H_2O)]@{Ca^{II}Cu^{II}_6[(S,S)-methox]_3(OH)_3} + 8H_2O (VO(acac)(H_2O)@4):$ Well-formed hexagonal green prisms of VO(acac)(H\_2O)@4, which were suitable for Xray diffraction, were obtained by soaking crystals of 4 (5.0 mg) in a saturated acetonitrile solution of VO(acac)\_2 for 72 hours. The crystals were washed with water, isolated by filtration on paper and air-dried (Table S3). Anal.: calcd for C<sub>41</sub>Cu<sub>6</sub>CaVH<sub>77</sub>S<sub>6</sub>N<sub>6</sub>O<sub>33</sub> (1846.8): C, 26.67; H, 4.20; S, 10.42; N, 4.55%. Found: C, 26.93; H, 4.09; S, 10.36; N, 4.51%. IR (KBr): v = 1613, 1605, 1591 cm<sup>-1</sup> (C=O). The same process can be followed, in a multigram-scale, using larger amounts of polycrystalline samples of 4.<sup>3</sup>

#### Impregnation of VO(acac)<sub>2</sub> in 4 and 5.

MOFs impregnation was carried out by suspending the corresponding MOF (100 mg) in a solution of 5 mL of acetonitrile with  $VO(acac)_2$  (10 mg), in a beaker equipped with a

magnetic stirrer. After five hours, MOF is filtered, washed with acetonitrile and dried under vacuum.

#### Supporting VO(acac)<sub>2</sub> on SiO<sub>2</sub>.

The catalyst was prepared by adding SiO<sub>2</sub> (530 mg), VO(acac)<sub>2</sub> (25.8 mg) and 50 mL of dry toluene in a round bottom flask equipped with a magnetic stirrer. This mixture was refluxed for 24 h. The material was vacuum-filtered, washed by reflux in dichloromethane (50 mL) and methanol (50 mL) and dried overnight in an oven at 120 °C. Then, the catalyst is obtained drying under vacuum. The content of vanadium obtained by ICP was 0.29%.

#### **Reaction procedures.**



The products 2 and 3 were prepared following the reaction scheme. Reagent 1 (0.5 mmol) was introduced in a sealed vial equipped with a magnetic stirrer and VO(acac)<sub>2</sub> (4 mg, 0.015 mmol) or VO(acac)(H<sub>2</sub>O)@4 (2 mg) and 1 mL of acetonitrile, and allowed to react for the required time at room temperature. After reaction is complete, filtration is carried out to eliminate the catalyst, the resulting mixture is dried under vacuum and the products obtained are characterised by GC-MS, IR, and/or NMR.

#### Compound characterization of the major compounds.

2,3-Epoxyhexan-1-ol **2a**.<sup>4</sup> GC-MS (m/z, M<sup>+•</sup> 116), major peaks found: 116, 71, 55, 43, 29. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 Hz)  $\delta$  0.95 (t, 3H, *J* = 7.2 Hz), 1.56-1.42 (m, 4H), 2.67-2.91 (m, 2H), 3.61 (dd, 1H, *J* = 12.6, 2.4 Hz), 3.91 (dd, 1H, *J* = 12.6, 2.4 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 Hz) 13.9 (CH<sub>3</sub>), 19.2 (CH<sub>2</sub>), 33.5 (CH<sub>2</sub>), 56.0 (CH), 58.5 (CH), 61.7 (CH<sub>2</sub>).

*Cinnamyl alcohol epoxide* **2b.**<sup>5</sup> GC-MS (m/z, M<sup>+•</sup> 150), major peaks found: 150, 148, 132, 117, 105, 91, 77, 63, 51, 28. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 Hz) *δ*7.73-7.34 (m, 5 H, Ph),

3.96 (m, 1H), 3.58-3.54 (m, 3H). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 101 Hz) δ 55.6 (CH), 61.2 (CH), 64.1 (CH<sub>2</sub>), 125.6 (CH), 128.2 (CH), 128.4 (CH), 135.4 (C).

(2-*Methyl-3-phenyloxiran-2-yl)methanol* **2c.**<sup>6</sup> GC-MS (m/z, M<sup>+•</sup> 164), major peaks found: 164, 145, 131, 117, 107, 90, 79, 63, 51, 39, 29. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 Hz)  $\delta$  1.2 (s, 3H), 2.01 (d, 1H, *J* = 1.6 Hz), 3.75-3.78 (m, 2H), 7.14-7.49 (m, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 Hz)  $\delta$  13.5 (CH<sub>3</sub>), 60.5 (CH), 64.1 (C), 65.2 (CH<sub>2</sub>), 126.4 (CH), 127.6 (CH), 128.1 (CH), 135.7 (C).

*1,2-Epoxyoctan-3-ol* **2d.**<sup>4</sup> GC-MS (m/z, M<sup>+•</sup> 144), major peaks found: 144, 131, 116, 101, 83, 71, 55, 43, 29. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 300 Hz) δ 0.89 (t, 3H, *J* = 6.6 Hz), 1.17-1.30 (m, 8H), 2.31 (m, 1H), 2.48 (m, 1H), 2.71 (m, 1H), 3.80 (m, 1H) <sup>13</sup>C NMR (CD<sub>3</sub>CN, 75 Hz) 73.1 (CH), 54.6 (CH), 43.5 (CH<sub>2</sub>), 34.3 (CH<sub>2</sub>), 31.8 (CH<sub>2</sub>), 24.9 (CH<sub>2</sub>), 22.5 (CH<sub>2</sub>), 13.9 (CH<sub>3</sub>).

2,3-Epoxygeraniol 2e.<sup>7</sup> GC-MS (m/z, M<sup>+•</sup> 170), major peaks found: 170, 168, 152, 139, 121, 109, 95, 82, 69, 55, 41, 27. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 101 Hz)  $\delta$  1.38 (s, 3H), 1.26-1.32 (m, 2H), 1.43-1.50 (m, 2H), 1.60 (s, 3H) 1.68 (d, 3H, *J* = 1.2 Hz), 2.99 (dd, 1H, *J* = 6.9, 4.5 Hz), 3.66-3.84 (2H, m), 5.08 (m, 1H). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 75 Hz)  $\delta$  16.9 (CH<sub>3</sub>), 17.8 (CH<sub>3</sub>), 23.8 (CH<sub>2</sub>), 25.8 (CH<sub>3</sub>), 38.6 (CH<sub>2</sub>), 61.3 (C), 61.6 (CH<sub>2</sub>), 63.0 (CH), 123.5 (CH), 132.3 (C).

3-Phenyloxiranylmethyl acetate **2g.**<sup>8</sup> GC-MS (m/z, [M• -H] 191), major peaks found: 191, 176, 164, 149, 131, 123, 107, 91, 77, 43. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 Hz) δ 2.09 (s, 3H), 3.27-3.30 (m, 1H), 3.85 (d, 1H, *J* = 2.0 Hz), 4.00 (dd, 1H, *J* = 6.4, 12.4 Hz), 4.48 (dd, 1H, *J* = 2.8, 12.4 Hz), 7.26-7.40 (m, 5H). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 101 Hz) 21.1 (CH<sub>3</sub>), 56.6 (CH), 60.1 (CH), 64.9 (CH<sub>2</sub>), 126.7 (CH), 129.6 (CH), 128.9 (CH), 137.4 (C), 171.4 (C).

(4-(*Prop-1-en-2-yl*)-7-oxabicyclo[4.1.0]heptan-1-yl)methanol **2h.**<sup>9</sup> GC-MS (m/z, M<sup>+•</sup> 168), major peaks found: 168, 150, 137, 125, 109, 93, 79, 67, 55, 41. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 Hz)  $\delta$  1.10-1.30 (m, 3H), 1.55-1.80 (m, 4H), 1.71 (brs, 3H), 1.93-1.99 (m, 1H), 3.17 (m, 1H), 3.45 (m, 1H), 4.68-4.72 (m, 2H). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 101 Hz) 21.1 (CH<sub>3</sub>), 25.4 (CH<sub>2</sub>), 26.9 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 37.9 (CH), 57.9 (CH), 66.2 (CH<sub>2</sub>), 68.9 (C), 109.5 (CH<sub>2</sub>), 150.3 (C).

*Cinnamaldehyde* **3b.**<sup>10</sup> GC-MS (m/z, [M<sup>+•</sup>-H] 131), major peaks found: 131.2, 103, 77, 51, 28. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 Hz) δ7.20-7.46 (m, 7H), 9.93 (s, 1H). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 101 Hz) δ125.6(CH), 128.0 (CH), 128.2 (CH), 128.4 (CH), 135.4 (C), 150.1 (CH), 195.8 (CH).

2-*Methyl-3-phenylacrylaldehyde* **3c.**<sup>11</sup> GC-MS (m/z, M<sup>+•</sup>-H] 145), major peaks found: 145, 131, 115, 103, 91, 78, 63, 51, 39, 29. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 Hz) δ 1.96 (d, 3H, *J* = 1.6 Hz), 7.14-7.49 (m, 6H), 9.46 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 Hz) δ 13.5 (CH<sub>3</sub>), 126.4 (CH), 127.6 (CH), 128.1 (CH), 135.7 (C), 138.3 (C), 150.1 (CH), 195,4 (CH).

*4-Nitro-cinnamaldehyde* **3f.**<sup>10</sup> GC-MS (m/z, M<sup>+•</sup> 177), major peaks found: 177, 160, 147, 130, 118, 102, 91, 77, 63, 51. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 Hz) δ 6.85 (dd, 1H, *J* = 7.6, 16.0 Hz), 7.61 (d, 2H, *J* = 8.8 Hz), 7.70 (d, 1H, *J* = 16.0 Hz), 8.27 (d, 2H, *J* = 8.8 Hz), 9.73 (d, 1H, *J* = 7.6 Hz). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 75 Hz) δ 123.9 (CH), 124.3 (CH), 129.0 (CH), 130.5 (CH), 131.3 (CH), 147.9 (CH), 190.3 (CH).

4-(*Prop-1-en-yl*)*cyclohex-1-ene-1-carbaldehyde* **3h.**<sup>12</sup> GC-MS (m/z, M<sup>+•</sup> 150), major peaks found: 150, 137., 121, 107, 93, 79, 67, 55, 41.

(*E*)-2-benzylideneheptanal **3i.**<sup>13</sup> GC-MS (m/z, [M<sup>+•</sup> -H] 201), major peaks found: 201, 189, 171, 159, 145, 131, 115, 107, 91, 79, 57, 41.

#### X-ray crystallographic data collection and structure refinement.

Crystal of **VO**(acac)(H<sub>2</sub>O)@4 with 0.14 x 0.12 x 0.12 mm as dimensions was selected and mounted on a MiTeGen MicroMount in Paratone oil and very quickly placed on a liquid nitrogen stream cooled at 90 K, to avoid the possible degradation upon dehydration or exposure to air. Diffraction data were collected on a Bruker-Nonius X8APEXII CCD area detector diffractometer using graphite-monochromated Mo-K<sub> $\alpha$ </sub> radiation ( $\lambda$  = 0.71073 Å), The data were processed through SAINT<sup>14</sup> reduction and SADABS<sup>15</sup> multiscan absorption software. The structure was solved with the SHELXS structure solution program, using the Patterson method. The model was refined with version 2018/3 of SHELXL against  $F^2$  on all data by full-matrix least squares.<sup>16</sup> As reported in the main text, the robustness of the 3D network, allowed the resolution of the crystal structure of  $VO(acac)(H_2O)@4$  adsorbates, being their crystals suitable for X-ray diffraction, even over one-step process of crystal-to-crystal transformation. Indeed, as previously reported, compound  $VO(acac)(H_2O)@4$  was synthesised by soaking crystals of precursor 4 in an acetonitrile solution of the  $[VO(acac)_2]$  complex during three days in open air. After that, it is reasonable to observe a diffraction pattern sometimes affected by expected internal imperfections of the crystals and thus a quite expected difficulty to perform a perfect correction of anisotropy, mainly affected by highly flexible, and thus disordered, thioether chains as terminal moiety (vide infra).

In the refinement, all non-hydrogen atoms of the MOF net, except the highly thermal disordered diethyl thioether chains from the methox ligand, and encapsulated vanadyl compound atoms, were refined anisotropically. The use of some C-C and C-S bond lengths restrains as well as vanadium-oxygen distance restrains, during the refinement, has been reasonable imposed and related to extraordinary flexibility of diethyl thioether chains from the methionine residues, which are dynamic components of the frameworks. In the refinement of crystal structures some further restrains, to make the refinement more efficient, have been applied, for instance ADP components have been restrained to be similar to other related atoms, using SIMU 0.04 for disordered sections or EADP for group of atoms expected to have essentially similar ADPs. In particular, acac<sup>-</sup> ligand exhibits statistical as well (see Fig. S7). Disordered sites for atoms C1V, C3V and C4V in refinement, belonging to the acetylacetonate ligand, reside in special positions resulting statistically disordered for symmetry reason. All the hydrogen atoms of the net were set in calculated position and refined isotropically using the riding model.

The occupancy factors of vanadium atoms have been defined in agreement with SEM and ICP–MS results (Table S2). The high thermal factors are likely related to the porosity of the net hosting vanadyl acetylacetonate complexes within very large pores.

The solvent molecules, as normally observed for such porous crystals, were highly disordered and only few of them were found from the  $\Delta F$  map. The quite large channels featured by this series of MOFs likely account for that.

A summary of the crystallographic data and structure refinement for  $VO(acac)(H_2O)@4$  crystal structure is given in Table S3. The comments for the alerts A and B are described in the CIF using the validation reply form (vrf). CCDC reference number is 2122007.

The final geometrical calculations on free voids and the graphical manipulations were carried out with PLATON<sup>17</sup> implemented in WinGX,<sup>18</sup> and CRYSTAL MAKER<sup>19</sup> programs, respectively.

ons, comparing nomoger	neous and netero	ogeneous catary	sts. ACIN: aceton	lurite
ОН —	0.75 mmol TBHP catalyst or not ACN (0.5 M), RT, 24h	O OH +		
0.5 mmol 1b		2b	3b	

**Table S1.** Blank experiments for cinnamyl alcohol epoxidation and dehydrogenation reactions, comparing homogeneous and heterogeneous catalysts. ACN: acetonitrile.

Catalyst	Conv% 1	Sel% 2	Sel% 3
None			
None	7.3	19.5	80.5
VO(acac) <sub>2</sub>	87.7	22.9	77.1
<b>4</b> <sup>a</sup>	15.3	26.1	73.9
<b>VO(acac)(H2O)@4</b> <sup>a</sup>	46.5	5.3	94.7
	VO(acac)2 4 <sup>a</sup> VO(acac)(H2O)@4 <sup>a</sup>	VO(acac)2       87.7         4 <sup>a</sup> 15.3         VO(acac)(H2O)@4 <sup>a</sup> 46.5	VO(acac)2       87.7       22.9         4 <sup>a</sup> 15.3       26.1         VO(acac)(H <sub>2</sub> O)@4 <sup>a</sup> 46.5       5.3

<sup>a</sup> 48 h reaction time.

VO(acac)(H <sub>2</sub> O)@4							
Metal	<b>Metal</b> % mass <sup>a</sup> Metal stoichiometr		% mass <sup>b</sup>	Metal stoichiometry <sup>b</sup>			
Cu	20.65	6.00	20.62	5.99			
Ca	2.13	0.98	2.24	1.03			
V	2.79 1.01		2.73	0.99			
VO(acac) <sub>2</sub> impregnated in <b>4</b>							
Metal % mass <sup>a</sup> Meta		Metal stoichiometry <sup>a</sup>	% mass <sup>b</sup>	Metal stoichiometry <sup>b</sup>			
Cu	20.58	5.98	20.68	6.01			
Ca	2.15	0.99	2.21	1.02			
V	0.68	0.25	0.72	0.26			
	VO(acac) <sub>2</sub> impregnated in 5						
Metal % mass <sup>a</sup> Metal stoichiometry		Metal stoichiometry <sup>a</sup>	% mass <sup>b</sup>	Metal stoichiometry <sup>b</sup>			
Cu	17.40	6.00	17.31	5.97			
Ca	1.92	1.05	1.83	1.00			
V	0.84 0.36		0.82	0.35			

**Table S2.** Selected data from the ICP–MS<sup>*a*</sup> and SEM/EDX<sup>*b*</sup> analyses for VO(acac)(H<sub>2</sub>O)@4 and VO(acac)<sub>2</sub> impregnated in MOFs 4 and 5.

Solid samples were digested with 0.5 mL of HNO<sub>3</sub> 69% at 60°C for 4 hours followed by the addition of 0.5 mL of HCl 37% and digestion 80°C for 1 hour. Metal stoichiometric is given according to formula unit.

Compound	VO(acac)(H <sub>2</sub> O)@4
Formula	$C_{41}H_{77}CaCu_6N_6O_{33}S_6V$
M (g mol <sup>-1</sup> )	1846.70
$\lambda$ (Å)	0.71073
Crystal system	hexagonal
Space group	$P6_3$
<i>a</i> (Å)	17.8884(17)
<i>c</i> (Å)	12.8853(13)
$V(\text{\AA}^3)$	3570.8(8
Ζ	2
$\rho_{\text{calc}} (\text{g cm}^{-3})$	1.718
$\mu \ (\mathrm{mm}^{-1})$	2.211
<i>T</i> (K)	90
$\theta$ range for data collection (°)	2.277 to 26.175
Completeness to $\theta = 25.0$	100%
Measured reflections	41658
Unique reflections (Rint)	4766 (0.0762)
Observed reflections $[I > 2\sigma(I)]$	2967
Goof	1.029
Absolute structure parameter (Flack)	0.20(3)
$R^{a}[I > 2\sigma(I)]$ (all data)	0.0775 (0.1332)
$wR^{b}[I > 2\sigma(I)]$ (all data)	0.2076 (0.2494)
CCDC	2122007

Table S3. Summary of crystallographic data for  $VO(acac)(H_2O)@4$ 

<sup>*a*</sup>  $R = \sum (|F_{\rm o}| - |F_{\rm c}|) / \sum |F_{\rm o}|$ . <sup>*b*</sup>  $wR = [\sum w(|F_{\rm o}| - |F_{\rm c}|)^2 / \sum w|F_{\rm o}|^2]^{1/2}$ .



**Fig. S1.** Plausible reaction mechanism for allylic alcohol epoxidation and dehydrogenation catalyzed by  $VO(acac)_2$ , and chemoselective rationalization.



**Fig. S2.** (a) Kinetics for the hydrogenation of **1b** (0.5 M) with TBHP (1.2 equivalents) catalyzed by VO(acac)<sub>2</sub> to give **2b** and **3b** in acetonitrile at room temperature (black squares), and other in the same conditions adding Ba(acac)<sub>2</sub>·xH<sub>2</sub>O (1.1 equivalent) (red circles). Error bars account for a 10% uncertainty. (b) <sup>1</sup>H NMR of the reaction crude with the corresponding signals of the acetylacetonate ligands in solution, indicated by the arrows.

b)



**Fig. S3.** Activation energies calculated for the epoxidation and dehydrogenation of cinnamyl alcohol **1b** (a) and 2-hexenol **1a** (b) under the indicated reaction conditions at different temperatures.



Town on string	Ducduct	Yield(%)=a+b·t(min)			
Temperature	Product	а	b	R <sup>2</sup>	
22	2a	0	0.289	0.9808	
52	<b>3</b> a	0	0.017	0.9119	
45	2a	0	0.531	0.9895	
43	<b>3</b> a	0	0.166	0.9975	
60	2a	0	1.122	0.9972	
00	<b>3</b> a	0	0.187	0.9921	
75	2a	0	1.028	0.9854	
75	<b>3</b> a	0	1.952	0.9697	

**Fig. S4.** Kinetic profiles to calculate the initial rates of reaction, calculated by linear regression for each temperature and measured for the alkene 1a using VO(acac)<sub>2</sub> in solution.



Tomponatura	Duoduot	Yield(%)=a+b·t(min)			
Temperature	Product	a	b	<b>R</b> <sup>2</sup>	
20	2b	0	0.090	0.8409	
50	3b	0	0.618	0.9708	
45	2b	0	0.166	0.9545	
43	3b	0	1.468	0.9955	
60	2b	0	0.348	0.9798	
00	3b	0	3.288	0.9941	
75	2b	-1.6	1.581	0.9564	
/3	<b>3</b> b	-7.4	8.342	0.9870	

**Fig. S5.** Kinetic profiles to calculate the initial rates of reaction, calculated by linear regression for each temperature and measured for the alkene **1b** using  $VO(acac)_2$  in solution.



Fig. S6. Scope of reactivity for different allylic alcohols under the indicated reaction conditions. We observed epoxides were formed when the allyl alcohol possess electron donating groups on the alkene (products 2a, 2c, and 2d), while aldehyde formation was favoured with electron withdrawing groups (3b, 3e, and 3f). Also, it was further validated that even a small change in the structure of the substrate is enough to favour the epoxidation, which agree with the slow difference in activation energy.



**Fig. S7.** Perspective view of the crystal structure of **VO**(acac)(H<sub>2</sub>O)@4 along *c* crystallographic axis, showing VO(acac)(H<sub>2</sub>O)<sup>+</sup> complexes well-packed within pores of the MOF 4. The 3D network is depicted as grey sticks, with the exception of copper and calcium, depicted as cyan and blue spheres, and ethyl chain and sulphur atoms from the methionine residue, which are represented as yellow sticks (carbon) and yellow spheres (sulphur). For the guest VO(acac)(H<sub>2</sub>O)<sup>+</sup> species hosted in the channels, vanadium, carbon and oxygen atoms are represented as purple, grey and red spheres, respectively. Crystallization water molecules have been omitted for the sake of clarity.



**Fig. S8.** Perspective details of a single pore of the crystal structure of **VO**(acac)(H<sub>2</sub>O)@4 along *c* crystallographic axis. The 3D network is depicted as grey sticks, with the exception of copper and calcium, depicted as cyan and blue spheres, and ethyl chain and sulphur atoms from the methionine residue, which are represented as yellow sticks (carbon) and yellow spheres (sulphur). For the guest  $VO(acac)(H_2O)^+$  species hosted in the channels, vanadium, carbon and oxygen atoms are represented as purple, grey and red spheres, respectively. Crystallization water molecules have been omitted for the sake of clarity.



**Fig. S9.** Top (a) and side (b) view of fragments of **VO**(acac)(H<sub>2</sub>O)@4 crystal structure highlighting the highly distorted coordination geometry around vanadium. The 3D network is depicted as grey sticks, with the exception of copper and calcium, depicted as cyan and blue spheres, and ethyl chain and sulphur atoms from the methionine residue, which are represented as yellow sticks (carbon) and yellow spheres (sulphur). For the guest VO(acac)(H<sub>2</sub>O)<sup>+</sup> species hosted in the channels, vanadium, carbon and oxygen atoms are represented as purple, grey and red spheres, respectively.



**Fig. S10.** Details of host-guest interactions in **VO**(acac)(H<sub>2</sub>O)@4: V···S interaction (purple dashed line) in VO(acac)(H<sub>2</sub>O)<sup>+</sup> a) and further V ··O<sub>water</sub> interaction with a second water molecule (red dashed line) residing near to the VO(acac)(H<sub>2</sub>O) moiety at a distance of 2.96(3) Å. The 3D network is depicted as grey sticks, with copper and calcium, depicted as cyan and blue spheres, and ethyl chain and sulphur atoms from the methionine residue, represented as yellow sticks (carbon) and yellow spheres (sulphur). For the guest VO(acac)(H<sub>2</sub>O)<sup>+</sup> species hosted in the channels, vanadium, carbon and oxygen atoms are represented as purple, grey and red spheres, respectively.



**Fig. S11.** Details of VO(acac)(H<sub>2</sub>O)<sup>+</sup> arrangement within pores and overlapping of some carbon atoms related to statistical disorder. The 3D network is depicted as grey sticks, with copper and calcium, depicted as cyan and blue spheres, and ethyl chain and sulphur atoms from the methionine residue, represented as yellow sticks (carbon) and yellow spheres (sulphur). For the guest VO(acac)(H<sub>2</sub>O)<sup>+</sup> species hosted in the channels, vanadium, carbon and oxygen atoms are represented as purple, grey and red spheres, respectively.



Fig. S12. (a) Calculated (bold lines) and experimental (solid lines) PXRD pattern profiles of 4 (blue) and VO(acac)(H<sub>2</sub>O)@4 (red) in the 2 $\theta$  range 2.0–50.0° at room temperature, and enlarged image in the range 10.0–50.0° (b). (c) Calculated (bold lines) and experimental (solid lines) PXRD pattern profile of VO(acac)(H<sub>2</sub>O)@4 after seven reuses in the catalytic epoxidation of 1c in the range 2.0–50.0°.



Fig. S13. Thermo-Gravimetric Analyses (TGA) of 4 (blue) and  $VO(acac)(H_2O)@4$  (red) under dry N<sub>2</sub> atmosphere.



Fig. S14. XPS spectra of  $VO(acac)_2$  (a) and  $VO(acac)(H_2O)@4$  (b).



Fig. S15. N<sub>2</sub> (77 K) adsorption isotherm for the activated compounds 4 (black) and VO(acac)(H<sub>2</sub>O)@4 (blue). Filled and empty symbols indicate the adsorption and desorption isotherms, respectively. The samples were activated at 348 K under reduced pressure for 19 h prior to carry out the sorption measurements. Both, 4 and VO(acac)(H<sub>2</sub>O)@4, exhibited an isotherm characteristic for microporous materials, with estimated Brunauer-Emmett-Teller (BET) surface areas of 455 (4) and 337 (VO(acac)(H<sub>2</sub>O)@4) m<sup>2</sup> g<sup>-1</sup>. As expected, after the VO(acac)(H<sub>2</sub>O) encapsulation we observed a reduction of N<sub>2</sub> uptake in VO(acac)(H<sub>2</sub>O)@4, respect 4. Nevertheless, VO(acac)(H<sub>2</sub>O)@4 still presents a sizeable porosity.

R <sub>1</sub>	VO(acac) <sub>2</sub> (3 mo OH VO(acac)-MOF (0.2	$\frac{100}{100}$ R <sub>1</sub>	Он	+ R1	
I	<sup>R</sup> 2 ACN (0.5M), RT, 2 1	4h	R <sub>2</sub> 2		R <sub>2</sub> 3
Entry	Reactive	Catalyst	Conv%	Sel%	Sel%
		j	1	2	3
1	Л	VO(acac) <sub>2</sub>	90.3	97.9	2.1
	1a	MOF*	36.0	50.0	50.0
2	ОН	VO(acac) <sub>2</sub>	100	22.9	77.1
	1b	MOF*	46.5	5.3	94.7
3	ОН	VO(acac) <sub>2</sub>	8.6	51.3	48.7
	lc	MOF	92.7	75.7	24.3
4	OH	VO(acac) <sub>2</sub>	89.4	83.1	16.9
	1d	MOF*	46.4	84.8	15.2
5		VO(acac) <sub>2</sub>	99.0	96.4	3.6
	le	MOF	88.6	84.9	15.1
6	ОН	VO(acac) <sub>2</sub>	100	0	85.6
	0 <sub>2</sub> N <sup>2</sup>	MOF*	32.5	0	100
7		VO(acac) <sub>2</sub>	2.5	81.0	0
	lg	MOF*	10.7	78.0	0
٩	ОН	VO(acac) <sub>2</sub>	91.0	41.1	31.0
0	1h	MOF*	87.4	52.1	31.3
0	ОН	VO(acac) <sub>2</sub>	30.0	0.0	100
7	(CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub> 1i	MOF*	12.6	0.0	100

0.75 mmol TBHP

Fig. S16. Scope of the reaction using VO(acac)H<sub>2</sub>O@4 or VO(acac)<sub>2</sub> as catalysts.\* 48 h reaction time.



Fig. S17. Left: Reuse of  $VO(acac)(H_2O)@4$  after washing with acetonitrile and drying. Right: Kinetics for the epoxidation of 1c (0.5 M) with TBHP (1.2 equivalents) catalysed by  $VO(acac)(H_2O)@4$  to give 2c and 3c in acetonitrile at room temperature (black squares) and after filtering the catalyst at 9 h reaction time (red circles).



**Fig. S18.** FT-IR spectra of **4** (red line), the fresh **VO**(**acac**)(**H**<sub>2</sub>**O**)@**4** (blue line) and after being used (pink line), are shown together with VO(acac)<sub>2</sub> (black line). At 960 cm<sup>-1</sup>, we observe the stretching vibration frequency of vanadyl group (V=O). It is one of the most intense and most characteristic. At 1280 cm<sup>-1</sup>, the stretching symmetric vibration of the ring (C-C-C) appears. In contrast, the stretching asymmetric vibration appears at 1520 cm<sup>-1</sup>. Finally, the stretching asymmetric vibration of C-O of the ring (C-C-C) can be seen at 1430 cm<sup>-1</sup>.<sup>20</sup>



Fig. S19. FT-IR spectra of VO(acac)(H<sub>2</sub>O)@4 before (fresh) and after used in different reactions (1h and 1i as starting materials).



Fig. S20. Catalytic results for the allylic alcohol epoxidation/dehydrogenation of aliphatic 1a (left) and aromatic 1b (rigth) alkenes using  $VO(acac)_2$  impregnated on 4 (black squares) and 5 (red dots).



Fig. S21. Left: Reuse of  $VO(acac)_2$  impregnated on 5 after washing with acetonitrile and drying. Right: Kinetics for the epoxidation of 1c (0.5 M) with TBHP (1.2 equivalents) catalyzed by  $VO(acac)_2$  impregnated on 4 to give 2c and 3c in acetonitrile at room temperature (black squares), and after filtering the catalyst at 24 h reaction time (red circles).



Fig. S22. Kinetics for the epoxidation of 1c (0.5 M) with TBHP (1.2 equivalents) catalyzed by  $VO(acac)_2@SiO_2$  to give 2c and 3c in acetonitrile at room temperature (black squares), and after filtering the catalyst at 50 min reaction time (red circles).

# Product **2h**:



Product **3h**:



Product 3i:



Fig. S23. GC-MS of products 2h, 3h and 3i.

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