



Gold Nanoparticle Immobilized Porous Manganese Oxide Microspheres As Heterogeneous Catalyst for Benzyl Alcohol Oxidation

Benzil Alkol Oksidasyonu için Heterojen Katalizör Olarak Altın Nanoparçacık Immobilize Edilmiş Gözenekli Manganez Oksit Mikroküreler

Kadriye Özlem Hamaloğlu[✉]

Department of Chemical Engineering, Hacettepe University, Ankara, Turkey.

ABSTRACT

A heterogeneous catalyst in the form of Au nanoparticles (Au NPs) immobilized porous manganese oxide (Mn_3O_4) microspheres was synthesized. Mn_3O_4 microspheres were obtained by sol-gel templating method. The heterogeneous catalyst ($Au@Mn_3O_4$) showed good performance when compared with similar catalysts in the oxidation of benzyl alcohol (BnOH). $Au@Mn_3O_4$ microspheres obtained by the decoration of Au NPs on Mn_3O_4 microspheres performed 99.4% of BnOH conversion and 100 % of benzaldehyde (BnCHO) formation yield. Also the heterogeneous catalyst showed a good stability and agglomeration resistance in the reusability experiments. There was no remarkable loss in the catalytic activity when the catalyst was reused up to 5 times.

Key Words

Manganese oxide, benzyl alcohol oxidation, gold nanoparticles, heterogeneous catalysis.

Öz

Altın nanopartiküllerle (Au NP'ler) dekore edilmiş gözenekli manganez oksit (Mn_3O_4) mikroküreleri formunda heterojen bir katalizör sentezlenmiştir. Mn_3O_4 mikrokürelerinin sentezi için sol-jel kalıplama yöntemi kullanılmıştır. Sentezlenen heterojen katalizör, benzil alkol (BnOH) oksidasyonunda benzer katalizörlerle karşılaştırıldığında iyi performans göstermiştir. Au NP'lerin Mn_3O_4 mikroküreleri üzerinde immobilizasyonu ile elde edilen heterojen katalizör ($Au@Mn_3O_4$) ile %99.4 BnOH dönüşümü ve %100 benzaldehit (BnCHO) oluşum verimi elde edilmiştir. Ayrıca heterojen katalizör, tekrar kullanılabilirlik deneylerinde iyi bir stabilite ve aglomerasyona karşı direnç göstermiştir. $Au@Mn_3O_4$ mikroküreleri, katalitik aktivitede kayda değer bir kayıp olmaksızın 5 kata kadar yeniden kullanılabilmiştir.

Anahtar Kelimeler

Manganez oksit, benzil alkol oksidasyonu, altın nanopartiküller, heterojen kataliz.

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Correspondence to: K.Ö. Hamaloğlu, Department of Chemical Engineering, Hacettepe University, Ankara, Turkey.

E-Mail: ozlemnaz@hacettepe.edu.tr

INTRODUCTION

Selective oxidation of benzyl alcohols to benzaldehyde (BnCHO) is one of most important processes in industry as BnCHO is used as an intermediate in chemical synthesis such as perfume and pharmaceuticals. Benzyl alcohol (BnOH) oxidation to BnCHO by using different catalysts had been a trend research topic in literature and industry [1, 2]. BnOH oxidation is performed by mixing the catalyst and the alcohol usually in organic solvent in the presence of oxygen or oxidant such as hydrogen peroxide or ter-butyl hydrogen peroxide [3].

In recent years, the usage of noble metal (such as Au, Pt, Pd, etc.) supported catalysts had been reported for BnOH oxidation [1-10]. There are problems during catalytic reactions due to aggregation and poor catalytic activity when only noble metal catalysts are used [9, 10]. Therefore to overcome these problems, different metal oxide supports like cerium dioxide [11-13], titanium dioxide [14-16], manganese oxide [17], vanadium oxide [18] and some other various metal oxides [19-22] have been used for the immobilization of noble metal nanostructures. Among these catalysts, Au nanostructures on supported metal oxides have been shown to be excellent catalysts in the benzyl alcohol oxidation. Catalytic activity of Au nanostructures in BnOH oxidation was influenced by the nature of metal oxide and immobilization methods [23, 24]. In oxidation reactions there is an attraction between gold nanostructures and metal oxide supports via their lattice oxygen vacancies [25, 26].

In this study, Mn_5O_8 microspheres were used as a support to synthesize a new heterogeneous catalyst ($Au@Mn_5O_8$ microspheres) for the selective oxidation of

BnOH to BnCHO. $Au@Mn_5O_8$ microspheres were characterized by SEM, XPS, XRD and BET and the catalytic performances in BnOH oxidation were correlated with the characterization results.

MATERIALS and METHODS

Materials

The chemicals used to synthesize poly(methacrylic acid-co-ethylene dimethacrylate), poly(MAA-co-EDMA) microspheres and Mn_5O_8 microspheres were supplied from Sigma-Aldrich (Milwaukee, WI, U.S.A) [27]. To derivatize Mn_5O_8 microspheres with amine groups, 3-aminopropyltriethoxysilane (APTES), triethylamine (TEA) and 2-propanol (Iso-PrOH) were also obtained from Sigma-Aldrich. To synthesize Au nanoparticles (Au NPs), chloroauric acid-trihydrate ($HAuCl_4 \cdot 3H_2O$, Sigma Chemical Co., St. Louis, MO, USA), sodium borohydride ($NaBH_4$, Sigma Chemical Co., St. Louis, MO, USA) were used. Benzyl alcohol (BnOH), diethylene glycol dimethyl ether (DEGDME), tert-butyl hydrogen peroxide (TBHP), and acetonitrile (ACN) were purchased from Sigma-Aldrich. Distilled deionized (DDI) water with a resistivity of 18 M Ω cm was used in all experiments.

Synthesis of $Au@Mn_5O_8$ microspheres

Poly(MAA-co-EDMA) microspheres were synthesized by multi-step micro-suspension polymerization by using poly(glycidyl methacrylate) (GMA) seed latex [27]. Staged shape templating method as given in the previous study was used by using poly(MAA-co-EDMA) microspheres as polymeric template to obtain Mn_5O_8 microspheres [27]. Calcination of organic-inorganic composite microspheres was performed at 410 °C for 4 h to remove polymeric template to obtain Mn_5O_8 microspheres.

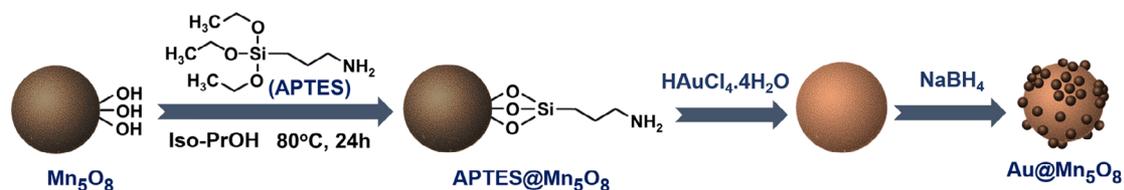


Figure 1. The route for the synthesis of $Au@Mn_5O_8$ microspheres.

The followed route used to synthesize Au@Mn₅O₈ microspheres is shown in Figure 1. The route consists of derivatization of manganese oxide microspheres and immobilization of gold nanoparticles (Au NPs) on microspheres. Prior to immobilization of Au NPs, Mn₅O₈ microspheres were derivatized with APTES to acquire amine groups according to the procedure given in a previous study [28]. Au NPs were immobilized on amine-derivatized Mn₅O₈ microspheres by impregnation method. In this method, Mn₅O₈ microspheres (100 mg) were added to 10 ml of HAuCl₄·3H₂O solution (1.3 M). After stirring the suspension for 2 h, 2.4 ml of NaBH₄ solution (0.1 M) was added and stirring was continued for 1 more hour. Au NPs immobilized-porous Mn₅O₈ microspheres (Au@Mn₅O₈) were then isolated by centrifugation and decantation with DDI water.

Characterization

The surface morphology of Au@Mn₅O₈ microspheres was determined by Scanning Electron Microscope (SEM) (Tescan, GAIA3+Oxford XMax 150 EDSWaltham, Oxford, UK). X-ray diffraction (XRD) patterns of Au@Mn₅O₈ microspheres were determined by X-ray diffractometer with CuKα1 radiation (λ) 1.540 nm operating at 30 mA and 40 kV (Scintag, a part of Thermo Fisher Scientific, Waltham, MA, U.S.A.). Pore size distribution, pore volume, pore size and specific surface area of Au@Mn₅O₈ microspheres were determined by a surface area and pore size analyzer (Quantachrome, Nova 2200E, UK), by using nitrogen adsorption/desorption method via the Brunauer-Emmett-Teller (BET) equation. Au content of Au@Mn₅O₈ were also determined by Inductively

Coupled Plasma – Mass Spectrometer (ICP-MS, ThermoFisher X series II, Thermo Fisher Scientific, USA).

Benzyl alcohol (BnOH) oxidation

The catalytic activity of the catalyst was studied by the oxidation of benzyl alcohol (BnOH). In these catalytic activity experiments, the heterogeneous catalyst (Au@Mn₅O₈ microspheres) was dispersed in 10 mL of DEGDME in a glass reactor containing 0.1 mL of BnOH and 0.15 mL of TBHP. The reactor was heated to 80°C in an oil bath under magnetic stirring. 100 µL of sample taken from reactor at different times was analyzed with a High-Pressure Liquid Chromatography (HPLC, Shimadzu, Japan) joint with UV detector (214 nm, SPD-10AV, Shimadzu, Japan) and 5 mm Silica column (250×4.60mm 5 micron, Phenomenex SphereClone). The flow rate of the mobile phase (composition: ACN/water: 10/90 % v/v) was 5 mL/min.

RESULTS and DISCUSSION

Characterization of catalysts

The information about the surface morphology and size distribution of Au@Mn₅O₈ microspheres was obtained by SEM photographs that are given in Figure 2. The microspheres were obtained in spherical form as seen in the Figure. From the SEM photo given in Figure 2A, the mean size of microspheres was obtained as 3.92±0.25 µm and the coefficient of variation (CV) was calculated as 6.35 %. The surface of the microspheres was rough due to their porous structure. (Figure 2B and Figure 2C)

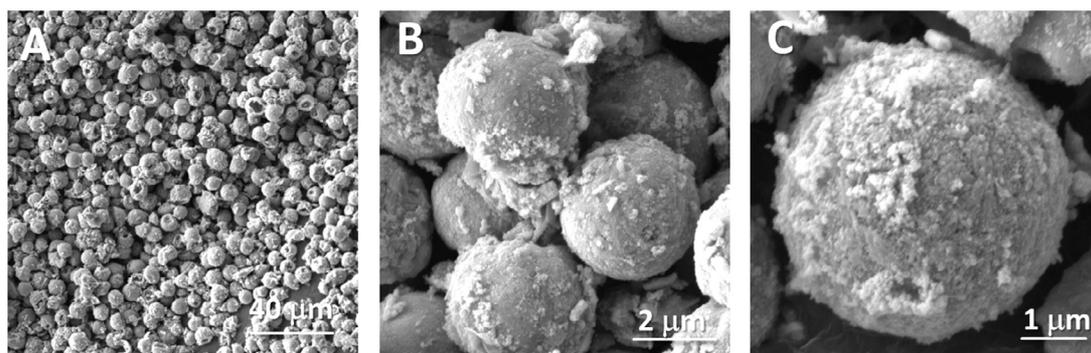


Figure 2. SEM photographs of Au@Mn₅O₈ microspheres with magnifications of (A) X2,500, (B) X25,000, (C) X50,000.

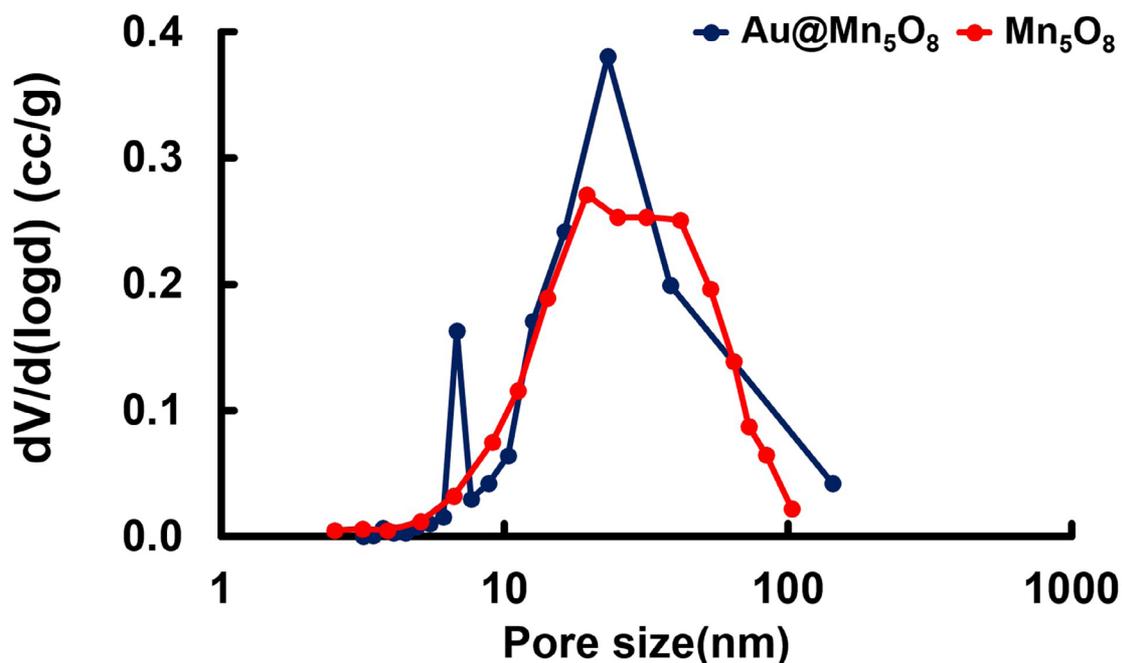


Figure 3. The pore size distribution curves of Mn₅O₈ and Au@Mn₅O₈ microspheres.

The pore-size distribution curves of Mn₅O₈ and Au@Mn₅O₈ microspheres were obtained by nitrogen adsorption-desorption method and are shown in Figure 3. The range for the pore-size distributions of both microspheres is between 2.5 - 143 nm. The specific surface areas of Mn₅O₈ and Au@Mn₅O₈ microspheres were found as 30.2 and 36.0 m²/g, respectively. The pore volume and specific surface area of Au@Mn₅O₈ microspheres were higher when compared with Mn₅O₈ microspheres due to the impregnation with Au NPs. Au atom content of Au@Mn₅O₈ microspheres was found as 5 % by ICP-MS. The content of Au atom within Au@Mn₅O₈ microspheres after fifth use was determined as 4.57 % which means that Au content of microspheres did not change after BnOH oxidation.

XRD spectra of Au@Mn₅O₈ microspheres synthesized using plain Mn₅O₈ microspheres are given in Figure 4. Au@Mn₅O₈ microspheres contains Mn₅O₈ (97 %) and Mn₉O₂ (3 %) phases. XRD spectrum of Au@Mn₅O₈ microspheres is coherent with the monoclinic Mn₅O₈ phase (JCPDS Card No. 39-1218, space group 12: C12/m1, unique-b, cell-1).

The survey XPS spectra of Au@Mn₅O₈ microspheres is given in Figure 5A and the surface atomic composi-

tions of Au@Mn₅O₈ microspheres are shown in Table 1. The peaks obtained at 529 and 284.0 eV belongs to O1s and C1s, respectively. Si2p and N1s peaks were also obtained at 100 and 400 eV, respectively, due to the derivatization of APTES. Also Mn2p peaks at 654.0 and 642.5 eV belonging to Mn2p_{1/2} and Mn2p_{3/2} were observed. Mn2p core level spectra is given in Figure 5B to show that the Mn₅O₈ microspheres has a mixed valence nature. By analyzing the deconvoluted core-level spectra for Mn2p scan, the surface percentages of all oxidation stages of Mn were calculated and are given in Table 1. The percentages of Mn(II), Mn(III) and Mn(IV) were found as 3.54, 16.57, 3.02 for Au@Mn₅O₈ microspheres, respectively. The multiple oxidation stages of manganese on Au@Mn₅O₈ microspheres was demonstrated within a calculation by using deconvoluted core-level spectra for Mn2p scan. This is also the evidence of the oxygen vacancies on the microspheres that results in the higher catalytic activity in BnOH oxidation. In addition to these peaks, the characteristic peaks at 84 eV and 88 eV were observed in the core level which belongs to Au4f (Figure 5C). Au atom content of Au@Mn₅O₈ microspheres was found as 2.72 % with respect to XPS spectra given in Figure 5A.

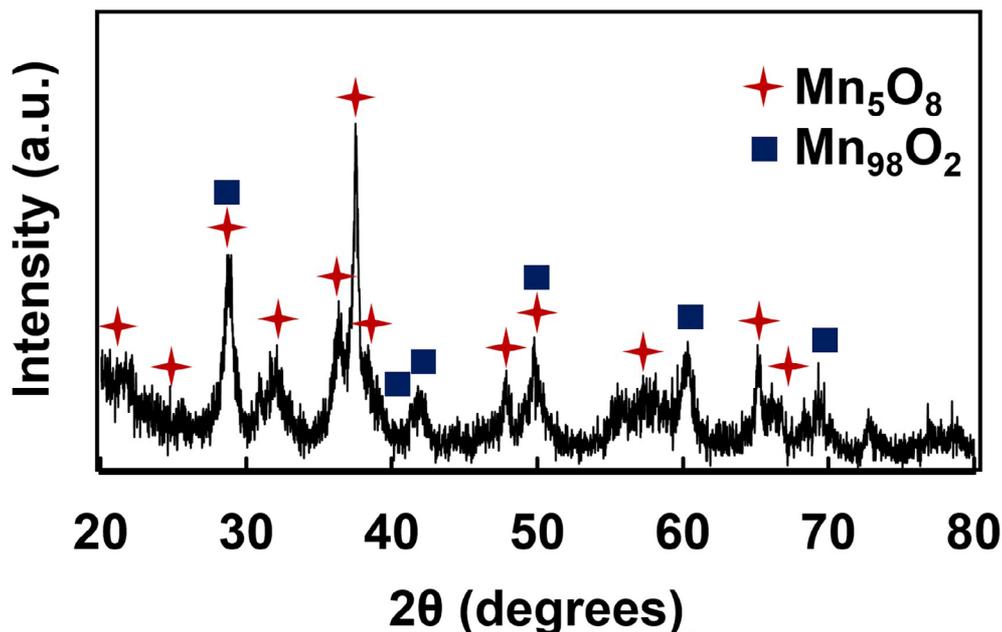


Figure 4. XRD patterns of Au@Mn₅O₈ microspheres.

Catalytic behaviour of Au@Mn₅O₈ microspheres in BnOH oxidation

In the BnOH oxidation mechanism, different products like BnCHO, benzyl benzoate and toluene are formed due to different pathways [29-32]. Generally, BnCHO can be obtained both by the dehydrogenation and disproportionation of alkoxy compounds or by the hydrolysis of BnOH [32]. The effects of oxidation conditions like initial BnOH concentration, catalyst amount and Au NP loading on conversion and formation yield were investigated.

The relation between the catalyst amount and initial BnOH concentration on BnOH conversion and BnCHO formation yield is given in Figure 6A and 6B, respectively. By increasing the catalyst amount, both the overall conversion and formation yield of BnCHO increased as expected (Figure 6A). However, both the overall BnOH conversion and BnCHO formation yield decreased by increasing BnOH concentration due to the decrease in the formation alkoxy compounds [30]. Highest values were obtained for the selectivity and the formation yield of BnCHO when the initial concentration of BnOH was 50 mM.

Figure 6C shows the effect of Au NP loading on conversion of BnOH and formation yield of BnCHO. The most appropriate Au NP loading percentage which provides the highest overall conversion and selectivity for BnCHO was found as 5.0 % (w/w). Increasing the Au NP loading percentage to 10.0 % (w/w) did not increase the BnOH conversion and the BnCHO formation yield. The reason of this situation could be the formation aggregates on the surface of microspheres.

The reusability of Au@Mn₅O₈ microspheres was determined by using the same catalyst for five consecutive runs. The decrease in the BnOH conversion and BnCHO formation yield are quite small after the first use. However, BnOH conversion and BnCHO selectivity decreased 20.5 and 12.7 %, respectively after five consecutive runs. These results show that the reusability of Au@Mn₅O₈ microspheres is satisfactory.

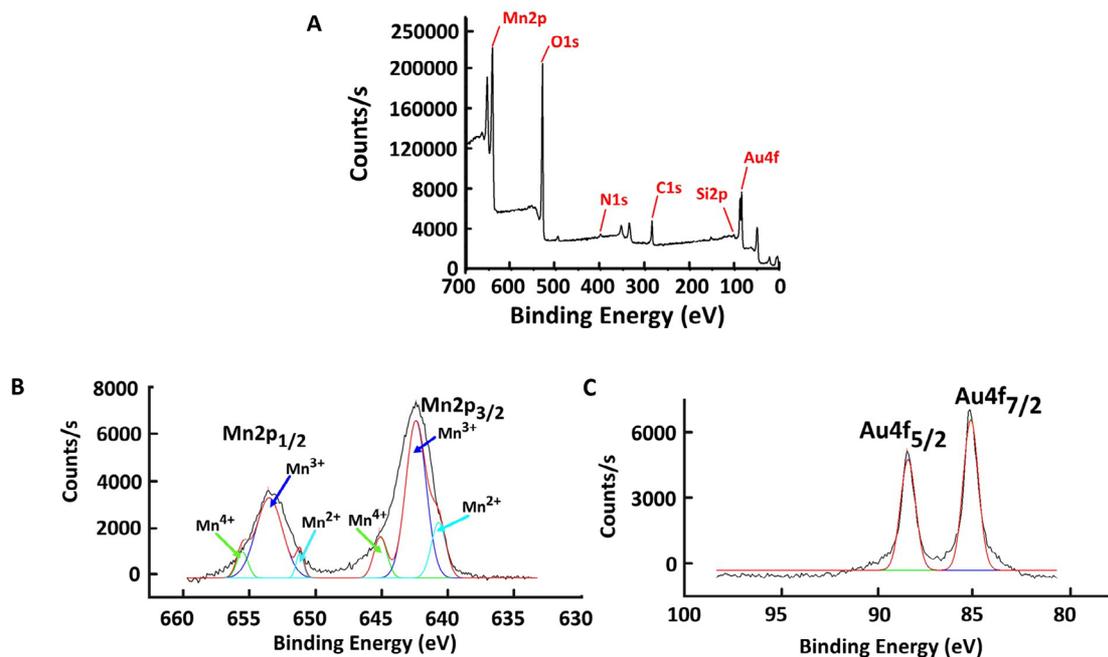


Figure 5. (A) Survey XPS spectra (B) Mn2p scan of core-level XPS spectra of (C) Au4f scan of core-level XPS spectra for Au@Mn₅O₈ microspheres.

Table 1. Surface atomic compositions of Au@Mn₅O₈ microspheres.

Sample	Surface percentages (%)								
	Mn 2p (Total)	Mn 2p (Mn(II))	Mn 2p (Mn(III))	Mn 2p (Mn(IV))	O 1s	C 1s	N 1s	Si 2p	Au 4f
Au@Mn ₅ O ₈	23.13	3.54	16.57	3.02	48.80	19.51	2.91	2.93	2.72

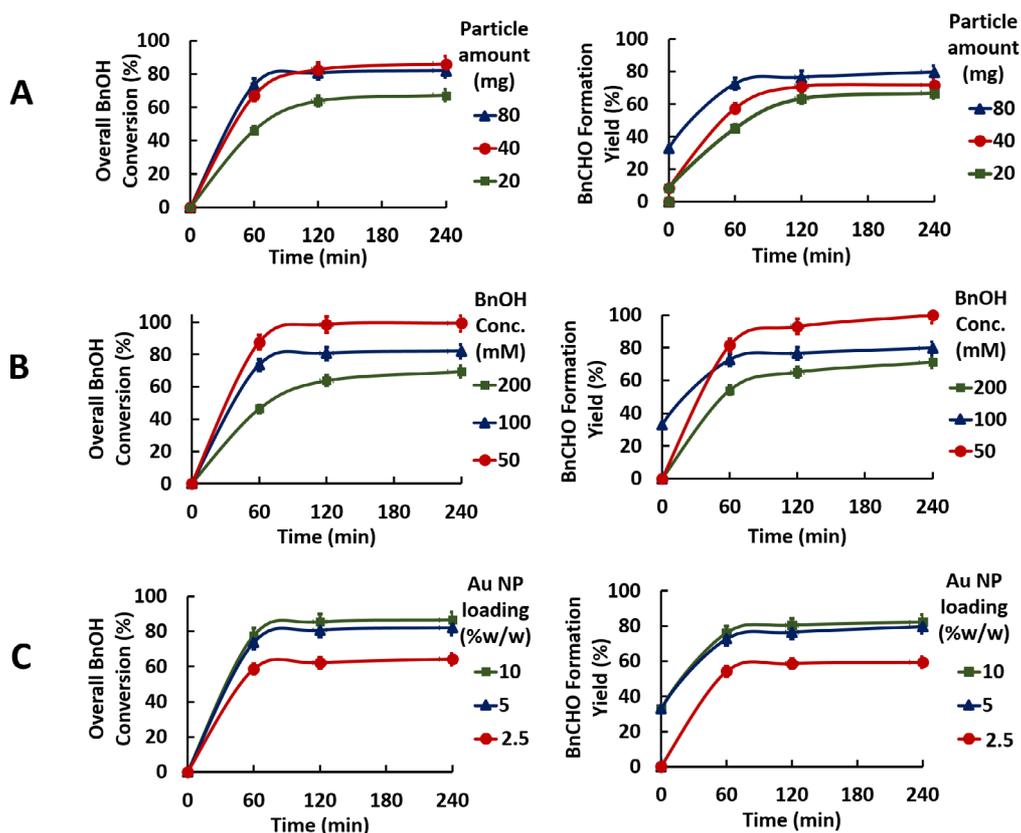


Figure 6. The effect of (A) catalyst amount, (B) initial BnOH concentration and (C) Au NP loading on BnOH conversion and BnCHO formation yield obtained by Au@Mn₅O₈ microspheres. Concentrations: TBHP: 150 mM, Reaction conditions: Volume: 10 mL, Temperature: 80 °C, Stirring rate: 400 rpm.

Conclusion

In this study, Mn₅O₈ microspheres as a suitable support material was used for the decoration of Au NPs as catalytic active centers by using ligand attachment protocols. Au@Mn₅O₈ microspheres as a reusable heterogeneous catalyst was used in the oxidation of BnOH and overall BnOH conversions and BnCHO formation yields were obtained up to 99.4 and 100 %, respectively. When compared with literature higher catalytic activity within BnOH conversion and BnCHO formation yield were observed with Au@Mn₅O₈ microspheres due to the synergistic relation between Au NPs and Mn₅O₈ microspheres. The higher catalytic activity can be related with mixed valence nature which cause an increase in the mobility of surface lattice oxygen. The protocol proposed in this study is also suitable for the preparation

of other heterogeneous catalysts by immobilizing different NPs on different supports for different catalytic applications.

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