



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 $\text{Ca}_9(\text{VO}_4)_5(\text{HVO}_4)(\text{OH})$, 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.

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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 $\text{Ca}_9(\text{VO}_4)_5(\text{HVO}_4)(\text{OH})$, 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 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (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 $11.6 \text{ m}^2 \text{ g}^{-1}$. 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. $\text{Ca}_9(\text{VO}_4)_5(\text{HVO}_4)(\text{OH})$, 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 $\text{V } 2p_{3/2}$. 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

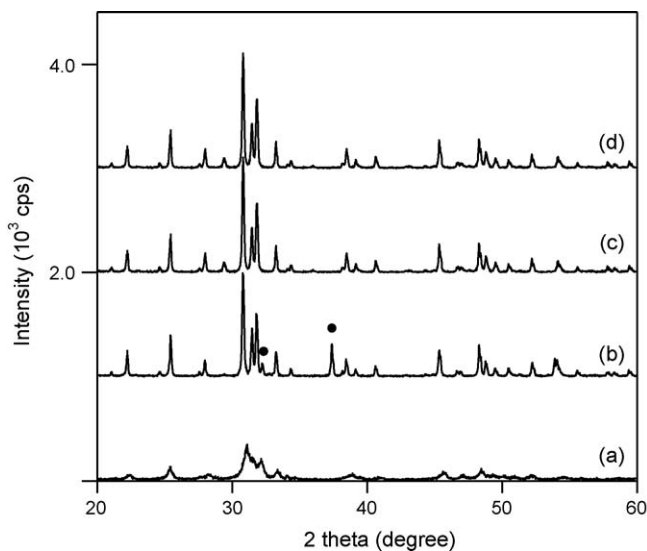


Fig. 1. The variation of XRD patterns: (a) uncalcined vanadium-apatite, (b) calcined vanadium-apatite, (c) VAP catalyst, and (d) recovered VAP catalyst after the aqueous Michael reaction. The peaks labeled (●) are originated from CaO.

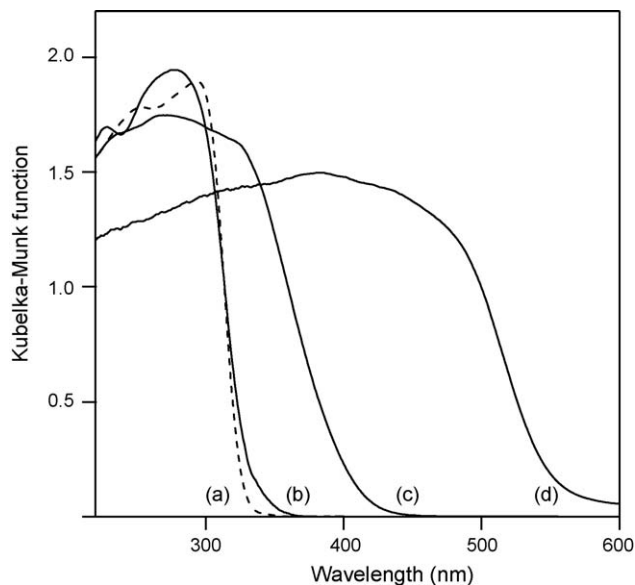


Fig. 2. Diffuse reflectance UV–vis spectra of (a) VAP catalyst, (b) Na_3VO_4 , (c) NaVO_3 , and (d) V_2O_5 .

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