

Vanadium phosphorus oxide composite as an efficient catalyst for hydrocarbon oxidations using tert-butyl hydroperoxide

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ABSTRACT

Calcined vanadium phosphorus oxide (VPO) prepared by an organic method is found to be an active and effective catalyst for the oxidation of various alkanes such as cyclohexane, n-hexane and cycloheptane in acetonitrile solvent using the environmentally benign oxidant, tert-butyl hydroperoxide, where the oxidation mechanism is believed to involve a reversible V^{4+}/V^{5+} redox cycle. This heterogeneous catalyst at the end of the reaction is easily separated by the least cost of the product. This reaction is investigated in a polar and nonpolar solvent with different dielectric constant. Cobalt metal is also used as a catalyst enhancer and TBHP as an oxidizing agent. After catalytic tests and determining the best catalyst and ideal amount of cobalt percent improvement, detection and analysis will be done by analyzing XRD, SEM, TGA, IR.

Keywords: Cyclohexane; VPO Catalyst; TBHP; Acetonitrile.

1. 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]. Partially oxygenated hydrocarbons are used as

building blocks in the manufacture of plastics and synthetic fibers. For example, oxidation products of cyclohexane, cyclohexanone and n-hexane 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 [3-5]. 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. Characterized rather extensively by various techniques such as, FT-IR, XPS, XRD and SEM. The better performance of this catalyst has been ascribed to the availability. We have very recently accomplished an unprecedented and efficient oxidation of cyclohexane over VPO catalyst using tert-butyl hydroperoxide in acetonitrile under an atmosphere

2. 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 $\frac{1}{4}$ 1.1) and refluxing for a further 6 h to give a light green precipitate. The precipitate was filtered off, dried at $110^\circ C$ over night and then calcined in air at $400^\circ C$ for 4 h. Oxidations of various alkanes were conducted in a 100 mL round-bottomed flask fitted with a reflux condenser and 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% tert-butyl hydroperoxide and the mixture was kept at $50-70^\circ C$ using a heating mantle with vigorous stirring under atmosphere. The reaction mixture was sampled at regular intervals and the aliquot extracted with ether [6, 7].

3. 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 [7]. 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 We have earlier found that calcined VPO catalyst prepared by the organic route is highly active for the oxidation of cyclohexane [8] using tert-butyl hydroperoxide and acetonitrile at $65^\circ C$ 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, tetra hydrofuran and dimethyl sulfoxide are not found to be useful. Acetonitrile activates tert-butyl hydroperoxide by forming a perhydroxyl anion (OOH), which nucleophilic ally attacks the nitrile to generate a peroxy-carboximidic acid intermediate which is a good oxygen transfer agent. Acetone also activates tert-butyl hydroperoxide [8] in a similar way but to a lesser extent than acetonitrile [9].

XRD spectra of the catalyst after calcination show high intensity peaks at 2θ values of 23.18, 28.48 and 29.98 characteristic of the presence of vanadyl pyrophosphate phase $((VO)_2P_2O_7)$ and also low intensity peaks at 2θ values of 22.08, 26.08 and 28.98 characteristic of $VOPO_4$ phase (Fig. 1) [10]. This suggests that vanadium in the calcined catalyst sample is predominantly in V^{4+} state with the presence of 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 cyclohexan 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 $(VO)HPO_4 \cdot 0.5H_2O$ at the solid-liquid interface which on calcination forms $(VO)_2P_2O_7$. The BET surface area of the calcined VPO catalyst is found to be $10 \text{ m}^2/\text{g}$.

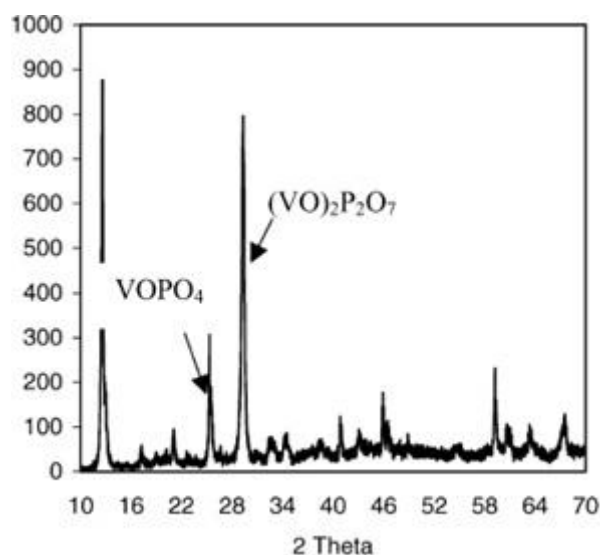


Fig 1. XRD spectra of the VPO catalyst.

The FE-SEM micrograph of the catalysts revealed that the samples possess a slate like morphology (Fig. 2). Further, aggregates without regular shapes are observed in VPO. This is the reason for the low surface area of the VPO catalyst than of Al-VPO. However, the morphology of VPO was not affected significantly by Aldoping.

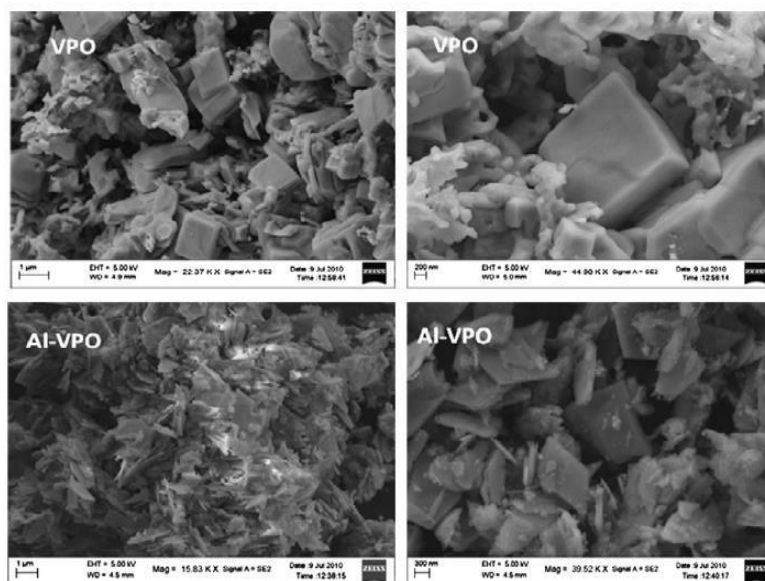


Fig 2. SEM micrograph of the VPO catalyst.

To accomplish better toluene conversion and maximum *p*-cymene selectivity, liquid-phase isopropylation of toluene was carried out over 5 wt.% Al-VPO catalyst at various reaction temperatures, and the results are depicted in Fig. 3 [9]. It has been found that the toluene conversion increases up to 150°C and remains constant thereafter. This could be attributed to the coke deposition caused by dealkylation, which in turn leads to the oligomerization of olefins. On the other hand, the increase in toluene conversion at lower temperatures may be due to the clustering of alcohols around the brønsted acid sites of the catalyst through H-bonding [10].

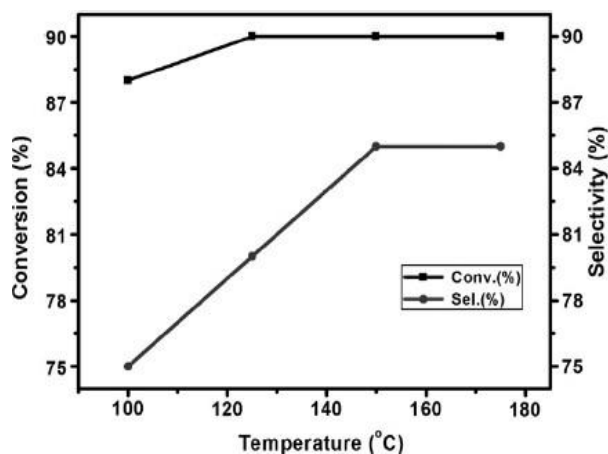


Fig 3. Conversion and selectivity at various reaction temperatures.

As a result, its dissociation to cyclohexan carbocations will be suppressed at higher temperatures. But at higher temperatures, the alcohols will have a decreased tendency to form molecular clusters, and so they can freely form carbonium ions via protonation.

4. Conclusions

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.

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