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Catalytic oxidation in green chemistry: A review

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Abstract

21st century global market place is moving towards sustainable development. Today's chemical industries need to give more focus for the planet through improving the environmental foot prints of fuels and chemical manufacturing processes. Oxidation and hydrogenation process are widely used in the production of chemicals and fuels. Oxidation processes are especially important to convert petroleum-based materials to useful petrochemicals of higher oxidation state. Oxidation process using eco-friendly oxidizing agents such as molecular oxygen, ozone and hydrogen peroxide (H_2O_2) are increasingg becoming important to improve the environmental sustainability.

Keywords: green chemistry, catalysis, (ep)oxidation, hydrogen peroxide, gold nanoparticles co-reagent, homogeneous, oxidants

Introduction

Green chemistry

"Green chemistry is design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances." Green chemistry used across the life cycle of a chemical products, including its designs, manufacture, used and ultimate disposal Green chemistry concept discovered by the scientist Poul Anastas and John C. Warner.

Basic principles of green chemistry

In 1998, Paul Anastas and John C. Warner published a set of principles to guide the practice of green chemistry. Nowdays, these 12 principles of green chemistry are considered are fundaments to contribute to sustainable development. The principles comprise instructions to implement new chemical products, new synthesis and new processes. These principles demonstrate the breadth of the concept of green chemistry are as follows –

Table 1

Principles	**Examples**
Prevention	Use of solvent less sample preparation technique
Atom economy	Hydrogenation of carboxylic acid to aldehyde using solid catalysts
Less Hazardous chemical synthesis	Adipic acid syn.by oxidation of cyclohexene using hydrogen peroxide
Designing safer chemicals	New. Less Hazardous pesticide
Safer solvent and auxiliaries	Supercritical fluid extraction syn.in ionic liquids
Design for energy efficiency	Polyolefins
Use of renewable feedstock	Production of surfactant
Reduce Derivatives	On fiber derivatization vs derivatization in solution in sample preparation
Catalysis	Efficiently Au (III) catalyzed syn of b- enaminones from 1,3-di carbonyl comp. And amine
Design for Degradation	Syn of biodegradable polymer
Real time analysis for pollution prevention	Use of in line analyzers for wastewater monitoring
Inherently safer chemistry	(DMC) is an environmentally friendly substitute.

Green oxidation catalysts

The Green Catalyst is most commonly associated with catalysts that are recoverable or prepared from readily available starting material.

Oxidation reactions involve the loss of electrons or the addition of oxygen and reduction is the opposite.

The controlled partial oxidation of hydrocarbons, comprising alkanes, alkenes and aromatics, is the single most important technology for the conversion of oil and natural gas-based feed stocks to industrial organic chemicals.

For economic reasons, these processes predominantly involve the use of molecular oxygen (dioxygen) as the primary oxidant. Their success depends largely on the use of metal catalyst to promote both the rate of reaction and the selectivity to partial oxidation products.

The pressure of increasingly stringent environmental regulation is also providing a stimulus for the deployment of catalytic oxidations in the manufacture of fine chemicals.

In principle, homogeneous as well as heterogeneous and bio- catalysts can be deployed in liquid phase oxidation but in practice, the overwhelming majority of processes are homogeneous, i.e. they involve the use of soluble metal salts or complexes as the catalyst.

The basic principles of catalytic processes depends on the use of soluble complexes as catalysts. The processes involved such as – the Wacker process, the Halcon process for the oxidation of alkenes with hydroperoxide and the process depends on molecular oxygen in addition to homogeneous method.

The increasing role of catalysis in organic chemistry in general and the ever increasingly environmental consideration provide a strong incentive to develop sustainable catalytic alternatives to stoichiometric reagents.

Oxidation catalysts can play a necessary role in breaking down the fractious compounds that are not degradable by biological substances.

Catalytic oxidation

Oxidation reaction represents a core industrial technology for the conversion of chemical feedstocks such as alkanes and alkenes, into fine chemicals, epoxides, dioles and alcohols.

The current use of stoichiometric oxidants including nitric acid, chromic acid, and its derivatives, permanganate, osmium tetroxide and hypochlorite is remarkably efficient but those processes involve higher costs, formation of toxic waste, and low atom efficiency due to stoichiometric factor.

Among the oxidation reaction, the formation of epoxides via the epoxidation of alkenes is important to obtain important products, such as alcohol, diols. Among the different strategies to achieve such transformation, bioinspired catalysts based on iron and manganese display interesting properties using H_2O_2 as oxidant.

Table 2: Bulk chemicals via catalytic oxidation

Product	Feedstock	Oxidant/product
Styrene	Benzene or Ethene	O_2/L
Terephthalic acid	p- Xylene	O_2/L
Ethene oxide	Ethene	O_2/G
Adipic acid	Benzene	O_2/L
Propene oxide	Propene	RO_2H/L

A} Oxidation of cyclooctene

Role of acetic acid (CH_3COOH)

To prove the need of carboxylic function as co-reagent in this catalysis, some tests with all complexes were done in absence of CH_3COOH. While no conversion was observed with the $[(L^3)FeCl_2](FeCl_4)$, complexes $(L^3)MnCl_2$, $(L^3)Mn(OTf)_2$ and $(L^3)Mn(p\text{-}Ts)_2$ were poorly active. These results showed the necessity of carboxylic function for this reaction. All complexes were then tested in presence of co reagent, either acetic acid either the SiO_2@COOH under identical experimental conditions.

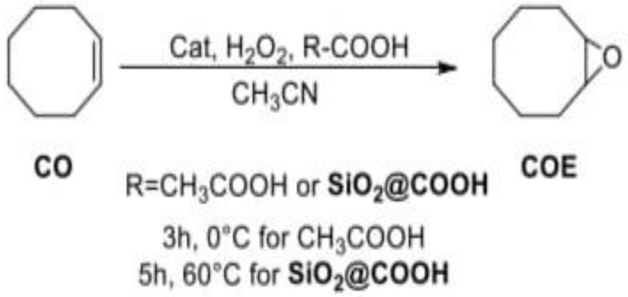

Fig 1: Catalysis oxidation of cyclooctene

CH_3COOH vs. SiO_2@COOH

In presence of the co-reagent, in all experimental conditions, (Reac.1 and Figure.1) all catalysts could achieve conversion of the CO, the best condition being in presence of acetic acid for all manganese complexes, while the conversion was better in presence of SiO_2@COOH in the case of the iron complex.

Effect of anion with CH_3COOH as co-reagent

Using CH_3COOH as a co-reagent (Figure1), the manganese complexes $(L^3)MnCl_2$, $(L^3)Mn(OTf)_2$ and $(L^3)Mn(p\text{-}Ts)_2$ gave a conversion of CO > 99%. However, the selectivity towards COE with $(L^3)Mn(OTf)_2$ and $(L^3)Mn(p\text{-}Ts)_2$ were around 60%, lower than $(L^3)MnCl_2$ around 81%. With those results, it can be concluded that the anion has an influence on the selectivity towards COE. It might due to the different acidity of the anion, the chloride being less basic than the two other ones. As we show, the ring opening might occur in presence of acid or base.

B} Catalysis oxidation of cyclohexene

The cyclohexene (CH) is very interesting substrate and it is starting material for synthesis of adipic acid. In terms of reactivity, the oxidation of CH is more complex. According to nature of the metal used within the reaction, two types of oxidations are possible: the allylic oxidation occurring on sp^3 C-H bonds and the epoxidation on the C=C double bond. Several products such as cyclohexene oxide (CHO), cyclohexane diol (CHD), cyclohexene-1-ol (CHol) and cyclohexen-1-one (CHone) are the most common products are observed (Reac. 2)

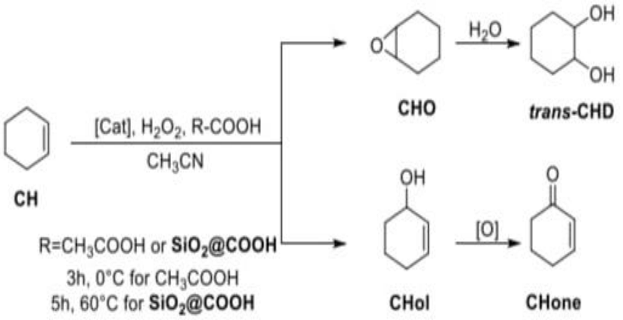

Fig 2: Catalysis oxidation of cyclohexene.

Mangnese complexes - CH_3COOH vs. SiO_2@COOH: -

All manganese complexes exhibited a high CH conversion in presence of CH_3COOH and final products that could be analysed are depending on the nature of the anion. While, manganese complexes such as $(L^3)MnCl_2$ gave exclusively the epoxide (CHO) with a relative good selectivity (89%), the $(L^3)Mn(OTf)_2$ and $(L^3)Mn(p\text{-}Ts)_2$ gave a small quantity of CHO (due to CHO opening with water) and CHone (coming from allylic oxidation).

When SiO_2@COOH are used, the CH conversion are lower, CHO being the only product synthesis with $(L^3)Mn(OTf)_2$ and $(L^3)Mn(p\text{-}Ts)$

From observation the presence of CH_3COOH or SiO_2@COOH have reverse effects in terms of selectivity according to nature of the nature of the anion of the Mn complexes with the$[(L^3)MnCl_2]FeCl_4$ complex, the mechanism seems to be radically different since the reaction with CH_3COOH as co-reagent did not give any expected product, but the use of SiO_2@COOH as co-reagent did improve the CH conversion but not in selective way since product originating from epoxidation and allylic oxidation were observed in almost equal quantities.

C} Catalysis oxidation of cyclohexanol

The cyclohexanol (CYol) is also a starting material of KA oil used for synthesis of adipic acid. In reactivity, the comparison with CH, the oxidation of CYol is not complicated and only one product is expected i.e. cyclohexanone (CYone) (Reac. 3).

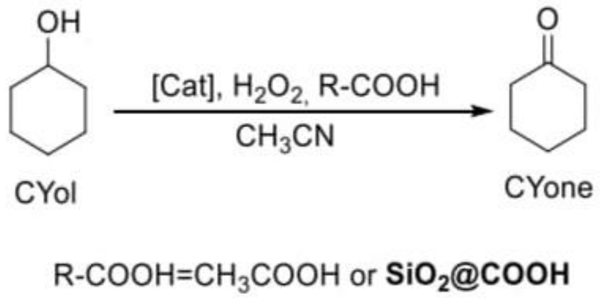

Fig 3: Catalysis oxidation of cyclohexanol

Mangnese complexes - CH_3COOH vs. SiO_2@COOH

In presence of CH_3COOH, the conversion of CYol was very high with a very high selectivity towards CTone. Mangnese complexes such as $(L^3)Mn(OTf)_2$ and $(L^3)Mn(p\text{-}Ts)_2$ are more reactive than $(L^3)MnCl_2$ due to strength ofmetal-anion bond or/and to the acid strength of the anion. Peroxide and carboxylic function reach easier the metal center because the free coordination site in $(L^3)Mn(OTf)_2$ and $(L^3)Mn(p\text{-}Ts)_2$ being more accessible than $(L^3)MnCl_2$

D} tugsten catalysts

As a phase transfer agent, a mixture of tungstate and phosphate in the presence of tetra alkylammonium salt catalysed epoxidation with H_2O_2 in two phase dichloroethane/ water as medium. The type of ammonium salt used with phosphate or tungstic acid catalyst is important.

The Noyori – system was observed to be an effective system for the oxidative cleavage of cyclic olefins to dicarboxylic acid using H_2O_2. (Reac.4). Cyclohexene afforded adipic acid in 93% isolated yield, thus providing a green route to adipic acid.

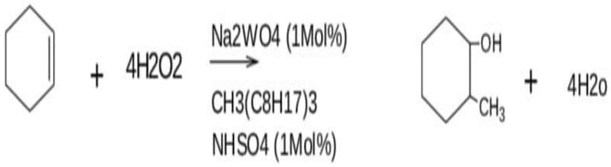

Fig 4: Oxidative cleavage of cyclohexene using tungstate catalyst.

E} Mangnese catalyst

Mangnese based catalysts involved an oxo- manganese complex (v) like active oxidant. In the presence of sodium bicarbonate the simple manganese sulphate is effective in promoting the epoxidation of alkenes with aqueous H_2O_2 using DMF or t-BuOH as solvents. In this system by *in – situ*, tetracarbonate is formed, thus minimizing the catalase activity of the Mn salt. Chan and coworkers introduced an imidazole – based ionic liquids in the Mn/ bicarbonate system in order to overcome the requirements of volatile organic co-solvents. (reac5).

The major disadvantage of these Mn salt system is 10 equivalents of H_2O_2 are still required to reach substantial conversion. Recently, it was found that by using peracetic acid as the oxidant $Mn^{11}(bipy)_2$ becomes an extremely active catalyst.

F} Gold catalyst

Recently, gold has appeared as one of the most active catalyst for alcohol oxidation and it is especially selective for poly- alcohols. In the case, gold nanoparticles are deposited on nanocrystalline cerium oxide, a TOF was obtained for the conversion of 1- phenyl ethanol into acetophenone at 160c (reac.6).

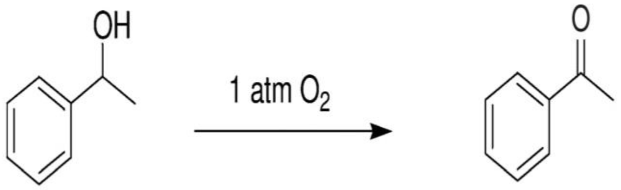

Fig 5: Au nanoparticles for alcohol oxidation

This catalyst is recyclable. Au is considered as the catalyst of choice for carbohydrate oxidation.

G} oxidation of alkanes

Classical autoxidation of tertiary C-H bonds in alkanes can afford the corresponding hydroperoxides in high selectivities. This is applied industrially in the conversion of pinnae to the corresponding hydroperoxide, an intermediate in the manufacture of pinanol

H} aromatic ring oxidation

Oxidation of aromatic ring is quit complicated for a number of reasons. Firstly, radical intermediate preferentially abstract hydrogen atoms from the aromatic side chain, rather than the nucleus. Secondly, the phenol products are much more reactive towards oxidation than the hydrocarbon substrates.

As a catalyst, $FeSO_2$, which is a Fenton catalyst, was applied in the presence of 5- carboxy – 2 – methylpyrazine N – oxide as ligand and a co-catalyst is trifluoro acetic acid (reac.8). Using 10 folds excess of benzene to hydrogen peroxide, 97% selectivity of phenol could be achieved at full conversion of H_2O_2.

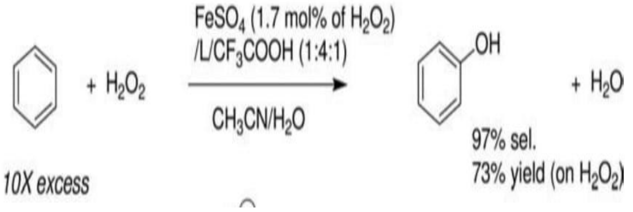

Fig 6: Direct oxidation of benzene to phenol using H_2O_2

Recently a solution was found to the problem over-oxidation by using aqueous organic solvent mixture. Similar results could be obtained by using aqueous- ionic liquid biphasic mixtures and iron – dodecane sulfonate salt as catalyst.

I} cyclooctene epoxidation

Corresponding epoxide, Cyclooctene oxide (COE) is known to be relatively stable towards ring-opening reactions therefore CO is interesting. Hydrolysis and ring opening might respectively gives cyclooctanediol and suberic acid. When the temperature reached to 80^0c then the oxidant (CO/TBHP ratio being 1:1.5) is added (Reac.10). In this whole reaction no organic solvent was added.

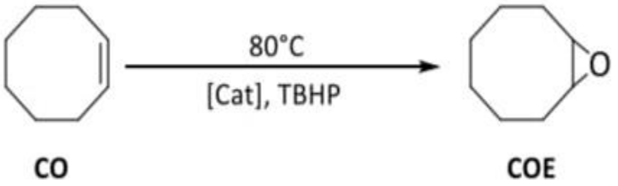

Fig 7: Catalyzed epoxidation of CO.

Catalyst were recovered by centrifugation and under the same experimental condition's catalyst are reused to test

Conclusion

Synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and environment. Chemical products should be designed to preserve efficacy of function while reducing toxicity. No vapour pressure and composed of entirely cations and anions. Good solvent properties and often facilitate chemical reactions without being transformed in process. Exhibit high thermal stability and wide working temperatures.

* The ultimate aim of green chemistry is to entirely cut down the stream of chemicals pouring into environment.

Multitude of possible combinations of cation and anion, they are susceptible to numerous permutations that allow various physical and chemical properties to be adjusted at will. It have negligible vapour pressure and miniscule flammability. Room temperature can be used as substitutes for aromatic solvents in chemical reactions and separation process.

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