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Nafion®-supported oxovanadium-catalyzed hydrophosphonylation of aldehydes under solventless conditions

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A Nafion® resin-supported oxovanadium(IV) catalyst was readily prepared via ion-exchange method. This solid vanadyl perfluorinated sulfonate catalyst was used as an efficient and recoverable catalyst for the hydrophosphonylation of various aldehydes under solventless conditions at room temperature. The catalyst could be recovered by simple filtration and reused without a significant loss of activity. Copyright © 2012 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: Pudovik reaction; hydrophosphonylation; Nafion®; vanadyl triflate

Introduction

The synthesis of α-hydroxyphosphonates has received much attention because of the important applications of these compounds in pest control, industrial chemistry, and catalysis.[1] In particular, α-hydroxyphosphonic acids have recently been found to exhibit several potent biological effects and pharmaceutical applications, such as the selective inhibition of the human immunodeficiency virus (HIV) protease, the regulation of a wide range of cellular processes through the inhibition of extracellular signal transduction, the regulation of plant growth, and the ability to mimic bio-phosphates; in addition, these compounds have antiviral, antibiotic, and anti-tumor activities.[2] These acids are also versatile precursors for the synthesis of other biological useful amino- and ketophosphonates.[3] The primary route to achieve these valuable α-hydroxyphosphonates is through the Pudovik reaction,[4] which involves the hydrophosphonylation of carbonyl compounds using dialkyl phosphonates or their labile tautomeric dialkyl phosphites as *P*-nucleophiles in the presence of Lewis acids or bases. In addition, the activation of the phospho-hydrogen (P−H) bond of the dialkyl phosphonates with oxo-functionality of an amphoteric oxo-metal complex, such as molybdenum oxylchloride (MoO_2Cl_2), benefits the formation of the labile phosphite tautomer and the subsequent phospho-aldol addition. This activation provides an alternative method to access various organophosphorus derivatives, although harsh conditions are required. The activation process starts with coordination of the P=O bond of the dialkyl phosphonate to molybdenum and a stepwise hydrogen transfer from the P−H to the oxo in Mo=O, generating the more labile phosphite–molybdate for the hydrophonylation (Fig. 1).[5]

The immobilization of metal catalysts on solid supports is highly desirable because of the increased ease of recovery and recycling, atom utility, and enhanced stability.[6] Among the solid-supported catalytic systems developed, perfluorinated sulfonic acid polymer, such as Nafion®-H and Nafion® SAC-13 (Nafion®-H, ion-exchange polymer on an amorphous silica nanocomposite), have been frequently employed as effective heterogeneous catalysts for a wide range of applications in organic transformation because of their superacidity and excellent thermal and chemical stability.[7] However, because of their superacidic character,[7g] functional group compatibilities under the required conditions are the major concern in their application in the synthesis of acid-sensitive and multi-functionalized molecules. In contrast, non-covalent immobilization of the metal cations on to the surface of Nafion would make the catalytic site of the corresponding catalyst more selective and specific, and it would make the catalytic process predictable and designable.[8] Thus unfavorable factors and side reactions during the reaction can be excluded. In addition, because of the super electron-withdrawing character of the perfluorinated carbon chains, the corresponding sulfonate anion is less coordinated than a normal sulfonate (e.g. TfO^-). Thus increased cationic character with enhanced Lewis acidity of the immobilized metal cations can be achieved.[9] Pioneering research on metal-immobilized Nafion catalysis has been conducted on the direct synthesis of nitrones via a one-pot condensation/oxidation processes with Nafion-immobilized molybdenum oxychloride ($MoOCl_4$) as the catalyst. The Nafion-immobilized $MoOCl_4$ was shown to be more reactive than its homogeneous analogue.[10]

Vanadyl triflate ($VO(OTf)_2$) is a water-stable and reusable Lewis acid that has been used as an efficient catalyst in a myriad of organic transformations.[11] The V=O unit (i.e. $^+V{-}O^-$) has an amphoteric character, and the partially positive V in V=O is sufficiently acidic to activate electrophiles.[12] Concurrently, the partial negative oxygen anion in V=O serves as a Lewis base to promote the subsequent proton transfer or proton extraction of protic

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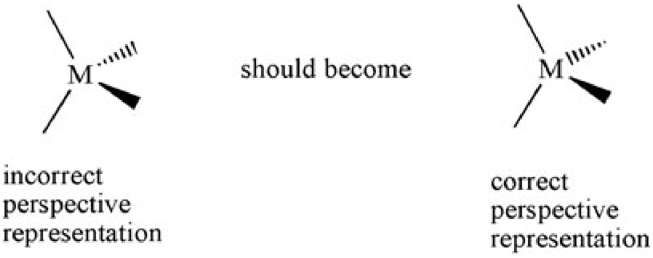


Figure 1. Activation of a dialkyl phosphite with the oxo-functionality of a high-valent oxymetal salt.

nucleophiles, facilitating the aza-, thia-, phospha-Michael-type 1,4-addition of α,β-unsaturated ketones, the acetalization and thioacetalization (1,2-addition) of carbonyl compounds, and nucleophilic acyl substitution (NAS) of anhydrides, esters, and carboxylic acids;[11a–c] this type of mechanism is known as the push–pull type mechanism for the reactant pair.[11a–e,h,j] Given the high P−H bond activation capacities of amphoteric V=O and Mo=O units and the enhanced catalytic ability of Nafion-supported $MoOCl_4$ compared with its homogeneous analogue, we sought to evaluate the catalytic efficiency of the hydrophosphonylation of aldehydes with dialkyl phosphonates using a vanadyl species immobilized on a Nafion ion-exchange polymer.

Experimental

General

^1H NMR and ^{13}C NMR spectra were recorded on a Jeol JVM-EX400 (400 MHz ^1H, 100 MHz ^{13}C) or Varian Unity Inova 500 (400 MHz ^1H, 100 MHz ^{13}C) spectrometer in deuterochloroform with chloroform as an internal reference unless otherwise stated. Chemical shifts are reported in ppm (δ). Coupling constants, *J*, are reported in Hz. Mass spectra were recorded with an ionization voltage of 70 or 20 eV unless otherwise stated. A Bruker EMX-10/12 spectrometer was used to acquire the spectra of electron paramagnetic resonance (EPR) of the supported oxovanadium catalysts at liquid nitrogen temperature (77 K) in thin quartz tubes operating at a frequency of 9.5 GHz (X-band) with a 100 kHz modulation frequency. X-ray photoelectron spectrometry (XPS) was performed on an ESCA PHI 1600 instrument using monochromatic Al-$K\alpha$ X-rays with a pass energy of 50 eV and the binding energies were referenced to the V $2p_{3/2}$ peaks at 520 eV, respectively. IR spectra were recorded with a Jasco FT/IR-410 FT-IR spectrometer in KBr pellet (0.005 g sample with 0.1 g KBr) scan number 8–36, resolution 2 cm^{-1}. Weight loss was evaluated by thermogravimetric analysis (TGA) in a Dynamic Q500 instrument in the temperature range 25–600 °C. Column (flash) chromatography was performed using 32–63 m silica gel. Solvents for extraction and chromatography were reagent grade. All reactions were run under nitrogen or argon atmosphere and the end products were isolated as spectroscopically pure materials.

Procedure for Nafion-V Preparation[9,10]

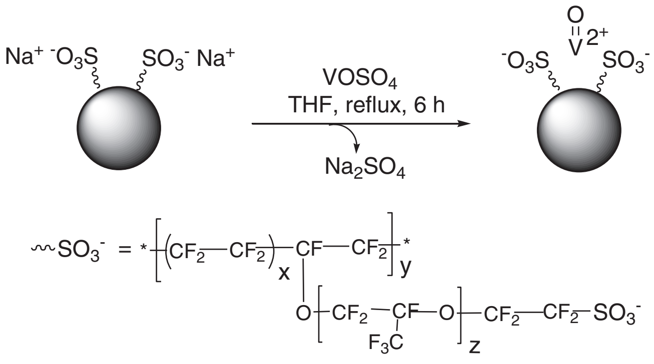
Suspended commercial Nafion® NR50 beads (2 g, 7–9 mesh, 2000–2800 μm) and excess amount of $VOSO_4.5H_2O$ (1.2 g, 4.74 mmol) were reacted in 50 ml refluxed ethanol for 24 h in the presence of sodium acetate (778 mg, 9.48 mmol) under a nitrogen atmosphere. The light-blue colored oxovanadium supported catalyst Nafion-V was separated by filtration and repeatedly washed with water and ethanol. The light-blue colored catalyst was dried under vacuum at 60 °C. The immobilized oxovanadium catalyst was characterized using EPR spectroscopy at liquid nitrogen temperature,[13] XPS analysis,[14] and IR analysis,[15] and the structure was confirmed using published reports. XPS (V_{2p}): 518 eV; IR (cm^{-1}): 3038 (s, broad, −OH), 1629 (s, H_2O), 1134 (s, SO_3^-), 1134 (s, $-CF_2-$), 994 (s, V=O). Metal loading was determined by TGA and was found to be 0.00126 mmol mg^{-1}. The unreacted $VOSO_4.5H_2O$ was recovered from the ethanol washes.

Procedure for Nafion-V_{powder} Preparation[9,10]

Suspended commercial Nafion® perfluorinated resin (2 g, 35–60 mesh, 25–425 μm) and excess amount of $VOSO_4.5H_2O$ (3.0 g, 11.85 mmol) were reacted in 50 ml refluxed ethanol for 24 h in the presence of sodium acetate (1.94 g, 23.7 mmol) under a nitrogen atmosphere. The dark-blue colored oxovanadium supported catalyst (Nafion-V_{powder}) was separated by filtration and repeatedly washed with water and ethanol. The dark-blue colored catalyst was dried under vacuum at 60 °C. The oxovanadium immobilized catalyst was characterized using EPR spectroscopy at liquid nitrogen temperature,[13] XPS analysis and IR analysis, and the structure was confirmed using published reports.[14,15] XPS (V_{2p}): 517 eV IR (cm^{-1}): 3062 (s, broad, −OH), 1627 (s, H_2O), 1136 (s, SO_3^-), (s, $-CF_2-$), 998 (s, V=O). Metal loading was determined by TGA and was found to be 0.0062 mmol mg^{-1}. The unreacted $VOSO_4.5H_2O$ was recovered from the ethanol washes.

General Procedure for the Hydrophosphonylation of Aldehyde and Catalyst Recovery

Under an argon atmosphere, Nafion-V_{powder} 8.1 mg (0.05 mmol, 5 mol% of V=O) was added to a dry tube containing 1.2 equiv. of dibenzyl phosphite (314.7 mg, 1.2 mmol, 266.7 μl) and 1.0 equiv. of the aldehyde (1 mmol). The reaction mixture was stirred at room temperature for the indicated period of time (Table 2). After completion of the reaction as monitored by TLC, 10 ml ethanol was added, and the catalyst was filtered off and washed with ethanol. The filtrate was concentrated, and the unreacted dibenzyl phosphite was recovered via distillation under reduced pressure (1.0 torr) using a Kügelrohr apparatus. The resulting crude product was recrystallized from ethanol solution or purified by column chromatography on silica gel with ethyl acetate/*n*-hexane (1:2–1:1) as eluents to give pure α-hydroxyphosphonates **1a–21a** in 64–95% yield. The recovered catalyst was dried under vacuum and reused for subsequent reactions without further purification.



Scheme 1. Immobilization of V=O to the Nafion support of Nafion-immobilized vanadyl catalysts.

Results and Discussion

Catalyst Preparation and Characterization

Immobilization of the vanadyl species on Nafion was carried out by the ligand exchange of Nafion beads (Nafion® NR50, 7–9 mesh) or Nafion powder (Nafion® perfluorinated resin, 35–60 mesh) with vanadyl sulfate ($VOSO_4.5H_2O$) in refluxed ethanol for 12 h (Scheme 1).[9,10,16] The immobilization of oxovanadium (VO^{2+}) on the Nafion supports was confirmed by EPR, XPS, and IR analysis (see supporting information). The X-band EPR spectra of Nafion® NR50 and Nafion® perfluorinated resin-supported oxovanadium(IV) polymers (Nafion-V and Nafion-V$_{powder}$, respectively) showed eight lines at liquid nitrogen temperature (77 K, Fig. 2) that were due to hyperfine splitting arising from the interaction of an unpaired electron and a ^{51}V nucleus with a nuclear spin number of $I = 7/2$.[13] This result confirms the presence of a single oxovanadium(IV) cation as the metallic center in the perfluorinated supports. It should be noted that the broad splitting lines that were observed for the Nafion-V$_{powder}$ catalyst due to the shorter distances between supported vanadium centers on the Nafion powder (which facilitate electron delocalization) suggest higher metal loading on the larger surface area of the Nafion-V$_{powder}$ catalyst.[13a]

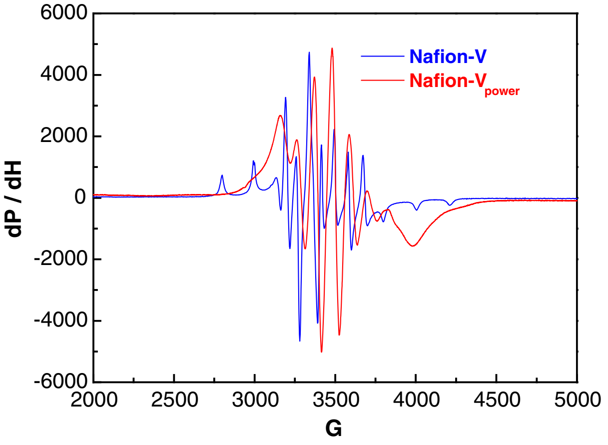
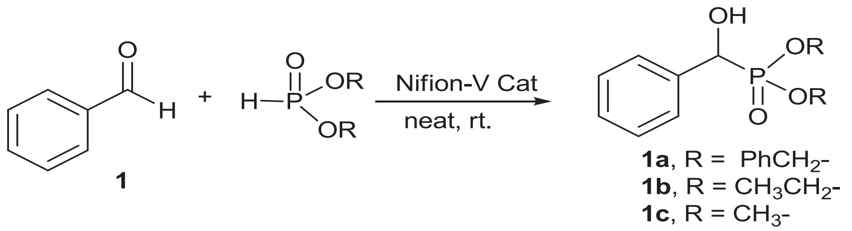


Figure 2. EPR spectra of the immobilization of oxovanadium (VO_2^+) on (a) Nafion beads (Nafion® NR50) and (b) Nafion powder (Nafion® perfluorinated resin). Experimental conditions: $V_{mw} = 9.49$ GHz; MW power = 10.1 mW; modulation amplitude = 8.0 G; time constant = 20.48 ms; conversion time = 40.96 ms; temperature = 77 K.

The XPS spectra of Nafion-V and Nafion-V$_{powder}$ catalysts at approximately 520 eV show the V $2p_{2/3}$ absorption bands and confirm that the vanadyl cations were properly immobilized on the Nafion supports (see supporting information). In addition, the IR spectra of the Nafion-V and Nafion-V$_{powder}$ catalysts exhibit absorption at ν 994 and 998 cm^{-1}, which are assigned to the ν (V=O) vibration.[15] The presence of ionic sulfate (SO_3^-) and difluoromethylene groups ($-CF_2-$) in both polymers was confirmed by the appearance of two bands: one around

Table 1. Hydrophosphonylation of benzaldehyde with dibenzyl phosphite catalyzed by Nafion-supported oxovanadium catalysts[a]



Entry	V catalyst	Run	Time (h)	Yield (%)[b]
1	VO(OTf)$_2$	1	24 (30)	84 (93)
2	MoO$_2$Cl$_2$	1	24	16 (92)[d]
3	Nafion-V (beads)	1	24	90
4	Nafion-V$_{powder}$	1	16 (28)[c]	94 (92)[c]
5	Nafion-V$_{powder}$	3	16	91
6	Nafion-V$_{powder}$	6	16	90
7	Nafion-V$_{powder}$	9	16	86
8	Nafion-V$_{powder}$	1	24	92[e]
9	Nafion-V$_{powder}$	1	24	90[f]
10	SiO$_2$—V	1	24	47
11	Nafion–MoCl$_4$	1	24	23
12	Nafion®-H powder	1	24	<10

[a] Reaction conditions: 5 mol% supported catalyst, benzaldehyde (1.0 mmol), dibenzyl phosphite (1.2 mmol, r.t., solvent-free conditions in nitrogen atmosphere.

[b] Isolated yield.

[c] 2 mol% Nafion-V$_{powder}$ was used.

[d] Reaction temperature: 60 °C.

[e] Diethyl phosphite was used.

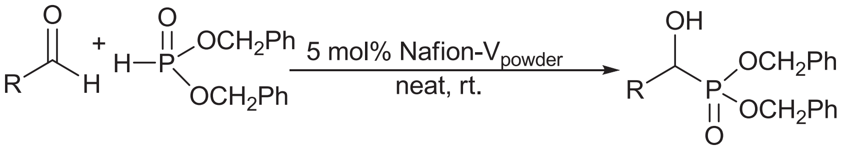
[f] Dimethyl phosphite was used.

1134–1136 cm^{-1} and the other around 1059–1061 cm^{-1}. The bands appearing at approximately 1600 cm^{-1} for both the Nafion-V and Nafion-V_{powder} catalysts may be assigned to the residence of molecular water in the polymer matrices of the Nafion.[15d] The metal loading on to the supports was found to be 0.0012 mmol mg^{-1} for Nafion-V catalyst and 0.0062 mmol mg^{-1} for Nafion-V_{powder} catalyst, as calculated by TGA (see supporting information).

Catalytic Reactivity for the Hydrophosphorylation Reaction and Catalyst Recovery

With the Nafion-supported oxovanadium catalysts (Nafion-V=O) in hand, we were keen to explore the catalytic activities for the hydrophosphonylation of dibenzyl phosphite with benzaldehyde in a 1.2:1.0 molar ratio under solvent-free conditions at room temperature in the presence of 5 mol% catalyst. The homogeneous $VO(OTf)_2$, silica-supported oxovanadium (SiO_2—V=O),[15b,c] dioxomolybdenum dichloride (MoO_2Cl_4), and Nafion-supported $MoOCl_4$ catalysts[10] were also tested for comparison (Table 1). The reaction results shown in Table 1 reveal that the Nafion-supported oxovanadium catalysts were far more efficient than silica-supported catalyst (SiO_2—V) and slightly more reactive then their homogeneous ($VO(OTf)_2$) analogues (Table 1; compare entries 3 and 4 with entries 10 and 1). Among supported oxovanadium catalysts, the Nafion-supported oxovanadium powder (Nafion-V_{powder}) was the most efficient catalyst owing to the larger surface area of the polymer and the high metal loading,[9] and the reaction was complete in 16 h with a 94% yield after chromatographic purification. Additionally, the catalyst loading could be reduced to 2 mol% to achieve 92% yield at the cost of a prolonged reaction time (Table 1, entry 4, in parentheses). Although the homogeneous $VO(OTf)_2$ catalyst has shown high catalytic reactivity toward hydrophosphonylation reaction, prolonged reaction time is required to drive the reaction to completion (Table 1, entry 1, in parentheses). On the other hand, when diethyl and dimethyl phosphite were used instead of dibenzyl phosphite, a longer reaction time was needed because of the slower dissolution of the diethyl and dimethyl phosphite with bezaldehyde (Table 1, entries 8 and 9). The amphoteric MoO_2Cl_2 has been reported to be an efficient catalyst for this reaction in neat conditions or in polar solvents at elevated temperature.[5] However, low yields were obtained when the reaction was performed at room temperature (Table 1, entry 2). In addition, the Nafion-supported amphoteric $MoOCl_4$ catalyst with increased Lewis acidity at the molybdenum center also showed inefficient catalytic reactivity (Table 1, entry 11). A control experiment using acidic Nafion powder was also carried out under the same conditions, and a yield of less than 10% was observed. This

Table 2. Reaction of dibenzyl phosphite with various aldehydes catalyzed by 5 mol% powder Nafion-V catalyst under solvent-free conditions.[a]



2-21

2a-21a

Entry	R	Time (h)	Yield (%)[b]
1	4-ClC_6H_4 (**2**)	20	92
2	4-$NO_2C_6H_4$ (**3**)	20[c]	90
3	2-BrC_6H_4 (**4**)	20	87
4	4-$MeOC(O)C_6H_4$ (**5**)	18	88
5	4-CNC_6H_4 (**6**)	9	95
6	4-$CH_3C_6H_4$ (**7**)	12	91
7	4-$CH_3OC_6H_4$ (**8**)	18	88
8	3-$CH_3OC_6H_4$ (**9**)	16	87
9	2-$CH_3OC_6H_4$ (**10**)	16	84
10	3-HOC_6H_4 (**11**)	24	82
11	4-$Me_2NC_6H_4$ (**12**)	30	64
12	1-Np (**13**)	12[c]	92
13	2-Furanyl (**14**)	12	94
14	2-Thiophenyl (**15**)	10	91
15	*trans*-PhCH=CH (**16**)	10	87
16	PhC&tbond;C (**17**)	10	82
17	$PhCH_2CH_2$ (**18**)	16	93
18	$(CH_3)_2CHCH_2$ (**19**)	16	92
19	Cyclohexyl (**20**)	20	90
20	$(CH_3)_3$ C (**21**)	24	86

[a]Reaction condition: 5 mol% supported catalyst, aldehyde (1.0 mmol), dibenzyl phosphonate (1.2 mmol, r.t., solvent-free conditions in nitrogen atmosphere.

[b]Isolated yield.

result suggests that the background reaction catalyzed by perfluorinated sulfonic acid can be excluded (Table 1, entry 12).

The advantages of this Nafion-V_{powder} catalytic system are that the catalyst can be recovered by simple filtration and reused for several runs (Table 1, entries 4–7), and that the reaction does not require the use of any organic solvent. Thus the catalytic protocol meets the standards of green chemistry from an environmental point of view. It is worth noting that a slight decrease in yield was observed after every three runs (Table 1, compare entries 5–7), indicating a loss of vanadium metal during the reaction and catalyst recovery processes. Further investigations of the leaching of vanadium metal during the recycle reactions were also carried out. TGA of recovered Nafion-V_{powder} catalyst after the ninth run showed that the V=O metal composition of the powder Nafion support was $0.0041\ \text{mmol mg}^{-1}$. This result indicates that approximately 2–3% of vanadium metal leached out of the support during each reaction cycle.

Hydrophosphonylation with Various Aldehydes

In addition to the parent benzaldehyde, various aromatic aldehydes with varying electron demands (heterocyclic, α,β-unsaturated, and propargyl) and aliphatic aldehydes were also tested in the hydrophosphonylation reaction catalyzed by 5 mol% recoverable Nafion-V_{powder} catalyst under solvent-free conditions (Table 2). In general, reactions with liquid aromatic aldehydes (entries 5–9 and 12–16) proceeded faster than those with solid aldehydes (entries 1–4 and 10–11) because of the easy blending of the liquid aldehydes with dibenzyl phosphite. Because solid aldehydes dissolve more slowly, a prolonged reaction time was necessary to achieve high yields. Substituted aromatic aldehydes with electron-withdrawing groups were found to be more reactive than aldehydes bearing electron-donating groups (compare entry 5 with entries 7–9, and compare entries 1–4 with entries 10 and 11). Acid-sensitive α,β-unsaturated cinnamyl and propargyl and heterocyclic furfuryl and thiophenyl aldehydes remained intact and showed high reactivities under the reaction conditions (entries 13–16). Aliphatic aldehydes, such as 3-phenyl ethanal, 3-methyl butanal, steric-hindered cyclohexyl carboxylic aldehyde and 2,2-dimethyl propanal, also reacted efficiently to generate the corresponding α-hydroxyl phosphonates in good to excellent yields in reasonable periods of time (entries 17–20).

It is noteworthy that aldehydes bearing a basic dimethylamino group, which serves as an acid inhibitor, could also be used even though a prolonged reaction time was required (entry 11). Therefore, the involvement of acidic co-catalysis could be excluded again from our catalytic system. In addition to aldehydes, hydrophosphonylation with sterically hindered acetophenone catalyzed by Nafion-V_{powder} was found sluggish even at elevated temperature. It should be noted that approximate 4–8% oxidation side products were observed during the reactions, especially in the reaction with electrodeficient aromatic aldehydes (entries 1–3, 5, and 14), α,β-unsaturated (entry 15), and propagyl aldehydes (entry16). These side reactions led to undesirable but synthetically useful α-keto-phosphonates, because of the high oxidation ability of the oxovanadium species in the presence of oxidants.[17]

Conclusions

We have developed a highly potent Nafion®-supported oxovanadium catalyst for the hydrophosphonylation of a wide range of aromatic and aliphatic aldehydes. This new catalytic protocol represents a mild and practical synthetic approach to achieve potentially biologically and pharmaceutically useful α-hydroxyphosphonates under mild conditions without using organic solvents. Furthermore, the solid perfluorinated oxovanadium catalyst can be easy recovered and recycled and therefore meets the standards of green chemistry.

Acknowledgements

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