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■ REVIEW ARTICLE

Catalytic Oxidation of Alcohols: A Review from the Perspective of Green Chemistry

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ABSTRACT: The oxidation of alcohols to carbonyl compounds is one of the most developed and investigated reactions in organic synthesis due to its easiness of conduct and the usefulness of its products. However, most current systems of oxidizing alcohols require stoichiometric oxidants that create large amounts of waste harmful to the environment. Thus, finding suitable catalytic systems for the specialized oxidation of different alcohols is desirable. This review critically examines various catalysts utilized in the catalytic oxidation of alcohols to carbonyl compounds within the framework of green chemistry. In short, traditional transition metal-based catalysts find their use in oxidizing various benzylic alcohols; TEMPO-based catalysts can be used for selective oxidation of primary alcohols to aldehydes or carboxylic acids under different conditions; biological enzymes apply to natural chemicals such as saccharides; and heterogeneous catalysts are recommended when dealing with reactive substrates in large scales.

KEYWORDS: Chemistry; Organic Chemistry; Catalysis; Oxidation; Alcohols.

■ Introduction

The oxidation of alcohols to carbonyl compounds has been a topic of prolonged interest due to the importance of the products of the reaction, such as aldehydes, ketones, and carboxylic acids, as crucial intermediates used to synthesize many pharmaceuticals, important industrial feedstocks, and fine chemicals.[1] However, the traditional catalysts required for this reaction are most commonly toxic transition metal compounds, such as palladium and ruthenium.[2,3] These pose challenges in terms of their recycling and environmental impact. Therefore, the need for finding sustainable catalysts to oxidize alcohols to carbonyl compounds is growing extensively. Of the currently used methods, the most promising method is utilizing air,[4,5] sodium hypochlorite,[6] hydrogen peroxide,[7] and other cheap and renewable materials as active terminal oxidants and certain redox-active compounds such as iron (III) nitrate as catalysts.[4] This way, minimal waste will be generated since the source of the oxidant is unlimited, and oxidation byproducts are harmless substances such as sodium chloride and water. However, the choice of catalyst becomes an important issue. On the one hand, the catalyst needs to be active enough to sustain for many runs and immune to catalyst poisoning. On the other hand, the catalyst is preferably recyclable and renewable and does not contain any heavy metals or substances harmful to the environment.[8] This contradiction emphasizes the need for designing and developing new renewable catalysts for oxidizing alcohols to carbonyl compounds.[9]

The catalytic oxidation of alcohols to carbonyl compounds is a reaction that accompanied human civilization from its birth. For instance, when wine is stored in a warm place for several months, it becomes vinegar as the enzymes in the acetic acid bacteria catalyze the oxidation of ethanol by air to form acetic acid.[10] Similarly, *Pleurotus ostreatus*, or the oyster mushroom, breaks down the wood it is attached to by a group of enzymes that catalyzes the oxidation and breaking down of lignin by oxygen.[11] Those ancient concepts were only well-developed in the near modern times. The first member of the acetic acid bacteria, Acetobacter aceti, was discovered and proven to be the cause of the conversion from wine to vinegar in 1864 by the famous microbiologist Louis Pasteur.[12] Likewise, laccase, the active enzyme in the oyster mushroom, was first studied by Gabriel Bertrand in the sap of a Japanese lacquer tree (for which the enzyme is named) in 1894.[13]

In the 20th century, nitroxyl radicals, the first class of manmade renewable catalysts, emerged: Two Soviet chemists synthesized (2, 2, 6, 6 - tetramethylpiperidin -1-yl) oxyl, commonly referred to as TEMPO,[14,15] and it was applied to catalytically oxidize alcohols in a mixed catalysis system after a few years.[16] Since then, various TEMPO-based mixed catalysis systems have been developed using cheaper or more efficient co-catalysts. Meanwhile, a series of noble metal complex catalyst systems also appeared, with ruthenium and palladium complexes taking the lead. Alongside homogeneous catalysis, there is also a growing interest in heterogeneous catalysts. Distinguished by their insolubility in most common organic solvents, heterogeneous catalysts can be easily separated and reused without a noticeable loss of catalytic activity. Examples of heterogeneous catalysts include nanoparticles, mainly consisting of transition metals and their oxides,[7,17] and a large category of metal coordination complexes known as metal-organic frameworks (MOFs).[18] Presently, systems suitable for different substrates are already available to chemists.

Despite the wide range of catalytic systems available, traditional metal-based catalytic systems remain a preferred choice for the oxidation of alcohols due to their high selectivity for specific substrates. This requires chemists to synthesize dif-

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ferent catalysts for different substrates, increasing time costs. Furthermore, designing catalysts that suit specific substrates requires expensive and rare ligands.[3] The aforementioned difficulties made recycling the valuable catalyst attractive, but most current catalysts are difficult to recycle. Addressing this research gap, this review study will outline all non-renewable and renewable catalysts applicable for the oxidation of alcohols, offering a comprehensive guide for catalyst design and selection.

General Mechanism of Oxidation Reactions:

Oxidation-reduction (redox) is one of chemistry's most widely occurring reactions. In organic chemistry, redox reactions specifically refer to the transfer of electrons from a nucleophile to an electrophile. For example, the oxidation of primary alcohols with a mild oxidant such as chromium trioxide proceeds as follows (Figure 1): The electron-rich oxygen in the alcohol attacks the electron-deficient hexavalent chromium in the chromium trioxide, forming a chromate ester. The hydrogen on the alpha-carbon of the alcohol is then removed, along with its electrons, and attached to one of the electrophilic chromium-oxygen double bonds. Finally, the chromate ester is broken apart by an E2 elimination to give the oxidized aldehyde/ketone product and tetravalent chromium species.[19] Unlike the primary and secondary ones, tertiary alcohols cannot be oxidized to their corresponding carbonyl compounds since the alpha-carbon is trisubstituted and does not have hydrogen attached.

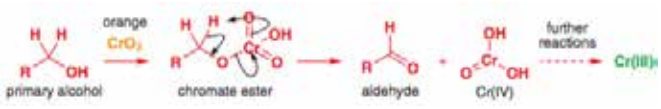

Figure 1: Reaction mechanism of the oxidation of primary alcohols by chromium trioxide as an example of an oxidation reaction.[19]

Non-renewable Catalysis: Transition Metal-based Catalysts:

Transition metal-based catalysts are the most maturely developed and extensively utilized class of catalysts for the oxidation of alcohols due to their high efficiency and selectivity. Platinum group metals are especially favored among all transition metals because they can form versatile complexes with many ligands that bring the molecule certain catalytic functions.[20] The two most frequently used platinum group metals are ruthenium and palladium, and rarely used metal-based catalysts are platinum and rhodium.

Ruthenium complex [RuHCl(CO)(PPh3)3]:

Ruthenium-based complexes are known for their combination of high catalytic efficiency and moderate cost compared to other rare metal catalysts. This study focuses on a novel example, [RuHCl(CO)(PPh_3)$_3$]. The aerobic oxidation of aryl alcohols by [RuHCl(CO)(PPh_3)$_3$] catalysis is performed in 90°C toluene under 1atm oxygen atmosphere, with 2-5mol% of ruthenium catalyst and 200mg 4Å molecular sieves added. Apart from the ruthenium catalyst, the reaction only requires cheap and easily attainable reagents such as toluene and molecular sieves. It also gives consistent yields up to 95% for various benzylic alcohols and fused-ring aryl alcohols, including those with halogens, electron-donating groups, and electron-withdrawing functional groups. The catalytic system also tolerates heterocyclic alcohols, distinguishing it from other powerful catalysts that oxidize those alcohols sluggishly and with poor yields. However, the catalytic system did not demonstrate great yields when oxidizing aliphatic alcohols.[3]

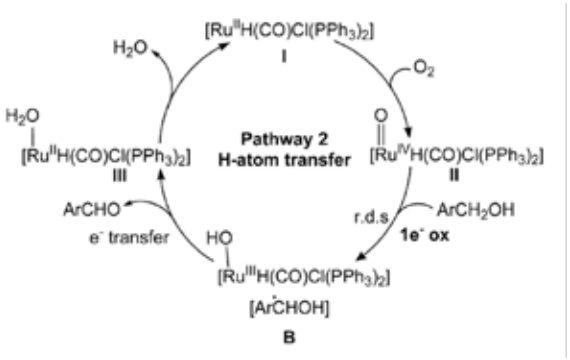

Figure 2: The pathway of the [RuHCl(CO)(PPh_3)$_3$]-catalyzed oxidation of aryl alcohols.[3]

The reaction pathway is shown in Figure 2. The ruthenium (II) complex is first oxidized by oxygen to form the corresponding ruthenium (IV) complex. This then accepts two hydrogens from the alcohol substrate and attaches them to the oxygen as the ruthenium center is reduced to (II). Finally, the resulting complex removes water and reforms the catalyst. Note that the activity of the catalyst may decrease after several runs due to the formation of [Ru(CO)$_3$(PPh_3)$_2$] and [RuH_2(CO)(PPh_3)$_3$], which are not catalytically active.[3] The main limiting factor to the availability of [RuHCl(CO)(PPh_3)$_3$] is the very high and unstable cost of its primary precursor, ruthenium (III) chloride. Thus, it is recommended for synthetic chemists to use [RuHCl(CO)(PPh_3)$_3$] in minute quantities when oxidizing benzylic and heterocyclic alcohols and recycling the ruthenium as inorganic ruthenium salts after use.

Palladium(II) acetate:

Palladium is even more widely employed than ruthenium due to its highly variable oxidation states and ability to complex with various organic ligands and substrates.[21] Palladium compounds are, for example, being used in the Suzuki coupling reaction. Still, it also applies to the catalytic oxidation of alcohols because of the ease of reaction procedures.[22] As an illustrative example, a palladium (II) acetate and pyridine catalytic system is discussed below. The typical reaction conditions are 5mol% palladium (II) acetate, 20mol% pyridine, and 0.5g 3Å molecular sieves combined in 10mL of toluene heated to 80°C under air/pure oxygen atmosphere for two hours. The oxidation to the corresponding aldehydes was nearly quantitative (92-100%) within only 2 hours of reaction for benzylic alcohols.[23] Furthermore, for most primary and secondary alcohols, even those with high steric hindrance, the reaction provided consistent yields (over 90%) without any carboxylic acid or ester products observed; at the same time, the common hydroxyl protection groups in the substrates are well-tolerated. Nevertheless, the catalytic system showed difficulty in oxidizing alkenic alcohols, perhaps due to the complexation of the alkene double bond to the palladium center of the catalyst,

and the problem was partially solved by adding an excess of pyridine.

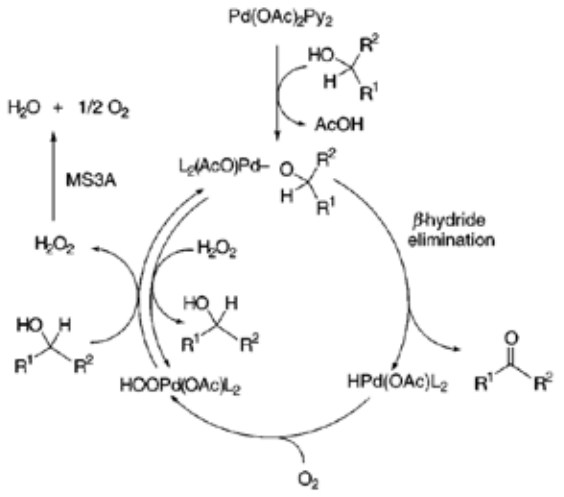

Figure 3: The mechanism of the aerobic oxidation of alcohols by the $Pd(OAc)_2$/pyridine system.[23]

As shown in Figure 3, the palladium (II) acetate first forms a complex with added complexing agents such as pyridine to form $Pd(OAc)_2(py)_2$, which further complexes with a molecule of the substrate alcohol to form a new palladium complex $(py)_2(AcO)Pd\text{-}(R^1C(OH)R_2)$ while losing a molecule of acetic acid. This complex undergoes a hydride elimination to give the ketone product, and a hydrogen atom fills the original alcohol ligand's place. The Pd-H bond then gets oxidized by atmospheric oxygen to form the hydroperoxide, which, in a reversible reaction, reacts with a molecule of the substrate alcohol to form hydrogen peroxide and $(py)_2(AcO)Pd\text{-}(R^1C(OH)R_2)$ again, continuing the catalytic cycle. The 3Å molecular sieves facilitate the removal of hydrogen peroxide as water and oxygen, promoting the forward reaction of the reversible process.[23] Similar to the mentioned ruthenium complex, palladium salts' high cost and toxicity also challenge this catalytic system. Still, it requires considerably less time to run (~2h compared to ~12h of Ru catalysis). It is much easier to set up (the Ru complex needs to be prepared before the experiment, while $Pd(OAc)_2$ and pyridine are commodity chemicals that can be easily obtained). This catalytic system is highly recommended for the oxidizing benzylic alcohols with various protection groups when high to quantitative yields are especially desired.

Renewable Catalysis: Homogeneous Catalysts:

Nitroxyl Radicals (TEMPO and its derivatives) Mixed Catalysis :

New renewable catalysts present distinct advantages over expensive, toxic, and challenging-to-recycle transition metal-based catalysts. Aminoxyl radicals, among many other catalysts such as enzymes and nanoparticles, stand out as one of the most promising renewable catalysts of the future due to their low production cost, versatile compatibility with substrates, and consistently high yields. The most frequently used and developed aminoxyl radical catalyst is (2,2,6,6-tetramethylpiperidin-1-yl) oxyl, or TEMPO for short. It is a versatile reagent that can be combined with other co-catalysts to form a series of active catalytic systems, each providing special properties for certain substrates.[6] The high catalytic activity of TEMPO is mainly due to the various oxidation states of the nitrogen atom: the reduced form (hydroxylamine), the intermediate form (N-oxyl radical), and the oxidized form (N-oxoammonium salt). The molecule can be oxidized and reduced readily, thus completing catalysis cycles.[24]

TEMPO/CuCl:

One of the first reported catalytic systems based on TEMPO is the TEMPO/CuCl system, which comprises 10mol%TEMPO as the primary catalyst, 10mol%CuCl as the co-catalyst, and operates at 25°C in DMF while bubbling oxygen gas (50-60 mL/min) through the solution. The system displays high selectivity towards benzyl alcohols and primary alcohols compared to secondary ones, with a mixture of 1-hexanol and cyclohexanol giving 60% conversion to 1-hexanal and 0% conversion to cyclohexanone after two hours. Also, the oxidation stops at the aldehyde stage cleanly without over-oxidation.[16]

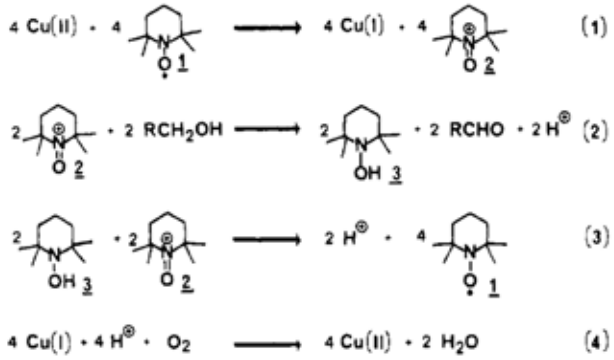

Figure 4: The simplified mechanism of the aerobic oxidation of primary alcohols by the TEMPO/CuCl system.[16]

The reaction mechanism of the catalytic system, shown in Figure 4, starts with the oxidation of copper (I) ions to copper (II) ions by atmospheric oxygen. Notably, this step generates water as a byproduct, indicating the reaction's feasibility in wet solvents. The copper (II) ions then oxidize the nitrogen on TEMPO to produce the corresponding N-oxoammonium salt, which reacts with the substrate alcohol to produce the aldehyde, hydrogen ions, and hydroxylamine. Finally, the hydroxylamine and the N-oxoammonium salt undergo a comproportionating reaction to yield TEMPO again.[16] Note that although the reaction involves both copper (I) and copper (II) ions as the reactive species, the original catalyst cannot be common copper (II) salts, e.g., $CuCl_2$, due to the excessive coordination of the chloride ion. This catalytic system's cheap and mild nature allows its widespread use in the oxidation of activated alcohols such as benzylic and allylic alcohols and selective oxidation of primary alcohols in the presence of secondary alcohols.

TEMPO derivatives/Fe(NO$_3$)$_3$/(Na,K)Cl:

The TEMPO derivatives/Fe(NO3)3/(Na,K)Cl system has become one of the most widely employed methods of catalytic aerobic oxidation of alcohols due to its cheap and easy-to-obtain reagents, mild reaction conditions, and outstanding adaptation to different substrates. The system consists of 10mol% (4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yl)oxyl (4-hydroxy-TEMPO), 10mol% NaCl, and 5mol% iron (III)

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nitrate nonahydrate in toluene under room temperature and 1atm oxygen or airflow. 4-hydroxy-TEMPO can be manufactured readily from the condensation reaction between acetone and ammonia[25] and thus is significantly cheaper than TEMPO while retaining most of the latter's catalytic properties. Due to its mild reaction conditions, the 4-hydroxy-TEMPO catalytic system is useful for specific functional groups sensitive to oxidation, especially propargylic and allylic alcohols. However, the main drawback of the system is its lengthy reaction time, typically between 5 and 24 hours when using 1mmol of the substrate.

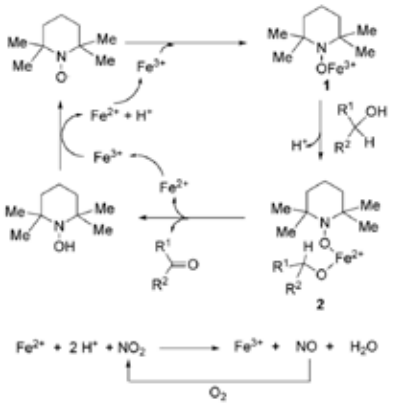

Figure 5: The reaction mechanism of the aerobic oxidation of alcohols by the TEMPO/$Fe(NO_3)_3$/(Na,K)Cl system.[5]

The mechanism proposed by Ma *et al*. in Figure 5 resembles the mechanism of the previous catalytic system involving copper salts but with iron (II) and iron (III) ions replacing the copper (I) and copper (II) ions, respectively. Ma *et al*. later discovered that if KCl was used instead of NaCl in the original protocol, the system affords carboxylic acids instead of aldehydes. Due to the larger radius of the potassium ion, it can bind and form complexes faster than the sodium ion, which enables the catalytic cycle to proceed to yield carboxylic acid instead of stopping at the aldehyde stage.[4]

Biological Catalysis:

Compared to man-made metal- and aminoxyl radical-based catalysts, biological catalysts such as enzymes gain unprecedented attention for their catalytic oxidation of alcohols due to their natural origin, cheap cost, and biocompatibility. They can be isolated from living organisms or made from readily available biomasses through simple processes, can be used in an aqueous environment, and require minimal workup after the reaction (a solvent extraction is more than enough).[26] The two most prominent biological catalysts are laccase and alcohol dehydrogenase. Although used directly industrially, these enzymes can combine with cocatalysts such as TEMPO and other biological molecules to form efficient catalytic systems in laboratories. For example, isosorbide, a bicyclic furan derivative produced from glucose and sorbitol, can be efficiently oxidized with air utilizing laccase and TEMPO in acetic acid to afford the corresponding diketone.[1]

Similarly, a combination of alcohol dehydrogenase, amine dehydrogenase, and nicotinamide adenine dinucleotide (NADH, a common redox-active biological molecule) as catalysts can convert primary and benzylic alcohols and ammonia to the corresponding enantiomerically pure amine with high yields.[27] The main drawback is the reactions' slow speed due to the limited solubility of oxygen gas in the reaction solvent. Introducing the oxygen gas in tiny bubbles can significantly elevate the reaction speed.[28] Overall, the biological catalytic systems show an advantage towards the oxidation of biological molecules such as saccharides to value-added products, so it is recommended to specialize them for the oxidation of sugars and similar compounds produced naturally in living organisms.

Renewable Catalysis: Heterogeneous Catalysts:

Heterogeneous catalysis has recently emerged as a new catalyst type in laboratories. Those catalysts have been used in industry to synthesize various essential chemicals, such as ammonia,[29] hydrogen,[30] and hydrogen cyanide.[31] Those catalysts exhibited advantages compared to homogeneous catalysts because they do not mix with the reactants or products, allowing for easier separation and recovery. However, heterogeneous catalysts only have limited applications in laboratories. The difficulties here are the slow reaction speed (typical hydrogenation requires 10-24 hours) and the reactive nature of the catalyst (Raney Ni and palladium on carbon are pyrophoric in air).[32] Over the years, new heterogeneous catalysts have been developed to overcome these problems, including metal-based nanoparticles and metal-organic frameworks (MOFs).[7,17,33]

Metal-based nanoparticles:

Metal-based nanoparticles are nanoparticles of transition metals and their oxides. In addition to the inherent redox-active properties of transition metals, nanoparticles have larger surface areas than regular transition metal compounds, resulting in higher catalytic activity.[34] For example, iron (II, III) oxide (magnetite) nanoparticles can be used catalytically with hydrogen peroxide to oxidize alcohols to carbonyl compounds. The most significant advantage of this system is its mild and easily attainable conditions: It uses water as a solvent and hydrogen peroxide as an oxidant, both of which are readily accessible compounds. Furthermore, the Fe_3O_4 nanoparticle catalysts can easily be removed and recycled with no apparent activity loss by placing a strong magnet near the reaction mix, decanting, and washing.[7]

Similarly, cobalt-palladium (Co-Pd) alloy nanoparticles also demonstrate those properties. The catalytic system is also conducted in water at similar temperatures and utilizes atmospheric oxygen as the terminal oxidant, leading to a nearly waste-free process. The catalyst particles can also be removed and recycled using a similar approach to the Fe_3O_4 nanoparticle.[17] One of the main drawbacks of nanoparticle catalysts is their complicated preparation, which involves inert atmospheres, precise time and temperature controls, and occasionally toxic and reactive reagents. Based on their cheap production costs and straightforward recycling process, nanoparticle catalysts are recommended for use when dealing with sensitive substrates in large quantities.[35]

Metal-Organic Frameworks (MOFs):

Metal-organic frameworks (MOFs) are a particular class of coordination compounds characterized by their crystalline polymeric structure constructed from metal ions and their organic ligands, known as linkers.[36] Common heterogeneous

catalysts, such as zeolites, also have a similar porous structure. Still, in addition to that, MOFs consist of transition metals and organic linkers, which can be modified to give the molecule redox-active properties. For example, the platinum group metals,[36-38] copper,[39] and gold[40] have been used in MOFs for aerobic catalytic oxidations of alcohols. The reaction conditions are similar to the homogeneous catalysts, and the catalysts can be recycled by simply filtering off and washing. The mutual problems of MOFs are their lengthy preparation and limited scope of substrates, as most current MOFs are only compatible with reactive benzyl alcohols.[33]

Conclusion

Outstanding processes have been made in novel, eco-friendly, and renewable pathways to efficiently and selectively oxidize various types of alcohol to carbonyl compounds under mild conditions and with high yields. The non-renewable transition metal-based catalysts such as palladium (II) acetate were developed and investigated first because they are similar in mechanism and effect to the traditional non-catalytic oxidizing agents. However, renewable catalysts' expansion became more preferential due to their relative impact on the environment. The first renewable catalyst systems, such as TEMPO/CuCl, abandoned the use of precious metals that are costly and difficult to recycle, and the later generations, like TEMPO/$Fe(NO_3)_3$/NaCl, improved the selectivity and efficiency of the oxidation reaction. Apart from those purely artificial catalysts, biological enzymes such as alcohol dehydrogenase played a critical role in converting biomasses into renewable commodity chemicals. More recently, several heterogeneous catalysts like metal-based nanoparticles also emerged, highlighted by their easiness of recycling and reuse. TEMPO-catalyzed aerobic oxidations are the future direction since they are maturely developed, have many variations, and are suitable for an extensive range of substrates. Although currently under development, heterogeneous catalysts are also the future direction because they can suit the need for large-scale production of pharmaceuticals. Although some obstacles still hinder the laboratory and industrial use of renewable catalysts, such as the lengthy reaction time and high recycling cost, the green, catalytic oxidation of alcohols is becoming increasingly significant.

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