

## Supplementary Information

### NH<sub>3</sub>-SCR of NO with novel active, supported vanadium-containing Keggin-type heteropolyacid catalysts

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#### Characterization of HPA-n POMs

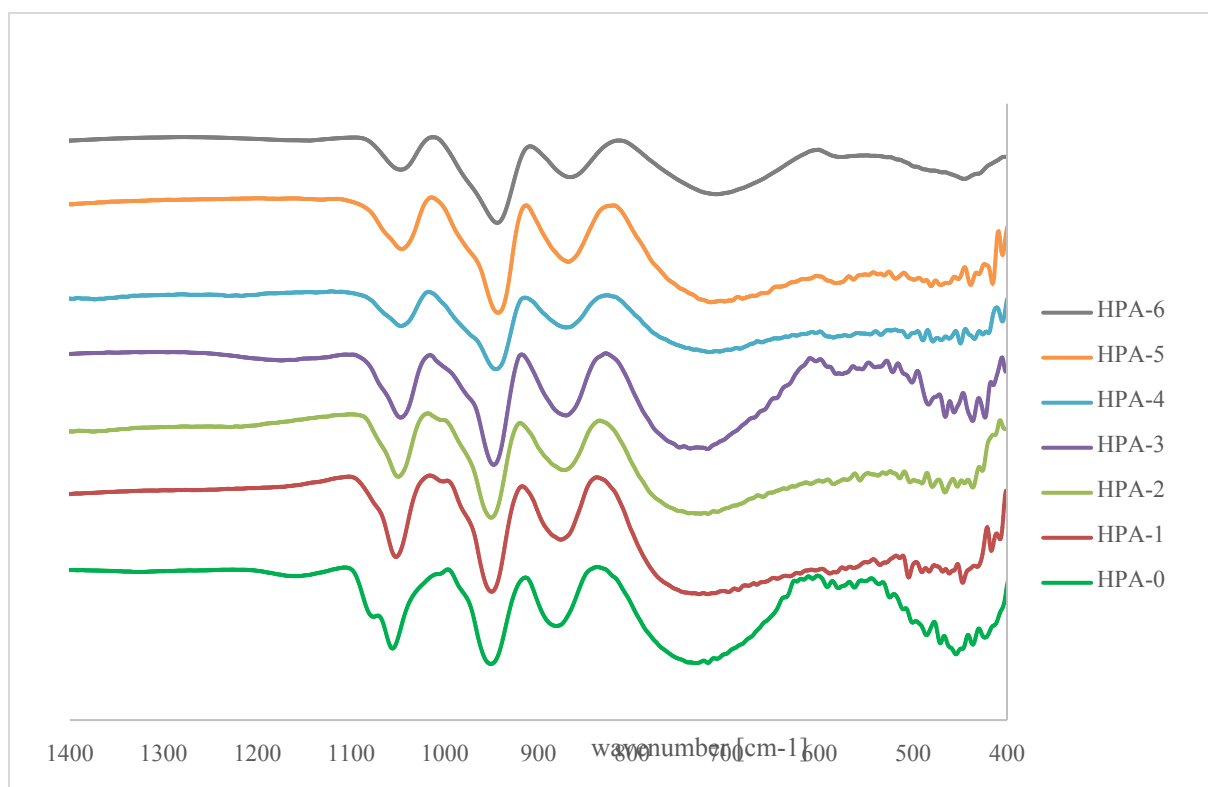
ICP-OES was used to determine the composition of the synthesized vanadium-substituted HPA-n Keggin-polyoxometalates. The results were adjusted considering one atom of phosphorous per Keggin unit according to the nature of the structure.

**Table S1:** Composition of the synthesized HPA-n polyoxometalates.

Material	Formula	P/V/Mo molar ratio <sup>a</sup>
HPA-0	H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	1 / 0 / 11.83
HPA-1	H <sub>4</sub> PV <sub>1</sub> Mo <sub>11</sub> O <sub>40</sub>	1 / 0.82 / 11.34
HPA-2	H <sub>5</sub> PV <sub>2</sub> Mo <sub>10</sub> O <sub>40</sub>	1 / 2.01 / 10.12
HPA-3	H <sub>6</sub> PV <sub>3</sub> Mo <sub>9</sub> O <sub>40</sub>	1 / 2.94 / 9.20
HPA-4	H <sub>7</sub> PV <sub>4</sub> Mo <sub>8</sub> O <sub>40</sub>	1 / 4.38 / 7.95
HPA-5	H <sub>8</sub> PV <sub>5</sub> Mo <sub>7</sub> O <sub>40</sub>	1 / 4.84 / 6.99
HPA-6	H <sub>9</sub> PV <sub>6</sub> Mo <sub>5</sub> O <sub>40</sub>	1 / 5.75 / 5.56

<sup>a</sup> Determined via ICP-OES.

Solid state FTIR ATR of the as-synthesized HPA-n catalysts was recorded in order to validate that they contained the Keggin structure. Figure S1 shows the FTIR spectra of the different HPA-n catalysts. All characteristic stretching vibrations of the Keggin oxoanion were observed at 1065 cm<sup>-1</sup> ( $\nu_{\text{as}}$  P-O<sub>a</sub>), 959 cm<sup>-1</sup> ( $\nu_{\text{as}}$  Mo-O<sub>d</sub>), 865 cm<sup>-1</sup> ( $\nu_{\text{as}}$  Mo-O<sub>b</sub>-Mo) and 771 cm<sup>-1</sup> ( $\nu_{\text{as}}$  M-O<sub>b</sub>-Mo).<sup>1</sup>



**Figure S1:** FTIR spectra of the synthesized HPA-n catalysts measured with a Jasco FT/IR-4100 spectrometer equipped with a PIKE GladiATR ATR-accessory.

### Characterization of the supported HPA-n POM catalysts

ICP-OES analysis was used to determine the metal content in the different supported catalysts.

**Table S2:** ICP-OES results of supported HPA-n catalysts.

Material	Mo [wt.%]	V [wt.%]
HPA-3/TiO <sub>2</sub>	6.48	1.61
HPA-3/ZrO <sub>2</sub>	6.73	2.09
HPA-3/SiO <sub>2</sub>	7.07	1.11
HPA-3/C	5.75	0.89
HPA-3/Al <sub>2</sub> O <sub>3</sub>	7.45	1.17
V <sub>2</sub> O <sub>5</sub> and HPA-0/TiO <sub>2</sub>	8.69	1.70

### Characterization of the pure support materials

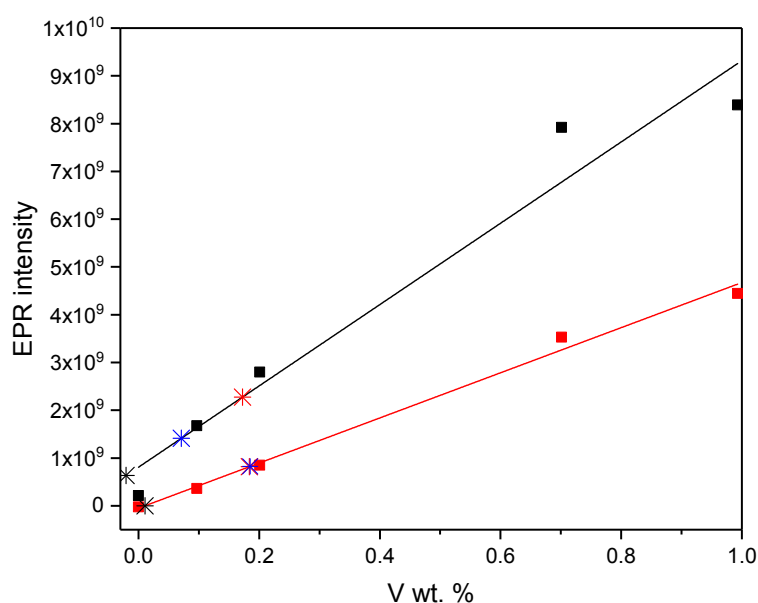
Specific surface area, pore volume and average pore diameter of all support materials were determined by N<sub>2</sub>-physisortion. Moreover, temperature-programmed desorption (TPD) of NH<sub>3</sub> measurements were performed to get more information regarding the acidity of the pure supports.

**Table S3:** Textural properties and NH<sub>3</sub>-TPD results of the different support materials.

Support material	BET surface area [m <sup>2</sup> g <sup>-1</sup> ]	Pore vol. [cm <sup>3</sup> g <sup>-1</sup> ]	Av. pore diameter [Å]	Ads. NH <sub>3</sub> [mmol g <sup>-1</sup> ]	T <sub>max</sub> [°C]
ZrO <sub>2</sub>	132.0	0.16	47.93	0.51	192.5
TiO <sub>2</sub>	82.9	0.25	114.52	0.15	166.0
SiO <sub>2</sub>	441.9	0.72	62.44	0.08	297.4
Al <sub>2</sub> O <sub>3</sub>	266.6	0.69	104.06	0.48	158.9
C	531.4	0.73	54.58	0.18	295.2

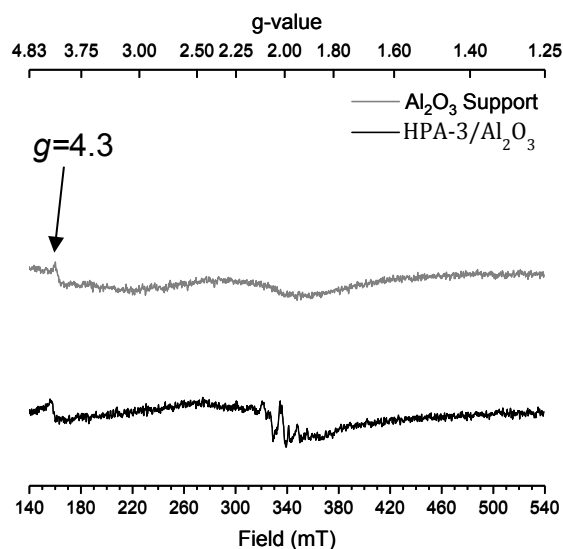
### In-situ EPR measurements

Quantification of active vanadium was carried out by EPR in two replicates (see below) on fresh HPA-3/TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>-HPA-0/TiO<sub>2</sub> and The HPA-3/Al<sub>2</sub>O<sub>3</sub> by referencing to EPR measurements of VOSO<sub>4</sub> in K<sub>2</sub>SO<sub>4</sub>. The results show HPA-3/TiO<sub>2</sub> catalyst contained 0.18 ± 0.01 wt.% EPR active [VO]<sup>2+</sup>, while V<sub>2</sub>O<sub>5</sub>-HPA-0/TiO<sub>2</sub> contained 0.13 ± 0.08 wt.% EPR active [VO]<sup>2+</sup>. HPA-3/Al<sub>2</sub>O<sub>3</sub> only gave a weak signal but it was estimated that it contained less than 0.05 wt.% EPR active [VO]<sup>2+</sup>. These amounts corresponded to 11, 8 and <4% of the total V measured by ICP being EPR active for the catalysts. The standard curves are given in Figure S2.



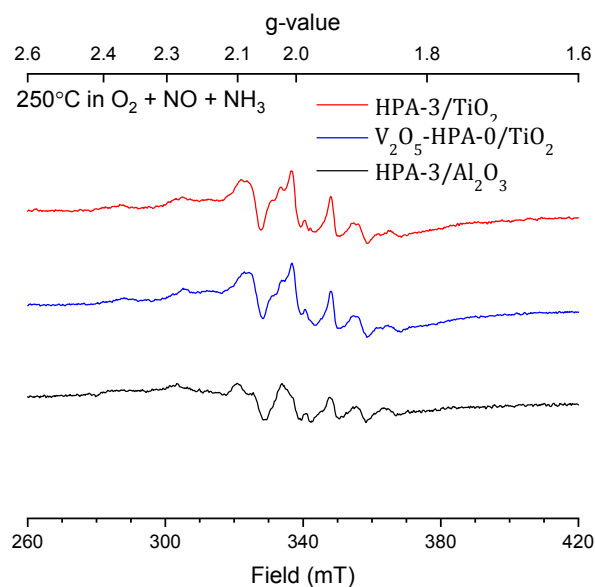
**Figure S2:** Standard curves for quantification of active vanadium by EPR at ambient conditions with no pre-treatment. Standards are shown as squares and samples as stars. The two curves represent two different series of measurements and are not directly comparable since the sample position and response differ between series.

A comparison of the EPR spectra of HPA-3/Al<sub>2</sub>O<sub>3</sub> and the Al<sub>2</sub>O<sub>3</sub> support itself showed that the signal observed at  $g = 4.3$  and a broad signal at  $g \approx 2$  was due to impurities on the support.



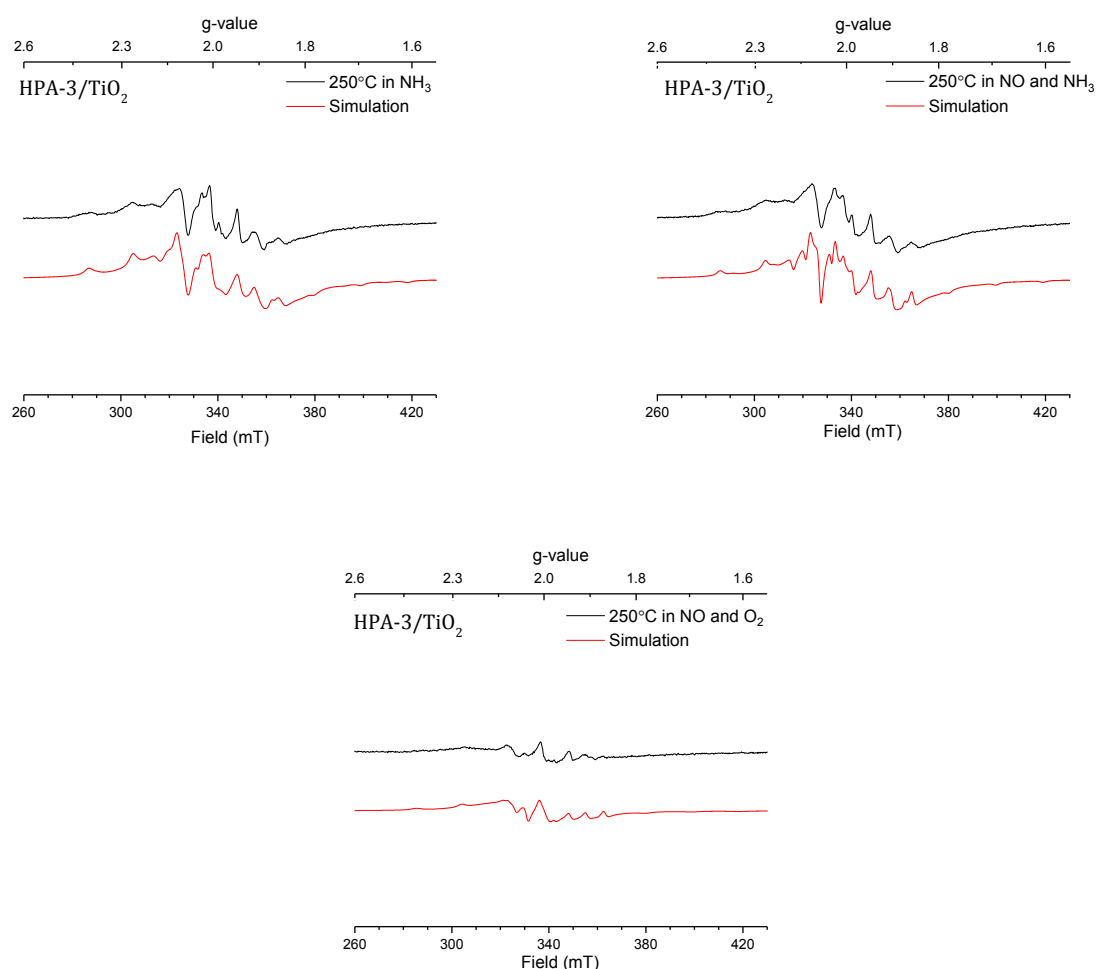
**Figure S3:** EPR spectra of the alumina support compared to HPA-3/Al<sub>2</sub>O<sub>3</sub> recorded at ambient conditions with no pre-treatment.

A comparison of EPR spectra of the samples during operando SCR conditions is shown in Figure S4. The spectra showed a difference in EPR active species between the Al<sub>2</sub>O<sub>3</sub>- and TiO<sub>2</sub> supported samples.



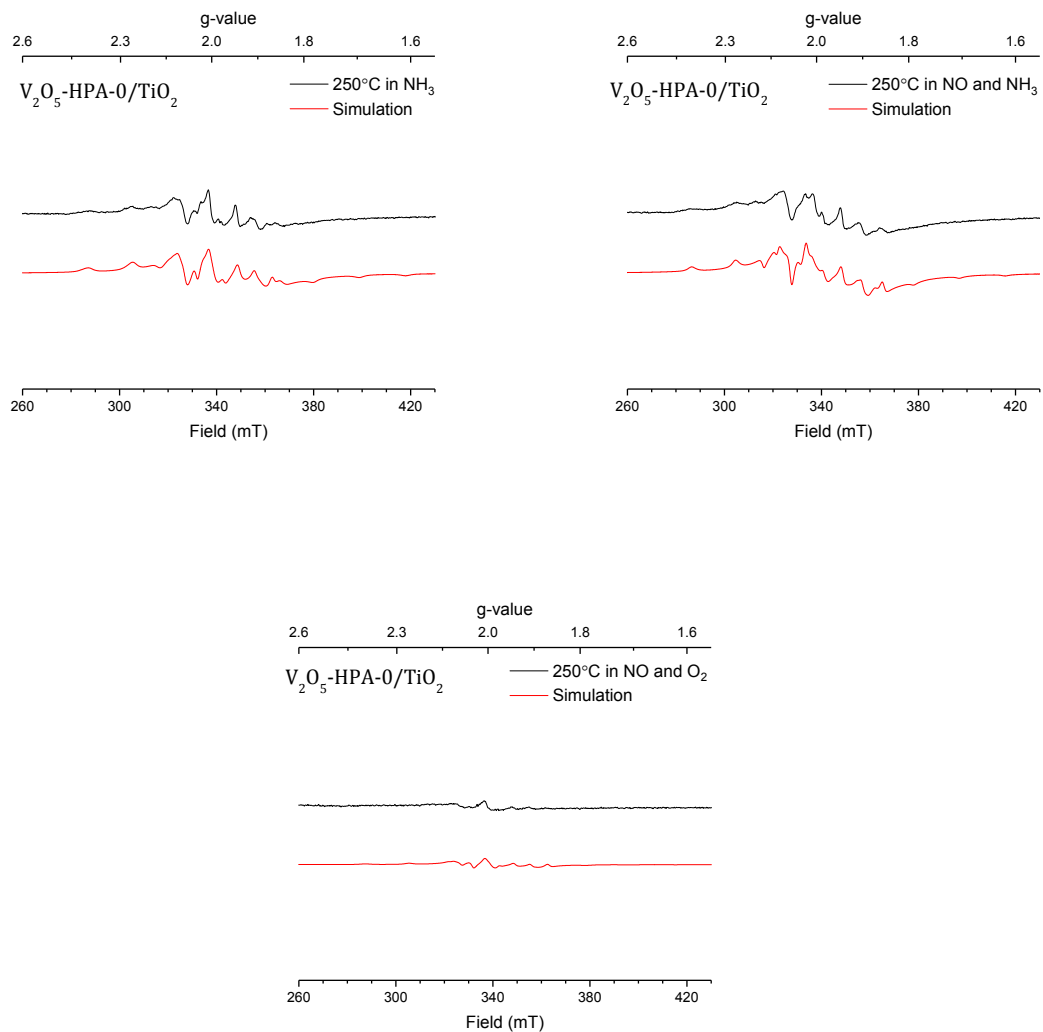
**Figure S4:** EPR spectra of the samples in 2.3 vol.% H<sub>2</sub>O, 4.5 vol.% O<sub>2</sub>, 500 ppm NO and 550 ppm NH<sub>3</sub> at 250 °C in balance He. Red line is the HPA-3 on TiO<sub>2</sub>, the blue line is V<sub>2</sub>O<sub>5</sub>-HPA-0/TiO<sub>2</sub> and the black line is HPA-3/Al<sub>2</sub>O<sub>3</sub>.

Selected EPR spectra from each sample were simulated using Matlab with the EasySpin 5.2.23 program. Simulations and spectra are shown in Figures S5-S7. Three different EPR active species, A, B and C were observed on the HPA-3/TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>-HPA-0/TiO<sub>2</sub> samples. The spin Hamiltonian values extracted from the simulated spectra of the reduced and oxidized samples are given in Table 2 of the main text. The simulations showed that for all the different conditions (SCR, NH<sub>3</sub>, NO/NH<sub>3</sub>, NO/O<sub>2</sub>) much of the signal intensity could be assigned to the [VO]<sup>2+</sup>-species denoted C, which had a broad signal at  $g = 1.96$  with unresolved hyperfine splitting and a large line width.

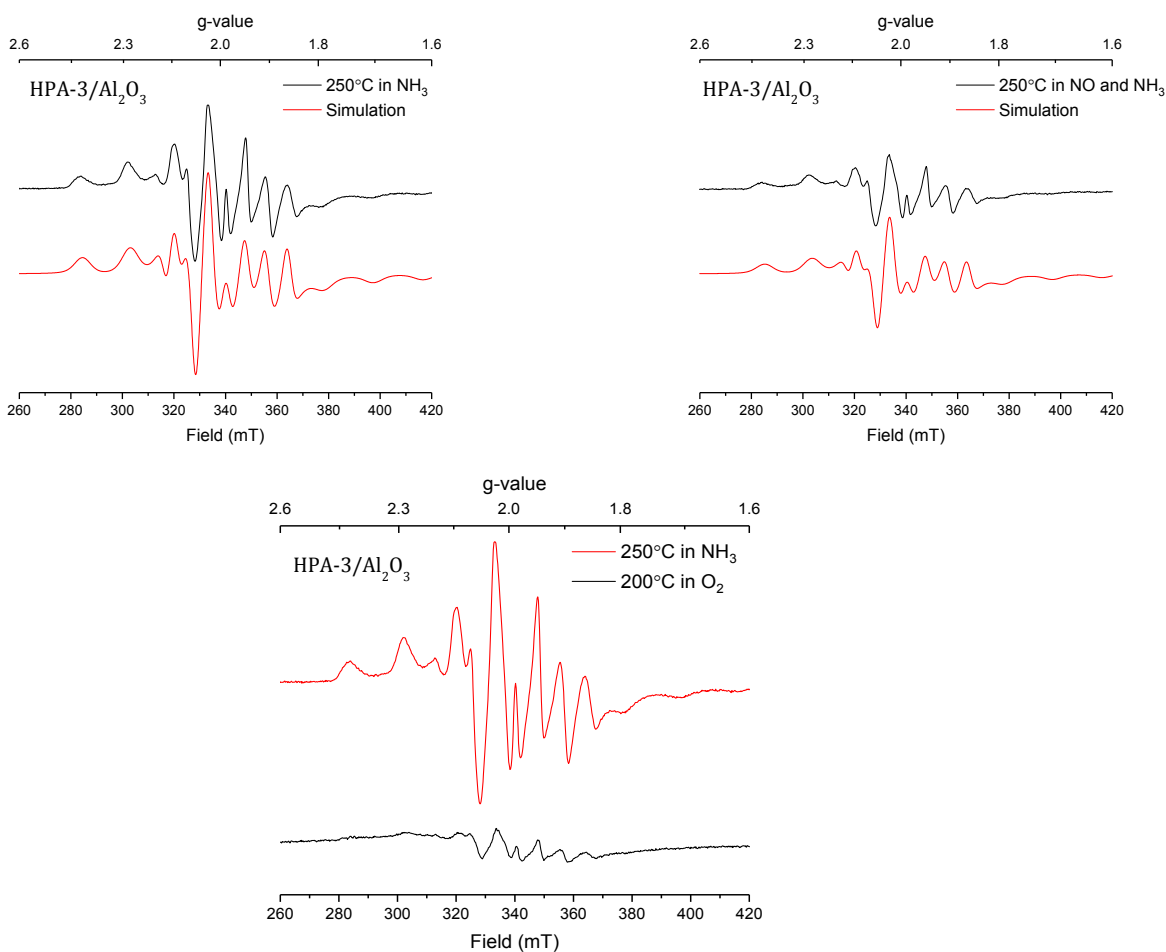


**Figure S5:** EPR spectra of HPA-3/TiO<sub>2</sub> (black lines) with the simulated spectra below (red lines). All flows were in balance He with 2.3 vol.% H<sub>2</sub>O, and with 500 ppm NO, 550 ppm NH<sub>3</sub> and 4.5 vol.% O<sub>2</sub> when indicated.

The EPR spectrum of HPA-3/Al<sub>2</sub>O<sub>3</sub> was compatible with a single vanadium species with varying intensity. The quantification of the signal for this sample was uncertain due to the low intensity of the initial spectrum and a non-vanadium impurity. Simulations and corresponding spectra are shown in Figure S7.



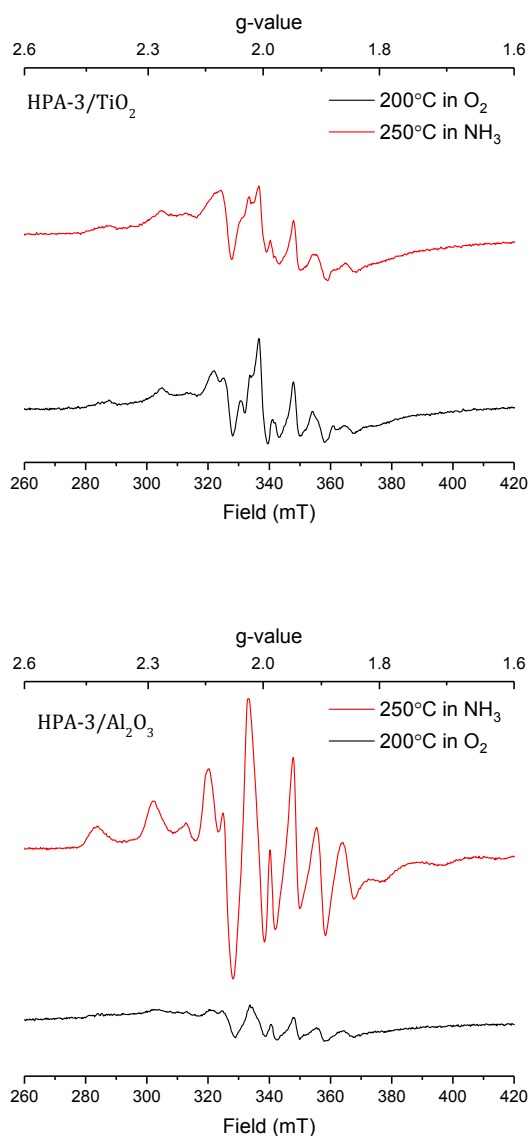
**Figure S6:** Recorded EPR spectra of  $V_2O_5$ -HPA-0/ $TiO_2$  (black lines) with the simulated spectra below (red lines). All flows were in balance He with 2.3 vol.%  $H_2O$ , and with 500 ppm  $NO$ , 550 ppm  $NH_3$  and 4.5 vol.%  $O_2$  when indicated.



**Figure S7:** Top spectra: EPR spectra of HPA-3/Al<sub>2</sub>O<sub>3</sub> (black lines) with the simulated spectra below (red lines). All flows were in balance He with 2.3 vol% H<sub>2</sub>O, and with 500 ppm NO, 550 ppm NH<sub>3</sub> and 4.5 vol.% O<sub>2</sub> when indicated Bottom spectrum: Comparison of EPR spectra under NH<sub>3</sub> and under O<sub>2</sub>.

### *Exposure of samples to NH<sub>3</sub> alone*

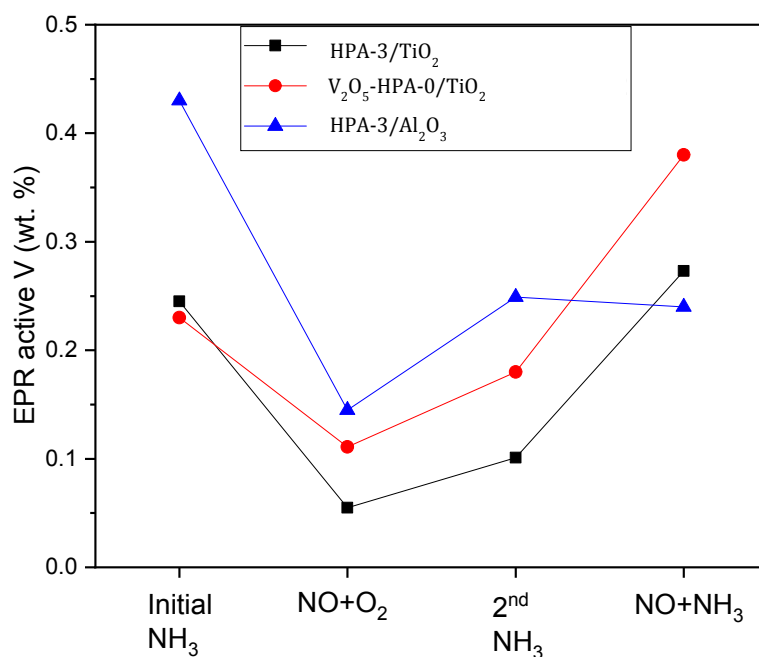
All samples were exposed to the same experimental protocol: They were first heated to 200 °C in O<sub>2</sub>, then exposed to 550 ppm NH<sub>3</sub> and 2.3 vol.% H<sub>2</sub>O in He at the same temperature and then heated to 250 °C in the same gas mixture. The exposure to NH<sub>3</sub> caused a significant increase in the intensity of the EPR signal for the HPA-3/Al<sub>2</sub>O<sub>3</sub>, see Figure S7, bottom. The increase corresponded to an increase in EPR active vanadium from less than 0.05 wt.% to a maximum of 0.43 wt.%. The resulting spectrum was axial and contained only one resolved EPR active vanadium species, with  $g_z = 1.979$ ,  $g_x = g_y = 1.927$  and  $A_z = 190$ ,  $A_x = A_y = 510$  MHz. After a few cycles between NO/NH<sub>3</sub> and NO/O<sub>2</sub> at 250 °C (see Figure 10 of the main text), the sample was exposed to NH<sub>3</sub> alone again. This time the intensity of the signal did not increase as much as before, and exposure to a mixture of NO/NH<sub>3</sub> did not increase the signal but rather decreased it a little, see Figure S9. Normally NO/NH<sub>3</sub> is considered the most reducing gas mixture and should give the highest intensity corresponding to the highest concentration of paramagnetic VO<sup>2+</sup>.



**Figure S8:** Top: EPR spectra of samples in 4.5 vol.% O<sub>2</sub> and 2.3 vol.% H<sub>2</sub>O in He at 200 °C (black lines). Bottom: The same samples after 30 min in 550 ppm NH<sub>3</sub> and 2.3 vol.% H<sub>2</sub>O at 250 °C (red lines). The total flow was maintained at 200 mL min<sup>-1</sup> and the spectra were normalized with respect to the mass of the samples.

For the TiO<sub>2</sub> supported samples the same protocol was followed. Exposure to NH<sub>3</sub> initially caused a moderate increase of intensity to 0.25 wt.% EPR active [VO]<sup>2+</sup>. The change was mainly in the broad unresolved signal at  $g = 1.96$  (species C) and a slight broadening of the lines, whereas only small changes to features of species A and B was observed. The distribution of the three observed species for the HPA-3/TiO<sub>2</sub> changed slightly when exposed to NH<sub>3</sub>. The increase in intensity was slow, however, and subsequent exposure to NO/NH<sub>3</sub> resulted in a faster and more significant increase.





**Figure S9:** Changes in amounts of EPR active vanadium at 250 °C in various conditions. Initial NH<sub>3</sub> represent the sample after exposure to 550 ppm NH<sub>3</sub> in 2.3 vol.% H<sub>2</sub>O and He balance on the sample that was heated in O<sub>2</sub>. NO/O<sub>2</sub> represent the sample exposed to 500 ppm NO and 4.5 vol.% O<sub>2</sub> in 2.3 vol.% H<sub>2</sub>O and He balance. 2<sup>nd</sup> NH<sub>3</sub> represent the sample when exposed to 550 ppm NH<sub>3</sub> for 30 min after the sample had been exposed to NO/O<sub>2</sub> for the TiO<sub>2</sub> supported samples and after NO/NH<sub>3</sub> for the Al<sub>2</sub>O<sub>3</sub> sample. NO/NH<sub>3</sub> represent the samples after exposure to 550 ppm NH<sub>3</sub> and 500 ppm NO in 2.3 vol.% H<sub>2</sub>O and He balance after 20 min for the TiO<sub>2</sub> supported samples and 30 min for the Al<sub>2</sub>O<sub>3</sub> sample.

**Table S4:** Summary of NO conversion ( $X_{NO}$ ), amount of converted NO ( $n_{NO,converted}$ ), amount of vanadium in the used catalyst ( $n_V$ ), Turnover frequency (TOF), catalytic rate constant ( $k$ ) and reaction rate ( $r$ ) at 250 °C.

T= 250 °C	$X_{NO}$	$n_{NO,converted}$ mol s <sup>-1</sup>	$n_V$ mol	TOF mol <sub>N<sub>2</sub></sub> / (mol <sub>V</sub> s)	$k$ cm <sup>3</sup> (mol <sub>V</sub> s) <sup>-1</sup>	$r$ mol (s*mol <sub>V</sub> )
HPA-0	1%	2,84E-12	-	-	-	-
HPA-1	7%	1,41E-11	3,86E-06	3,65E-06	1,70E+05	3,22E-03
HPA-2	19%	3,61E-11	7,82E-06	4,61E-06	2,29E+05	4,31E-03
HPA-3	25%	4,83E-11	1,20E-05	4,02E-06	2,08E+05	3,69E-03
HPA-4	26%	5,03E-11	1,62E-05	3,09E-06	1,61E+05	2,84E-03
HPA-5	33%	6,31E-11	2,06E-05	3,07E-06	1,67E+05	2,84E-03
HPA-6	36%	6,94E-11	2,51E-05	2,77E-06	1,54E+05	2,55E-03

TOF was calculated using equation S1:

$$TOF = \frac{\dot{n}_{Products}}{n_{Vanadium}} = \frac{\dot{n}_{NO, converted}}{n_{Vanadium}} \quad (S1)$$

#### Reference:

1. Albert, J.; Lüders, D.; Bösmann, A.; Guldi, D. M.; Wasserscheid, P., Spectroscopic and electrochemical characterization of heteropoly acids for their optimized application in selective biomass oxidation to formic acid. *Green Chemistry* **2014**, *16* (1), 226-237.doi: 10.1039/C3GC41320A