Supplementary Information

Novel metal oxide of CuO-ZnO nanocatalyst efficiently catalyzed synthesis of 2-amino-4*H*-chromenes in water

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General

All products were identified by comparison of their spectroscopic data (NMR, IR) and physical data with authentic samples. Chemicals were purchased from Merck chemical company. Yields refer to isolated pure products. The IR spectra were recorded on a Perkin Elmer 781 Spectrophotometer. All the NMR spectra were recorded on a Bruker Advance 400 MHz. Yields refer to isolated pure products.

Catalyst Characterization

The specific surface area of the catalyst was analyzed by N₂ adsorption-desorption using BET method. BET tests were carried out using an automated gas adsorption analyzer (Tristar 3020, Micromeritics). Prior to BET tests the samples were degassed under vacuum at 150 °C for 2 h. The XRD analysis was performed using an X-ray diffractometer (Bruker AXS D8) with a Cu-K α monochromatized radiation source in the range $2\theta = 10\text{--}80^\circ$, in order to study the structure and crystallinity of the catalysts.

The average crystallite size of the samples was determined based on Scherrer equation. Scanning electron microscopy (SEM) was performed by a HITACHI S-4160 instrument in order to study the morphology of the catalysts. High resolution transmission electron microscopy (HRTEM) analysis was performed using a JEOL JEM-2100 (200 kV) microscope. More than 200 particles are measured in order to obtain particle size distribution of the prepared catalyst.

Catalyst Preparation

The 20 wt% CuO supported ZnO nanocatalyst was prepared by co-precipitation method. An aqueous solution of 0.5 M $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ was added drop by drop into a mixture of 0.03 M $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solutions under vigorous mixing. The resulted solution was kept at pH=8.5 for 15 min at constant temperature of 65°C. Afterwards, the suspension was filtered and washed with warm distilled water. The precipitates were dried at 100°C overnight followed by calcination at 300°C for 3h. Also, a ZnO support was prepared under the same condition for the supplementary tests. The prepared catalyst is denoted as 20CuO-ZnO, where 20 is the content of CuO in wt.%.

General Procedure for the Synthesis of 2-Amino-4*H*-Chromenes

A mixture of 2-naphtol (1 mmol), malononitrile (1 mmol), benzaldehyde (1 mmol) and 0.05 g of 20CuO-ZnO catalyst was stirred in water at reflux condition for the proper times, according to Table 2. After reaction completion (moitored by TLC), the resulting mixture was chilled, filtered and, hot ethanol was added. The filtrate was evaporated and dryness. Then, the solid residue was recrystallized in hot ethanol to give the pure product. The recovered catalyst was washed with hot ethanol, dried and stored for

another consecutive reaction run. The spectral and analytical data for the new compounds are as following:

Table 3, entry 12: mp: 229-231 °C; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3351, 3329, 3193, 3063, 2189, 1657, 1591, 1517, 1464, 1403, 1237, 1181, 1084, 1022, 969, 861, 808, 739. ^1H NMR (DMSO- d_6 , 400 MHz), δ (ppm): 5.65 (s, 1H), 7.07 (t, 2H, $J=7.2$ Hz), 7.15 (s, 2H), 7.31 (d, 1H, $J=8.8$ Hz), 7.38-7.45 (m, 2H), 7.60 (d, 3H, $J=7.6$ Hz), 7.93 (t, 2H, $J=8.8$ Hz). ^{13}C NMR (DMSO- d_6 , 100 MHz), δ (ppm): 37.85, 56.87, 11.50, 117.28, 120.18, 122.23, 123.29, 125.50, 127.88, 129.20, 129.27, 130.37, 130.58, 131.24, 133.20, 144.85, 147.52, 160.24. Elem. Anal. Found: C, 63.75 %; H, 3.52 % N, 7.49 % (calculated for $\text{C}_{20}\text{H}_{13}\text{N}_2\text{OBr}$: C, 63.67 %; H, 3.47 %; N, 7.42 %).

Table 3, entry 13: mp: 260-262 °C; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3423, 3331, 2996, 2935, 2827, 2181, 1652, 1591, 1515, 1459, 1400, 1298, 1263, 1231, 1185, 1133, 1085, 1030, 914, 832, 746. ^1H NMR (DMSO- d_6 , 400 MHz), δ (ppm): 5.46 (s, 1H), 6.80 (d, 1H), 7.05(t, 4H), 7.60 (s, 2H), 7.72-7.75 (m, 4H), 9.89 (s, 1H). ^{13}C NMR (DMSO- d_6 , 100 MHz), δ (ppm): 37.88, 56.91, 105.95, 113.67, 113.89, 117.70, 120.32, 122.50, 125.74, 129.17, 130.10, 130.26, 130.75, 132.62, 133.24, 144.75, 148.10, 157.04, 160.04. Elem. Anal. Found: C, 61.16 %; H, 3.39 % N, 7.19 % (calculated for $\text{C}_{20}\text{H}_{13}\text{N}_2\text{O}_2\text{Br}$: C, 61.08 %; H, 3.33 %; N, 7.14 %).

Table 3, entry 14: mp: 290-292 °C; IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3610, 3458, 3349, 3205, 3070, 2185, 1656, 1585, 1524, 1407, 1343, 1220, 1169, 1079, 1030, 809, 725, 677. ^1H NMR (DMSO- d_6 , 400 MHz), δ (ppm): 5.38 (s, 1H), 6.98 (d, 2H, $J=9.08$ Hz), 7.11 (d, 1H, $J=8.84$ Hz), 7.17 (s, 2H), 7.57 (t, 1H, $J=8.44$ Hz), 7.63 (d, 1H, $J=7.44$ Hz), 7.73 (d, 1H, $J=8.56$ Hz), 7.79 (d, 1H, $J=8.92$ Hz), 8.4 (s, 2H), 10.00 (s, 1H). ^{13}C NMR (DMSO- d_6 ,

100 MHz), δ (ppm): 37.99, 57.20, 105.77, 112.65, 113.38, 117.45, 120.50, 121.48, 122.00, 125.44, 129.97, 130.49, 130.57, 132.06, 133.88, 147.61, 147.89, 148.13, 156.75, 160.02. Elem. Anal. Found: C, 66.93 %; H, 3.69 % N, 11.76 % (calculated for $C_{20}H_{13}N_3O_4$: C, 66.85 %; H, 3.64 %; N, 11.69 %).

Table 3, entry 15: mp: 274-276 °C; IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3475, 3333, 3068, 2867, 2187, 1648, 1588, 1509, 1452, 1413, 1295, 1267, 1238, 1216, 1186, 1083, 1035, 907, 831, 769. ^1H NMR (DMSO- d_6 , 400 MHz), δ (ppm): 5.05 (s, 1H), 6.94 (s, 2H), 7.04-7.14 (m, 7H), 7.71-7.78 (m, 2H), 9.84 (s, 1H). ^{13}C NMR (DMSO- d_6 , 100 MHz), δ (ppm): 38.13, 58.29, 106.17, 113.65, 113.97, 115.82, 116.03, 117.60, 120.97, 125.74, 129.20, 129.28, 129.81, 130.65, 132.49, 142.22, 147.73, 156.87. Elem. Anal. Found: C, 72.37 %; H, 3.99 % N, 8.49 % (calculated for $C_{20}H_{13}N_2O_2F$: C, 72.28 %; H, 3.94 %; N, 8.43 %).

Table 3, entry 16: mp: 288-290 °C; IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3391, 3327, 3195, 2971, 2228, 2187, 1657, 1591, 1516, 1450, 1414, 1297, 1269, 1238, 1219, 1186, 1140, 1082, 1046, 834, 765. ^1H NMR (DMSO- d_6 , 400 MHz), δ (ppm): 5.21 (s, 1H), 6.93 (d, 2H), 7.08 (d, 2H, $J = 8.94$ Hz), 7.33 (d, 2H, $J = 8.50$ Hz), 7.74-7.81 (m, 5H), 9.91 (s, 1H). ^{13}C NMR (DMSO- d_6 , 100 MHz), δ (ppm): 38.38, 56.14, 105.61, 109.58, 112.59, 113.26, 117.31, 118.76, 120.31, 125.33, 128.05, 129.76, 130.34, 132.03, 132.89, 147.48, 150.90, 156.62, 159.91. Elem. Anal. Found: C, 73.41 %; H, 3.90 % N, 12.44 % (calculated for $C_{21}H_{13}N_3O_2$: C, 74.32 %; H, 3.86 %; N, 12.38 %).

Figure 1. XRD patterns of (a) ZnO, and (b) 20CuO/ZnO nanocatalyst.

Figure 2. (a) N_2 adsorption/desorption isotherms, and (b) pore size distributions, of ZnO and 20CuO/ZnO samples.

Figure 3. SEM micrographs of (a,b) ZnO, and (c,d) 20CuO-ZnO samples.

Figure 4. (a,b) TEM image, (c) particle size distribution, and (d) EDS analysis, of 20CuO-ZnO nanocatalyst.

Table 3, entry 12

Table 3, entry 13

Table 3, entry 14

Table 3, entry 15

Table 3, entry 17