Synthesis and catalytic evaluation of PVP-CeO_2/rGO as a highly efficient and recyclable heterogeneous catalyst for multicomponent reaction in water

Shaheen Siddiqui and Zeba N. Siddiqui*

Department of Chemistry, Aligarh Muslim University, Aligarh 202002, Uttar Pradesh, India

*Corresponding author

E-mail: siddiqui_zeba@yahoo.co.in

zns.siddiqui@gmail.com

General Experimental details

Melting points of the synthesized compounds were taken in a Stuart SMP30 instrument and are uncorrected. The IR spectra were recorded on Perkin Elmer RXI spectrometer using KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance III 400 MHz spectrometer using tetramethylsilane (TMS) as an internal standard and $DMSOd_6/CDCl_3$ as solvent. ESI-MS was recorded on a Quattro II (ESI) spectrometer. Elemental analyses (C, H and N) were conducted using the Elemental vario EL III elemental analyser. TGA data were obtained with a DSC-60 Shimadzu instrument. TG Analysis was performed in the temperature range 0–750°C at a constant heating rate of 20 °C min^{-1} in a nitrogen atmosphere. X-ray diffractograms (XRD) of the catalyst were recorded on a Shimadzu 6100 X-ray diffractometer in the range of 2θ = 10–80°, with a scan rate of 8°/min. SEM-EDX characterization of the catalyst was performed on a JEOL JSM-6510 scanning electron microscope equipped with an energy-dispersive X-ray spectrometer operating at 20 kV. X-ray photoelectron spectroscopy (XPS) analysis was performed on spectrometer (Model no. PHI 5000 Versa Prob II, FEI Inc.) with Auger Electron Spectroscopy (AES) module and C60 sputter gun. The high resolution spectra was measured with pass energies of 23.5 eV and 0.025eV step. TEM analysis was performed on JEM-2100 F Model (ACC. Voltage: 200 kV) electron microscope. ICP-AES analysis was performed using ARCOS-Simultaneous ICP-AES spectrometer.

The Green metric analysis of the synthesized compounds (4a-j)

A. Formula used for the calculations:

The following formulae were used for evaluating green chemistry metrics such as atom economy (AE), carbon efficiency (CE), reaction mass efficiency (RME), overall efficiency (OE), process mass intensity (PMI) solvent intensity (SI) and E-factor.

1. % Atom Economy (AE) *= (Mol Wt. of desired product/ Mol Wt. of all reactants) × 100*

2. % Carbon Efficiency (CE) *= (Amount of carbon in the product)/ Total carbon present in reactant) × 100*

3. % Reaction Mass Efficiency (RME) *= (Mass of isolated product)/ Total mass of reactants) × 100*

4. % Overall Efficiency (OE) *= (RME/AE) × 100*

5. % Process Mass Intensity (PMI) *= (Total mass of input materials in a process)/ Mass of product)*

6. ***Solvent Intensity (SI)*** *= (Total mass of input solvents in a process)/ Mass of product)*

7. ***E-Factor*** *= PMI-1*

Recycling experiment of the catalyst

A mixture of 5-acetyl-1,3-dimethylbarbituric acid **1** (1 mmol), 3-nitrobenzaldehyde **2a** (1 mmol), *o*-phenylene diamine **3a** (1 mmol) and PVP-CeO_2/rGO was taken in a round bottom flask (50 ml) and stirred in water at room temperature for 10 min. After completion of the reaction, the reaction mixture was cooled and the products were extracted using ethyl acetate (5 mL). The catalyst being insoluble in ethyl acetate was separated by filtration, washed thoroughly with ethyl acetate (2× 10 mL), dried and reused **(Figure 1S)**.

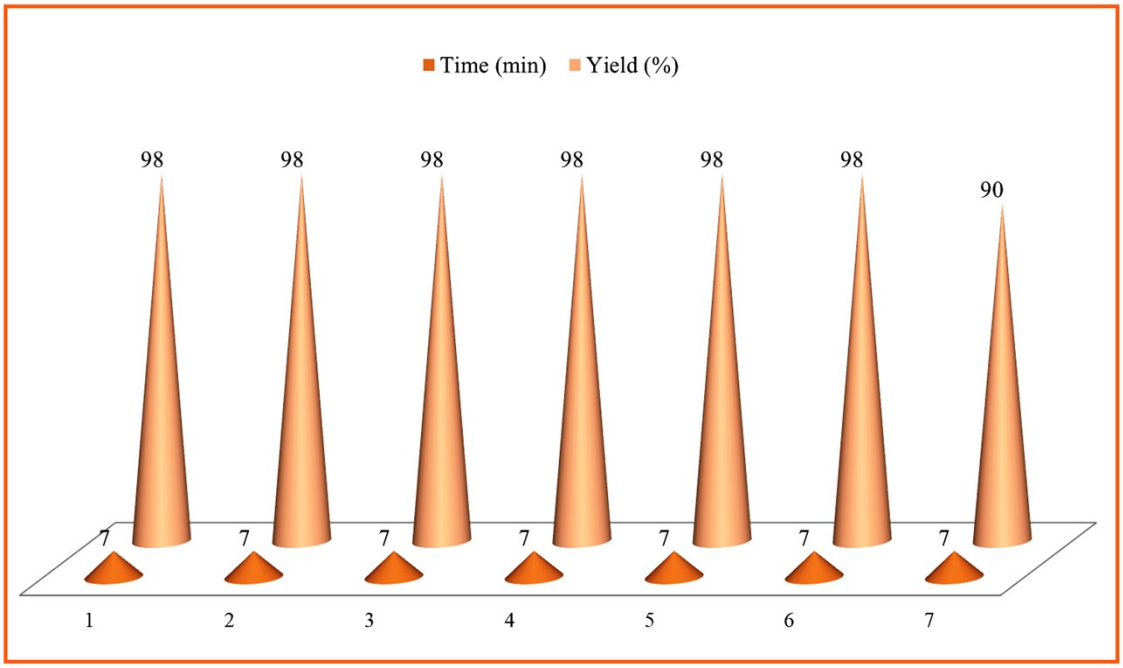

Figure 1S. Recycling study of PVP-CeO_2/rGO

Spectral data of compounds

5-(4-(5-chloro-3-methyl-1-phenyl-1H-pyrazol-4-yl)-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-ylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (**4a)**

Yellow solid; m.p.: 192-195 °C; IR (KBr) (*v*max, cm^{-1}): 3384, 3269, 3126, 2984, 1727, 1692, 1197. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.44 (s, 3H, CH_3), 3.02 (t, 1H, CH), 3.20, 3.34 (s, 6H, 2xCH_3), 4.36 (d, 2H, CH_2), 4.60 (d, 1H, CH), 6.74-7.66 (m, 9H, ArH) 12.09 (s, 2H, NH). ^{13}C NMR (100 MHz): δ 12.287, 29.542, 29.889, 48.271, 53.218, 114.363, 119.748, 121.304, 124.878, 125.467, 126.210, 126.547, 128.518, 129.644, 129.914, 130.113, 134.092, 137.173, 144.947, 147.267, 150.093, 163.780, 171.121. ESI-MS (m/z) 490.15 (M^++1). Anal.Calcd ($C_{25}H_{23}ClN_6O_3$): C, 61.15; H, 4.72; N, 17.12. Anal. Found ($C_{25}H_{23}ClN_6O_3$): C, 61.16; H, 4.73; N, 17.13.

1,3-dimethyl-5-(4-(3-methyl-5-phenoxy-1-phenyl-1H-pyrazol-4-yl)-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-ylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (**4b)**

Yellow solid; m.p.: 195-197 °C; IR (KBr) (*v*max, cm^{-1}): 3374, 3269, 2928, 1703, 1646. ^{1}H NMR (DMSO-d_6, 400 MHz): 2.51 (s, 3H, CH_3), 2.94 (t, 1H, CH), 3.16, 3.35 (s, 6H, 2xCH_3), 4.44 (d, 2H, CH_2), 4.85 (d, 1H, CH), 6.77-7.55 (m, 14H, ArH) 13.74 (s, 2H, NH). ^{13}C NMR (100 MHz): δ 13.580, 29.297, 29.801, 53.232, 114.348, 119.658, 122.2210, 122.661, 122.943, 124.382, 126.304, 126.782, 128.164, 129.716, 130.106, 134.022, 137.672, 145.090,

147.658, 150.247, 153.331, 155.604, 164.137, 171.137. ESI-MS (m/z) 548.22 (M^++1). Anal.Calcd ($C_{31}H_{28}N_6O_4$): C, 67.87; H, 5.14; N, 15.32. Anal. Found ($C_{31}H_{28}N_6O_4$): C, 67.86; H, 5.15; N, 15.32.

1,3-dimethyl-5-(4-(3-nitrophenyl)-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-ylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (**4c)**

Yellow solid; m.p.: 225-227°C; IR (KBr) (*v*max, cm^{-1}): 3369, 2925, 1702, 1631. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 3.004 (t, 1H, CH), 3.304, 3.362 (s, 6H, 2xCH_3), 4.373 (d, 2H, CH_2), 4.553 (d, 1H, CH), 6.896-7.353 (m, 8H, ArH) 13.808 (s, 2H, NH). ^{13}C NMR (100 MHz): δ 27.740, 28.001, 30.873, 90.830, 120.866, 121.714, 122.648, 122.968, 124.602, 127.498, 128.576, 129.813, 139.470, 146.355, 148.464, 151.104, 162.803, 166.212, 170.226. ESI-MS (m/z) 421.14 (M^++1). Anal.Calcd ($C_{21}H_{19}N_5O_5$): C, 59.85; H, 4.54; N, 16.62. Anal. Found ($C_{21}H_{19}N_5O_5$): C, 59.84; H, 4.55; N, 16.62.

1,3-dimethyl-5-(4-(2-nitrophenyl)-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-ylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (**4d)**

Yellow solid; m.p.: 210-212 °C; IR (KBr) (*v*max, cm^{-1}): 3366, 2952, 1710, 1650. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 3.27 (t, 1H, CH), 3.34 (s, 6H, 2xCH_3), 4.14 (d, 2H, CH_2), 4.34 (d, 1H, CH), 6.93-8.04 (m, 8H, ArH) 13.75 (s, 2H, NH). ^{13}C NMR (100 MHz): δ 29.601, 32.801, 49.187, 57.455, 114.178, 120.808, 124.790, 126.102, 127.457, 127.535, 128.198, 134.079, 137.463, 145.583, 148.408, 150.871, 164.122, 171.695. ESI-MS (m/z) 421.14 (M^++1). Anal.Calcd ($C_{21}H_{19}N_5O_5$): C, 59.85; H, 4.54; N, 16.62. Anal. Found ($C_{21}H_{19}N_5O_5$): C, 59.84; H, 4.55; N, 16.62.

5-(4-(4-chlorophenyl)-8-methyl-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-ylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione **(4e)**

Light yellow solid; m.p.: 180-182 °C; IR (KBr) (*v*max, cm^{-1}): 3369, 2924, 1706, 2984, 1643. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.53 (s, 3H, CH_3), 3.03 (t, 1H, CH), 3.30, 3.38 (s, 6H 2xCH_3), 4.31 (d, 2H, CH_2), 4.51 (d, 1H, CH), 6.70-8.33 (m, 7H, ArH) 13.85 (s, 2H, NH). ^{13}C NMR (100 MHz): δ 21.952, 29.619, 34.997, 47.063, 63.041, 122.990, 123.096, 128.458, 129.005, 132.046, 132.203, 134.307, 134.548, 137.763, 138.908, 142.340, 149.924, 164.901, 171.026, 171.172. ESI-MS (m/z) 424.13 (M^++1). Anal.Calcd ($C_{22}H_{21}ClN_4O_3$): C, 62.19; H, 4.97; N, 13.19. Anal. Found ($C_{22}H_{21}ClN_4O_3$): C, 62.19; H, 4.98; N, 13.20.

5-(4-(4-methoxyphenyl)-8-methyl-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-ylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione **(4f)**

Light yellow solid; m.p.: 161-163 °C; IR (KBr) (*v*max, cm^{-1}): 3374, 2937, 1713, 2976, 1648. ^1H NMR (DMSO-d_6, 400 MHz): δ 2.601 (s, 3H, CH_3), 3.012 (t, 1H, CH), 3.517, 3.585 (s, 6H, 2x CH_3), 4.392 (d, 2H, CH_2), 4.01 (s, 3H, CH_3), 4.540 (d, 1H, CH), 7.071-8.052 (m, 7H, ArH), 13.828 (s, 2H, NH). ^{13}C NMR (100 MHz): δ 21.046, 29.974, 30.450, 49.338, 55.691, 62.733, 114.625, 115.641, 126.624, 132.707, 133.437, 134.984, 135.242, 137.054, 142.374, 150.766, 158.892, 165.712, 170.837, 171.125. ESI-MS (m/z) 420.18 (M^++1). Anal.Calcd ($C_{23}H_{24}N_4O_4$): C, 65.70; H, 5.76; N, 13.34. Anal. Found ($C_{23}H_{24}N_4O_4$): C, 65.71; H, 5.75; N, 13.33.

5-(4-(5-chloro-3-methyl-1-phenyl-1H-pyrazol-4-yl)-8-methyl-4,5-dihydro-1H benzo[b][1,4]diazepin-2(3H)-ylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione **(4g)**

Yellow solid; m.p.: 205-207 °C; IR (KBr) (*v*max, cm^{-1}): 3399, 2922,1711, 1661. ^1H NMR (DMSO-d_6, 400 MHz): 2.51 (s, 3H, CH_3), 2.86 (s, 3H, CH_3), 3.20 (t, 1H, CH), 3.34 (s, 6H, 2xCH_3), 4.23 (d, 2H, CH_2), 4.43 (d, 1H, CH), 6.56-7.38 (m, 8H, ArH) 12.39 (s, 2H, NH). ^{13}C NMR (100 MHz): δ 12.895, 21.318, 29.364, 33.458, 48.889, 53.956, 119.407, 124.296, 126.496, 129.088, 129.633, 129.703, 132.265, 134.256, 134.894, 137.195, 137.650, 142.230, 147.655, 150.375, 164.614, 171.177. ESI-MS (m/z) 504.16 (M^++1). Anal. Calcd ($C_{25}H_{23}ClN_6O_3$): C, 61.15; H, 4.73; N, 17.12. Anal. Found ($C_{25}H_{23}ClN_6O_3$): C, 61.16; H, 4.72; N, 17.13.

1,3-dimethyl-5-(8-methyl-4-(3-methyl-5-phenoxy-1-phenyl-1H-pyrazol-4-yl)-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-ylidene)pyrimidine-2,4,6(1H,3H,5H)-trione **(4h)**

Light yellow solid; m.p.: 208-210 °C; IR (KBr) (*v*max, cm^{-1}): 3381, 2922, 1710, 2993, 1650. ^1H NMR (DMSO-d_6, 400 MHz): 2.50 (s, 3H, CH_3), 2.61 (s, 3H, CH_3), 2.99 (t, 1H, CH), 3.41, 3.62 (s, 6H, 2xCH_3), 4.14 (d, 2H, CH_2), 4.29 (d, 1H, CH), 7.35-8.19 (m, 13H, ArH) 13.39 (s, 2H, NH). ^{13}C NMR (100 MHz): δ 13.146, 21.183, 28.738, 29.049, 34.050, 52.799, 119.057, 122.074, 122.558, 122.910, 124.265, 126.511, 129.137, 129.471, 132.062, 134.287, 134.670, 137.308, 142.844, 147.104, 150.209, 153.277, 155.029, 164.039, 171.209, 171.839. ESI-MS (m/z) 562.23 (M^++1). Anal.Calcd ($C_{32}H_{30}N_6O_4$): C, 68.30; H, 5.37; N, 14.95. Anal. Found ($C_{32}H_{30}N_6O_4$): C, 68.31; H, 5.37; N, 14.94.

1,3-dimethyl-5-(8-methyl-4-(3-nitrophenyl)-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-ylidene)pyrimidine-2,4,6(1H,3H,5H)-trione **(4i)**

Light yellow solid; m.p.: 225-227 °C; IR (KBr) (*ν*max, cm^{-1}): 3361, 2937, 1702, 1639. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.60 (s, 3H, CH_3), 2.99 (t, 1H, CH), 3.46, 3.54 (s, 6H, 2xCH_3), 4.48 (d, 2H, CH_2), 4.58 (d, 1H, CH), 6.95-8.22 (m, 7H, ArH) 13.67 (s, 2H, NH). ^{13}C NMR (100 MHz): δ 22.826, 30.915, 36.293, 48.122, 67.599, 121.578, 122.112, 128.977, 132.345, 133.181, 133.784, 133.827, 137.603, 139.870, 143.083, 147.473, 151.190, 165.239, 171.631. ESI-MS (m/z) 435.15 (M^++1). Anal.Calcd ($C_{22}H_{21}N_5O_5$): C, 60.69; H, 4.86; N, 16.09. Anal. Found ($C_{22}H_{21}N_5O_5$): C, 60.68; H, 4.87; N, 16.08.

1,3-dimethyl-5-(8-methyl-4-(2-nitrophenyl)-4,5-dihydro-1H-benzo[b][1,4]diazepin-2(3H)-ylidene)pyrimidine-2,4,6(1H,3H,5H)-trione **(4j)**

Yellow solid; m.p.: 230-232 °C; IR (KBr) (*ν*max, cm^{-1}): 3364, 2954, 1702, 1646. ^{1}H NMR (DMSO-d_6, 400 MHz): 2.51 (s, 3H, CH_3), 3.01 (t, 1H, CH), 3.51, 3.59 (s, 6H, 2xCH_3), 4.35 (d, 2H, CH_2), 4.47 (d, 1H, CH), 6.96-7.99 (m, 7H, ArH) 13.68 (s, 2H, NH). ^{13}C NMR (100 MHz): δ 21.245, 29.716, 31.223, 57.923, 124.338, 127.404, 129.256, 132.128, 134.231, 134.257, 134.295, 138.053, 141.450, 148.039, 150.747, 165.005, 169.872, 170.292. ESI-MS (m/z) 435.15 (M^++1). Anal.Calcd ($C_{22}H_{21}N_5O_5$): C, 60.69; H, 4.86; N, 16.09. Anal. Found ($C_{22}H_{21}N_5O_5$): C, 60.68; H, 4.87; N, 16.08.