

Chapter - 3

Heterogeneous Nanocomposites in Benzyl Alcohol Oxidation

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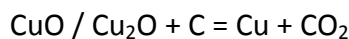
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Abstract— *This chapter briefly discusses the importance of alcohol oxidation (benzyl alcohol) and its mechanism in the different metal-based supported catalyst. The difficulties in such oxidation process have also been emphasized. The role of zeolite in such oxidation process has also been discussed in this chapter*

Introduction

A Brief Review on Oxidation-Reduction Process

Oxidation is a phenomenon in which an element or a molecule binds to an electronegative element, i.e., the element or the molecule loses an electron. It is a process that is also characterized by the addition of oxygen or removal of hydrogen from the element. The history of oxidation-reduction reactions dates 7500-4500 years back, during the copper/bronze age. In the presence of carbon, copper ores were heated to produce copper metals (reduction) and carbon dioxide (oxidation).^{1,2}

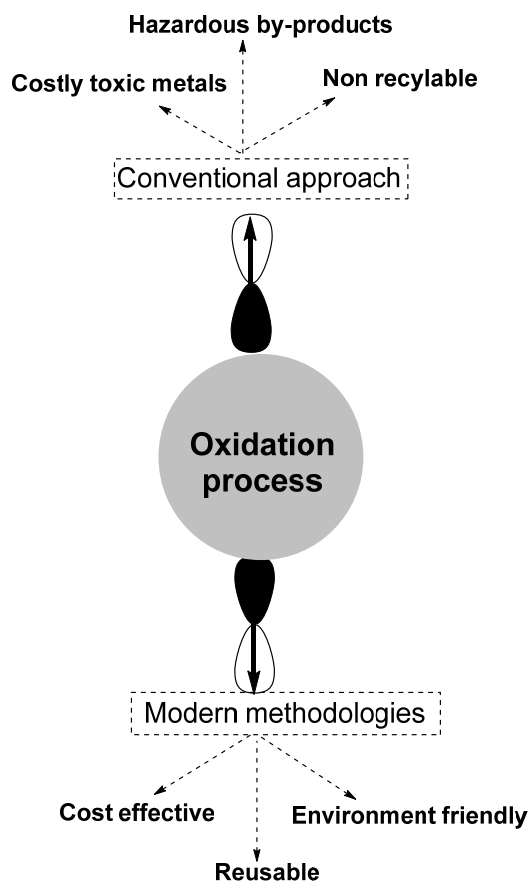


A similar process was also applied to iron ores during the Iron age (4500-3500 years back). The most important step in understanding the oxidation-reduction reactions dates back to the eighteenth century when Joseph Priestley prepared oxygen in the laboratory by heating mercury oxide to form elementary mercury and oxygen. This reaction was also an oxidation-reduction reaction, as mercury was reduced and the oxide ion was oxidized. Antoine Lavoisier, the Father of Chemistry, recognized that when substances are burned, they combine with oxygen. He even schemed out that food burns in our body to give off carbon dioxide and produce energy for all the bodily processes.^{1,2}

Oxidation processes are mainly used by the chemical industries to produce useful chemical reagents from different petroleum-based feedstock. Nowadays, keeping the importance of environmental safety, most of the pharmaceutical industries are limiting the use of different toxic reagents in such oxidation process due to several issues like disposal problems and other several reasons related to toxic organic solvents. The development of any procedures requires satisfying the green principles and also by considering sustainable chemistry. So to cope with such problems, various researchers are nowadays devoting their time and research for the development of several strategies. A pictorial diagram for the benefits of the modern and conventional approach is shown below.^{3,4}

In modern synthetic chemistry, selective catalytic oxidation of benzyl alcohols to the corresponding benzaldehyde is one of the most important processes. That is why, many research has been reported to find out the

new and effective catalyst, for this type of oxidation reaction.⁵⁻⁷ Due to the large surface-area-to-volume ratios, nanoparticles have been explored extensively in a diverse field of many important organic catalysis. For example, Ru,⁸ Au,⁹⁻¹¹ Pd,¹²⁻¹⁴ Cu,¹⁵⁻¹⁷ and Pd-Au alloy catalyst¹⁸⁻²⁰ have been used efficiently for alcohol oxidation processes. Out of these NPs, Pd NPs has drawn more attention due to their outstanding catalytic activity.^{21,22}



Pd NPs are susceptible to aggregate and form Pd black due to their high surface energy.²³ This is why static Pd NPs over porous support is considered as the most important method to overcome this aggregation

problem. So far, immobilization into various inorganic substances such as SiO_2 ²⁴ and solid support like MOF, and graphene sheets are some of the typical methods to provide support to Pd NP.²⁵ Incorporation of such NPs are achieved by solid-state dispersion method, which is a green and solvent-free method.²⁶ Bimetallic catalyst has the potential to oxidize the benzyl alcohol to its subsequent aldehyde. It was reported by Enache *et al.* using 2.5% Au-2.5% Pd/C with the TOF 24 s^{-1} .²⁷ Meenakshisundaram *et al.* synthesized bimetallic Au-Pd/ TiO_2 catalyst for the oxidation of benzyl alcohol. They also reported that the rate of oxidation over the bimetallic catalyst is greater than monometallic Pd catalyst.²⁸

Alcohol oxidation

Oxidation is an essential chemical reaction in the synthesis of organic compounds and also plays an important role in the development of many essential chemicals from biomass. The use of heterogeneous catalysts and molecular oxygen to oxidation reaction provides a clean and green alternative pathway to conventional, traditional, hazardous chemical oxidants. The oxidation of alcohols to their subsequent carbonyl compound is one of the essential transformations in the synthesis of organic compounds. Recently a review of transformations of alcohols by bio catalyst²⁹ and heterogeneous photo catalyst³⁰ has been reported. In this chapter, we have focused on the selective oxidation of alcohols on the supported metal catalysts, because of the easy recovery of heterogeneous catalyst from the product and capacity for recyclability.

The oxidation of alcohol to an aldehyde on a heterogeneous catalyst can proceed in three ways. At first, the absorption of alcohol on the surface of the metal takes place producing an adsorbed metal-alkoxide. Secondly, the elimination of β -hydride occurs to produce a carbonyl species and a metal hydride. At the last step, the oxidation of metal hydride occurs to regenerate the metal surface.

Benzyl Alcohol Oxidation

Formation of carbonyl compounds by selective oxidation of benzyl alcohols is one of the most important conversions for laboratory synthesis, as well as industrial production; because carbonyl compounds are universal intermediates for the synthesis of pharmaceuticals and fine chemicals. The reaction is likely to play a significant role in developing value-added chemicals from biomass shortly, as the oil reserves are depleting, which has led to considerable growth of interest in developing sustainable alternatives to petroleum-derived fuels and chemicals.³¹

To test for catalyst reactivity, benzyl alcohol is generally used as a test substrate. Benzyl alcohol popularity as a probe molecule results from its extremely high reactivity and lesser amounts of by-products formation. Like many other alcohols, oxidation of benzyl alcohol proceeds via an aldehyde intermediate to the acid as a final product as depicted in Figure 1. Metal catalysts that are typically used for benzyl alcohol oxidation are Pt, Pd, and Au, etc.

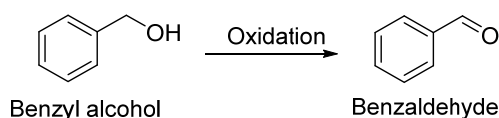
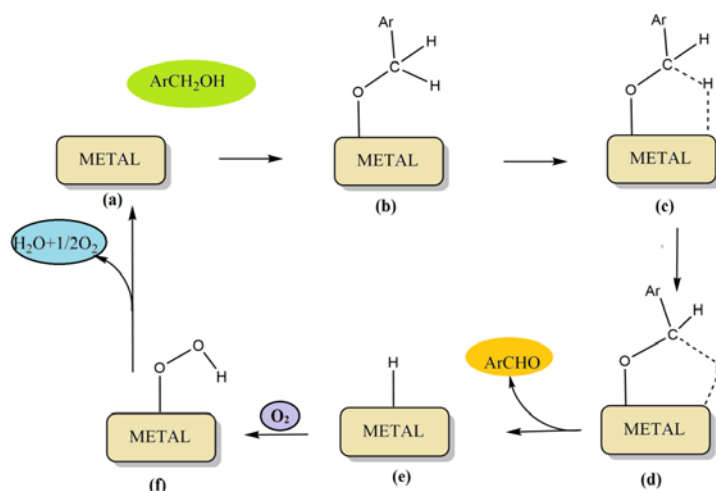


Figure 1. Reaction scheme for benzyl alcohol oxidation.

Mechanism

Alcohol oxidation to aldehyde over heterogeneous catalyst occurs in three steps, as shown in Scheme 1.

1. adsorption of primary alcohol on the metal surface takes place, producing metal alkoxide. The formation of metal alkoxide species is known for the selective oxidation of primary alcohols. In another contradiction, Mori *et al.* reported the same reaction rate for benzyl alcohol and 1-phenyl ethanol oxidation on a Pd catalyst, yet proposed the similar metal alkoxide intermediate.³²
2. it is followed by β -hydride elimination to produce a carbonyl species and a metal hydride. This step is widely regarded as the second step of oxidation of alcohol on a metal catalyst, forming a carbonyl group and a metal hydride.^{33,34} The Hammett methodology has been applied by some groups to find the mechanism of oxidation of benzyl alcohol and to confirm the elimination of β -hydride step.³⁵ Finally, oxidation of metal hydride takes place in the presence of dioxygen to regenerate metal surface.
3. the metal-hydride oxidation proceeds via a peroxide intermediate formation to generate water and oxygen molecules.



Scheme 1. Mechanism for alcohol oxidation on metal surface, (a) Alcohol adsorbs on the metal surface, (b) formation of an alkoxide, (c) and (d) β -hydride elimination, (e) metal hydride formation after release of carbonyl compounds, and (f) formation of metal hydroperoxide intermediate in the presence of oxygen, and subsequent regeneration of the catalytically active metal surface.

Yamaguchi *et al.*³⁶ and Fristrup *et al.*³⁷ have employed Hammett's theory to confirm the β -hydride elimination step for benzyl alcohol oxidation. Mori *et al.* further ascertained the last two steps of the benzyl alcohol oxidation, i.e., the oxidation of metal hydride via peroxide intermediate.

Effect of Various Catalysts on Benzyl Alcohol Oxidation

Palladium catalyst

The role of the support for Pd catalyst was investigated by Mori *et al.*³² and Chen *et al.*³⁴. Mori *et al.* found that conversion of benzyl alcohol and the selectivity of benzaldehyde depended on support; with the help of catalysts having the hydroxyapatite (HAP) support has the highest

conversion. The other examined supports (Al_2O_3 , SiO_2 , and C) produced the aldehyde with selectivity less than 50%, and the most selective was Pd/ SiO_2 with the conversion up to 71%. The conversion with the highest rate was achieved over Pd/ Al_2O_3 , though the selectivity was the lowest. The Pd/C produced the conversion with the lowest selectivity. The effect of Pd particles size on benzyl alcohol oxidation has been probed by Chen *et al.* by varying the ratio of $\text{SiO}_2:\text{Al}_2\text{O}_3$ in a mixed oxide support to tune the size of Pd particles in the range of 2-10 nm.³⁴ The size of the Pd nanoparticle got decreased upon decreasing the $\text{SiO}_2:\text{Al}_2\text{O}_3$ that might be due to the overall strength of interactions of the Pd precursor with the support. Though the variation of $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio changed the relative acidity of the support, the change in activity can be related only to Pd NPs. A TOF with maximum value was found at an average metal particle with the size ranges between 3-4 nm, indicating that oxidation of benzyl alcohol over Pd might be sensitive to structure, which was noted by Mori *et al.*³² in their work on Pd supported on HAPN. The catalyst which is optimized (Pd particle sizes of 4.3 nm and 3.6 nm) shows high TOF (2.53 s^{-1} and 2.45 s^{-1} , respectively) and it also has high selectivity to the aldehyde in a solvent-free condition.

Uozumi *et al.* used novel support, an amphiphilic resin, in the aqueous alcohols oxidation.³⁸ The resin was found to be highly hydrophobic in its pores, so organic molecules can diffuse from the aqueous media into the matrix where the Pd nanoparticles is anchored to catalyze the oxidation reaction. A mixture of benzyl alcohol and catalyst was refluxed in water

under atmospheric pressure of O₂ gives a high yield of the aldehyde. The selectivity with a high rate to the aldehyde in an aqueous medium is interesting, especially because successive oxidation to the carboxylic acid readily happens in water. The hydrophobic nature of the resin stops aldehyde conversion in water over Pd. The role of solvent was investigated by Villa *et al.*³⁹ They used Pd over carbon nanotubes or on activated carbon. The reaction rate was higher in cyclohexane than in water. It is significant to note that the Pd leaching from the support into the liquid was ample in this study, 25% for Pd/CNTS and 28% for Pd/AC. From the above results, it seems that the support material for Pd nanoparticles can have a considerable effect on the selectivity of the product. Most importantly, the suitable choice of support can subdue the successive oxidation of aldehyde to carboxylic acid in aqueous solution.

Bimetallic catalysts

Alloying of many metals can enhance the rate of the reaction and can alter the selectivity of product. In another report, the alloying of Au and Pd reduces the leaching of Pd from the supported catalyst.³⁹ Production of bimetallic catalysts for oxidation of benzyl alcohol is focused mainly on Pt, Au, Pd, and Ag-based catalysts. The highest rate of oxidation of benzyl alcohol was reported by Enache *et al.* in 2006 using 2.5% Au-2.5% Pd/C with the TOF found to be 24 s⁻¹. The addition of Au to Pd nanoparticles made better selectivity towards aldehyde formation in comparison to their monometallic Pd counterparts. The primary rate of bimetallic catalyst was lower than that of the monometallic Pd. This specified that the TOF for the

monometallic Pd catalyst was greater than 24 s^{-1} which is very higher than any other reports for Pd catalyst for oxidation of benzyl alcohol. An improvement of the reaction rate over Pd, Au, and Au-Pd and Au-Pt bimetallic catalyst supported on carbon was reported by Dimitratos *et al.*⁴⁰

Effect of Bimetallic Catalyst over Support

The amalgamation of different metals and their effect on increasing the catalytic activity of various oxidation reactions have already been reported. It has been found that alloying of two metals prevents leaching of the active sites from the support. Sometimes, the symbiosis effects displayed by the two bimetallic counterparts substantially enhances the reaction process. Meenakshisundaram *et al.*²⁸ synthesized Pd-Au bimetallic TiO_2 support for benzyl alcohol oxidation and found that the bimetallic alloy showed higher activity than individual Pd and Au catalysts. Out of the various supports such as hydroxyapatite, C, Al_2O_3 , SiO_2 , metal oxides, zeolites, etc., inorganic mantles, the aluminosilicates (FAU-Y) has been found as the most stable support for anchoring different kinds of metal-oxides, bimetallic nanoparticles, ligands, etc. The main efficiency of this support lies in its large surface area, shape selectivity and further, suppresses the formation of by-products.⁵⁻⁷ Recently, hybrid materials with zeolites/CNT has also gained much attention due to its increased conductivity, hydrophobicity, thermal stability, increased surface area, etc.

Conclusion

In conclusion, the importance of benzyl alcohol in industries as well as in academics has been discussed in this chapter along with its mechanism in

the different metal-based supported catalyst (Pd, Au, Ru, etc.). Various limitations in such oxidation process have also been included along with the several recent signs of progress with the transition metal-based catalysts. The importance of different metal-supported nanocomposites has also been debated in this chapter.

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