Research Article

Synthesis, Characterization, and Relative Study on the Catalytic Activity of Zinc Oxide Nanoparticles Doped MnCO$_3$, –MnO$_2$, and –Mn$_2$O$_3$ Nanocomposites for Aerial Oxidation of Alcohols

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Zinc oxide nanoparticles doped manganese carbonate catalysts [X% ZnO$_x$–MnCO$_3$] (where $X = 0$–7) were prepared via a facile and straightforward coprecipitation procedure, which upon different calcination treatments yields different manganese oxides, that is, [X% ZnO$_x$–MnO$_2$] and [X% ZnO$_x$–Mn$_2$O$_3$]. A comparative catalytic study was conducted to evaluate the catalytic efficiency between carbonates and oxides for the selective oxidation of secondary alcohols to corresponding ketones using molecular oxygen as a green oxidizing agent without using any additives or bases. The prepared catalysts were characterized by different techniques such as SEM, EDX, XRD, TEM, TGA, BET, and FTIR spectroscopy. The 1% ZnO$_x$–MnCO$_3$ calcined at 300°C exhibited the best catalytic performance and possessed highest surface area, suggesting that the calcination temperature and surface area play a significant role in the alcohol oxidation. The 1% ZnO$_x$–MnCO$_3$ catalyst exhibited superior catalytic performance and selectivity in the aerial oxidation of 1-phenylethanol, where 100% alcohol conversion and more than 99% product selectivity were obtained in only 5 min with superior specific activity (48 mmol·g^{-1}·h^{-1}) and 390.6 turnover frequency (TOF). The specific activity obtained is the highest so far (to the best of our knowledge) compared to the catalysts already reported in the literatures used for the oxidation of 1-phenylethanol. It was found that ZnO$_x$ nanoparticles play an essential role in enhancing the catalytic efficiency for the selective oxidation of alcohols. The scope of the oxidation process is extended to different types of alcohols. A variety of primary, benzylic, aliphatic, allylic, and heteroaromatic alcohols were selectively oxidized into their corresponding carbonyls with 100% convertibility without overoxidation to the carboxylic acids under base-free conditions.

1. Introduction

Selective catalytic oxidation of alcohols to corresponding carbonyl compounds is one of the most pivotal functional group transformations in organic chemistry [1–6]. The oxidation products such as aldehyde and ketone derivatives are important precursors and intermediates in the cosmetics, perfumery, flame-retardants, insecticides, confectionary, biofuels, and pharmaceutical industries [7–11]. Usually, conventional oxidation of alcohols was conducted using toxic and expensive stoichiometric oxidizing agents such as CrO$_3$, KMnO$_4$, NaClO, Na$_2$Cr$_2$O$_7$, SeO$_2$, and Br$_2$ and leads to producing harmful by-products [12, 13]. In contrast, using clean and low cost oxidizing agents, such as aqueous hydrogen peroxide and particularly molecular oxygen to produce water, is the only side product and has gained growing interest from the sustainable and green chemistry point of views [14, 15]. In this context, noble metals such as gold [16–20], palladium [21], platinum [22–24], ruthenium [25, 26], and rhodium [27, 28] have been used as a heterogeneous catalyst for the alcohol oxidation with high catalytic activities and selectivities. Beside their high costs, these precious metals also have serious toxicity issues and difficulty in preparation and rarity of these noble metals makes these catalysts

impractical for industrial applications [29, 30]. Therefore, huge efforts have been made in order to replace these expensive noble metal catalysts with cheaper and plentiful nonnoble metals, for example, copper [31, 32], cobalt [33, 34], nickel [35–37], iron [38, 39], vanadium [40], silver [41, 42], chromium [43], molybdenum [44, 45], rhenium [46], and zirconium [47], for selective oxidation of alcohols. The metal, metal oxide, and mixed metal oxide nanoparticles catalysts were also found to be highly effective for the catalytic oxidation of alcohols. In addition, it has been widely reported that the catalytic activity of mixed metal oxide nanoparticles catalysts was remarkably enhanced upon doping with other metals, maybe because the metal nanoparticles possess huge surface area [48, 49].

Manganese carbonate ($MnCO_3$) has being considered one of the inexpensive and most stable metal oxides with high catalytic performance. Because $MnCO_3$ has various leads such as being most active, being stable, having low cost, and being environmental friendly catalyst, $MnCO_3$ and manganese oxides have been widely castoff as a catalyst or catalyst support for the catalytic oxidation of alcohols into carbonyls [50–53]. Moreover, it has several features, such as being highly active, stable, inexpensive, and ecofriendly catalyst [51–56]. However, different types of manganese oxide, mixed manganese oxide, and noble metal doped/supported Mn oxides were widely employed for the catalytic oxidation of numerous organic substrates, for instance, oxidation of naphthalene to carbon dioxide [57], oxidation of carbon monoxide to CO_2 [58, 59], oxidation of toluene to CO_2 [60], oxidation of ethylene and propylene to CO_2 [61], oxidation of cyclohexane to cyclohexanol and cyclohexanone [62], oxidation of alkyl aromatics to ketones [63], oxidation of 4-tert-butyltoluene to 4-tert-butylbenzaldehyde [64], and oxidation of formaldehyde to CO_2 [65].

In continuation of our efforts on the use of different mixed metal oxide nanoparticles as an efficient catalyst for the selective oxidation of alcohols in presence of molecular O_2 [18, 32, 41, 48, 49], we demonstrate herein a facile and straightforward procedure for the preparation of ZnO_x NPs doped manganese carbonates or oxides employed for oxidation of secondary alcohols with environmentally friendly oxidizing agent such molecular O_2 which produces water as the only by-product under base-free conditions. The reaction circumstances have been optimized with different weight percentages of ZnO_x, reaction times, calcination temperatures, reaction temperatures, and catalyst amounts using oxidation of 1-phenylethanol into acetophenone as a reaction model. The as-prepared catalyst was employed for oxidation of different types of alcohols. It was found that most of alcohols that were used in this study were completely converted to their corresponding aldehydes or ketones in extremely short reaction time without overoxidation to the acids. Moreover, the prepared catalysts have been characterized by several types of techniques, like scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and Brunauer-Emmett-Teller (BET) surface area measurement spectroscopies.
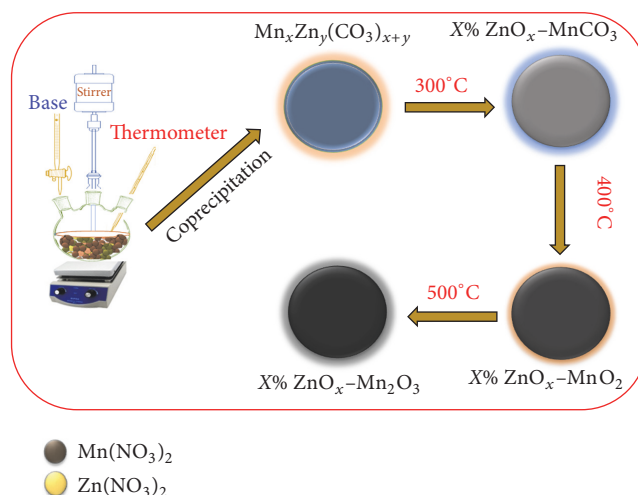
Scheme 1: Graphical illustration of the synthesis of the X% ZnO_x–$MnCO_3$ oxide and other products formed.

2. Experimental Section

2.1. Preparation of the Catalysts. ZnO_x NPs doped $MnCO_3$ catalysts of the type X% ZnO_x–$MnCO_3$ (where $X = 0, 1, 3, 5$, and 7) were prepared by coprecipitation method where % X denotes w/w%. Stoichiometric amount of manganese (II) nitrate tetrahydrate ($Mn(NO_3)_2 \cdot 4H_2O$) and zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) was dissolved in distilled water. About 100 mL of the mixture of solutions was taken in a glass three-necked round-bottom flask. The resulting mixture was heated to 80°C, while stirring using a mechanical stirrer and 0.5 M solution of sodium hydrogen carbonate ($NaHCO_3$) was added dropwise until the solution attained a pH 9. The solution was continued to stir at the same temperature for about 3 hours and then left on stirring over night at room temperature. The solution was filtered by centrifugation and the solid product obtained was dried at 70°C overnight; this upon calcination at different temperatures yielded different catalysts, which were used for comparative study of catalytic properties. A pictorial illustration is given in Scheme 1.

2.2. Characterization Techniques. Scanning electron microscopy (SEM) and elemental analysis (energy dispersive X-ray analysis: EDX) were carried out using Jeol SEM model JSM 6360A (Japan). This was used to determine the morphology of nanoparticles and its elemental composition. Fourier transform infrared (FTIR) spectra were registered on a Perkin-Elmer 1000 FTIR instrument (Waltham, MA, USA); the samples were prepared in KBr pellets. Transmission electron microscopy (TEM) was carried out using Jeol TEM model JEM-1101 (Japan), which was used to determine the shape and size of nanoparticles. Powder X-ray diffraction studies were carried out using Altima IV [Make: Regaku] X-ray diffractometer. BET surface area was measured on a NOVA 4200e surface area and pore size analyzer. Thermogravimetric analysis was carried out using Perkin-Elmer Thermogravimetric Analyzer 7.
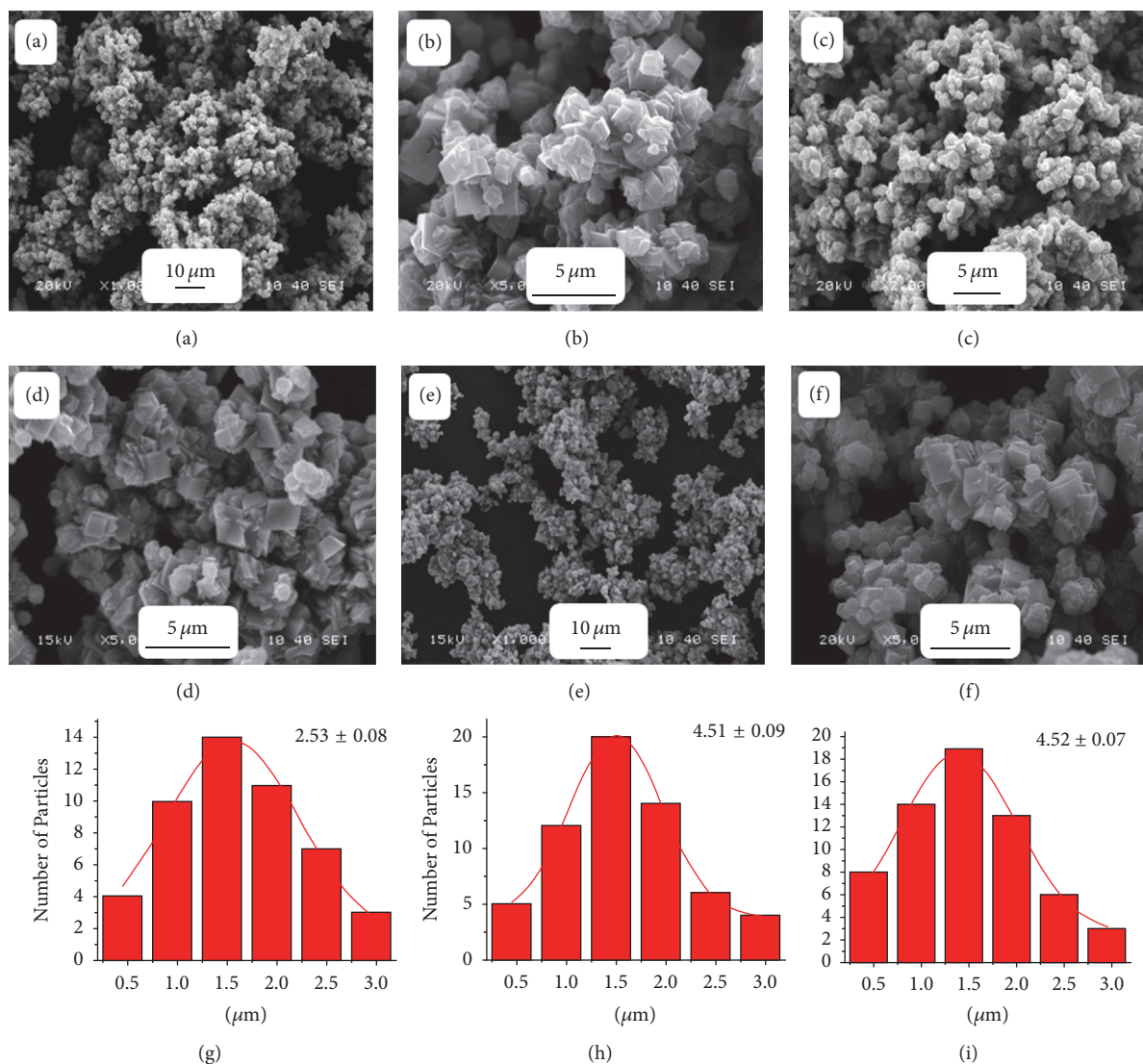
FIGURE 1: SEM analysis of the catalysts calcined at (a)-(b) 300°C; (c)-(d) 400°C; (e)-(f) 500°C; (a)-(b) overview image for as-prepared 1% ZnO_x–$MnCO_3$; (c)-(d) overview image of 1% ZnO_x–MnO_2; (e)-(f) overview image of 1% ZnO_x–Mn_2O_3; (g) particle size distribution of 1% ZnO_x–$MnCO_3$; (h) particle size distribution of 1% ZnO_x–MnO_2; (i) particle size distribution of 1% ZnO_x–Mn_2O_3.

2.3. Typical Procedure for Alcohol Oxidation. Liquid-phase oxidation of 1-phenylethanol was performed in glass flask equipped with a magnetic stirrer, reflux condenser, and thermometer. In a typical experiment, a mixture of the 1-phenylethanol (2 mmol), toluene (10 mL), and the catalyst (0.3 g) was transferred in a glass three-necked round-bottomed flask (100 mL); the resulting mixture was then heated to desired temperature with vigorous stirring. The oxidation experiment was started by bubbling oxygen gas at a flow rate of 20 mL/min into the reaction mixture. After the reaction, the solid catalyst was filtered off by centrifugation and the liquid products were analyzed by gas chromatography to determine the conversion of the alcohol and product selectivity by GC, 7890A, Agilent Technologies Inc., equipped with a flame ionization detector (FID) and a 19019S-001 HP-PONA column.

3. Results and Discussion

3.1. Characterization of the Catalysts. The as-synthesized catalysts surface morphology was analyzed by using scanning electron microscopy (SEM). The SEM images of the as-synthesized catalysts calcined at different temperatures, 1% ZnO_x–$MnCO_3$ at 300°C, 1% ZnO_x–MnO_2 at 400°C, and 1% ZnO_x–Mn_2O_3 at 500°C, exhibited morphology as shown in Figures 1(a)–1(e). The SEM image of the catalysts discloses well defined and spherical shaped morphology. Furthermore, it is observed that the morphology of the catalysts did not vary with the different calcination temperatures but it varies with size of the particles; as the calcination temperature increases ZnO_x NPs size increases and also the spherical shaped morphology of all the catalysts clearly exhibited in Figures 1(a)–1(e). The particle size distribution of SEM micrographs
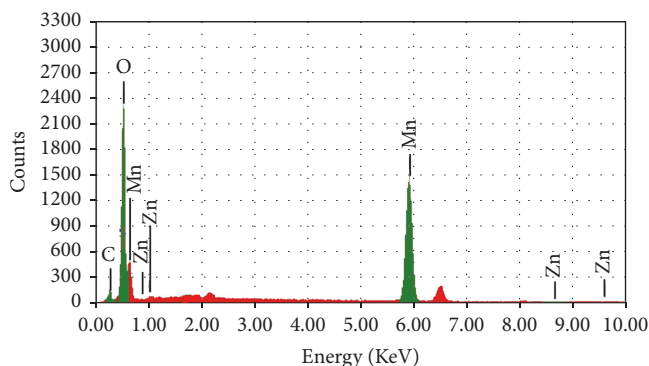
FIGURE 2: EDX analysis of the as-synthesized catalysts calcined 1% $ZnO_x–MnCO_3$.

FIGURE 3: XRD pattern of the catalyst 1% $ZnO_x–MnCO_3$ uncalcined and catalyst calcined at different temperatures 1% $ZnO_x–MnCO_3$; 1% $ZnO_x–MnO_2$; and 1% $ZnO_x–Mn_2O_3$.

of the as-synthesized catalysts, 1% $ZnO_x–MnCO_3$ calcined at different temperatures, 1% $ZnO_x–MnCO_3$ at 300°C, 1% $ZnO_x–MnO_2$ at 400°C, and 1% $ZnO_x–Mn_2O_3$ at 500°C, was assessed by using the program software J as shown in Figures 1(g)–1(i). The particle size was found to be approximately equal to 2.53, 4.51, and 4.79 μm in the catalyst precalcined at 300, 400, and 500°C correspondingly. From the attained results, it is noticed that while there is a variation in particle sizes among the precalcined catalysts 1% $ZnO_x–MnCO_3$ at 300°C and 1% $ZnO_x–MnO_2$ at 400°C, there is a merely small difference in the particle sizes among the precalcined catalysts 1% $ZnO_x–MnO_2$ at 400°C and 1% $ZnO_x–Mn_2O_3$ at 500°C.

3.2. Energy Dispersive X-Ray Spectroscopy (EDX) Analysis.
The elemental composition of the catalyst 1% $ZnO_x–MnCO_3$ at 300°C was investigated using energy dispersive X-ray spectroscopy (EDX). The intense signal at 5.5–6 keV strongly recommends that "Mn" was the major element, which has an optical absorption in this range due to the surface plasmon resonance (SPR). The signals at 0.8, 1.1, 8.6, and 9.6 strongly endorse that "Zn" was the element. It was also prominent that the other signals were also attained in the range 0.0–0.5 keV which denotes the typical absorption of carbon and oxygen. The found values of composition percentage of the Zn, Mn, and O_2 present in the catalyst were nearly identical to the values of the composition castoff in preparing the catalyst shown in Figure 2.

3.3. X-Ray Diffraction (XRD) Analysis.
The as-prepared catalysts crystal structure was analyzed by using X-ray diffraction (XRD). The XRD images of the catalysts 1% $ZnO_x–MnCO_3$ uncalcined and calcined at different temperatures, 1% $ZnO_x–MnCO_3$ at 300°C, 1% $ZnO_x–MnO_2$ at 400°C, and 1% $ZnO_x–Mn_2O_3$ at 500°C are shown in Figure 3. The found diffraction signals confirmed that as-synthesized catalysts are in crystalline nature. The calcined catalysts conceded various phases of manganese oxide alongside with the traces of ZnO_x. The uncalcined catalyst shows patterns which were obtained to be in agreement with the standard XRD data of rhodochrosite syn-$MnCO_3$ (JCPDS number 44-1472). With the calcination at 300°C the XRD pattern exhibits the existence of rhodochrosite D-$MnCO_3$ (JCPDS number
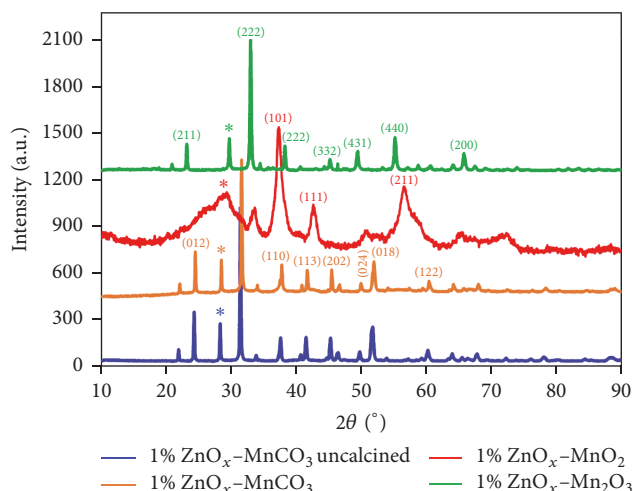
1-0981). Subsequently when the calcination temperature was further increased to 400°C the XRD spectra attained were in agreement with pyrolusite MnO_2 (JCPDS number 24-0735). When the catalyst was calcined at 500°C the XRD pattern obtained was in agreement with bixbyite-Mn_2O_3 (JCPDS number 2-0909). The reflections noticed with symbol asterisk (∗) might be owing to the occurrence of ZnO_x. The as-synthesized nanocomposite catalysts have been matched with known compounds stated in the literature.

3.4. Fourier Transform Infrared Spectroscopy (FTIR) Analysis.
The FTIR spectrum was used to classify the functional groups on the surface of the as-synthesized catalyst. The FTIR spectra of the catalysts at different calcination temperatures (300, 400, and 500°C), that is, 1% $ZnO_x–MnCO_3$, 1% $ZnO_x–MnO_2$, and 1% $ZnO_x–Mn_2O_3$, correspondingly are displayed in Figure 4. High wavenumber zone displays stretching vibrations of the surface hydroxyl group and physisorbed water. The characteristic bands of νOH located around 3475 cm^{-1} were found to be in the 300, 400, and 500°C calcined catalyst. The intensity of these bands decreases as the calcination temperature increase demonstrates the decrease of the existence of OH group and H_2O on the catalyst surface. The absorption band at around 1635 cm^{-1} resembles fingerprint bending vibration modes of hydroxyl groups [83]. Therefore, it can be said that OH group in the catalyst surface acts a significant part in the 1-phenylethanol oxidation, in which the 1% $ZnO_x–MnCO_3$ catalyst displays the highest catalytic performance associated with the other calcination temperatures [84]. In case of 300°C calcination temperature, the presence of a sharp peak at nearly 1356 cm^{-1} is a fingerprint for surface carbonate (CO_3^{-2}) group which confirmed the occurrence of carbonate group in the surface of the catalyst and these results are in good agreement with EDX and XRD results [85, 86]. In case of 400 and 500°C, that is, 1% $ZnO_x–MnO_2$ and 1% $ZnO_x–Mn_2O_3$ correspondingly, the absorption peak
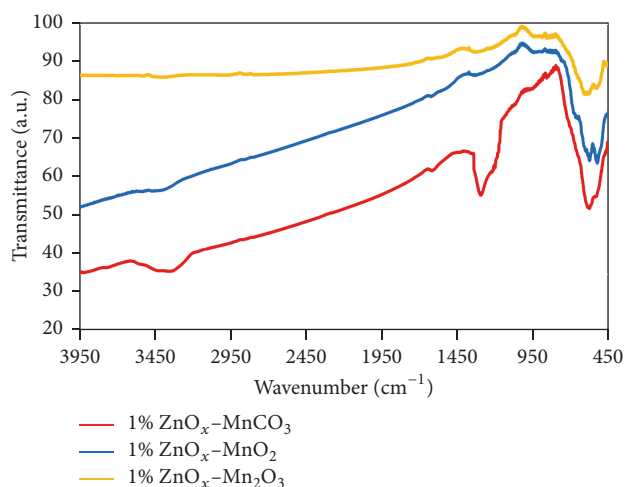
FIGURE 4: FTIR spectra of the catalyst calcined at different temperatures 1% ZnO_x–$MnCO_3$; 1% ZnO_x–MnO_2; and 1% ZnO_x–Mn_2O_3.

at around $1356\,cm^{-1}$ representing carbonate group almost disappears, maybe owing to manganese carbonate converted to manganese oxides at elevated temperature. Sharp peaks are attained in the range of 520–$610\,cm^{-1}$ typical for different oxides of manganese [87, 88].

3.5. High-Resolution Transmission Electron Microscopy (HRTEM) Analysis.
The HRTEM images of catalysts calcined at different temperatures, 1% ZnO_x–$MnCO_3$ at 300°C, 1% ZnO_x–MnO_2 at 400°C, and 1% ZnO_x–Mn_2O_3 at 500°C, are displayed in Figures 5(a)–5(c). Moreover, the HRTEM image reveals that the calcination temperature plays significant role in particle size. The particles size and agglomeration of the as-synthesized catalyst increase with increase of calcination temperature. It might also be owing to the decomposition of $MnCO_3$ to manganese oxide. The interplanar distance estimated from the HRTEM image of the catalysts calcined at 300°C (Figure 5(a)) revealed d-spacing of $0.29\,nm$ and $0.23\,nm$ resembles the (104) and the (110) planes of rhombohedral $MnCO_3$. The sample calcined at 400°C revealed d-spacing of $0.25\,nm$ resembled the (201) planes of MnO_2 (Figure 5(b)). For the sample calcined at 500°C (Figure 5(c)), the most noticeable lattice spacing resembles the (200) plane of α-Mn_2O_3.

3.6. Thermal Gravimetric Analysis.
For the as-synthesized catalyst calcined at different temperatures, 1% ZnO_x–$MnCO_3$ at 300°C, 1% ZnO_x–MnO_2 at 400°C, and 1% ZnO_x–Mn_2O_3 at 500°C, thermal stability was investigated by thermogravimetric analysis (TGA) as displayed in Figure 6. The thermogram of the as-synthesized catalyst calcined at 300°C demonstrates that the catalyst is steady up to 415°C with very insignificant percentage of weight loss that is less than 3%, due to the exclusion of volatile surface-absorbed water and volatile impurities. The highest loss of weight percentage was noticed by nearly 10%–12% in the temperature range of about 420–600°C which appears to be due to the loss of CO_2 of $MnCO_3$ to form MnO_2 and further oxidation of
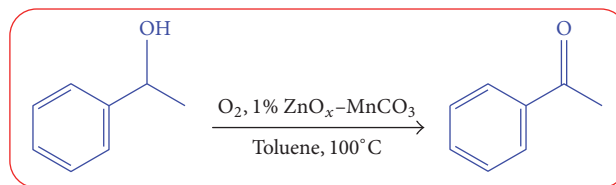
SCHEME 2: Aerial oxidation of 1-phenylethanol into acetophenone.

MnO_2 to Mn_2O_3 as indicated from the literature by Zhu et al. [89]. When the temperature is increased up to 800°C, the highest weight loss is noticed around 14%. Furthermore, the as-synthesized catalyst calcined at 400°C exhibited the maximum total weight loss percentage around 9% when the catalyst was heated up to 800°C, whereas in the case of the catalyst calcined at 500°C it displayed weight loss percentage of around 4%. Consequently, the catalysts displayed a thermal stability up to around 415°C and a marginally thermal stability decrease attained with raise in temperature.

3.7. Surface Area Measurements.
The surface area of the as-synthesized catalysts was studied using BET surface area analysis, in order to determine the surface area and to understand the relationship between surface area and catalytic activity of the as-prepared catalyst for the oxidation of 1-phenylethanol. Table 1 displayed that the specific surface area of the prepared catalyst calcined at different calcination temperature such as 300°C, 400°C, and 500°C, that is, 1% ZnO_x–$MnCO_3$, 1% ZnO_x–MnO_2, and 1% ZnO_x–Mn_2O_3, respectively, was about 120.26, 69.83, and $21.79\,m^2{\cdot}g^{-1}$, respectively. It can be observed that the catalyst with composition 1% ZnO_x–$MnCO_3$ calcined at 300°C has higher specific surface area than the catalyst obtained by calcining the prepared material at higher temperatures, that is, 400°C and 500°C. The results obtained suggest that at higher calcination temperatures there is a decrease in the surface area due to the sintering. Thus, this may partially be responsible for high catalytic performance in case of the catalyst calcined at 300°C, while in case of 400 and 500°C calcination treatment, there is a considerable decrease in the specific surface area, maybe due to agglomeration of ZnO_x NPs, which has negative effect on the catalyst functioning, which leads to poor alcohol conversion. From the above findings, it can be said that both calcination treatment and the surface area of the synthesized catalyst play a crucial role in the surface area of the synthesized catalyst, which in turn affects the working of the catalyst.

3.8. Catalytic Evaluation.
In order to get effective results, the various parameters such as various percentages weight of ZnO_x, reaction time, calcination temperature, catalyst amount, and reaction temperature were optimized as shown in Tables 1–4. For this purpose, the oxidation of 1-phenylethanol was chosen as a substrate model (Scheme 2).

3.8.1. Influence of Calcination Temperature.
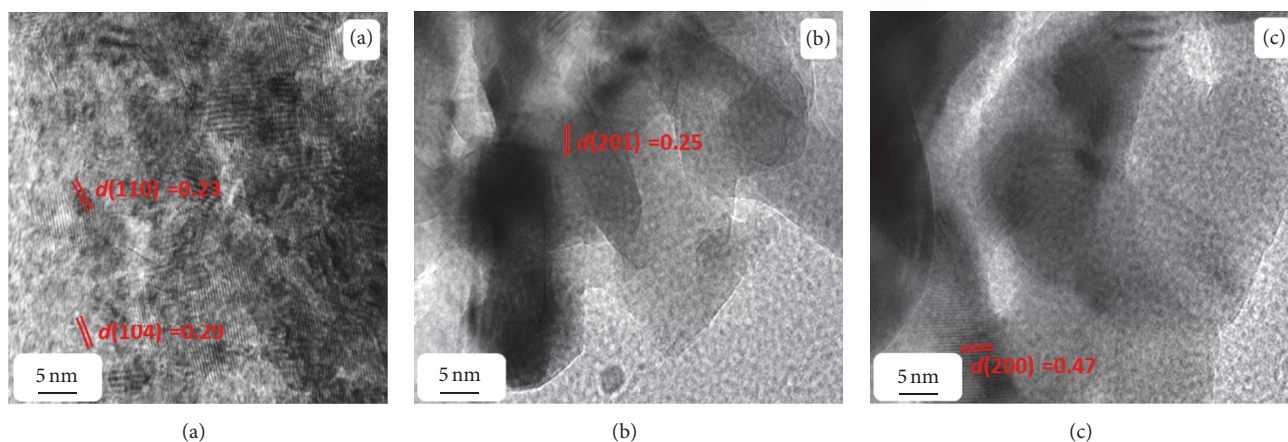The effect of calcination temperature on the oxidation of 1-phenylethanol

FIGURE 5: The HRTEM images of catalyst calcined at different temperatures: (a) 1% ZnO_x–$MnCO_3$; (b) 1% ZnO_x–MnO_2; and (c) 1% ZnO_x–Mn_2O_3.

TABLE 1: Catalytic oxidation of 1-phenylethanol in different calcination temperatures of the prepared catalysts.[a]

Entry	Catalyst	T (°C)	SA (m^2 g^{-1})	Conv. (%)	Sp. activity (mmol·g^{-1}·h^{-1})	TON	TOF (h^{-1})	Sel. (%)
1	1% ZnO_x–$MnCO_3$	300	120.26	100.00	22.22	54.25	180.83	>99
2	1% ZnO_x–MnO_2	400	69.83	81.49	18.11	44.21	147.37	>99
3	1% ZnO_x–Mn_2O_3	500	21.79	55.94	12.43	30.35	101.16	>99

[a] Reaction conditions: 2 mmol of 1-phenylethanol, 300 mg of catalyst, oxygen with rate 20 mL/min, reaction temperature at 100°C, 10 mL of toluene, and 18 min of reaction time.

TABLE 2: Effect of different weight % of ZnO_x on the 1-phenylethanol oxidation.[a]

Entry	Catalyst	Conv. (%)	Sp. activity (mmol·g^{-1}·h^{-1})	TON	TOF (h^{-1})	Sel. (%)
1	0% ZnO_x–$MnCO_3$	78.31	17.40	/	/	>99
2	1% ZnO_x–$MnCO_3$	100.00	22.22	54.25	180.83	>99
3	3% ZnO_x–$MnCO_3$	92.43	20.54	18.08	60.27	>99
4	5% ZnO_x–$MnCO_3$	72.29	16.06	10.85	36.17	>99
5	7% ZnO_x–$MnCO_3$	60.14	13.36	7.70	25.67	>99

[a] Reaction conditions: 2 mmol of 1-phenylethanol, 300 mg of catalyst, calcination temperature at 300°C, oxygen with rate 20 mL/min, reaction temperature at 100°C, 10 mL of toluene, and 18 min of reaction time.
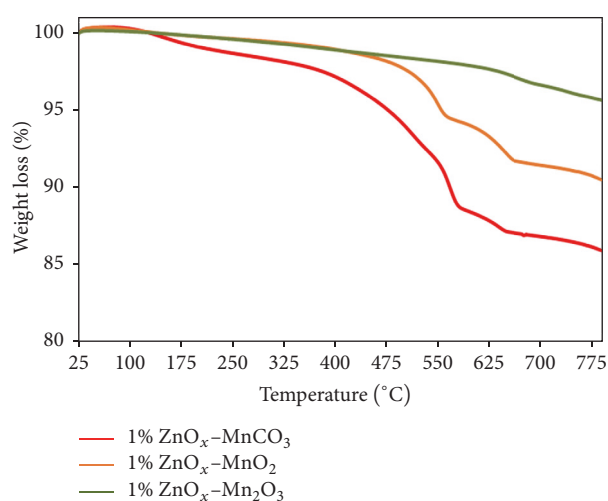

FIGURE 6: TGA of as-synthesized catalyst calcined at different calcination temperatures 300°C, 400°C, and 500°C; 1% ZnO_x–$MnCO_3$; 1% ZnO_x–MnO_2; and 1% ZnO_x–Mn_2O_3.

has been examined. The synthesized catalyst calcined at different temperatures such as 300°C, 400°C, and 500°C. The catalysts showed high product selectivity during all oxidation experiments (above 99%). Notwithstanding the oxidation of 1-phenylethanol is strongly affected by calcination temperature. The obtained results concluded that the applied calcination treatment has a marked inhibiting effect on the oxidation process by decreasing the alcohol conversion [90, 91]. For example, the catalyst calcined at 300°C, that is, 1% ZnO_x–$MnCO_3$, exhibits the highest alcohol conversion (100%) along with 22.22 mmol·g^{-1}·h^{-1} specific activity and 180.83 h^{-1} TOF, within 18 min of the reaction (Table 1, entry 1), while catalysts calcined at 400 and 500°C, that is, 1% ZnO_x–MnO_2 and 1% ZnO_x–Mn_2O_3, respectively, gave a lower conversion of 81.49% and 55.94%, respectively, under similar circumstances (Table 1, entries 2, 3). It is worth mentioning that these observations correlate with the BET surface area results of the prepared catalyst. 1% ZnO_x–$MnCO_3$, 1% ZnO_x–MnO_2, and 1% ZnO_x–Mn_2O_3 were 120.26, 69.83, and

TABLE 3: Effect of reaction temperature on the oxidation of 1-phenylethanol using 1% ZnO_x–$MnCO_3$ as the catalyst.[a]

Entry	T (°C)	Conv. (%)	Sp. activity (mmol·g^{-1}·h^{-1})	TON	TOF (h^{-1})	Sel. (%)
1	20	36.07	8.01	19.57	65.23	>99
2	40	52.84	11.74	28.67	95.57	>99
3	60	69.12	15.36	37.50	125.0	>99
4	80	84.69	18.82	45.94	153.13	>99
5	100	100.0	22.22	54.25	180.83	>99

[a]Reaction conditions: 2 mmol of 1-phenylethanol, 300 mg of catalyst, calcination temperature at 300°C, oxygen with rate 20 mL/min, 10 mL of toluene, and 18 min of reaction time.

TABLE 4: The effect of the catalyst 1% ZnO_x–$MnCO_3$ amount on the catalytic efficiency.[a]

Entry	Catalyst amount (mg)	Conv. (%)	Sp. activity (mmol·g^{-1}·h^{-1})	TON	TOF (h^{-1})	Sel. (%)
1	100	40.58	97.39	66.05	792.60	>99
2	200	56.13	67.36	45.67	548.04	>99
3	300	70.98	56.78	38.51	462.12	>99
4	400	86.01	51.61	34.96	419.52	>99
5	500	100	48.0	32.55	390.6	>99

[a]Reaction conditions: 2 mmol of 1-phenylethanol, calcination temperature at 300°C, oxygen with rate 20 mL/min, reaction temperature at 100°C, 10 mL of toluene, and 5 min of reaction time.

21.79 m^2·g^{-1}, respectively. As we mentioned, the prepared catalyst 1% ZnO_x–$MnCO_3$ exhibited the highest alcohol conversion and possessed the highest surface area among all other calcination temperatures. In contrast, the catalyst calcined at 400, that is, 1% ZnO_x–MnO_2, and 500°C, that is, 1% ZnO_x–Mn_2O_3, provided lesser activity and lower surface area. Therefore, it can be deduced that the catalytic activity is strongly influenced by calcination temperature of the catalyst. So we chose to use the catalyst calcined at 300°C, that is, 1% ZnO_x–$MnCO_3$, as the best calcination temperature to optimize other parameters. The results including 1-phenylethanol conversion, surface area, specific activity, turnover number (TON), turnover frequency (TOF), and acetophenone selectivity over the prepared catalyst were summarized in Table 1 and plotted in Figure 7.

3.8.2. Influence of the Amount of ZnO_x Promotor.
In order to get the best catalytic performance, the influence of % ZnO_x on the reaction yield was studied by varying load of ZnO_x on $MnCO_3$ support ranging from 0 to 7% and the graphical representation of the results has been shown in Figure 8 and listed in Table 2. The results showed that undoped $MnCO_3$ catalyst, that is, 0% ZnO_x–$MnCO_3$, gives about 78.31% conversion of 1-phenylethanol along with specific activity of 17.40 mmol·g^{-1}·h^{-1} within 18 min (Table 2, entry 1). However, after ZnO_x NPs doping on $MnCO_3$, the catalytic efficiency has been remarkably enhanced, where the 1% ZnO_x–$MnCO_3$ catalyst exhibits a full alcohol conversion under identical reaction conditions and the calculated specific activity was found to be 22.22 mmol·g^{-1}·h^{-1} and 180.83 h^{-1} TOF (Table 2, entry 2), whereas as the weight percentage of ZnO_x is further increased, the catalysts 3% ZnO_x–$MnCO_3$, 5% ZnO_x–$MnCO_3$, and 7% ZnO_x–$MnCO_3$ provided a lower alcohol conversion of 92.43, 72.29, and
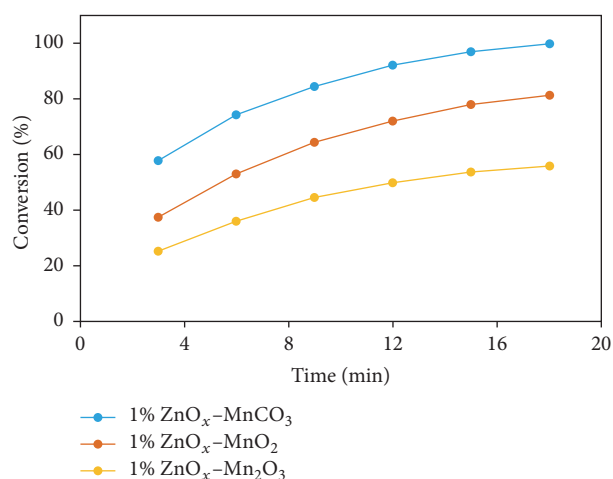

FIGURE 7: Graphical illustration of 1-phenylethanol oxidation using catalyst calcined at different calcination temperature.

60.14%, respectively. Additionally, the specific activity, TON, and TOF were found to decrease with increased ZnO_x content in the catalyst (Table 2, entries 3–5), although the selectivity towards acetophenone was more than 99% for all reactions. As illustrated in Figure 8, the ZnO_x NPs play a fundamental role in improving the catalytic performance for the selective oxidation of 1-phenylethanol. Moreover, as % ZnO_x increases the conversion of 1-phenylethanol decreases, probably due to the agglomeration of ZnO_x NPs in the catalyst surface or to a blocking of active sites as indicated by the results of the BET analysis. The results indicate that 1% ZnO_x–$MnCO_3$ catalyst was the best among all catalysts synthesized. Hence, we choose to use 1% ZnO_x–$MnCO_3$ in the further studies.
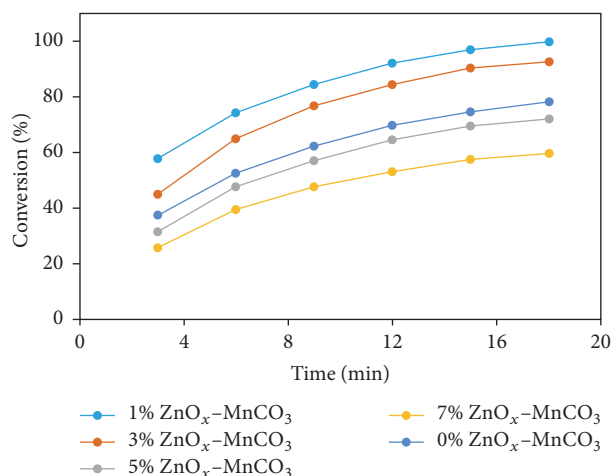
FIGURE 8: The effect of different weight % ZnO_x on the 1-phenylethanol oxidation.

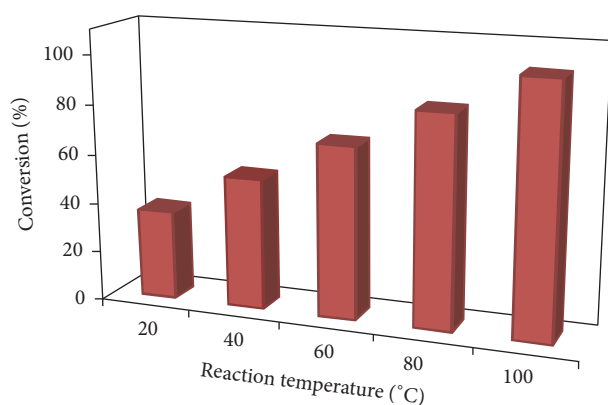FIGURE 9: Catalytic performance of 1% ZnO_x–$MnCO_3$ catalyst as a function of reaction temperature.

FIGURE 10: Catalytic activity of 1% ZnO_x–$MnCO_3$ catalyst as a function of catalyst amount.

3.8.3. Influence of Temperature. The effect of reaction temperature on the conversion of 1-phenylethanol and the acetophenone selectivity was investigated by considering five different temperatures in the range of 20–100°C. The results including alcohol conversion, specific activity, TON, TOF, and product selectivity have been summarized in Table 3 and plotted in Figure 9. The acetophenone selectivity was almost unchanged (>99%), whereas the conversion of 1-phenylethanol strongly depends on the reaction temperature. For instance, at low reaction temperature of 20°C, a relatively low alcohol conversion of 36.07% has been obtained (Table 3, entry 1). As expected, the high temperature contributed to a higher oxidation rate and led to the remarkable improvement of catalytic activity of the prepared catalyst. A full conversion of 1-phenylethanol was achieved at 100°C within relatively short reaction time (18 min) under identical reaction conditions (Table 3, entry 5). In addition, when the reaction temperature increased, the specific activity, TON, and TOF were also increased as shown in Table 3. Therefore, 100°C was chosen to be an optimum reaction temperature in this study to achieve highest catalytic performance.
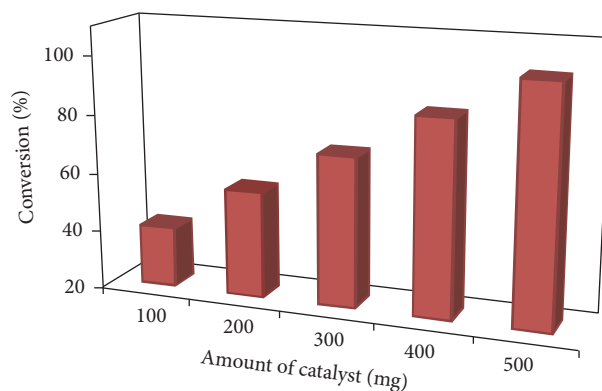
3.8.4. Influence of Catalyst Amount. The 1-phenylethanol conversion and the selectivity of acetophenone using different catalyst amounts were also evaluated, and the results are illustrated in Table 4 and Figure 10. The oxidation reaction was carried out in presence of 100, 200, 300, 400, and 500 mg of 1% ZnO_x–$MnCO_3$ catalyst under the optimized reaction conditions. It is noteworthy that the catalytic activity of the as-synthesized catalyst is directly proportional to the catalyst amounts. According to Table 4, the alcohol conversion increased from 40.58% to 100% by increasing the catalyst amount from 100 to 500 mg within short reaction time (5 min), whereas the product selectivity was almost unchanged during all oxidation processes (above 99%). Moreover, a blank reaction has also been examined in the absence of the catalyst. It was found that no formation of acetophenone was obtained, indicating that the catalyst is necessary for the oxidation of 1-phenylethanol.

Furthermore, in order to show the superior catalytic activity of the present catalytic system, the effectiveness of our catalytic system has been compared with the ones already reported in the scientific literature in the oxidation of 1-phenylethanol (Table 5). Obviously, the as-synthesized 1% ZnO_x–$MnCO_3$ is the most efficient catalyst among all the listed catalysts. Herein, the prepared catalyst has been used for 1-phenylethanol oxidation and exhibited a full conversion and selectivity within extremely short reaction time of 5 min at 100°C and highest specific activity (48 mmol·g^{-1}·h^{-1}) compared to all other listed catalysts. In contrast, all listed catalysts take a very long reaction time to completely oxidize 1-phenylethanol and require higher reaction temperature. For instance, Hosseini-Sarvari et al. [76] have prepared Ag nanoparticles doped ZnO support (Ag/ZnO) and used it as a catalyst for selective oxidation of alcohols to their corresponding carbonyls. The nano Ag/ZnO catalyst provided 90% conversion of 1-phenylethanol and more than 99% selectivity of acetophenone along with 30 mmol·g^{-1}·h^{-1} specific activity after long reaction time of 6 h at 100°C. In another example, Nepak and Darbha [70] reported liquid-phase selective alcohol oxidation over Au–Pd NPs doped in sodium titanate nanotubes (NaTNTs) as a catalyst. The Au–Pd/NaTNT catalyst exhibited 1-phenylethanol conversion of 84% and product

TABLE 5: A comparison between performance of our catalytic system and earlier reported catalysts for 1-phenylethanol oxidation.

Catalyst	Conv. (%)	Sel. (%)	T (°C)	Time	Sp. activity (mmol·g^{-1}·h^{-1})	Ref.
1% ZnO$_x$–MnCO$_3$	100	>99	100	5 min	48.0	This work
Cu/AlO(OH)	99	97	27	5 h	8.08	[66]
VOSO$_4$/TEMPO	99	96	80	2 h	37.78	[67]
SSDT	90	>99	reflux	1 h	1.8	[68]
Au/MgO	97	>99	130	2 h	19.4	[69]
Au–Pd/NaTNT	84	86	120	10 h	42.0	[70]
CdS-MTA	40	>99	5	1.5 h	0.60	[71]
Au–Pd/LDH	>99	>99	80	1.5 h	6.67	[72]
Au/TiO$_2$	100	>99	110	24 h	0.83	[73]
Fe(NO$_3$)$_3$·9H$_2$O/ABNO	87	>99	RT	4 h	5.44	[74]
FeCl$_3$-imine@SiO$_2$	90	>99	80	6 h	3.26	[75]
Ag/ZnO	90	>99	100	6 h	30.0	[76]
CoTE4PyP-MT	92	89	70	2 h	30.67	[77]
Mn(III)-salen	46.9	>99	20	40 min	5.77	[78]
5 wt% Ir/TiO$_2$	97	95	80	48 h	0.40	[79]
Ru/CaO–ZrO$_2$	>99	>98	40	6 h	1.67	[80]
CeCrO$_3$	100	100	90	6 h	15.15	[62]
Ru/Mg–LaO	96	>99	80	4 h	2.4	[81]
CoAl$_2$O$_4$	63.45	83.25	80	8 h	0.79	[34]
Fe$_3$O$_4$	76	>99	80	18 h	1.4	[82]

selectivity of about 86%, and the specific activity of this conversion was about 42 mmol·g^{-1}·h^{-1} within long reaction time of 10 h at higher reaction temperature of 120°C. As a result, the prepared 1% ZnO$_x$–MnCO$_3$ catalyst has been found to be the best choice for the alcohol oxidation.

3.9. Recycling Studies. The reusability of the catalyst has considerable importance from both commercial and academic point of view. In order to evaluate the recyclability and the stability, the oxidation of 1-phenylethanol was performed 5 times under optimum reaction conditions with the recycling of 1% ZnO$_x$–MnCO$_3$ catalyst and results are shown in Figure 11. After the first use of the catalyst in the oxidation of 1-phenylethanol to give acetophenone, the toluene was evaporated and fresh toluene was added and the mixture was filtered by centrifugation to recover the catalyst. The filtered catalyst was washed sequentially with toluene. The results revealed that the 1% ZnO$_x$–MnCO$_3$ catalyst was reused for at least 5 cycles with no appreciable decrease in its activity being observed and selectivity remained unchanged throughout all runs. During the five recycling reactions, the conversion of 1-phenylethanol decreased gradually from 100% to 92.37%, possibly due to the mass loss during the filtration method [92, 93]. Therefore, results indicate an excellent recyclability and stability of the as-prepared catalyst.

3.10. Oxidation of Different Types of Alcohols over 1% ZnO$_x$–MnCO$_3$ Catalyst. For evaluation of the catalyst capabilities, a variety of alcohols including secondary, benzylic aliphatic, primary allylic, and heteroatomic alcohols were subjected to oxidation with molecular O$_2$ under the optimized circumstances (Table 6, entries 1–26). The optimal
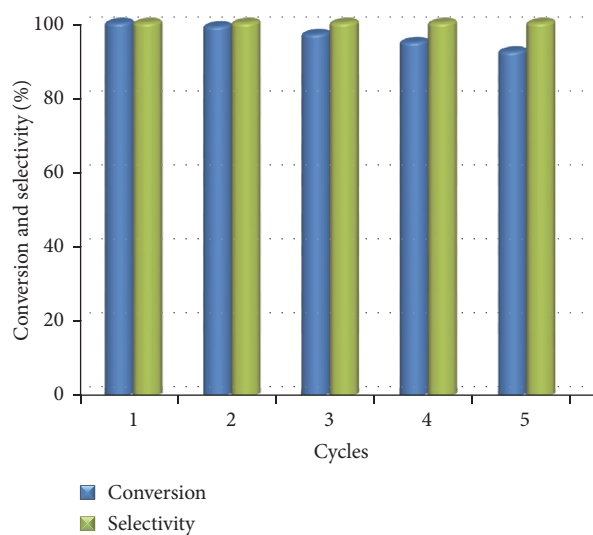

FIGURE 11: Recyclability of 1% ZnO$_x$–MnCO$_3$ for the aerial oxidation of 1-phenylethanol (reaction conditions: 2 mmol of 1-phenylethanol, calcination temperature at 300°C, oxygen with rate 20 mL/min, 0.5 g of catalyst, 10 mL of toluene, reaction temperature at 100°C, and 5 min of reaction time).

reaction conditions include 2 mmol of alcohol in 10 mL toluene with 20 mL/min oxygen flow rate and 100°C reaction temperature in presence of 1% ZnO$_x$–MnCO$_3$ catalyst (0.5 g) calcined at 300°C. The results are summarized in Table 6. The results showed that all secondary aromatic alcohols were selectively oxidized into their corresponding ketones with 100% convertibility under optimized circumstances (Table 6,

TABLE 6: Oxidation of different types of alcohols over 1% ZnO$_x$–MnCO$_3$ catalyst.[a]
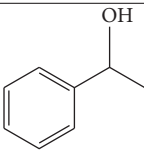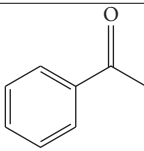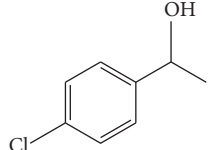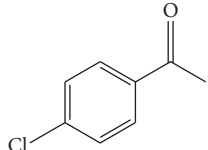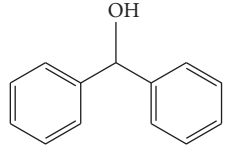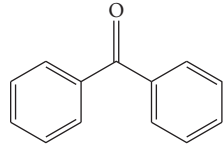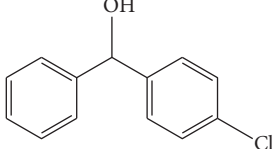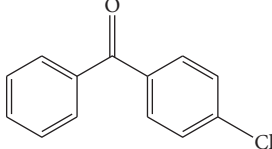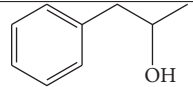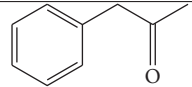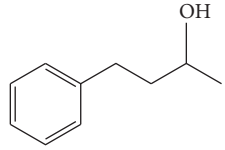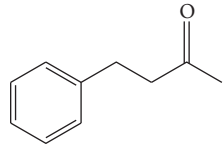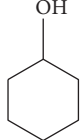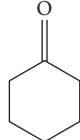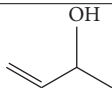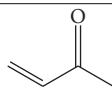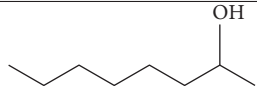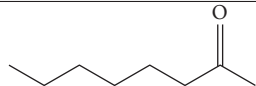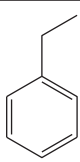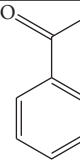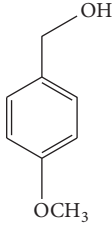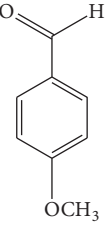
R. number	Reactants	Products	Time (min)	Conv. (%)	Sel. (%)
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2			8	100	>99
3			4	100	>99
4			6	100	>99
5			10	100	>99
6			13	100	>99
7			30	100	>99
8			80	100	>99
9			85	100	>99
10			4	100	>99
11			4	100	>99

TABLE 6: Continued.
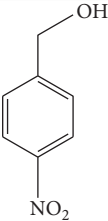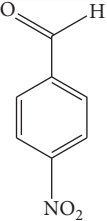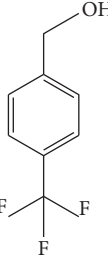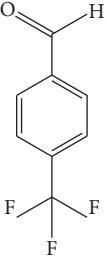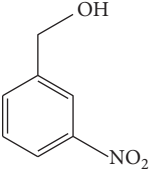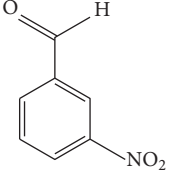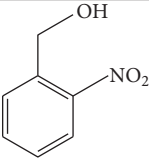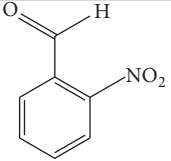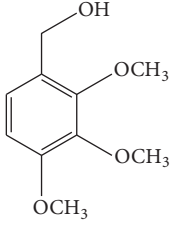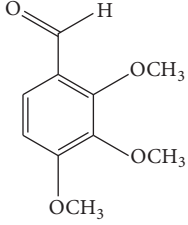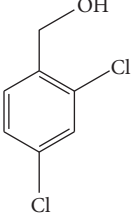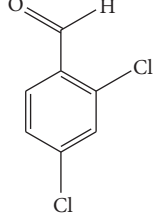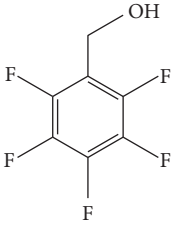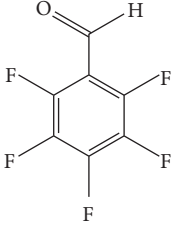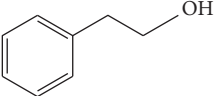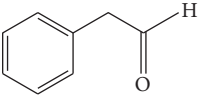
R. number	Reactants	Products	Time (min)	Conv. (%)	Sel. (%)
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13			8	100	>99
14			8	100	>99
15			11	100	>99
16			9	100	>99
17			12	100	>99
18			15	100	>99
19			10	100	>99

TABLE 6: Continued.

R. number	Reactants	Products	Time (min)	Conv. (%)	Sel. (%)
20			20	100	>99
21			7	100	>99
22			20	100	>99
23			35	100	>99
24			70	100	>99
25			75	100	>99
26			90	100	>99

[a] Reaction conditions: 2 mmol of alcohol, 0.5 g of catalyst, calcination temperature at 300°C, oxygen with rate 20 mL/min, reaction temperature at 100°C, and 10 mL of toluene.

entries 1–6). Additionally, an excellent selectivity (above 99%) towards ketones has been obtained throughout all oxidation processes and no by-products were found in the reaction mixture. It is noteworthy that the benzhydrol was demonstrated to be the most reactive among all secondary aromatic alcohols and gave 100% conversion after 4 min, while the 4-chlorobenzhydrol gave 100% conversion after longer reaction time, maybe because 4-chlorobenzhydrol contains electron-withdrawing group that deactivate the phenyl ring by decreasing the electron density (Table 6, entries 3 and 4). Furthermore, 1-phenylethanol and its derivatives also afforded complete conversion and more than 99% selectivity in relatively short reaction times (Table 6, entries 1 and 2). Commonly, the oxidation of aliphatic alcohols is much more difficult than aromatic ones [94–96]. Indeed, our catalytic protocol was also found to be effective for oxidation of secondary aliphatic alcohols to their corresponding ketones under the similar reaction conditions (Table 6, entries 7–9).

As expected, it was necessary to increase reaction time, because the oxidation of secondary aliphatic alcohols is more difficult than secondary aromatic alcohols; for example, 2-octanol required relatively longer reaction time (85 min) for complete oxidation to 2-octanone (Table 6, entry 9).

In order to exploit the applicability of the present catalytic system and to generalize the scope of the oxidation process, the oxidation reaction has extended to various types of alcohol such as primary aromatic, allylic, heteroaromatic, and aliphatic alcohols. Generally, all primary aromatic alcohols could be oxidized rapidly to the corresponding aldehydes with complete conversions within very short reaction times (Table 6, entries 10–22). Moreover, more than 99% selectivity to corresponding aldehydes has been achieved in most of oxidation reactions and no other products were detected in the reaction mixture because no overoxidation to carboxylic acids occurred. The oxidation of the primary benzylic alcohols was strongly influenced by the electronic properties of

the substituents on the benzyl group. In general, the oxidation rate of aromatic alcohols with electron-releasing groups was relatively higher than that of alcohols with electron-withdrawing group [13, 97, 98]. For instance, oxidation of an aromatic alcohol containing electron-donating group such 4-methoxylbenzyl alcohol gave 100% conversion only in 4 min (Table 6, entry 11), while oxidation of alcohol bearing electron-withdrawing group like 4-(trifluoromethyl)benzyl alcohol afforded 100% conversion within longer reaction time (8 min) (Table 6, entry 13). On the other hand, *para*-substituted alcohols have higher activities relative to *ortho*- and *meta*-substituent, probably because the *para*-position has minimum steric hindrance compared to other positions [99, 100]. For an example, *para*-nitrobenzyl alcohol was fully oxidized into its corresponding aldehyde within 7 min (Table 6, entry 12), while *meta*- and *ortho*-nitrobenzyl alcohol were completely oxidized after longer times, 8 and 11 min, respectively (Table 6, entries 14 and 15). Steric hindrance is another essential factor that affects the rate of the oxidation processes; the bulky groups such as 4-CF$_3$, 2,4-DiCl, 2,3,4-TriOMe, and 2,3,4,5,6-pentaflouro attached to benzyl alcohol decrease the performance of the oxidation reaction, maybe because of the steric resistance that impedes the oxidation of the alcohols bearing bulky substituents (Table 6, entries 13, 16–18). Cinnamyl alcohol, an example of allylic alcohols, has been completely oxidized to cinnamaldehyde with more than 99% cinnamaldehyde selectivity within 7 min (Table 6, entry 21). A heteroaromatic alcohol such as furfuryl alcohol has been converted to furfural within 20 min, with complete conversion and product selectivity (Table 6, entry 22). Furthermore, compared to primary aromatic alcohols, the oxidation of primary aliphatic alcohols exhibited relatively low reactivity towards oxidation reaction (Table 6, entries 23–26). In this regard, the oxidation of cyclohexanemethanol, 5-Hexen-1-ol, octan-1-ol, and citronellol into their corresponding aldehydes occurs in slightly longer reaction times (Table 6, entries 23–26). As a result, it can be said that the aerobic oxidation of alcohols catalyzed by 1% ZnO$_x$–MnCO$_3$ has been affected by two factors, electronic and steric effects.

4. Conclusions

In conclusion, ZnO$_x$ NPs doped MnCO$_3$ was found to be an efficient catalyst towards the catalytic oxidation of alcohols to carbonyls with molecular O$_2$ as a clean oxidant without using any additive or base. Interestingly, the ZnO$_x$ NPs play a fundamental role in the catalytic performance because the oxidation rate has remarkably improved after doping ZnO$_x$ NPs on MnCO$_3$. A complete 1-phenylethanol conversion can be accomplished within extremely short reaction time of only 5 min along with 48 mmol·g^{-1}·h^{-1} specific activity and 390.6 TOF. The obtained specific activity is much higher than that reported in earlier literatures. Additionally, wide range of benzylic, aliphatic, allylic, primary, and secondary alcohols has been studied for aerobic oxidation into their corresponding aldehydes and ketones with excellent alcohols conversion within relatively short reaction times under mild reaction conditions. Furthermore, the very high product selectivity (>99%) has been achieved for most of alcohols used in this work. The as-prepared catalyst can be recycled and reused for five times without any obvious loss of catalytic activity and the selectivity remained almost unchanged. This catalytic system offers several advantages including complete alcohol conversions and extremely high specific activities and selectivity towards products in extremely short reaction times by using ecofriendly, low cost, selective, facile synthesis, and reusable heterogeneous catalyst will make this system useful and applicable for the selective oxidation of alcohols.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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