Silver decorated multi-walled carbon nanotubes as a heterogeneous catalyst in the sonication of 2-aryl-2,3-dihydroquinazolin-4(1H)-ones

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Silver decorated multi-walled carbon nanotubes as a heterogeneous catalyst in the sonication of 2-aryl-2,3-dihydroquinazolin-4(1H)-ones

J. Safari,* S. Gandomi-Ravandi

In the present study, an attempt has been made to synthesize 2-aryl-2,3-dihydroquinazolin-4(1H)-ones from sonication of anthranilamide and aldehyde as precursors in the presence of Ag-CNTs as a novel catalyst. This work consistently has the advantages of excellent yields, short reaction times, and simple experimental and work-up procedures. The heterogeneous catalyst could be recovered and recycled several times without any loss of its activity.

Introduction

2,3-Dihydroquinazolines are an important class of heterocycles with a wide range of pharmacological and biological activities. Additionally, these compounds can easily be oxidized to their quinazolin-4(3H)-one analogs, which they themselves are important biologically active compounds. In view of these useful properties, development of a simple, environmentally benign, high-yielding, and clean method is on demand to synthesize 2,3-dihydroquinazolin-4(1H)-ones. Several strategies were already developed for their synthesis: (a) condensation of anthranilamide with an aldehyde or ketone using p-toluenesulfonic acid as catalyst; (b) desulfurization of 2-thioxo-4(3H)-quinazolinones; (c) reaction of isatoic anhydride with Schiff-bases; (d) one-step conversion of 2-nitrobenzamides to 2,3-dihydro-4(1H)-quinazolinones; (e) condensation of anthranilamide with benzyl; (f) two-step synthesis starting from isatoic anhydride and amines, then was annulated with ketones; (g) a one-pot three-component condensation of isatoic anhydride, aldehydes and amines. However, there is a need for a greener and milder method that might work under efficient conditions.

Since their discovery in 1991, carbon nanotubes (CNTs) have been at the forefront of nanoscience and nanotechnology because of their remarkable electrical, mechanical, thermal, and optical properties. Carbon nanotubes (CNTs) are a promising material for many potential applications because of their unique structure and properties. Carbon nanotubes are often applied as electrocatalysis support due to their unique structure and morphology, high electrochemical stability and conductivity. Recently, many studies have been devoted to prepare CNTs–metal composites because of the improvement of the electrical and mechanical properties of composite. The advantages of using CNTs as supports are getting better size and dispersion of transition metal catalysts on their surface in electrocatalytic reactions. On the other hand, among all metals, extreme interest has been attracted to Ag due to their superior optical, electrical, physical, and catalytical properties. Silver supported on CNTs (Ag–CNTs) has attracted significant attention owing to their wide applications as catalyst, electrodes, optical limiters, and advanced materials. There are several methods to prepare well-defined Ag nanoparticles (NPs) supported on multi-walled carbon nanotubes (MWCNTs) including thermal decomposition (solid-state reaction), gamma irradiation, DC electrophoresis, surface chemical reduction, and wet-chemical method. Recent studies showed that modifying CNTs surface by chemical treatments is a general protocol to obtain well-fined catalyst nanoparticles on CNTs. Chemical modification, especially using acid with creation of defects and covalent on the external walls by oxidative process, is the simplest and most inexpensive method to promote the properties of CNTs. In sonochemistry, ultrasound is defined as sound waves with a frequency of 20 kHz or more. Ultrasonic irradiation is potentially simpler, cleaner, milder, safer and greener than other sources and forms purer products. These effects of ultrasound arise from acoustic cavitations resulting from the continuous formation, growth and implosive collapse of the bubbles in a liquid medium, which is resulted in an instantaneously high temperature and pressure pulse at local
These cavitation bubbles grow in a process called ‘rectified diffusion’. Small amounts of gas go from the medium into the cavity (cavitation bubble) during its expansion phase in this process and the gas is not fully expelled during compression. Thus chemical reactions occur with enhancement in the mass transfer.64

We have been specifically interested in the synthesis of heterocycles containing the 2-aryl-2,3-dihydroquinazolin-4(1H)-one backbone. Therefore, an original and novel Ag-CNTs-catalyzed US-activated synthesis of 2-aryl-2,3-dihydroquinazolin-4(1H)-one was devised from an o-aminobenzamide compound and a substituted/ unsubstituted aldehyde in an efficient reaction (Scheme 1). However, there are no reports on the use of Ag-CNTs for synthesis of 2-aryl-2,3-dihydroquinazolin-4(1H)-ones under ultrasonic irradiation. Here, we hope to report the effect of ultrasonic irradiation for the highly efficient synthesis of 2-aryl-2,3-dihydroquinazolin-4(1H)-ones in the presence of Ag-CNTs reagent as a reusable catalyst in high yields.

Scheme 1. Sonication of anthranilamide and aldehyde with Ag-CNTs as catalyst

Results and discussion

For the first time, Ag-CNTs nanocomposites were studied to improve the catalytic activity of CNTs in the synthesis of quinazolinones on a laboratory scale. In order to explore the generality and scope of this new catalyst, anthranilamide with aromatic aldehydes were investigated in a model reaction in ethanol as solvent under the ultrasonic irradiation. The results were summarized in Table 1. As it is shown in this table both type of aldehydes led to desired 2-aryl-2,3-dihydroquinazolin-4(1H)-one under ultrasonic irradiation. The application of ultrasonic irradiation in reactions using heterogeneous catalyst is a promising technique. Compared with traditional methods, this technique is more convenient and easily controlled. The advantages of ultrasound procedures are consist of good yields, short reaction times, high selectivity and mild reaction conditions. The intense local temperature and high pressure produced during cavitation promoted the reaction yield. These directly help in shortening the time span of reactions and increasing the yield of products. The use of Ag-CNTs catalyst in conjunction with ultrasonic heating is a standard technology used in this context.

Table 1. Catalytic condensation of anthranilamide with aromatic aldehydes under ultrasound irradiation in 75 °C

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Time (min)</th>
<th>Yield (%)</th>
<th>Product</th>
<th>Mp (°C)</th>
</tr>
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<tr>
<td>1</td>
<td>H</td>
<td>5</td>
<td>97</td>
<td>3a</td>
<td>216–218</td>
</tr>
<tr>
<td>2</td>
<td>2-OH</td>
<td>20</td>
<td>86</td>
<td>3b</td>
<td>222–224</td>
</tr>
</tbody>
</table>

We also investigated the recyclability of the catalyst under above conditions using model reaction between benzaldehyde and anthranilamide. Figure 1 revealed the reusability of catalyst without the significant loss in its catalytic activity.

Figure 1. Reusability of the catalyst in the model reaction under sonochemical conditions

As shown in Figure 2, the rate of cyclocondensation depended on temperature. Thus, the reaction temperature is an important factor: the yield of the reaction was determined at various temperatures and found to grow with increasing temperature mostly to 75 °C. When the reaction was performed at 35 °C, the rate of the reaction was very slow and at higher temperatures than 75 °C the yield of 3a compound was significantly reduced. The general decrease in reaction rates at higher temperatures apparently was due to thermal degradation effects. A temperature of 75 °C was observed to be optimum for this studied reaction. In order to demonstrate the advantages of ethanol in the cyclization reaction of anthranilamide with aldehyde derivatives, as shown in Table 2, a series of parallel reactions were performed in various solvents.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Time (min)</th>
<th>Yield (%)</th>
<th>Product</th>
<th>Mp (°C)</th>
<th>Found</th>
<th>Reported</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2,4-Cl2</td>
<td>10</td>
<td>92</td>
<td>3c</td>
<td>167–169</td>
<td>51</td>
<td>165–167</td>
</tr>
<tr>
<td>4</td>
<td>4-F</td>
<td>12</td>
<td>90</td>
<td>3d</td>
<td>203–204</td>
<td>56</td>
<td>203–205</td>
</tr>
<tr>
<td>5</td>
<td>4(NMe2)</td>
<td>21</td>
<td>87</td>
<td>3e</td>
<td>208–210</td>
<td>55</td>
<td>210–212</td>
</tr>
<tr>
<td>6</td>
<td>4-Br</td>
<td>15</td>
<td>90</td>
<td>3f</td>
<td>195–197</td>
<td>50</td>
<td>197–199</td>
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<tr>
<td>7</td>
<td>2-NO2</td>
<td>6</td>
<td>96</td>
<td>3g</td>
<td>193–194</td>
<td>56</td>
<td>190–192</td>
</tr>
<tr>
<td>8</td>
<td>2,3-Cl2</td>
<td>9</td>
<td>93</td>
<td>3h</td>
<td>223–225</td>
<td>50</td>
<td>225–227</td>
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<tr>
<td>9</td>
<td>3-Cl</td>
<td>10</td>
<td>92</td>
<td>3i</td>
<td>185–187</td>
<td>31</td>
<td>188–188</td>
</tr>
<tr>
<td>10</td>
<td>2-OH</td>
<td>17</td>
<td>87</td>
<td>3j</td>
<td>173–174</td>
<td>31</td>
<td>173–175</td>
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<tr>
<td>11</td>
<td>2,3-(OMe)</td>
<td>15</td>
<td>90</td>
<td>3k</td>
<td>239–241</td>
<td>32</td>
<td>238–240</td>
</tr>
<tr>
<td>12</td>
<td>2-F</td>
<td>10</td>
<td>89</td>
<td>3l</td>
<td>265–267</td>
<td>33</td>
<td>266–267</td>
</tr>
</tbody>
</table>
In order to investigate the effect of intensity of ultrasonic power on reaction, the reaction was also performed at powers of the ultrasonic bath (20, 40, 60, 80 and 90 W). Increase of ultrasonic power led to higher yield and shorter reaction time. The results were shown in Table 4.

**Table 4. The effects intensity of ultrasonic power on time and yield of the synthesis of 3a**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Power (W)</th>
<th>Time (min)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>35</td>
<td>65</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>25</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>20</td>
<td>89</td>
</tr>
<tr>
<td>4</td>
<td>80</td>
<td>5</td>
<td>97</td>
</tr>
<tr>
<td>5</td>
<td>90</td>
<td>5</td>
<td>94</td>
</tr>
</tbody>
</table>

Figure 3 shows the XRD spectra of the oxidized MWCNTs, Ag nanoparticles, and Ag-CNT composites. The presented diffractogram exposes that the synthesized Ag/CNT nanocomposites are crystalline and no impurity was found. The diffraction peaks identify the sample as a mixture of Ag NPs and MWCNTs. The peak around (2θ ≈26.1°) was related to the structure of MWCNTs, while the peaks at about (2θ ≈38.37°), (2θ ≈44.55°), (2θ ≈64.68°) and (2θ ≈77.67°) corresponded to Ag (200), (111), (220) and (311). Particle size of the silver nanoparticles on CNTs using Scherrer’s formula is calculated 19.63 nm.

The SEM images presented in Figure 4 indicate the nonstructural characterization of the CNT and silver–carbon nanotube composite samples. As it is obvious from Figure 4(a), the average diameter of carbon nanotubes was found 17.58 nm. The size distribution of Ag nanoparticles attached to the CNTs was found to be 19.6 nm of diameter. SEM images suggest that the Ag nanoparticles mostly are attached to carbon nanotubes and are not localized within the channels of nanotubes.
In order to investigate the crystallinities of the Ag-D CNT nanocomposites, Raman spectroscopy was used. Two peaks at approximately 1307 cm$^{-1}$ (D band) corresponding to the vibrations of C atoms and 1584 cm$^{-1}$ (G band) corresponding to the stretching mode on the graphite plane are clearly observed in Figure 5. It represents also the lower region of the Raman spectra for the Ag-MWCNT; it appears a peak at 519 and 965 cm$^{-1}$ correlated to the stretching modes of Ag-C. The intensity ratio of D-band to G-band (ID/IG ratio) has a linear relation with the structural properties and crystallinity of MWNTs. After Ag loading, the ID/IG ratio of the MWCNTs has been decreased from 1.86 to 1.66. This decrease in the intensity ratio indicates the reduction of structure defects and the enhancement of atomic ordering or crystalloid of the MWCNTs.

Figure 5. Raman spectroscopy of oxidized carbon nanotubes and Ag-MWCNTs composites

Figure 6 shows FTIR spectra of acid treatment MWCNTs with a broad peak at 3438 cm$^{-1}$ which can be attributed to the OH stretching mode. Carbonyl group at 1726 cm$^{-1}$ can be because of oxidation of MWCNTs surface through purification. The C=C stretching band is assigned at 1578 cm$^{-1}$, and methylene group (CH$_2$) stretching bands at 2919 cm$^{-1}$ and 2849 cm$^{-1}$ are appeared for oxidized MWCNTs. The band appearing at 526 cm$^{-1}$ is due to Ag-C stretching mode.

Figure 6. FT-IR spectroscopy of acid treatment CNTs and Ag-MWCNTs composites

Attenuated total reflectance (ATR FT-IR) spectra of modified MWCNTs and MWCNT supported with Ag nanoparticles are presented in Figure 7. The peaks of surface functional groups of acid modified MWNTs such as the C=O stretching vibration, C=C and C–H vibration mode and the hydroxyl group are indicated. Moreover, it is presented the Ag-C stretching vibration in 615 cm$^{-1}$.
Figure 7. ATR FT-IR spectra of acid treatment CNTs and Ag-MWCNTs composites

The formation of the products can be explained by a plausible mechanism as shown in Scheme 2. It seems that enhancing the electrophilicity of the carbonyl group in aldehyde has occurred using supported metal. Then, the intermediate I is formed by the reaction of 2-aminobenzamide and activated aldehyde. After intermediate I dehydration, the imine intermediate II is produced. On the other hand, the part of imine in this intermediate could be activated by metal. Then, intermediate III could be prepared by intramolecular nucleophilic attack of the amide nitrogen on activated imine group. In the following, the products are afforded by a 1,5-proton transfer.

Scheme 2. Proposed reaction mechanism in synthesis of quinazolinones

We herein report very high activity of Ag-CNTs catalyst system in the cyclocondensation of o-aminobenzamide with various aldehydes to prepare 2-aryl-2,3-dihydroquinazolin-4(1H)-ones in ethanol under ultrasound conditions. We feel this protocol will be useful to synthesize numerous fused heterocyclic compounds because of its simple experimental procedure and excellent yields. The structures of these compounds were established by comparing their physical and spectral data with authentic samples in the literature.

Experimental

All the commercially available reagents were obtained from Merk, Aldrich and Fluka, and generally were used without further purification. MWNTs with outer diameter of CNT 10 and 20 nm were purchased from Nanotech Port Co. (Taiwan). These MWNTs were produced via the chemical vapor deposition (CVD, or sometimes called catalytic pyrolysis) method. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker DRX–400 spectrometer, chemical shifts are expressed in δ parts per million with reference to TMS. IR spectra of all the compounds were recorded on a Perkin Elmer FT–IR 550 spectrophotometer. All melting points (m.p.) were determined on an Electrothermal MK3 apparatus, expressed in °C and are uncorrected. Analytical thin layer chromatography (TLC) on silica gel plates containing UV indicator was employed routinely to follow the course of reactions and to check the purity of products. Ag-CNTs composite materials were characterized by a scanning electron microscope (KYKY SEM model EM3200, operated at a 25 kV). Also, the obtained nanocatalysts were characterized by XRD on a Bruker D8 Advance X-ray diffraction (XRD) diffractometer (CuK, radiation, λ= 0.154056 nm and 40 kV voltage), at a scanning speed of 2°/min from 10° to 100° (20). The Raman spectra were measured on a Bruker SENTERRA spectrometer with spectral range: 200-3500 cm$^{-1}$ and Laser wavenumber 785 nm.

Preparation of Ag-CNT composites

Silver mirror reaction (Tollens reaction), which was used to generate reflective silver mirrors on solid supports, is a chemical route which can be extended to nanometer region to generate silver coatings on nanosized objects such as carbon nanotubes. Ag-CNTs were prepared according to reported procedures in the literature. In short, CNTs were dissolved in the mixture of 98% sulfuric acid and 70% nitric acid (volumetric ratio 3:1) at 50 ºC under ultrasonication for 16 h. Then, MWNTs were centrifuged and washed with distilled water, then were dried under vacuum oven at 100 ºC for 24 h. After that, 10 g modified CNTs was mixed with 30 ml 38% formaldehyde, 200 ml absolute ethyl alcohol, and 200 ml deionized water. With vigorously stirring at 30 ºC, a mixture of 200 ml silver nitrate (AgNO$_3$) solution of 35 g/1 and 400 ml 25% ammonia solution (production of the ammonia solution of silver [Ag(NH$_3$)$_2$]) was dropped into above CNT–formaldehyde–alcohol–water solution. The pH value was kept in 8–9. Finally, the product was collected by centrifuging, was washed by de-ionized water twice, and was dried in vacuum oven at 60 ºC (Figure 7).
all products were identified by comparing of their physical and spectroscopic data with those reported in the literature.

Conclusions

These studies develop a straightforward and efficient approach to synthesize 2-aryl-2,3-dihydroquinazolin-4(1H)-ones using ultrasound-accelerated reaction in the presence of anthranilamide and aryl aldehydes as precursors and Ag-CNTs as reusable and heterogeneous catalyst. The short reaction times, high yields, reusability of catalyst and easy work up procedure are some advantages of this method. We think that our approach will be useful to design the libraries of quinazolinone congeners and to study relationship between their structure and activity. Combining the nanocomposites as catalyst and ultrasound irradiation is presented as an alternative method to produce 2-aryl-2,3-dihydroquinazolin-4(1H)-ones due to the mild conditions of this system.

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Notes and references

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Figure 7. Schematic diagram to form Ag nanoparticles along the MWCNTs

Ultrasound-induced condensation of anthranilamide and aldehydes

A mixture of anthranilamide (1 mmol), aromatic aldehydes (1 mmol) and catalytic amount of Ag-CNTs (0.04 g) was stirred in 5 mL ethanol as solvent and was irradiated under silent conditions by ultrasound for required reaction time. The completion of the reaction was monitored by TLC using chloroform: methanol (1:3) as eluent. Then, the catalyst was removed by filtering and was washed with distilled water. It could be reused and subjected to a second run of reaction. The resulted solution was cooled to ice water, was filtered, dried, and recrystallized from ethanol to afford the corresponding product. All products were identified by comparing of their physical and spectroscopic data with those reported in the literature.

References

27. D. J. Guo, H. L. Li, Carbon 2005, 43(6), 1259-64.