# **Supporting Information for:**

# Vanadium Catalyst on Isostructural Transition Metal-, Lanthanide- and Actinide-based Metal-Organic Frameworks for Alcohol Oxidation

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# Chemicals

**Linker synthesis.** 1,4-dioxane, dichloromethane, hexane, tetrahydrofuran (THF), ethyl acetate and methanol were purchased from Fischer Scientific (Schaumburg, IL). 1,3,5-tribromo-2,4 6-trimethylbenzene, acetone, (4-(methoxycarbonyl)phenyl) boronic acid, pinacol, potassium phosphate, magnesium sulphate and hydrochloric acid were purchased from Sigma Aldrich. Pd(PPh<sub>3</sub>)<sub>4</sub> was purchased from Strem Chemicals. Water was obtained from a deionized water source provided by Northwestern University. Unless otherwise stated, all commercial chemicals were used without further purification unless otherwise mentioned.

**MOFs synthesis.** Ammonium Cerium(IV) Nitrate (Ce  $(NH_4)_2(NO_3)_6$ ), Zirconium(IV) dichloride oxide octahydrate (ZrOCl<sub>2</sub>·8H<sub>2</sub>O), Hafnium(IV) chloride (HfCl<sub>4</sub>) and Thorium(IV) nitrate (Th(NO<sub>3</sub>)<sub>4</sub>·6H<sub>2</sub>O) were used as metal salts to synthesize isostructural NU-1200. Zirconium(IV) chloride and Hafnium(IV) dichloride oxide were used to synthesize single crystals. All the metal salts, *N*, *N*-dimethylformamide (DMF), *N*, *N*-diethylformamide (DEF), hydrochloric acid, acetone and trifluoroacetic acid were purchased from Sigma Aldrich.

**Chemicals used in the solvothermal deposition in MOFs (SIM).** Methanol was purchased from Fischer Scientific and used as soaking solvent, vanadyl(IV) acetylacetonate was purchased from Sigma Aldrich and used as metal precursor without further purification. Hydrogen peroxide, V, Zr, Hf, Ce and Th ICP standards were purchased from Sigma Aldrich. Concentrated nitric acid was purchased from VWR Scientific, LLC. (Chicago, IL). Ultrapure deionized water was obtained from a Millipore Milli-Q-Biocel A10 instrument.

**Catalysis.** 4-methoxybenzyl alcohol, acetone and dichlorobenzene were purchased from Sigma Aldrich. Anhydrous toluene and triethylamine were purchased from Fischer Scientific. O<sub>2</sub> used during the catalysis were ultra-high purity grade 5 and were obtained from Airgas Specialty Gases

# **Analytical techniques**

Nuclear Magnetic Resonance (NMR) spectra (<sup>1</sup>H and <sup>19</sup>F). All the <sup>1</sup>H spectra were collected on a Bruker

Avance III 500 MHz system equipped with DCH CryoProbe and automated with a BACS-60 autosampler. Chemical shifts for <sup>1</sup>H spectra were referenced using internal solvent resonances and reported relative to tetramethylsilane (TMS). For the <sup>19</sup>F spectra, 0.5 mg sample were tested on a fully automated 400 MHz Bruker Avance III HD system equipped with SampleXpress autosampler. 5  $\mu$ L of 1 vol% 1-bromo-3,5-bis(trifluoromethyl)benzene in DMSO solution was added and used as internal standard to calculate the exact amount of the modulator in the MOFs.

*Inductively-coupled plasma optical emission spectroscopy (ICP-OES)*. The V loading amount was confirmed by Varian Vista-MDX model ICP-OES spectrometer (Varian, Walnut Creek, CA) with a CCD detector and Ar plasma that covers 175-785 nm range. For the sample preparation, 2-3 mg materials were digested in 1 mL concentrated HNO<sub>3</sub> by heating in a 2~5 mL Biotage (Uppsala, Sweden) SPX microwave reactor (software version 2.3, build 6250) at 100 °C for 15 minutes. After that, 500  $\mu$ L of the solution was taken out and then diluted to a final volume of 15 mL with Millpore H<sub>2</sub>O and analyzed for V (310.23, 292.402, 290.882 and 309.311 nm), Zr (327.305, 339.198, 349.621 and 343.823 nm), Hf (339.98, 232.247 and 277.336) and Ce (404.076 and 535.353) content as compared to standard solutions.

*Inductively Coupled Plasma Mass Spectrometry (ICP-MS).* For the V-Th-NU-1200, the sample was tested on ICP-MS which is a quadrupole-based inductively coupled plasma mass spectrometer for the detection of most elements in the ppt-ppb concentration range (0.001 - 1000 ppb), equipped with a CETAC ASX260 120-position (15-mL conical tubes) autosampler.

**Powder X-ray Diffraction (PXRD)**. PXRD patterns were recorded at room temperature on a STOE-STADIMP powder diffractometer equipped with an asymmetric curved Germanium monochromator (CuK $\alpha$ 1 radiation,  $\lambda = 1.54056$  Å) and one-dimensional silicon strip detector (MYTHEN2 1K from DECTRIS). The generator was set to be 40 kV and 40 mA. The activated powder was measured in transmission geometry in a rotating holder with the intensity data from 1 to 30 degrees. The scan step was set to be  $2\theta = 4^{\circ}$  while the scan time was 30 s.

*Brunauer–Emmett–Teller (BET) Surface Area and porosity analysis.* The dry MOFs were activated at 120 °C for 12 h under vacuum on a Micromeritics Smart Vac Prep (for Ce-NU-1200, the activation condition is 100 °C for 12 h). N<sub>2</sub> sorption isotherms were then measured on a Micromeritics Tristar II 3020 (Micromeritics, Norcross, GA) instrument at 77 K. Pore size distributions curves were calculated by using DFT calculations according to a carbon slit-pore model with a N<sub>2</sub> kernel.

*Thermogravimetric analysis (TGA).* Thermal stability of M-NU-1200 and V-M-NU-1200 was tested by TGA which was carried out on a TA Instruments Discovery TGA equipped with a Stanford Research Systems QMS200 gas analyzer (MS). Before the measurement, every sample was activated at 120 °C under high vacuum for 12 h to remove the solvent in the material. After that, samples were run with a heating rate of 5 °C/min from room temperature to 600 °C under air flow (20 mL/min).

*Diffuse Reflectance Infrared Fourier Transform Spectra (DRIFTS) measurements.* Nicolet 6700 FTIR spectrometer (Thermo Scientific) equipped with an MCT detector and a Harrick praying mantis accessory was used to collect infrared (IR) spectra. Before the measurement, every sample was activated at 120 °C under high vacuum for 12 h so as to remove the solvent in the material. The spectra were collected at 1 cm<sup>-1</sup> resolution over 64 scans with solid KBr as the background.

*Raman spectroscopy.* Raman spectra of all the samples were recorded at room temperature by using a HORIBA LabRAM HR Evolution Confocal Raman Spectroscopy with Olympus 100 × microscope objective with a 532 nm laser.

*Solid State* <sup>51</sup>*V Nuclear Magnetic Resonance (NMR) spectra.* The spectrum was collected by Bruker Avance III HD 400 MHz solid nmr system (Hg400) at room temperature with a spinning rate of 15 K Hz and 16384 scans.

*Diffuse Reflectance Ultraviolet vis spectroscopy (DR UV-vis)*. Diffuse reflectance UV-vis spectra were collected in the wavelength range of 200-800 nm under ambient conditions by using Shimadzu UV-3600 with a Harrick Praying Mantis diffuse reflectance accessory. Polytetrafluoroethylene (PTEF) powder was used as a perfect reflector for baseline measurement, and the sample (~ 1mg) were diluted in PTEF powder for the measurements. The obtained reflectance spectra were converted to absorption spectra according to the Kubelka–Munk function  $F(R\infty)$ , edge energies for V-M-NU-1200 were also calculated. <sup>S1</sup>

*Scanning electron microscopy (SEM) images.* SEM images of all the samples were collected on a Hitachi SU8030 FESEM (Dallas, TX) microscope at Northwestern University's EPIC/NUANCE facility. For preparation, around  $\sim$ 1 mg sample was soaked in the acetone and sonicated for 10 min to disperse the powder. The samples were then dropped on the SEM sample holder to dry in the air. Before the measurement, samples were coated with OsO<sub>4</sub> to  $\sim$ 9 nm thickness to increase the electrical conductivity.

*Energy dispersive spectroscopy (EDS) line scans.* EDS line scans were collected concurrently with SEM images

*X-ray photoelectron spectroscopy (XPS).* Measurements were carried out at the KECKII/NUANCE facility at NU on a Thermo Scientific ESCALAB 250 Xi equipped with an electron flood gun and a scanning ion gun. XPS data was analyzed using Thermo Scientific Avantage Data System software and all spectra were referenced to the C1s peak (284.8 eV)

*Electron paramagnetic resonance (EPR).* Continuous wave EPR measurements were performed with a Bruker Elexsys E580-X EPR spectrometer, equipped with a super-high Q resonator (ER4122-SHQE). The spectra were obtained using non-saturating microwave power at room temperature.

The V<sup>4+</sup> EPR spectrum of V-Zr-NU-1200 after 2 hours/5 hours of catalysis was fit using Easyspin.<sup>S2</sup> The spectrum was fit using a slightly rhombic g-tensor  $g = [1.9755 \ 1.9769 \ 1.9302]$  and a slightly rhombic Hyperfine tensor A = [190 201 520.5] MHz. The rhombicity in g- and A- tensors suggests that the coordination environment of the Vanadium is slightly rhombic.

#### Single-crystal X-ray crystallography.

Single-crystal X-ray structure analyses were carried out using a Bruker Kappa APEX II CCD detector equipped Cu K $\alpha$  ( $\lambda$  = 1.54178 Å) microsource with MX optics. The single crystals were mounted on MicroMesh (MiTeGen) with paratone oil. The structures were determined by direct methods (SHELXT 2014/5)<sup>S3</sup> and refined by full-matrix least-squares refinement on F2 (SHELXL-2017/1)<sup>S4</sup> using the Yadokari-XG <sup>S5</sup> or Olex2<sup>S6</sup> software package. Refinement results are summarized in Table S1 and Table S4. Crystallographic data in CIF format have been deposited in the Cambridge Crystallographic Data Centre (CCDC) under deposition number CCDC-1876021(Hf-NU-1200), 1899941 (V-Zr-NU-1200) and 1899942 (V-Hf-NU-1200). The data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.)

#### Refinement details of V-Zr-NU-1200 and V-Hf-NU-1200

Prior to the structural refinements of the vanadium sites, the V-Zr-NU-1200 framework atoms were first located and refined. Because the electron densities of acac ligand were also clearly observed on the chelating position of the MOF nodes, the atoms of acac were located and refined using some thermal and structural restraints (DFIX, ISO, SIMU; the number of acac per  $Zr_6$  node was estimated to be 1.0, which is consistent with the NMR result (Figure S4c) before the vanadium site refinement. Residual electron density close to the terminal oxygen atoms (O4) on the node was assigned as the vanadium site and occupancy was determined by structural refinements. The V occupancy was estimated to be 0.1, which corresponds to 0.8

vanadium per the  $Zr_6$  node. The total of crystallographically determined vanadium content (0.8 V/Zr<sub>6</sub>) is in good agreement with the data obtained from ICP-OES analysis (1.28 ± 0.1 V/Zr<sub>6</sub>). After assigning the vanadium sites, the refinement of VO2 units were conducted using some thermal and structural restraints for V1. Additional residual electron density peaks being assigned to disordered vanadyl oxygen (O6 and O6A) and terminal oxygen on vanadium. For V-Hf-NU-1200, the vanadium atom and the disordered vanadyl oxygen atoms (O5 and O5A) were determined in the same fashion but the lower data quality did not allow for the assignment of terminal oxygen atoms. Some thermal and structural restraints (DFIX and ISO) were used for their refinements. The disordered non-coordinated solvents were removed using the PLATON SQUEEZE program. Refinement results are summarized in Table S4.

## **Experimental section**

#### Ligand synthesis.

4,4',4''-(2,4,6-trimethylbenzene-1,3,5-triyl)tribenzoic acid (TMTB) was synthesized according to the literature with some modification.<sup>57</sup> 5.3 g (15 mmol) 1,3,5-tribromo-2,4,6-trimethylbenzene, 21 g (75 mmol) methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate and 22.5 g K<sub>3</sub>PO<sub>4</sub> were added into a 1000 mL two-necked, round-bottomed Schlenk flask. 600 mL dioxane and 40 mL H<sub>2</sub>O were then added into the flask with N<sub>2</sub> bubbling for 30 min, after that, 750 mg Pd(PPh<sub>3</sub>)<sub>4</sub> was added into the solution and bubbled for another 30 min. The flask was equipped with a water condenser and reflux under the nitrogen and 98 °C for 3 days. The solvent was removed using rotary evaporator and water and CH<sub>2</sub>Cl<sub>2</sub> was used to extract the resulting solid mixture for three times with MgSO<sub>4</sub> drying the organic phase. The solvent that was evaporated mostly was then purified by the column chromatography over the silica gel with the developing agent of ethyl acetate: hexanes= 1: 20. The final product was in ~75% yield (4.0 g) based on 1,3,5-tribromo-2,4,6-trimethylbenzene.

This product was then added into a 500 mL Schlenk flask with 120 mL THF and 120 mL methanol. After that, 70 mL 10 M NaOH aqueous solution was added into the solution. The mixture was stirred under reflux overnight. After the THF and methanol were evaporated, the solution was then acidified to give white product, which was washed with DI water for several times to get pure TMTB of 3.6 g with a yield of 90%. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>)  $\delta$ 8.03 (d, J = 8.3 Hz, 6H), 7.37 (d, J = 8.3 Hz, 6H), 1.62 (s, 9H).

# **Characterization section**

Table S1. Crystallographic data of Hf-NU-1200

	Hf-NU-1200
Empirical formula	$C_{40}H_{28}Hf_3O_{16}$
Formula weight	1300.09
Temperature/K	100
Crystal system	cubic
Space group	Pm-3m
a/Å	28.0224(8)
b/Å	28.0224(8)
c/Å	28.0224(8)
a/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	22004.7(19)
Z	6
$\rho_{calc}g/cm^3$	0.589
μ/mm <sup>-1</sup>	2.138
<b>F(000)</b>	3672.0
Crystal size/mm <sup>3</sup>	$0.05 \times 0.05 \times 0.03$
Radiation	MoKa ( $\lambda = 0.71073$ )
20 range for data collection/°	3.25 to 41.178
Index ranges	$-27 \le h \le 27,  -24 \le k \le 27,  -20 \le l \le 27$
<b>Reflections collected</b>	47827
Independent reflections	2234 [ $R_{int} = 0.1092$ , $R_{sigma} = 0.0335$ ]
Data/restraints/parameters	2234/3/85
Goodness-of-fit on F <sup>2</sup>	1.066
Final R indexes [I>=2σ (I)]	$R_1 = 0.0605, wR_2 = 0.1394$
Final R indexes [all data]	$R_1 = 0.0967, wR_2 = 0.1739$
Largest diff. peak/hole / e Å <sup>-3</sup>	1.33/-1.52



Figure S1. a)  $N_2$  isotherms and b) pore size distribution curves of isostructural NU-1200s as c) showed the volumetric pore size distribution

Table S2. Surface area and pore volume before and after normalizing to volumetric surface areas and total

	_			
materials	$S_{BET}(m^2/g)^a$	S <sub>BET</sub> (m <sup>2</sup> /cm <sup>3</sup> ) <sup>b</sup>	pore volume(cm³/g) <sup>c</sup>	pore volume(cm <sup>3</sup> /cm <sup>3</sup> )
Zr-NU-1200	2380	1082	1.54	0.70
Hf-NU-1200	1750	1030	1.19	0.70
Ce-NU-1200	1900	986	1.19	0.62
Th-NU-1200	1300	1106	0.91	0.77

pore volumes of all isostructural MOFs

<sup>*a*</sup> S<sub>BET</sub> was calculated in P/P<sub>0</sub> range of 0.05 ~ 0.3, <sup>*b*</sup> density for Ce-NU-1200 and Th-NU-1200 were roughly calculated based on Zr-NU-1200 and Hf-NU-1200 using their density and molecule weight, <sup>*c*</sup> total pore volume was calculated at P/P<sub>0</sub>=0.99.



Figure S2. SEM images of a) Zr-NU-1200; b) Hf-NU-1200; c) Ce-NU-1200 and d) Th-NU-1200 with similar particle size



**Figure S3.** <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O) spectrum of four isostructural a) M-NU-1200 and b,c) V-M-NU-1200, which were digested by diluted NaOD solution (0.1 M)



**Figure S4.** <sup>19</sup>F NMR (500 MHz, D<sub>2</sub>SO<sub>4</sub>) spectrum of a) four isostructural M-NU-1200 and b) V-Ce-NU-1200

The <sup>1</sup>H NMR showed that there were 3.2 formates per node in Zr-/Hf- NU-1200 but only 0.5 and 0.25 formates per node in Ce-/Th-NU-1200, respectively. However, <sup>19</sup>F NMR showed only Ce-NU-1200 contained around 1.6 trifluoroacetate per node, which is because HCl was not used to activate this sample due to stability issues.

samples	before (V/M <sub>6</sub> )	after (V/M <sub>6</sub> )
V-Zr-NU-1200	$1.28 \pm 0.12$	$1.24 \pm 0.08$
V-Hf-NU-1200	$1.07{\pm}~0.08$	$1.01 \pm 0.11$
V-Ce-NU-1200	$1.24 \pm 0.10$	$1.22 \pm 0.05$
V-Th-NU-1200	$1.06 \pm 0.13$	$0.99 \pm 0.11$

Table S3. ICP results of catalysts before and after 5 h oxidation

ICP result showed that the loadings were calculated to be  $1.3 \pm 0.1$ ,  $1.1 \pm 0.1$ ,  $1.2 \pm 0.1$  and  $1.1 \pm 0.1$  V for V-Zr-NU-1200, V-Hf-NU-1200, V-Ce-NU-1200 and V-Th-NU-1200, respectively. No vanadium decrease was found during the leaching test, indicating the stability of the catalysts.



**Figure S5.** SEM images of a) V-Zr-NU-1200 b) V-Hf-NU-1200 c) V-Ce-NU-1200 and d) V-Th-NU-1200 before catalysis with EDS line scans of metals and V (red).



Figure S6. PXRD patterns of M-NU-1200 and V-M-NU-1200



Figure S7. Gravimetric N2 isotherms of M-NU-1200 and V-M-NU-1200



Figure S8. TGA curves of a) bare M-NU-1200 and b) V-M-NU-1200



S13



Figure S9. Gravimetric pore size distribution of M-NU-1200 and V-M-NU-1200

**Figure S10.** DRIFT spectra of M-NU-1200 and V-M-NU-1200. b), d), f), and h) show the OH stretches of the materials.



Figure S11. Raman spectra of M-NU-1200 (black) and V-M-NU-1200 (red). a) Zr-NU-1200 and V-Zr-NU-1200; b) Hf-NU-1200 and V-Hf-NU-1200; c) Ce-NU-1200 and V-Ce-NU-1200; d) Th-NU-1200 and V-Th-NU-1200.



**Figure S12**. 400 MHz <sup>51</sup>V NMR spectra of (a) V-Zr-NU-1200 and (b) V-Hf-NU-1200 were collected at RT with spinning rate of 15 K Hz and 16384 scans. The main peak around 610 ppm is consistent with vanadium species of grafted monomer from literature.<sup>S8</sup> Due to the paramagnetic nature of Ce<sup>3+</sup>, it prevented us from a comparison across our series.



**Figure S13.** Diffuse reflectance UV spectra of M-NU-1200 (black) and V-M-NU-1200 (red). a) Zr-NU-1200 and V-Zr-NU-1200; b) Hf-NU-1200 and V-Hf-NU-1200; c) Ce-NU-1200 and V-Ce-NU-1200; d) Th-NU-1200 and V-Th-NU-1200. The peaks for Ce-NU-1200 and V-Ce-NU-1200 seemed different from the other three which is due to the yellow color of the materials.



**Figure S14.** Calculation of the edge energies of vanadium in V-M-NU-1200 from the X-intercept of the linear fit at the edge of absorption from DRUV.



Figure S15. V-XPS spectra of V-M-NU-1200: a) V-Zr-NU-1200; b) V-Hf-NU-1200; c) V-Ce-NU-1200; d) V-Th-NU-1200

	V-Zr-NU-1200	V-Hf-NU-1200
Empirical formula	$C_{10.63}H_7O_{5.2}V_{0.1}Zr_{0.75}$	$C_{10.63}H_7Hf_{0.75}O_5V_{0.1}$
Formula weight	291.37	353.62
Temperature/K	200.0	250
Crystal system	cubic	cubic
Space group	Pm-3m	Pm-3m
a/Å	28.2644(4)	28.2300(3)
b/Å	28.2644(4)	28.2300(3)
c/Å	28.2644(4)	28.2300(3)
α/°	90	90
β/°	90	90
$\gamma/^{o}$	90	90
Volume/Å <sup>3</sup>	22579.8(10)	22497.4(7)

Table S4. Crystallographic data of V-Zr-NU-1200 and V-Hf-NU-1200

Z	24	24	
$\rho_{calc}g/cm^3$	0.514	0.626	
µ/mm <sup>-1</sup>	2.085	4.142	
<b>F(000)</b>	3472.0	4009.0	
Crystal size/mm <sup>3</sup>	$0.21\times 0.21\times 0.1$	$0.08\times0.06\times0.05$	
Radiation	$CuK\alpha$ ( $\lambda = 1.54178$ )	$CuK\alpha$ ( $\lambda = 1.54178$ )	
$2\Theta$ range for data collection/°	4.422 to 130.424	11.3 to 100.874	
Index renges	$-33 \le h \le 28,  -33 \le k \le 32,  -33 \le$	$-28 \le h \le 24,  -28 \le k \le 28,  -24 \le$	
index ranges	$1 \leq 32$	$l \leq 26$	
<b>Reflections collected</b>	98182	57996	
Indonandant reflections	3769 [ $R_{int} = 0.0581$ , $R_{sigma} =$	2350 [ $R_{int} = 0.0756$ , $R_{sigma} =$	
independent renections	0.0207]	0.0202]	
Data/restraints/parameters	3769/32/112	2350/65/98	
Goodness-of-fit on F <sup>2</sup>	2.692	3.040	
Final R indexes [I>=2σ (I)]	$R_1 = 0.1458,  wR_2 = 0.5059$	$R_1 = 0.1894, wR_2 = 0.6168$	
Final R indexes [all data]	$R_1 = 0.1608, wR_2 = 0.5590$	$R_1 = 0.2150, wR_2 = 0.6381$	
Largest diff. peak/hole / e Å $^{-3}$	2.32/-1.66	1.35/-2.28	



**Figure S16.** Different side views of the crystal structure for a) V-Zr-NU-1200 and b) V-Hf-NU-1200. The vanadium atoms are disordered in two crystallographically-equivalent positions on every pair of adjacent

terminal oxo groups.



Figure S17. Kinetic plot of 100% conversion vs. reaction time of 4-methoxylbenzyl alcohol oxidation for V-Zr-NU-1200 with error bars.



**Figure S18.** Stability tests of all the catalysts with 3 times recycling experiments. The reduction of the conversion after each time is due to the weight loss of the catalysts when recycled, however, the TOFs didn't change.

Table S5. XPS parameters of the vanadium species on all the catalysts

samples V 2P <sub>3/2</sub> (5+)	$V 2P_{1/2}(5+)$	<b>O1s(1)</b>	O1s(2)
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V 7., NH 1200	B.E. (eV)	517.5	524.9	531.8	530.9
V-ZF-INU-1200	FWHM (eV)	2.5	3.5	2.8	3.1
V HE NH 1300	B.E. (eV)	517.6	525.0	531.9	530.6
V-HI-NU-1200	FWHM (eV)	2.3	3.2	2.4	2.5
V.C. NIL 1200	B.E. (eV)	517.7	525.1	531.9	530.4
v-Ce-NU-1200	FWHM (eV)	2.05	3.5	2.3	1.8
17 TE NIL 1400	B.E. (eV)	517.5	524.9	531.9	530.6
v-1n-NU-1200	FWHM (eV)	2.3	3.5	2.5	2.8

Table S6. XPS parameters of the vanadium species on V-Zr-NU-1200 and V-Ce-NU-1200 after 5 h's

reaction before	exposed to	o oxygen/	air
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samples		V 2P <sub>3/2</sub> (5+)	$V 2P_{1/2}(5+)$	$V 2P_{3/2}(4+)$	$V 2P_{1/2}(4+)$
V-Zr-NU-1200-5 h's	B.E. (eV)	517.4	524.8	516.4	523.2
reaction	FWHM (eV)	2.1	1.9	2.6	2.1
V-Ce-NU-1200-5 h's	B.E. (eV)	517.5	524.8		
reaction	FWHM (eV)	1.9	2.2		



**Figure S19.** Comparison of the metal valance change before and after the V loading and catalysis: a-c) Zr-NU-1200; e-f) Ce-NU-1200

The valance for the Zr didn't change after the vanadium deposition and the catalysis, however, Ce showed a valance decrease after the V loading but show only little change after the reaction (Totally Ce<sup>4+</sup> in



Figure S20. EPR spectra of V-Zr-NU-1200 in different stages



Figure S21. EPR spectra of V-Ce-NU-1200 in different stages. For both of the catalysts, after wash, only very small amount of  $V^{4+}$  still can be observed.



Figure S22. XPS of vanadium species on V-Zr-NU-1200 a) after reaction at different conditions before exposed to air, b) after reaction in  $N_2$  atmosphere and c) after reaction without base.



Figure S23. Scheme diagram of the V species structure on the node

**Figure** S23 showed the depositing way of the vanadium species and also the mechanism of the relationship of the catalytic activity with the supports. By depositing the vanadium species between two hydroxyl groups, the catalytic property of the vanadium can be affected easily through the supports. The mechanism can be described as followed: With a strong electron-withdrawing ability, the M-O bond (①) tends to be a strong bond and the O-V bond (②) will be weak while V=O (③) will be a strong bond. In this case, in the V=O bond, the vanadium will be exhibited negative charge while the oxygen exhibited positive charge, therefore, the oxygen on V=O can easily withdraw an electron from the substrate. Thus, with a stronger electronwithdrawing ability seems can start the reaction easier.



**Figure S24**. Reaction of V-M-NU-1200 with 4-methoxybenzyl alcohol. a) V=O as the active site b) V-OH as the active site. For mechanism (a), the V=O was the active site while mechanism (b) showed the V-OH will be the active site. Both mechanisms indicate that having a strong electron-withdrawing property will make the vanadium catalysts can easily start the reaction and thus have a high initial rate. Since  $V^{3+}$  appear in the mechanism, XPS measurement was carried out on a sample (V-Zr-NU-1200) with careful preparation in the glovebox after reaction and purging with N<sub>2</sub>. However, we were unable to detect  $V^{3+}$ . To check if this is due to sample processing and/or the transfer between glovebox and XPS instrument, XPS measurement of VCl<sub>3</sub> which was stored in glovebox also prepared for the test. However, no  $V^{3+}$  was detectable from the standard as well, indicating that the V<sup>3+</sup> most likely was oxidized to V<sup>4+</sup> during the transfer to the XPS instrument.

Table S7 Detailed va	lues of electrone	gativity calcul	ation
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metals	<b>IE</b> ( <b>eV</b> ) <sup>S10</sup>	<b>EA</b> (eV) <sup>S10</sup>	electronegativity (eV)
Zr	$80.35  (\mathrm{Zr}^{4+} \rightarrow \mathrm{Zr}^{5+})$	$34.42  (\mathrm{Zr}^{3+} \rightarrow \mathrm{Zr}^{4+})$	57.4
Hf	68.37 (Hf <sup>4+</sup> →Hf <sup>5+</sup> )	33.37 (Hf <sup>3+</sup> →Hf <sup>4+</sup> )	50.9
Ce	$36.9(\mathrm{Ce}^{3+}\rightarrow\mathrm{Ce}^{4+})/65.55(\mathrm{Ce}^{4+}\rightarrow\mathrm{Ce}^{5+})$	$20.2(\mathrm{Ce}^{2+}\rightarrow\mathrm{Ce}^{3+})/36.91(\mathrm{Ce}^{3+}\rightarrow\mathrm{Ce}^{4+})$	28.6/51.2
Th	58.04 (Th <sup>4+</sup> →Th <sup>5+</sup> )	28.65 (Th <sup>3+</sup> →Th <sup>4+</sup> )	43.3

The values for the ionization energy and electron affinity in eV from +3 to +4 and +4 to +5 are taken from the NIST website on atomic values. The calculation of the electronegativity was based on the following

equation:

Mulliken scale: 
$$X(M) = \frac{IE + EA}{2}$$

Where IE means ionization energy and EA represents electron affinity.



Figure S25. PXRD patterns of M-NU-1200 and V-M-NU-1200 before and after catalysis. The parent

framework stays intact upon metal deposition and during catalysis



Figure S26. Pore size distribution of M-NU-1200 and V-M-NU-1200 before and after catalysis



Figure S27. V-XPS spectra of V-M-NU-1200 after catalysis: a) V-Zr-NU-1200; b) V-Hf-NU-1200; c) V-

# Ce-NU-1200; d) V-Th-NU-1200

samples		V 2P <sub>3/2</sub> (5+)	$V 2P_{1/2}(5+)$	<b>O1s(1)</b>	O1s(2)
V-Zr-NU-1200	B.E. (eV)	517.5	524.8	531.8	530.6
after oxi.	FWHM (eV)	2.2	3.5	2.7	2.6
V-Hf-NU-1200	B.E. (eV)	517.4	524.8	531.9	530.4
after oxi.	FWHM (eV)	2.2	3.5	2.5	2.4
V-Ce-NU-1200	B.E. (eV)	517.8	525.2	531.8	530.2
after oxi.	FWHM (eV)	2.2	3.5	2.3	1.8
V-Th-NU-1200	B.E. (eV)	517.5	524.9	531.9	530.4
after oxi.	FWHM (eV)	2.3	3.5	2.5	2.3

Table S8. XPS parameters of the vanadium species on all the catalysts after catalysis



Figure S28. XPS spectra (Zr/ Hf/ Ce/ Th) of V-M-NU-1200 before and after catalysis: a, b) V-Zr-NU-1200

c, d) V-Hf-NU-1200 e, f) V-Ce-NU-1200 g, h) V-Th-NU-1200

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