Mater. Environ. Sci. 5 (S1) (2014) 2122- 2128
ISSN : 2028-2508
CODEN: JMESCN
MPE14

Natural phosphate as heterogeneous catalyst for oxidation of cyclic ketones to keto acids in environmentally friendly media

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Received 7 Dec 2013, Revised 16 July 2014, Accepted 17 July 2014

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Abstract

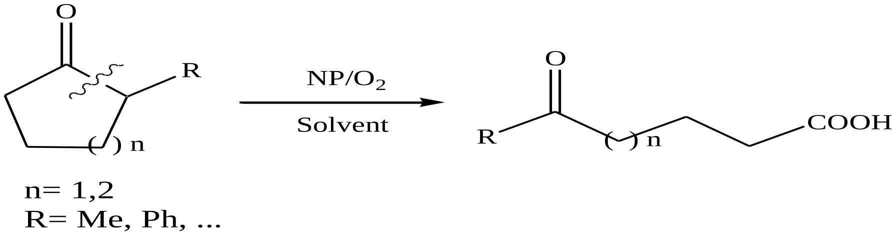
A novel method for the selective oxidation of cycloalkanones to keto acids has been developed employing the natural phosphate (NP) as heterogeneous catalyst and molecular oxygen as clean oxidant. The effects of solvent nature and reaction times on oxidation were fully considered. The catalyst can be easily recovered and efficiently reused. The selectivity observed at high conversions of various cyclic ketones, coupled with the use of the mild conditions and inexpensive oxidant, can make this process very attractive in the fine chemical synthesis.

Keywords: Heterogeneous catalysis, oxygen molecular, C-C bond cleavage, cycloalkanones.

1. Introduction

The oxidative cleavage of cyclic ketones and their substituted derivatives is the main pathway for the synthesis of diacids and keto acids on both the laboratory and industrial scales [1, 2]. Oxidations of organic compounds by dioxygen have been reported for a number of homogeneous transition-metal catalysts [3-5]. α–substituted cycloalkanones are oxidised to keto acids by copper (II)/dioxygen/acetic acid/water system [6]. Recently, rather unsophisticated catalyst precursors and heteropolyacids $H_{3+n}[PMo_{12-n}V_nO_{40}].yH_2O$ have been used for the preparation of oxo acids under very mild conditions (T = 60°C, $p(O_2) = 10^3$ mbar) [2,7]. However, it is well-known that the separation of the homogeneous catalyst from the products is not easy. In order to overcome this problem, nafion®-supported vanadium-oxo species have been prepared and characterised; they were used as catalyst precursors for the aerobic cleavage of C-C bonds mainly in 2-methylcyclohexanone (**1**) and 2-hydroxycyclohexanone to afford carboxylic acids derivatives [8].

In this paper, we report on a comparative study for the oxidation of **1** to 6-oxoheptanoic acid (**2**), by dioxygen in the presence of natural phosphate (Scheme 1), which is not soluble either in an aqueous phase or in organic solvents such as MeOH, AcOH, etc. The natural phosphate was used to promote numerous organic transformations [9-15] and has shown that its mild basic and acidic properties can be exploited in many synthetic applications [16-21].



Scheme 1: Oxidative cleavage of α-substituted cycloalkanones.

2. Experimental

2.1. Preparation and characterisation of NP

Natural phosphate, used in this work, comes from an ore extracted in the region of Khouribga (Morocco) and is treated by techniques involving attrition, sifting, calcination, washing, and recalcination, as described in previous papers [22]. Natural phosphate exists under several mineralogical classes [23], but generally they belong to the family of phosphocalcic apatite ($Ca_{10}(PO_4)_6F_2$ fluoroapatite in its pure state). The chemical composition of the treated NP is: P (34.24%), Ca (54.12%), C (1.13%), Mg (0.68%), Si (2.24%), Al (0.46%), Fe (0.36%), F (3.37%), S (2.21%), Na (0.92%), K (0.04%) and several metals (Zn, Cu, Cr, V) in the ppm range, and its structure is similar to that of fluoroapatite. The surface area of NP is 1.4 m^2g^{-1} (nitrogen adsorption) and its total pore volume is V_T = 0.0055 cm^3g^{-1}.

2.2. Reaction procedure

All catalysis tests were carried out using the Schlenk techniques (20 mL) which was attached to a vacuum line with a manometer and a gas inlet. The reaction vessel was charged at atmospheric pressure and heated in an oil-bath (60 ± 0.5 °C). Dioxygen uptake can be determined using a gas burette system connected to the reactor. The mixture was analysed by GC (Girdel Chromatograph (FID)). The products were identified by GC- MS (RTX5- MS). Product yields were determined by using heptanoic acid as internal standard. The catalyst recycling was accomplished by simple filtration, washing with the reaction solvent, drying under vacuum and heating at 100 °C for 1 hour before reuse. All compounds and solvents were purchased from commercial sources and they received no further treatment.

For instance, the Schlenk was charged with NP (0.1 g) and AcOH/H_2O (5 mL, 4.5:0.5). Then, the substrate (0.8 mmol) was added. The vessel was immersed in a bath preheated at 60 °C, and the mixture was magnetically stirred under O_2 for the time indicated in the tables. In all cases, the oxidation medium was heterogeneous.

3. Results and discussion

3.1. Oxidation of 2-methylcylohexanone

A solvent effect on the oxidation of 2-methylcyclohexanone, **1**, with pure dioxygen and natural phosphate was studied thoroughly; the main obtained results are summarised in table 1.

Table 1: Oxidative cleavage of 2-methylcyclohexanone with NP/O_2[a]: solvent effect

Entry	Solvent (mL)	n (O_2) (mmol)	Time (h)	Conversion [b] (%)	6-oxoheptanoic acid, **2**, yield [b] (%)
1	MeOH (5)	0.25	24	28	25
2	MeOH/H_2O (4.5/0.5)	0.38	20	40	37
3	CH_3CN (5)	0.49	24	50	47
4	CH_2Cl_2 (5)	0.60	24	66	65
5	THF (5)	0.28	24	29	28
6	THF/H_2O (2.5/2.5)	0.60	10	61	60
7	AcOH (5)	0.59	24	60	58
8	AcOH/H_2O (4.5/0.5)	0.87	12	90	88
9	AcOH/H_2O (2.5/2.5)	0.61	24	50	48
11	H_2O (5)	0.47	24	48	46
12[c]	AcOH/H_2O (4.5/0.5)	0	24	0	0

[a] *Reaction conditions: substrate (0.8 mmol), NP (0.5 g), T = 60°C, p(O_2) = 0.1 MPa.*
[b] *Conversions and yields were determined using GC analysis.*
[c] *Reaction carried out in the absence of NP.*

We have tested many solvents with different properties (non-polar, polar protic and polar aprotic), in order to find the best media of our oxidation. Thus, moderate conversions and yields are observed using MeOH, CH_3CN, CH_2Cl_2 and THF (entries 1-6). In aqueous media, the conversion reaches only 48% after 24 hours of reaction time (entry 11) and with pure acetic acid (AcOH); slightly lower values are obtained (entry 7). The best result is

obtained with AcOH/H_2O (4.5 mL/0.5 mL) giving 90% conversion after 12 h (entry 8). Probably, this mixture provides good acidity for the medium of reaction which promotes the enolisation of the 2-methylcyclohexanone. The enol form is a key step for the oxidation of ketones [24]. Moreover, the addition of 0.5mL of water is the optimum for activation the surface of NP [25] (see Figure 1). The molar ratio of oxygen uptake to substrate of about 1 is in favour of a single oxidative cleavage process.
The kinetic curves of the O_2 consumption in the oxidation of **1** using NP as catalyst and various reports of AcOH/H_2O show that the best activity of our catalyst is obtained with volume report AcOH/H_2O= 4.5/0.5 (Figure 1).

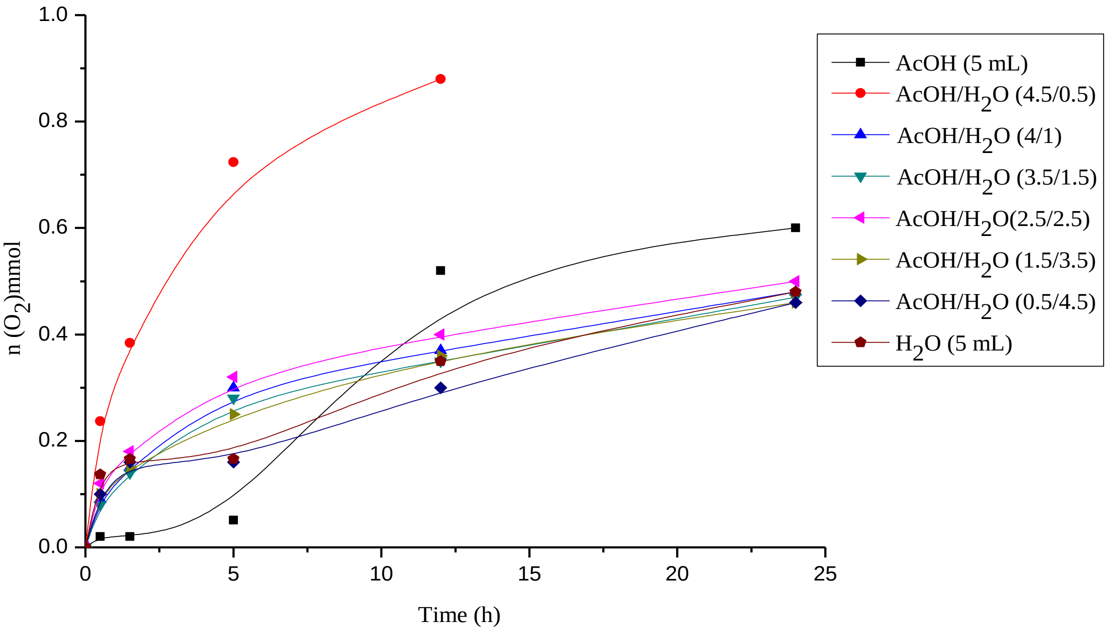


Figure 1: Kinetic curves of the O_2 consumption with NP/AcOH-H_2O/O_2 system in oxidation of 2-methylcyclohexanone.

It is worthwhile to emphasise that the keto acid is inert to degradation by NP/O_2 system and NP has no catalytic effect under anaerobic conditions. This means that in the present reaction dioxygen plays a decisive role. Blank experiments performed in the absence of NP show that the keto acid cannot be synthesised (entry 12).
The effect of weight on the starting catalyst was also studied. With AcOH/H_2O (4.5mL/0.5mL), the initial concentration of 2-methylcyclohexanone was kept constant while the natural phosphate weight was varied. The yield obtained at different initial NP weights in the 0.1-1g range did not vary remarkably. However, when the quantity of NP was greater than 0.5g, the reaction rate was increased (Figure 2). It should be noted, that for less than 0.1g of the NP this reaction does not take place. This may be ascribed to insufficient numbers of active centres on NP.
On the other hand, we have studied the reaction temperature effect. Thus, the temperature increase from ambient to 80 °C, within the limits imposed by the choice of solvent, led to a faster consumption of O_2 at 80°C. However, the optimal yield (88%) was obtained after 12 hours of reaction at 60°C (Table 2). At high temperature (80 ºC) the destruction of some reaction products could be the origin of this decrease in yield and the over-absorption of O_2 (entry 3). The short reaction time observed may be due to activation of the catalytic sites of NP by heat. It should be noted that the NP remains active at ambient temperature.

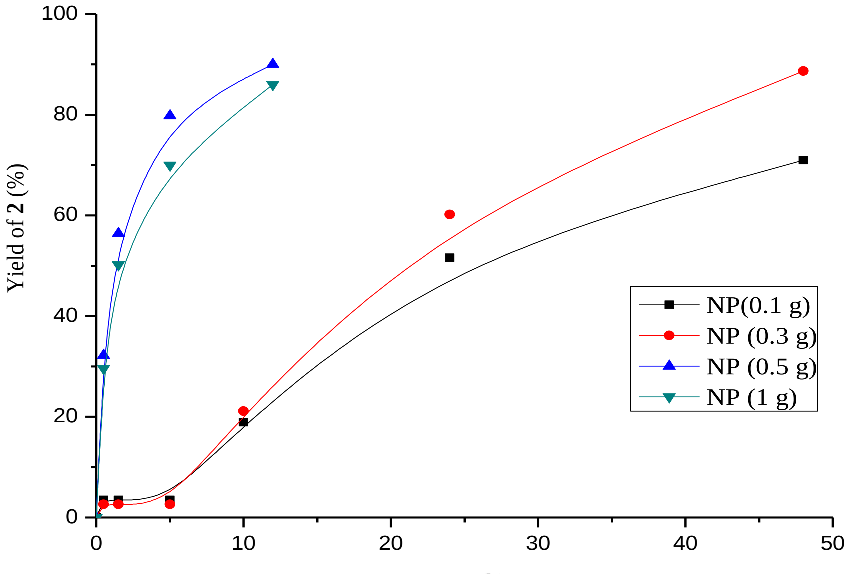


Figure 2: Effect of various masses of NP on the yields of the oxidation of 2-methylcyclohexanone.

Table 2: Oxidative cleavage of 2-methylcyclohexanone with NP/O_2[a]: reaction temperature effect

Entry	Temperature (°C)	Time (h)	mmol O_2/ mmol **1**	Conversion[b] (%)	Yield[b] in **2** (%)
1	r. t.	24	1	58	57
2	60	12	1.08	90	88
3	80	12	1.5	93	51

[a] *Reaction conditions: substrate (0.8 mmol), NP (0.5 g), AcOH/H_2O (4.5/0.5, mL), p(O_2) = 0.1 MPa.*
[b] *Conversions and yields were determined using GC analysis.*

We would like to emphasise that the crystallographic structure of the NP was not altered in our conditions. Thus, the X-ray diffractograms of NP after oxidation reaction obtained in the classical angle range ($10 \leq 2\theta \leq 70°$), show peaks corresponding to apatite type phosphates (Figure 3).

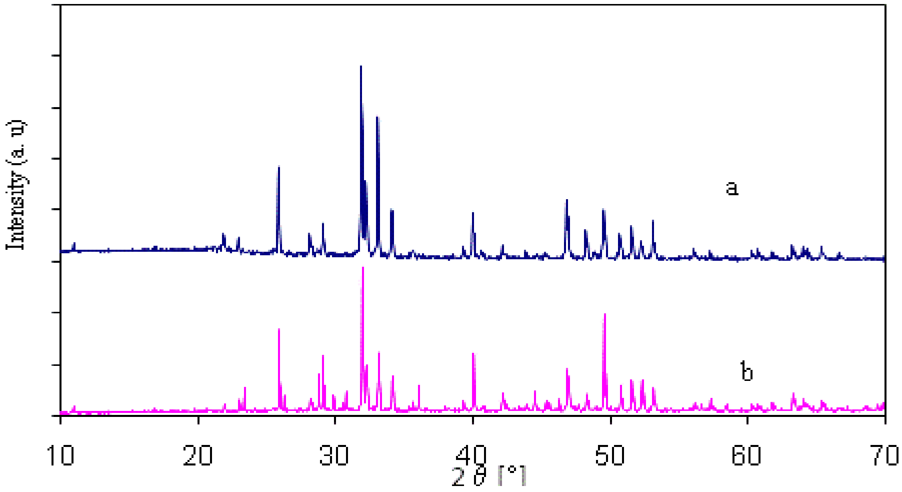


Figure 3: X-ray diffractogram of NP before (a) and after (b) oxidation reaction.

The IR spectra of NP after oxidation reaction shows the characteristic bands at 1000 and 600 cm^{-1} which may be assigned to $\nu_3(PO_4^{3-})$ and $\nu_4(PO_4^{3-})$ groups [26] (Figure 4). Other IR data (solid, cm^{-1}): 3439 cm^{-1} (H_2O sorbed) and 1450 cm^{-1} $\nu_2(CO_2)$ groups adsorbed from the atmosphere.

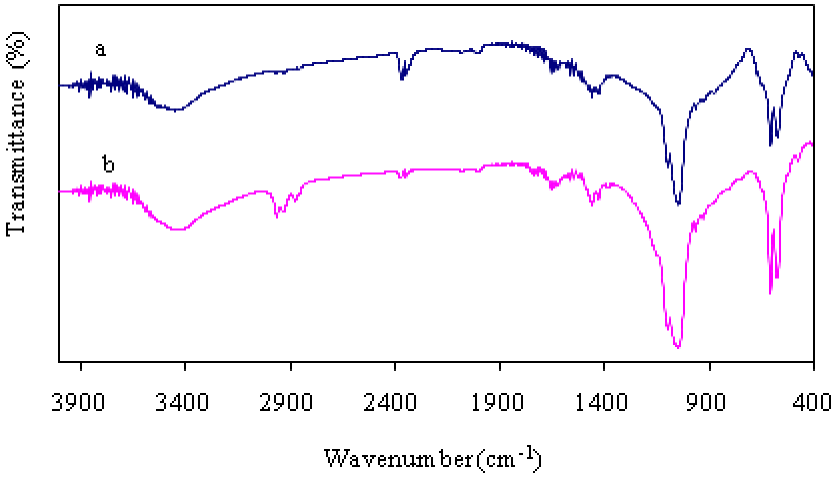


Figure 4: IR spectra of NP before (a) and after (b) oxidation reaction.

It should be noted that the SEM images of NP show the some modification in the particles morphology of the NP after oxidation reaction. Thus, the examination of these images reveals that the NP, before catalysis reaction, is characterised by microparticles in the ovoid form or hexagonal rods (Figure 5a). After catalysis, we observe the same forms which are partially broken (Figure 5b) through the friction effect of particles among one another during the reaction.

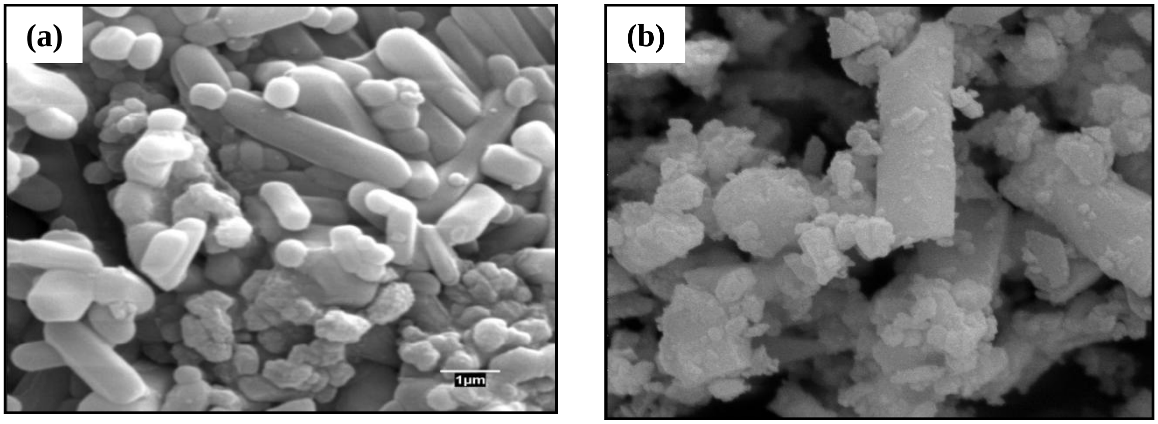


Figure 5: Scanning electron microscopy (SEM) images of NP before (a) and after (b) oxidation reaction.

The main advantage of this catalysis oxidation, over the remarkable ability of NP, is that allow us to reuse the catalyst in an inexpensive solvent. Indeed, it was recycled four times without any loss in activity and selectivity (Figure 6). This means that the structure of the active centers is maintained from one test to another.

3.2. Oxidation of other cycloalkanones

The use of the catalytic system, natural phosphate/dioxygen/acetic acid/water exhibited high catalytic activity for the oxidation of other substituted cycloalkanones bearing one alkyl radicals, a phenyl or hydroxyl groups (Table 3). No oxidation products were detected in the absence of the NP catalyst.

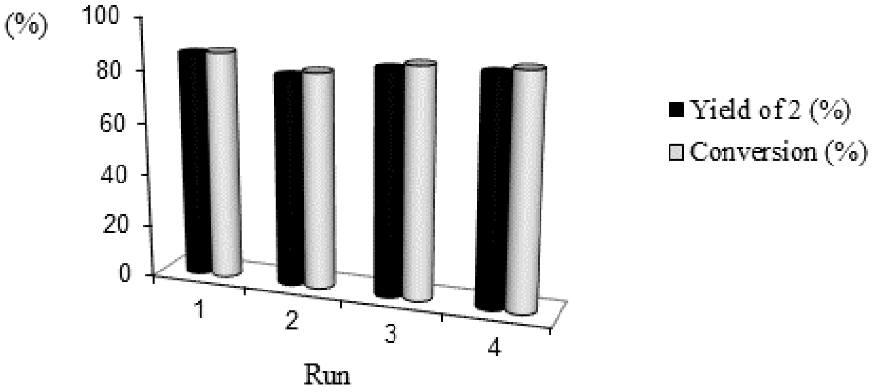


Figure 6: Catalytic performances of the catalyst after recycling in the C-C cleavage of **1**.

Treatment of methyl 2-oxocyclopentanecarboxylate gives 6-methoxy-5,6-dioxohexanoic acid in high yields (88%, 12 h, entry 1), and the 2-phenylcyclohexanone produces mainly 6-phenyl-6-oxohexanoic acid Ph-CO-$(CH_2)_4$-COOH (58 %, 24 h, entry 2). In the last case, the reaction rate is slower if it is compared to oxidation of 2-methylcyclohexanone (entry 4); this is probably due to the significantly attractor effect of phenyl group. The oxidative cleavage of 2-hydroxycyclohexanone to produce adipic acid (entry 3), and the concentration of this compound was measured after esterification by addition of ethereal diazomethane. This result opens interesting perspectives for a more selective synthesis of adipic acid, based on a forced conversion of cyclohexanone to 2-hydroxycyclohexanone.

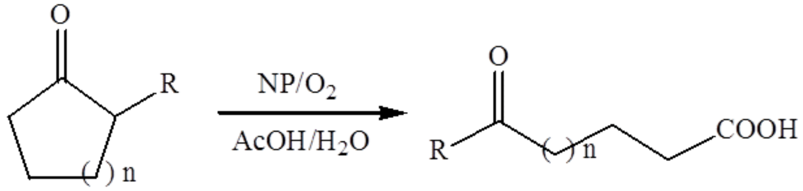


Table 3: Catalytic oxidation of cycloalkanones by NP/AcOH-H_2O/O_2[a]

Entry	Cycloalkanone	n (O_2) (mmol)	Time (h)	Conversion[b] (%)	Product yield[b] (%)
1	n = 1, R = CO_2Me	0.90	12	90	88
2	n = 2, R = Ph	0.60	24	60	58
3	n= 2, R = OH	0.90	24	88	86
4	n = 2, R = Me	0.87	12	90	88

[a] *Reaction conditions: substrate (0.8 mmol), AcOH/H_2O (4.5/0.5, mL), NP (0.5 g), T = 60°C, p(O_2) = 0.1 MPa.*
[b] *see Table 1.*

Conclusion

In this work, we have demonstrated that NP/AcOH-H_2O/O_2 catalytic system is an environmentally friendly process for the selective oxidation of α-substituted cycloalkanones to linear oxo acids. We have found also that the catalytic system has a similar behaviour towards previously described systems involving vanadium catalysts or stoichiometric oxidants which generate a large amount of solid toxic waste. Moreover, this reaction condition might also represent a perfect alternative to the process carried out in liquid phase, which is characterised by a no longer acceptable environmental impact.

Acknowledgements-This work was partly supported by the Comité mixte franco-marocain (PICS N°562). M. D. thanks the CNRST of Morocco for the allocation of a Bourse excellence grant.

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