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Original Research Article

Green and selective oxidation of alcohols using MnO_2 nanoparticles under solvent-free condition using microwave irradiation

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Alcohol oxidation using metal oxides
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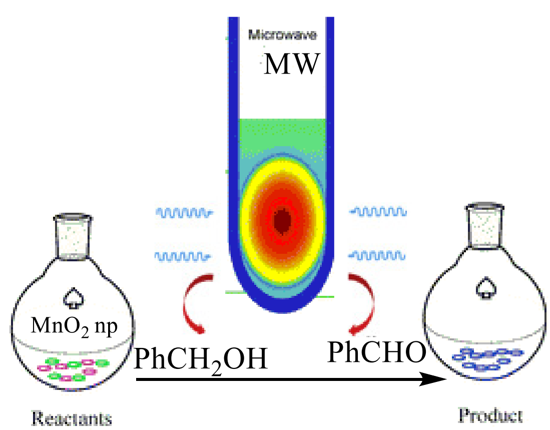
ABSTRACT

Alcohols are selectively oxidized to aldehydes using active manganese dioxide (MnO_2) nanoparticles under solvent-free condition using microwave irradiation. The complete conversion of the alcohols to their corresponding aldehydes was achieved successfully within only 15 seconds of irradiation in microwave oven. The products of oxidation were characterized by TLC, IR, and Tollens' 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.

Graphical Abstract



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Introduction

The oxidation of 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 such as Julia and Witting reaction to produce alkenes, hemicacetals, and acetal formation, imine (Schiff base) formation, *etc*. The first direct oxidation of alcohols to aldehydes is the use of usual oxidizing agents such as Jones reagent potassium dichromate ($K_2Cr_2O_7$) 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 pyridinium chlorochromate (PCC) are the 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.

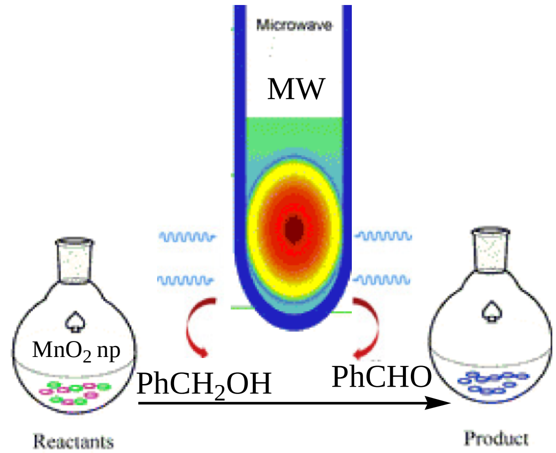
Recently, most of the nanomaterial has been used as a heterogeneous catalyst due to their unique physical properties. The developing catalysts have economic and green behavior attracted by researchers. There are several metal oxide nanoparticles has been used as a catalyst for converting alcohols to aldehyde and vice versa, including copper [1], nickel [2] and manganese [3]. Karzan *et al.* [2] reported the conversion of benzyl alcohol to benzyl aldehyde by using nickel oxide nanoparticles. They indicated that the catalytic activity of nickel nanoparticle for oxidation alcohols. Also, the manganese nanoparticles are utilized as efficient catalysts for oxidation and decomposition of chemical compounds such as catalytic decomposition of hydrogen peroxide [4], as a water oxidizing catalyst in nature [5] at the same time manganese 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 several applications in the different fields such as sensors [7], molecular adsorption [8], removal of CO from hydrogen rich fuel cell [9], lithium batteries [10] and ion exchange [11].

In this study, we report a green, fast and selective oxidation of variety of alcohols to their corresponding aldehydes using active MnO_2 nanoparticles on silica under solvent-free condition using microwave irradiation (Scheme 1).

Experimental

Materials and methods

Scheme 1. Graphical reaction of alcohol oxidation



Alcohols were purchased from Sigma-Aldrich. MnO_2 nanopartcles prepared and provided by Karzan [4]. The purity of the products and reactions checked by TLC on silica gel PolyGram SILG/UV 254 plates. Ordinary microwave oven used for heating the reactions, model type Lynx 2090. IR spectroscopy conducted at Raparin University, Department of Chemistry.

General procedure

The selected alcohol (1 mole/eq.) was mixed with manganese dioxide MnO_2 nanoparticles 1.1 mole/eq.) in solid state without solvent. The mixture was placed in microwave oven and irradiated for 15-45 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 iodin 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.
The general reaction is.

Results and Discussion

Synthesis and characterization of MnO_2 nanoparticles

The MnO_2 Nps has been synthesized according to previously published work [4]. The characterization of synthesized nanopartcles by scanning electron microscopy (SEM) indicated that the morphology of MnO_2 Nps are not uniform and existence of the different shape of nanopartcles due to agglomeration and electronic dispersive X-ray (EDX) confirmed the purity and chemical composition of synthesized nanopartcles. Also, the average crystalline particle size of MnO_2 nanopartcles has been indicated by XRD techniques which was 14 nm as shown in Figure 1 and Table 1. The MnO_2 nanoparticles are considered as the most interesting in the catalytic fields. MnO_2 NPs have a high surface area and prefect dispersed due to their particle size, which leads to availability more active sides to role as catalyst in organic reactions. Also, MnO_2 NPs are one of the most stable metal oxide nanoparticles in the air and high temperature. The biocompatibility of MnO_2 NPs is very important oxidech making them environmentally friendly and safe utilizing them in the different application filed.

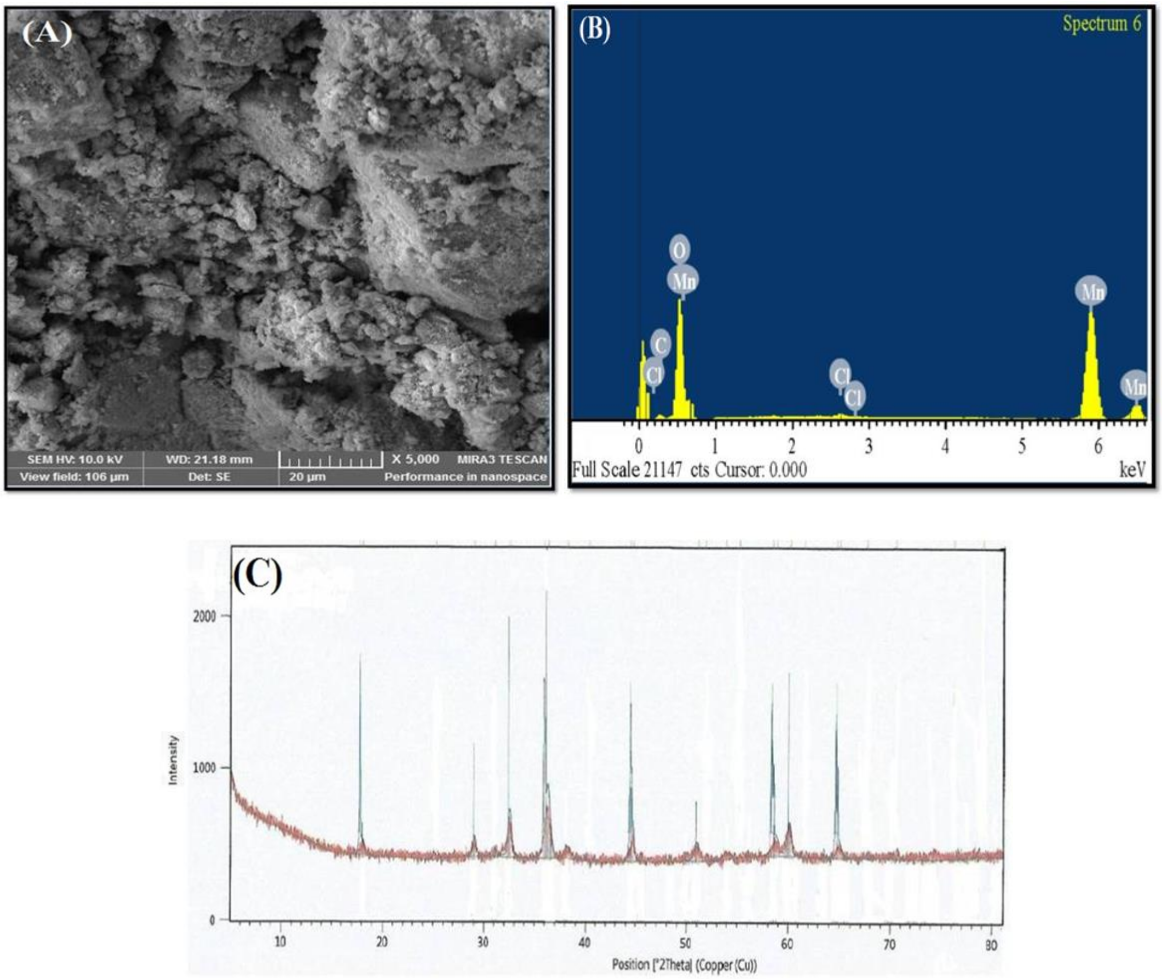


Figure 1. Characterization of MnO_2 nanopartcles using a) SEM, b) EDX and C) XRD techniques

Table 1. Chemical composition of synthesized MnO_2 Nanopartcles

Element	Weight%	Atomic%
C K	4.43	10
O K	35.56	60.23
Cl K	0.62	0.48
Mn K	59.38	29.29
Total	100	

Selective oxidation of alcohols into corresponding aldehydes using MnO_2 nanoparticles catalyst

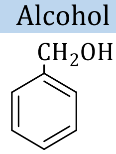
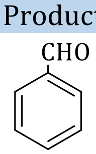
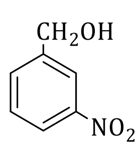
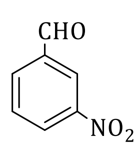
An active MnO_2 nanoparticle was found has a potential to oxidize alcohols to their corresponding aldehydes selectively in excellent yield without further oxidation to carboxylic acids. The reaction procedure is completely green, and easy to be conducted in the laboratory. The simple microwave irradiation oven was used as a heating source to conduct the reaction in solid state under solvent-free reaction. Microwave irradiation has been very popular recently to enhance chemical reactions, as it has several advantages like performing the reaction homogeneously, the less reaction time required, and most of the time gives a chance to perform the reaction under solvent-free condition.

Table 2 shows the selective oxidation of different alcohols into the corresponding aldehydes using manganese dioxide nanoparticles on silica under solvent free condition using microwave irradiation.

The reaction completion was monitored by thin layer chromatography (TLC) (5:1 petroleum ether/ethyl acetate as eluting solvent, and iodin solution as stain). As can be seen from the TLC Figure 2, the top spot belongs to the benzaldehyde (P), while the starting material (s) showed the lower spot just above the base line due to high polarity of alcohol. This confirms the total conversion of alcohol to aldehyde.

The same reaction was conducted under reflux for 2 hrs at 80 °C in oil bath, gave the benzaldehyde in 84% yield. This experiment 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. Figure 3 shows the TLC for the benzaldehyde under two different reaction conditions. The P1 spot represents the produced benzaldehyde under reflux, and P2 represents the produced benzaldehyde under microwave irradiation. As can be seen, the TLC of both of the spots is identical, which means both of the methods gave the same product. This confirms that, our new method an alternative green method for oxidation of variety of alcohols.

Table 2. Selective oxidation of alcohols into corresponding aldehydes over MnO_2 nanoparticles catalyst

Alcohol	Time (Sec.)	Product	Conversion	Selectivity	Yield
	15		100	>99	98
	20		100	>99	97

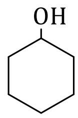
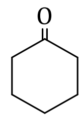
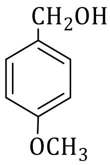
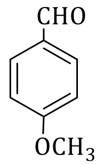
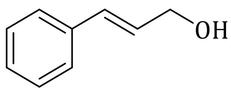
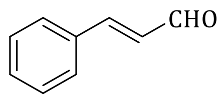
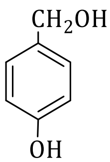
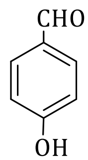
	45		100	>99	93
	15		100	>99	94
	30		100	>99	94
	30		100	>99	90

Figure 2. Thin layer chromatography (TLC) of benzaldehyde

Figure 3. Thin layer chromatography (TLC) of benzaldehyde under different reation condition

Tollens 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 aldehydes from corresponding alcohols Scheme 2.

$$AgNO_3 + NaOH \longrightarrow Ag_2O \xrightarrow{NH_4OH} Ag(NH_3)_2OH + RCHO \longrightarrow Ag + RCOONH_4 + NH_3 + H_2O \longrightarrow \text{Silver mirror}$$

Scheme 2. Tollens' test reaction for benzaldehyde

IR spectroscopy was also used for further confirmation the success of the reaction. IR spectroscopy for 3-nitro benzaldehyde showed clearly the C=O stretching band at 1701 cm^{-1} which is less than the usual value of C=O is stretching band of aldehydes. This is due to conjucation with the aromatic ring, leads to reduce the vibrational frequency. Two bands appeared at 2785 and 2878 cm^{-1}, the first band is for the C-H stretching. The aldehyde functional group and the later is the overtone of C-H deformation of the aldehyde functional group. Disappearance of the OH stretching band was also an indication of the success of the reaction. There is a weak and broad shoulder band at 3369 cm^{-1} represents the overtone of the carbonyl group Figure 4.

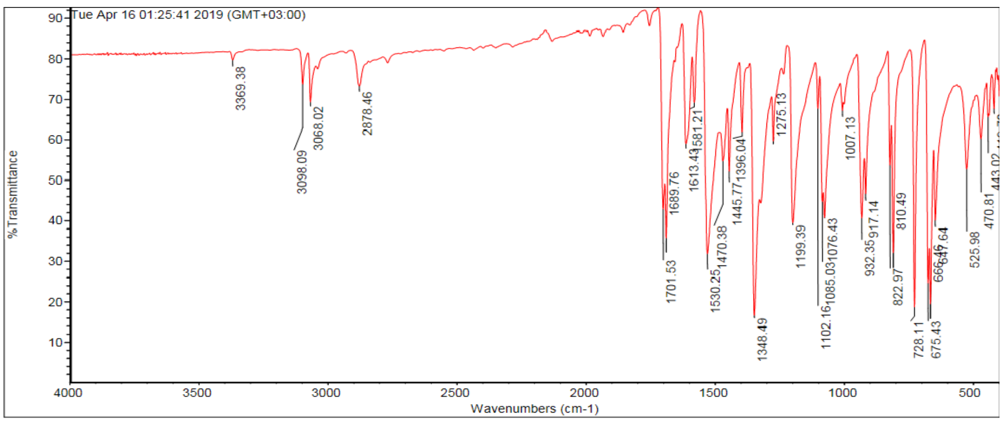


Figure 4. IR spectrum of 3-nitrobenzaldehyde

Conclusions

A series of alcohols were selectively oxidized to their corresponding aldehydes using environmentally friendly catalyst "active manganese dioxide (MnO_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 safe material, and reducing waste of hazardous material in the environment. The average time of a complete conversion of alcohols to their corresponding aldehydes with high yields carried out between 15-45 seconds by using microwave irradiation only. The important advantages of the present method; are fast, mild, green, easy procedure, and could be applied for oxidation of variety of alcohols such as (aromatic, primary, secondary alcohols) to aldehydes without further oxidation to carboxylic.

Disclosure Statement

No potential conflict of interest was reported by the authors.

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