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Catalysis Today 111 (2006) 349–353
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Vanadomolybdophosphoric acid/fluorapatite solid-phase system for aerobic oxidative dehydrogenation

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Abstract

We developed a solid-phase-oxidation-system using FAp disperse phase and vanadomolybdophosphoric acid ($H_{3+n}PV_nMo_{12-n}O_{40}$: PV*n*) catalysts with molecular oxygen as a new green reaction system. The PV4/FAp system was an efficient and recyclable solid–catalyst system for solvent-free oxidative dehydrogenation of α-terpinene to *p*-cymene under 1 atm of molecular oxygen at 50 °C. The catalytic activity in the solid-phase system was comparable to that in the homogeneous liquid-phase system with acetonitrile. Even if under air conditions, PV4/FAp system was able to promote the catalytic dehydrogenation at room temperature sufficiently.

Keywords: Vanadomolybdophosphoric acids; Aerobic dehydrogenation; Fluorapatite; Solvent-free; Molecular oxygen; Recyclable catalyst; Green chemistry

1. Introduction

The search for environmentally benign alternatives to the conventional reaction process using organic solvents has been of great significance in green sustainable chemistry [1]. Recently we have developed a new reaction system using a harmless solid disperse phase, instead of organic solvents, as an environmentally benign oxidation system. By use of the solid phase system of a polyoxometalate catalyst/fluorapatite disperse phase (FAp)/urea–H_2O_2 without organic solvents, the epoxidation of alkenes and allylic alcohols and the selective oxidation of sulfides proceed smoothly at ambient temperature and pressure [2–5]. Practically, FAp powder was simply mixed with reactants without organic solvents and the oxidation proceeded in the powdery solid state without stirring. Our solid-phase system is a convenient green process, a solvent-free catalytic reaction, using a harmless solid disperse phase and reusable solid-catalyst phase, without heating or cooling, without special apparatus.

In the system, FAp phase is used not for fixation of a catalyst but for dispersion of reactants instead of organic solvents. The use of FAp as a disperse phase remarkably enhances the solvent-free catalytic oxidations with solid urea–H_2O_2. This is because FAp moderately interacts with both inorganic and organic reactants due to its exchange ability of cation and anion and affinity for organic compounds, in addition to resistance to oxidations.

Polyoxometalates have been recently attracted as an environmentally benign catalyst in homogeneous and heterogeneous liquid-phase oxidations because of high stabilities for oxidants [6,7]. In the FAp phase system with urea–H_2O_2 a variety of polyoxometalates showed effective and different catalytic activities from those in the well-known liquid-biphasic system with aqueous hydrogen peroxide; in the former solid-phase system Keggin-type of molybdophosphates was superior to the tungstophosphates, in reverse order to the latter conventional method [4,5]. In the solid-phase system, the formation of new active species retaining the parent cluster structure was elucidated by solid state NMR and FT-IR spectroscopic studies. Characteristic activities of the parent-cluster-sized active species are expected in the system.

Molecular oxygen as well as hydrogen peroxide is the environmentally benign and low waste oxidant. Keggin-type of vanadomolybdophosphoric acid–catalytic system, discovered in the 1970s, is efficient and versatile for oxidations with molecular oxygen [8]. Using the catalytic system, recently, the oxidative dehydrogenation of cyclic dienes to the aromatic compounds using $H_5PV_2Mo_{10}O_{40}$ catalyst has been in detail

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0920-5861/$ – see front matter
doi:10.1016/j.cattod.2005.10.060

studied in homogeneous solution with organic solvents by Neumann and co-workers [9–11]. Instead of the solvents, FAp or other solid disperse phases would be applicable to the catalytic dehydrogenation. We now report herein a solid-phase-oxidation-system using FAp disperse phase and vanadomolybdophosphoric acid ($H_{3+n}PV_nMo_{12-n}O_{40}$: PV*n*) catalysts with molecular oxygen as a new green reaction system.

2. Experimental

2.1. Catalysts and solid disperse phase

A series of Keggin-type of vanadomolybdophosphoric acids (PV*n*: $H_{3+n}PV_nMo_{12-n}O_{40}$, $n = 1–5$) was available from Japan New Metals Co. Ltd. and Nippon Inorg. Colour & Chem. Co. Ltd. In all PV*n* catalysts, the compositions of P:V:Mo were 1:*n*:12 − *n* from elemental analyses, respectively. The used PV*n* catalysts except PV1 were the average of some vanadium-substituted mixtures and/or vanadium regio-isomers.

Fluorapatite powders, $Ca_{10}(PO_4)_6F_2$ (particle size, 5–20 μm; specific surface area, 8–12 m^2/g), were available from Taihei Chem. Ind. Co. Ltd., and used as a solid-disperse phase.

2.2. The catalytic activities of vanadomolybdophosphoric acids/solid disperse phase in the aerobic dehydrogenation of α-terpinene

The catalytic oxidative dehydrogenation of α-terpinene to *p*-cymene was carried out under solid-phase conditions as follows: 1 mol% of PV*n* catalyst was simply mixed with solid disperse phase powder (0.50 g) in 35 mL of the test tube capped with septum. The solid-catalyst phase was permeated with the liquid substrate (0.5 mmol) after being fully replaced with molecular oxygen. After shortly mixing, the reaction test tube was left at 50 °C without stirring. The dehydrogenation was followed by gas chromatography using an internal standard.

2.3. The oxidative dehydrogenation using PV4/FAp solid-phase system

For isolation of the product and the recycled use of solid-catalyst phase, the reaction was carried out using 300 mL flask capped with septum in three times molar scale as above. For the dispersion of the catalyst on FAp phase we used two methods: mixing with the catalyst powder (dry method) and mixing with acetone solution of the catalyst and evaporation (wet method).

Isolation procedures were as follows: after the reaction, extraction of the solid reaction mixture with *n*-hexane, filtration and evaporation of the solvent were carried out to obtain the product without further purification. As another isolation method, direct distillation from the solid reaction mixture was carried out under vacuum. The product was identified by ^{1}H NMR.

Recycle use of PV4/FAp solid-catalyst phase: The used solid-catalyst phase was recovered after extraction or distillation of the product, dried at room temperature under vacuum and was reused to the reaction.

3. Results and discussion

3.1. Effect of FAp solid phase on catalytic activities of vanadomolybdophosphoric acids (PVn)

The effect of FAp as a solid disperse phase was investigated on the catalytic dehydrogenation of α-terpinene to *p*-cymene in the presence of molecular oxygen without solvents. A series of Keggin-type vanadomolybdophosphoric acids ($H_{3+n}PV_nMo_{12-n}O_{40}$, PV*n*) with substitution number of vanadium $n = 1–5$ was used as a catalyst. The catalytic activities of PV*n*/FAp were compared with the yields of *p*-cymene formed at 50 °C after 1 h (Fig. 1).

All of PV*n* catalysts dispersed on FAp phase catalyzed the dehydrogenation of α-terpinene to *p*-cymene under 1 atm of oxygen atmosphere at 50 °C under powdery solid-phase conditions without organic solvent. In a series of PV*n* catalysts, the catalytic activities of PV3 and PV4 remarkably increased in the presence of FAp phase. The yields of *p*-cymene were 40% and 74%, respectively. In contrast, in the absence of FAp phase, the reaction mixtures were in a liquid–solid heterogeneous state and the reactions hardly proceeded under the similar reaction conditions. In all the cases of PV*n* catalysts ca. 10% yields of *p*-cymene were at best formed. Thus, FAp was found to be an effective disperse phase for the catalytic oxidation using molecular oxygen as well as hydrogen peroxide.

3.2. Effect of some solid disperse phases on catalytic activities of PVn

Instead of FAp disperse phase, hydroxyapatite (HAp), ZrO_2 and CeO_2 powders were used in the PV*n*-catalyzed oxidative dehydrogenation and their effectiveness as solid disperse phase was compared (Fig. 1).

HAp, $Ca_{10}(PO_4)_6(OH)_2$, and FAp, $Ca_{10}(PO_4)_6F_2$, were calcium phosphates having the same crystal structures but somewhat different chemical properties. Interestingly, there was a marked difference in effectiveness of disperse phases

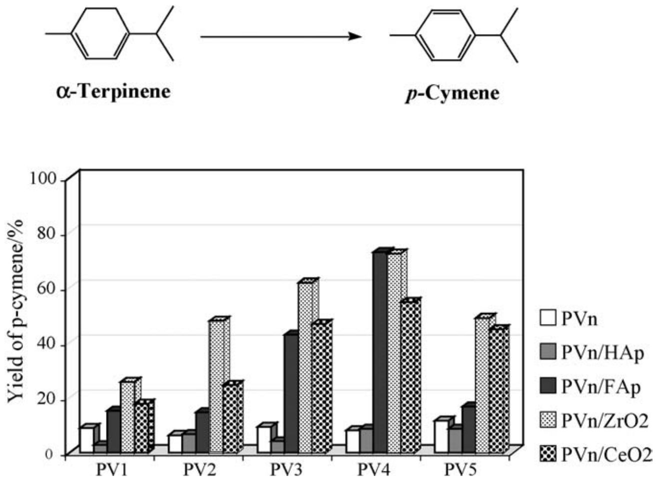


Fig. 1. The oxidative dehydrogenation of α-terpinene using PV*n*/solid phase/O_2 system (at 50 °C for 1 h).

between HAp and FAp: HAp rather diminished the catalytic activities, whereas FAp enhanced ones.

ZrO_2 and CeO_2 crystals are able to absorb and disperse oxygen in the crystal lattice. These solid powders were effective for the solid-phase oxidation with molecular oxygen. ZrO_2 and CeO_2 solid phases, similarly to FAp, increased the activities of PV*n*s. In the use of ZrO_2, PV*n*s showed higher activities than those in the use of FAp, although PV4 showed the similar highest activity in both cases. The differences in catalytic activity among PV2–5 series (ZrO_2, 48–72%; CeO_2, 25–55% yields) were smaller than that in FAp solid-phase (FAp, 15–73% yields).

The used solid disperse phases except for HAp enhanced the catalytic activities of a series of PV*n*, and in all the cases PV4 catalyst showed the highest activity. Both PV4/FAp and PV4/ZrO_2 were found to be the most effective solid catalytic phases for the oxidative dehydrogenation.

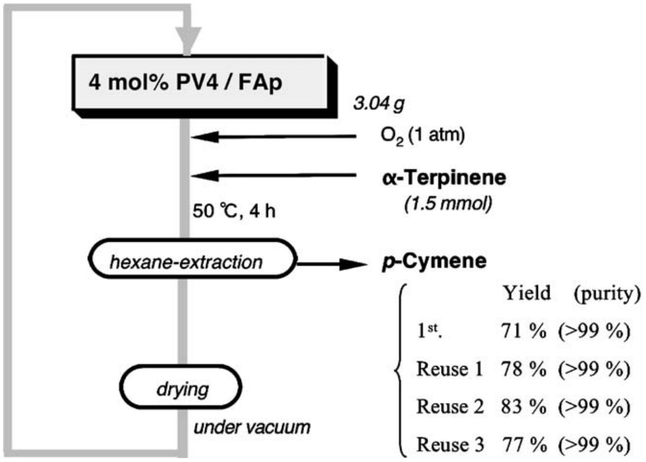


Fig. 2. Recycle use of PV4/FAp catalytic system.

3.3. *Recycle use of PV4/FAp solid-catalyst phase*

In both of PV4/FAp and PV4/ZrO_2 with the highest activities, the PV4/FAp solid-phase system was selected for the recycle use from a view of green chemistry, because FAp is environmentally harmless disperse phase in comparison with ZrO_2.

PV4 catalyst/FAp solid-phase was an efficiently recyclable solid-catalyst phase for the dehydrogenation of α-terpinene. The flowchart of the recycled reaction system procedure was simple as shown in Fig. 2; after extraction of the product with hexane, the recovered solid-catalyst phase was dried under vacuum, and again permeated with the substrate to start the next reaction in the presence of molecular oxygen. Under the mild reaction conditions of 1 atm of oxygen at 50 °C for 4 h, the solid-phase reactions using 4 mol% of PV4/FAp phase proceeded completely to afford 70–80% yields of *p*-cymene in the first and the reused three runs.

As a recyclable system, the reaction using 2 mol% of PV2 dissolved in nonvolatile polyethylene glycol (PEG) has been reported recently (100% GC yield of *p*-cymene from α-terpinene was obtained under 2 atm of oxygen at 100 °C for 16 h) [11]. Compared with the homogeneous liquid-phase reaction, our solid-phase system has advantages of mild reaction conditions of low temperature without pressure of oxygen and simple reaction procedures of product-separation and reuse.

3.4. *Utility of PV4/FAp solid-phase system in the aerobic dehydrogenation of α-terpinene*

The results in the catalytic dehydrogenation of α-terpinene under milder various reaction conditions are summarized in Table 1. Using PV4/FAp/O_2 solid-phase system, the dehydrogenation of α-terpinene was completed under 1 atm of oxygen without heating at 25 °C after 24 h (Runs 7 and 8). By hexane-extraction a 77% yield of *p*-cymene was obtained. In the case, a 66% yield of the product with high purity was obtained by direct distillation of the solid reaction mixture (Run 8).

It is desirable that the catalytic dehydrogenation is performed at ambient temperature and pressure with molecular

Table 1
The oxidative dehydrogenation of α-terpinene using PV4/FAp solid-phase system

Run[a]	Oxidant	Catalyst	Solid phase	Method[b]	Temperature (°C)	Time (h)	Conversion (%)[c]	*p*-Cymene (%)[d]
1	O_2	PV4	FAp	D	50	1	90	(73)
2	O_2	PV4	none		50	1	8	(8)
3	O_2	PV4	FAp	D	25	19	92	(61)
4	O_2	PV4	none		25	19	14	(14)
5	Air	PV4	FAp	D	25	19	30	(26)
6	O_2	PV4	FAp	W	50	6	>99	70
7	O_2	PV4	FAp	W	25	24	>99	78
8	O_2	PV4	FAp	W	25	20	>99	66[e]
9	Air	PV4	FAp	W	25	72	>99	85

[a] Reaction conditions of Runs 1–5: substrate/PV4/FAp/O_2 = 1.0 mmol/0.01 mmol/0.50 g/1 atm; reaction conditions of Runs 6–8: substrate/PV4/FAp/O_2 = 1.5 mmol/0.03 mmol/1.50 g/1 atm; reaction conditions of Run 9: substrate/PV4/FAp/air = 1.5 mmol/0.03 mmol/1.50 g/1 atm.

[b] D: dry method; W: wet method.

[c] Determined by GC.

[d] Isolated yields by hexane-extraction unless otherwise noted. Values in parentheses are GC yields using an internal standard.

[e] Isolated yields by distillation.

oxygen in air instead of 100% replacement of molecular oxygen. In the PV4/FAp solid-phase system, the reaction proceeded at 25 °C even in air to obtain an 85% yield of *p*-cymene after 72 h (Run 9).

3.5. Comparison with homogeneous liquid-phase reactions

The oxidative dehydrogenation has been reported under homogeneous liquid-phase conditions using acetonitrile or polyethylene glycol solution of $H_5PV_2Mo_{10}O_{40}$ (PV2) [9–11]. For evaluation of our solid-phase system, we examined the catalytic activities of the PV*n* catalysts ($n = 1–5$) in acetonitrile or PEG under the similar reaction conditions (1 mol% PV*n*/1 mL of solvent/1 atm of O_2 at 50 °C) to the solid-phase conditions (Fig. 3). In the use of 1% H_2O–acetonitrile all the PV*n* catalysts catalyzed the reaction under homogeneous liquid-phase conditions but in the only case of PV5 under heterogeneous conditions because of poor solubility. All the catalysts showed high activities (45–78% yields) and PV4 was also the most effective in the solution. In the use of PEG, all the catalysts did not completely dissolve in PEG at 50 °C and were not effective for the reaction under the mild conditions (ca. 20% yields at 50 °C after 2 h). In the case, the stronger conditions such as the reported one are needed [11].

In a series of the PV*n* catalysts, it was found that the order of the catalytic activities was PV4 > PV3 > PV2 in the solid-phase system and also in the acetonitrile system, and that the PV4/FAp and the PV4/ZrO_2 solid-phase systems without solvents showed similar high catalytic activities to the PV4–acetonitrile homogeneous system. The PV*n*/FAp solid-phase system showed considerable difference in catalytic activity among PV2–4 series compared with PV*n*/ZrO_2 solid-phase system and the PV*n*–acetonitrile system. In the use of PV4 and PV2, the yields of *p*-cymene at 50 °C after 1 h were 73%/15% (FAp), 72/48 (ZrO_2) and 78/60 (acetonitrile), respectively.

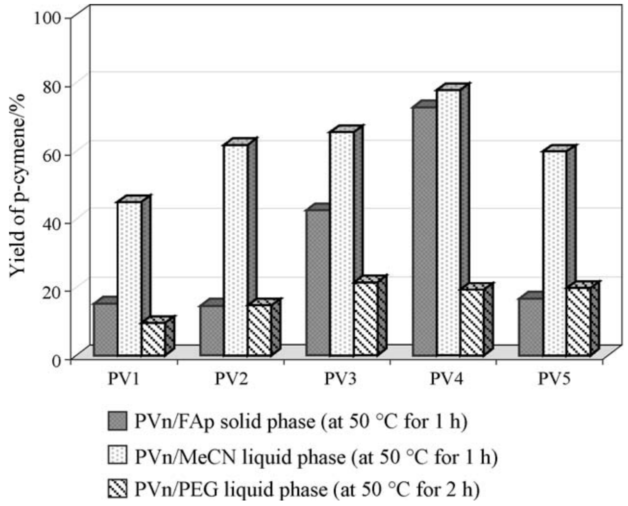


Fig. 3. The oxidative dehydrogenation of α-terpinene using PV*n*–liquid-phase system.

3.6. O_2-oxidative dehydrogenation using PVn dispersed on solid phase

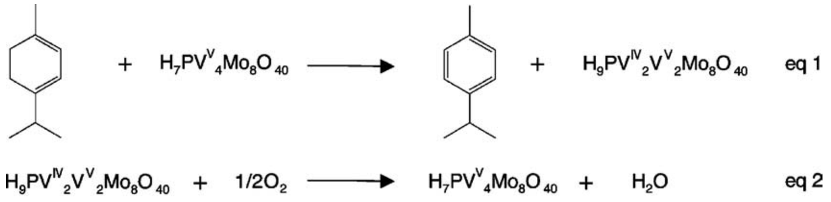
PV*n*–catalytic system contains two processes of the dehydrogenation with PV*n* (oxidized form) and regeneration of the reduced catalyst to the oxidized form with molecular oxygen [8]. In a homogeneous acetonitrile solution of PV2, the latter process is rate-determining step [10]. This is easily undertaken through changing the color of PV2 solution with progressing the dehydrogenation.

In our solid-phase systems using FAp and ZrO_2, similar color changes were recognized to the liquid-phase reaction. At starting the reaction with addition of the substrate, immediately, the color of the catalyst solid-phase turned from orange (oxidized form of the catalyst) to green–blue-tone (the reduced form). Then the color of the solid reaction mixture slowly changed and finally turned to yellow-brownish. This point showed completing the reaction. Thus, probably the solid-phase reaction proceeds in the catalytic two-processes-mechanism, similarly to the liquid-phase reaction (Fig. 4). The rate-determining step would be regeneration of the reduced catalyst with molecular oxygen.

Although the solid-phase system may contain two similar processes to the liquid-phase system, the form of PV*n* catalyst acting in the oxidation should be different from that in the liquid system. The solid particles of the catalyst dispersed on the solid phase is concerned as the aggregated Keggin-clusters in the oxidation, whereas one Keggin-cluster dissolved in acetonitrile solution is concerned. In the solid-phase system, it is considered that on average a partial site of one PV*n* cluster in the aggregated clusters may act in Eq. (1), on the analogy of the formation of new peroxo-active species in the polyoxometalates/FAp/urea–H_2O_2 system [3]. Recently, Matveev et al. [12] have reported that under acidic aqueous solution conditions, PV*n* with higher *n* increases the oxidation potential to promote the oxidation more easily in the limited case of early incomplete reduction of $PV^{V}n$ to $PV^{V}n\text{–}mV^{IV}m$ ($n = 2–4$, $m = 0.5$). In the solid-phase system such incomplete reduction and regeneration of PV*n*, by action of the limited site of the clusters, may occur repeatedly to catalyze the dehydrogenation. Therefore, the order of the activities of PV4 > PV3 > PV2 would be observed corresponding to the oxidation potentials. This phenomenon must be induced by the stabilization of the catalyst cluster with solid disperse phase.

The ratio of catalytic activities of PV4/PV2 was smaller in the ZrO_2 system than that in the FAp system. This is due to enhancement of the reoxidation of the reduced PV2 with sufficient adsorption–dispersion of molecular oxygen by ZrO_2. On the other hand, high catalytic activities of PV*n*s ($n = 2–6$) observed in the acetonitrile system may be attributed to solubility of molecular oxygen, oxidation potentials of PV*n*s and reduction degree of PV*n* in acetonitrile.

As it is known that in strongly acidic aqueous solution VO_2^+ cation is easy to dissociate from parent PV*n* cluster with higher *n* and that in the case the oxidation is complicated, stable PV2 has been usually used for aerobic oxidations and extensively studied [6]. In the present solid-phase systems, however, PV4



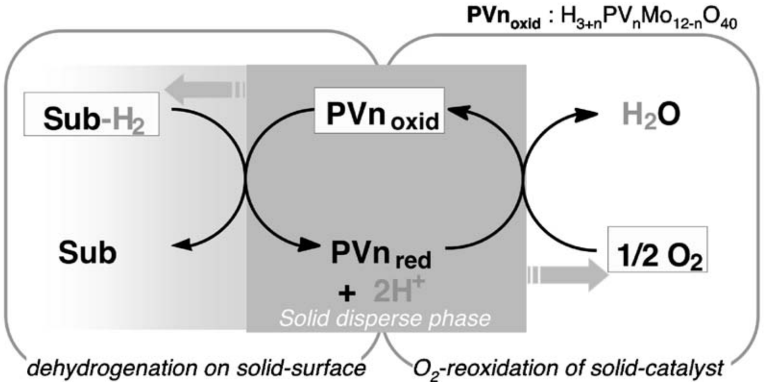


Fig. 4. Solvent-free PV*n*/solid phase/O_2 catalytic system.

showed high stability and high catalytic activity. Taking account of the action of the limited site of the clusters, PV4 in the solid-phase systems should be active rather than acetonitrile liquid-phase system.

As a role of solid-disperse phase of PV*n* series, stabilization and dispersion of PV*n* clusters, and enhancement of the rate-determining step, the reoxidation with molecular oxygen are required. The FAp system might not more efficiently enhance the reoxidation of the reduced PV*n* because of weaker adsorption of molecular oxygen than the ZrO_2 system. However, like the effect observed in the polyoxometalates/FAp/urea–H_2O_2 system, FAp should contribute to the aerobic oxidation in the points of affinity to organic compounds, stability of dispersing catalysts and proximity of the reactants. Spectroscopic studies on the structural variation of PV*n* catalysts in the reaction are in detail under way.

4. Conclusions

Vanadomolybdophosphoric acid dispersed on FAp phase (PV4/FAp) was an effective and recyclable solid-phase system for solvent-free oxidative dehydrogenation of α-terpinene under 1 atm of molecular oxygen at moderate temperature. The catalytic activity in the solid-phase system was comparable to that in the homogeneous liquid-phase system. Even if under air conditions, PV4/FAp system may be applicable to the dehydrogenation at room temperature.

Acknowledgements

This research was supported by the Grant-in-Aid for Scientific Research from Ministry of Education, Culture, Sports, Science and Technology of Japan.

We thank Japan New Metals Co. Ltd. for the supply of vanadomolybdophosphoric acids.

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