Vanadium phosphorus oxide as an efficient catalyst for hydrocarbon oxidations using hydrogen peroxide

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Calcined vanadium phosphorus oxide (VPO) prepared by an organic route is found to be an active and effective catalyst for the oxidation of various alkanes such as cyclopentane, cyclohexane, *n*-hexane, cycloheptane, cyclooctane, cyclodecane and adamantane in acetonitrile solvent using the environmentally benign oxidant, hydrogen peroxide, where the oxidation mechanism is believed to involve a reversible V^{4+}/V^{5+} redox cycle.

Introduction

Oxidation of hydrocarbons is a key process in the chemical industry due to the wide ranging utility of the ensuing functionalized compounds as raw materials and intermediates in industrial and pharmaceutical chemistry.[1] Small, partially oxygenated hydrocarbons are used as building blocks in the manufacture of plastics and synthetic fibers. For example, oxidation products of cyclohexane, cyclohexanone and cyclohexanol are important raw materials for the production of adipic acid and caprolactam used for the manufacture of nylon.[2] Current processes for the production of these highly desired oxygenates in many cases involve stringent conditions, which may include high temperatures and pressures, strong acids, free radicals and corrosive oxidants.[3,4] Although these processes are currently being utilized they have low energy efficiencies as well as generating environmentally hazardous waste and by-products. Increased environmental concerns in recent years call for environmentally benign oxidants like molecular oxygen or hydrogen peroxide rather than organic peroxides and stoichiometric metal oxides, which have been widely employed until now.[4] The importance of hydrocarbon oxidation is evidenced by the large number of research papers appearing on this subject over a variety of homogeneous and heterogeneous catalytic systems and employing different oxidants such as hydrogen peroxide, *t*-butyl hydroperoxide and molecular oxygen. Notable catalysts for this oxidation include Na–GeX zeolite, titanium-containing mesoporous materials such as TS-1 and Ti-MCM-41 and metal-containing AlPO redox molecular sieves.[5–8] A recent review article by Schuchardt *et al.* acknowledges that efficient cyclohexane oxidation continues to be a challenge in spite of several research attempts.[9] Some attempts have been made for the oxidation of cyclohexane[10] and cyclooctane[11] under supercritical CO_2 medium, but with not much improvement in the conversion and selectivity. A few other studies describe the oxidation of other cycloalkanes such as cyclopentane, cycloheptane, cyclooctane and adamantine.[12–16] Therefore, a major challenge in this field is to find reaction pathways that afford the primary product with high selectivity at high conversion of the hydrocarbon.

Vanadium phosphorus oxide (VPO) is an efficient catalyst for the vapor phase *n*-butane oxidation to maleic anhydride.[17] This catalyst has been synthesized by various methods and characterized rather extensively by various techniques such as Raman, FT-IR, ^{31}P NMR, XPS, LEIS, EPR, *etc.* The better performance of this catalyst has been ascribed to the availability and easy switching (reversible sequential reduction and reoxidation) between the different oxidation states of vanadium on the catalyst surface. It is also known that the heterolytic oxygen transfer catalyzed by vanadium can operate by either high-valent peroxometal complexes or *via* oxometal species, depending on the substrate. Most of the literature has been focused only on *n*-butane oxidation, perhaps due to the commercial importance and success of maleic anhydride production using this catalyst. Amorphous microporous homogeneously mixed oxides of Ti, V, Fe, Zr, Cu, Mo, Co and Cr on silica (TiO_2–SiO_2, V_2O_5–SiO_2, Fe_2O_3–SiO_2, ZrO_2–SiO_2, CuO–SiO_2, Mo_2O_5–SiO_2, Co_2O_3–SiO_2 and Cr_2O_3–SiO_2) have been studied for cyclohexane oxidation using *t*-butyl hydroperoxide as the oxidant, however, with less than 10% conversion.[18] We have very recently accomplished an unprecedented and efficient oxidation of cyclohexane over VPO catalyst using H_2O_2 in acetonitrile under a nitrogen atmosphere.[19] The catalyst has not been well-explored for other hydrocarbon oxidations, which is a very important and challenging area. This paper focuses on this area, *viz.*, the utility of a well-characterized catalyst for a new and wide-ranging application such as oxidation of hydrocarbons, especially the C5–C10 cycloalkanes, in an environmentally benign oxidation protocol involving aqueous hydrogen peroxide in nitrogen atmosphere.

Results and discussion

The VPO catalysts are prepared by a variety of methods, all of which, however, eventually result in the same active phase. The most important of the synthesis steps is the initial preparation of the active phase precursor, vanadyl hydrogen phosphate hemihydrate, $(VO)HPO_4{\cdot}0.5H_2O$, which is then thermally decomposed and activated inside a reactor. The two main methods for the preparation of this precursor involve the reduction of V^{5+} (V_2O_5) to V^{4+} either in water by HCl or hydrazine or the reduction in an organic phase (2-butanol) in the presence of another reducing agent such as benzyl alcohol. The catalyst prepared by the organic route is rather more popular. Therefore, vanadium phosphorus oxide (VPO) with a P:V

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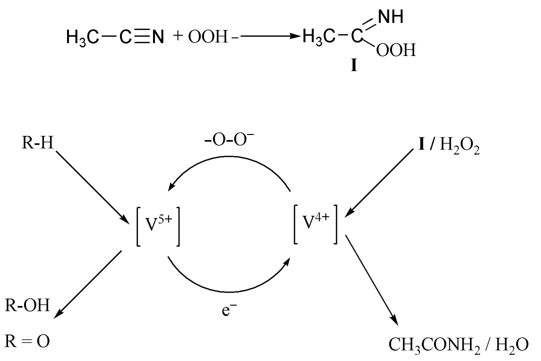
ratio of 1.1 was prepared by the organic route. XRD spectra of the catalyst after calcination showed high intensity peaks at 2θ values of 23.1°, 28.4° and 29.9°, characteristic of the presence of the $(VO)_2P_2O_7$phase, and also low intensity peaks at 2θ values of 22.0°, 26.0° and 28.9°, characteristic of the $VOPO_4$ phase.[17] This shows that the vanadium in the calcined catalyst sample was predominantly in the V^{4+} state with a small amount of V^{5+} species. The mechanism of formation of this phase involves the solubilization of V^{5+} through the formation of vanadium alcoholate followed by its reduction to V_2O_4 by the organic alcohol (benzyl alcohol). On the addition of H_3PO_4, V_2O_4 reacts with H_3PO_4 to form $(VO)HPO_4 \cdot 0.5\ H_2O$ at the solid–liquid interface, which on calcination forms $(VO)_2P_2O_7$.[20] The BET surface area of the calcined VPO catalyst is found to be 10 $m^2\ g^{-1}$.

We have earlier found that calcined VPO catalyst prepared by the organic route is highly active for the oxidation of cyclohexane using hydrogen peroxide and acetonitrile at 65 °C under nitrogen atmosphere where the maximum activity is obtained at a substrate-to-catalyst ratio of 385.[19] Acetone is also found to be another successful solvent. However, the reaction is much slower in solvents such as 1,4-dioxane and methanol whereas other solvents such as dichloromethane, methyl *t*-butyl ether, tetrahydrofuran and dimethyl sulfoxide are not found to be useful. Acetonitrile activates H_2O_2 by forming a perhydroxyl anion (OOH^-), which nucleophilically attacks the nitrile to generate a peroxycarboximidic acid intermediate (Scheme 1, **I**), which is a good oxygen transfer agent.[21] Acetone also activates H_2O_2 in a similar way but to a lesser extent than acetonitrile. In addition, acetonitrile and acetone have a comparatively good solubility power for both the organic substrate as well as the aqueous H_2O_2.

The use of the VPO catalysts for the oxidation of other similar substrates was explored by extending the reaction to a variety of other alkanes such as cyclopentane, methyl cyclohexane, isopropyl cyclohexane, *n*-hexane, cycloheptane, cyclooctane, *n*-octane, cyclodecane and adamantane; the results are presented in Table 1. Apparently, the VPO catalysts are effective for the oxidation of many of these substrates, which are usually difficult to accomplish. The oxidation protocol using VPO catalyst, however, is not useful for the selective oxidation of linear alkanes. For example, *n*-hexane gets over-oxidized (entry 5) whereas *n*-octane undergoes negligible oxidation (entry 8). On the other hand, cycloalkanes show very encouraging results. Approximate turnover numbers are also estimated on the assumption that all the vanadium in the catalyst sample was in the form of $(VO)_2P_2O_7$. The presence of a substituent in the carbon ring decreases the reactivity (entries 3 and 4). The higher the size of the substituent, the lower is the conversion. Most of the substrates studied formed their corresponding ketones as the major product with negligible or no formation of the respective alcohol, except cyclohexane (entry 2) and adamantane (entry 10). To the best of our knowledge, this kind of effective oxidation protocol for the oxidation of various cycloalkanes over any given catalyst has not been reported earlier and hence is very promising. This oxidation protocol is also much cleaner than the traditional oxidation processes using stoichiometric oxidants and peracids, which would produce copious amounts of undesired by-products. The catalyst preparation is also relatively simple and does not involve the use of any expensive precursor materials. The percentage of H_2O_2 consumed is determined by iodometric titration[22] after the end of each experiment and found to be in the range of 93–95%. This suggests that more than a stoichiometric amount of H_2O_2 is utilized in the reaction, which could be due to the non-selective thermal decomposition of H_2O_2 to oxygen and water at the reaction temperature.[23]



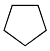
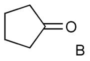
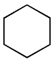
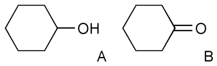
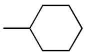
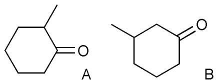
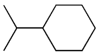
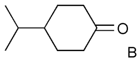
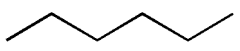
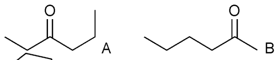
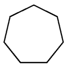
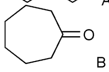
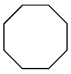
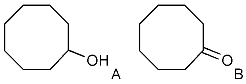
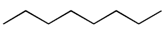
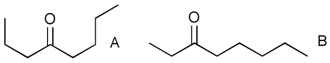
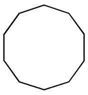
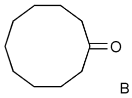
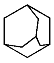
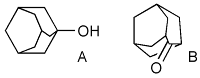
Scheme 1

The VPO catalyst is, however, soluble in the reaction mixture, forming a homogeneous solution and therefore not recoverable for recycling. Nevertheless, we have demonstrated that cyclohexane oxidation could be successfully carried out repeatedly by the addition of new batches of substrate along with the solvent and oxidant to the previous reaction mixture.[19] The same is found to be true also in the case of the other substrates studied here. The activity is found to decrease with successive batches, however, the reaction could be successfully completed by extending the reaction time.

XRD analyses show that the calcined VPO catalysts is composed mainly of the vanadyl pyrophosphate ($(VO)_2P_2O_7$) phase with a small amount of the $VOPO_4$ phase as if the latter is dispersed on a vanadyl pyrophosphate (VPP) support. P/V ratios in the precursor higher than the stoichiometric one stabilize the $(VO)_2P_2O_7$ phase from re-oxidation in the reactant atmosphere as well as during calcination in air at high temperatures.[20] VPO catalysts have a higher surface P/V ratio than the bulk P/V ratio, suggesting that they may be terminated by a distorted VPP structure, where the excess amount of phosphorus is positioned between the vanadyl units and the phosphate groups.[24] This may lead to the generation of more Lewis (V^{4+}) and Bronsted (P–OH) acid sites on the catalyst surface, which are stabilized due to the large cohesion of VO_6 pseudo-octahedra in the bi-dimensional framework at the surface. This stability is more pronounced in catalysts prepared in organic media. It is also observed that maximum catalytic performance requires a certain degree of disorder in the VPP lattice.[25] This is further supported by the improved catalytic efficiency observed for the tribomechanically treated crystallized VPP catalysts.[26] Catalysts calcined at lower temperatures (<750 °C) contain V^{5+} microdomains on the surface and isolated V^{5+} sites in the sublayers of the vanadyl pyrophosphate structure.[27] It may also be possible that different phases present in the calcined catalyst can cooperate to enhance the catalytic activity.

It is therefore expected that the mechanism of oxidation over VPO catalysts may involve a reversible V^{4+}/V^{5+} redox cycle as illustrated in Scheme 1.[19,28] Excess phosphorus at the surface stabilizes the pyrophosphate framework (V^{4+}) so that the V^{4+}/V^{5+} redox cycle is maintained in a dynamic equilibrium. This is why the reaction works better under nitrogen atmosphere than in the presence of air/O_2 as the availability of oxygen hinders the reduction of V^{5+} species to V^{4+}. The decrease in the conversions for methyl cyclohexane (entry 3, Table 1) and isopropyl cyclohexane (entry 4, Table 1) is in accordance with the expected cyclic intermediate on the catalyst surface as per the above mechanism and the effect of steric restrictions to form the transition state complex leading to the oxygenated products. The presence of excess phosphorus prevents the oxidation of the surface (and the bulk) to the β-$VOPO_4$ phase, which has a deleterious effect on catalyst performance.[29] The redox mechanism is also evident from the color of the reaction mixture wherein the initial green color of the reaction mixture (V^{4+}) slowly changes to greenish-yellow to brown (V^{5+}), which further changes to green (V^{4+}). In other words, it appears that dispersed V^{5+} species

Table 1 Oxidation of various hydrocarbons over VPO catalysts using H_2O_2 under N_2[a]

Entry	Alkane	Products	T/°C	Time/h	% Conversion	TON	% Selectivity A	% Selectivity B
1[b]			50	4	23	22	–	100
				8	35	33	–	100
				20	48	46	–	100
2			65	4	70	135	49	51
				8	84	162	50	50
				20	96	185	50	50
3			65	4	16	31	50	50
				8	27	52	52	48
				20	36	69	49	51
4			70	4	2	4	–	100
				8	4	8	–	100
				20	8	15	–	100
5			65	4	10	19	100	00
				8	80	154	22	12[c]
6			70	4	46	88	–	100
				8	55	106	–	90[d]
				20	56	108	–	93[d]
7			70	4	45	87	12	76[d]
				8	47	90	–	78[d]
				20	47	90	–	78[d]
8			70	4	0	–	–	–
				8	4	8	53	47
				20	6	12	49	51
9			70	4	21	40	–	100
				8	24	46	–	100
				20	28	54	–	100
10[e]			70	4	13	25	73	27
				8	17	33	69	31[f]
				20	25	48	49	30[f]

[a] Substrate = 12.5 mmol, acetonitrile = 10 mL, catalyst = 10 mg, H_2O_2 = 7 g. [b] Catalyst = 20 mg. [c] Remaining acids (formic acid = 30%, acetic acid = 11%, propanoic acid = 26%). [d] Remaining acid products. [e] Acetonitrile = 20 mL. [f] Remaining adamantane-1,3-diol, TON = turn over number, number of molecules of product formed per active site.

in combination with $(VO)_2P_2O_7$ (V^{4+}) is important for the oxidation of cyclohexane whereas the V^{5+} act as a dynamic oxidizing center. Calcination of the catalyst at high temperature results in more β-$VOPO_4$ phase, which is detrimental to the catalytic activity.

In summary, the calcined VPO catalyst with a P/V ratio 1.1 is found to be a very active catalyst for the oxidation of alkanes, especially cycloalkanes such as cyclopentane, cyclohexane, cycloheptane, cyclooctane, cyclodecane and adamantane, to their respective oxygenates using hydrogen peroxide under nitrogen atmosphere. The active center for the oxidation is believed to be $(VO)_2P_2O_7$ sites (V^{4+}) in combination with dynamic V^{5+} sites involving a reversible redox cycle. The VPO catalyst can also be successfully reused for the reaction.

Experimental

Vanadium phosphorus oxide (VPO) catalyst with a P/V of 1.1 was prepared by refluxing an appropriate quantity (10 g) of V_2O_5 in a mixture of isobutanol (30 mL) and benzyl alcohol (15 mL) for 12 h, followed by addition of the required quantity of 85% H_3PO_4 (P/V = 1.1) and refluxing for a further 6 h to give a light green precipitate.[17,20] The precipitate was filtered off, dried at 110 °C overnight and then calcined in air at 400 °C for 4 h.

The VPO catalyst was characterized by X-ray diffraction analysis using a Siemens D5000 diffractometer with a Cu-Kα radiation running at 40 kV/30 mA in the 2θ range of 10° to 80° with a step size of 0.05°. The single-point BET surface area of the catalyst was determined using N_2 adsorption at −196 °C (77 K) using a Micromeritics Auto Chem. II instrument (Model 2920).

Oxidations of various alkanes were conducted in a 100 mL round-bottomed flask fitted with a reflux condenser and a magnetic stirrer. In a typical reaction procedure, 12.5 mmol substrate was mixed with 10 mg of calcined VPO catalyst, 10 mL solvent and 50 mmol of 30% hydrogen peroxide and the mixture was kept at 50–70 °C using a heating mantle with vigorous stirring under nitrogen atmosphere. The reaction mixture was sampled at regular intervals and the aliquot extracted with ether. The organic layer was analyzed by a Hewlett–Packard 6890 gas chromatograph using an HP-5 5% phenyl methyl siloxane capillary column (30 m × 20 μm × 0.25 μm) and a quadrupole mass filter equipped HP 5973 mass selective detector. The aqueous phase was also analyzed to detect any acid formation using an HPLC (Finnigan-mat-LCQ) system using a Supelcogel™ H 59346 column (25 cm × 4.6 mm) with a water–phosphoric acid solution as the eluent. The conversion and product selectivities reported are based on the GC yield. Quantification of the oxygenated products was obtained using a multi-point calibration curve for each product.

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