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Eco-Friendly and Solvent-Less Mechanochemical Synthesis of ZrO₂–MnCO₃/N-Doped Graphene Nanocomposites: A Highly Efficacious Catalyst for Base-Free Aerobic Oxidation of Various Types of Alcohols

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Abstract: In recent years, the development of green mechanochemical processes for the synthesis of new catalysts with higher catalytic efficacy and selectivity has received manifest interest. In continuation of our previous study, in which graphene oxide (GRO) and highly reduced graphene oxide (HRG) based nanocomposites were prepared and assessed, herein, we have explored a facile and solvent-less mechanochemical approach for the synthesis of N-doped graphene (NDG)/mixed metal oxide (MnCO₃-ZrO₂) ((X%)NDG/MnCO₃-ZrO₂), as the (X%)NDG/MnCO₃-ZrO₂ nano-composite was synthesized using physical grinding of separately synthesized NDG and pre-calcined (300 °C) MnCO₃-ZrO₂ via green milling method. The structures of the prepared materials were characterized in detail using X-ray powder diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM), Energy Dispersive X-Ray Analysis (EDX), Fourier-transform infrared spectroscopy (FTIR), Raman, Thermogravimetric analysis (TGA), and N2 adsorption-desorption isotherm analysis. Besides, the obtained nanocomposites were employed as heterogeneous oxidation catalyst for the alcohol oxidation using green oxidant O₂ without involving any surfactants or bases. The reaction factors were systematically studied during the oxidation of benzyl alcohol (PhCH₂OH) as the model reactant to benzaldehyde (PhCHO). The NDG/MnCO₃-ZrO₂ exhibits premium specific activity $(66.7 \text{ mmol} \cdot \text{g}^{-1} \cdot \text{h}^{-1})$ with 100% conversion of PhCH₂OH and > 99.9% selectivity to PhCHO after only 6 min. The mechanochemically prepared NDG based nanocomposite exhibited notable improvement in the catalytic efficacy as well as the surface area compared to the pristine MnCO₃–ZrO₂. Under the optimal circumstances, the NDG/MnCO₃–ZrO₂ catalyst could selectively catalyze the aerobic oxidation of a broad array of alcohols to carbonyls with full convertibility without over-oxidized



side products like acids. The NDG/MnCO₃–ZrO₂ catalyst were efficiently reused for six subsequent recycling reactions with a marginal decline in performance and selectivity.

Keywords: ZrO₂; MnCO₃; N-doped graphene; nanocomposites; catalyst; alcohols

1. Introduction

Nitrogen doping is considered as one of the essential ways of carbon functionalization. It leads to alteration of several properties of carbonaceous materials due to the numerous structural defects occurring with doping of 'N' and with further doping of catalytically active metal nanoparticles (NPs) there is an improvement of the electronic density, such modifications lead the formation of a new class of compounds, called graphene-based nanocomposites, which make carbonaceous materials useful in many fields [1,2]. N-doping of graphene not only produces an outstanding alternative for the dispersion of metal NPs on the graphene layer as it significantly influences the growth mechanism of NPs, which assists in controlling the size and morphology of the NPs, but also helps the uniform dispersion of NPs, prohibits the agglomerating and restacking of graphene sheets which seizes the decline in its surface areas an essential parameter for heterogeneous catalysts involved in a variety of organic transformations [3–5]. Theoretical calculations have revealed that the anchored N sites can affect the binding energy between metallic nanoparticles indicating that the N-doping of graphene played a significant role in catalytic processes owing to the changed N sites anchoring metals or metal oxides [6].

Among the various uses of heterogeneous catalysts, the catalyst employed for the preparation of pivotal precursors such as aldehydes and ketones via the oxidation of alcohols has attracted great interest [7]. Traditionally, this transformation not only involves very expensive, corrosive, and hazardous oxidants (e.g., permanganate, hypervalent iodine, chromium oxides or hypochlorite, etc.) and harsh reaction conditions but also generates a large quantity of deleterious and toxic materials against the requirements of green chemistry [8,9]. Hence, it was necessary to find an environmentally friendly catalytic oxidation methodology using inexpensive oxidants as well as inexpensive non-noble metals, such as aqueous H_2O_2 , oxygen molecule which has attracted significant interest in the field of green and sustainable chemistry [10]. Recently, utilizing noble precious metal catalysts to catalyze the oxidation of alcohol has been widely studied gold, palladium, ruthenium, platinum [11,12]. Nonetheless, various limitations and safety concerns are related to these processes, like high prices and rareness these precious metals [13]. Therefore, considerable efforts have been made to explore plentiful and inexpensive non-noble metals including nickel, cobalt, vanadium, copper, molybdenum, osmium, chromium, cerium, zirconium, iron, zinc, and rhenium as oxidation catalysts for alcohol oxidation [14]. In particular, manganese oxide is one of the cheapest and most stable metal oxides with superior catalytic efficacy and broadly utilized as a support material/catalyst for catalytic alcohol oxidation. Furthermore, it has been widely reported that the catalytic efficacy of metal and/or metal oxide nanoparticles (NPs) catalysts noticeably enhanced upon doping with other metals possibly owing to synergistic effects between them in addition to the huge increment of the surface area [15].

In general, incorporation of carbonaceous material along with transition metal nanoparticles have found to be much effective catalysts for the alcohol oxidation, particularly graphene and its derivatives. These catalysts have attracted extensive interest owing to their enormous potential in several applications, such as batteries, solar cells, supercapacitors, catalysis, drug delivery, sensors, hydrogen storage, electronics, and water purification [16,17].

Our group has studied extensively various catalyst and their carbonaceous nanocomposites [18,19]. In our previous study, we have displayed that zirconia acts a highly effective promoter to the $MnCO_3$, and the $MnCO_3$ –(1%)ZrO₂ calcined at 300 °C. It displayed outstanding catalytic efficacy for aerobic oxidation of alcohols using environmentally-friendly oxidant O₂. We further modified it with HRG

and GRO and the catalytic performance was studied [20]. In continuation of the study of exploring effects of various carbonaceous materials on the catalytic performance, we explored the use of N-doped graphene (NDG) in which we prepared the novel (X%)NDG/ZrO₂–MnCO₃ nanocomposites by mixing of separately synthesized N-doped graphene oxide (NDG) and pre-calcined ZrO_2 –MnCO₃ NPs using an eco-friendly mechanochemical ball milling procedure. The ball milling method assists with decrease the size of NPs and inhibits agglomeration. The as-obtained materials have been thoroughly characterized by various spectroscopic and microscopic techniques, including FESEM, EDX, XRD, FT-IR, and Raman. The N₂-adsorption analysis have been carried out to identify the surface area of the as-synthesized nanocomposites. The thermal degradation of the nanocomposites was investigated by using TGA analysis. The as-obtained catalysts have been investigated for the catalytic oxidation of a different array of alcohols to realize the impact of NDG in the catalytic protocol. To the best of our knowledge, this is the first report of a catalytic system wherein ZrO_2 –MnCO₃ is doped with NDG and evaluated as an oxidation catalyst and especially, highlighting the impact of NDG in the catalytic system as a dopant

2. Results and Discussion

2.1. Characterizations

The crystallographic structure and crystallinity of the as-synthesized samples was determined via XRD technique. Figure 1 displays XRD analyses of the pristine graphite, graphene oxide (GRO), N-doped graphene (NDG), MnCO₃–(1%)ZrO₂, and (1%)NDG/MnCO₃–(1%)ZrO₂ nanocomposite. The XRD diffractogram of the pure graphite illustrates the high crystalline degree with an intensesingle reflection at 26.6° which assigned to (0 0 2) crystal plane with inter planar-spacing of 3.4 Å [21]. However, the degree of crystallinity of GRO is lower in comparison with graphite a wide diffraction peak centered at 11.7°, which is a fingerprint peak of GRO (Figure 1b). The evanescence of the graphite diffraction line at 26.6° and emergence of a new reflection at approximately 11.7° with (0 0 2) crystal plane, confirming the efficient oxidation of graphite to GRO [22]. This shift leads to an increment in an interplanar distance from 3.4 to 6.5 Å for graphite and GRO, respectively, maybe because of the inclusion of oxygenic possessing groups between the graphitic layers upon oxidation reaction [23]. For respective NDG, a wide diffraction peak at approximately 24.6° with (0 0 2) crystal plane has observed, which is a feature peak of NDG and evanescence of the peak at 11.7°, indicating the complete reduction of GRO to NDG [24]. For (1%)NDG/MnCO₃-(1%)ZrO₂ nanocomposite, all diffraction signals are readily indexed as rhodochrosite D-MnCO₃ (JCPDS card no.1-0981) in addition to characteristic diffraction reflection of NDG at about 24.6° [25]. The above observations indicated that the (1%)NDG/MnCO₃-(1%)ZrO₂ nanocomposite was successfully prepared.

Thermal stability was examined by using thermal-gravimetric analyses (TGA) to assess the thermal behavior of (1%)NDG/MnCO₃-(1%)ZrO₂ and compared with the thermal degradation of its precursors like graphite, GRO and un-doped catalyst (without graphene) MnCO₃-(1%)ZrO₂. Figure 2 plots the TGA graphs of the prepared samples in the temperature range of (25–800 $^{\circ}$ C) under an N₂ atmosphere. The TGA results displayed that the TGA graph of graphite exhibits a weight loss of ~1%. Whilst, the thermal degradation of GRO is much lower relative to the graphite sample attributed to the presence of labile oxygenic possessing groups on the surface of GRO [26]. For respect GRO, at lower than 100 °C, a slight weight loss (about 4%) was observed because of the vaporization of moisture and H₂O molecules. Then, from 200 to 390 °C, an essential weight loss of 44% occurs owing to the elimination of oxygen functional groups. Eventually, a weight loss takes place from 390 to 800 °C could be assigned to the pyrolysis of the graphene skeletons [27]. The thermogram of the NDG shows an overall weight loss of about 30%, attributed to the reduction of most oxygen-possessing groups. The (1%)NDG/MnCO₃–(1%)ZrO₂ nanocomposite exhibits a 28% weight loss as compared to the 30% weight loss exhibited by the NDG. Moreover, thermal stability of the $MnCO_3$ -(1%)ZrO₂ nanocatalyst is stable at high temperature but with the doping of NDG in the $MnCO_3$ -(1%)ZrO₂ catalyst i.e., (1%)NDG/MnCO₃-(1%)ZrO₂ nanocomposite slightly decreases.



Figure 1. XRD diffractograms of (**a**) graphite, (**b**) GRO, (**c**) NDG, (**d**) MnCO₃–(1%)ZrO₂ and (**e**) (1%) NDG/MnCO₃–(1%)ZrO₂ samples.



Figure 2. TGA curves of (a) graphite, (b) GRO, (c) NDG, (d) $MnCO_3-(1\%)ZrO_2$ and (e) (1%)NDG/MnCO_3-(1%)ZrO_2 nanocomposites.

FTIR spectra of GRO, NDG, and (1%)NDG/MnCO₃–(1%)ZrO₂ samples are plotted in Figure 3. In the spectra of pristine GRO, the wideband is situated at approximately 3440 cm⁻¹, related to O–H stretching vibrations of adsorbed H₂O and –COOH groups. The intense peak at 1738 cm⁻¹ was indexed as C=O stretching vibrations of –COOH groups, and peak centered at 1630 cm⁻¹ related to stretching modes of carbonaceous skeletal (C=C) in the un-oxidized graphitic areas [28]. Moreover, three peaks centered at 1060, 1226, and 1395 cm⁻¹ appeared owing to vibrations of O-possessing groups such C–O (alkoxy), C–O–C (epoxy) and C–OH groups, correspondingly. NDG fingerprint peaks were observed at 1560 and 3432 cm⁻¹ associated with N–H bond vibrations, and the peak at 1150 cm⁻¹ belongs to the C–N bond [29], and other peaks belonging to oxygenated groups disappeared [23]. However, the comparision of the GRO spectrum with (1%)NDG/MnCO₃–(1%)ZrO₂ nanocomposite distinctly displays the efficient reduction of most of the oxygen containing functional groups. The strong absorption peaks at 1060, 1226, and 1395 cm⁻¹ disappeared, implying that the oxygenated functionalities on GRO surfaces were almost eradicated. Moreover, a weak peak at 1635 cm⁻¹ can be assigned to (C=C) stretching vibrations, besides, the (1%)NDG/MnCO₃–(1%)ZrO₂ nanocomposite exhibits two peaks at 860 and 1448 cm⁻¹, which are a fingerprint peaks for manganese carbonate [30], furthermore,

two peaks at 1560 and 3432 cm⁻¹ correspond to N–H bond vibrations and the peak at 1150 cm⁻¹ assigned to the C–N bond. Ultimately, the strong peak at 580 cm⁻¹ is related to Mn–O vibrations [31].



Figure 3. FTIR analysis of (a) GRO, (b) NDG, and (c) (1%)NDG/MnCO₃-(1%)ZrO₂ samples.

The morphology of the nanocomposite was studied and a high-resolution field emission scanning electron microscopy (FE-SEM) images of NDG and the (1%)NDG/MnCO₃–(1%)ZrO₂ is illustrated in Figure 4. Figure 4a shows the sheet-like structure of NDG as a continuous crumpled membrane organized as layers. Figure 4b–d show the crumbled NDG sheets construct a network of nanoparticles. MnCO₃–(1%)ZrO₂ nanoparticles are clustered over the NDG sheets. Particle-size of the metal oxide nanoparticles was calculated from Figure 4c using ImageJ software program and is found to be 44 nm (Figure S2). The distribution of (1%)NDG/MnCO₃–(1%)ZrO₂ over NDG was clearly resolved by a high-resolution FE-SEM elemental mapping via EDX analysis (Figure 5). The elemental mapping of (1%)NDG/MnCO₃–(1%)ZrO₂ at the rectangular area shown in Figure 5 reveals the uniform distribution of O (turquoise), N (green), C (purple), Zr (yellow) and Mn (red) atoms throughout the 7 μ m sized cross-section. Atomic percentages from EDX (Figure S1) elemental analysis on the same cross-section of the nanocomposite were found to be 57.54%, 1%, 32.34%, 7.95% and 1.16% for C, N, O, Mn and Zr respectively which is in correspondence with the line scan profile. Further the nanocomposite material was investigated using Inductively coupled plasma (ICP) analysis to find out the composition and the percentage of ZrO₂ was found to be 1 mol%.

To measure the surface areas of prepared materials and to find out its relevance with the catalytic performance for aerobic PhCH₂OH oxidation N₂ adsorption-desorption analysis was carried out. Table 1 revealed that the surface area of pure MnCO₃–(1%)ZrO₂ catalyst is about 133.6 m²/g. However as estimated, the surface areas of the nanocomposites after doping them with graphene such as NDG, GRO and HRG were substantially increased to 243.7 m²/g, 229.5 m²/g, and 211.0 m²/g, respectively. Notably, the attained catalytic data aligned well with surface area analysis outcomes. Unsurprisingly, the catalytic efficacy after inclusion the catalyst with NDG, GRO and HRG i.e., (1%)NDG/MnCO₃–(1%)ZrO₂, (1%)GRO/MnCO₃–(1%)ZrO₂ and (1%)HRG/MnCO₃–(1%)ZrO₂, respectively, also noticeably improved. Subsequently, it could be deduced that the introduction of graphene (NDG, GRO, or HRG) into the catalytic system had a positive influence on surface areas of prepared nanocomposites, which inevitably leads to enhance the catalytic efficacy of the as-obtained catalysts. Interestingly, the (1%)NDG/MnCO₃–(1%)ZrO₂ catalyst possesses the highest surface area among all other prepared graphene based catalysts and yielded also higher alcohol conversion, whereas, the other synthesized graphene based catalysts showed lower catalytic activity as well as surface area.



Figure 4. FE-SEM images of (**a**) NDG showing sheets like structures, and (**b**–**d**) (1%)NDG/MnCO₃– (1%)ZrO₂.



Figure 5. FE-SEM elemental mapping and line scan profile of (1%)NDG/MnCO₃-(1%)ZrO₂.

Raman spectroscopy is employed to characterize graphite derivatives, since it is useful in studying bond vibrations in carbon hybridization and disorder or defect in crystal structure. Here we studied the Raman spectra of GRO, NDG, and (1%)NDG/MnCO₃-(1%)ZrO₂ and results are shown in Figure 6. GRO shows two prominent peaks in a typical Raman spectrum, the G band at 1605 cm⁻¹ arising due to the E_{2g} phonon of the sp² C atoms, and a D band at 1338 cm⁻¹ due to the breathing mode of κ -point phonons of A_{1g} symmetry. The G band is common for all sp^2 carbon forms, and it arises from the C-C bond stretch [32]. The D band is a measure of disorder, which may be due to the presence of defects such as vacancies, grain boundaries, and amorphous carbon species [33], while the G band is Raman allowed vibrations of sp^2 carbon due to the C-C bond stretching [32]. Disorder is determined by the intensity ratio between the disorder induced D band and the Raman allowed G band (I_D/I_G) . Furthermore, in NDG and (1%)NDG/MnCO₃-(1%)ZrO₂, the G band is seen at 1595 cm⁻¹, and 1592 cm⁻¹, and the D band at 1328 cm⁻¹, and 1328 cm⁻¹ for NDG and (1%)NDG/MnCO₃-(1%)ZrO₂ respectively. The G band in NDG is red shifted to a lower wave number due to the replacement of oxygen through N doping, which results owing to the formation of pyridinic, pyrrolic and graphitic N instead of sp^2 carbon atoms [34]. The D band in GRO is broadened due to the reduction in size of the sp² domains by the creation of defects, vacancies, and distortions during oxidation. The increase of I_D/I_G from 1.09 (GRO) to 1.19 (NDG) confirms the embedding of heterogeneous nitrogen atoms into the graphitic planes. Further, the ratio of I_D and I_G is lower in the (1%)NDG/MnCO₃-(1%)ZrO₂ comparing to the value of NDG, the indicates the partial restoration of sp^2 domains [35].



Figure 6. Raman spectra of (a) GRO, (b) NDG and (c) (1%)NDG/MnCO₃-(1%)ZrO₂ samples.

2.2. Catalytic Activities

From the point of view of green and eco-friendly chemistry, molecular O_2 was employed as the environmentally-benign oxidant to selectively oxidize PhCH₂OH to PhCHO as the model substrate under mild and alkali-free conditions. Various catalysts were prepared by varying the wt.% of NDG in the nanocomposite. Besides, several factors have been optimized, for example, operating temperature, catalyst quantity, and reaction time, as presented in Figures 7–10 and Tables 1 and 2.



Figure 7. Graphical representation of PhCHO oxidation over (a) $MnCO_3-(1\%)ZrO_2$, (b) (1%)NDG/MnCO₃-(1%)ZrO₂, (c) (3%)NDG/MnCO₃-(1%)ZrO₂, (d) (5%)NDG/MnCO₃-(1%)ZrO₂ and (e) (7%)NDG/MnCO₃-(1%)ZrO₂ catalysts.



Figure 8. Graphical illustration of comparative PhCHO oxidation using (1%)HRG/MnCO₃-(1%)ZrO₂, (1%)GRO/MnCO₃-(1%)ZrO₂ and (1%)NDG/MnCO₃-(1%)ZrO₂ catalysts.



Figure 9. Impact of varying temperature on PhCH₂OH conversion over (a) $MnCO_3$, (b) $MnCO_3$ –(1%) ZrO_2 and (c) (1%)NDG/MnCO₃–(1%) ZrO_2 catalysts.



Figure 10. Impact of varying catalyst dosage on the PhCH₂OH conversion over (**a**) MnCO₃, (**b**) MnCO₃–(1%)ZrO₂ and (**c**) (1%)NDG/MnCO₃–(1%)ZrO₂ catalysts.

Entry	Catalyst	S. A. (m ² /g)	Con. (%)	Specific Activity (mmol·g ⁻¹ ·h ⁻¹)	Sel. (%)
1	NDG	485.6	2.7	1.8	>99
2	MnCO ₃	70.5	41.6	27.7	>99
3	$MnCO_3$ -(1%) ZrO_2	133.6	73.1	48.8	>99
4	(1%)NDG/MnCO3-(1%)ZrO2	243.7	100.0	66.7	>99
5	(1%)GRO/MnCO ₃ -(1%)ZrO ₂	229.5	96.8	64.6	>99
6	(1%)HRG/MnCO ₃ -(1%)ZrO ₂	211.0	89.3	59.6	>99

Table 1. Aerobic oxidation o	f PhCH ₂ OH over	various catalys	sts.
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Conditions: 2 mmol PhCH₂OH, 15 mL toluene, O₂ 20 mL/min, 300 mg catalyst, 100 °C and 6 min.

Entry	Catalyst	Conv. (%)	Specific Activity (mmol·g ⁻¹ ·h ⁻¹)	Sel. (%)
1	NDG	2.7	1.8	>99
2	MnCO ₃ -(1%)ZrO ₂	73.1	48.8	>99
3	(1%)NDG/MnCO ₃ -(1%)ZrO ₂	100.0	66.7	>99
4	(3%)NDG/MnCO ₃ -(1%)ZrO ₂	95.1	63.4	>99
5	(5%)NDG/MnCO ₃ -(1%)ZrO ₂	84.8	56.6	>99
6	(7%)NDG/MnCO ₃ -(1%)ZrO ₂	65.6	43.8	>99

Table 2. Catalytic results of different catalysts.

Conditions: 2 mmol PhCH₂OH, 15 mL toluene, O₂ 20 mL/min, 300 mg catalyst, 100 °C and 6 min.

2.2.1. Impact of wt.% of NDG

In general, the effectiveness of the catalyst for the oxidation of alcohol can be remarkably fine-tuned after utilizing graphene or its derivatives as a support or promoter [14,36]. Hence, for this study, we selected our previously reported catalyst i.e., $MnCO_3$ –(1%)ZrO₂, and co-doped with NDG to improve the catalytic efficacy and to compare effects of incorporating NDG in the catalytic system.

Firstly, we tested the catalytic performance of pristine NDG for selective oxidation of PhCH₂OH in presence of oxygen molecule as an oxidant at 100 °C and no conversion product is obtained indicating that that NDG is not an active catalyst for the PhCH₂OH oxidation. Nonetheless, the catalytic performances of different (X%)NDG/MnCO₃–(1%)ZrO₂ nanocomposites, (where, X = 0 - 7) have been assessed for oxidation of PhCH₂OH and the achieved data are collected in Table 2 and presented in Figure 7. As noticed in Table 2 and Figure 7, the catalyst MnCO₃–(1%)ZrO₂ (without NDG) gave about

73.1% conversion of PhCH₂OH within 6 min. Nevertheless, after doping MnCO₃–(1%)ZrO₂ catalyst with 1 wt.% of NDG, i.e., (1%)NDG/MnCO₃–(1%)ZrO₂ afforded maximum catalytic activity among all other nanocomposites with various weight percentages of NDG. The (1%)NDG/MnCO₃–(1%)ZrO₂ gave 100% conversion of PhCH₂OH within a very short time (6 min) and exceptional specific activity of 66.7 mmol·g⁻¹·h⁻¹. Moreover, it was noticed that upon further raising the weight% of NDG to 3 wt.% led to a slight decline in the PhCH₂OH conversion to 95.1%. While the nanocomposites with 5 wt.% and 7 wt.% of NDG gave 84.8% and 65.6% alcohol conversion, respectively, at similar catalytic circumstances. The decline in catalytic activities on increasing the amount of NDG might be due to the blocking impact of NDG that could cover or block the active sites of the nanocatalyst, attributed to the high wt.% of NDG, however, the selectivity of PhCHO remains constant (i.e., > 99%). As a result, it was stated that the NDG doping of the catalytic system had an explicit impact on enhancing the effectiveness of our catalytic methodology for the current oxidation process.

2.2.2. Effects of Various Graphene Derivatives

Furthermore, we also compared the catalytic activity of nanocomposites of MnCO₃–ZrO₂ NPs with various graphene derivatives (i.e., NDG, HRG, and GRO) for PhCH₂OH oxidation to realize the impact of the graphene in the catalytic system. The obtained catalytic data are outlined in Table 1 and plotted in Figure 8. Initially, we have tested pure MnCO₃ catalyst for aerobic oxidation of $PhCH_2OH$ under the above-mentioned conditions, a 41.6% alcohol conversion within reaction period of 6 min was obtained, however after doing it with 1 wt.% of ZrO_2 in MnCO₃ i.e., MnCO₃-(1%)ZrO₂, the catalytic activity markedly raised, and yielded 73.1% PhCH₂OH conversion at the identical catalytic conditions. Moreover, further modifications carried out by utilizing NDG as a catalyst dopant, i.e., (1%)NDG/MnCO₃–(1%)ZrO₂ nanocomposite had slightly higher catalytic efficacy than the catalysts doped with GRO and HRG i.e., (1%)GRO/MnCO₃-(1%)ZrO₂ and (1%)HRG/MnCO₃-(1%)ZrO₂ nanocomposites, respectively. The (1%)NDG/MnCO₃-(1%)ZrO₂ nanocomposite yields full transformation of PhCH₂OH in addition to a superior specific activity of 66.7 mmol g^{-1} ·h⁻¹ within an extremely short period (6 min). The GRO-based catalyst exhibits good activity could be due to the myriad O-possessing groups in GRO assisted the oxidation of PhCH₂OH [37]. However, with respect to HRG, the (1%)HRG/MnCO₃-(1%)ZrO₂ displays higher performance by comparing with un-doped catalyst i.e., MnCO₃-(1%)ZrO₂ catalyst, presumably ascribed to the increment in the adsorption between π -electrons on the aromatic ring in alcohol substrates and π -electrons on the HRG's surface by π - π interactions near the MnCO₃-(1%)ZrO₂ nanocatalyst [14]. The superior activity of the NDG based nanocomposite can be attributed to the existence of the N groups in the NDG surface, as well as the extra electronic density compared to carbon atoms due to the 'N' atoms [38]. Finally, the presence of NDG can be responsible for additional defects in the crystalline MnCO₃–ZrO₂ nanocatalysts which promotes the effectiveness of the nanocomposites. The reasonable mechanism for catalytic enhancement can be further studied.

2.2.3. Impact of Operating Temperature

Operating temperature generally plays a crucial role in the catalytic methodology and had a marked influence on the catalyst's effectiveness. Hence, various reactions were conducted at several temperatures (20, 40, 60, 80 and 100 °C), catalyzed by MnCO₃, MnCO₃–(1%)ZrO₂ and (1%)NDG/MnCO₃–(1%)ZrO₂ catalysts while other experimental factors were kept constant. As observed in Figure 9, the operation temperature had a positive impact on the catalytic activities of all catalysts utilized in this work, whereas excellent selectivity towards PhCHO maintained almost motionless (> 99.9%). Figure 9 reveals that the optimal catalyst achieved maximum performance is (1%)NDG/MnCO₃–(1%)ZrO₂ catalyst. The conversion improved from 37.4% to 100% when the operating temperature rose from room temperature to 100 °C. In this ambient temperature circumstances assisted intermolecular collisions and activated molecules, thereby decreasing mass transfer limitations among molecules [39]. As a result of the above experiments and as it has been reported [40] that the selectivity of the benzaldehyde decreases at temperatures above 100 °C, hence, 100 °C was regarded as the optimal reaction temperature for further optimization experiments.

2.2.4. Impact of Catalyst Dose

Catalyst quantity is highly crucial for any catalytic transformation using a catalyst. To assess the effect of varying amount of catalysts (MnCO₃, MnCO₃–(1%)ZrO₂ and (1%)NDG/MnCO₃–(1%)ZrO₂), diverse catalyst dosages like 0.05, 0.10, 0.15, 0.20, 0.25 and 0.30 g were taken with maintaining other catalytic variables unaltered and the attained results are represented in Figure 10. When the catalyst dosage was zero i.e., the oxidation transformation conducted in the absence of the catalyst, no formation of the oxidative product (i.e., PhCHO) has been detected by Gas chromatography (GC), indicating the as-prepared catalyst is indispensable for the current transformation. Noticeably, the conversion of PhCH₂OH raised dramatically as the quantity of catalysts rose from 0.50 to 0.30 g. Meantime, the product selectivity was roughly constant through all oxidation reactions (>99%). The catalytic results distinctly demonstrated that the (1%)NDG/MnCO₃–(1%)ZrO₂ nanocomposite exhibits optimal performance towards this transformation among all catalysts used in this study, the PhCH₂OH conversion enhanced gradually from 30.1% to 100% after the catalyst amount was increased from 50 to 300 mg within 6 min at 100 °C. The reason was that the increment in catalyst quantity provided more active sites, which led to accelerating the rate of PhCH₂OH oxidation.

Under the optimal circumstances, a blank reaction without reactant (PhCH₂OH) has performed over (1%)NDG/MnCO₃–(1%)ZrO₂ using the toluene as a solvent to emphasize that there is no impact of solvent in oxidation of PhCH₂OH. No oxidation product (PhCHO) has been observed as predicted, showing that the PhCHO is generated only results from the catalytic oxidation of PhCH₂OH and not from oxidation toluene. Besides, to elucidate the key role of the oxidant (oxygen molecule), the process was carried out catalyzed by (1%)NDG/MnCO₃–(1%)ZrO₂ catalyst in presence of air without bubbling molecule O₂. At optimal catalytic conditions, the achieved data disclosed that just 28.3% PhCH₂OH conversion has been obtained, which is considerably lower compared to 100% convertibility obtained when the transformation is carried out in presence of oxygen molecule.

2.3. Reusability Tests

The reusability and durability are regarded as a pivotal factor for industrial applications of heterogeneous catalysts. To investigate the recyclability of the (1%)NDG/MnCO₃–(1%)ZrO₂, oxidation of PhCH₂OH was carried out six consecutive runs at optimum operation conditions (Figure 11). The recyclability data revealed that we were able to efficiently recycle the prepared catalyst for six cycles with no notable loss in its efficacy after every recycling run. It could be observed from Figure 11 that after six runs of recycling reactions, the conversion of PhCH₂OH merely decreased from 100% to 91.2% after 6 recycles. The slight decline in the alcohol conversion might be ascribed to the slight mass loss of catalyst through the collecting and filtration process [41]. Notably, the selectivity towards PhCHO through all recycling reactions is found to be >99.9%. Therefore, the achieved data indicated that the as-synthesized catalyst was recyclable and highly stable for this transformation.

The catalytic activity for base-free aerobic oxidation of PhCH₂OH to PhCHO over (1%)NDG/MnCO₃–(1%)ZrO₂ catalyst in this study and other previous published graphene containing catalysts was compared in Table 3. Compared with other graphene containing catalysts listed in Table 3, the (1%)NDG/MnCO₃–(1%)ZrO₂ catalyst in this study exhibited the highest catalytic efficiency in terms of conversion, selectivity, specific activity and reaction time. The (1%)NDG/MnCO₃–(1%)ZrO₂ catalyst showed the full transformation of PhCH₂OH to PhCHO and > 99% selectivity of PhCHO within a very short time only 6 min with outstanding specific activity (66.7 mmol·g⁻¹·h⁻¹). As observed in Table 3, other graphene-possessing catalysts afforded a much longer time for a complete transformation of PhCH₂OH and lower specific activity compared to the prepared catalyst. This can be attributed to the increase in defects, vacancies and distortions in the NDG, which might have played a role in enhancement of the catalytic performance. Very recently, Ramirez-Barria et al. [38] have successfully

synthesized Ru NPs deposited on NDG (4%Ru (CO)/NDG) and employed for aerobic oxidation of PhCH₂OH in presence of O₂. The 4%Ru (CO)/NrGO catalyst shows only 46% conversion of PhCH₂OH and selectivity to PhCHO was about > 99% with a lower specific activity of 6.4 mmol·g⁻¹·h⁻¹ within a much longer reaction time of 24 h with respect to the prepared catalyst. In another example, Sun and his group [42] reported liquid-phase oxidation of PhCH₂OH over Au–Pd/Fe–Graphene catalyst in presence of O₂ as an oxidant. The Au–Pd/Fe–Graphene yields 89.5% conversion, 87.5% selectivity and the specific activity of 6.7 mmol·g⁻¹·h⁻¹ after long period of 4 h.



Figure 11. Recyclability results of (1%)NDG/MnCO₃–(1%)ZrO₂ catalyst for PhCH₂OH oxidation. Conditions: 2 mmol PhCH₂OH, 15 mL toluene, O₂ 20 mL/min, 0.3 g catalyst, 100 °C and 6 min.

Table 3. Comparative results of the PhCH ₂ OH oxidation catalyzed by various grap	hene containing
catalysts.	

Catalyst	Т. (°С)	Time (h)	Conv. (%)	Sel. (%)	Specific Activity (mmol·g ⁻¹ ·h ⁻¹)	Ref.
(1%)NDG/MnCO ₃ -(1%)ZrO ₂	100	0.1	100	>99	66.7	Herein
(1%)GRO/MnCO ₃ -(1%)ZrO ₂	100	0.1	100	>99	64.6	[20]
(1%)HRG/MnCO ₃ -(1%)ZrO ₂	100	0.1	100	>99	59.6	[14]
4%Ru (CO)/NDG	90	24	46	>99	6.4	[38]
MCG-700	100	8	89.5	97.3	4.5	[43]
Au–Pd/Fe–Gr	110	4	89.1	87.5	6.7	[42]
Au NPs/NG	70	6	67	40	0.4	[44]
MnO ₂ /GRO	110	3	97	100	1.6	[45]
Sn–W/RGO	80	3	94.0	94.4	15.7	[46]
Ag NPs/GOSH	80	24	61	58	5.1	[47]
Cu NPs@rGO	80	16	<99	98.6	8.3	[48]
Pd NPs/GRO	110	6	36	34.1	1.0	[49]
1 wt.% RGO/MnCoO	140	2	78	100	12.6	[50]
Au NPs/RGO	100	8	65	93	5.4	[41]
GRO/Fe3O4/HPW	70	3	99	100	16.7	[51]
GO-100	80	5	100	100	1.1	[52]

To expand the general applicability of $(1\%)NDG/MnCO_3-(1\%)ZrO_2$ catalyst, a wide array of aromatic, primary, secondary, aliphatic, heterocyclic and allylic alcohols were selectively oxidized to the corresponding aldehydes and ketones using the optimal experimental conditions as displayed in Table 4. It was noted that all the primary aromatic alcohols were favorably transformed into the respective aldehydes with 100% conversion during short times (Entries 1–22). Meanwhile, the chemoselectivities to aldehydes and ketones remained consistent (higher than 99%) for all alcohols in this work and no over-oxidized byproducts such as carboxylic acids were observed. Evidently, the catalytic data revealed that electronic effects played a crucial role in this process. It has been found that the electron-rich

benzylic alcohols bearing electron-donating derivatives have higher reactivity and exhibiting relatively shorter reaction times, whereas the time for the benzyl alcohols carrying electron-withdrawing groups is comparatively longer. The decline in the catalytic activity for alcohol bearing electron-withdrawing group is possibly caused by the reduction of electron-density on the benzene ring caused by the negative induction effect, which was detrimental to the enhancement of catalytic performance in alcohol oxidation [46]. For instance, oxidation of benzylic alcohol possessing electron-releasing substituent like p-methoxybenzyl alcohol was totally oxidized to p-methoxy benzaldehyde within 6 min (Entry 3), while, *p*-(trifluoromethyl)benzyl alcohol, which bears an electron-withdrawing group, needed comparatively longer time (15 min) (Entry 13). Moreover, p-substituted aromatic alcohols exhibit higher activities compared to *o*- and *m*-positions could be attributed to the fact the *p*-position possesses minimal steric hindrance compared with other positions [53]. For instance, *p*-nitrobenzyl alcohol was entirely converted to its respective aldehyde within 12 min (Entry 10), whereas *m*- and *o*-nitrobenzyl alcohol were fully oxidized after comparatively longer periods (17 and 20 min, correspondingly, Entries 13 and 15). Moreover, the steric hinderance plays an essential role in catalytic performance due to the existence of bulky substituents (trimethoxy, dichloro and pentafluoro) associated to the aromatic ring decreases the oxidation rate efficiency and required longer reaction time (Entries 16–18). It was noteworthy that the oxidation of cinnamic alcohol as an example for allylic alcohol was selectively converted into cinnamic aldehyde within only 12 min (Entry 19). Additionally, heterocyclic alcohol such as furfuryl alcohol were also successfully transformed into furfural with 100% conversion and selectivity (Entry 20). Furthermore, the as-synthesized catalyst is also efficient for the oxidation of secondary benzylic alcohols with full conversion and selectivity towards ketones under identical conditions (Entries 23–28).

Predominantly, the oxidation of aliphatic alcohols is much more difficult compared with aromatic ones [54]. Fortunately, the present catalytic strategy has also applicable to the oxidation of primary aliphatic alcohols to corresponding aliphatic aldehydes (Entries 27–30). For example, complete oxidation of 1-octanol and citronellol were obtained by prolonging the time of reaction (Entries 29 and 30). As expected, the oxidation of secondary aliphatic alcohols exhibited lower effectiveness by comparing with the secondary aromatic alcohols towards this transformation (Entries 31 and 32). Distinctly, it is indispensable to elongate the time of reaction, attributed to the oxidation of aliphatic secondary alcohols is more complicated than that of aromatic counterparts. As anticipated, complete conversion of 1-phenylethanol occurs within just 8 min, whilst the total oxidation of 2-octanol took place after a comparatively longer time of 120 min (Entries 21 and 32). Therefore, it could be stated that the current aerobic methodology over (1%)NDG/MnCO₃–(1%)ZrO₂ nanocomposite has strongly affected by dual factors, electronic and steric effects. The above observations revealed that (1%)NDG/MnCO₃–(1%)ZrO₂ catalyst could be successfully applied for a wide range of alcohols with different structures.

S. No.	Reactant	Product	Time (min)	Conv. (%)	Sel. (%)
1	OH	O H	6	100	>99.9
2	OH CH ₃	O H CH ₃	7	100	>99.9

Table 4. Aerobic oxidation of various	alcohols catalyzed b	y (1%)NDG/MnCO3	$-(1\%)ZrO_2$
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Table 4. Cont.

S. No.	Reactant	Product	Time (min)	Conv. (%)	Sel. (%)
3	OH OCH ₃		6	100	>99.9
4	OH CH ₃	O H CH ₃	8	100	>99.9
5			10	100	>99.9
6	Br	Br	9	100	>99.9
7	OH		11	100	>99.9
8	OH F	O F	10	100	>99.9
9	OH	O H	11	100	>99.9
10	OH NO ₂		12	100	>99.9

Table 4. Cont.

S. No.	Reactant	Product	Time (min)	Conv. (%)	Sel. (%)
11	OH CH ₃	O H CH ₃	14	100	>99.9
12	CI	CI	14	100	>99.9
13	OH NO ₂	O H NO2	17	100	>99.9
14	OH F F F	O F F F F	15	100	>99.9
15	OH NO ₂		20	100	>99.9
16	OH OCH ₃ OCH ₃	O H OCH ₃ OCH ₃	17	100	>99.9
17	OH CI		18	100	>99.9
18			24	100	>99.9
19	ОН		12	100	>99.9

Table 4. Cont.

S. No.	Reactant	Product	Time (min)	Conv. (%)	Sel. (%)
20	ОН	С О Н	25	100	>99.9
21	OH	o C	8	100	>99.9
22	CI OH	CI	10	100	>99.9
23	OH		10	100	>99.9
24	UH CI		15	100	>99.9
25	ОН		14	100	>99.9
26	OH	° C	18	100	>99.9
27	ОН	ОН	30	100	>99.9
28	ОН	° ⊢ H	100	100	>99.9
29	~~~~он	о Ц	110	100	>99.9
30	CH ₃ OH H ₃ C CH ₃		130	100	>99.9
31	OH		40	100	>99.9
32	OH	°	120	100	>99.9

Conditions: 2 mmol alcohol, 0.3 g (1%)NDG/MnCO₃–(1%)ZrO₂ catalyst, 15 mL toluene, O₂ 20 mL/min, 100 °C and 6 min.

3. Experimental Section

3.1. Preparation of GRO and NDG

Initially, GRO was prepared from pristine graphite through the Hummers oxidation process [55], thereafter, GRO was reduced by utilizing ammonium hydroxide and hydrazine hydrate to NDG and the full synthetic procedure was given in the supporting data.

3.2. Preparation of (X%)NDG Doped MnCO₃–(1%)ZrO₂ Nanocomposites

Initially, the ZrO₂ nanoparticles doped MnCO₃ were prepared through co-precipitation process by mixing stoichiometric volumes of Mn(NO₃)₂ and Zr(NO₃)₂ solution in a round-bottom flask at 95 °C with vigorous stirring followed by addition of 0.5 M of NaHCO₃ until the pH reaches to 9.0 for 3 h. The stirring was continued all night at RT. The resultant solution was filtered utilizing centrifugation and dried at 60 °C all night. The obtained sample was annealed in a muffle furnace at 300 °C and ZrO₂ nanoparticles doped MnCO₃ (i.e., MnCO₃–(1%)ZrO₂) was obtained. Thereafter, the separately prepared NDG was dried in an oven at 60 °C and initially ground in a planetary mill. Then varying amount of NDG are mixed with MnCO₃–(1%)ZrO₂ in a planetary mill to obtain (X%)NDG doped MnCO₃–(1%)ZrO₂ nanocomposites i.e., (X%)NDG/MnCO₃–(1%)ZrO₂. And all experimental details related to the ball-mill process are mentioned in the supporting data.

3.3. Characterizations

The as-obtained samples are characterized using many common techniques and all instrumental details are mentioned in the supporting data.

3.4. Catalytic Investigations

The typical experiment for aerobic alcohol oxidation according to the method presented in our previous literature [18].

3.5. Recovery Tests

After finishing the first experiment, the used catalyst was filtered utilizing simple centrifugation, then washed sequentially with toluene and dried at 115 °C for 3 hr for recycling reaction at the optimum conditions.

4. Conclusions

Present work discusses the design of a mechanochemical process for the synthesis of NDG doped MnCO₃-(1%)ZrO₂ nanocomposites, that is efficacious, low cost, and environmental-friendly and the as-prepared nanocomposites were employed for aerobic alkali-free oxidation of different kinds of alcohols with excellent effectiveness and selectivity. This is the first report wherein we demonstrate the exploitation of nitrogen-doped graphene (NDG) as a co-dopant in a catalytic system, which is different from the traditional use where it is used as a support. Additionally, we have compared the catalytic performance of (1%)NDG/MnCO₃–(1%)ZrO₂, with MnCO₃–(1%)ZrO₂, (1%)GRO/MnCO₃-(1%)ZrO₂ and (1%)HRG/MnCO₃-(1%)ZrO₂ for the oxidation of PhCH₂OH with nature-friendly oxidant O_2 in the absence of any hazardous additives or bases. The results demonstrated the (1%)NDG/MnCO₃-(1%)ZrO₂, possesses higher catalytic performance than pure MnCO₃-(1%)ZrO₂ (without graphene), GRO/MnCO₃-(1%)ZrO₂ and HRG/MnCO₃-(1%)ZrO₂ nanocomposites. The achieved enhanced catalytic performance of the (1%)NDG/MnCO₃-(1%)ZrO₂ nanocomposite might be due to the NDG presence, which affects the interaction between nitrogen groups on the surface of graphene and $MnCO_3$ -(1%)ZrO₂ nanocatalysts, the occurrence of graphene sheets develops several defects in the crystal lattice, it leads to increase of aromatic substrate adsorption, near the catalytic sites and it could improve the interactions between the surface of NDG and acidic

substrates that leads to superior catalytic properties. The catalyst (1%)NDG/MnCO₃–(1%)ZrO₂ exhibits outstanding catalytic performance (100% conversion and > 99% selectivity to PhCHO) for aerobic, base-free oxidation of PhCH₂OH during an extremely short time. The excellent specific activity (66.7 mmol·g⁻¹·h⁻¹) is considerably higher than that reported in previous publications. The merits of this aerobic catalytic approach are as follows: (a) facile eco-friendly method, (b) abundant, cheap and green oxidant, (c) no usage of harmful surfactants or alkalis, (d) mild reaction conditions, (e) low percentage of graphene, (f) inexpensive reusable catalyst, (g) extremely high convertibility, specific activity, and selectivity, (h) very fast transformation and (i) applicable to an array of alcohols.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/10/1136/s1, Figure S1: EDX spectrum of (1%) NDG/MnCO₃–(1%) ZrO₂ nanocomposite. Figure S2: Particle size distribution of (1%)NDG/MnCO₃–(1%)ZrO₂ nanocomposite.

Author Contributions: S.F.A. and J.V.S.K. designed the project; M.K. (Mufsir Kuniyil). M.E.A., M.K. (Mujeeb Khan) and W.A.A.-M. helped to write the manuscript; M.K. (Mufsir Kuniyil) and M.R.S. performed the experimental section and some part of characterization; A.K., M.B. and H.M.N.I. performed the some part of characterization; J.V.S.K., A.A.-W. and M.R.H.S. provided scientific guidance for successful completion of the project and helped to draft the manuscript. All authors read and approved the final manuscript.

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