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Substrate Oxidation Prompted by Solvent Dissociation: The Role of Peroxo-Vanadate and Ag- π Interaction

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ABSTRACT

Silver-sulphur hydroxo-peroxo vanadate species generated from silver-sulphur-oxido vanadium cluster favoured by the heterolytic dissociation of C-CN bond of acetonitrile was found to be highly active for selective oxidation of benzyl alcohol at low temperature and in presence of hydrogen peroxide. The *in situ* generated active peroxo-vanadium species was well characterized via electrospray ionization technique and various spectrochemical analyses. Benzyl alcohols with different substituents were successfully and selectively oxidized to its corresponding aldehydes. The reactions were highly solvent selective and it proceeded well only in acetonitrile. The formation of the product even in presence of free radical trapping agent revealed for the non-free radical mechanism. Density functional theory (DFT) calculations on the mechanism of benzyl alcohol oxidation suggested that Ag- π interaction played a significant role in stabilizing the intermediates and transition states.

1. Introduction

Oxidation of benzyl alcohol (BA) to benzaldehyde is one of the well known reactions that are being mostly studied due to the high applicability of benzaldehyde in pharmaceutical industries [1–4]. The dehydrogenation process although looks to be simple but from practical point of view it is much difficult to have control over the desired product [5–7]. In maximum cases the benzaldehyde formation is accompanied by over-oxidation of benzaldehyde to benzoic acid and thereby lowers the selectivity [8–10]. From kinetic modelling study it was also revealed that the oxidation of BA proceeded through different pathways leading to different by-products like toluene, benzoic acid and benzyl benzoate [11,12]. The main disadvantage associated with the reaction is the use of oxidant like H₂O₂ which follows the free radical mechanism and limits the product selectivity [8,13]. So, current emphasis has been made to develop a reaction pathway that would bypass the classical free radical mechanism [14–16]. Reaction through benzylic C-H bond activation is considered to be an alternate approach to have control over the autoxidation process [17]. Some success has been obtained in case of the reaction where the metals like silver (Ag) acts as co-catalyst to activate the benzylic C-H bond and lowers the activation barrier [17,18].

Out of the various transition metal catalysts, oxides of vanadium or

vanadium metal complexes are also known to be effective catalyst for such oxidation process [19–21]. However, they demands for some costly reaction conditions to bring out the selectivity in the product formation [19–21]. Hence feasibility of the vanadium-based catalyst in this particular reaction is less emphasized. At the same time silver (Ag) supported in various metal oxides although known to be efficient catalyst for various organic transformations [22] but its involvement in BA oxidation with vanadium oxides are so far not explored in literature. Furthermore, metal- π interactions [23,24] are ubiquitous in nature and play a significant role in organometallic catalysis [25,26]. But such effect is not well understood in BA oxidation and involvement of Ag through Ag- π interaction [27] during BA oxidation has not been reported to best of our knowledge.

Apart from depending on the type of catalyst or metals, the oxidation of BA is also hampered by various physical parameters like temperature, solvent etc., [8]. High temperature condition results in loss of selectivity and hence catalyst that could promote such reaction at low temperature is more desirable [28–30]. The solvents can also play vital role in modulating the suitable reaction path [31]. However, the dissociation of solvent like acetonitrile (CH₃CN) for generation of active species during the BA oxidation is less known. Therefore, the current study is mostly focussed on the formation of an active peroxo-vanadate species from a silver-sulphur oxido vanadium cluster via the heterolytic

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