

## Supplementary Information

### Supported monomeric vanadium catalyst for dehydration of amides to form nitriles

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#### Experimental

##### 1) General

Vanadium trichloride was purchased from Wako Pure Chemical Co., Ltd. Hydrotalcite (AD 500NS) was purchased from Tomita Pharmaceutical Co., Ltd. All amides were commercially available. Mesitylene was purified before use. Inductively coupled plasma measurements were performed using a Nippon Jarrell-Ash ICAP-575 Mark II spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL JNM-AL400 instrument. GC analyses were performed on a Shimadzu GC-2014 chromatograph using a column packed with KOCL-3000T or Silicone Gum SE-30 (Nishio Industry Co., Ltd.). V K-edge X-ray absorption spectra were recorded at SPring-8, JASRI, Harima, Japan at room temperature using a fluorescence yield collection technique at the beam line (01B1) station with an attached Si (111) monochromator. Detailed data analysis was performed using the REX 2000 program ver. 2.5.7 (RIGAKU). Fourier transformation (FT) of the

$k^3$ -weighted EXAFS (extended X-ray absorption fine structure) data was performed to obtain the radial structural function. UV-visible spectra were measured using a JASCO V-570.

## 2) Reaction Procedures

A typical procedure for the dehydration of **1** by V/HT catalyst was as follows: V/HT (0.1 g, 0.04 mmol V) and *o*-toluamide (1.0 mmol) were placed in a Schlenk tube, followed by addition of mesitylene (3 mL), and the reaction mixture was vigorously stirred at 180 °C in 10 h with the removal of water. After the dehydration reaction, the yield was determined by GC analysis with biphenyl as an internal standard.

**Product purification:** after the dehydration reaction, the supernatant of the reaction mixture was separated by centrifuge and the catalyst was washed with hexane (5 mL). The combined solution was subjected to silica gel column (Wakogel C-200). Mesitylene was removed by elution with hexane, and then the nitrile product was eluted by hexane/ethyl acetate = 1:1. After evaporation of the eluent, the residue was distilled with Kugelrohr or recrystallized to give the pure product.

Isolation of 4-cyanopyridine was conducted as follows. After the dehydration reaction, solid catalyst was removed by filtration and the filtrate was extracted with water. Further, the product was extracted again with ethyl acetate. The extract was dried with MgSO<sub>4</sub> and evaporated. The residue was recrystallized to afford 4-cyanopyridine as a white crystal.

**Product identification:** all products are commercially available. The products were determined by GC and NMR. GC retention times and  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts of products agreed with those of authentic samples.

### 3) Characterization of V/HT

Figure 1S shows the V K-edge X-ray absorption near-edge structure (XANES) spectra of V compounds. All of the XANES spectra have a sharp pre-edge peak around 5470 eV and an absorption edge around 5480 eV. The absorption edge was assigned to  $\text{V}^{\text{V}}$  species and the pre-edge peak is attributed to 1s-3d dipole transitions allowed by destruction of the inversion symmetry around the V atom. In the Fourier transformation of the V K-edge  $k^3$ -weighted EXAFS spectrum of V/HT (Figure 2S), only one peak near 1.7 Å, corresponding to the V-O single shell, was detected. In the UV-vis diffuse reflectance spectra of V/MgO and V/HT, charge-transfer bands at 300 and 260 nm were detected (Figure 3S). The band at 340 nm in the V/ $\text{Al}_2\text{O}_3$  and V/ $\text{TiO}_2$  spectra was attributed to polymeric vanadium species.

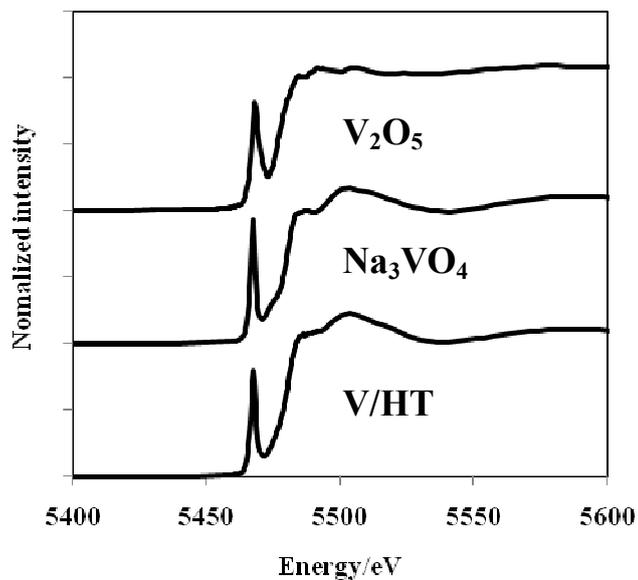


Figure 1S. V K-edge XANES spectra of V compounds.

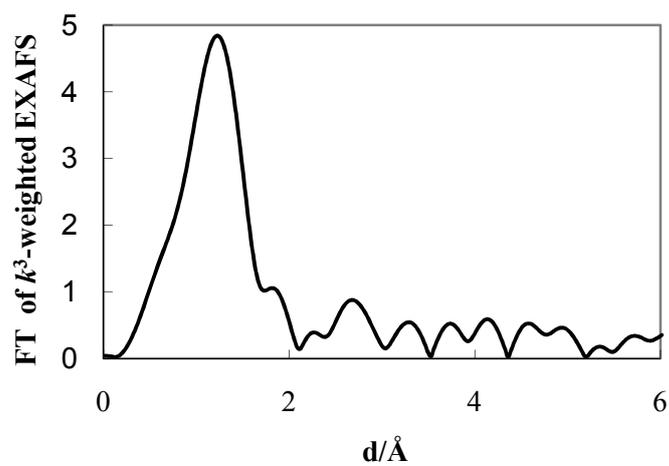


Figure 2S. Fourier transform of  $k^3$ -weighted V K-edge EXAFS of V/HT.

**Table 1S** A curve-fitting result of V K-edge EXAFS of V/HT

Sample	Shell	CN <sup>a</sup>	R[Å] <sup>b</sup>	Δσ[Å <sup>2</sup> ] <sup>c</sup>
V/HT	V-O	4.1	1.68	0.047
Na <sub>3</sub> VO <sub>4</sub>	V-O	4.0	1.70	-

<sup>a</sup> Coordination number. <sup>b</sup> Interatomic distance. <sup>c</sup> Δσ is the difference between the Debye-Waller factor of the sample and that of the reference sample.

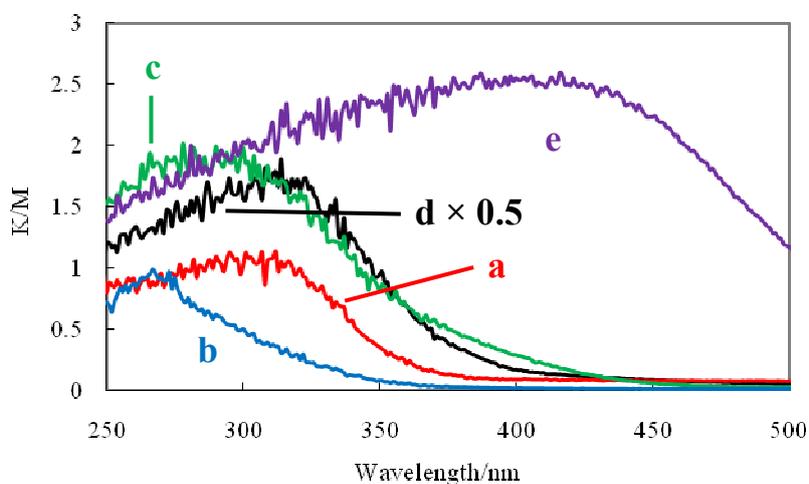
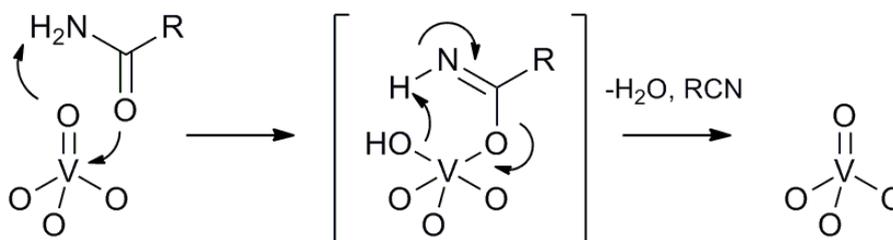


Figure 3S. Diffuse reflectance UV-vis spectra of a) V/HT, b) V/MgO, c) V/Al<sub>2</sub>O<sub>3</sub>, d) V/TiO<sub>2</sub> and e) V/SiO<sub>2</sub>.



Scheme 1S. Proposed mechanism of dehydration of amide by V/HT.