TRANSITION METAL NANOPARTICLES IN OXIDATION REACTIONS OF ALCOHOLS USING MICROWAVE IRRADIATION: A GREEN CHEMISTRY APPROACH

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Abstract: Green chemistry with its twelve principals would like to see change in the convention synthesis and the use of less toxic starting materials. Green chemistry would like to increase the efficiency of synthetic method to use less toxic solvents, reduce the stages of synthetic routes and minimize waste as far as practically possible. In this way, chemical synthesis will be part of the effort for sustainable development. Microwave assisted synthesis has revolutionized chemicals synthesis. Small molecules can be built in a fraction of the time required by conventional methods. Alcohols are selectively oxidized to aldehyde using active cerium dioxide (CeO_2) nanoparticles under solvent free using microwave irradiation. The complete conversion of the alcohols to their corresponding aldehydes was achieved successfully within 25-55 seconds of irradiation in microwave oven. The products of oxidation were characterized by TLC,IR and Tollen's reagent test, which showed the characteristic results of the desired aldehydes.This method is found to be fast , green and a very easy procedure that could be applied for the oxidation of alcohols to aldehydes without further oxidation to carboxylic acids.

Keywords–Transition metal, oxidation, alcohol, microwave irradiation, Green chemistry.

I.INTRODUCTION

The term green chemistry becoming the world wide term used to describe the design of chemical products and processes that reduce or eliminate the use of generation of substances hazardous to human health. The term was coined by the US environmental protection agency and has been defined as; the utilization of a set of principles that reduce or eliminate the use or generation of hazardous substances in the design, manufacture and application of chemical product. The oxidation of aliphatic and aromatic alcohols to the carbonyl compounds (Aldehydes and Ketones) are one of the most common reactions in organic synthesis , because of their role to be involved in a variety of organic reactions like Julia and Witting reaction to produce alkenes, hemiacetals and acetal formation, imine (Schiffs base) formation etc. The first direct oxidation of alcohols to aldehydes is the usual oxidizing agents such as Jones reagent potassium dichromate (K_2CrO_7) or potassium permanganate ($KMnO_4$) but the reaction could not be controlled and undergoes further oxidation to produce carboxylic acid, and it is limited due to several safety issues.

In the last few decades, the uses of mild oxidizing agents have attracted researchers in the organic chemistry field to apply for the oxidation of alcohols to aldehydes without further oxidation to carboxylic acids. The uses of chromium reagents such as Collin reagent and pyridium chlochromate (PCC) are most common mild oxidizing agents that are used , but again , these compounds are associated with difficulties in working up the reaction, further oxidation to carboxylic acids and some health and safety issues. The enveloping catalysts have economic and green behavior attracted by researchers. There are several metal oxide nanoparticles has been used as a catalyst for converting alcohols to aldehyde and vice-versa, including copper [1], nickel [2] and manganese [3],Karzan *etal.*[2] reported the conversion of benzyl alcohol; to bezaldehyde by using nickel oxide nanoparticlaes.They indicated that the catalytic activity of nickel nanoparticles for oxidation of alcohols. Also, the manganese nanoparticles are utilized as efficient catalysts for oxidation and decomposition of chemical

compounds such as catalytic activity of catalytic decomposition of hydrogen peroxide [4], as a water oxidizing catalyst in nature [5] at the same time cerium nanoparticles like other metal nanoparticles playing important role in the conversion of the most organic alcohols to aldehyde [6]. Despite of its catalytic characteristics, it has been several applications in their fields such as sensors [7].Molecular adsorption [8], removal of CO from hydrogen rich fuel cell [9], lithium batteries [10] and ion exchange [11] and [12].

In the present study, herewith report a green, fast and selective oxidation of various alcohols to their corresponding aldehydes using active CeO_2 nanoparticles on silica under solvent –free condition using microwave irradiation. **(Scheme1)**.

(CeO_2Nanoparticles) + Benzyl alcohol → Benzaldehyde

Reactants Product

Scheme 1. Reaction of alcohol oxidation

II. *EXPERIMENTAL*

Materials and methods

Alcohols were purchased from Loba Chemie Pvt.Ltd.,Tarapur. CeO_2 nanoparticles prepared and provided by Karzan [4].The purity of the products and reactions checked by TLC on silica gel plates. The microwave oven used for heating the reactions, model type Godrej GME725CF1 PZ. IR spectroscopy conducted at C-MET, Pune.

General procedure

The selected alcohol (1mole/eq.) was mixed with cerium dioxide CeO_2 nanoparticles 1.1 mole/eq. in solid state without solvent. The mixture was placed in microwave oven and irradiated for 25-55 seconds depending on the type of the alcohol. The completion of the reaction was confirmed by monitoring thin layer chromatography using petroleum ether/ethyl acetate 5:1 as eluting solvent and iodine stain. After completion of the reaction, the product was extracted with ethyl acetate, filtered off to remove the residue, and the solvent was evaporated to give the product.

III. RESULTS AND DISCUSSION

Synthesis and characterization of CeO_2 nanoparticles

The CeO_2 nanoparticles has been synthesized according to previously published work [4].The characterization of synthesized nanoparticles by scanning electron microscopy (SEM) indicated that the morphology of CeO_2 nanoparticles are not uniform and existence of the different shape of nanoparticles due to agglomeration and electronic dispersive X-ray (EDX) confirmed the purity and chemical composition of synthesized nanoparticles. The cerium dioxide nanoparticles are considered as the most interesting in the catalytic fields.CeO_2 nanoparticles have a high surface area and prefect dispersed due to their particle size, which leads to nanoparticlas are one of the most stable metal oxide nanoparticles in the air and high temperature. The biocompatibility of CeO_2 nanoparticles is very important oxides making them environmentally friendly and safe utilizing them in the different application filed.

Selective oxidation of different alcohols into corresponding aldehydes using CeO_2 nanoparticles catalyst

An active CeO_2 nanoparticles were found has a potential to oxidize alcohols to their corresponding aldehydes selectivity in excellent yield without further oxidation to carboxylic acids. The reaction procedure is completely green, and easy to be conducted in the laboratory. The simple microwave irradiation oven was used as heating source to conduct the reaction in solid state under solvent –free condition. Microwave irridation has been very popular recently to enhance chemical reactions as it has several advantages like performing the reaction homogenously, the less reaction time requires, and most of the time gives a change to perform the reaction under solvent-free condition. Table-1 shows the selective oxidation of different alcohols into the corresponding aldehydes using cerium dioxide nanoparticles on silica under solvent free condition using microwave irradiation.

The reaction completion was monitors by thin layer chromatography [TLC] (5:1) petroleum ether/ethyl acetate as eluting solvent, and iodine solution as strain. This confirms the total conversion of alcohol to aldehyde.

The same reaction was conducted under reflux for 1.5 hr at 70^0C in oil bath, the benzaldehyde in 95% yield. This experimental was conducted in order to study the effect of reaction condition on the yield of the reaction and product formation, in comparison to our new method of oxidation. As can be seen, the TLC of both of the spots is identical, which means both of the method gave the same product. This confirms that, our new

method an alternative green method for oxidation of several of alcohols. The conversion of alcohols to corresponding aldehydes was 100 percentage.

Table 1. Selective oxidation of different alcohols into corresponding aldehydes using CeO_2 nanoparticles catalyst

Alcohol	Reaction Time (Sec)	Product	Yield
Benzyl alcohol	25	Benzaldehyde	95
m-Nirtobenzyl alcohol	30	m-Nirtobenzaldehyde	96
Cyclohexenol	55	Cyclohexanone	90
P-Methoxybenzyl alcohol	25	P-Methoxybenzaldehyde	90
P-Hydroxybenzyl alcohol	40	P-Hydroxybenzaldehyde	92

Tollen's qualitative and specific test for aldehydes was also conducted and showed positive test to the reagent by forming a clear silver mirror. This also confirms the formation of aldehyde from alcohol shown in **Scheme 2.**

$AgNo_3 + NaOH \rightarrow Ag_2O \rightarrow Ag(NH_3)_2OH + RCHO \rightarrow Ag\downarrow + RCOONH_4 + NH_3 + H_2O \rightarrow$ Silver mirror

Scheme 2. Tollens test reaction for benzaldehyde

IR spectroscopy was also used for further confirmation the success of the reaction.IR spectroscopy for benzaldehyde showed clearly the C=O stretching band at 1701 cm^{-1} which is less than usual value C=O is stretching band of aldehydes.

IV. CONCLUSIONS

A series of alcohol were selectively oxidized to their corresponding aldehydes using environmentally friendly catalyst "active cerium dioxide (CeO_2) nanoparticles" under solvent free condition using microwave irradiation in a very short time and the use of less mole equivalents to perform the reaction. Such conversion has been interested in the field of green chemistry due to the use of same material, and reducing waste of hazardous material in the environment. The average time of a complete conversion of alcohols to their corresponding with high yields carried out between 25-55 seconds by using microwave irradiation only. The important advantage of the present method: are fast, mild, green, easy procedures, and could be applied for oxidation of variety of alcohols such as primary or secondary alcohols to aldehydes without further oxidation to carboxylic acid.

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V.REFERENCES

[1] A.Hamza., D.Srinivas., *Catal.Lett*.,128:434.,(2009).

[2]K.A.Omar., S.G.Tahir., A.S.Saadi., *Indian J.Naturai Sci*., 7:11248.,(2016).

[3]K.Dhanalaxmi.,R.Singuru.,S.K.Kundu.,B.M.Reddy.,A.Bhaumik.,J.Mondal.,*J.RSC.Adv*.,6:36728.,(2016).

[4]K.A.Omar., *Int. J. of Res. in Engineering and Tech.*, 2.241., (2014).

[5]M.M.Najafpour.,F.Rahimi.,E.M.Aro.,C.H.Lee.,*J.R.Soc.,Interface*.,9:2383.,(2012).

[6]J.Fei.,L.Sun.,C.Zhou.,*Nanoscale Res.Lett.*,12:23.,(2017).

[7] V.Kumar., K.Singh. S.Panwar., S.K.Mehta.,*Int.NanoLet*t,7:123,(2017).

[8] S.A.Majetich.,*Jin Y.Science*., 284:470.,(1997).

[9]L.Kang., Z.H.Liu.,*Spectochim.Acta.A.Mol.Biomol.Spectrosc*.,67:864.,(2007).

[10]U.Heiz.,F.Vanolli.,A.Sanchez.,*J.Am.Chem.Sco*.,120:9668. , (1998).

[11] S.G.Taher.,K.A.Omar., B.M.Faqi-Ahmad., *AJGC*., **(4)**,231-238.,(2020).

[12]V.Y.Sonawane., *JETIR*.,**7(3)**,157-159.,(2020).