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Supplementary Information for

Synthesis of 5-substituted 1H-Tetrazole using nano ZnO/Co_3O_4 catalyst

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Experimental section

Materials

All reagents were of analytical grade, purchased from M/S S. D. Fine Chemicals Pvt. Ltd. and used without further purification. All products were characterized by MS analysis (GC-MS Shimadzu QP 2010). 5 phenyl 1H-tetrazole was characterized by H^1 NMR and CHNS.

Preparation of Catalysts

All the mixed metal oxides were prepared by taking 1:1 mole ratio of their precursors. 6 mmol of the metal precursor was used for every synthesis. Nano ZnO/Co_3O_4 mixed metal oxide is synthesized by simple precipitation method under ultrasonication. Zinc acetate and cobalt acetate in 1:1 mole ratio were dissolved in 0.1 N HCl and precipitate is obtained by dropwise addition of aqueous ammonia. The whole procedure of precipitation was carried out under ultrasonication. Titanium tetraisopropoxide and cerium nitrate were used as precursors for preparation of TiO_2 and CeO_2. The bulk metal oxides and mixed metal oxides were prepared by adding aqueous ammonia solution to the solutions of respective precursors. This addition was carried out without ultrasonication. The pH of the solution is adjusted between 8-9.

Characterization of nano ZnO/Co_3O_4

The X-ray diffractograms were obtained (XRD, MINI FLEX RIGAKU MODEL) with Cu K-α radiation (1.5418 A°) with scanning rate of 2^o per min from 2^o to 80^o. Particle size and external morphology of the prepared particles were observed on a Transmission Electron Microscope (TEM) (Philips CM 200, operating at 20 – 200 kV accelerating voltage and having resolution upto 2.4 A^o). Surface morphology and EDAX (Energy Dispersive X-Ray Spectroscopy) analysis was done by using Field Emission Gun-Scanning Electron Microscopes (FEG-SEM) JSM-7600F model operating at accelerating voltage 0.1 to 30 kV, Magnification x25 to 1,000,000 and having resolution 1.0 nm - 1.5 nm (15kV). To analyze the chemical structure, the FT-IR spectrum was recorded by using the Fourier Transform Infra-Red Spectroscopy (FT-IR) in the range of 400-4000 cm^{-1} frequency range on a Perkin-Elmer Spectrophotometer (100 Spectrochem Series). The laser Raman spectrum was obtained on a Jobvin-Yvon-Horiba (HR800UV) Raman spectrometer at ambient conditions equipped with laser supplying the excitation line at 514.5 nm with 1–20 mW. NH_3-TPD of the catalysts was conducted with Micromeritics AutoChem II 2920 automated catalyst characterization system. A sample of few mg was placed in a quartz reactor and heated at 500 ◦C

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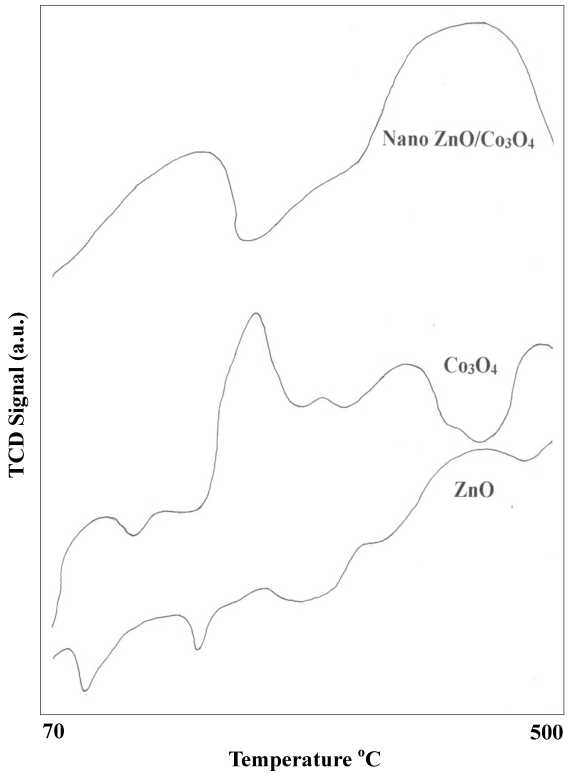

NH_3-TPD of the prepared catalysts

Typical procedure for preparation of 5-substitited 1H-tetrazole

In 25 mL round bottom flask taken a mixture of benzonitrile (1 mmol, 0.103 g), sodium azide (1.5 mmol, 0.0975g) and 3 mL DMF was added. Further 50 mg catalyst was added to the reaction mixture. The reaction mixture was heated to 120-130 ^oC for 12 h. After completion of the reaction the catalyst was separated by centrifugation and subsequently washed with dichloromethane. The reaction mixture was diluted with water and the product was extracted by dichloromethane (3 × 10 cm^3). The filtrate was diluted with 4 N HCl (20 ml), stirred vigorously and extracted with dichloromethane (3 × 10 cm^3).

Organic layer was dried over anhydrous sodium sulphate and was evaporated under reduced pressure to give the product. The product was purified by column chromatography by using pet ether and ethyl acetate solvent system. The purified product was then confirmed by its spectral analysis after analyzing by IR, ^1H NMR and mass spectra.

Characterization of 5-substitited 1H-tetrazole

$_1H$ NMR (300MHz, $CDCl_3$): δ = 8.01-8.04 (m, 2H), 7.57-7.61 (m, 3H), 3.42 (m, 1H)

MS (70 eV): *m/z* (%) = 146 (M+, 16.2%), 118 (100.0%), 103 (12.4%), 90.95 (47.1%), 77 (31.7%), 62.9 (24.4%) and 51 (12.3%).

CHNS = Anal. Calcd for $C_7H_6N_4$: C, 57.53; H, 4.14; N, 38.34. Found C, 57.76; H, 4.74; N, 38.77.