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Alcohol Oxidation by Vanadium Catalysts

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ABSTRACT: Oxidation of various alcohols such as benzyl alcohol, 1-phenylethanol, and cyclohexanol was studied over vanadium catalysts using tert-butyl hydroperoxide as an oxidant. Vanadium complexes with catecholates or pyrazine 2-carboxylate ligands were prepared and characterized by Fourier transform infrared spectroscopy, ^1H nuclear magnetic resonance spectroscopy, ultraviolet-visible spectroscopy, and elemental analysis. The effect of solvent was investigated. It was found that when the oxidation reaction was performed in toluene solvent, benzyl alcohol was oxidized to benzaldehyde without any overoxidation to benzoic acid; on the contrary, in acetonitrile solvent, both benzaldehyde and benzoic acid were formed. The catalytic activity of some vanadium phosphorus oxides was also compared, and the results showed that higher product yields were obtained when using acetonitrile as the solvent than using toluene.

KEYWORDS: oxidation, vanadium, alcohol, catalysts, reaction, elemental, spectroscopy

I. INTRODUCTION

A review indicated that Dipicolinate vanadium(V) alkoxide complexes $(\text{dipic})\text{V}(\text{V})(\text{O})(\text{OR})$ (OR = isopropoxide (1), n-butanoxide (2), cyclobutanoxide (3), and α -tert-butylbenzylalkoxide (4)) react with pyridine to afford vanadium(IV) and 0.5 equiv of an aldehyde or ketone product. The role of pyridine in the reaction has been investigated. Both NMR and X-ray crystallography experiments indicate that pyridine coordinates to 1, which is in equilibrium with $(\text{dipic})\text{V}(\text{V})(\text{O})(\text{O}(\text{i})\text{Pr})(\text{pyr})$ (1-Pyr). Kinetic studies of the alcohol oxidation suggest a pathway where the rate-limiting step is bimolecular and involves attack of pyridine on the C-H bond of the isopropoxide ligand of 1 or 1-Pyr. The oxidations of mechanistic probes cyclobutanol and $[1,2]$ α -tert-butylbenzylalcohol support a two-electron pathway proceeding through a vanadium(III) intermediate. The alcohol oxidation reaction is promoted by more basic pyridines and facilitated by electron-withdrawing substituents on the dipicolinate ligand. The involvement of base in the elementary alcohol oxidation step observed for the dipicolinate system is an unprecedented mechanism for vanadium-mediated alcohol oxidation and suggests new ways to tune reactivity and selectivity of vanadium catalysts.[3,4]

In another study, Dipicolinate vanadium(V) alkoxide complexes $(\text{dipic})\text{V}(\text{V})(\text{O})(\text{OR})$ (OR = isopropoxide (1), n-butanoxide (2), cyclobutanoxide (3), and α -tert-butylbenzylalkoxide (4)) react with pyridine to afford vanadium(IV) and 0.5 equiv[5,6] of an aldehyde or ketone product. The role of pyridine in the reaction has been investigated. Both NMR and X-ray crystallography experiments indicate that pyridine coordinates to 1, which is in equilibrium with $(\text{dipic})\text{V}(\text{V})(\text{O})(\text{O}(\text{i})\text{Pr})(\text{pyr})$ (1-Pyr). Kinetic studies of the alcohol oxidation suggest a pathway where the rate-limiting step is bimolecular and involves attack of pyridine on the C-H bond [7,8] of the isopropoxide ligand of 1 or 1-Pyr. The oxidations of mechanistic probes cyclobutanol and α -tert-butylbenzylalcohol support a two-electron pathway proceeding through a vanadium(III) intermediate. The alcohol oxidation reaction is promoted by more basic pyridines and facilitated by electron-withdrawing substituents on the dipicolinate ligand. The involvement of base in the elementary alcohol oxidation step observed for the dipicolinate system is an unprecedented mechanism for vanadium-mediated alcohol oxidation and suggests new ways to tune reactivity and selectivity of vanadium catalysts.[9,10]

In another research Oxidation of various alcohols is studied in liquid phase under nitrogen atmosphere over vanadium phosphorus oxide catalyst in an environmentally friendly protocol using hydrogen peroxide. The catalyst and the method are found to be suitable for the selective oxidation of a variety of secondary aliphatic, alicyclic and aromatic alcohols to the corresponding ketones. The catalyst is soluble in the reaction mixture, however, it could be reused by the addition of new batch of substrate along with the solvent and oxidant to the previous reaction mixture. The reaction mechanism is expected to involve a redox cycle in which V^{4+} in combination with dynamic V^{5+} sites are acting as the active centers. The active V^{4+} phase is expected to be a vanadium complex with oxo and phospho ligands.[11,12]

Vanadium complexes have been used extensively to catalyze olefin and alcohol oxidation. However, their application in C-H oxidation has not been well-studied. We report herein that commercially available Cp₂VCl₂ catalyzes benzylic C-H oxidation selectively and effectively, giving no aromatic oxidation products. Mixed-valence vanadium oxide particles grafted onto a variety of oxide supports. In these catalysts V₆O₁₃ species with mixed oxidation states (V⁴⁺ or V⁵⁺) are believed to be catalytically active sites. These catalysts successfully enable alcohol oxidation to selectively



produce aldehydes and ketones using O₂ as the oxidant. The catalytic process is driven by visible light irradiation at room temperature and, most importantly, progresses with negligible overoxidation. The catalysts can even selectively oxidize aliphatic alcohols, which are much more challenging to control in comparison to aromatic analogues.[13,14] They can also be applied to the activation and oxidation of the otherwise stable C–H bonds of saturated aromatic hydrocarbons, such as toluene and xylene, under irradiation. Both experimental results and density functional theory (DFT) simulations suggest the formation of V₆O₁₃-alkoxide species as the initial step in the catalytic cycle. The V₆O₁₃-alkoxide then acts as the light harvester, being excited by light of wavelength shorter than 550 nm. Facile room-temperature C–H bond cleavage in the excited state V₆O₁₃-alkoxide in the presence of O₂ leads to the carbonyl-containing products. [15,16] These findings demonstrate an example of light-driven selective oxidation of diverse alcohols via in situ formation of photoresponsive V₆O₁₃-alkoxide species. This catalytic process is especially valuable for the synthesis of temperature-sensitive products and represents an alternative pathway to many conventional thermal oxidation reactions.

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,[17,18] we find that the VO(PO₃)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(PO₃)₂ showed remarkable catalytic activity with respect to other catalytic system; conversion and selectivity with respect to aldehyde is 97 and 99%, respectively.[19,20]

II. DISCUSSION

Keggin-type heteropolyoxometalates has been used as catalysts for the oxidation of benzylic alcohols and secondary alcohols to the corresponding carbonyl compounds using environment-friendly H₂O₂ as oxidant at room temperature. The catalysts used in this study exhibit high selectivity in the oxidation of alcohols with no over-oxidation and formation of carboxylic acids. For vanadium(V)-substituted heteropolyoxometalates [H_{x-2}PV_xW_{12-x}O₄₀]⁵⁻ (x= 4 for POM 1 and 6 for POM 2), the catalytic activity decreases with increasing number of vanadium atoms in the catalyst.[21,22]

Fluidized bed reactors as an option to avoid the well-known hot spot temperatures. However, owing to their low mechanical resistance, un-supported iron molybdates are not suitable for this configuration.

Currently, research is focused on finding a suitable catalyst. Until now, low surface area silica seemed to be the best support, but the activity of this supported iron molybdate is much lower than that of the un-supported material.[23,24] The replacement of part of the Mo by other elements (such as V, Sb, P, Sn and Mn) could probably lead to more active supported catalysts. Nevertheless, there is a need for more re-search in this area

Vanadium oxides have redox properties that make them very interesting catalysts for oxidation reactions, especially in the highest oxidation states (V₂O₅). For instance, when using bare powdered V₂O₅ at 50% methanol conversion the main product is formaldehyde, whereas at higher conversion methylformate is the main product.8 Different kinds of vanadates have been extensively investigated by Wachs et al.;9-11 more specifically, in a patent[25,26] they claimed that bulk metal vanadates possess higher activity than the traditional MoO₃-Fe₂(MoO₄)₃ catalysts for methanol selective oxidation, thus making it possible to use them at lower temperatures while maintaining selectivity and also avoiding the problems related to catalyst deactivation by volatilization. Among the catalysts tested, those that performed better (at methanol conversion higher than 96%) were CrVO₄, NbVO₅ and Ni₃(VO₄)₂ with 90.4, 90.0 and 94.0% selectivity to formaldehyde, respectively (at 300 °C and a methanol-oxygen-helium feed gas composition of 6 : 13 : 81 mol%).

In another investigation by Wachs and co-workers[27] on methanol oxidation over bulk FeVO₄ and supported 4% V₂O₅-a-Fe₂O₃, it was found that both surfaces are similar and consist of VO_x species which are the catalytically active sites.



III. RESULTS AND CONCLUSIONS

The study was performed with temperature-programmed IR spectroscopy comparing the individual oxides, supports and the bulk catalyst while methanol was being adsorbed. They found that in all cases the species CH_3OH^* and CH_3O^* are present on the catalyst surface with the exception of the acidic $\alpha\text{-Fe}_2\text{O}_3$, yielding dimethyl ether (DME).

Instead, for V_2O_5 , FeVO_4 and supported 4% $\text{V}_2\text{O}_5\text{-}\alpha\text{-Fe}_2\text{O}_3$, both surface intermediates gave rise mainly to HCHO (see Scheme 8.1). The results were confirmed with HR-TEM[28] images showing an amorphous VO_x -enriched layer of 1 nm at the outer surface of the bulk FeVO_4 catalysts and also by the increased V : Fe atomic ratio in the surface of the FeVO_4 particles found in the elemental analysis by electron energy loss spectroscopy (EELS).

Recently, a catalyst formulation containing V and Sb supported on silica was patented by Wacker Chemie, 14 claiming a high yield for methanol oxidation to formaldehyde (92,1%), which is of great importance in moving towards fluidized bed technology.[29,30]

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