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Creation of a monomeric vanadate species in an apatite framework as an active heterogeneous base catalyst for Michael reactions in water

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ABSTRACT

Vanadium-apatite containing the VO_4^{3-} species was synthesized. Several characterization techniques such as XRD, TEM, XPS, ESR, UV–vis DRS, V K-edge XAFS, ^{51}V MAS NMR, Raman spectroscopy, and CO_2 TPD revealed that the vanadium-apatite was $Ca_9(VO_4)_5(HVO_4)(OH)$, abbreviated to VAP, covered with calcium oxide. This surface-coated calcium oxide phase could be removed by washing with water and then, the monomeric V-OH species having the strong Brønsted basicity were generated on the surface of VAP. The strong basicity of the solid VAP-catalyzed efficient Michael reaction in water solvent. Furthermore, VAP was found to be applicable to the direct synthesis of pyrazolinone derivatives using aryl hydrazines and diethyl ethoxymethylenemalonate.

1. Introduction

One powerful solution in the Green & Sustainable Chemistry movement is the replacement of traditional synthetic methods, which use harmful stoichiometric reagents that produce vast amounts of waste, with clean and simple catalytic alternatives with high atom efficiency and low E-factors [1–4]. Catalytic chemistry, therefore, is of ever-increasing importance because catalyst is a key element in material transformations at atomic and molecular levels, which are an essential realm of chemistry and chemical processes. Conducting reactions under aqueous conditions provides advantages such as reduced pollution, low cost, and simplicity in process and handling. Additionally, unique reactivity and selectivity that cannot be achieved under dry conditions are often observed in aqueous organic reactions due to the hydrophilic and hydrogen-bonding properties of water, even when solid catalysts are employed [5–7]. Development of water-tolerant solid catalysts is a strong motivation in the field of heterogeneous catalysis, however, typical solid Lewis bases do not function under aqueous conditions because the surface base sites are severely poisoned by water. Few studies on solid Brønsted base catalysts have been reported despite the potential of hydroxyl anions to promote organic transformations [8].

Vanadium is one of the most important metals in catalysis because of its versatile redox potential, unique oxygen-transfer ability, and highly Lewis acidic properties [9–12]. Capitalizing on these characteristics, a diverse array of oxidative transformations have been developed [13,14], but the use of vanadium catalysts in carbon–carbon bond-forming reactions has lagged far behind other transition metal catalysts [15,16]. The precise control of the architecture of active vanadium centers is expected to lead to the discovery of new synthetic methods involving fascinating and atom-economical carbon–carbon bond formations.

Hydroxyapatites (HAPs) possess Ca^{2+} sites surrounded by PO_4^{3-} tetrahedra parallel to the hexagonal axis, and have attracted considerable interest in view of their potential usefulness as biomaterials, adsorbents, and ion exchangers [17]. However, few excellent applications as catalysts or catalyst supports have emerged so far. We have disclosed a new strategy for the design of high-performance heterogeneous catalysts using apatite compounds [18]. The choice of HAPs as catalyst supports is motivated by the following advantages: (i) well-defined monomeric active species can be immobilized on their surface, on the basis of high ion exchange ability and adsorption capacity; (ii) the nonporous structure can help to overcome the problems of mass transfer limitation; and (iii) weak acid–base properties prohibit side reactions induced by the support itself.

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In recent our report, vanadium-apatite containing VO_4^{3-} species in the whole apatite matrix was synthesized, and which could act as a highly efficient heterogeneous catalyst for green organic syntheses such as Michael, Knöevenagel, and Henry reaction in water [19]. Motivated by the unique catalytic activity of the vanadium-apatite in the aqueous media, we herein attempted the full characterization of the substituted vanadium species in apatite matrix and the mechanistic investigation of the above reactions. Namely, spectroscopic analyses revealed that the above vanadium-apatite was $Ca_9(VO_4)_5(HVO_4)(OH)$, abbreviated to VAP, covered with the calcium oxide. This surface-coated calcium oxide phase could be removed by washing with water and then, the monomeric V-OH species having the strong Brønsted basicity were generated on the surface of VAP, which promoted sufficiently Michael reaction. Furthermore, this strong Brønsted basicity of the VAP catalyst was found to be applicable to the direct synthesis of pyrazolinone derivatives using aryl hydrazines and diethyl ethoxymethylenemalonate.

2. Experimental

The vanadium-apatite was synthesized by modification of a previously reported procedure [20]. A mixture of $CaSO_4 \cdot 2H_2O$ (11.5 g, 66.8 mmol) and Na_3VO_4 (7.36 g, 40.0 mmol) in aqueous solution (100 mL) was refluxed for 2 h with excess NaOH (5.0 g). The white slurry was then cooled to room temperature, filtered, washed with a large amount of deionized water and dried overnight at 110 °C. The resulting white powder was calcined at 800 °C for 3 h under air, followed by washing with hot water using Soxhlet's extractor overnight, yielding the VAP catalyst as a white powder.

3. Characterization of VAP catalyst

Based on elemental analysis, the amounts of Ca and V for the VAP catalyst were found to be 33.76 and 28.61 wt%, respectively. The Brunauer–Emmett–Teller (BET) surface area of the VAP catalyst was found to be $11.6\, m^2\, g^{-1}$. The XRD patterns of the vanadium-apatite and VAP catalyst are shown in Fig. 1. The uncalcined vanadium-apatite showed an amorphous phase (Fig. 1a), whereas the vanadium-apatite calcined at 800 °C for 3 h exhibited sharp peaks together with small peaks of a CaO phase at around 32° and 38° (Fig. 1b). From TEM images of the calcined vanadium-apatite, it can be observed that the surface is covered with an amorphous CaO phase as a bright region in a dark field [21]. The Ca/V ratio at various depths of the calcined vanadium-apatite was determined by XPS etched by an Ar ion laser. First, enrichment of Ca at the surface was observed due to the presence of the CaO phase. As the etch treatment was continuously repeated, the Ca/V ratio decreased, but then increased again. It seems that the calcined vanadium-apatite consists of three phases: CaO, a non-stoichiometric apatite shell, *e.g.* $Ca_9(VO_4)_5(HVO_4)(OH)$, and a stoichiometric apatite core under the surface [17]. After washing with hot water, the XRD spectrum of the VAP catalyst showed the disappearance of the CaO phase (Fig. 1c), and the Ca/V ratio of the VAP was estimated to be 1.50 in agreement with the non-stoichiometric value of the apatite component.

The electron spin resonance (ESR) spectrum of a vanadium species in VAP was completely silent. In XPS, the VAP showed a binding energy value almost identical to that of V_2O_5 (516.8 and 516.6 eV, respectively) for V $2p_{3/2}$. In their diffuse reflectance UV–vis spectra (Fig. 2), VAP did not exhibit a 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 polymeric octahedrally coordinated species [22–24]. In V K-edge X-ray absorption near edge structure (XANES) spectra [21], VAP showed a strong pre-edge peak comparable to those seen for Na_3VO_4 [25–27]. Table 1 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 (5470 eV). The energy positions of the pre-edge peak, of the main absorption of the 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. In the Fourier transforms (FT) of k^3-weighted 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 (Fig. 3). These results show that *the vanadium species in the VAP exists in an isolated tetrahedral geometry with an oxidation state of* +5.

Fig. 4 shows the solid-state wide-line ^{51}V NMR spectrum of VAP. It is well known that resonances located between −500 and −700 ppm correspond to vanadium in a tetrahedral coordination

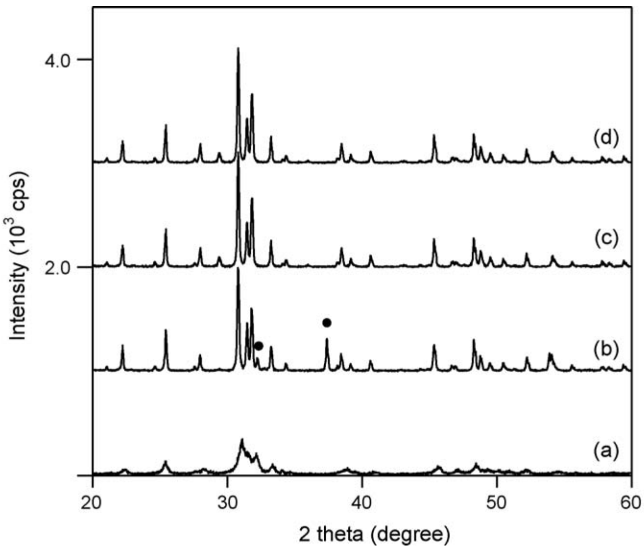


Fig. 1. The variation of XRD patterns: (a) uncalcined vanadium-apatite, (b) calcined vanadium-apatite, (c) VAP catalyst, and (d) recovered VAP catalyst after the aqueous Michael reaction. The peaks labeled (●) are originated from CaO.

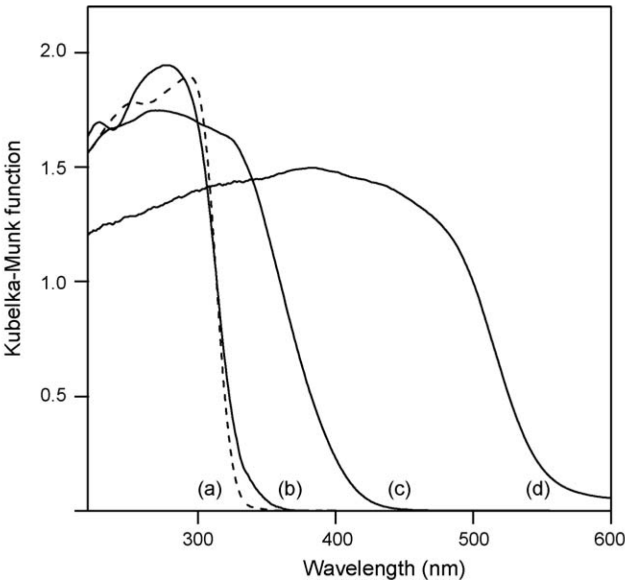


Fig. 2. Diffuse reflectance UV–vis spectra of (a) VAP catalyst, (b) Na_3VO_4, (c) $NaVO_3$, and (d) V_2O_5.

Table 1
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_2O_5	0.0	10.8	30.1
K_3VO_4	−0.9	12.0	16.3
NH_4VO_3	−0.6	11.4	26.6
$VO(acac)_2$[c]	−1.5	10.8	13.8
$VOSO_4{\cdot}nH_2O$[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 V_2O_5 (5470 eV).
[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.

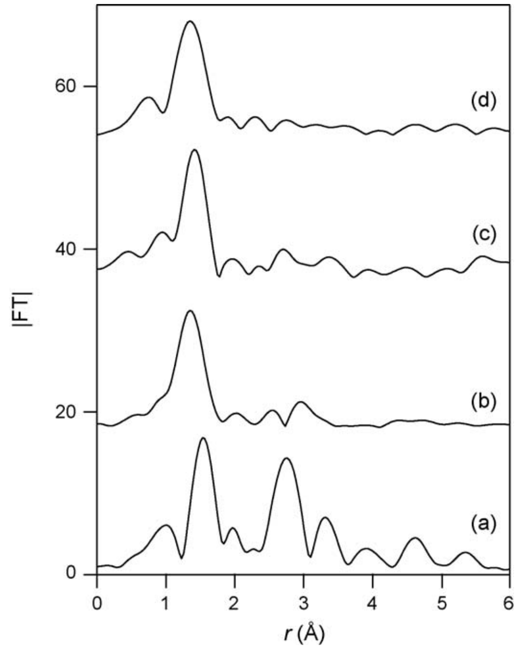


Fig. 3. Fourier transformation of the k^3-weighted V K-edge EXAFS spectra of (a) V_2O_5, (b) K_3VO_4, (c) VAP catalyst, and (d) recovered VAP catalyst. EXAFS were transformed in the range of 3.5–12.0 Å. The phase shift was not corrected. The peak at 1.5 Å corresponds to V=O and V–OH shells.

[28]. The main peak appears at −596 ppm, implying a 4-coordinated geometry of vanadium in the apatite matrix, which is in agreement with the results of UV–vis DRS or EXAFS analysis. Nabavi et al. reported that analysis of a distorted tetrahedral vanadate with a short vanadyl bond showed large upfield shifts [29]. The peak at −602 ppm in Fig. 4 suggests distortion in the vanadium tetrahedron that is probably caused by the calcium deficiency. In the Raman spectrum of the calcined VAP [21], a strong band was observed at 859 cm^{-1} for an isolated V=O stretching vibration [30]. In addition, the bands appearing at 823 and 795 cm^{-1} were attributed to V=O stretching vibrations of distorted vanadate species such as HVO_4 or H_2VO_4. As these results show, *the present methodology of catalyst preparation is a promising protocol for creation of a non-stoichiometric apatite phase containing stable and isolated tetrahedral vanadates on an apatite surface.*

4. VAP-catalyzed aqueous Michael reaction

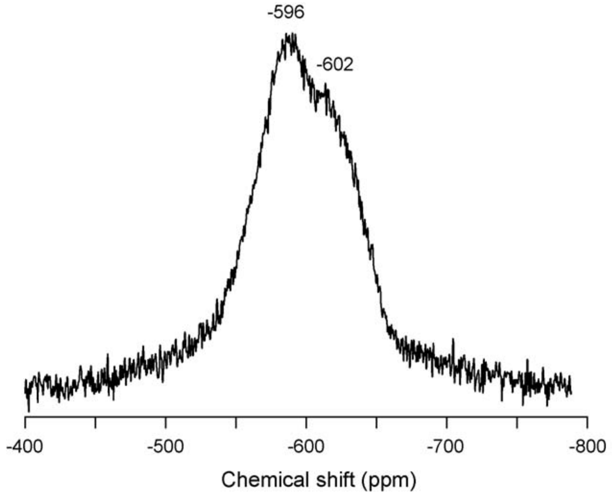
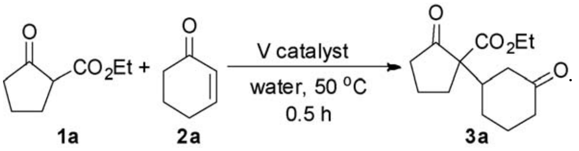


Fig. 4. A solid-state wide-line ^{51}V NMR spectrum of VAP catalyst.

The Michael reaction of 1,3-dicarbonyl compounds with activated enones provides access to 1,5-dioxo synthons, which can be easily transformed into cyclohexanone derivatives for use as important intermediates in steroid and terpenoid synthesis [31,32]. Traditionally, this reaction is promoted by strong bases such as alkali metal alkoxides or hydroxides [33–35]. In some cases, however, various side and subsequent reactions, *e.g.* ester solvolysis, aldol cyclizations, and retro-Claisen-type decompositions, result in low selectivity. One way to address these drawbacks is to avoid basic reaction conditions. To achieve this, a number of catalytic systems employing neutral conditions have been developed [36,37].

In order to investigate the abilities of the VAP catalyst, the Michael reaction of ethyl 2-oxocyclopentanecarboxylate (**1a**) with 2-cyclohexen-1-one (**2a**) was carried out as a model reaction at 50 °C in various solvents, and the results are summarized in Table 2. It is noteworthy that VAP showed the highest catalytic activity for the Michael reaction only under aqueous conditions, giving ethyl 2-oxo-1-(3-oxocyclohexyl)cyclopentanecarboxylate

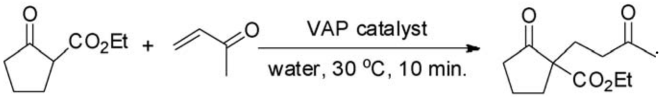
Table 2
Michael reaction of **1a** with **2a** in water solvent[a].



Entry	Catalyst	V valency	Solvent	Convn (%)[b]	Yield (%)[b]
1	VAP	+5	Water	>99	>99
2	VAP	+5	1,2-DCE[c]	66	66
3	VAP	+5	Toluene	56	54
4	VAP	+5	Ethanol	35	33
5[d]	Uncalcined vanadium-apatite	+5	Water	38	36
6	Na_3VO_4	+5	Water	41	39
7	K_3VO_4	+5	Water	33	32
8	$NaVO_3$	+5	Water	0	0
9	$VO(acac)_2$	+5	Water	0	0
10	$V(acac)_3$	+4	Water	0	0
11	V_2O_5	+4	Water	0	0
12	$VOSO_4{\cdot}nH_2O$	+3	Water	0	0
13	VCl_3	+3	Water	0	0
14[e]	HAP	–	Water	0	0
15	None	–	Water	0	0

[a] **1a** (1 mmol), **2a** (1.5 mmol), catalyst (V: 0.012 mmol), solvent (3 mL).
[b] Determined by GC using an internal standard technique.
[c] Dichloroethane.
[d] Vanadium leaching was observed.
[e] HAP (0.05 g) was used as a catalyst.

Table 3
Recycle experiment of VAP-catalyzed aqueous Michael reaction[a].



Entry	Run number	Convn (%)[b]	Yield (%)[b]
1	Fresh	>99	>99
2	1st reuse	>99	98
3	2nd reuse	>99	>99
4	3rd reuse	>99	>99
5	4th reuse	>99	>99

[a] Donor (5 mmol), acceptor (5.5 mmol), VAP (0.05 g), H_2O (5 mL), 30 °C, 10 min.
[b] Determined by GC using an internal standard technique.

(**3a**) in quantitative yield within 30 min in the various solvent screening reactions (entries 1–4). In the XRD profile of recovered VAP catalyst, the peak profile maintained the original pattern (Fig. 1d). The reaction did not proceed at all without the VAP catalyst (entry 15). Comparisons of the catalytic activities of VAP with those of various vanadium compounds in water solvent are also listed in Table 2. Orthovanadate derivatives containing isolated +5 valent VO_4 tetrahedra, such as Na_3VO_4 and K_3VO_4, also gave **3a** in moderate yields of 39 and 32%, respectively (entries 6 and 7). However, these catalysts underwent severe deactivation caused by the structural change from monomeric to polymeric species during the reaction: the presence of charge-transfer bands at wavelengths longer than 320 nm was confirmed by UV–vis spectroscopy. The use of other vanadium reagents did not afford any products (entries 8–13) and the reaction did not proceed in the presence of HAP by itself (entry 14). These results support the contention that the presence of monomeric +5 valent vanadate species on a solid surface plays a key role in the success of the aqueous Michael reaction. No spectral changes were observed in the V K-edge EXAFS data of the recovered VAP (Figs. 3d and 2Sg in Appendix A), which shows that the vanadium species remained in the monomeric state throughout the reaction.

The catalyst was found to be reusable at least four times without any reduction in activity during the reaction of **1a** and **2b** (Table 3). To further demonstrate the effectiveness of the VAP, the catalyst was removed by filtration from the reaction of **1b** with **2b** after 55% conversion. Continuation of the reaction for 1 h under identical reaction conditions afforded no product. Any vanadium leached in the aqueous phase was in amounts small enough to be undetectable by ICP analysis. These results show that this reaction proceeds on the VAP surface and does not involve dissolved vanadium species.

More significantly, the use of 0.008 g of the VAP catalyst under aqueous conditions allowed 32.2 g (200 mmol) of **1a** to react with 15.4 g (210 mmol) of **2b** in a highly effective manner, giving a 92% isolated yield (41.6 g) of **3b** at 40 °C in 1.5 h, as highlighted in Scheme 1. It has been reported that the surface density of the PO_4^{3-} species of the HAP is 5 PO_4^{3-} nm^{-2} [38]. Adapting this calculation method, the amount of the VO_4^{3-} in the spent VAP was estimated to be 0.096 mmol g^{-1} for the surface area. Based on the surface vanadium content, the VAP catalyst showed a high TON of 260400 and TOF of 48 s^{-1}. The TON and TOF values of the VAP catalyst are the highest reported for transition metal catalyzed Michael reactions to date, *e.g.*, hydroxyapatite-supported La complex (LaHAP) catalyst (TON 4500, TOF 500 h^{-1}) [39,40], montmorillonite-enwrapped Sc (Sc^{3+}-mont) (1000, 29 h^{-1}) [41], and montmorillonite-enwrapped Cu (Cu^{2+}-mont) (400, 28.5 h^{-1}) [42], $RuH_2(PPh_3)_4$ (33.3, 66.6 h^{-1}) [43], $Yb(OTf)_3/SiO_2$ (17, 0.7 h^{-1}) [44], $CeCl_3{\cdot}7H_2O/NaI$ (5, 0.8 h^{-1}) [45], $Ni(acac)_2$ (100, 100 h^{-1}) [46], Fe-mica (100, 5 h^{-1}) [47], $InCl_3$ (10, 1.7 h^{-1}) [48], $Yb(OTf)_3$ (100, 1.4 h^{-1}) [49] and $FeCl_3{\cdot}6H_2O$ (100, 100 h^{-1}) [50]. We conclude that the present vanadium-based catalytic system allows for simple and practical organic synthesis while meeting the increasing criteria for environmentally friendly chemical processes in the synthesis of fine chemicals and pharmaceuticals.

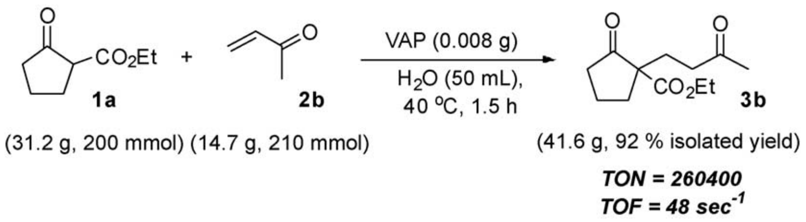
5. Mechanistic investigation

In our previous report, we determined the surface basicity of VAP catalyst by CO_2 TPD method. The surface basicity of VAP is stronger than that of the calcined vanadium-apatite before washing. For example, the base amount in the VAP was approximately 0.32 mmol g^{-1}, which was two orders of magnitude greater than that of the catalyst without treatment with hot water (6.6×10^{-3} mmol g^{-1}). Furthermore, in the reaction of **1a** with **2b**, an addition of 1.5 equiv. of benzoic acid based on the amount of surface vanadium species resulted in a significant decrease in product yield from 99 to 37%. These results show that the *removal of the CaO phase from the surface and generation of the non-stoichiometric apatite phase by water treatment produces a distorted vanadate species, e.g. a V-OH species, on the surface of the VAP catalyst that acts as a Brønsted base site.*

The difference FT-IR spectrum of the VAP [21], upon treatment with **1b**, showed a shift of the ν(C═O) band toward 1520 cm^{-1} in comparison to the free ν(C═O) band of **1b** at 1718 cm^{-1}, along with new peaks at 1645, 1419, and 1363 cm^{-1} assigned to the acetylacetonato-vanadium species [51]. These results are in agreement with the formation of a 1,3-diketonate vanadium species on the VAP surface. The suggested mechanism of the VAP-catalyzed Michael reaction is as follows. *In situ* generation of an extremely active V–OH species abstracts an α-proton from the donor to form a 1,3-diketonato vanadium species on the surface. An acceptor subsequently coordinates to a vacant site of the vanadium species through a carbonyl oxygen, and alkylation and hydrolysis then take place, affording the Michael adduct and, regenerating the V–OH species. The hydrophilic nature of the VAP and the structural robustness of the isolated VO_4 tetrahedron units on the solid surface offer the possibility of performing a diverse array of base-mediated reactions under aqueous conditions.

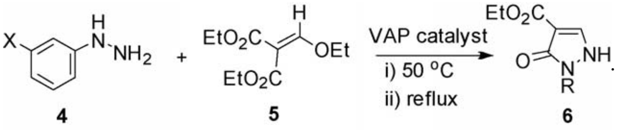
6. Application to one-pot synthesis of pyrazolinones

Pyrazole derivatives have a broad spectrum of biological activities and are used as fungicides, pesticides, anti-inflammatory,



Scheme 1. 200 mmol-scale reaction using VAP catalyst.

Table 4
One-pot synthesis of pyrazolinone catalyzed by VAP[a].



Entry	X	Time (h)	Convn of **4** (%)[b]	Yield (%)[c]
1	–Br	3	>99	69
2	–Me	3	>99	72
3	$-NO_2$	1.5	>99	74

[a] Reaction conditions: (i) pretreatment: VAP (V: 0.02 mmol), **4** (1 mmol), K_2CO_3 (0.55 mmol), H_2O (10 mL), 50 °C, Ar, 10 min. (ii) **5** (1.1 mmol), reflux, Ar.
[b] Determined by TLC.
[c] Isolated yield.

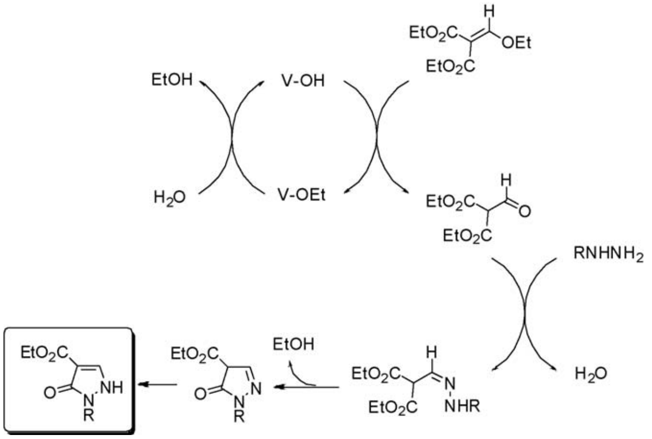


Fig. 5. Plausible reaction pathway of pyrazolinone synthesis catalyzed by VAP.

antipyretic, and antibacterial agents, etc. [52]. Various pyrazolinone esters could be synthesized from the corresponding aryl hydrazine (**4**) and diethyl ethoxymethylenemalonate (**5**) using an excess of homogeneous base such as aqueous K_2CO_3, NaOH, or sodium ethoxide [53]. From the standpoint of green organic syntheses, environmentally friendly alternatives using solid base catalysts are desired.

In exploring the utility of VAP, we found that the strong basic property of the VAP was applicable to the direct synthesis of pyrazolinone derivatives using aryl hydrazines and diethyl (ethoxymethylene)malonate [21]. 3-Nitrophenyl hydrazine hydrogen chloride was combined with a stoichiometric amount of K_2CO_3 to remove HCl in water at 50 °C, and then VAP and **5** were added successively. The reaction mixtures were refluxed for 1.5 h, then the solid VAP catalyst was removed by filtration. Recrystallization of the residue gave 4-ethoxycarbonyl-1-(3-nitrophenyl)-3-pyrazolin-5-one in 74% isolated yield. Aryl hydrazine derivatives of 3-Me and 3-Br hydrazines were also applicable, giving good yields of the corresponding pyrazolinones, as shown in Table 4.

A plausible reaction pathway of the pyrazolinone synthesis is shown in Fig. 5. VAP acts as a base catalyst in the first step of the deprotection of malonate **5**, in which a stoichiometric amount of base such as K_2CO_3 and NaOEt, was traditionally used. The second step is a known cyclization to the pyrazolinone [54]. Conclusively, VAP can act as a strong solid base catalyst to replace the classical synthetic route using an excess amount of bases.

7. Conclusions

VAP, which contains isolated vanadate species has been developed as an extremely active base catalyst for Michael reactions and one-pot synthesis of pyrazolinones under aqueous conditions. Our catalytic system possesses remarkably attractive features for organic syntheses: (i) high catalytic efficiency under mild reaction conditions, (ii) a simple procedure that allows for large-scale operation, (iii) no requirement for organic solvents, and (iv) easy separation and recycling of the solid catalyst.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2009.08.018.

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