

# Synthesis, characterization and study of catalytic activity of Silver doped ZnO nanocomposite as an efficient catalyst for selective oxidation of benzyl alcohol

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**Abstract.** Powder samples of Ag/ZnO nanocomposite containing different amounts of Ag were synthesized by co-precipitation method. The synthesized samples were characterized by XRD, SEM, EDX and TEM techniques. The XRD results revealed that all the samples show wurtzite hexagonal phase of ZnO. The TEM micrographs of the samples showed that size of Ag-ZnO nanoparticles was in the range of 30–50 nm. Catalytic activity was tested using liquid-phase selective oxidation of benzylic alcohols to aldehydes. The influence of some parameters such as optimum weight of Ag, catalyst dosage, oxidant and various solvents were studied. The superior catalytic performance of the Ag/ZnO nanocomposite was observed in microwave condition compared to that performed in reflux condition. The catalysts were recycled three times in the oxidation of alcohols and little change in the conversion efficiency was observed. The highly dispersed Ag metal particles on ZnO surface was considered to be responsible for the catalytic activity.

**Keywords.** Ag/ZnO nanocomposite; selective oxidation; benzyl alcohol; heterogeneous catalysis.

## 1. Introduction

The heterogeneous catalysis is recently extended to synthetic organic chemistry for production of fine chemicals and pharmaceuticals.<sup>1</sup> Heterogeneous catalysts are convenient to use on a large scale, present a high surface area of the catalytically active phase and also have many other advantages such as separation and recycling process compared to homogeneous catalysts.<sup>2</sup> Among the organic reactions performed under heterogeneous catalysis, selective oxidation reactions are extensively applied in synthetic organic chemistry. The selective oxidation reactions represent one of the most important classes of organic transformations in chemical synthesis.<sup>3,4</sup> The catalytic oxidation of alcohols is particularly fascinating because this reaction can be utilized in the production of carbonyl compounds. Carbonyl compounds such as acetophenone are precursors for some pharmaceuticals, drugs, vitamins, fragrances alcohols, esters and useful in the food processing or cosmetics industry and are important intermediates in many complex syntheses.<sup>2</sup> Today, heterogeneous catalytic systems are available for the selective oxidation of different alcohols to the

corresponding carbonyl compounds.<sup>4,5</sup> Also, molecular oxygen is an interesting oxidant for oxidative reactions due to their obvious economic and ecological advantages, and it has been utilized in oxidation of alcohols with transition metals.<sup>6</sup> Heterogeneous catalysts for oxidation of alcohols are usually based on noble metals such as Pd<sup>7,8</sup> Au<sup>9–11</sup> Ru<sup>12,13</sup> Pt<sup>14–16</sup> and Ag<sup>17–23</sup> or combinations of them.<sup>24–27</sup> The oxidation reactions are carried out in liquid or liquid-like phases. Furthermore, heterogeneous oxidations of alcohols over metal oxide catalysts have also been studied. The studied catalysts are the oxides of magnesium,<sup>28–30</sup> copper,<sup>31</sup> cerium,<sup>32–34</sup> titanium,<sup>35–39</sup> tungsten,<sup>40</sup> cobalt,<sup>41</sup> vanadium,<sup>42</sup> molybdenum,<sup>43</sup> niobium,<sup>44,45</sup> and zinc.<sup>6,46,47</sup> Recently semiconductor metal oxides nanoparticles have been widely used for heterogeneous oxidation of alcohols to the corresponding carbonyl compounds. Among semiconductor metal oxides, TiO<sub>2</sub> has a great potential in organic synthesis.<sup>39,48–53</sup> For instance, Higashimoto *et al.*<sup>49,50</sup> have reported that the photocatalytic oxidation of benzyl alcohol and its derivatives into corresponding aldehydes proceeded at high conversion and selectivity on a TiO<sub>2</sub> photocatalyst under O<sub>2</sub> atmosphere. Wang *et al.*<sup>53</sup> studied the selective oxidation of alcohols to aldehydes and ketones over TiO<sub>2</sub>-supported gold nanoparticles with good yields and

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selectivities. In another report, Marotta *et al.*<sup>39</sup> have studied the selective oxidation of benzyl alcohol to benzaldehyde in aqueous solution by the  $\text{TiO}_2/\text{Cu(II)}$ /solar system. Metal oxide nanoparticles have different physical and chemical properties compared to its bulk material because of their high surface area. Furthermore, the surface of semiconductor metal oxides such as  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{ZnO}$  exhibit both Lewis acid and Lewis base characters. They are good adsorbents for a wide variety of organic compounds, and increase the reactivity of the reactants.<sup>54</sup>  $\text{ZnO}$  is a very interesting metal oxide as it has surface properties which are potentially favourable for diverse organic reactions. Nano-sized Zinc oxide an inexpensive, non-toxic and easily available Lewis acid catalyst is another semiconductor metal oxide which has been widely used as catalyst in organic transformations.<sup>47,54–56</sup> In our previous published research works,<sup>57–63</sup> we synthesized some catalytic systems and activities of the prepared catalysts were described in relation to different reactions. In the present work, we investigated the synthesis of efficient Ag-ZnO nanocomposites for oxidation of benzylic alcohols to the corresponding aldehydes or ketone under reflux and microwave irradiation. Oxidation reactions are studied in various operating conditions such as silver loading, catalyst loading, temperature, solvent, oxidizing agent effect and quantities of alcohols. We are interested in exploring the utility of Ag-ZnO-nanoparticles as a recyclable, economical, cheap and commercially available catalyst for the oxidation of benzylic alcohols. Operational simplicity, non-toxic catalytic system, practicability, high yields of products, good reusability, easy separation cost efficient and simple work-up procedure are the worthy benefits of this protocol.

## 2. Experimental

### 2.1 General remarks

Zinc acetate, silver nitrate and sodium carbonate (from Merck, Germany) are all analytical grades and used without further purification. Deionized water was used in all the experiments.

### 2.2 Preparation of ZnO and Ag/ZnO heterostructure nanocrystals

The pure and Ag-doped ZnO nanoparticles were prepared by co-precipitation method using the precursors of zinc, silver by the reaction of  $\text{Zn}^{2+}$ ,  $\text{Ag}^+$  and  $\text{OH}^-$  in an aqueous medium. Zinc acetate dihydrate

( $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ ) was used as zinc oxide source. The co-precipitation is one of the most successful techniques for synthesis of ZnO powders. To prepare pure ZnO and Ag-doped ZnO, the following steps were followed. In a typical procedure, 0.01 mol of zinc acetate dihydrate was dissolved in 50 mL of deionized water with stirring for half an hour, thus making precursor solution A. Then, 0.01 mol of sodium carbonate was dissolved in 50 mL of deionized water with stirring for half an hour, making precursor solution B. In order to make ZnO nanoparticles, solution A was added dropwise into the solution B while stirring the solution for half an hour. Subsequently, a precipitation was obtained. Then, the resultant precipitate was filtered and washed several times by deionized water. Finally, the obtained precipitation was dried at  $80^\circ\text{C}$  and then calcinated at  $300^\circ\text{C}$  for 2 h. To prepare Ag-doped ZnO, the above procedure was repeated. In the synthesis procedure of Ag-ZnO, certain amounts of silver nitrate (3, 5 and 7 wt% with respect to zinc acetate dihydrate) were dissolved in deionized water under vigorous stirring ( $\sim 200$  rpm) and then the solution was added into the solution of zinc acetate dihydrate/deionized water dropwise. In order to make Ag-doped ZnO, solution of zinc acetate dihydrate/silver nitrate was added dropwise to a solution of sodium carbonate under constant stirring for half an hour. The resultant precipitate was separated by filtration and washed several times by deionized water and so obtained precipitation was dried at  $80^\circ\text{C}$  and then calcinated at  $300^\circ\text{C}$  for 2 h. The nanoparticles thus synthesized were then used for further experimental exploration, i.e., catalytic oxidation of benzylic alcohols.

### 2.3 Catalytic test

A certain amount of catalysts (30 mg) was placed in the two necked, round-bottomed flask and then 1 mmol of alcohol and 10 mL of solvent (acetonitrile, dichloromethane and ethanol) were introduced into the reactor through a septum. The catalytic experiments were carried out under reflux and microwave condition under atmospheric pressure and magnetic stirring, using t-BHP 70%, (0.3–0.5 mL) or hydrogen peroxide 30% (0.3 mL) as oxidant. The progress of the reaction was followed using thin layer chromatography. After the reaction was run for the desired time, the products were filtered out from the catalyst and then oxidation products were analyzed using a gas chromatograph with a GC capillary column HP 6890 and a FID detector.

### 2.4 Characterization techniques

To investigate the morphology of the pure and Ag-doped samples scanning electron microscopy (SEM)

images were obtained on a Philips XL30 equipped with an energy dispersive (EDS) microanalysis system for compositional analysis of the doped samples. For the SEM analysis, samples were covered with Au. The particles sizes were obtained by transmission electron microscope (TEM) images on a Philips CM10 instrument with an accelerating voltage of 100 kV. X-ray diffraction measurements were recorded by a Philips PW1840, X-ray diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ), scan rate 0.02  $2\theta$ /s and within a range of  $2\theta$  of 10 to 70 degree at room temperature.

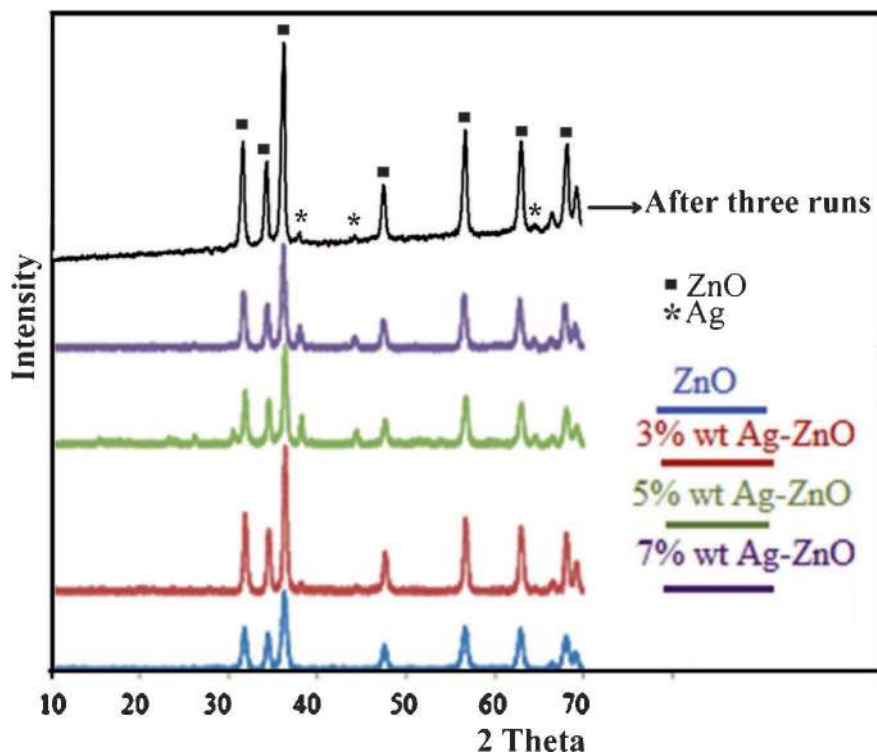
### 3. Results and Discussion

#### 3.1 Crystal structure of ZnO and Ag/ZnO heterostructure nanocrystals

The XRD patterns of the as-synthesized samples are shown in figure 1. All the materials showed a hexagonal wurtzite crystal structure and high crystallinity of ZnO. The XRD patterns of all the Ag-doped ZnO catalysts are almost similar to that of ZnO, suggesting that there is no change in the crystal structure upon silver doping process. All XRD patterns in Ag-ZnO samples obviously show two sets of diffraction peaks, indicating that the as-synthesized products are composite materials with high crystallinity. Those marked with

“■” can be indexed to hexagonal wurtzite ZnO, while the others marked with “\*” can be indexed to face-centered-cubic (fcc) metallic Ag. No other crystalline impurities are observed in the patterns. The XRD patterns of 5% and 7% Ag-ZnO shows that the intensity of the Ag diffraction peak increased, showing aggregation of the Ag particles on the surface of ZnO. In addition, there is no remarkable shift of Ag-ZnO diffraction peaks, implying that no  $\text{Zn}_{1-x}\text{Ag}_x\text{O}$  solid solution is formed and the change of the lattice parameters of ZnO nanocrystals should be negligible.<sup>64</sup> After three cycles, the catalyst 3% Ag-ZnO was washed, and then characterized using XRD. The results showed that Ag-ZnO still showed a hexagonal wurtzite crystal structure. On the other hand, the XRD patterns of Ag-ZnO nanocomposite after three runs showed that silver nanoparticles were present on the surface of the catalyst and the grain-boundary stability was similar to the as-prepared samples.

The preparation of nano Ag-ZnO was carried out by zinc acetate dihydrate as zinc precursor. The excess acetate anion adsorbed on the surface of Ag-ZnO could act as a capping agent, which favoured grain-boundary stability in the as-prepared catalyst. This type of complexation of acetate anion on the surface of Ag-ZnO may be responsible for the decrease in the crystallite size of catalyst in this synthesis.

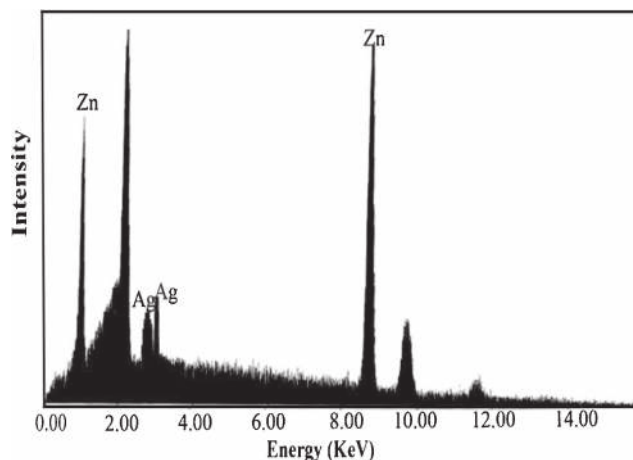


**Figure 1.** XRD patterns of ZnO and Ag-ZnO nanocomposite with different Ag contents and after three cycles.

### 3.2 Morphology analysis

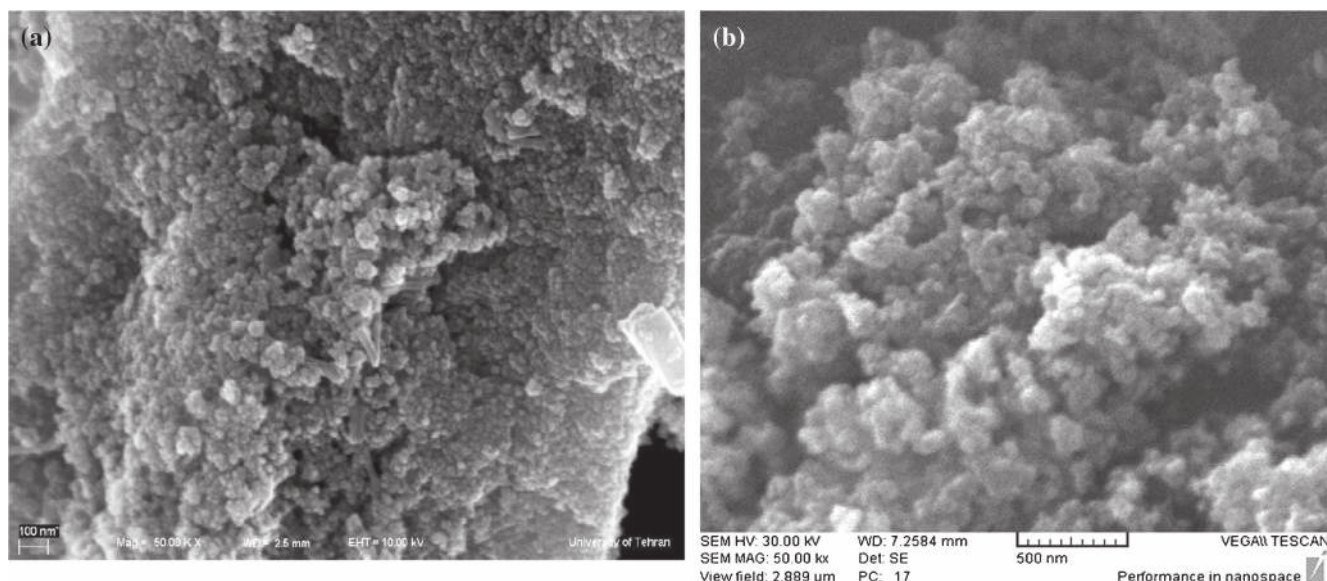
In order to investigate the morphology of the obtained samples, comparison between the SEM images of the ZnO and 3% wt Ag-ZnO is illustrated in figure 2. In figure 2A, typical SEM image of ZnO nanoparticles is shown. The image reveals that most of them are irregularly shaped and relatively spherical with dimensions that are less than 100 nm. Figure 2B shows the SEM image of 3% Ag-ZnO nanoparticles. The Ag-ZnO sample shows a surface morphology similar to that of the bare ZnO. The particles in this sample have relatively a sphere-like morphology and the nanoparticles were composed of agglomerates of Ag-ZnO particles. To check the chemical composition of the synthesized ZnO nanocomposite, an energy-dispersive X-ray (EDX) spectroscopy analysis was performed. Figure 3 shows the EDX spectroscopy for 3% Ag-ZnO nanocomposite. The existence of the Ag dopant can be clearly observed in the spectrum.

In order to obtain detailed information about the exact size and morphology of the as-synthesized samples, TEM images are presented. Figure 4 depicts transmission electron micrographs of ZnO nanoparticles, 3% wt Ag-ZnO and 3% wt Ag-ZnO after three runs. TEM image of ZnO particles (figure 4A) shows that the ZnO consists of nanoparticles with average size of 20–70 nm. The TEM image of Ag-ZnO shows the shape of the Ag-doped ZnO nanoparticles, observed as aggregates with average particle size of 30–50 nm (figure 4B). The TEM image of the sample shows the Ag/ZnO heterostructure nanocrystals

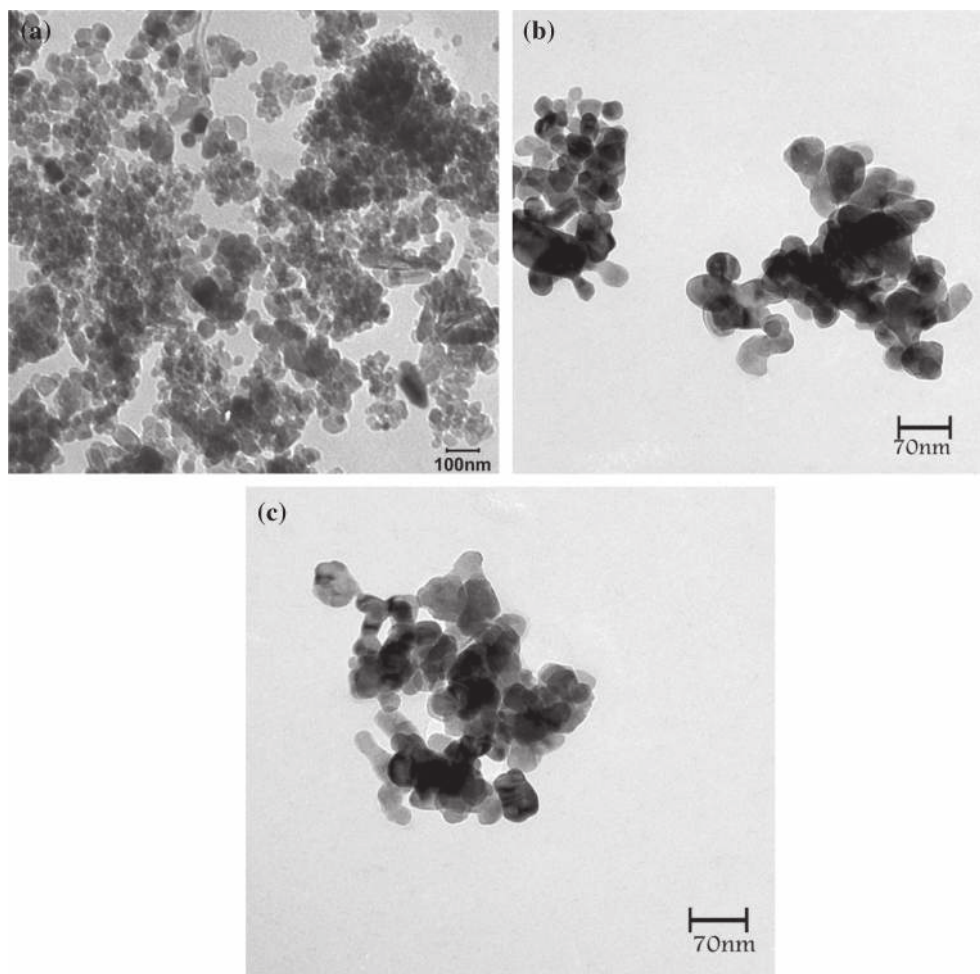


**Figure 3.** EDS analysis of 3 wt% Ag-ZnO.

consisting of metallic Ag nanoparticles. The black dots are Ag nanoparticles and Ag aggregates are not found in our TEM observations, indicating that all metallic Ag nanoparticles are highly dispersed in ZnO nanocrystals. It is obvious that the diameters of Ag nanoparticles are in the range of 20–40 nm. After three reaction cycles, the catalyst 3% Ag-ZnO was washed, and then characterized using TEM analysis. Figure 4C shows the TEM image of 3% wt Ag-ZnO after three cycles of reaction. The TEM image of sample shows the Ag/ZnO heterostructure consisting of metallic Ag nanoparticles and the grain-boundary stability was achieved in the as prepared catalyst. On the other hand, TEM image showed no obvious changes in the surface morphology indicating that the catalyst had good mechanical stability.



**Figure 2.** SEM images of: (A) ZnO and (B) 3 wt% Ag-ZnO nanocomposite.



**Figure 4.** TEM images of: (A) ZnO, (B) 3% wt Ag-ZnO nanocomposite and (C) 3% wt Ag-ZnO after three cycles.

### 3.3 Catalytic activity study

We studied the oxidation of different types of alcohols, including primary and secondary benzylic alcohols. They were efficiently oxidized to their corresponding carbonyl compounds with Ag-ZnO as the catalyst. The catalytic oxidation was carried out at both reflux and microwave condition. In the presence of pure ZnO catalyst, the oxidation of alcohols was also tested and result is shown in table 1.

**3.3a Effect of Ag doping concentration on catalytic properties of Ag/ZnO:** To evaluate the catalytic activity of the ZnO and Ag-doped ZnO and determine the optimum amount of Ag doping, oxidation experiments on benzhydrol (Diphenylmethanol) were carried out by different Ag amounts of doped samples ranging from 1 to 7 wt%, and the results are given in table 1. As shown in table 1, Ag loading had a remarkable effect on benzhydrol conversion. It can be seen that the conversion increased with increasing load of Ag during the

oxidation process. The oxidation reaction takes place on the pure ZnO with low conversion, but with the increase of Ag content in Ag-ZnO catalysts, the conversion of alcohol increased significantly. In fact, the catalyst properties are closely associated with the amount of metal active sites and the size of Ag. Higher Ag loading obviously ensures sufficient active Ag sites.<sup>10</sup> As shown in table 1, the 3 wt% Ag-doped ZnO sample had suitable catalytic efficiency and the optimal Ag doping is 3 wt%. It is reported that the supported Ag catalyst needs an induction period to reach its optimal activity. The presence of induction time indicates that the metallic Ag particles on the catalyst surface are required to be activated at the initial stage and the oxygen molecules adsorbed on the metallic Ag is dissociated to create an oxidized Ag surface ( $\text{Ag}^+$ ) for the oxidation of benzyl alcohol.<sup>17,18</sup> After 15 min, the conversion reaches a constant value of more than 85%.

Since, support ZnO has very low catalytic activity (table 1), it is believed that the pre-adsorbed oxygen and oxygen species from oxidized Ag surface are

**Table 1.** Oxidation of benzhydrol in presence of ZnO and Ag-ZnO with different Ag doping concentration under reflux condition (1 mmol benzhydrol, 30 mg catalyst, 0.4 mL TBHP and 10 mL acetonitrile).

Samples	Time (min)	Conversion (%)
No catalyst	45	5
ZnO	30	10
1 wt% Ag-ZnO	15	60
3 wt% Ag-ZnO	15	85
5 wt% Ag-ZnO	15	85
7 wt% Ag-ZnO	15	90



**Scheme 1.** Schematic reaction mechanism of benzyl alcohol oxidation on Ag-ZnO nanocomposite.

responsible for the alcohol oxidation. Oxidized Ag species are dispersed on the surface of dominant metallic Ag particles.<sup>17</sup> Metallic Ag seems to have a higher affinity for gaseous O<sub>2</sub>. The oxidized Ag surface on the supported metallic Ag was proposed to be an active site for the oxidation of benzyl alcohol.<sup>18</sup>

Based on the aforementioned considerations, a plausible schematic model of the active sites of the supported Ag catalyst is proposed for catalytic oxidation of benzyl alcohol and illustrated in scheme 1.

In the selective oxidation of benzyl alcohol, the gaseous oxygen molecules can be adsorbed on the surface of the metallic Ag particle and dissociate to form the atomic oxygen species such as O<sub>ad</sub><sup>-x</sup> through electron transfer from the metallic Ag particles.<sup>17,18</sup> The surface of supported metallic Ag will be positive-charged with formation of Ag<sup>+</sup> species.

The atomic oxygen species on the surface of Ag first migrate to the ZnO surface to react with the activated alcohol molecules adsorbed on the ZnO, leading to the formation of an electron-rich state (Ag<sup>+</sup> + e<sup>-</sup> → Ag<sup>0</sup>) on the Ag particle surfaces. The generated atomic oxygen species with nucleophilic character activate the C–H and O–H bonds in benzyl alcohol to produce corresponding aldehyde. However, the oxidation of benzyl

alcohol occurs not only on the Ag particle surface but is also dependent on the ZnO support. If the metal and support are separated from each other, transportation of oxygen species would be inhibited.

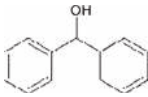
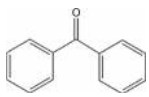


**3.3b Effect of catalyst weight:** The effect of 3 wt% Ag-ZnO weight on the oxidation of the benzhydrol was studied in the weights of 20, 30 and 40 mg (table 2). It is notable that catalytic activity is proportional to the amount of the catalysts. A negligible conversion of benzhydrol (only 5%) was obtained in the absence of the catalysts, indicating that the presence of catalyst is necessary for the benzhydrol oxidation (table 1). A small but significant increase in the rate of the catalytic oxidation observed with an increase in the catalyst weight from 20 to 40 mg. On the other hand, the conversion increased from 60 to 90% by increasing the catalyst amount from 20 to 40 mg. In the higher amount of the catalyst, the chances are better for the reactants (benzhydrol and TBHP) to react before diffusing out of the catalysts surface. Consequently, the extent of oxidation of benzhydrol increases on increasing the catalyst amount and suitable efficiency (85%, after 15 min) of benzhydrol was obtained at catalyst dosage of 30 mg.

**3.3c Effect of reaction temperature on oxidation process:** The catalytic activity of 3 wt% Ag-ZnO catalyst was investigated on the oxidation of the alcohols at reflux condition (80°C) and room temperature (25°C) (tables 3 and 4). The results show that the catalytic activity of Ag-ZnO nanocomposites at reflux condition is much higher than the room temperature. It can be seen that conversion of benzhydrol and benzyl alcohol largely increased at reflux condition. Therefore, high temperature favours the reaction as the benzhydrol conversion increased from 40 to 85% and also benzyl alcohol conversion increased from 30 to 90% when the temperature was elevated from 25°C to 80°C. Therefore, reflux condition (80°C) was considered the optimum reaction temperature. As shown in table 1, under reflux condition, benzyl alcohol and its derivatives substituted by –Cl, –Br, –NO<sub>2</sub>, –CH(CH<sub>3</sub>)<sub>2</sub>, –CH(OH)CH<sub>3</sub>

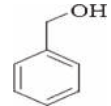

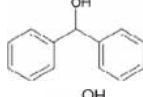
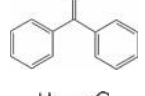
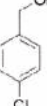
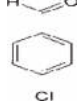
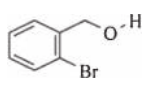
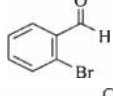
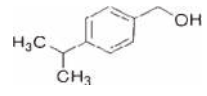
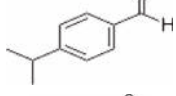
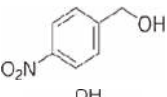
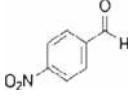
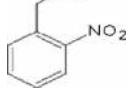
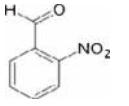
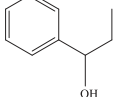
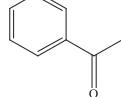
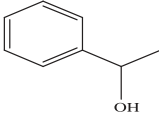
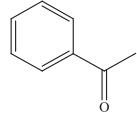
**Table 2.** Oxidation of benzhydrol in presence of different amount of 3 wt% Ag-ZnO (1 mmol benzhydrol, 30 mg catalyst, 0.4 mL TBHP and 10 mL acetonitrile).

Catalyst weight	20 mg	30 mg	40 mg
Conversion (%)	60%	85%	90%

**Table 3.** Oxidation of benzhydrol and benzyl alcohol in presence 3 wt% Ag-ZnO at room temperature (1 mmol alcohols, 30 mg catalyst, 0.4 mL TBHP and 10 mL acetonitrile).

Entry	Substrate	Product	Time(min)	Conversion %	GC Yield %
1			60	40	35
2			60	30	27

**Table 4.** Oxidation of benzylic alcohols to their corresponding carbonyl compounds using 3 wt% Ag-ZnO under reflux condition (1 mmol alcohols, 30 mg catalyst, 0.4 mL TBHP and 10 mL acetonitrile).

<sup>a</sup> Entry	Substrate	Product	Time (min)	Conversion	GC Yield %
1			30	90	77
2			15	85	80
3			5	95	90
4			15	85	80
5			15	90	85 <sup>c</sup>
6			45	40	35
7			45	30	25
8			30	90	86
9			30	90	84

**Table 5.** Oxidation of benzhydrol and benzyl alcohol in presence different solvents (3 wt% Ag-ZnO, reflux, (1 mmol alcohols, 30 mg catalyst, 0.4 mL TBHP and 10 mL acetonitrile, 15 min).

Solvents	Acetonitrile	Ethanol	Dichloromethane
Benzhydrol (conversion %)	85	60	40
Benzyl alcohol (conversion %)	90	40	30

**Table 6.** Oxidation of benzhydrol and benzyl alcohol in presence t-BHP and H<sub>2</sub>O<sub>2</sub> (3 wt% Ag-ZnO, reflux, 1 mmol alcohols, 30 mg catalyst, 0.4 mL TBHP and H<sub>2</sub>O<sub>2</sub> and 10 mL acetonitrile).

Oxidant Alcohols	t-BHP		H <sub>2</sub> O <sub>2</sub>	
	time	conversion%	time	Conversion %
Benzhydrol	15	85	60	40
Benzhyl alcohol	15	70	60	30

**Table 7.** Reusability of 3 wt% Ag-ZnO for oxidation of benzhydrol and benzyl alcohol (reflux, 1 mmol alcohols, 30 mg catalyst, 0.4 mL TBHP and 10 mL acetonitrile).

Reusability Alcohols	Run 1		Run 2		Run 3	
	Time (min)	Conversion (%)	Time (min)	Conversion (%)	Time (min)	Conversion (%)
Benzhydrol	15	80	15	75	15	67
Benzhyl alcohol	15	70	15	65	15	55

and-CH(OH)C<sub>2</sub>H<sub>5</sub> groups were converted to corresponding aldehydes with different conversion and yield on Ag-ZnO, while no other products were observed.

**3.3d Effect of different solvents:** To investigate the effect of solvents in the catalytic activity of the Ag-doped ZnO, oxidation of the benzhydrol and benzyl alcohol was studied in various other solvents e.g., acetonitrile, ethanol and dichloromethane (table 5). It can be seen that, acetonitrile is a suitable solvent for the oxidation reaction. As shown in table 5, the best results were obtained when acetonitrile was used as the solvent. However, in the presence of acetonitrile 85% and 70% conversion were achieved for benzhydrol and benzyl alcohol. Ethanol and dichloromethane were also used as the solvent where a 60% and 40% of conversion was observed in benzhydrol in 15 min. It can be concluded that the polarity index of acetonitrile (acetonitrile: 5.8, ethanol: 5.2 and dichloromethane: 3.1) is higher than other solvents and strong polarity of solvent may be useful for the oxidation of alcohols (table 5).

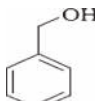

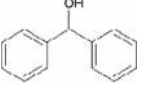
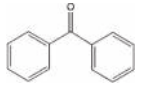

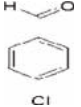
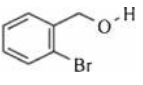
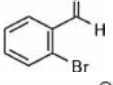
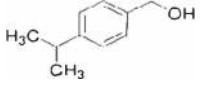
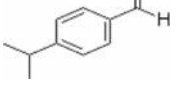
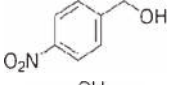
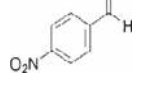
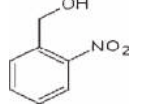
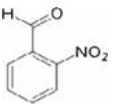
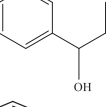
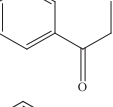
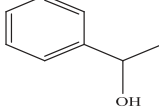
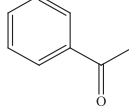
**3.3e Effect of oxidants:** The utilization of oxidants plays a crucial role in the oxidation process. To evaluate the oxidants' effect in the catalytic activity of the Ag-doped ZnO, oxidation of the benzhydrol and benzyl alcohol was studied in presence of two oxidants

e.g., tetrabutyl hydroperoxide (t-BHP) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (table 6). The results show that the catalytic activity of Ag-ZnO nanocomposites in presence of t-BHP (t-BHP/alcohol molar ratio of 0.25) is much higher than that of H<sub>2</sub>O<sub>2</sub>. Maximum conversion and good reaction time was obtained by t-BHP while H<sub>2</sub>O<sub>2</sub> is not found to be effective for the oxidation of alcohols. Actually, when H<sub>2</sub>O<sub>2</sub> was utilized for the oxidation of alcohols, most of H<sub>2</sub>O<sub>2</sub> molecules were decomposed into O<sub>2</sub> and the reaction time was prolonged.<sup>60</sup>

**3.3f Reusability of catalytic systems:** The reusability of the synthesized catalysts is a significant factor from environmental and economical points of view. In heterogeneous catalysts the leaching of metal is a main problem, which leads to loss of catalyst activity on subsequent uses. In order to investigate the stability of the catalytic systems, recycling experiments were performed. The catalyst after reaction were recovered by centrifugation and washed with deionized water and ethanol, then dried and reused for catalytic reaction under the similar conditions. The catalytic activity of the Ag-doped ZnO decreased when the recovered catalytic system was reused for further catalytic reactions and in the third cycle, the conversion was reduced to nearly 67% and 55% for benzhydrol and benzyl respectively, as shown in table 7.



**Table 8.** Oxidation of benzylic alcohols to their corresponding carbonyl compounds using 3 wt%Ag-ZnO under microwave condition (1 mmol alcohols, 30 mg catalyst, 0.4 mL TBHP and 10 mL acetonitrile).

Entry	Substrate	Product	Time(min)	Conversion	GC Yield %
1			3	70	65
2			3	80	75
3			2	90	87
4			2.5	90	82
5			2.5	90	85
6			3	50	40
7			3	30	25
8			2.5	90	85
9			2.5	80	78

**3.3g Effects of reaction conditions and reaction time (comparison of oxidation of alcohols under microwave and reflux conditions):** In order to study the influence of the reaction conditions, oxidation experiments were assayed in different conditions e.g., reflux and microwave (tables 4, 8). Microwave method has shown the best results in shorter time. The reaction rate is highest in the microwave state and is lower in the reflux condition. Table 8 summarizes the main results for the oxidation of benzyl alcohol under microwave irradiation using Ag-ZnO catalyst. As shown in table 8, compared with reflux procedure, in microwave reaction, benzylic alcohol and its derivatives were successfully converted to their corresponding aldehydes with higher conversion at very short time. Results showed that good conversions of starting material (>50%) were obtained after 2–3 min of reaction. The use of microwaves

reduced times of reaction (from 30 h to 3 min) as well as increased the conversion of starting material in the oxidation under relatively similar reaction conditions. This demonstrates that the microwave irradiated synthesis is superior to that of conventional methods in terms of reaction time and energy consumption. The production yields for the microwave reaction were a little lower but comparable to those achieved by reflux process. Whereas the microwave reaction were meaningfully shorter, it was difficult to maintain a constant temperature; though, the reflux condition was heated more slowly. The advantages of microwave synthesis are that the reactions under dielectric heating show higher yields and purities, and in many cases the microwave synthesis is considered as environment friendly method for organic transformation.<sup>65</sup> The advantage of microwaves as novel and cleaner reaction

tool has been presented to reduce the reaction times and energy consumption together with an increase in production yields and selectivity.<sup>66,67</sup>

#### 4. Conclusion

In order to perform effective, selective liquid-phase oxidation of benzyl alcohols, Wurtzite ZnO nanocomposite that was doped with silver was synthesized using co-precipitation method in a single step. The Ag-ZnO showed high activity and conversion in the oxidation of benzyl alcohol to benzaldehyde. The catalytic activity increased as the silver loading increased. The most suitable conditions such as shorter reaction time, acetonitriles as solvent, temperature of 80°C, catalyst amount of 30 mg, TBHP/alcohol molar ratio of 0.25, Ag loading of 3% were obtained in reflux condition. It is a useful strategy for the synthesis of aldehydes or ketones, without the formation of carboxylate compounds. Results also showed that the catalytic activity of Ag-ZnO nanocatalyst at microwave condition is much higher than that of reflux condition. The reactivity order of the alcohols examined in this work was that aromatic alcohols like benzhydrol were more reactive than aliphatic alcohols. The reusability of the ZnO supported with silver was ascertained and catalytic performance of the regenerated catalyst was comparable to that of the fresh catalyst.

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