Application of CdO nanocatalyst in the acetylation of benzyl alcohols and degradation of sulfathiazole as a green approach

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**Abstract**

CdO nanoparticles (CdO NPs) were prepared with a template. The nanoparticles were characterized by XRD, scanning electron microscopy (SEM), diffuse reflectance spectroscopy (DRS), and energy dispersive X-ray spectroscopy (EDX). The XRD pattern revealed that the final product has a cubic phase and its particle size diameter is 36.4 nm. The morphology of CdO is nanospherical. The catalytic activity of a CdO nanoparticle in the acetylation of benzyl alcohols was studied. The formation of products proceeds on the catalysts with predominantly strong base sites. The degradation of sulfathiazole antibiotic in the presence of CdO NPs was also investigated under ultraviolet irradiation. Various experimental parameters, such as initial sulfathiazole concentrations, initial CdO concentration and initial pH, were investigated. According to the results, this method has the potential to perform well in the removal of sulfathiazole.

**Keywords:**
Nanospherical CdO Nanoparticle Acetylation Sulfathiazole Degradation

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1. Introduction

During the past decade, interest in chemical reactions occurring at metal oxide-aqueous solution interfaces has increased significantly because of their importance in a variety of fields. These fields include atmospheric chemistry, heterogeneous catalysts and photocatalysts, chemical sensors, corrosion, environmental chemistry and geochemistry, metallurgy and ore beneficiation, metal oxide crystal growth, soil science, semiconductor manufacturing and cleaning, and tribology. Cadmium oxide (CdO) is a transparent conducting material with a direct band gap of 2.5 eV [1]. In this study, CdO was chosen as a low cost material with higher chemical stability, wide spread availability, and use in several important applications [2-8].

There have been previous reports on the synthesis of CdO NPs for nanowires and nanoﬁlms by chemical co-precipitation or sonochemical methods [9,10]. Liu et al. have synthesized CdO nanoneedles by chemical vapour deposition [11]. Zou et al. have prepared CdO NPs using the micro-emulsion method employing anionic surfactants Aerosol-OT (AOT) reverse micelles [12].

The acetylation of –OH group provides an efficient route for the synthesis of compounds with industrial value and for the production of medicines, ﬂavors, fragrances, solvents, food preservers, plasticizers, and cosmetics among others [13-15]. The acetylation of alcohols and phenols has been typically performed using acetic anhydride or acetyl chloride in the presence of either base [16-19] or acid catalysts [20-34]. Sulfathiazole (STZ) is extensively used in aquaculture, livestock production and also in human medicine to treat bacterial, protozoal and fungal infections [35-39]. The introduction of these compounds into the environment through anthropogenic sources can constitute a potential risk for aquatic and terrestrial organisms. Only four review articles on oxidation technologies for the removal of antibiotics in the aquatic environment have been published [40-42].

In the present work, we converted a solution of benzyl alcohol to benzyl acetate with the same selectivity as on a basic CdO catalyst to optimize the concentration of the catalyst in an aqueous solution. The other aim of this work was to investigate sulfathiazole degradation under UV irradiation. The chemical structure of the drug is given in Figure 1.

2. Experimental methods

2.1. Apparatus

Phase identification of the fabricated samples was carried out with a Holland Philips X-ray diffraction CuKα (λ=1.5417 Å) in the radiation range of 20-80°. A Field emission scanning electron micrograph (SEM), Holland Philips XL30 microscope, was used to observe the morphology and elemental analysis of the samples. Spectrophotometric measurements were conducted using an UV-Vis Shimadzu 2101 spectrophotometer equipped with an Acermate 486 SX/25D computer and thermostically matched 10-mm quartz cells. Infrared spectra were recorded on a Jasco FT-IR spectrometer equipped with a liquid nitrogen-cooled HgCdTe (MCT) detector and a KBr beam splitter.

2.2. Preparation of CdO NPs

7.2 mmol (0.29 mg) NaOH was dissolved in 36 mL of distilled water under stirring. Then, 7.2 mmol (1.001 mg) of the template, hexamethylenetetramine, was added to the solution. Cd(CH₃COO)₂H₂O (1 mmol, 0.27 mg) was added to the mixture. The mixture was reﬂuxed for 4 h in 80 °C. After cooling to room temperature, the precipitate was collected by ﬁltration and washed several times with distilled water and ethanol. The CdO NPs were collected by centrifugation and drying of the precipitate at room temperature.

2.3. Procedure

For the acetylation of alcohols, a mixture of the alcohol (1 mmol), acetic anhydride (1.2 mmol, 1.5 mL) and nanocatalyst (0.08 g) in CH₂Cl₂ (10 mL) was stirred as a slurry at room temperature. The completion of the reaction, was determined by TLC, after which the mixture was ﬁltered to recover the nanocatalyst.
The solvent was then removed under vacuum to give the crude product as a residue. The crude product was purified by column chromatography over silica gel to afford the pure desired products in high yield.

3. Results and discussion

3.1. Characterization of nanoparticles

The diffraction patterns of CdO are shown in Figure 2. The crystallite size of the prepared sample was calculated using the Scherrer formula: \[ D = \frac{0.9\lambda}{\beta \cos \theta} \] [43]. The CdO NPs have an average particle size of 36.4 nm.

The diffraction peaks values at 2\( \theta \) are 33.08, 38.43, 55.31, 65.90 and 69.28° corresponding to pure CdO and matching the (111), (200), (220), (311), and (222) planes, which having a cubic structure (JCPDS Card No.05-0640). This indicates the formation of CdO NPs. Elemental analysis of the sample was performed by energy dispersive X-ray spectroscopy (EDS). The surface morphology of the prepared pure CdO was studied using SEM (Figure 2). The EDS spectra confirm the absence of impurities in the CdO NPs (Figure 3).

3.2. Optical properties

In general, the existence of impurities, synthesis method, crystalline network, and average crystal size of the semiconductor are the main factors affecting band-gap energy [44,45]. The band-gap energy of CdO has been reported to be approximately 2.9 eV. Band gap energy of the loaded samples was estimated by the Kubelka-Munk function using Eq. (1).

\[
(\alpha h\nu)^2 = \beta (E_g - h\nu)
\]

Where \( E_g \) is the band gap of the proposed semiconductor (eV), \( h \) is the Planck’s constant (J s), \( \nu \) (or \( \lambda \)) is the frequency (or wavelength) of the used light (s\(^{-1}\) or nm), \( \beta \) is the absorption constant, and \( \alpha \) is the absorption coefficient defined by Beer–Lambert’s law as \( \alpha = \left( \frac{2.303\times\text{Abs}}{d} \right) \), where \( d \) and Abs are the sample thickness and sample absorbance, respectively. The band gap can be determined by extrapolating the linear portion of the \((\alpha h\nu)^2 \) vs \( h\nu \) curve. From Eq. (1), the optical band gap is determined by extrapolation of the graph to the x-axis.
3.3. Photocatalytic results

The efficiency of the UV/CdO photocatalytic process to remove STZ from an aqueous solution was investigated in this paper. To determine the photocatalyst effect, two experiments in the absence (Figure 5a) and presence (Figures 5b-d) of catalyst were conducted. In the absence of catalyst, the degradation of STZ was less than 15% within 2 h. The effect of different parameters, such as pH, on the STZ adsorption in CdO was also examined. A decrease in pH had a strong effect on the degradation of STZ. In the presence of CdO, the highest degradation was observed at a pH of about 3. At an acidic pH, the sulfur atom in the sulfonamide molecule can be mineralized to SO$_4$^{2-}, whereas the nitrogen of the molecule can be mineralized either to NH$_3$ or NO$_2^-$ and/or NO$_3^-$ [46] and these anions can give rise to a gradual decrease in pH until the molecule is degraded. It is possible that after adsorption onto CdO surface the STZH$^+$ ions take part in a direct photocatalytic process as acceptors of excited electrons. The degradation of STZ was higher than 80% within 2 h.

To investigate the effect of CdO concentration on photocatalytic efficiency, a set of experiments was performed with different concentrations of CdO in a range from 0.2–1.1 g/L. The results showed that the optimum concentration of CdO catalyst is 1.0 g/L.

Recently, mineral oxides have proven to be useful to chemists in both the laboratory and industry due to the good activation of adsorbed compounds and reaction rate enhancement, selectivity, easier work-up and recyclability of the supports and the eco-friendly, green reaction conditions [47,48]. According to the results obtained from the metal oxides tested, TiO$_2$, SiO$_2$,
Al\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{2}O\textsubscript{3} and Ag\textsubscript{2}O were unable to promote benzylation of ethanol while CaO and MgO gave large amounts of benzoic acid from the hydrolysis of the benzoyl chloride. As can be seen in Table 1, the most efficient catalyst was ZnO [49].

Herein, the performances of the CdO nanocatalyst containing different amounts of CdO were evaluated for the acetylation of alcohols. The selective acetylation of benzylic alcohols containing electron-withdrawing and electron-donating substituents with acetic anhydride was also investigated using the CdO catalyst. The results revealed that the benzylic alcohols bearing electron-donating groups have the most reactivity and are converted to the corresponding products in the shortest reaction times with the highest yield (91-98%). The possible mechanism for the acetylation of alcohols in the presence of CdO as the catalyst is shown in Scheme 1.

The results revealed that the best outcomes are obtained in the presence of 0.05 g of the CdO nanocatalyst at room temperature. The acetylation of benzylic alcohols was confirmed with the FT-IR spectra (Figure 7). In all of the alcohols (a-e), it can be seen that the O–H stretching vibration frequency of the alcohols is located at 3100-3300 cm\textsuperscript{-1}. In addition, the stretching vibrations of the carbonyl groups (C=O) of the esterification products appeared at 1650-1750 cm\textsuperscript{-1}.

4. Conclusions

In this paper, a simple and efficient protocol for the acetylation of alcohols was developed using a CdO nanocatalyst. The results obtained proved that for all investigated systems there is a connection between the amount of sorbed substance on the surface of the catalyst and its catalytic activity (Table 2). The proposed method has high reaction rates and excellent yields with no adverse side-reactions. The prepared nano CdO had more advantage in promoting the yields of product formation compared with other ordinary metal oxides (Table 1). Our results showed the number of atomic surfaces of nanopowder particles are a large fraction of the total; therefore, the catalytic activity of metal oxide is improved. Compared with several other catalysts reported for this transformation, the CdO nanocatalyst promoted the reaction effectively to give the desired product in high yield over a short reaction time.

Since sulfonamides, including difficult biodegradable sulfa-drugs, can be removed from wastewater using the photodegradation process, oxidation of the antibiotic STZ by photolytic and photocatalytic processes using the CdO was investigated. It has been assumed that the radical pathway is a dominant mode of STZ degradation in the combined UV photolysis system. Our experiments have shown that the presence of CdO in the UV/CdO photocatalysis system had a positive influence on the degradation of STZ. The results showed that the system is most efficient at 30 mg/L and 0.02 g/L concentrations of STZ and CdO nanoparticles in acidic conditions, respectively.

### Acknowledgments

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### Table 1. Benzoylation of ethanol with benzoyl chloride in the presence of metal oxide [49].

<table>
<thead>
<tr>
<th>Entry</th>
<th>Metal Oxide</th>
<th>Time/ Temp. (h/oC)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>5/40</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>SiO\textsubscript{2}</td>
<td>5/40</td>
<td>52</td>
</tr>
<tr>
<td>3</td>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>5/40</td>
<td>37</td>
</tr>
<tr>
<td>4</td>
<td>MgO</td>
<td>5/40</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>CaO</td>
<td>5/40</td>
<td>63</td>
</tr>
<tr>
<td>6</td>
<td>TiO\textsubscript{2}</td>
<td>5/40</td>
<td>24</td>
</tr>
<tr>
<td>7</td>
<td>Ag\textsubscript{2}O</td>
<td>5/40</td>
<td>40</td>
</tr>
<tr>
<td>8</td>
<td>ZnO</td>
<td>5/40</td>
<td>93</td>
</tr>
<tr>
<td>9</td>
<td>Nano-ZnO</td>
<td>10/25</td>
<td>93</td>
</tr>
<tr>
<td>10</td>
<td>Nano-Fe\textsubscript{2}O\textsubscript{3}</td>
<td>15/25</td>
<td>91</td>
</tr>
</tbody>
</table>
Fig. 7. FT-IR spectra of a) benzyl alcohol, b) 2-methyl benzyl alcohol, c) 2-nitro benzyl alcohol, d) 4-chloro-benzyl alcohol, and e) 4-hydroxy-benzyl alcohol and corresponding esteric products. In all figures the stretching vibrations of carbonyl groups (C=O) of corresponding products are shown with arrows.

Table 2. Selective acetylation of benzyl alcohols in the presence of different concentrations of CdO nanocatalyst.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>product</th>
<th>Reaction time (30 mg)</th>
<th>Reaction time (50 mg)</th>
<th>Reaction time (70 mg)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅CH₂OH</td>
<td>C₆H₅CH₂OAc</td>
<td>15</td>
<td>10</td>
<td>10</td>
<td>98</td>
</tr>
<tr>
<td>p-Cl-C₆H₄CH₂OH</td>
<td>p-Cl-C₆H₄CH₂OAc</td>
<td>55</td>
<td>30</td>
<td>40</td>
<td>94</td>
</tr>
<tr>
<td>o-NO₂-C₆H₄CH₂OH</td>
<td>o-NO₂-C₆H₄CH₂OAc</td>
<td>70</td>
<td>45</td>
<td>50</td>
<td>91</td>
</tr>
<tr>
<td>o-CH₃-C₆H₄CH₂OH</td>
<td>o-CH₃-C₆H₄CH₂OAc</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>96</td>
</tr>
<tr>
<td>p-OH-C₆H₄CH₂OH</td>
<td>p-OH-C₆H₄CH₂OAc</td>
<td>20</td>
<td>10</td>
<td>5</td>
<td>92</td>
</tr>
</tbody>
</table>

Reaction conditions: alcohol 1 mmol, acetic anhydride 1.2 mmol, catalyst 0.03, 0.05 and 0.07 g, room temperature, CH₂Cl₂ as solvent.
References


