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Tetrahedron 60 (2004) 9031–9036

Calcium phosphate-vanadate apatite (CPVAP)-catalyzed aerobic oxidation of propargylic alcohols with molecular oxygen

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Received 21 June 2004; revised 4 August 2004; accepted 4 August 2004

Available online 1 September 2004

Abstract—Calcium phosphate-vanadate apatite (CPVAP) works effectively as a catalyst for the aerobic oxidation of propargylic alcohols to the corresponding carbonyl compounds under an atmospheric pressure of molecular oxygen. Moreover, CPVAP can be readily separated by filtration and reused at least 10 times without appreciable loss of the catalytic activity.

1. Introduction

For the increasing environmental and economical concerns in recent years, it is now essential for chemists to search environmentally benign catalytic reactions as many as possible. The organic reaction using heterogeneous catalyst is one of the suitable methods for realizing green and sustainable chemistry and much attention has been paid to it because of its reusability and the ability to minimize the toxic wastes.[1,2] Recently, metal-immobilized hydroxyapatite has been developed by Kaneda and co-workers, in which the aerobic oxidation of organic compounds was well studied.[3] Especially, ruthenium and palladium-hydroxyapatite (RuHAP or PdHAP) were revealed to be excellent catalysts for the aerobic oxidation of alcohols, amines, and silanes.[3a–d]

We have so far studied the oxidation of alcohols using molecular oxygen as a sole reoxidant, in which both homogeneous and heterogeneous Pd-catalytic systems were disclosed to be quite effective for the oxidation of various kinds of alcohols.[2d,e,4] We also found the effective oxidation system for propargylic alcohols consisting of an oxovanadium complex such as $VO(acac)_2$, molecular sieves 3 Å (MS3A), and molecular oxygen in acetonitrile,[5,6] the oxidation of which was unsuccessful with Pd catalysts. We have now tried to heterogenize this vanadium system for reuse of the catalyst from the viewpoint of green and sustainable chemistry, and eventually we disclosed that calcium phosphate-vanadate apatite (we abbreviate this as CPVAP), prepared by the reported method,[7] could be used as a recyclable catalyst for the aerobic oxidation of propargylic alcohols. The CPVAP has been known to be formed by partial substitution of PO_4^{3-} by VO_4^{3-} in hydroxyapatite as a highly stable, isomorphic compound $Ca_{10}(PO_4)_{6-x}(VO_4)_x(OH)_2$.[7] Herein, we report the CPVAP-catalyzed oxidation of propargylic alcohols under an atmospheric pressure of oxygen.

2. Results and discussion

First, the oxidation of 1-phenyl-2-propyn-1-ol (**1a**) (0.5 mmol) was examined using the catalytic amount of CPVAP (25 mg, 0.073 mmol (15 mol% to **1a**) as vanadium) in acetonitrile (1 mL) at 80 °C under an atmospheric pressure of oxygen similar to the reaction conditions of homogeneous catalytic system that we previously reported.[5] The reaction, however, did not proceed efficiently to give the corresponding ketone **2a** even after a longer reaction time (Table 1, entries 1–3). On the other hand, **2a** was obtained in high yield at higher temperature using benzonitrile as solvent in the presence of the doubled amount of CPVAP (50 mg, 0.15 mmol as vanadium) (entry 4). Other solvents such as toluene, chlorobenzene, and *n*-butyronitrile were also examined (entries 5–7), because benzonitrile was not easy to be removed after the reaction due to its high boiling nature. When *n*-butyronitrile was used as solvent, **2a** was obtained in a similar high yield as in

Keywords: Vanadium; Oxidation; Propargylic alcohols; Molecular oxygen; Hydroxyapatite.
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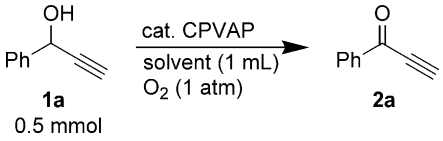
doi:10.1016/j.tet.2004.08.004

Table 1. Optimization of the reaction



Entry	Solvent	Temperature (°C)	Reaction time (h)	CPVAP (mg)	Conversion of **1a** (%)	Yield of **2a** (%)[a]
1	Acetonitrile	80	3	25[b]	16	10
2	Acetonitrile	80	24	25	24	16
3	Acetonitrile	80	72	25	35	34
4	Benzonitrile	100	20	50[c]	99	82
5	Toluene	100	20	50	38	38
6	Chlorobenzene	100	20	50	78	53
7	*n*-Butyronitrile	100	20	50	92	85
8[d]	*n*-Butyronitrile	100	20	50	0	0

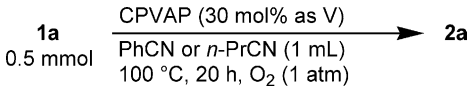
[a] Based on **1a** employed.
[b] 15 mol% as V to **1a**.
[c] 30 mol% as V to **1a**.
[d] Under N_2 (1 atm).

the use of benzonitrile (entry 7). The reaction under nitrogen atmosphere did not proceed at all (entry 8), showing that the presence of oxygen is essential for this reaction.

Next, we examined recycling of the catalyst. At first, the oxidation of **1a** in benzonitrile was carried out in the presence of CPVAP (50 mg, 0.15 mmol as vanadium) at 100 °C for 20 h under oxygen atmosphere. After the reaction, CPVAP was separated by filtration from the reaction mixture, and the collected CPVAP was washed with diethyl ether and dried under vacuum at room temperature before use for the next run. The yield of **2a** was determined by GLC analysis. As a result, CPVAP could be reused at least 10 times keeping in high catalytic activity (Table 2). Similar phenomenone was also observed using *n*-butyronitrile as solvent also shown in Table 2.

The oxidation of some propargylic alcohols was examined in *n*-butyronitrile as solvent. Typical results are listed in Table 3. When the reaction was carried out under an atmospheric pressure of air, **1a** was also converted to **2a** in good yield although it proceeded slower than the same reaction under molecular oxygen (entry 2). Among 1-aryl-2-propyn-1-ols, those having a chloro or methyl substituent at *m*- or *p*-position on aromatic nuclei (**1e–1h**) were efficiently oxidized to give the corresponding ketones in high yields (entries 6–9), while the oxidation of the alcohols having a substituent at *o*-position (**1b–1d**) was slower (entries 3–5). This tendency was also observed when propargylic alcohol having a 1-naphthyl substituent (**1i**) was compared with that having 2-naphthyl one (**1j**) (entries 10 and 11). Propargylic alcohol having a vinylic substituent at the α-position (**1k**) gave the corresponding ketone in low yield under this condition (entry 12). Primary propargylic alcohol **1l** was converted to the corresponding aldehyde in good yield (entry 13). The oxidation of propargylic alcohols having an alkyl substituent at the α-position (**1m–1o**) gave the corresponding ketones in low yields (entries 14, 17, and 18). Longer reaction time and higher reaction temperature did not improve much the product yields (entries 15 and 16).

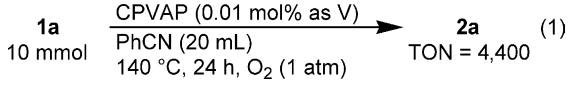
Table 2. Recycling of the catalyst



Run	Conversion of **1a** (%)[a]	Yield of **2a** (%)[a,b]
1	99 (92)	82 (85)
2	99 (84)	78 (82)
3	99 (84)	83 (80)
4	99 (84)	86 (81)
5	99 (83)	87 (82)
6	95 (79)	92 (74)
7	95	91
8	92	88
9	94	92
10	86	86
11	88	87

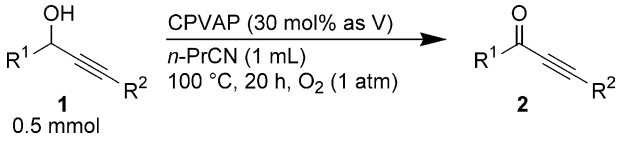
[a] The results using *n*-butyronitrile as solvent are shown in parentheses.
[b] Based on **1a** employed.

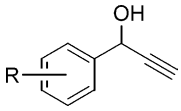
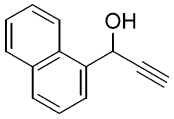
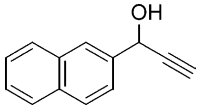
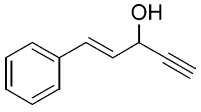
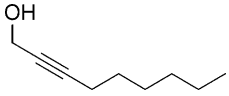
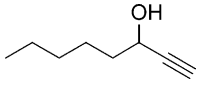
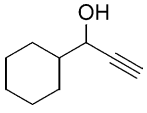
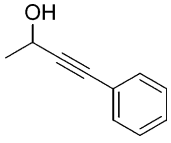
The amount of the catalyst could be reduced in the oxidation of some propargylic alcohols listed in Table 3 which smoothly reacted to give the corresponding carbonyl compounds in good yields (Table 4). Although the higher reaction temperature was needed, the turnover number (TON) reached to 4,400 when the reaction was carried out in benzonitrile at 140 °C under S/C = 10,000 for 24 h (Eq (1)).



We next investigated a time profile of the oxidation of **1a** under the conditions shown in Table 4. The product yield gradually increased and reached to maximum after ca. 20 h (Fig. 1). When CPVAP was removed by filtration from the reaction mixture after 9 h and the heating of the filtrate was continued under the same conditions, the yield of **2a** did not improve at all. Further, no leaching of vanadium into the filtrate was detected by ICP (inductivity coupled plasma) atomic emission analysis. These results clearly show that

Table 3. CPVAP-catalyzed aerobic oxidation of propargylic alcohols



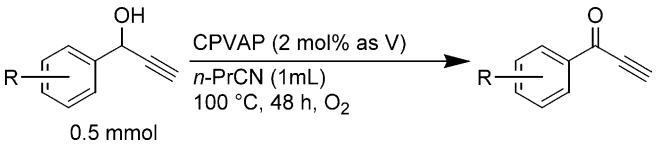
Entry	Substrate		Conversion of **1** (%)	Yield of **2** (%)[a]
1		**1a** R=H	89	85[b]
2[c]		**1a** R=H	73	64[b]
3		**1b** R=2-Cl	59	56
4		**1c** R=2-Me	80	53
5		**1d** R=2-OMe	55	41
6		**1e** R=3-Cl	89	79
7		**1f** R=3-Me	99	99
8		**1g** R=4-Cl	99	91
9		**1h** R=4-Me	98	87
10		**1i**	72	52
11		**1j**	87	87
12		**1k**	99	31[d]
13		**1l**	74	66
14		**1m**	31	20[b]
15[e]		**1m**	79	41[b,d]
16[f,g]		**1m**	—	31[b,d]
17		**1n**	89	37
18		**1o**	50	24

[a] Based on an alcohol employed.
[b] GLC yield.
[c] Under air (1 atm).
[d] Many unidentified products were also observed.
[e] For 48 h.
[f] For 96 h.
[g] Benzonitrile was used as solvent at 120 °C.

any vanadium species do not leach to the solution and the oxidation may proceed on the surface of the solid catalyst.

Lastly, we investigated the catalytic activity of other transition metal-containing hydroxyapatites. The results are summarized in Table 5. The use of vanadium hydroxyapatite (VHAP) prepared by Kaneda's method[8] as a catalyst gave **2a** in moderate yield (entry 2). When RuHAP and PdHAP, which were known to be efficient catalysts for the aerobic oxidation of alcohols,[3a,c] were used as catalysts, **2a** was not obtained at all (entries 3–6).

Table 4. Reducing of the catalyst



Entry	Substrate	Yield of **2** (%)[a]	TON
1[b]	**1a**	97	48.5
2	**1e**	78	39
3	**1f**	72	36
4	**1g**	89	44.5
5	**1h**	82	42

[a] Based on an alcohol employed.
[b] For 24 h.

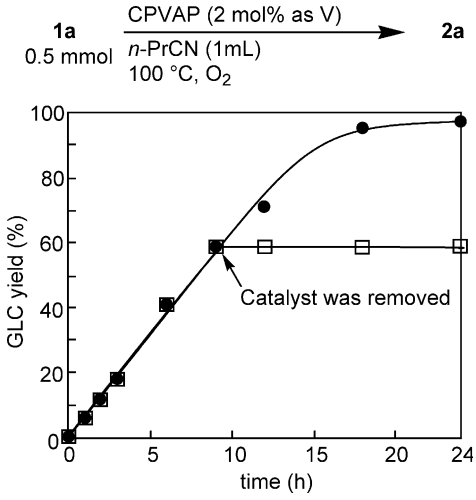


Figure 1. Time profile of CPVAP-catalyzed aerobic oxidation of **1a**.

3. Conclusion

In summary, we found that calcium phosphate-vanadate apatite (CPVAP) worked effectively as a catalyst for the aerobic oxidation of propargylic alcohols to the corresponding carbonyl compounds under an atmospheric pressure of molecular oxygen. Moreover, CPVAP was readily separated by filtration and could be reused at least 10 times.

4. Experimental

4.1. General

NMR spectra were recorded on JEOL EX-400 (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz) instruments for solutions in $CDCl_3$ with Me_4Si as an internal standard: the following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet. GLC analyses were performed on a Shimadzu GC-14A instrument (25 m×0.33 mm, 5.0 mm film thickness, Shimadzu fused silica capillary column HiCap CBP10-S25-050) with a flame-ionization detector and helium as carrier gas. Analytical thin-layer chromatography (TLC) was performed with Merck silica gel 60 F-254 plates. Column chromatography was performed with Merck silica gel 60. ICP atomic emission analysis for the vanadium content in the CPVAP was performed with a Shimadzu ICPS-1000 sequential plasma spectrometer.

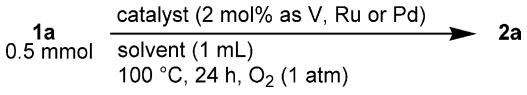
4.2. Materials

Commercially available organic and inorganic compounds were used without further purification except for the solvent. Alcohols **1a**, **1m**, **1o** are commercial products and purified by normal methods just before use. Alcohols **1b**–**1l** and **1n** were prepared from the corresponding aldehydes and lithium acetylides or alkynylmagnesium bromides, purified by column chromatography on silica gel (eluent; *n*-hexane–ethyl acetate) and identified by ^{1}H NMR and ^{13}C NMR. All propargylic alcohols and the corresponding aldehydes and ketones are known compounds. Ketone **2m** is commercial products. Selected spectral data of alcohols and carbonyl compounds are shown below. Spectral data of other alcohols and carbonyl compounds were shown in the previous report.[5b]

4.2.1. 1-(*o*-Tolyl)-2-propyn-1-ol.[9] (1c, Table 3, entry 4) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (br s, 1H (OH)), 2.44 (s, 3H), 2.64 (d, J=2.4 Hz, 1H), 5.61 (d, J=2.4 Hz, 1H), 7.17–7.27 (m, 3H), 7.65–7.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.9, 62.2, 74.7, 83.2, 126.2, 126.3, 128.5, 130.7, 135.8, 137.7.

4.2.2. 1-(2-Methoxyphenyl)-2-propyn-1-ol.[10] (1d, Table 3, entry 5) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.60

Table 5. Comparison with results using other transition metal containing hydroxyapatite as catalyst



Entry	Catalyst	Solvent	Conversion of **1a** (%)	Yield of **2a** (%)[a]
1	CPVAP	*n*-Butyronitrile	97	97
2	VHAP[b]	*n*-Butyronitrile	49	39
3	RuHAP[b]	Toluene	62	2[c]
4	RuHAP[b]	*n*-Butyronitrile	10	5
5	PdHAP[b]	Benzotrifluoride	100	0[c]
6	PdHAP[b]	*n*-Butyronitrile	100	0[c]

[a] Based on alcohol employed.
[b] Prepared by following the method described by Kaneda et al.[3a,3c,8]
[c] Many unidentified products were also observed.

(d, J=2.4 Hz, 1H), 3.15 (br s, 1H (OH)), 3.88 (s, 3H), 5.69 (d, J=2.4 Hz, 1H), 6.90 (d, J=8.3 Hz, 1H), 6.97 (td, J=8.3, 1.5 Hz, 1H), 7.31 (td, J=7.8, 1.5 Hz, 1H), 7.56 (dd, J=7.8, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 60.9, 74.0, 83.0, 110.7, 120.7, 127.7, 128.1, 129.7, 156.5.

4.2.3. 1-(3-Chlorophenyl)-2-propyn-1-ol.[11] (1e, Table 3, entry 6) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (br s, 1H (OH)), 2.70 (d, J=2.2 Hz, 1H), 4.54 (d, J=2.2 Hz, 1H), 7.31–7.44 (m, 3H), 7.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.7, 75.3, 82.7, 124.6, 126.7, 128.6, 129.8, 134.4, 141.7.

4.2.4. 1-(*m*-Tolyl)-2-propyn-1-ol.[9] (1f, Table 3, entry 7) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 2.37 (br s, 1H (OH)), 2.65 (d, J=2.4 Hz, 1H), 5.41 (s, 1H), 7.15 (d, J=7.3 Hz, 1H), 7.25–7.36 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 64.4, 74.7, 85.6, 123.6, 127.2, 128.5, 129.2, 138.3, 139.8.

4.2.5. 1-(4-Chlorophenyl)-2-propyn-1-ol.[10] (1g, Table 3, entry 8) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (d, J=2.4 Hz, 1H), 2.87 (br s, 1H (OH)), 5.40 (d, J=2.4 Hz, 1H), 7.33 (dt, J=8.3, 2.2 Hz, 2H), 7.45 (dt, J=8.3, 2.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.5, 75.1, 83.0, 127.8, 128.6, 134.2, 138.3.

4.3. General procedure for the preparation of calcium phosphate-vanadate apatite (CPVAP)

Calcium phosphate-vanadate apatite (CPVAP) $Ca_{10}(PO_4)_{6-x}(VO_4)_x(OH)_2$ (x=3.1) was prepared by following the method described by Boechat et al.[7] To a solution of $Ca(NO_3)_2\cdot 4H_2O$ (15.8 g, 66.7 mmol) in H_2O (60 mL) in a 500 mL three-necked round bottomed flask was added a solution of VCl_3 (8.6 g, 54.4 mmol) in H_2O (brown solution, 30 mL). The mixture was then brought to pH 11–12 with 28% ammonia solution in H_2O (dark brown solution) and thereafter diluted to 120 mL. In a separate flask, a solution of $(NH_4)_2HPO_4$ (5.3 g, 40.0 mmol) in H_2O (100 mL) was brought to pH 11–12 with 28% ammonia solution in H_2O and then diluted to 160 mL. This $(NH_4)_2HPO_4$ solution was added dropwise from dropping funnel to the above $Ca(NO_3)_2/VCl_3$ solution with stirring for 30 min. After the addition, the mixture was heated to 95 °C for 10 min. After cooling, it was filtered and the separated solid was washed with water (20 mL×7). This solid was dried at 80 °C for 15 h and calcined at 500 °C for 3 h to give 9.1 g of CPVAP as a pale brown solid. The vanadium content in the CPVAP was 2.9 mmol g^{-1} estimated by ICP atomic emission analysis.

Hydroxyapatite-supported vanadium, ruthenium and palladium were prepared by treatment of hydroxyapatite (HAP)[12] with VCl_3, $RuCl_3$ and $PdCl_2(MeCN)_2$ at room temperature in water or acetone by following the methods described by Kaneda et al.[3a,c,8]

4.4. General procedure for the CPVAP-catalyzed oxidation of porpargylic alcohols with molecular oxygen

To a suspension of CPVAP (50 mg, 0.15 mmol as vanadium) in benzonitrile or *n*-butyronitrile (1 mL) in a 20 mL Schlenk flask was added a propargylic alcohol (0.5 mmol). Oxygen gas was then introduced into the flask from an O_2 balloon under atmospheric pressure and then the mixture was stirred vigorously for 20 h at 100 °C under oxygen. After the reaction, the mixture was cooled to room temperature and CPVAP was separated by filtration through a glass filter. The amount of the product was determined by GLC analysis using bibenzyl as an internal standard. For isolation of the product the solvent was evaporated and the residue was purified by column chromatography on SiO_2 (*n*-hexane–ethyl acetate as an eluent) and identified by ^{1}H NMR and ^{13}C NMR.

4.4.1. 1-(*o*-Tolyl)-2-propyn-1-one.[13] (2c, Table 3, entry 4) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.63 (s, 3H), 3.38 (s, 1H), 7.27 (d, J=7.1 Hz, 1H), 7.35 (t, J=7.1 Hz, 1H), 7.48 (td, J=7.5, 1.5 Hz, 1H), 8.27 (dd, J=7.5, 1.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 79.5, 81.6, 125.9, 132.1, 133.2, 133.7, 134.6, 140.8, 178.7 (C=O).

4.4.2. 1-(2-Methoxyphenyl)-2-propyn-1-one.[14] (2d, Table 3, entry 5) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.39 (s, 1H), 3.93 (s, 3H), 7.00–7.06 (m, 2H), 7.55 (ddd, J=8.3, 7.3, 2.0 Hz, 1H), 8.06 (dd, J=7.8, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.8, 79.3, 82.1, 112.1, 120.1, 125.7, 133.1, 135.4, 159.9, 175.8 (C=O).

4.4.3. 1-(3-Chlorophenyl)-2-propyn-1-one.[15] (2e, Table 3, entry 6) Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.49 (s, 1H), 7.45 (t, J=7.8 Hz, 1H), 7.61 (ddd, J=7.8, 2.0, 1.0 Hz, 1H), 8.04 (td, J=7.8, 1.0 Hz, 1H), 8.12 (t, J=2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 79.8, 81.5, 127.7, 129.5, 129.9, 134.3, 135.0, 137.4, 175.8 (C=O).

4.4.4. 1-(*m*-Tolyl)-2-propyn-1-one.[14] (2f, Table 3, entry 7) Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.42 (s, 1H), 7.39 (t, J=7.8 Hz, 1H), 7.45 (d, J=7.8 Hz, 1H), 7.95 (s, 1H), 7.98 (d, J=7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 80.3, 80.5, 127.1, 128.5, 129.9, 135.2, 136.1, 138.5, 177.4 (C=O).

4.4.5. 1-(4-Chlorophenyl)-2-propyn-1-one.[15] (2g, Table 3, entry 8) Orange solid; mp: 96.0–97.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.47 (s, 1H), 7.48 (dt, J=8.8, 2.0 Hz, 2H), 8.10 (dt, J=8.8, 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 79.9, 81.2, 129.0, 130.9, 134.4, 141.1, 175.9 (C=O).

4.5. General procedure for recycling of the catalyst

Recovered CPVAP by filtration from the former run of the oxidation of porpargylic alcohols was washed with diethyl ether and dried under vacuum at room temperature before use for the next run.

Acknowledgements

We thank Professor Masashi Inoue and Dr. Shinji Iwamoto (Kyoto University) for their help in ICP atomic emission analysis to measure vanadium contents in CPVAP. The financial support from Japan Science and Technology Corporation (JST) is also acknowledged.

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