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Monodisperse Pt NPs@rGO as Highly Efficient and Reusable Heterogeneous Catalyst for the Synthesis of 5-substituted 1H-tetrazole Derivatives

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Monodisperse Pt NPs@rGO catalyst showed excellent yield and shortest reaction time for the synthesis of 5-Substituted 1H-tetrazoles
Monodisperse Pt NPs@rGO as Highly Efficient and Reusable Heterogeneous Catalyst for the Synthesis of 5-substituted 1H-tetrazole Derivatives

İbrahim Esirden\textsuperscript{a},\textsuperscript{t} , Esma Erken\textsuperscript{b},\textsuperscript{t} , Muharrem Kaya\textsuperscript{b},\textsuperscript{*,} and Fatih Sen\textsuperscript{b},\textsuperscript{**}

Monodisperse platinum nanoparticles supported with reduced graphene oxide (Pt NPs@rGO) are stable, isolable, bottleable, long-lived, highly efficient and exceptional reusable heterogeneous catalyst for the synthesis of 5-substituted 1H-tetrazoles from sodium azide and various aromatic nitriles with great catalytic performance. Pt NPs@rGO have been used for the first time for these types of synthesis reactions and these NPs were characterized by transmission electron microscopy (TEM), the high resolution electron micrograph (HRTEM), X-ray diffraction (XRD), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). All prepared tetrazole compounds were obtained with highest yield by using current heterogeneous catalyst and characterized by melting points, FT-IR, \textsuperscript{1}H-NMR, \textsuperscript{13}C-NMR and HRMS analyzes.

Result and discussion

Monodisperse Pt NPs@rGO have been prepared by sonochemical reduction method as given experimental section and their preliminary characterization was performed by TEM, HRTEM, XRD, AFM and XPS methods.

X-ray diffraction (XRD) pattern of Pt NPs@rGO are illustrated in Fig. S1. The peak at around 24.7° is raised from the graphite (002) plane of rGO. 2θ = 39.79, 46.24, 67.72, 81.56 and 85.97 diffraction peaks are due to Pt (111), (200), (220), (311), (320) planes of the face-centered cubic (fcc) crystal lattice of \textsuperscript{102}.
platinum, respectively. (JCPDS-ICDD, Card No. 04-802). The Pt (220) diffraction peak of the prepared Pt NPs@rGO is used to calculate the lattice parameter values and average crystallite size of the metal particles. The lattice parameter value of the resulting Pt NPs@rGO was calculated as 3.910 Å by considering Pt (220) diffraction peak from the following equation.21

\[
\sin \theta = \frac{\lambda \cos \theta}{2a}
\]

where \(a\) is the lattice parameter (Å); \(\lambda\) is the wavelength (1.54056 Å); \(\beta\) is the full width half-maximum of respective diffraction peak (rad); \(\theta\) is the angle at the position of peak maximum (rad).

Furthermore, the average crystallite platinum particle size of the prepared catalyst was calculated to be about 3.92 ± 0.60 nm using following Scherrer equation with XRD as Pt (220)22;

\[
d(\text{Å}) = \frac{k\lambda}{\beta \cos \theta}
\]

Atomic force microscopy (AFM) was also used to observe the height diameter distributions shown in Fig. S2. The AFM height diameter of the Pt NPs@rGO is found to be 4.05 nm which is in good agreement with the dimensions get by XRD and TEM.

X-ray photoelectron spectroscopy (XPS) was used to designate the surface compositions and chemical oxidation states of Pt in the nanocatalysts. To that end, the Pt 4f region of spectrum was analysed and the fitting of XPS peak was performed by Gaussian-Lorentzian method and the relative intensity of the species was estimated by calculating the integral of each peak. Accurate binding energies (±0.3 eV) were decided by referencing to the C 1s peak at 284.6 eV at XPS spectrum. Fig. S3 shows the Pt 4f photoelectron spectrum which comprise of two pairs of doublet. The most intense doublet at about 71.1 eV is a signature of metallic platinum26, 27 and the other doublet at about 74.6 eV is most likely by very small fraction of oxidized Pt\textsuperscript{IV} species possibly due to unreduced Pt precursor or PtOx species formed along the catalyst exposure to the atmosphere as shown in Table S1. The ratios of Pt(0) to Pt(IV) for the monodisperse Pt NPs@rGO were calculated as 3.72 from the relative peak area of the Pt 4f spectrum.

It is worth mentioning that Pt NPs are often used as a catalyst in alcohol oxidation, dehydrogenation, super-capacitors, hydrogen storage, batteries and sensor but its use as a catalyst for synthesizing 5-substituted 1H-tetrazoles from nitriles and sodium azide has not been reported before.

The general synthesis method shown in Scheme 1 was employed to prepare the tetrazole compounds (Table 1, entries 3a-j). Tetrazole compounds were prepared by means of a one-pot reaction producing highest yields and providing a simple work-up procedure. Aromatic nitriles \( \text{1} \) were converted into tetrazoles with the sodium azide \( \text{2} \) in the molar ratio of 1:1.5 using monodisperse Pt NPs@rGO as the catalyst and various solvents. By changing the nature of the substituents present in the aromatic nitrile components, a rather large chemical diversity can be incorporated in tetrazoles (Scheme 1; Table 1). These several substituents are included in the compounds of nitro, aldehyde, halogen (Cl, Br), methyl, pyridine moiety and acetonilide (Table 1).

We also investigated the effects of the solvent on the model reaction (Table S2, entries 1-5). The model reaction was performed in DMF, DMSO, ethanol, toluene and water. The reactions gave poor yields when water, ethanol and toluene were used as solvents. Therefore, these solvents were determined not to be suitable for this model reaction. Even though the phenyl tetrazole was obtained in a moderate yield and a long reaction time in DMSO, the reaction in DMF was performed in a shortest reaction time with the best yield. Therefore, it can be thought that DMF is a superior solvent compared to the others.

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**Fig. 1.** High resolution transition electron micrograph and particle size histogram of a Pt NPs@rGO

TEM image of Pt NPs@rGO are given in Fig. 1, they show the presence of monodisperse Pt NPs@rGO in the range of 3.57–4.35 nm with a mean diameter of 3.9±0.41 nm. In addition, the high resolution electron micrograph (HRTEM) of the catalyst is shown in Fig. 1. HRTEM results indicated that most of particles are in spherical shape, and no agglomerations are observed in our catalyst. Fig. 1 also displays the representative atomic lattice fringes obtained by high resolution transmission electron microscopy for monodisperse Pt NPs@rGO. Moreover, the chosen area HRTEM image of Pt NPs@rGO displays the highly crystalline feature of 4.0 this Pt NPs@rGO with a crystalline spacing of 0.227 nm which is very close to nominal Pt (111) spacing of 0.228 nm.23-25
Scheme 1. Synthesis of 5-substituted 1H-tetrazoles

Table 1. The synthesis of 5-substituted 1H-tetrazoles with Pt NPs@rGO

<table>
<thead>
<tr>
<th>Entry</th>
<th>Product</th>
<th>Reaction time (h)</th>
<th>Yield (%)</th>
<th>TON</th>
<th>TOF (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>![Product Image]</td>
<td>0.5</td>
<td>96</td>
<td>32.07</td>
<td>64.14</td>
</tr>
<tr>
<td>3b</td>
<td>![Product Image]</td>
<td>1</td>
<td>95</td>
<td>31.67</td>
<td>31.67</td>
</tr>
<tr>
<td>3c</td>
<td>![Product Image]</td>
<td>3</td>
<td>97</td>
<td>32.33</td>
<td>10.78</td>
</tr>
<tr>
<td>3d</td>
<td>![Product Image]</td>
<td>2.5</td>
<td>98</td>
<td>32.67</td>
<td>13.07</td>
</tr>
<tr>
<td>3e</td>
<td>![Product Image]</td>
<td>1.5</td>
<td>94</td>
<td>31.33</td>
<td>20.89</td>
</tr>
<tr>
<td>3f</td>
<td>![Product Image]</td>
<td>1.5</td>
<td>92</td>
<td>30.67</td>
<td>20.45</td>
</tr>
<tr>
<td>3g</td>
<td>![Product Image]</td>
<td>0.4</td>
<td>99</td>
<td>33.07</td>
<td>82.68</td>
</tr>
<tr>
<td>3h</td>
<td>![Product Image]</td>
<td>4</td>
<td>90</td>
<td>30.07</td>
<td>7.52</td>
</tr>
<tr>
<td>3i</td>
<td>![Product Image]</td>
<td>5</td>
<td>89</td>
<td>29.67</td>
<td>5.93</td>
</tr>
</tbody>
</table>
The concentration of the catalyst plays a crucial role in the success of the reactions in terms of the rate and the yields, and these experiments are summarized in Table 2. In the absence of catalyst the phenyl tetrazole was obtained 0 % yield in room temperature (24 h), ≤ 8 % yield in 50 °C and 12 % yield in 75 °C (24 h). Increasing the catalyst to 1, 2, 3, 4 and 5 mol % resulted in increasing the reaction yields to 77, 85, 96, 96 and 96 % the reaction times varied from 0.3 to 24 hours. The phenyl tetrazole product was obtained in the model reaction in the presence of 3 mol % Pt NPs@rGO in DMF in a highest yield (96%) and shortest time (0.5 h). Use of just 3 mol % Pt NPs@rGO in DMF is enough to afford an efficient synthesis. In conclusion, the best catalyst amount was determined to be 3 mol % Pt NPs@rGO (Table 2, entry 6).

Table 2. Optimization of conditions for preparation of 5-substituted 1H-tetrazoles using Pt NPs@rGO as a catalyst in DMF

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (mol %)</th>
<th>Time (h)</th>
<th>Temperature (°C)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>24</td>
<td>r.t.</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>None</td>
<td>24</td>
<td>50</td>
<td>≤ 8</td>
</tr>
<tr>
<td>3</td>
<td>None</td>
<td>24</td>
<td>75</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>None</td>
<td>3</td>
<td>75</td>
<td>77</td>
</tr>
<tr>
<td>5</td>
<td>None</td>
<td>2</td>
<td>75</td>
<td>85</td>
</tr>
<tr>
<td>6</td>
<td>None</td>
<td>0.5</td>
<td>75</td>
<td>96</td>
</tr>
<tr>
<td>7</td>
<td>None</td>
<td>0.4</td>
<td>75</td>
<td>96</td>
</tr>
<tr>
<td>8</td>
<td>None</td>
<td>0.3</td>
<td>75</td>
<td>96</td>
</tr>
</tbody>
</table>

Table 3 indicates the comparison of the activity of the different heterogeneous catalysts with that of prepared Pt NPs@rGO by considering the yield for the reaction. We observed that the current Pt NPs@rGO catalyst gives best catalytic activities (the highest TOF and TON values), highest reusability and shortest reaction time performances than the other catalysts in literature such as nanocrystalline ZnO, Nano CSMIL, ZnO nanoflakes, CuFe2O4 nanoparticles, Mesoporous ZnS, CoY zeolite, Ag NPs, Graphene, Graphene oxide/ZnO nanocomposites as shown in Table 3. The prepared monodisperse Pt NPs@rGO have been also compared with PtCl4 which is the precursor material of Pt NPs@rGO. When we used PtCl4 as a precatalyst and Pt NPs@rGO as a catalyst under the same conditions for the preparation of 5-substituted 1H-tetrazoles, we observed 74 % and 96 % yield, respectively (Table 3). This case can be explained that the sole stabilizer present in PtCl4 system is the weakly coordinating chloride anion cannot provide enough stabilization for the preparation of 5-substituted 1H-tetrazoles. During the presence of tripropylamine and rGO, the Pt NPs are found to be determined towards agglomeration over months. It shows that tripropylamine and rGO are powerful stabilizing and supporting agent for the Pt NPs. After the washing of the Pt NPs with dry ethanol for removing surplus ligand, they can be isolated readily as solid by evaporation of solvent under vacuum atmosphere.

Table 3. Comparison of various heterogeneous nanocatalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Temperature (°C)</th>
<th>Yield (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nanocrystalline ZnO</td>
<td>14</td>
<td>120-130</td>
<td>72, 662</td>
<td>20a</td>
</tr>
<tr>
<td>2</td>
<td>Nano CSMIL</td>
<td>7</td>
<td>120</td>
<td>87</td>
<td>20b</td>
</tr>
<tr>
<td>3</td>
<td>ZnO nanoflakes</td>
<td>14</td>
<td>125</td>
<td>87</td>
<td>20c</td>
</tr>
<tr>
<td>4</td>
<td>CuFe2O4 nanoparticles</td>
<td>12</td>
<td>120</td>
<td>82, 756</td>
<td>20d</td>
</tr>
<tr>
<td>5</td>
<td>Mesoporous ZnS</td>
<td>36</td>
<td>120</td>
<td>86</td>
<td>20e</td>
</tr>
<tr>
<td>6</td>
<td>CoY zeolite</td>
<td>14</td>
<td>120</td>
<td>90, 77.5c</td>
<td>20f</td>
</tr>
<tr>
<td>7</td>
<td>Ag NPs</td>
<td>8</td>
<td>120</td>
<td>92</td>
<td>20i</td>
</tr>
</tbody>
</table>
To understand the scope and effectiveness of the monodisperse Pt NPs@rGO, different substituents benzonitriles were selected and used in the determined conditions. These [3+2] cycloaddition reactions play a vital role on the nitrile compound activity. 5-Substitute 1H-tetrazoles were obtained in a shorter time with very good yields than electron-withdrawing functional groups containing benzonitriles (table 1, entries 3b-f) and heteroaromatic nitriles compound such as 4-pyridinecarbonitrile (table 1, 3g) while benzonitriles containing electron-donating groups (table 1, entry 3h-j) converted to tetrazoles in longer reaction times. For example, such aromatic nitriles as –NO$_2$, –Br, –Cl and –CHO, which contain electron-withdrawing groups, react faster in better yields when compared to the nitriles containing electron-donating groups like –CH$_3$, –NHAc. In fact, 4-pyridinecarbonitrile was transformed into the tetrazole compound in a much shorter period of time with a very good yield. All the products were characterized by melting points, FT-IR, $^1$H-NMR, $^{13}$C-NMR and HRMS analyzes. (Fig. S4-S10)

**Table 4. Reusability performance of Pt NPs@rGO**

The model reaction (benzonitrile, NaN$_3$ in a 1:1.5 molar ratio in DMF) was performed successfully within 0.5 h in the presence of 3 mol % heterogeneous Pt NPs@rGO in the first run. Pt NPs@rGO, which recovered by centrifuges after each reaction, can be reutilized for 6 consecutive times in the new batch experiments without influential yield loss and produce products with purities similar to those achieved in the first run. As a conclusion, the reusability performances of the prepared monodisperse Pt NPs@rGO have been compared with the others reported in literature and it was found that to the best of our knowledge our Pt NPs@rGO have the best reusability performances as shown in Table 4.

A sensible mechanism is shown in Scheme 2. In the beginning, coordination of nitrogen atoms of nitrile compounds with Pt NPs@rGO forms complex I which expedites the cyclization step. The [3+2] cycloaddition among the C≡N bond of nitrile compound and azide ion gets place easily to form the intermediate step II. Later Pt NPs@rGO were separated by using centrifugation. The pH of the solution was adjusted in between 2-2.5 and was formed the determined 5-substituted 1H-tetrazole (step III).

![Scheme 2. A sensible mechanism for the formation of tetrazoles](image-url)
Experimental Section

The preparation of monodisperse Pt NPs@rGO

Pt NPs@rGO were synthesized from sonochemical reduction method. Summarizing this method, superhydride and ethanol were used to reduce the mixture of 0.25 mmol of PtCl₄ lysed in small amount of dehydrated tetrahydrofuran and 0.25 mmol of tripropylamine ligand. The observation of a brown-black color in the solution indicates the formation of Pt NPs. Lastly, in the room temperature, the solid Pt NPs was dried under vacuum. rGO was obtained by the hydrazine reduction of GO which was synthesized from graphite powder using modified Hummer’s method (Supplementary section). The prepared platinum nanoparticles were mixed in a 1:1 ratio with rGO by using tip sonicator.

General procedure for preparation of tetrazole derivatives (3a-j) using monodisperse Pt NPs@rGO as the catalyst

A mixture of nitrile (0.5 mmol), sodium azide (1 mmol), and monodisperse Pt NPs@rGO (3 mol %) was stirred at 75 °C in DMF (1.5 mL) for 0.5 h. The progress of the reaction was monitored by thin layer chromatography. After completion, the reaction mixture was cooled to room temperature and the catalyst was separated from centrifugation. Reaction mixture was treated with ~5 mL HCl (4 mol L⁻¹). The resultant organic layer was separated and the aqueous layer was extracted with ethyl acetate (2x15 mL). Ethyl acetate extract concentrated under reduced pressure. The combined product obtained was recrystallized from acetic acid to afford pure 5-Phenyl 1H-tetrazole.

Conclusions

Easy, effective and practical synthetic method has been developed for the synthesis of 5-Substituted 1H-tetrazoles via the successive [3+2] cycloaddition reactions of the various aryl nitrile compounds and sodium azide in the presence of novel, stable, exceptional reusable, isolable, bottleable, long-lived and highly efficient monodisperse Pt NPs@rGO as the catalyst. This nano sized heterogeneous catalyst showed excellent catalytic activity for the synthesis of 5-Substituted 1H-tetrazoles most likely due to high monodispersity, low crystalline particle size, high chemical surface area and high % Pt (0) contents of the prepared Pt NPs@rGO. This reusable catalyst offers advantages like simple work-up and highest yield. Furthermore, the given methodology is efficient and environmentally benign. This method, which enabled 5-substituted 1H-tetrazoles to be prepared in excellent yields and shortest reaction times, would be a rather attractive synthetic method in near future.

Acknowledgements

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Notes and references

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Note: † These authors contributed equally to this work.