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Liquid phase catalytic oxidation of benzyl alcohol to benzaldehyde over vanadium phosphate catalyst

Gobinda Chandra Behera, K.M. Parida*

Colloids and Materials Chemistry Department, Institute of Minerals and Materials Technology (CSIR), Bhubaneswar 751013, Orissa, India

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ABSTRACT

Vanadium phosphate (VPO) is well known as a heterogeneous catalyst in gas phase oxidation reactions. Till date, this material has not drawn much attention for its application in liquid phase reactions. This paper briefly highlights our recent research on vanadyl metaphosphate concerning its fabrication, characterization and application towards liquid phase oxidation of benzyl alcohol to benzaldehyde using tert-butyl hydroperoxide (TBHP) as the oxidant. In our preliminary catalytic studies, we find that the $VO(PO_3)_2$ exhibits extraordinarily high activity and selectivity in oxidation of benzyl alcohol under mild conditions. The benzyl alcohol conversion is largely increased but the selectivity for benzaldehyde is slightly decreased with the increase in reaction period or temperature. The present catalyst $VO(PO_3)_2$ showed remarkable catalytic activity with respect to other catalytic system; conversion and selectivity with respect to aldehyde is 97 and 99%, respectively.

1. Introduction

Vanadium phosphate materials continue to attract attention of researchers as a well studied heterogeneous catalyst. Recent interest in VPO solid materials stems from their structural diversity and potential application in catalysis and material science. An astonishing variety of novel phases of this material arises due to versatility of vanadium in terms of its variable oxidation states (III, IV, V) and co-ordination geometry (tetrahedral, square pyramidal and octahedral). There are many well characterized, crystalline VPO phases were identified whose structure and catalytic properties have been well documented. Some of the most widely studied are the V^{5+} vanadyl ortho phosphate (α-, β-, γ-, δ-, ε- and ω-$VOPO_4$) and $VOPO_4{\cdot}2H_2O$), and the V^{4+} vanadyl hydrogen phosphates ($VOHPO_4{\cdot}4H_2O$, $VOHPO_4{\cdot}0.5H_2O$, $VO(H_2PO_4)_2$), vanadyl pyrophosphate ($(VO)_2P_2O_7$) and vanadyl metaphosphate ($VO(PO_3)_2$).

The $(VO)_2P_2O_7$ catalyst and its precursor $VOHPO_4{\cdot}0.5H_2O$ phase have been extensively studied, including preparation procedures, activation conditions, crystal structures, activity and catalytic kinetics [1–9]. On the other hand, the crystalline $VO(PO_3)_2$ catalyst is mostly a combination of amorphous $VO(PO_3)_2$, monoclinic α-$VO(PO_3)_2$ [10] and tetragonal β-$VO(PO_3)_2$ phases [11]. The crystalline $VO(PO_3)_2$ was obtained from calcination of $VO(H_2PO_4)_2$ phase under air flow conditions. The catalytic performance of both $VO(PO_3)_2$ and $(VO)_2P_2O_7$ have been evaluated in gas phase reactions such as oxidations, oxidative dehydrogenations and ammoxidations [12–19]. However, $VO(PO_3)_2$ catalyst has shown poor catalytic performance in gas phase oxidation of *n*-butane to maleic anhydride when compared to high catalytic performance of $(VO)_2P_2O_7$ catalyst. The poor catalytic performance of $VO(PO_3)_2$ catalyst in *n*-butane oxidation has made to test its application in other reactions.

Liquid phase oxidation of benzyl alcohol is a hot topic in modern organic synthesis. The design and development of a catalyst with high conversion and selectivity for partial oxidation must also be carried out with regard to the preservation of oil related resources. For selective oxidation reactions, there is tremendous challenge to prevent over oxidation of the products, which are often more sensitive to be oxidized than the reactants. The direct oxidation of benzyl alcohol to benzaldehyde is such type of reaction. Benzaldehyde is a chief raw material in the synthesis of other organic compounds, ranging from pharmaceuticals to plastic additives. It is also an important intermediate for the processing of perfume and flavoring compounds and in the preparation of certain aniline dyes.

Several methods are available for alcohol oxidations using metal salts in the form of homogeneous catalysis [20–26] or supported metal ions as heterogeneous catalysts [27–31]. However the common methods of alcohol oxidation may use toxic, corrosive, expensive oxidants such as chromium (VI), and setting up a severe condition, like high pressure or temperature, using strong mineral acids.

Structural stability, heterogeneity, deactivation rates and recyclability of the solid acid catalysts are still critical impending to the liquid phase reaction's impact on solid catalyst [32]. Although

* Corresponding author. Tel.: +91 674 2581636 425; fax: +91 674 2581637.
E-mail address: paridakulamani@yahoo.com (K.M. Parida).

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