

RESEARCH PAPER

## Ag/ZnO Nanocomposites: Preparation, Characterization and Investigation of the Catalytic Activity for Oxidation of Toluene in Liquid Phase

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### ABSTRACT

In this research, Ag/ZnO nanocomposites were prepared and characterized by transition electron microscopy (TEM), the energy dispersive X-ray spectrum (EDS) and X-ray diffraction patterns (XRD). These nanocomposites were used as catalysts for the oxidation of toluene to benzaldehyde and benzoic acid with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and tert-butylhydroperoxide (TBHP) as oxidizing agent in the liquid phase. For these Ag/ZnO nanocomposites, acetonitrile was used as a solvent, since all the reagents dissolved and show the highest yields. The oxidation products of toluene are benzaldehyde and benzoic acid. The results of this study showed that oxidant and the catalyst type affected the efficiency of toluene oxidation. TBHP was found to be better oxidizing agent than H<sub>2</sub>O<sub>2</sub>, since higher efficiency of product were observed when TBHP was used. The catalytic performance of 2.5%Ag/ZnO nanocomposite was better than the 1% and 5%Ag/ZnO nanocomposites. Under the optimal reaction conditions, the catalytic system of 2.5%Ag/ZnO nanocomposite gave about 76.3% efficiency of toluene.

#### How to cite this article

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### INTRODUCTION

Volatile Organic Compounds (VOCs) propagated from industrial reactions and automobile are not only detrimental to human health since they are malodorous, mutagenic and/or carcinogenic but also because they can create poisonous photochemical oxidants and suspended particulate substances through photochemical reactions. Many countries have already enacted rigorous rules to reduction VOC propagation [1]. In order to effective elimination VOCs, different technologies have been developed, including adsorption, bio-destruction, membrane separation, thermal combustion and photo-catalytic oxidation [2]. Among these technologies, catalytic oxidation is investigated as the most promising process for reduction VOCs' propagation. Indeed, catalytic oxidation might

be acted at temperatures much lower compared to thermal combustion. The advantage of the low temperature oxidation is the decrease of fuel consumption, especially for large volumes of diluted VOC contaminated air. The optimization of the catalyst formulation is not simple task due to the large diversity of VOCs and the complexity of VOC-containing mixtures. Primarily, the catalyst has to allow ignition temperatures as low as possible. In addition, it has to be very active, because of the low concentration of VOCs and the large volumes to be treated, and also highly selective in the sense that only desired product should be made. Eventually, the catalyst has to resist the reaction conditions over long periods of operation, i.e., has to be thermally stable.

Toluene is a typical aromatic hydrocarbon with

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three primary C-H bonds that is undesirable to the environment and can be oxidized to various useful chemical materials, such as benzyl alcohol, benzaldehyde, benzoic acid and benzoate [3]. Among these materials, benzaldehyde is the most favorable and value-added product due to its large importance in human life [4]. In the medicinal industries, it is utilized for the production of intermediates for amipiphilicin, ephedrine, chloramphenicol, etc. [5,6]. It is also a main intermediate for production the certain aniline dyes, processing the perfume and flavoring compounds [7]. Traditionally, benzaldehyde is mainly manufactured by chlorination of the  $-CH_3$  group of toluene followed by saponification [8]. This reaction strongly suffers from too much waste causing environmental difficulties due to the advantage of a remarkable amount of chlorine. In addition, it is associated with the equipment corrosion and manufacture of poisonous acidic waste [9]. The Rhodia, Dowand Snia-Viscosa reactions were utilized as industrial realization of the liquid phase oxidation of toluene with homogeneous metal salt catalysts, but the halogen ions and acidic solvents were involved in these reactions [10–12].

Various oxidants such as TBHP and  $H_2O_2$  are used in presence of transition metal compounds as homogeneous catalysts for this oxidation reaction. But, the environmental limitation and the catalyst separation is one of the important problems in the homogeneous catalysts. In order to avoid these problems, heterogeneous catalysts are under intensive investigation. In these catalysts, alumina, silica, zirconia, active carbon, zeolites and zinc oxide are commonly used as the supports [13–15]. Bulk oxides in general cannot be used in industrial reactions as they impart poor thermal stability that lead to fast decomposition of the catalyst [16]. Hongpei Wang et al. [17] have investigated the catalytic oxidation of toluene with nano-sized  $\gamma$ -alumina supported CuO and  $MnO_x$  as catalyst. In another report, Guan Huang and coworkers have used manganese tetraphenylporphyrin (Mn TPP) supported on chitosan (CTS) for catalytic oxidation of toluene with molecular oxygen as oxidant. Mn TPP/CTS containing 2 mg of Mn TPP as a catalyst showed excellent catalytic performance of up to 5.9% toluene conversion and 96% selectivity for benzaldehyde and benzyl alcohol in the toluene oxidation [18]. A cost-effective method for the selective oxidation of toluene to benzaldehyde

was developed based on immobilized  $CoO_x$  on  $SiO_2$  catalyst with predominating cobaltous ions in the presence of N-hydroxyphthalimide (NHPI) and hexafluoropropan-2-ol (HFIP) using ambient molecular oxygen at room temperature. A toluene conversion of 91% and a selectivity to benzaldehyde of 68% were realized [19]. CuMn mixed oxides catalysts doped with La were prepared following a co-precipitation method and used for the catalytic oxidation of toluene. These catalysts exhibit the best catalytic activity, with a 90% conversion temperature of 255°C [20]. However, to the best of our knowledge, there is no report for application of Ag/ZnO nanocomposites for catalytic oxidation of toluene with  $H_2O_2$  and TBHP. Here, we synthesized Ag/ZnO nanocomposites by the chemical precipitation method. In this strategy the size is control by arrested precipitation technique. The basic trick has been to synthesis and studies the nanomaterial in situ i.e. in the same liquid medium avoiding the physical changes and aggregation of tiny crystallites. Also studied their catalytic abilities in the oxidation of toluene with TBHP and  $H_2O_2$  as the oxidant in the liquid phase.

## MATERIALS AND METHODS

### *Chemicals and materials*

Zinc nitrate hexahydrate (MERK), silver nitrate (Fluka; >99.0%), polyethylene glycol (PEG-4000), sodium borohydride (MERK) and ammonium hydroxide solution used in this work, all were of analytical grade.

### *Preparation of catalysts*

#### *Preparation of ZnO nanoparticles*

ZnO nanoparticles were synthesized by the chemical precipitation method. Experimental details were as follows: firstly, 3 g polyethylene glycol (PEG-4000) as surfactant was dissolved in 30ml of distilled water. Secondly, 2.98 g of Zinc nitrate hexahydrate ( $Zn(NO_3)_2 \cdot 6H_2O$ ) was added slowly to the above solution under the stirring, resulting in the formation of a clear solution. Thirdly, ammonium hydroxide solution was dropped into the mixing solution until the pH value reached 7, which immediately resulted in the formation of white precipitates in the beaker. Then kept at 60°C for 1 h under stirring, the as-produced precipitates were filtered, washed with alcohol and distilled water for several times. Lastly, the obtained white precipitate dried in an oven at 100°C overnight and calcined in air at 600°C for 2 h.

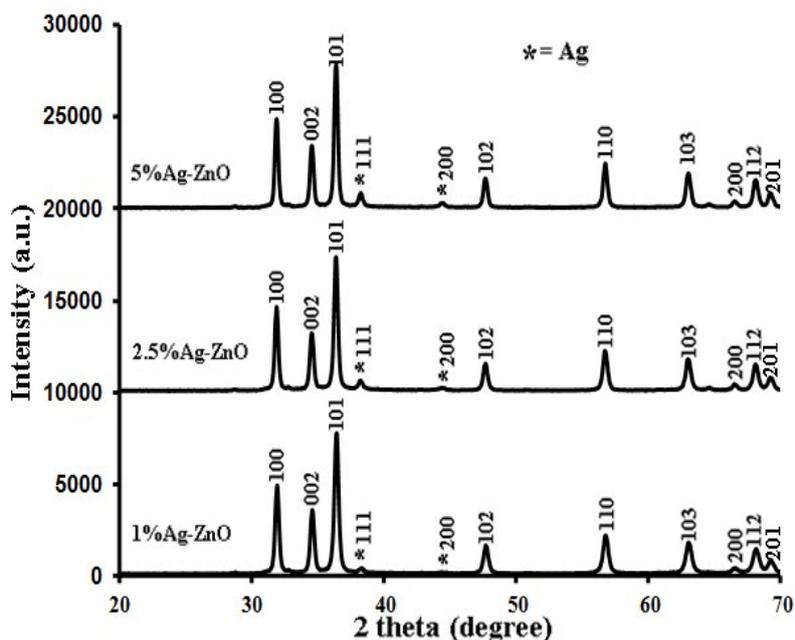


Fig. 1. XRD patterns of the Ag/ZnO nanocomposites with different Ag loadings.

#### Preparation of Ag/ZnO nanocomposites

Ag/ZnO nanocomposites were prepared by a chemical reduction technique. Various amounts of  $\text{Ag}^+$  ions, prepared by dissolving silver nitrate salt in distilled water, then the solutions were added into the suspension of ZnO such that the  $\text{Ag}^+$  concentration was of 1, 2.5 and 5 at.% in relation to ZnO. Sodium borohydride ( $\text{NaBH}_4$ ) solution (freshly prepared) was then added dropwise with vigorous stirring. The reduction of Ag from  $\text{Ag}^+$  to  $\text{Ag}^0$  was confirmed by the darkening of the solution. The suspensions were then filtered, washed and dried to give Ag deposited ZnO catalysts.

#### Experimental procedure

In a typical procedure, a mixture of 0.25 g catalyst, 20 ml solvent of acetonitrile and 32 mmol toluene was stirred under nitrogen in a 50 ml round bottom flask equipped with a condenser and a dropping funnel at room temperature for 30 min. Then 15 mmol of TBHP (tert-butylhydroperoxide) or  $\text{H}_2\text{O}_2$  (30% in  $\text{H}_2\text{O}$ ) was added as oxidizing reagents. The resulting mixture was then refluxed for 8 h under  $\text{N}_2$  atmosphere. After filtration, the solid was washed with solvent and then the reaction mixture was analyzed by gas chromatograph (GC). Products identification was done with gas chromatography mass spectrometry (GC-MS) and confirmed by comparison of their

retention times with authentic commercial samples of these compounds.

#### Characterization

X-ray powder diffraction (XRD) patterns of the samples were recorded using a Bruker Advance D8 Diffractometer with Cu K $\alpha$  radiation ( $\lambda=0.154$  nm). Chemical analysis of the samples was done by energy dispersive X-ray (EDX) analysis joined to a Philips XL 30 scanning electron microscope. Transmission electron microscopy (TEM) measurements were performed on a LEO 912 AB TEM operated at 120 kV. Products of these oxidation reactions were analyzed by GC (Shimadzu 8A) and were identified by GC-MS (Finnigan TSQ-7000).

## RESULTS AND DISCUSSION

#### Characterization of the catalysts

Fig. 1 shows XRD patterns of the Ag/ZnO nanocomposites with different Ag loadings. All the diffraction can be indexed as the typical hexagonal wurtzite structure of ZnO with lattice constants in agreement with the values in the standard card (JCPDS 36-1451). diffractions associated with Ag metal were also observed ( $38.1^\circ$ ,  $44.3^\circ$  and  $64.4^\circ$ ) which were all consistent with the reported values (JCPDS 04-0783), indicating that the product was the composites of Ag and ZnO. diffractions

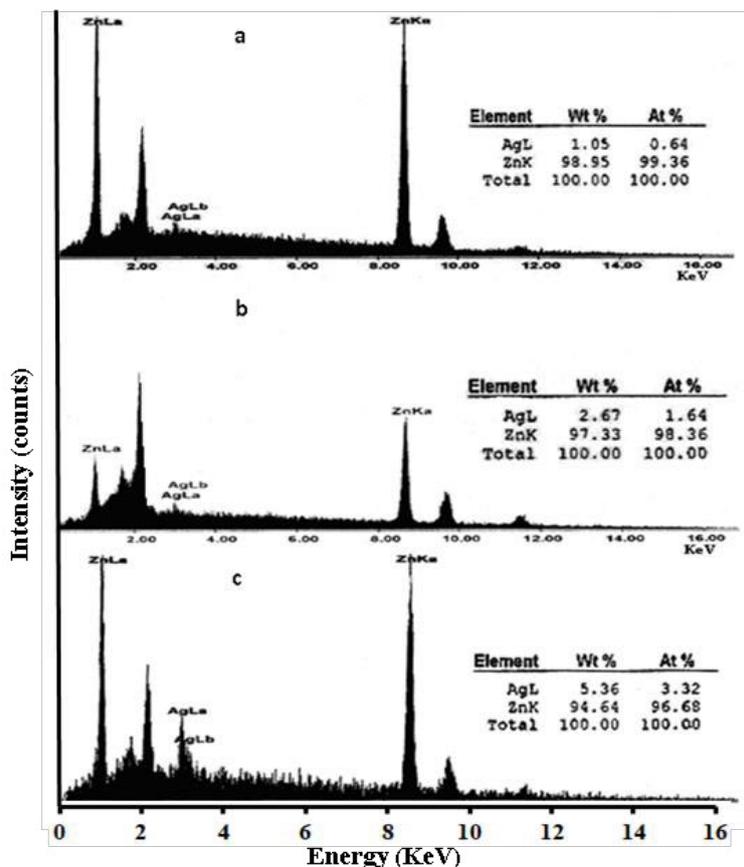


Fig. 2. EDS diagrams of the Ag/ZnO nanocomposites with different Ag loadings: (a) 1%Ag/ZnO (b) 2.5%Ag/ZnO (c) 5%Ag/ZnO.

associated with Ag metal were observed after loading of 1 % Ag and increased in intensity with increasing Ag loading. No diffractions were observed corresponding to silver oxide phases in the Ag/ZnO nanocomposites. Its average crystal size is determined to be 75 nm according to Scherrer equation ( $D = k\lambda / \beta \cos \theta$ ).

The energy dispersive X-ray spectrum (EDS) analysis of the nanocomposites was performed in order to determine the loading amount of Ag. Fig. 2 depicts the EDS spectrum of the products. It can be seen that the values of loaded Ag are near to 1%, 2.5% and 5%. Also, no other impurity peak is found in XRD and EDS spectra, indicating that the products are pure.

Fig. 3 shows the TEM images of Ag/ZnO nanocomposites. Based on the images, all the Ag nanoparticles were uniformly dispersed on the surface of ZnO, with a well-distributed spherical particles with the diameter ranging from 50 to about 80 nm. It can be seen that small spherical nanoparticles of Ag are found on all the three

supports after Ag deposition.

#### Catalytic oxidation of toluene

Based on the earlier studies on the oxidation of toluene, TBHP was used as an oxidizing agent [21], this oxidizing agent was found to cause minimal destruction of Ag/ZnO nanocomposite, and to give better selectivity of the products. For comparative purposes,  $H_2O_2$  was also used as an oxidizing agent. The solvent of acetonitrile was employed for the catalysis, since all the reagents dissolved and show the highest yields.

The performance of the synthesized nanocomposites as a heterogeneous catalysts for the oxidation of toluene was investigated using hydrogen peroxide and tert-butylhydroperoxide as oxidizing reagents (Table 1). In all the cases, the only products observed were benzaldehyde and benzoic acid. In the presence of 2.5 wt.% Ag/ZnO nanocomposite, conversion percentage of toluene was 76.3% with TBHP as an oxidant. Contrastive experiment result show that toluene oxidation

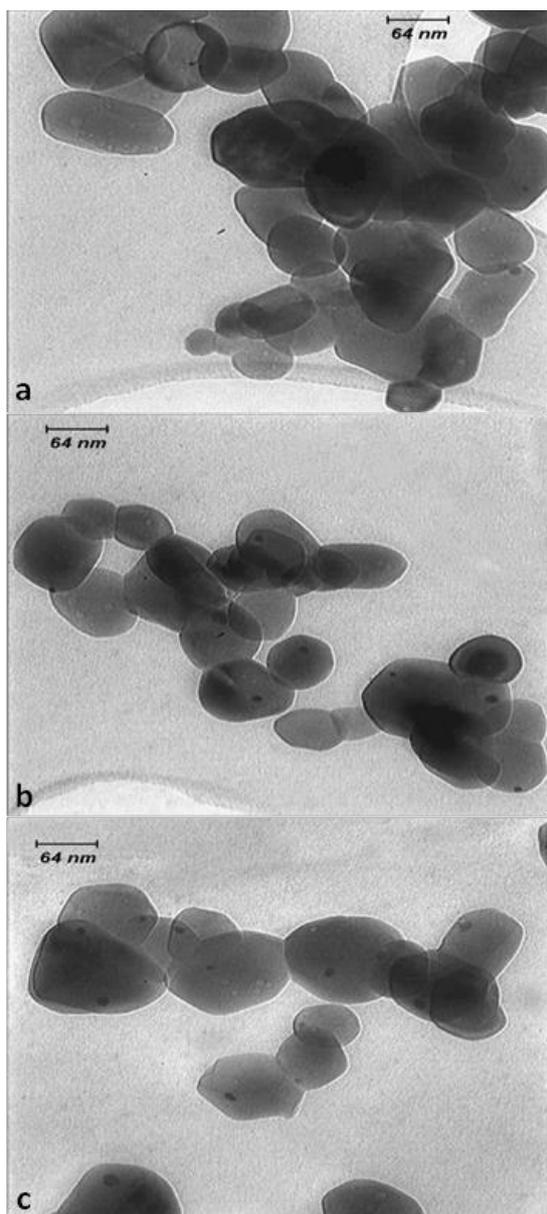


Fig. 3. TEM images of the Ag/ZnO nanocomposites with different Ag loadings: (a) 1%Ag/ZnO (b) 2.5%Ag/ZnO (c) 5%Ag/ZnO.

with TBHP and  $H_2O_2$  did not occur with removing of the catalyst under the same reaction condition. This indicated that Ag/ZnO nanocomposites acted catalysis during toluene oxidation. B. Du et al. [22] reported that with simple and efficient zeolite catalyst and in the presence of  $H_2O_2$  oxidant, a conversion percent of around 32% of toluene with selectivity of 25% benzaldehyde, 20.8% benzyl alcohol and 27.5% benzoic acid was obtained. They

also concluded that benzoic acid was obtained as the main product.

To investigate the catalytic power of reused Ag/ZnO nanocomposites, the nanocomposite used in each catalytic oxidation was isolated from the reaction mixture for reuse later. The experimental results showed that Ag/ZnO nanocomposites could be reused several times. These results proved that Ag/ZnO nanocomposites possessed good reusable catalysis.

#### *Influences of reaction time on toluene oxidation reaction*

In this experiment, the change in conversion (%) of toluene in the presence of TBHP oxidant and 2.5% Ag/ZnO nanocomposite was monitored and plotted with respect to time (Fig. 4). The reaction was carried out at reflux temperature for 8 h with 0.25 g catalyst and 32 mmol toluene and 15 mmol TBHP in a round bottom flask and some samples was drawn out at regular intervals and analyzed by GC. Fig. 4 shows that with increasing the time, the conversion of toluene was enhanced continuously until 76.1% and then remains constant after 7 h, therefore duration about 7-8 h is proper reaction time.

#### *Influences of the loading amount of Ag on toluene oxidation reaction*

For investigation of the loading effect Ag on the conversion and selectivity of the products three nanocomposites were tested. In Table 1, details of the conversion and selectivity of the products for each nanocomposite are shown. It is observed that maximum conversion occurs with the catalyst of 2.5% Ag/ZnO. It is known that Ag nanoparticles can be highly dispersed on ZnO nanoparticles at 2.5 wt.% loading. A drop of conversion of toluene of the nanocomposite with higher loadings than 2.5 wt.% is possibly due to a more reduction of the specific surface area of the nanocomposite. With these optimum conditions, the order of catalytic activities is as follows:

2.5% Ag/ZnO > 5% Ag/ZnO > 1% Ag/ZnO.

#### *Influences of oxidant type on toluene oxidation reaction*

Fig. 5 shows that the reactivity of the toluene toward oxidation with TBHP and  $H_2O_2$  on Ag/ZnO nanocomposites depend on type of oxidant. tert-Butylhydroperoxide was found to be a more convenient oxidizing reagent due to weaker O-O bond

Table 1. Results of the toluene oxidation using Ag/ZnO nanocomposites as catalysts.

Catalyst	Oxidant	Conversion toluene (%)	Product selectivity (%)	
			Benzaldehyde	Benzoic acid
1% Ag/ZnO	TBHP	48.7	25	75
1% Ag/ZnO	H <sub>2</sub> O <sub>2</sub>	40.3	70	30
2.5% Ag/ZnO	TBHP	76.3	29	71
2.5% Ag/ZnO	H <sub>2</sub> O <sub>2</sub>	64.6	72	28
5% Ag/ZnO	TBHP	64.5	25	75
5% Ag/ZnO	H <sub>2</sub> O <sub>2</sub>	53.5	73	27
ZnO	TBHP	27.8	25	75
ZnO	H <sub>2</sub> O <sub>2</sub>	20.3	70	30

Reaction condition: 0.25 g catalyst, toluene 32 mmol, oxidant 15 mmol, solvent acetonitrile, reflux temperature, reaction time 8 h, Conver. = (mole of toluene reacted/moles of toluene in the feed) × 100. Selec.i = (moles of toluene converted to i/moles of toluene reacted) × 100.

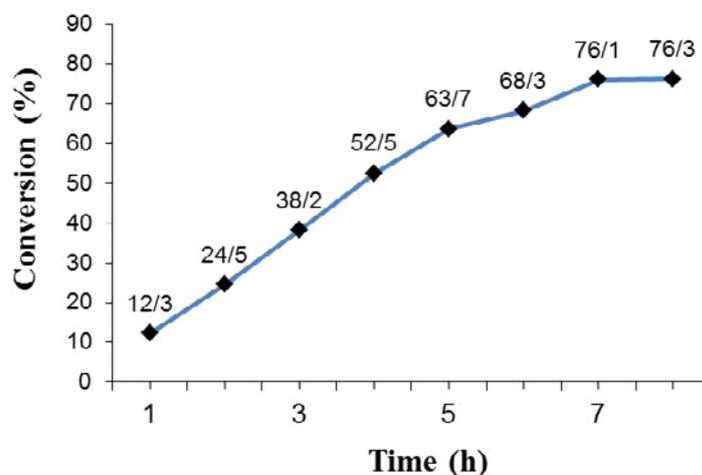


Fig. 4. The effect of reaction time on toluene conversion.

than hydrogen peroxide. In this regard, it is worth noting that using H<sub>2</sub>O<sub>2</sub> as reactant the complexes (both encapsulated and unsupported Ag) lose their characteristic color during the course of the reaction.

Oxidation of toluene with TBHP gave benzoic acid as the main product and benzaldehyde as by-product. When the oxidant was changed to hydrogen peroxide, benzaldehyde obtained as the main product. Although both TBHP and

H<sub>2</sub>O<sub>2</sub> oxidize toluene in the presence of Ag/ZnO nanocomposites, but TBHP give more oxidation of toluene under the similar conditions, which leads to the production of benzoic acid.

#### Comparison of catalytic power of ZnO-supported Ag with that unsupported Ag

The experimental data of toluene oxidation catalyzed by the ZnO-supported Ag or unsupported

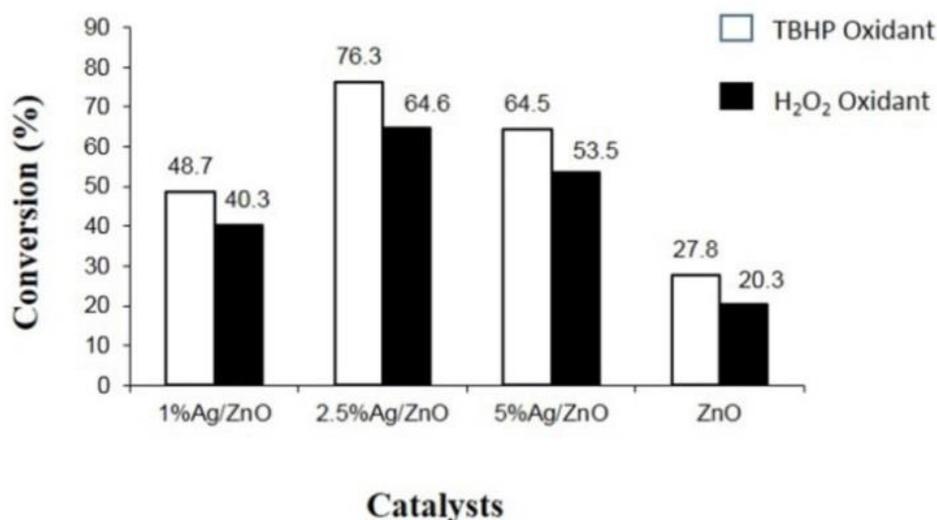


Fig. 5. The effect of oxidant type on toluene conversion in the presence of various catalysts.

Ag in the presence of TBHP oxidant shows that the partial oxidation of toluene catalyzed by Ag supported on ZnO nanoparticles had better conversion than that of unsupported Ag nanoparticles. When 2.5% Ag/ZnO nanocomposite was used as catalyst, the toluene conversion was 76.3%. However, when the unsupported Ag nanoparticles was used as the catalyst, the toluene conversion was 35.9%. The result confirms the high stability of Ag nanoparticles on the ZnO surface or in the ZnO pores.

## CONCLUSION

Ag/ZnO nanocomposites have been synthesized and were well characterized. Catalytic activities of these nanocomposites have been investigated for the selective oxidation of toluene to benzaldehyde and benzoic acid using TBHP and H<sub>2</sub>O<sub>2</sub> as the oxidant, in the presence of acetonitrile solvent. Based on results, TBHP was found to be a more convenient oxidizing reagent. We found that 2.5 wt.% Ag/ZnO nanocomposite was a good heterogeneous catalyst for the oxidation of toluene with TBHP under our experimental conditions and could achieve about 76.3% conversion of toluene and selectivity of 29% benzaldehyde and 71% benzoic acid. According to the results, time has a crucial effect on the catalytic activity, so we were optimized the time and after 7 h the best results was shown in oxidation reaction of toluene. The recycling investigations exhibited that Ag/ZnO nanocomposites was recyclable, and could behave

as a truly heterogeneous catalyst.

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

## REFERENCES

1. Popova M, Szegedi Á, Cherkezova-Zheleva Z, Mitov I, Kostova N, Tsoncheva T. Toluene oxidation on titanium- and iron-modified MCM-41 materials. *Journal of Hazardous Materials*. 2009;168(1):226-32.
2. Zhang C, Guo Y, Guo Y, Lu G, Boreave A, Retailleau L, et al. LaMnO<sub>3</sub> perovskite oxides prepared by different methods for catalytic oxidation of toluene. *Applied Catalysis B: Environmental*. 2014;148-149:490-8.
3. Wang Y, Li H, Yao J, Wang X, Antonietti M. Synthesis of boron doped polymeric carbon nitride solids and their use as metal-free catalysts for aliphatic C–H bond oxidation. *Chem Sci*. 2011;2(3):446-50.
4. Kesavan L, Tiruvalam R, Rahim MHA, bin Saiman MI, Enache DI, Jenkins RL, et al. Solvent-Free Oxidation of Primary Carbon-Hydrogen Bonds in Toluene Using Au-Pd Alloy Nanoparticles. *Science*. 2011;331(6014):195-9.
5. Acharyya SS, Ghosh S, Tiwari R, Sarkar B, Singha RK, Pendem C, et al. Preparation of the CuCr<sub>2</sub>O<sub>4</sub> spinel nanoparticles catalyst for selective oxidation of toluene to benzaldehyde. *Green Chem*. 2014;16(5):2500-8.
6. Lu X, Yuan Y. Copper-containing hexagonal mesoporous silicas for styrene epoxidation using tert-butylhydroperoxide. *Applied Catalysis A: General*. 2009;365(2):180-6.

7. Lv J, Shen Y, Peng L, Guo X, Ding W. Exclusively selective oxidation of toluene to benzaldehyde on ceria nanocubes by molecular oxygen. *Chemical Communications*. 2010;46(32):5909.
8. Partenheimer W. Methodology and scope of metal/bromide autoxidation of hydrocarbons. *Catalysis Today*. 1995;23(2):69-158.
9. Ghosh S, Acharyya SS, Tripathi D, Bal R. Preparation of silver-tungsten nanostructure materials for selective oxidation of toluene to benzaldehyde with hydrogen peroxide. *J Mater Chem A*. 2014;2(38):15726-33.
10. Nomiya K, Hashino K, Nemoto Y, Watanabe M. Oxidation of toluene and nitrobenzene with 30% aqueous hydrogen peroxide catalyzed by vanadium(V)-substituted polyoxometalates. *Journal of Molecular Catalysis A: Chemical*. 2001;176(1-2):79-86.
11. Wang F, Xu J, Li X, Gao J, Zhou L, Ohnishi R. Liquid Phase Oxidation of Toluene to Benzaldehyde with Molecular Oxygen over Copper-Based Heterogeneous Catalysts. *Advanced Synthesis & Catalysis*. 2005;347(15):1987-92.
12. Carrell TG, Cohen S, Dismukes GC. Oxidative catalysis by Mn4O46+ cubane complexes. *Journal of Molecular Catalysis A: Chemical*. 2002;187(1):3-15.
13. Badieli A R, Gholami J, Mohammadi Ziarani G, Abbasi A R, Direct oxidation of benzene to phenol in liquid phase by H<sub>2</sub>O<sub>2</sub> over vanadium catalyst supported on highly ordered nanoporous silica. *J Nanostructures*. 2011; 1(1): 69-75.
14. Torkian L, Amereh E, Nano sized Ni/TiO<sub>2</sub> @ NaX zeolite with enhanced photocatalytic activity. *Journal of Nanostructures*. 2016; 6(4): 307-311.
15. Ebadi A, Shojaei S, Synthesis, characterization and catalytic performance in the selective oxidation of alcohols by metallophthalocyanines supported on zinc oxide nanoparticles. *Journal of Nanostructures*. 2017; 7(1): 57-63.
16. Routray K, Reddy KRSK, Deo G. Oxidative dehydrogenation of propane on V<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts: understanding the effect of support by parameter estimation. *Applied Catalysis A: General*. 2004;265(1):103-13.
17. Wang H, Lu Y, Han Y, Lu C, Wan H, Xu Z, et al. Enhanced catalytic toluene oxidation by interaction between copper oxide and manganese oxide in Cu-O-Mn/γ-Al<sub>2</sub>O<sub>3</sub> catalysts. *Applied Surface Science*. 2017;420:260-6.
18. Huang G, Luo J, Deng CC, Guo YA, Zhao SK, Zhou H, et al. Catalytic oxidation of toluene with molecular oxygen over manganese tetraphenylporphyrin supported on chitosan. *Applied Catalysis A: General*. 2008;338(1-2):83-6.
19. Shi G, Xu S, Bao Y, Xu J, Liang Y. Selective aerobic oxidation of toluene to benzaldehyde on immobilized CoOx on SiO<sub>2</sub> catalyst in the presence of N-hydroxyphthalimide and hexafluoropropan-2-ol. *Catalysis Communications*. 2019;123:73-8.
20. Pan J, Du W, Liu Y, Cheng Y, Yuan S. Lanthanum-doped Cu Mn composite oxide catalysts for catalytic oxidation of toluene. *Journal of Rare Earths*. 2019;37(6):602-8.
21. Grootboom N, Nyokong T. Iron perchlorophthalocyanine and tetrasulfophthalocyanine catalyzed oxidation of cyclohexane using hydrogen peroxide, chloroperoxybenzoic acid and tert-butylhydroperoxide as oxidants. *Journal of Molecular Catalysis A: Chemical*. 2002;179(1-2):113-23.
22. Du B, Kim S-I, Lou L-L, Jia A, Liu G, Qi B, et al. A simple and efficient zeolite catalyst for toluene oxidation in aqueous media. *Applied Catalysis A: General*. 2012;425-426:191-8.