Novel vanadium phosphate phases as catalysts for selective oxidation

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Abstract. In our effort to induce novel modifications in the structure of some important vanadium phosphate phases used as selective oxidation catalysts, it has been observed that metal ions such as Zn$^{2+}$, Ni$^{2+}$, Pd$^{2+}$ can be incorporated into the vanadyl hydrogen phosphate VOHPO$_4$$\cdot$$0$$\cdot$$5$$\cdot$$2$O phase in very different ways depending upon the medium of preparation. It has been found that the metal ions are either substituted into the lattice with retention of structure of the parent compound or intercalated between the layers of a new mixed-valent phase. These new metal-incorporated phases are catalytically active and the palladium incorporated compound in particular displays shape selective catalysis for different oxidation and reduction reactions. In another approach, the preparation of VOHPO$_4$$\cdot$$0$$\cdot$$5$H$_2$O has been modified to give a novel crystalline phase containing mixed-valent vanadium and having NH$_3$ species bound to the lattice. This phase could be a potential catalyst for ammoxidation reactions. In addition, novel mesostructured vanadium phosphate phases have been prepared using a long-chain amine as the templating agent involving a ligand templating mechanism of formation.

Keywords. Vanadium phosphate; selective oxidation; structure modification.

1. Introduction

One of the most important applications of selective oxidation catalysts is the functionalization of alkenes and aromatics because of the ease and economy with which they can be obtained from petroleum$^1$. However, the trend now is to functionalize alkanes directly since they are relatively even more economical and readily available raw materials.

The major challenge in the selective oxidation of hydrocarbons is that thermodynamics favours total oxidation and the C–H bonds in the initial reactant are generally stronger than those in the intermediate products which makes them prone to rapid further oxidation$^2$. The key step therefore is to stop the oxidation at the desired compound through kinetic control. This can be done only by designing the nature of active sites of the catalyst such that it is able to control the relative rates of different reaction pathways – accelerating the steps leading to the desired product and hindering those which give unwanted products.

Presently, the only selective gas-phase alkane oxidation that has been commercialized is the oxidation of butane to maleic anhydride$^3$. One major advantage in this reaction is that the stability of the product is higher than that of the starting alkane. However, the apparent paradox of catalytic chemistry, that higher yield and selectivity to maleic

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anhydride are obtained in the oxidation of \( n \)-butane than in the oxidation of butenes, opens up the possibility that with a suitable choice of catalyst it may be possible to obtain a better performance in the selective oxidation of other alkanes rather than the corresponding alkene.

Catalysts used for selective oxidation are generally oxides, and vanadium and molybdenum oxides are the most widely used ones for the selective oxidation of alkanes. Amongst these the most preferred element is vanadium. A vanadium pyrophosphate phase \((\text{VO})_2\text{P}_2\text{O}_7\) is commercially used as catalyst for the selective oxidation of butane to maleic anhydride. Vanadium phosphorous oxides (VPO) have also shown promising results as heterogeneous catalysts in the selective oxidation of propane to acrylic acid, pentane to maleic and phthalic anhydride, and in the oxidative dehydrogenation of ethane, propane etc.\(^4\)

Vanadium phosphates constitute a very interesting class of layered compounds which exist in a wide range of structural forms both due to the variable valency of vanadium as well as the large diversity in the bonding of the \( \text{VO}_6 \) octahedron and the \( \text{PO}_4 \) structural units.\(^5\) Several phases containing vanadium in +5, +4 and +3 oxidation states are known. In all these compounds the layers are held together by hydrogen bonding or by weak Van der Waal’s interactions. These layered compounds are therefore amenable for intercalation reactions.

In the present work we describe different approaches that have been adopted to synthesise novel phases in the VPO system as well as modify the structures of some known catalytically important vanadium phosphate phases. In addition the catalytic activity of some of these new and modified phases have been investigated.

2. Experimental section

2.1 Preparation of metal incorporated phases

The \( \text{VOHPO}_4\cdot0.5\text{H}_2\text{O} \) phase was prepared by a published method\(^6a\) involving the reduction of an aqueous slurry of \( \text{V}_2\text{O}_5 \) with \( \text{NH}_2\text{OH}\cdot\text{HCl} \) followed by the addition of a stoichiometric amount of 85% phosphoric acid (P:V = 1:1). In the preparation of the intercalation compounds, the relevant metal salt was added to the \( \text{V}_2\text{O}_5 \) slurry (V/M = 1:0.2, M = Zn, Ni, Pd). The zinc, nickel and palladium incorporated compounds are coded as \( \text{A/Zn}, \text{A/Ni} \) and \( \text{A/Pd} \) respectively. However, in the synthesis in organic medium\(^6b\), the reduction of \( \text{V}_2\text{O}_5 \) was carried out by isobutanol-benzyl alcohol mixture and the relevant metal salts were added in the same atomic ratio of P:V:M = 1:1:0.2. The metal intercalates were coded as \( \text{O/Zn}, \text{O/Ni} \) and \( \text{O/Pd} \).

2.2 Synthesis of new phases through modification of conventional procedures

For the preparation of a new phase the conventional method for the preparation of \( \text{VOHPO}_4\cdot0.5\text{H}_2\text{O} \) in aqueous medium was modified as described above by introducing a time delay between the onset of the reduction of \( \text{V}_2\text{O}_5 \) with hydroxylamine hydrochloride and the addition of phosphoric acid. The final phases were then isolated in the usual manner as described above in the preparation of \( \text{VOHPO}_4\cdot0.5\text{H}_2\text{O} \). The phases obtained at different delay times of 0 to 10 min are referred to as \( \text{P-0}, \text{P-1}, \text{P-2}, \text{P-3}, \text{P-4}, \text{P-5}, \text{P-6}, \text{P-7}, \text{P-8}, \text{P-9}, \text{P-10} \) respectively.