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Supplementary file

Solventless Mechanochemical Fabrication of ZnO–$MnCO_3$/N-Doped Graphene Nanocomposite: Efficacious and Recoverable Catalyst for Selective Aerobic Dehydrogenation of Alcohols Under Alkali-Free Conditions

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2.2. Preparation of (1%)ZnO–$MnCO_3$/(X%-NDG) Nanocomposites

Approximately, 1.98 g of ZnO nanoparticles–$MnCO_3$ and 0.02 g of NDG powder were milled using Fritsch Pulverisette P7 (Idar-Oberstein, Germany) planetary ball mill. The NDG powder, ZnO nanoparticles–$MnCO_3$ and stainless steel balls (5 mm diameter) with the ball to powder weight ratio of 11:1 were introduced into the stainless steel container. The milling of the powder was performed for 16 h. In order to maintain the temperature inside the container, the milling process was paused at regular intervals.

2.3. Characterizations

Scanning electron microscopy (SEM) and elemental analysis (Energy Dispersive X–Ray Analysis: EDX) were carried out using FE-SEM (JSM 7600F JEOL, Japan). This was used to determine the morphology of nanoparticles and its elemental composition. Powder X–ray diffraction studies were carried out using D2 Phaser X-ray diffractometer (Bruker, Germany), Cu Kα radiation (k = 1.5418 A°). Fourier Transform Infrared Spectroscopy (FTIR) spectra were recorded as KBr pellets using a Perkin- Elmer 1000 FTIR spectrophotometer. BET surface area were measured by N_2 adsorption-desorption isotherm at liquid nitrogen temperature (-196 °C) using Micromeritics (Gemini VII, 2390 surface area and porosity USA). Sample was degassed at 120 °C for 3 h using N_2 gas.

2.4. Catalytic Evaluation Tests

Liquid-phase oxidation of benzyl alcohol has conducted in a three-necked glass flask equipped with a magnetic stirrer, reflux condenser, and thermometer. In a typical experiment, a mixture of the benzyl alcohol (2 mmol), toluene (10 mL), and the catalyst (300 mg) has transferred in a three-necked round-bottomed flask (100 mL), the resulting mix-

ture is then heated to desired temperature with vigorous stirring along with bubbling oxygen gas at a flow rate of 20 mL.min^{-1} into the reaction mixture. After the reaction, the solid catalyst has filtered off by centrifugation and the liquid products analyzed by gas chromatography to determine the conversion and product selectivity by (GC, 7890A) Agilent Technologies Inc, equipped with a flame ionization detector (FID) and a 19019S-001 HP-PONA column.

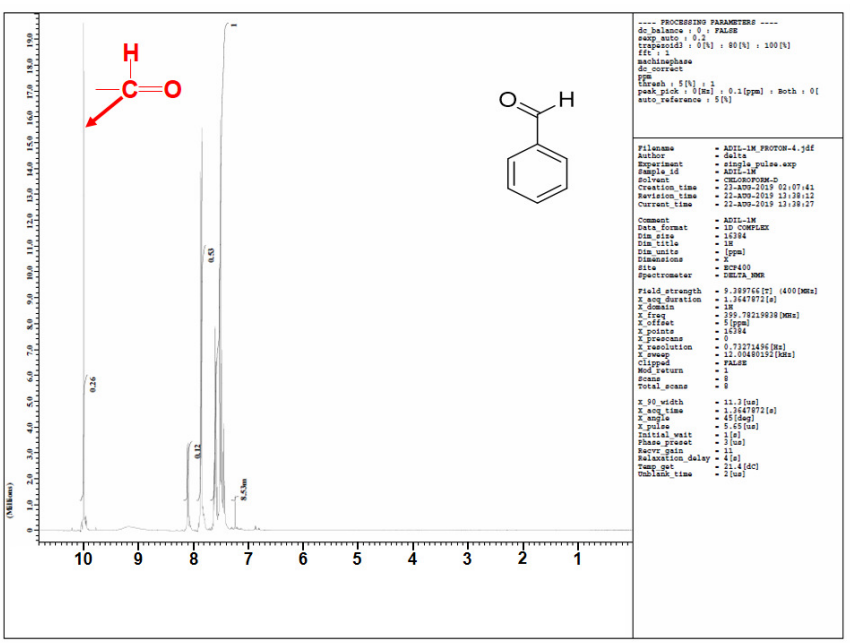

Figure S1. ^{1}HNMR spectra for the product (benzaldehyde) obtained after selective oxidation of benzyl alcohol.

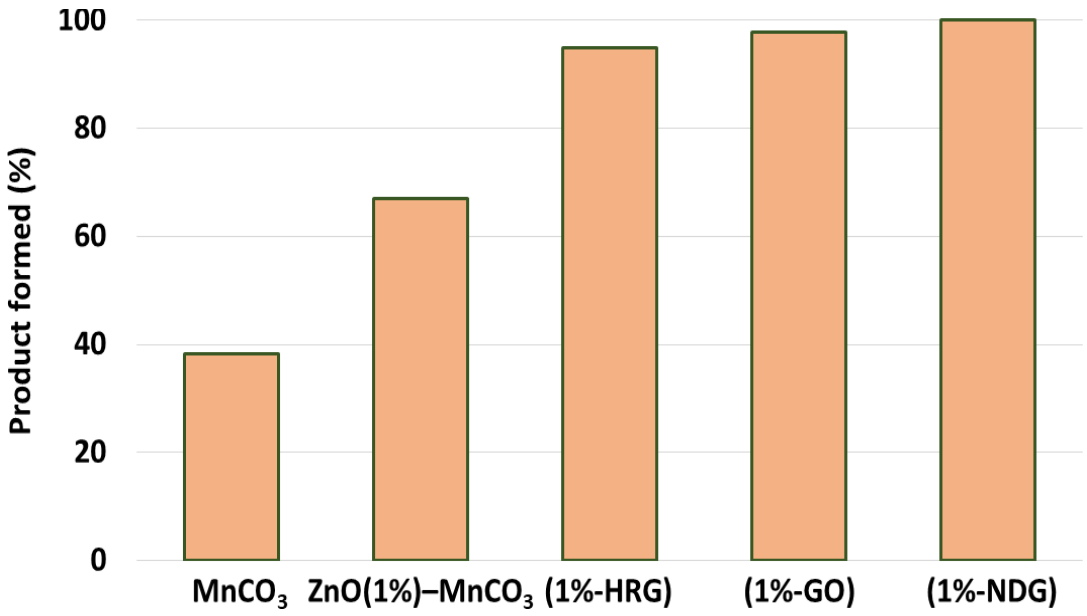

Figure S2. Comparative graphical illustration of percentage of benzaldehyde (BH) formed using $MnCO_3$, ZnO(1%)-$MnCO_3$ and their various graphene based composites within 5 minutes.