A microemulsion route to fabrication of mono- and bi-metallic Cu/Zn/γ-Al₂O₃ nanocatalysts for hydrogenation reaction

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Abstract. This research’s pioneering aim is to address the preparation of Cu and Cu/Zn nanocatalysts supported on alumina using microemulsion route. To do so, stable colloidal systems of Cu and Zn nanoparticles were firstly prepared in a W/O microemulsion system. The formulated microemulsions were formed from copper nitrate and zinc nitrate as a source of metals, cyclohexane as oil phase, and AOT as an anionic surfactant. To confirm the formation of Cu and Zn colloidal systems after ions reduction, Dynamic Light Scattering (DLS) method was used. From the DLS results, it was found that the nanoparticles’ average size for colloidal suspension system was about 2 nm. Finally, γ-Al₂O₃ was added to the colloidal systems to make Cu/Al₂O₃ or Cu-Zn/Al₂O₃ nanocatalysts. The resulted nanocatalysts were characterized by FE-SEM and XRD techniques. The prepared nanocatalysts were tested for hydrogenation reaction of an unsaturated aldehyde in a batch reactor and mild condition.

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1. Introduction

Due to nanoparticles’ small size, nanomaterial systems exhibit novel chemical, physical, magnetic, electronic, and surface properties, which drastically differ from bulk properties. Basically, these novel properties depend on size and size distribution. Rodemer published a valuable review to discuss why nanomaterials are different [1]. In this review, two types of size-dependent effects have been discussed. The first is quantum confinement effect of materials and the second type is surface effect. It should be noted that these effects can also change the physical and mechanical properties of composite materials [2,3]. Heilitag and Niederberger [4], published a review article from some selected papers to discuss the fascinating world of nanoparticles and their applications. Hasan [5] also presented the types and synthesis of nanoparticles in a review article. As it is confirmed, one of the most important applications of the nanomaterials is the catalyst use. In recent years, some valuable research and review articles have been also published to introduce catalytic applications of nanomaterials [6-8]. Obviously, the catalytic phenomena are related to materials’ component types of the catalyst as well as surface and size of the materials.

It is well known that the control over the size of nanoparticles is dependent on the preparation method. There are many chemical approaches, such as sol-gel [9,10], microemulsion [11,12], chemical precipitation [13], and hydrothermal [14] methods, to prepare nanoparticles, among which the microemulsion method
is an ideal route to control the particle size with the best monodispersity. Microemulsions are transparent and thermodynamically stable systems composed of oil, water, surfactant, and sometimes cosurfactant. Water-in-Oil microemulsion systems (W/O) consist of nanometer-sized domains of water, stabilized by a monolayer of surfactant(s), dispersed in a continuous oil phase. One of the most interesting research works in the microemulsion field is the use of a structured reaction medium for the preparation of nanoparticles [15,16]. The microemulsion method allows for the synthesis of uniform and size-controlled nanoparticles for many applications.

Nanocatalysts represent a class of nanotechnological products which are increasingly used in academic and industrial researches [17,18]. This class of the materials is produced with different well-known methods. Recently, the microemulsion method, as a simple and energy-efficient method, for the preparation of nanocatalysts has been introduced. In this method, the resulting particles are affected by the oil-water interface membrane, hindering the aggregation of particles. Thus, the particle size or even the morphology of the resulted catalysts can be controlled precisely [19-21].

Selective hydrogenation of unsaturated aldehydes to the corresponding product is an important reaction in an industrial area [22-24]. In fact, the hydrogenation of α, β-unsaturated carbonyls into saturated carbonyls is comparatively easy to achieve because thermodynamics favor the hydrogenation of the C=O bonds; therefore, research efforts were directed mainly at improving the selectivity to unsaturated alcohols. Research efforts in this area were directed mainly at developing hydrogenation processes based on heterogeneous catalysis. In the last decade, many academic investigations were carried out in this field because hydrogenations of unsaturated aldehydes were chosen as model reactions to establish relations between selectivity and catalyst structure. Gallegote and Richard published a review article on selective hydrogenation of α, β-unsaturated aldehydes [25]. Recently, Murzin et al. [26] published a review paper to discuss the chemoselective hydrogenation of unsaturated aldehydes and ketones over heterogeneous catalyst.

2-ethyl-2-hexanol or 2-Ethyl-3-Propyl Acrolein (EPA) is a colorless or yellowish unsaturated aldehyde commonly used as a raw material to prepare 2-ethylhexanol. The possible hydrogenation reactions of EPA are shown in Scheme 1.

As observed, the products of the hydrogenation reaction include 2-ethylhexanal (EHA) and 2-ethylhexanol (2EH), in which the latter is a complete hydrogenation product as a saturated alcohol.

In spite of a large number of catalysts suggested in recent years for hydrogenation of EPA [26], there is no report on nanocatalysts for this process prepared by microemulsion systems. To continue our research works on nanomaterials and nanocatalysts based on microemulsion systems [27-30], in this work, Cu and Cu/Zn nanocatalysts were prepared using microemulsion system. The prepared nanocatalysts were characterized by FE-SEM and XRD techniques. The selective heterogeneous hydrogenation of EPA was investigated by the resulted nanocatalysts. We hope to offer a novel nanocatalyst type in the field of industrial applications.

2. Experimental section

2.1. Materials

Cu(NO₃)₂·3H₂O and Zn(NO₃)₂·6H₂O as a source of metals, cyclohexane, and hydrazine (N₂H₄) were purchased from Merck. γ-Al₂O₃ was obtained from Japan Aerosil, with a surface area of 110 m²/g. The anionic surfactant sodium bis-(2-ethylhexyl) sulfosuccinate (AOT) with purity of 96% was purchased from Acros Company and used as received. All of the solutions were prepared by deionized water. 2-ethyl-3-propyl acrolein (EPA) was purchased from Sigma-Aldrich.

2.2. Synthesis of Cu and Zn colloidal suspensions

Colloidal suspensions of Cu and Zn nanoparticles were prepared in a w/o microemulsion containing cyclohexane as the continuous oil phase and AOT as a surfactant. A suitable amount of aqueous solution of Cu(NO₃)₂·3H₂O and Cu(NO₃)₂·3H₂O was added to 0.1 M of surfactant solution in cyclohexane such that [H₂O]/[Surfactant] = 5. This microemulsion sample was equilibrated for 3 hours with stirring; afterwards, Cu and Zn ions were reduced by the addition of a separate microemulsion system containing N₂H₄. The molar ratio of N₂H₄: Cu/Zn was kept at 1:10:1. After 4 hours of stirring to ensure complete mixing and reduction, the reaction was considered complete. Dynamic Light Scattering (DLS) was used to monitor the formation of the nanoparticles.

2.3. Preparation of Cu/Zn/γ-Al₂O₃

γ-Al₂O₃, as a supporting material on which to adsorb
Cu and Zn nanoparticles, was added to the prepared colloidal suspension in a 50:1 Al₂O₃:Cu/Zn mass ratio. After the addition of the alumina, the colloidal system was destabilized by the slow addition of THF to 3 times the volume of the initial colloidal dispersion. Subsequently, the final Cu/Zn/γ-Al₂O₃ products were dried at room temperature for 24 hours and calcined for 1 hour at 600°C to remove adsorbed organic materials.

2.4. Catalysis characterization
The X-Ray Diffraction (XRD) experiment on catalysts was carried out at room temperature by a Philips diffractometer with a 40 kV generator tension and 30 mA generator current with Cu Kα radiation (Cu Kα1:1.54056 Å, Cu Kα2:1.54439 Å). The 2θ angular region between 10° and 100° was explored at a step time of 2.0 s.

In order to characterize the structure of the fractured surface of the nanocomposites, the Field Emission Scanning Electron Microscope (FE-SEM) was applied using a MIRA 3 XUM instrument.

2.5. Catalytic study
In order to test the synthesized nanocatalyst in hydrogenation reaction of EPA, as an unsaturated aldehyde, a special reactor was constructed in our lab. An autoclave was equipped with a mechanical stirrer, a pressure gauge, a thermocouple, and an inlet valve of reaction mixture (Figure 1). In the first time, 1.0 g of the nanocatalyst was reduced in a H₂ flow (100 ml/min) in the reactor at 300°C for 2 h prior to the reaction initiation. Then, the reaction was started with 3 ml of EPA and 20 ml of 2-propanol under H₂ atmosphere at 200°C and 8 bar for 3 h. The experimental setup is shown in Figure 1. Finally, the reaction products were analyzed by gas chromatography method (VARIYAN 3800) equipped with FID detector and DB-1 column. Selectivity was calculated by the following expression:

\[ S_i = \frac{C_i}{\sum C_i}, \]

where \( C_i \) is the concentration of product i and \( C_t \) is the total concentration of the products.

3. Results and discussion
3.1. DLS analysis of the nanocolloid system
In order to confirm the formation of copper or zinc nanoparticles by water-in-oil microemulsion system and also to clarify the stability and monodispersity of nanoparticles as key and beneficial factors to their applicability, dynamic light scattering (nano zeta size-90, malvern instrument) was employed. In this method depending on the shape of the nanoparticles, for spherical particles, the hydrodynamic radius of the particle \( R_H \) can be calculated from its diffusion coefficient by the Stokes-Einstein equation:

\[ D = \frac{k_B T}{6\pi \eta R_H}. \]  

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature of the suspension, and \( \eta \) is the viscosity of the surrounding media. The instrument operated at a scattering angle of 90°. In all measurements, 1 ml of particle suspensions was employed and placed in a 10 mm × 10 mm quartz cuvette. A typical DLS result of Cu nanoparticles is shown in Figure 2 as the particle number distribution. As seen in Figure 2, the size of suspension metal nanoparticles is in the range of 1-2 nm. It should be noted that the suspensions were not monomodal and spherical as observed from intensity distribution.

![Figure 1.](image1.png) An autoclave manufactured and designed in lab, which was used in hydrogenation of unsaturated aldehydes.

![Figure 2.](image2.png) DLS result for copper nanocolloid system.
3.2. X-ray diffraction spectroscopy of the prepared nanocatalyst

XRD patterns of γ-Al₂O₃, Zn/γ-Al₂O₃, and Cu-Zn/γ-Al₂O₃ samples are shown in Figure 3. The main reflection data shown in Figure 3(a), related to γ-Al₂O₃, have been confirmed by literature data [22]. Unfortunately, the peaks related to the copper or zinc nanoparticles in Figure 3(b) and (c) are not sharp because the amount of loaded copper or zinc on the alumina cannot be enough to be detected clearly. However, from the change in the patterns of Figure 3(a) to (c), it can be concluded that the copper and zinc particles have been grown on the alumina surface; however, they may be in an amorphous structure. The presence of these nanoparticles will be confirmed by FE-SEM analysis in the next section.

3.3. FE-SEM analysis of the prepared nanocatalysts

To determine the size of copper or zinc nanoparticles dispersed on Al₂O₃, the scanning electron microscope was performed on the prepared nanocatalyst. The obtained images are shown in Figure 4. It was found that the catalyst kept the layer structure of γ-Al₂O₃ support. As seen, copper or zinc nanoparticles’ sizes dispersed on alumina are in the range of about 20 to 40 nm with a very well distribution. It should be noted that, after precipitation of Cu and Zn particles, which are less than 5 nm in a colloidal form and calcined at 600°C, these metal nanoparticles were changed to an oxide form and coagulated to about 20 to 40 nm particles.

3.4. Catalytic activity results

The hydrogenation reaction of EPA on the new type

![Figure 3. XRD patterns of (a) γ-Al₂O₃ powder, (b) Zn/γ-Al₂O₃, and (c) Cu-Zn/γ-Al₂O₃.](image)

![Figure 4. FE-SEM images of (a) γ-Al₂O₃, (b) Cu/γ-Al₂O₃, and (c) Cu-Zn/γ-Al₂O₃.](image)
of Cu and Cu/Zn based on γ-Al2O3 nanocatalysts, prepared in microemulsion systems, has been investigated in a certain condition. The obtained results show different conversion and selectivity of the EHA and 2EH products. It is obvious that, in the microemulsion method, the initial concentration of the precursor affects the particle size and activity of the nanocatalyst [31]. Therefore, the effects of initial concentration of Cu precursor on the conversion and selectivity corresponding to EHA and 2EH products over Cu/γ-Al2O3 nanocatalyst have been investigated. On the other hand, in a bi-metallic nanocatalyst of Cu/Zn, prepared in the microemulsion system, the effects of metals mole ratio on the conversion and selectivity corresponding to EHA and 2EH products over Cu/Zn/γ-Al2O3 nanocatalyst have been investigated.

3.4.1. Effect of initial concentration of Cu precursor on the catalytic activity of Cu/γ-Al2O3

The results of hydrogenation reaction of EPA over the Cu/γ-Al2O3 nanocatalyst, prepared at different concentrations of Cu precursor in a microemulsion system, are reported in Table 1. As can be seen, by increasing Cu(NO3)2 concentration as a source of Cu nanoparticles, the total conversion of the hydrogenation reaction and selectivity related to EHA and 2EH increase simultaneously. It is obvious that by increasing the amount of Cu nanoparticles loaded on the alumina support, the active area of the catalyst will increase. On the other hand, the results showed that by increasing the initial concentration of Cu(NO3)2 more than 1.0 M, the catalytic activity did not change significantly. This behavior may be due to the coagulation of Cu nanoparticles on the alumina support during nanocatalyst preparation.

3.4.2. Effect of CuZn mole ratio on the catalytic activity of Cu/Zn/γ-Al2O3

For all of the fabricated nanocatalysts with different mole ratios of Cu/Zn at fixed precursors’ concentration of 0.1 M, the conversion and selectivity corresponding to EHA and 2EH were obtained, summarized in Table 2. As an excellent result, Cu/Zn/γ-Al2O3 bi-metallic nanocatalyst shows a better performance in the EPA hydrogenation reaction, compared to Cu/γ-Al2O3 at lower concentration of precursor in the same conditions. In our previous work [30], it was approved that the bi-metallic nanocomposite with a controlled size can be synthesized in a microemulsion system. Then, it can be concluded that Cu and Zn metals are dispersed on the alumina support at a nanometric range, as observed in FE-SEM image (Figure 4(b)). This observation confirms that both of Cu and Zn nanoparticles act as an active site role of the nanocatalyst and promote the catalytic activity. Furthermore, Cu/Zn/γ-Al2O3 with a mole ratio of 3:1 shows higher selectivity and conversion due to the key and vital role of Cu nanoparticles with a high catalytic activity in an employed reaction. The catalytic behaviour was investigated in other molar ratios containing 4:1 and 5:1 mole ratios, while no remarkable change was manifested in the obtained conversion, demonstrating that the 3:1 is the best mole ratio for Cu/Zn/γ-Al2O3 nanocatalyst.

4. Conclusion

The prime focus of the present research was the introduction of a new type of Cu/γ-Al2O3 and Cu/Zn/γ-Al2O3 nanocatalysts successfully fabricated by the microemulsion system. In order to evaluate the catalytic activity of the prepared nanocatalyst, the hydrogenation reaction of EPA was employed. It was verified that the initial concentration of Cu precursor affected the catalytic activity of Cu/γ-Al2O3 nanocatalyst and the higher catalytic activity observed at 0.1 M of Cu(NO3)2. On the other hand, for the bi-metallic nanocatalyst of Cu/Zn/γ-Al2O3, the mole ratio of 3:1 Cu/Zn shows the best performance in catalytic hydrogenation reaction. The obtained results may be useful to investigate these types of nanocatalysts as potential candidates for hydrogenation reactions.

**Nomenclature**

<table>
<thead>
<tr>
<th>AOT</th>
<th>Anionic surfactant sodium bis-(2-ethylhexyl) sulfosuccinate</th>
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<tbody>
<tr>
<td>EPA</td>
<td>2-ethyl-2-hexanal or 2-ethyl-3-propyl acrolein</td>
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<tr>
<td>EHA</td>
<td>2-ethylhexanal</td>
</tr>
<tr>
<td>2EH</td>
<td>2-ethylhexanol</td>
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DLS  Dynamic Light Scattering
XRD  X-Ray Diffraction
FE-SEM  Field Emission-Scanning Electron Microscope

References


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