

Supporting Information for

**Highly Efficient C-C Bond-Forming Reactions in Aqueous Media
Catalyzed by Monomeric Vanadate Species in an Apatite Framework**

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Table of Contents

1. General Procedure	(S2)
2. Characterization of the VAp Catalyst	(S3)
3. Product Identification	(S8)
4. Experimental Section	(S10)
5. Reuse of the VAp Catalyst in the Michael Reaction	(S12)
6. References and Notes	(S13)

1. General Procedure

All chemical compounds were purified by the standard procedures before use. Analytical GLC was performed by Shimadzu GC-8APF and GC-1700 with flame ionization detector equipped with KOCL3000T, Silicone UC W-98, Silicone OV-1, Silicone OV-17 packed, and CPB-20 capillary columns. ^1H and ^{13}C NMR spectra were obtained on JEOL GSX-270 or JNM-AL400 spectrometers at 270 or 400 MHz in chloroform- d_1 with TMS as an internal standard. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-700 Mass Spectrometer. Products were confirmed by the comparison of their GC retention time, mass, ^1H and ^{13}C NMR spectroscopy with those of authentic samples. Purities of isolated products were determined by ^1H NMR. Substrates and solvents were commercially obtained from Tokyo Kasei, WAKO, Aldrich (reagent grade).

Powder X-ray diffraction patterns were recorded using Philips X'Pert-MPD with Cu $K\alpha$ radiation. Diffuse reflectance UV-vis spectra were recorded on JASCO V-550 spectrometer equipped with integration spheres at room temperature. BaSO_4 was used as a standard reflection sample. Inductively coupled plasma measurement was performed by Nippon Jarrell-Ash ICAP-575 Mark II. X-ray photoelectron spectroscopy were recorded on Shimadzu ESCA-KM using $\text{MgK}\alpha$ radiation. Powder samples were pressed to be attached on carbon tape and mounted on a sample folder. Binding energy (B. E.) was calibrated using the C 1s photoelectric peak at 284.6 eV. X-ray absorption (XAS) experiments were carried out on the beam line 9C at Photon Factory in National Laboratory for High Energy Physics (KEK-PF), Tsukuba, Japan, with a ring energy of 2.5 GeV. XAFS data of the samples were collected by the EXAFS facilities installed at BL9C in transmission mode at room temperature with an Si(111) two-crystal monochromator. BET surface area was determined by N_2 adsorption measurement at 77 K using BELSORP 18PLUS-SP analyser (Bel Japan, Inc.). Prior to the measurements, each catalyst was dried at 673 K for 8 h in vacuo. Raman spectrum was obtained on the

JASCO NRS-3100 spectrometer. ESR spectra were recorded at the X-band using a Bruker EMX-10/12 spectrometer. TEM micrographs were obtained with Hitachi H-800 type microscope. A solid-state wide-line ^{51}V NMR spectra were recorded on CMX-300W Infinity with VOCl_3 as a standard. CO_2 -TPD of the samples was carried out in a flow-type fixed bed reactor using Japan BEL TPD-77 instrument. The TPD profiles was obtained from 100 °C to 800 °C at a heating rate of 10 °C/min in a vacuum with a turbo molecular pump and an ion pump. The small portion of desorbed gases was introduced into the chamber to analyze after adsorption of an excess CO_2 at room temperature by Anelva AQA100R quadrupole mass spectrometer. He was continuously introduced into the system during the TPD run, and peak intensity of each mass was normalized to that of He.

2. Characterization of the VAp Catalyst

Figure S1 shows transmission electron microscopy (TEM) images of the VAp calcined at 800 °C. The VAp covered with amorphous CaO phase was observed as a bright region in a dark field. The electron spin resonance (ESR) spectrum of a vanadium species in the VAp was completely silent. In X-ray photoelectron spectroscopy (XPS), the VAp showed a binding energy almost identical values to that of V_2O_5 (516.8 eV and 516.6 eV, respectively) for V $2p_{3/2}$. In their UV-vis diffuse reflectance spectra (DRS), the VAp did not exhibit the charge-transfer band at wavelength regions longer than 320 nm, which suggests that the vanadium oxide moieties exist in a highly dispersed state in the apatite matrix with an absence of polymerized octahedrally coordinated species (Figure S2).¹

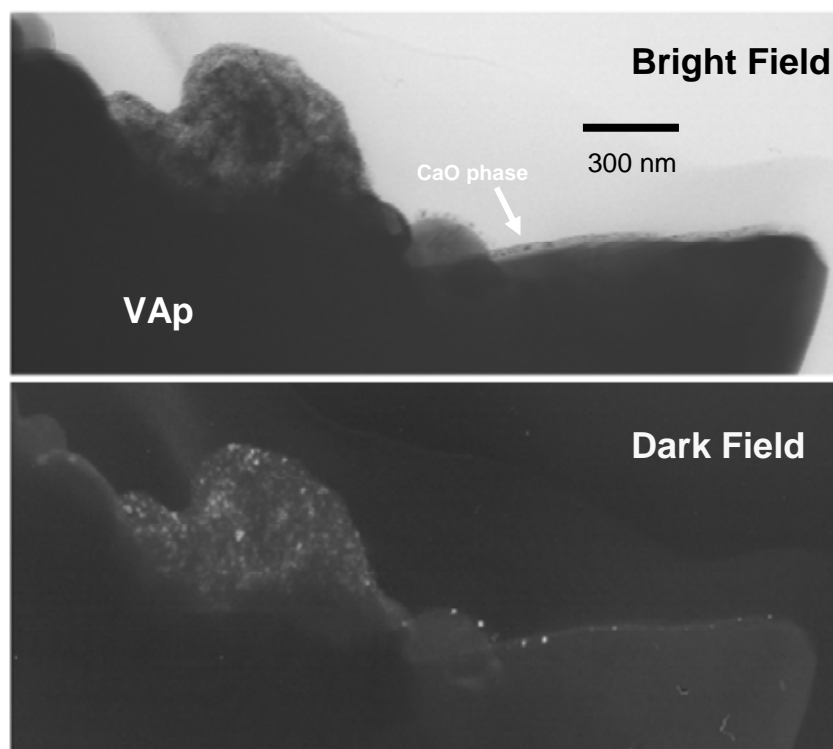


FIGURE S1. TEM image of the VAp catalyst: bright field (top), and dark field image (bottom).

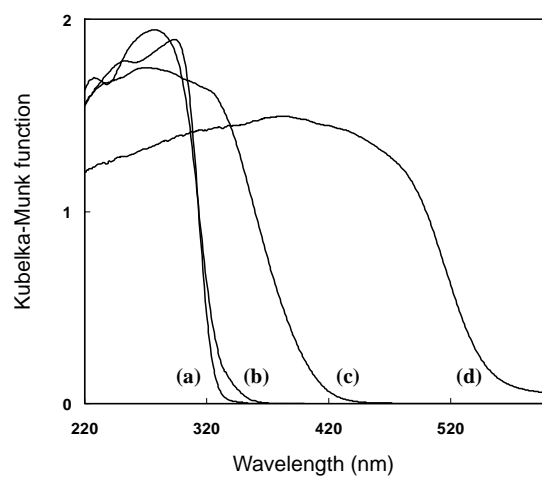


FIGURE S2. Diffuse Reflectance UV-vis spectra of (a) VAp, (b) Na_3VO_4 , (c) NaVO_3 , and (d) V_2O_5 .

In V K-edge X-ray absorption near edge structure (XANES) spectra, the VAp showed a strong pre-edge peak comparable to those seen for Na_3VO_4 (Figure S3).² Table S1 summarizes the features of the XANES spectra. The energy offset was taken with respect to the position of the pre-edge peak of V_2O_5 . The energy positions of pre-edge peak, of the main absorption of edge, and of the peak due to the $1s-4d$ dipole-allowed transition in the VAp were in good agreement with those observed for Na_3VO_4 , respectively. In the Fourier transforms (FT) of k^3 -weighted extended X-ray absorption fine structure (EXAFS) data, peaks due to V–O–V bonds in the second coordination sphere, detectable at around 2.8 Å for V_2O_5 , were not observed for either Na_3VO_4 or VAp (Figure S4).

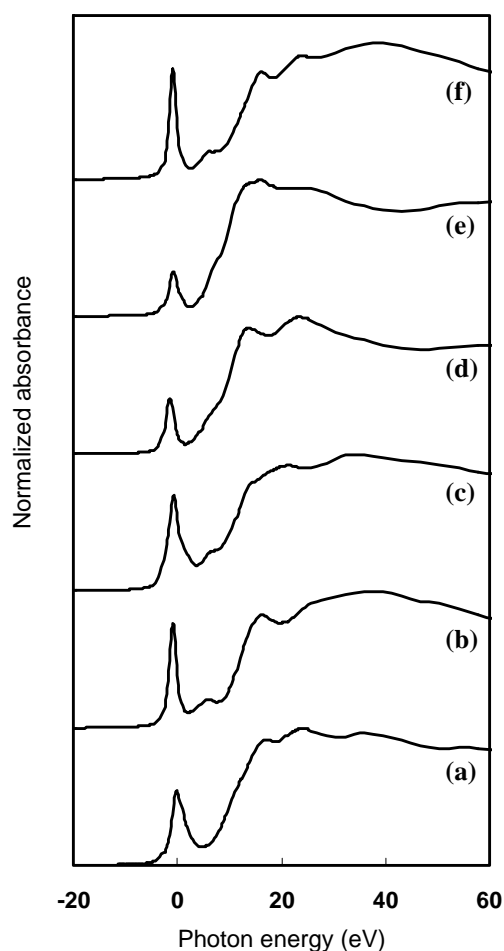


FIGURE S3. Vanadium K-edge XANES spectra of (a) V_2O_5 , (b) K_3VO_4 , (c) NH_4VO_3 , (d) $\text{VO}(\text{acac})_2$, (e) $\text{VOSO}_4 \cdot n\text{H}_2\text{O}$, and (f) VAp. Each spectrum was normalized to the height of edge jump. Energy offset is taken to be the position of the pre-edge peak of the V_2O_5 .

Table S1. Energy Positions of the Pre-edge Peak, the Edge, and 1s-4p Transition in V K-edge XANES Spectra^a

V compounds	relative energy positions / eV		
	pre-edge peak	edge ^b	1s-4p transition
V ₂ O ₅	0.0	10.8	30.1
K ₃ VO ₄	-0.9	12.0	16.3
NH ₄ VO ₃	-0.6	11.4	26.6
VO(acac) ₂ ^c	-1.5	10.8	13.8
VOSO ₄ ·nH ₂ O ^c	-0.9	9.9	16.4
VAp	-0.9	12.9	16.3

^a Energy offset was taken at the pre-edge peak position of V₂O₅. ^b Determined from the position of the second maximum of the derivative of XANES curve.

^c Note that formal charge of V in these compounds is tetravalent.

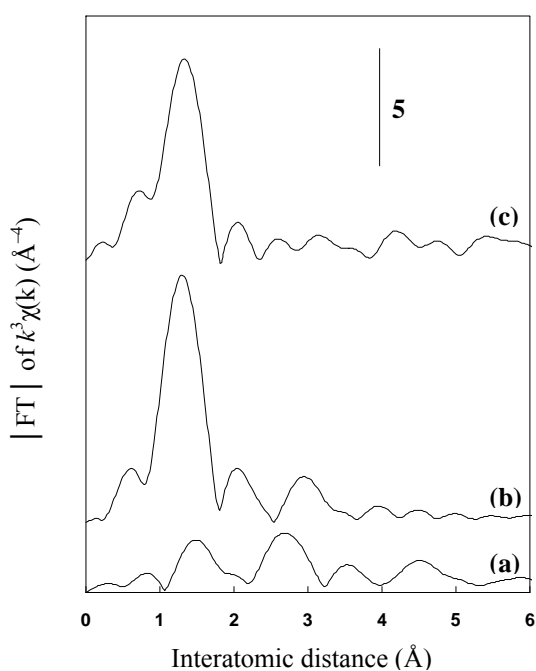


Figure S4. Fourier transformation of the k^3 -weighted V K-edge EXAFS spectra of (a) V₂O₅, (b) K₃VO₄, and (c) VAp. EXAFS were transformed in the range of 3.5-11.0 Å. The phase shift was not corrected. The peak at 1.5 Å corresponds to V=O and V-OH shells.

Figure S5 shows the solid-state wide-line ^{51}V NMR spectrum of the VAp calcined at 800 °C.³ It is well known that the resonances located between –500 and –700 ppm correspond to vanadium in a tetrahedral coordination.⁴ The main peak appears at –596 ppm, implying 4-coordinated geometry of vanadium in the apatite matrix, which is in agreement with the results of UV-vis DRS or XAFS analysis. Nabavi and co-workers reported that analysis of a distorted tetrahedral vanadate with a short vanadyl bond showed large upfield shifts.⁵ The peak at –602 ppm in Figure S5 suggests distortion in the vanadium tetrahedron which is probably caused by the calcium deficiency. In the Raman spectrum of the VAp calcined at 800 °C as shown in Figure S6, a strong band was observed at 860 cm^{-1} for an isolated $\text{V}=\text{O}$ stretching vibration.⁶ In addition, the bands appeared at 823 and 780 cm^{-1} were attributed to $\text{V}=\text{O}$ stretching vibrations of distorted vanadate species such as HVO_4 or H_2VO_4 .

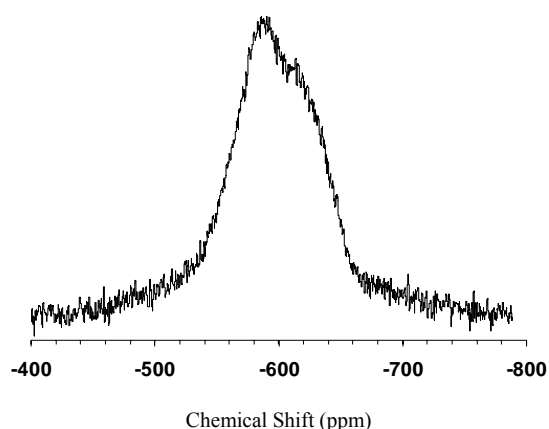


FIGURE S5. A solid-state wide-line ^{51}V NMR spectrum of the fresh VAp catalyst

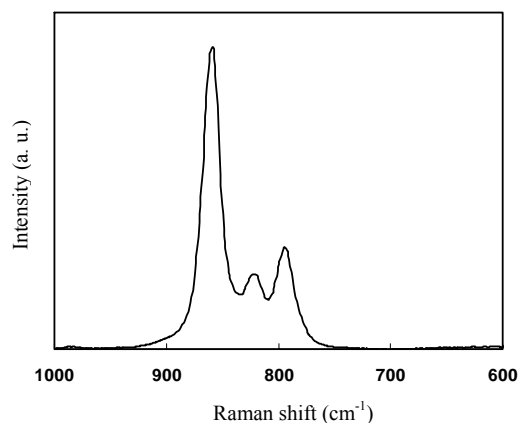


FIGURE S6. Raman spectrum of the VAp calcined at 800 °C for 3 h

3. Product Identification

The products showed spectra in an excellent agreement with the reported data. CAS registry number and references are shown below.

TABLE 1.

2-oxo-1-(3-oxocyclohexyl)-cyclopentanecarboxylic acid ethyl ester (3a);⁷ CAS registry No. [170969-99-0]

TABLE 2.

2-oxo-1-(3-oxobutyl)-cyclopentanecarboxylic acid ethyl ester (3b) (entry 1);⁸ CAS registry No. [61771-81-1]

1-(ethoxycarbonyl)-2-oxo-cyclopentanepropanoic acid methyl ester (3c) (entry 2);⁷ CAS registry No. [177664-80-1]

1-(2-cyanoethyl)-2-oxo-cyclopentanecarboxylic acid ethyl ester (3d) (entry 3);⁷ CAS registry No. [4668-82-0]

2-oxo-1-(3-oxobutyl)-cyclohexanecarboxylic acid ethyl ester (entry 4);⁸ CAS registry No. [61771-80-0]

2-acetyl-5-oxo-hexanoic acid ethyl ester (3e) (entry 5);⁸ CAS registry No. [35490-05-2]

2-acetyl-2-methyl-5-oxo-hexanoic acid ethyl ester (entry 6);⁹ CAS registry No. [28793-08-0]

β -oxo- α -(3-oxobutyl)-benzenepropanoic acid ethyl ester (entry 7);⁹ CAS registry No. [92582-13-3]

2-acetyl-2-(3-oxobutyl)-cyclohexanone (entry 8);⁸ CAS registry No. [121506-76-1]

3-acetyl-3-methyl-2,6-heptanedione (entry 9);⁸ CAS registry No. [73843-15-9]

3-acetyldihydro-3-(3-oxobutyl)-2(3H)-furanone (entry 10);¹¹ CAS registry No. [176101-57-8]

3-acetyltetrahydro-2-oxo-3-furanpropanoic acid methyl ester (entry 11);¹² CAS registry No. [280568-02-7]

3-acetyltetrahydro-2-oxo-3-furanpropanenitrile (entry 12);¹² CAS registry No. [351031-99-7]

(3-oxobutyl)-propanedioic acid diethyl ester (entry 13);¹³ CAS registry No. [4761-26-6]

methyl(3-oxobutyl)-propanedioic acid diethyl ester (entry 14);¹⁴ CAS registry No. [10433-88-2]

TABLE 3.

(2E)-2-cyano-3-phenyl-2-propenoic acid methyl ester (6a) (entry 1);¹⁵ CAS registry No. [3695-84-9]

(2E)-2-cyano-3-(4-methoxyphenyl)-2-propenoic acid ethyl ester (entry 2);¹⁶ CAS registry No. [2017-87-0]

(2E)-3-(4-chlorophenyl)-2-cyano-2-propenoic acid ethyl ester (entry 3);¹⁶ CAS registry No. [2169-68-8]

(2E)-2-cyano-2-octenoic acid ethyl ester (entry 4);¹⁶ CAS registry No. [91340-21-5]

(2E)-2-cyano-2-decenoic acid ethyl ester (entry 5);¹⁷ CAS registry No. [192705-39-8]

(2E)-2-cyano-3-cyclohexyl-2-propenoic acid ethyl ester (entry 6);¹⁶ CAS registry No. [90913-43-2]

(2E, 4E)-2-cyano-5-phenyl-2,4-pentadienoic acid ethyl ester (entry 7);¹⁶ CAS registry No. [41109-95-9]

(αE)-α-(phenylmethylene)-benzeneacetonitrile (entry 8);¹⁶ CAS registry No. [16610-80-3]

(2E)-3-phenyl-2-(phenylsulfonyl)-2-propenenitrile (entry 9);¹⁶ CAS registry No. [129200-96-0]

TABLE 4.

2-nitro-1-(nitromethyl)ethyl-benzene (entry 1);¹⁸ CAS registry No. [117538-84-8]

1-nitro-4-[2-nitro-1-(nitromethyl)ethyl]-benzene (entry 2);¹⁸ CAS registry No. [117538-89-3]

1-chloro-4-[2-nitro-1-(nitromethyl)ethyl]-benzene (entry 3):¹⁸ CAS registry No. [852159-30-9]

1-methoxy-4-[2-nitro-1-(nitromethyl)ethyl]-benzene (entry 4):¹⁸ CAS registry No. [117538-86-0]

4-nitro-3-(nitromethyl)butyl-benzene (entry 5):¹⁸ CAS registry No. [757237-59-5]

2-nitro-1-(nitromethyl)ethyl-cyclohexane (entry 6):¹⁸ CAS registry No. [885053-34-9]

4. Experimental Section

Deuteration of Various Ketones by Use of VAp Catalyst (TABLE 5)

After deuteration procedure described below, the signals of the corresponding α -protons disappeared in ^1H NMR, showing complete deuteration. Reaction procedure, CAS registry number, and HRMS value of each products are shown below.

3-Pentanone-2,2,4,4- d_4 (entry 2): CAS registry No. [6400-97-1]

Into a reaction vessel with VAp (0.05 g) and deuterium oxide (5 mL) were placed 3-pentanone (**8**) (0.43 g, 5 mmol), and stirred at 50 °C under Ar atmosphere. After 2 h, the VAp catalyst was readily separated from the reaction mixture by a centrifuge. The reaction mixture was extracted with diethylether. The organic layer was dried over MgSO_4 , filtered, concentrated, and distilled. 3-Pentanone-2,2,4,4- d_4 [94 % atom D] was obtained. Further treatment of the isolated product with the VAp catalyst and D_2O in the same manner gave analytically pure 3-pentanone-2,2,4,4- d_4 (**9**) (0.39 g, 100 % atom D, 86 % isolated yield). HRMS (EI): m/z calcd for $\text{C}_5\text{H}_6\text{D}_4\text{O}$ 90.0979. Found: 90.0983.

1-Indanone-2,2- d_2 (entry 3): CAS registry No. [10036-02-9]

Into a reaction vessel with VAp (0.05 g) and deuterium oxide (5 mL) were placed 1-indanone (0.66 g, 5 mmol), and stirred at 50 °C under Ar atmosphere. After 2 h, the VAp catalyst was readily separated from the reaction mixture by a centrifuge. The reaction mixture was extracted with diethylether. The organic layer was dried over MgSO_4 , filtered, concentrated, and distilled to give 1-indanone-2,2- d_2 [91 % atom D].

Further treatment of the isolated product with the VAp catalyst and D₂O in the same manner gave analytically pure 1-indanone-2,2-*d*₂ (0.63 g, 100 % atom D, 94 % isolated yield). HRMS (EI): *m/z* calcd for C₉H₆D₄O 134.0699. Found: 134.0701.

Cyclohexanone-2,2,6,6-*d*₄ (entry 4): CAS registry No. [1006-03-7]

Into a reaction vessel with VAp (0.05 g) and deuterium oxide (5 mL) were placed cyclohexanone (0.49 g, 5 mmol), and stirred at 50 °C under Ar atmosphere. After 2 h, the VAp catalyst was readily separated from the reaction mixture by a centrifuge. The reaction mixture was extracted with diethylether. The organic layer was dried over MgSO₄, filtered, concentrated, and distilled. Cyclohexanone-2,2,6,6-*d*₄ [79 % atom D] was obtained. Further treatment of the isolated product with the VAp catalyst and D₂O in the same manner gave cyclohexanone-2,2,6,6-*d*₄ (0.63 g, 98 % atom D, 93 % isolated yield). Treatment of the isolated product again with the VAp catalyst and D₂O in the same manner gave cyclohexanone-2,2,6,6-*d*₄ (0.63 g, 100 % atom D, 88 % isolated yield). HRMS (EI): *m/z* calcd for C₆H₆D₄O 102.0979. Found: 102.0967.

Aqueous Michael Reaction of 1a with 2e Catalyzed by VAp

A mixture of **1a** (0.16 g, 1 mmol), **2b** (0.28 g, 5 mmol), VAp (0.05 g), and water (5 mL) was stirred at 50 °C. After 24 h, the VAp was separated by a centrifuge, and the reaction mixture was extracted with diethylether, washed with brine, and then dried over MgSO₄. Diethylether was removed under the reduced pressure, the residue was treated with acetic anhydride (5 mL) at 100 °C under Ar atmosphere. After 2.5 h, ice water (30 mL) was added. The reaction mixture was extracted with diethylether, washed with brine, and then dried over MgSO₄. Diethylether was removed under the reduced pressure, the residue was distilled to give 0.21 g (84 % isolated yield) of analytically pure 4-acetoxy-8-oxo-bicyclo[3.2.1]octane-1-carboxylic acid ethyl ester (**3f**) (colorless oil) (**3f**):¹⁹ CAS registry number [67496-39-3].

A Procedure for the Synthesis of *o*-Benzylphenol Using VAp in Water

A mixture of 2-cyclohexen-1-one (0.10 g, 1 mmol), benzaldehyde (0.11 g, 1 mmol), VAp (0.05 g), and water (5 mL) was stirred at 150 °C using a pressure tube. After 12 h, the VAp catalyst was separated from the reaction mixture by a centrifuge. The reaction mixture was extracted with diethylether, and then dried over MgSO₄. Removal of diethylether under the reduced pressure, followed by recrystallization (*n*-hexane and ethylacetate) afforded analytically pure *o*-benzylphenol (**7**) (0.14 g, 78 % isolated yield).²⁰ CAS registry number [28994-41-4].

Synthesis of MgV₂O₇²¹

α -Magnesium pyrovanadate (Mg₂V₂O₇) was prepared from Mg(OH)₂ and NH₄VO₃. An appropriate amount of Mg(OH)₂ powder was added to a basic aqueous solution (1% NH₄OH) containing NH₄VO₃. The suspension was evaporated to dryness while being stirred and then finally dried at 110 °C. The resulting solid was calcined at 823 K for 6 h, 873 K for 6 h, 923 K for 6 h, 973 K for 17 h and then again 973 K for 17 h. The solid was finely ground after each calcination.

5. Reuse of the VAp Catalyst in the Michael Reaction

Upon completion of the Michael reaction of **1a** with **2b** under the conditions described in Table 2, the VAp catalyst was readily separated from the reaction mixture by a centrifuge and the spent VAp was washed with acetone and dried before reuse. The above recycling procedures were repeated four times in the same manner as in the first run. The results of the reuse experiment was shown in Figure S7.

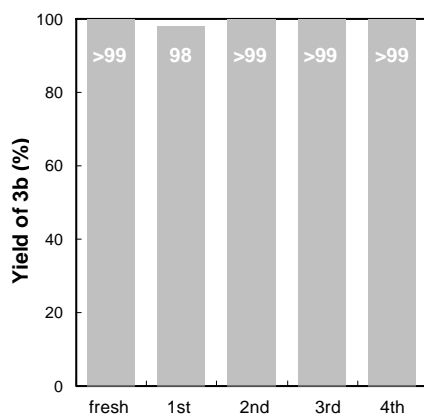


Figure S7. Recycling experiments of the VAp-catalyzed the aqueous Michael reaction of **1a** with **2b**.

6. References and Notes

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