Article

Selective Oxidation of Cinnamyl Alcohol to Cinnamaldehyde over Functionalized Multi-Walled Carbon Nanotubes Supported Silver-Cobalt Nanoparticles

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Abstract: The selective oxidation of alcohols to aldehydes has attracted a lot of attention because of its potential use in agrochemicals, fragrances, and fine chemicals. However, due to homogenous catalysis, low yield, low selectivity, and hazardous oxidants, traditional approaches have lost their efficiency. The co-precipitation method was used to synthesize the silver-cobalt bimetallic catalyst supported on functionalized multi-walled carbon nanotubes (Ag-Co/S). Brunauer Emmet Teller (BET), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), and X-ray diffraction (XRD) were used to characterize the catalyst. For the oxidation of cinnamyl alcohol (CA) with O_2 as an oxidant, the catalyst's selectivity and activity were investigated. The impacts of several parameters on catalyst's selectivity and activity, such as time, temperature, solvents, catalyst dosage, and stirring speed, were comprehensively studied. The results revealed that in the presence of Ag-Co/S as a catalyst, O_2 could be employed as an effective oxidant for the catalytic oxidation of cinnamyl alcohol to cinnamaldehyde (CD) with 99% selectivity and 90% conversion. In terms of cost effectiveness, catalytic activity, selectivity, and recyclability, Ag-Co/S outperforms the competition. As a result, under the green chemistry methodology, it can be utilized as an effective catalyst for the conversion of CA to CD.

Keywords: silver-cobalt bimetallic catalyst; CNTs; selective oxidation; cinnamyl alcohol; cinnamaldehyde

1. Introduction

The functional transformation of molecules to carbonyl compounds contributes significantly to the organic synthesis. The selective oxidation of alcohols in the presence of different stoichiometric reagents, such as chromium and manganese has been well investigated [1]. The oxidation of cinnamyl alcohol, a simple aromatic allylic alcohol, is one of the most studied heterogeneously catalyzed oxidation reactions. The carbonyl compound cinnamaldehyde is a significant chemical intermediate in organic transformations and has a wide range of applications in the food and fragrance industries. It is also used in animal repellant, plant protection against nematodes, flea repellent, and antibacterial agent. The

synthesis of metal catalysts for the catalytic the oxidation of target molecules in the presence of molecular oxygen as an oxidant has received more attention due to the atom economy and related environmental issues under the protocol of green chemistry. Few catalysts with suitable reactivity and stability are currently available for large-scale applications of aerobic oxidation of alcohols. So far, monometallic catalysts with platinum-group metals have dominated for the oxidation of cinnamyl alcohol. Furthermore, bimetallic nanoparticles have also received significant attention in comparison to monometallic particles because of their multifunctionalities, selectivity, and activity, and their use in a variety of research fields such as optics, water purification, electronics, and catalysis [2,3]. As a result, scientists are interested in synthesizing bimetallic nanoparticles in various shapes in order to improve their efficiency through different approaches, such as chemical approaches, sol-gel and precipitation methods [4]. Silver-cobalt (Ag-Co) bimetallic nanoparticles has become notable in several industries and various fields of science including catalysis, biotechnology and energy storage [5]. Hydrothermal reduction, sol-gel, and co-precipitation procedures have been used to prepare the bimetallic Ag-Co nanoparticles [6].

Erdogan and his co-workers used a co-precipitation approach to synthesize Ag-Co bimetallic nanoparticles and examined their role in the oxidation of carbon monoxide [7]. Alonso et al. investigated the antiseptic properties of Co and Ag mono metallic nanoparticles as well as Ag/Co composites [8]. Lima et al. prepared bimetallic nanoparticles of silver and cobalt in various molar ratios and studied their ability to reduce oxygen in alkaline environments [9]. Herein, the Ag and Co nanoparticles were synthesized through co-precipitation method and supported on functionalized multi walled carbon nanotubes [10]. The functionalized multi walled carbon nanotubes (FCNTs) was used as a support for nanoparticles due to its mechanical properties, stability, surface area, comparatively excessive oxidation stability, conductivity and selectivity [11]. Ag and Co bimetallic nanoparticles on the surface of FCNTs (Ag-Co/S) were used to catalyze the oxidation of cinnamyl alcohol to cinnamaldehyde. According to the literature review, the utilization of Ag-Co/S for the oxidation of cinnamyl alcohol in this study is a novel strategy because the supported nanoparticles showed increased selectivity, % conversion, recyclability, and stability. This FCNTs-supported Ag-Co catalyst, on the other hand, might be used well in industries for alcohol oxidation.

2. Results and Discussion

2.1. Characterization of of Ag-Co/S Nanoparticles

The supported nanoparticles were morphologically studied using SEM. Figure 1 shows that silver and cobalt bimetallic nanoparticles are present on the surface of FCNTs in a well-dispersed form. Kazici et al. [12] also conducted a similar investigation and reported the same findings. The existence of silver, cobalt, carbon, and oxygen was confirmed in the elemental composition of the supported bimetallic nanoparticles, as shown in ,. Metal oxide production and MWCNTs functionalization with organic acids (COOH) caused oxygen peaks in the results. The Ag-Co/S surface area measured by BET was 217.5 m^2/g, which is consistent with the literature. The MWCNTs are identified by the diffraction peak at $2\theta = 26.1$ in Figure 3. The diffraction peaks at $2\theta = 38.1°$, 66° and 78.4° correspond to Ag crystal lattices, while the peaks at $2\theta = 41°$, 44°, 47° and 76° correspond to cobalt crystal lattices. Kanwal et al. [13] also studied Co-Ag nanoparticles and found similar results.

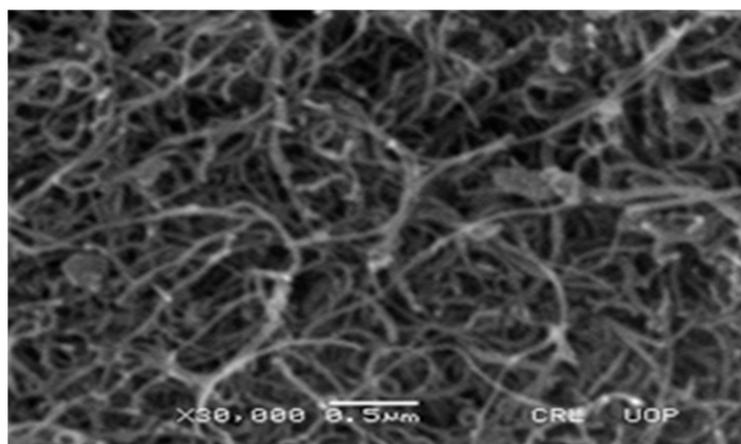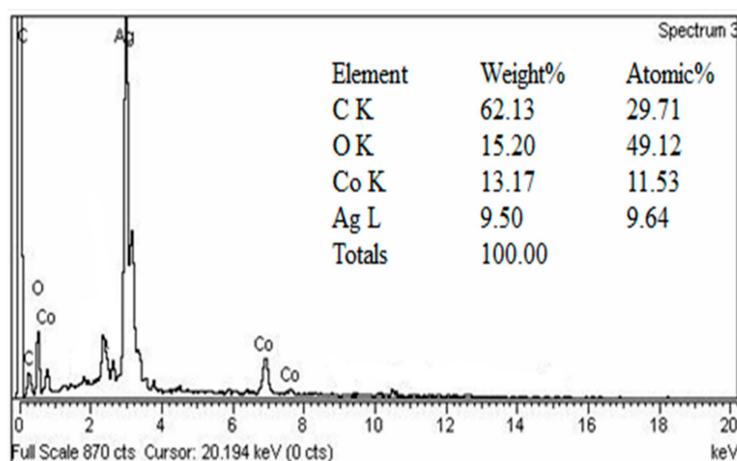**Figure 1.** Scanning electron microscopy (SEM) image of Ag-Co/S nanoparticles.

Element	Weight%	Atomic%
C K	62.13	29.71
O K	15.20	49.12
Co K	13.17	11.53
Ag L	9.50	9.64
Totals	100.00	

Full Scale 870 cts Cursor: 20.194 keV (0 cts)

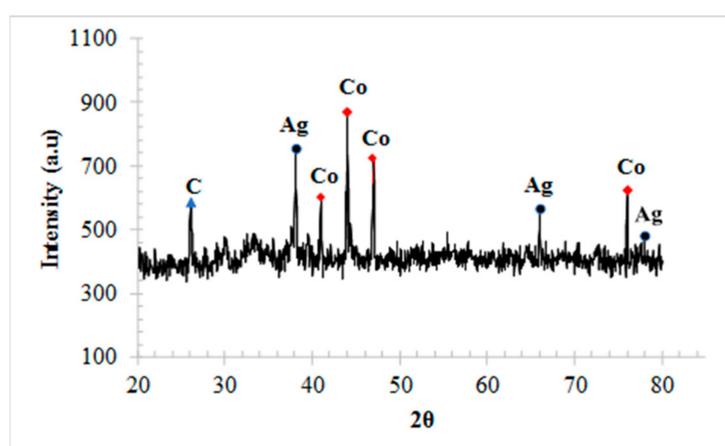**Figure 2.** Energy dispersive X-ray spectrum of Ag-Co/S nanoparticles.

Figure 3. X-ray diffractometry image of Ag-Co/S nanoparticles.

2.2. Oxidation of Cinnamyl Alcohol as a Model Reaction

To confirm the absence of autocatalysis of cinnamyl alcohol, a substrate solution (CA in ethanol) was introduced in the reactor without Ag-Co/S, and the percent conversion and selectivity were calculated at 75 °C, 750 rpm, 760 torr (O2), and 80 min. The reaction was next studied in the presence of Ag-Co/S in order to determine its catalytic effect on

CA oxidation under the same experimental circumstances. Furthermore, multiple tests were carried out to study the effect of various parameters on percent conversion and selectivity, such as time duration, temperature, catalyst quantity, solvent, stirring speed, and recyclability. The percent conversion and selectivity were calculated by applying Equations (1) and (2).

$$\% \ Conversion = \frac{moles \ of \ reactant \ disappeared}{moles \ of \ initial \ reactant} \times 100 \tag{1}$$

$$\% \ Selectivity = \frac{C_{compound}}{\sum C_{product}} \times 100 \tag{2}$$

In the current investigation, Ag-Co/S was determined to be an outstanding catalyst in terms of selectivity and perecnt conversion when compared to the other reported catalysts (Table 1).

Table 1. Comparative study of the catalytic performance of our synthesized nanoparticles to that reported in the literature for the oxidation of CA to CD.

Catalysts	Conv/Sel (%)	Reaction Conditions	References
Bi-Pt/AC	34/84	Temp; 60 °C, Solvent; Toluene, Time; 2 h	[14]
Fe$_2$O$_3$/AC	44/89	Temp; 80 °C, Solvent; Water, Time; 2 h	[15]
Bi-Pt/Alumina	>90/>90	Temp; 100 °C, Detergents;	[16]
Au–Pd/TiO$_2$	82/64	Temp; 100 °C, Solvent; Toluene, Time; 7 h	[17]
Ag-Co/S	90/99	Temp; 75 °C, Solvent; Ethanol, Time; 80 min	The current research

2.3. Impact of Different Reaction Parameters

2.3.1. Effect of Time

To study the effect of time on both percent conversion and selectivity of the oxidation of CA to CD, the reaction was periodically monitored. The reaction was carried out at 75 °C with 25 mg of the catalyst added to the substrate solution (1 mmole CA/10 mL ethanol) at 1 atm and 750 rpm stirring. Figure 4 showed that the percent conversion and selectivity grew in a linear fashion up to 80 min, after which both percent conversion and selectivity gradually dropped due to the formation of by-products, as demonstrated by GC. As a result, the remaining processes were assigned an optimal response time of 80 min. A comparable study was conducted by Zhao et al. [18].
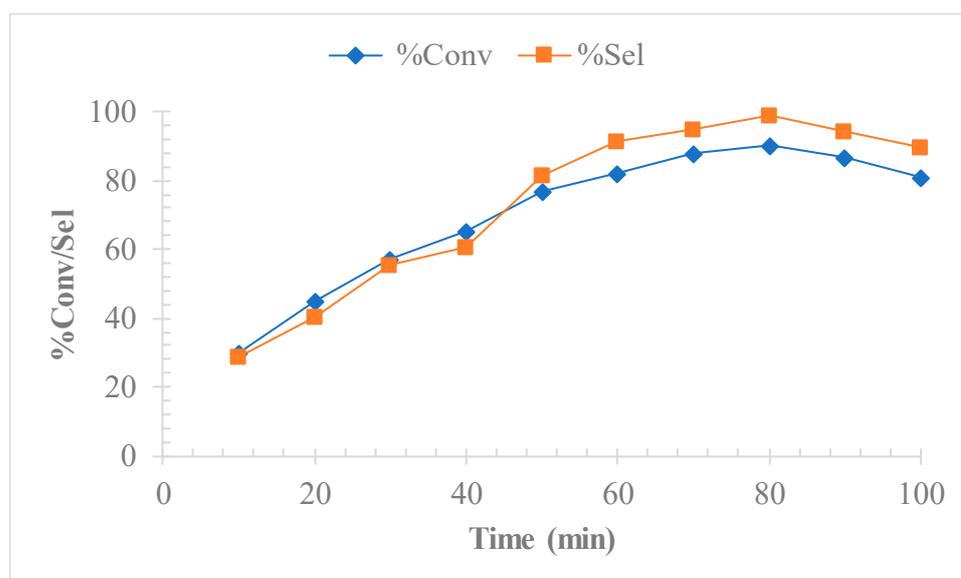
Figure 4. Time effect on percent conversion and selectivity of CA to CD with Ag-Co/S as a catalyst. Conditions of Reaction: CA; 1 mmol, Cat; 25 mg, Stirring speed; 750 rpm, oxidant; O_2 (760 torr), and temperature; 75 °C.

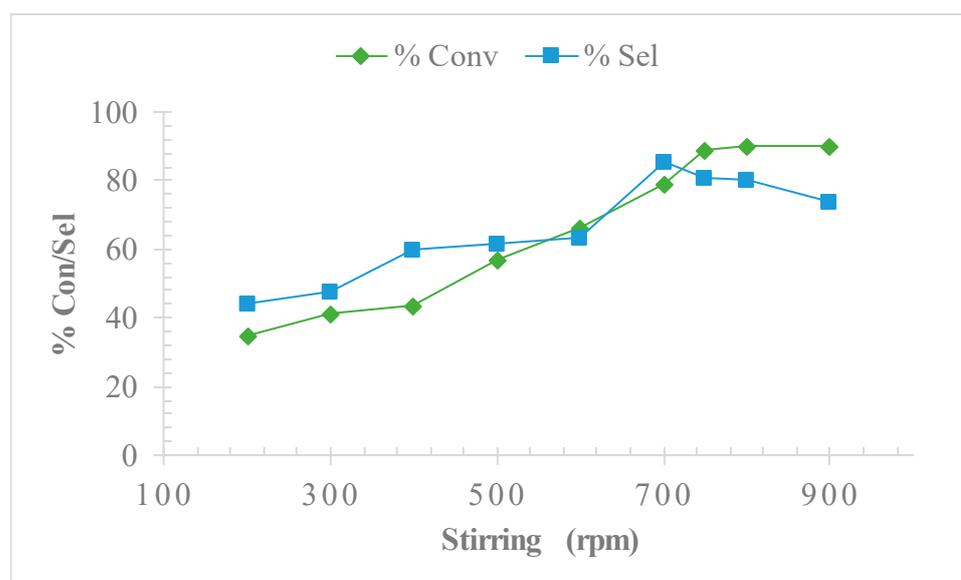### 2.3.2. Effect of Temperature

The temperature has a significant effect on percent conversion and selectivity. By adopting experimental conditions constants, both percent conversion and selectivity for cinnamyl alcohol to cinnamaldehyde oxidation were investigated at temperatures ranging from 25 to 100 °C in the presence of ethanol as a solvent. As demonstrated in Figure 5, both percent conversion and selectivity rose until 75 °C, after which they both declined due to solvent evaporation and the generation of by-products. As a result, for CA to CD oxidation, all subsequent reactions were carried out at 75 °C. Wu et al. conducted a similar analysis and found that cinnamaldehyde had a maximum selectivity of 64 percent at 100 °C [17].
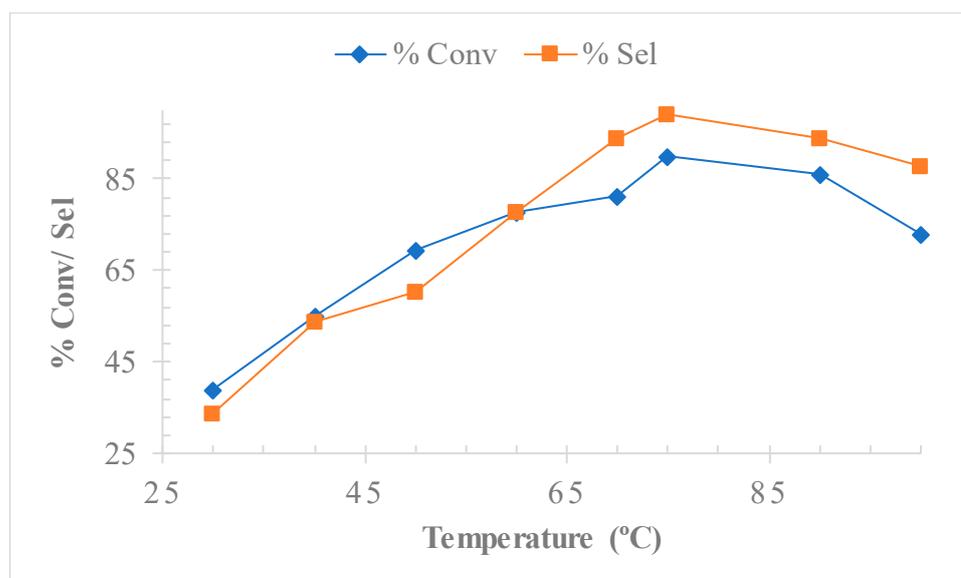
Figure 5. Effect of temperature on percent conversion and selectivity of CA to CD in the presence of Ag-Co/S. Conditions of reaction: Cat; 25 mg, CA; 1 mmol in 10 mL solvent, Solvent; ethanol, Oxidant; O_2 (1 atm), Time; 80 min, Stirring speed; 750 rpm.
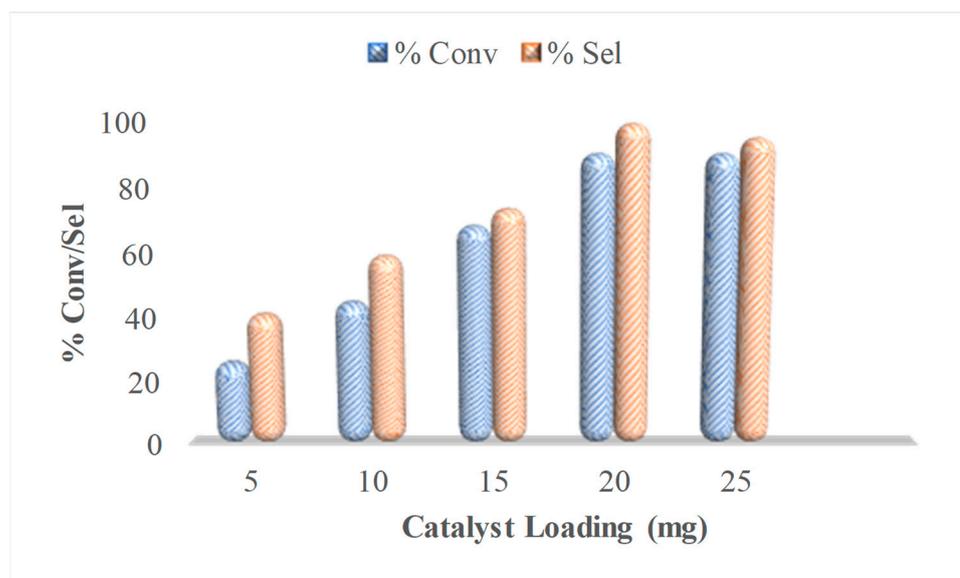
2.3.3. Effect of Stirring Speed

The stirring speed has a considerable effect on the percent conversion and selectivity of CA to CD. The experiment was carried out with a range of stirring speeds (200–1000 rpm) while keeping all other experimental variables constant in order to optimize the stirring speed. Figure 6 indicated that percent conversion and selectivity both increased in the early phases, with the maximum percent conversion and selectivity occurring between 750 and 800 rpm, and a little drop occurring above 800 rpm due to by-product production. All subsequent trials were carried out at a stirring speed of 750 rpm to eliminate the probability of mass transfer. Sadiq et al. synthesized cinnamaldehyde, which is consistent with the findings of this study [19].

Figure 6. Effect of stirring speed on percent conversion and selectivity of CA to CD in the presence of Ag-Co/S. Conditions of reaction: Cat; 25 mg, CA; 1 mmol, Solvent; ethanol, Oxidant; O_2 (1 atm), Time; 80 min, Temperature; 75 °C.

2.3.4. Catalyst Dose Study

By maintaining the entire parameters constant, a catalyst dose study was done to evaluate the percent conversion and selectivity of CA to CD oxidation. Up to 25 mg of catalyst, the percent conversion rose linearly with the amount of catalyst used, with no decrease in selectivity. A catalyst dose of 25 mg resulted in a maximum conversion of 90% with 99 percent selectivity, as illustrated in Figure 7. Due to the adsorption of oxidized products on the surface of the Ag-Co/S catalyst, increasing the catalyst loading causes a noticeable decrease in both conversion and selectivity. As a result, subsequent experiments were carried out using 25 mg of the catalyst. Breen et al. also used the Ir/C catalyst for the selective hydrogenation of CD to CA [20].

Figure 7. The effect of catalyst quantity on percent conversion and selectivity of CA to CD in the presence of Ag-Co/S. Conditions of reaction: CA; 1 mmol, Solvent; ethanol, Time; 80 min, Temperature; 75 °C; Oxidant; O_2 (1 atm), Stirring Speed; 750 rpm.

2.3.5. Effect of Solvents

As shown in Figure 8, the nature of solvents has a significant impact on the conversion of CA to CD. This graph compares the effects of several solvents such as water, n-hexane, acetonitrile, toluene, and ethanol on the conversion of CA to CD while maintaining all other variables constant. Among the solvents used, ethanol yielded the highest conversion rate. Acetone, water, acetonitrile, toluene, and ethanol were seen in ascending order of percent conversion. The solubility of oxygen in different solvents has an impact on the CA to CD conversion. Guo et al. studied the effect of solvents on the catalytic hydrogenation of CD to CA and came to the same conclusion [21]. Nyamunda et al. investigated the influence of different solvents on the selectivity of cinnamaldehydes and found that cinnamaldehyde had an 84 percent selectivity [14].
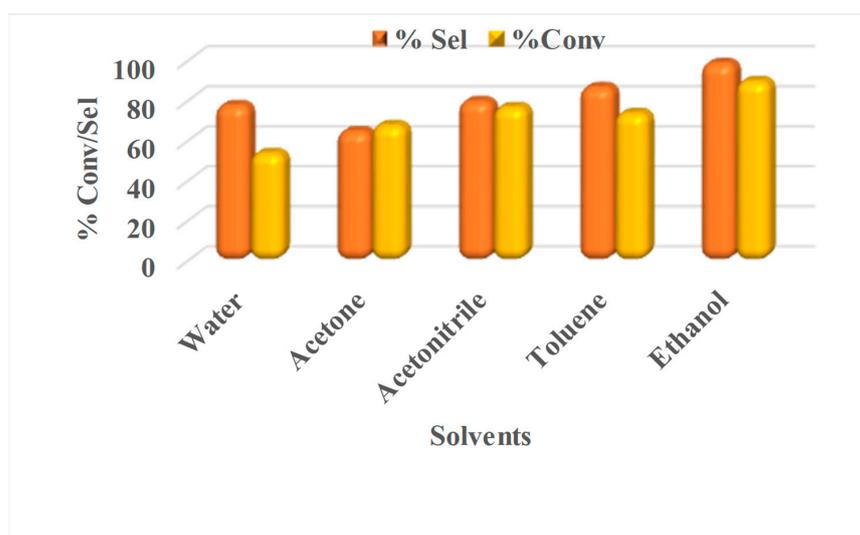
Figure 8. The effect of various solvents on percent conversion and selectivity of CA to CD in presence of Ag-Co/S. Conditions of reaction: Cat; 25 mg, CA; 1 mmol, Solvent; ethanol, Oxidant; O_2 (1 atm), Time; 80 min, Stirring speed; 750 rpm, Temperature; 75 °C.

2.4. Leaching and Recyclability of Ag-Co/S

To ensure that the solvents were inert, Ag-Co/S was mixed and stirred in them at optimal conditions. The appearance of a single signal in the chromatograph confirmed the solvents' inert nature. CA was added to the filtrate and stirred under the same experimental conditions to check the heterogeneous nature of the catalysts. There was no CA to CD conversion, indicating that Ag-Co/S was stable in the chosen solvents and had true heterogeneous behavior. The reaction took place when 25 mg of Ag-Co/S was added to the solution (CA/ethanol) under the given conditions, and cinnamaldehyde was produced in a significant amount with 90% conversion. In ethanol, the recyclability of Ag-Co/S was tested. The catalyst was separated from the reaction mixture, washed, and dried at about 100 °C before being exposed to the cinnamyl alcohol solution for up to five cycles without experiencing any noticeable decrease in catalytic activity in terms of percent selectivity, but a 10% decrease in conversion was observed (Figure 9). These results suggested that Ag-Co/S can be used effectively several times for the oxidation of cinnamyl alcohol. Sadiq et al., on the other hand, investigated the recyclability and stability of Zn-Mn bimetallic nanoparticles as a catalyst for CA to CD oxidation under mild reaction conditions [20].
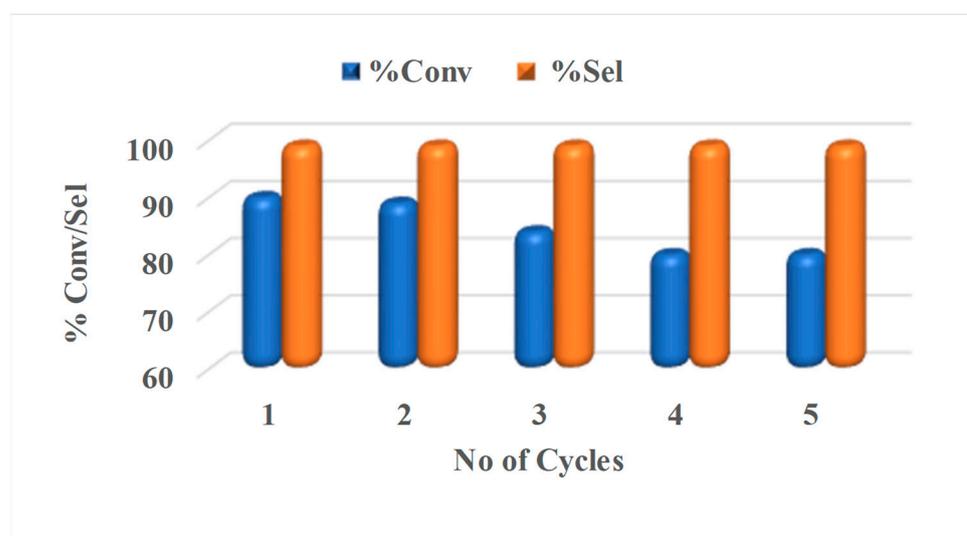

Figure 9. Reusability of Ag-Co/S for oxidation of CA to CD.

3. Materials and Methods

3.1. Materials and Chemicals

The chemicals and reagents used in this study were of high purity (Sigma Aldrich, Saint Louis, MO, USA, Alfa Aesar, Thermo Fisher, Kandel, Germany, and Merck, New Jersey, United States). The multi-walled carbon nanotubes (MWCNTs; O.D. × L 6–13 nm × 2.5–20 μm) were furnished by Sigma Aldrich. Gases such as oxygen and nitrogen were supplied by the British Oxygen Company (BOC), West Wharf Karachi, Pakistan. To remove traces from the applied gases, certain filters such as (C.R.S.Inc.202223) and (C.R.S.Inc.202268) were used.

3.2. Synthesis of Ag-Co/S Catalyst

Following the co-precipitation approach, equimolar solutions of metal salts such as $AgNO_3 \cdot 2H_2O$ and $CoCl_2 \cdot 2H_2O$ (0.01 M) were prepared and titrated against ammonium hydroxide (NH_4OH). As a result, dense metal hydroxides developed in the form of precipitates. The precipitates were filtered, washed with deionized water several times, and then treated with 0.1 N HCl in a modified Soxhlet apparatus using a glass thimble until the pH was neutral. Then it was let to dry overnight. Chemically altering the surface of carbon nanotubes (CNTs) can give them a desired feature. In general, functionalization has been

accomplished through the use of oxidants such as HNO_3, $KMnO_4$, and others. Carboxyl groups, on the other hand, serve to functionalize CNTs defects and ends. The present goal of the study was to design a simple and quick approach for functionalizing carbon nanotubes. For the functionalization of multi-walled carbon nanotubes (MWCNTs) with an amine-containing group, we used a covalent chemical method. As a result, MWCNTs were treated with *p*-aminobenzoic acid to make them functional. Functionalized multi-walled carbon nanotubes (FCNTs) were separated by centrifugation, washed multiple times with deionized water until pH was neutral, and then dried for 12 h at 100 °C. The synthesized silver-cobalt nanoparticles were dispersed in ethanol/water (50% *v/v*) and a specific amount of FCNTs were added to the suspension to incorporate the prepared bimetallic nanoparticles on the $FCNT_S$. At room temperature, the resultant mixture was sonicated for an hour. Bimetallic nanoparticles of silver and cobalt supported on FCNTs were separated by centrifugation, washed, dried and stored in a desiccator [22].

3.3. Characterization of Ag-Co/S Catalyst

The morphology of the catalyst Ag-Co/S was investigated using scanning electron microscopy (SEM, JSM 5910, JEOL, Tokyo, Japan). Elemental analysis of the supported nanoparticles was carried out by Energy dispersive X-ray spectroscopy (EDX, JSM 5910, JEOL, Tokyo, Japan). X-Ray diffractometer (XRD, JDX-3532, JEOL, Tokyo, Japan) with operating voltage of 20–40 kV and 2θ range of 0–160° was used to analyze the phase of nanoparticles. The BET surface area of the Ag-Co/S nanoparticles was measured using a surface area and pore size analyzer (NOVA2200e, Quantachrome, Boynton Beach, FL, USA).

3.4. Catalytic Test

In a 100 mL three necked double walled round bottom batch reactor with a quick fit thermometer and a condenser, a substrate solution (CA/10 mL ethanol) and 25 mg Ag-Co/S as a heterogeneous catalyst were added. As shown in Scheme 1, the reaction mixture was vigorously stirred (200–1000 rpm) for 80 min at 75 °C while delivering a steady supply of oxygen (40 mL/min). For the analysis of the reaction mixture, two types of analytical methods were applied. Gravimetric and gas chromatographic methods. In gravimetric method, phenyl hydrazine was used for the detection of the product. The supported nanoparticles were separated from reaction mixture and then 1 mL of phenyl hydrazine was added to 10 mL reaction mixture. This resulted in the formation of a precipitate in an hour, which was filtered out and dried at 70–80 °C. Gas chromatography (GC, Clarus 580, Perkin Elmer, Waltham, MA, USA) with a flame ionized detector and capillary column (cross-linked methyl siloxane capillary column; length: 30 m, ID: 0.32 mm, and film thickness: 0.25 μm) was used to measure percent conversion and selectivity. A nitrogen generator (G6010E, Parker Domnick hunter, Team Valley Trade Est, NE11 0PZ Gateshead, UK) and a hydrogen generator (PGXH2 100, Perkin Elmer, Waltham, MA, USA) were used to provide nitrogen and hydrogen gases. In gas chromatographic technique, the sample was spiked with authentic standard, the sharpening of the given peak at that particular retention time, confirmed the formation of the desired product.
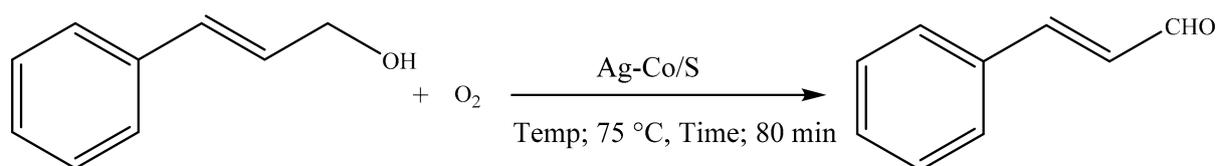
Scheme 1. Oxidation of CA to CD with 25 mg catalyst, 10 mL substrate solution (1 mmole of CA/10 mL ethanol) at 75 °C for 80 min under stirring 750 rpm in the presence of O_2.

4. Conclusions

In the present study, Ag-Co/S was synthesized effectively by co-precipitation method and characterized through SEM, EDX, XRD, and the BET surface area analyzer. The prepared nanoparticles were tested as a heterogeneous catalyst for the selective oxidation of CA to CD using different solvents such as water, acetone, acetonitrile, toluene and ethanol under mild reaction conditions in the presence of cost effective and ecofriendly oxidant. The Ag-Co/S has shown increased potential in terms of percent conversion (90%) with selectivity (99%) at optimal conditions such as catalyst; 25 mg, cinnamyl alcohol; 1 mmol, solvent; ethanol, temperature; 75 °C, time; 80 min, stirring speed; 750 rpm and oxidant; O_2 at 1 atm. The Ag-Co/S is a potent heterogeneous catalyst for the oxidation of cinnamyl alcohol to cinnamaldehyde because of their ease of preparation, high catalytic activity, cost effectiveness, heterogeneous behavior, and recyclability. Future research into the kinetics of adding an oxidant as well as changing the catalyst support could result in major changes in catalyst selectivity/activity and may diverse their applications in organic transformation of other alcohols.

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Data Availability Statement: No data associated with this publication to be link. All the data associated in presented in this paper.

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