Research Article

Comparative Catalytic Evaluation of Nano-ZrO$_x$ Promoted Manganese Catalysts: Kinetic Study and the Effect of Dopant on the Aerobic Oxidation of Secondary Alcohols

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This work reports the zirconia (ZrO$_x$) nanoparticles doped MnCO$_3$ catalysts prepared by facile and simple coprecipitation technique and the synthesis of zirconia-manganese carbonate [X% ZrO$_x$–MnCO$_3$] (where X% = 0–7%) catalyst which upon calcination at 400°C is converted to zirconia-manganese dioxide [1% ZrO$_x$–MnO$_2$] and when calcined at 500°C is converted to zirconia-manganic trioxide [1% ZrO$_x$–Mn$_2$O$_3$]. A comparative catalytic study was performed to investigate the catalytic efficiency between carbonate and oxides for the selective oxidation of 1-phenylethanol by using molecular O$_2$ as a clean oxidant. The influence of several parameters such as w/w% of ZrO$_x$, reaction time, calcination temperature, catalyst amount, and reaction temperature has been thoroughly examined using oxidation of 1-phenylethanol as a model substrate. The 1% ZrO$_x$–MnCO$_3$ precalcined at 300°C exhibited the best catalytic efficiency. It was found that ZrO$_x$ nanoparticles also play an essential role in enhancing the effectiveness of the catalytic system for the aerobic oxidation of alcohols. Furthermore, the physical and chemical properties of synthesized catalysts were evaluated by microscopic and spectroscopic techniques. An extremely high specific activity of 40 mmol·g^{-1}·h^{-1} with a 100% conversion of oxidation product and selectivity of >99% was achieved within extremely short reaction time (6 min).

1. Introduction

The catalytic oxidation of alcohols to carbonyl compounds is one of the most valuable and significant organic transformations in synthetic chemistry from the scientific and manufacturing perspective [1–5]. The oxidation products are significant intermediates in perfumes, confectionary, flame-retardants, dyestuffs, cosmetics, agrochemical, and pharmacological industries [6–9]. Conventionally, the oxidation of alcohols into their respective carbonyl compounds is achieved by adding stoichiometric quantities of chromate, hypochlorite, or permanganate as oxidants, which are not environmentally friendly as they are toxic and corrosive in nature [10, 11]. Moreover, the desired organic transformation requires harsh conditions such as high temperature and pressure. This process also has some drawbacks, it generates a huge quantity of pollutant and toxic by-products [12, 13]. In comparison, water is the only by-product, by using eco-friendly and low cost oxidants, such as molecular O$_2$ to produce carbonyl compounds, so this approach has gained significant attention from the economic and environmental prospective [14, 15]. Furthermore, there are many oxidation catalysts prepared by employing noble metals, such as gold [16–21], palladium [22–25], platinum [26, 27], rhodium [28, 29], and ruthenium [30, 31], which have been extensively utilized for the aerial oxidation of alcohols with high catalytic performances. Consequently, a significant effort has been made in order to explore eco-friendly and low cost catalysts
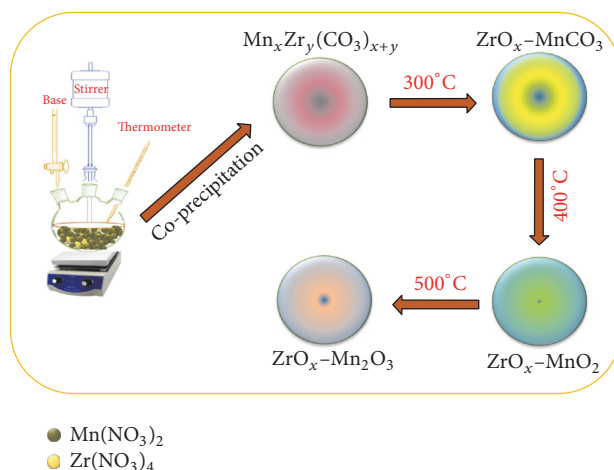
such as nonnoble metals like copper [32–34], cobalt [35–37], nickel [38–40], iron [41, 42], vanadium [43], silver [44], chromium [45, 46], molybdenum [47, 48], rhenium [49], and zinc [50–52] for aerobic oxidation of alcohols. In addition, it has been extensively reported that the catalytic activity of mixed metal oxide nanoparticles catalysts enhanced remarkably upon doping with other metals probably due to the extremely high surface area of metal nanoparticles [53, 54].

Furthermore, manganese carbonate and various mixed manganese oxide and noble metal doped/supported "Mn" oxides were extensively employed for the oxidation of numerous organic compounds, for instance, oxidation of naphthalene [55], carbon monoxide [56, 57], toluene [58], olefins [59], ethylene and propylene [60], cyclohexane [61], benzene [62], alkyl aromatics [63], nitrogen monoxide [64], and formaldehyde [65].

We have earlier reported mixed metal oxides [19, 44, 53, 54] and metal oxides doped with other transition metals nanoparticles as catalyst such as Ag NPs doped manganese dioxide [44]. With the continued interest in our studies to find new and improved catalysts we carried out a comparative study of ZrO_x–$MnCO_3$ or ZrO_x–Mn_2O_3 for the oxidation of primary alcohols [66] and it was found that the ZrO_x–$MnCO_3$ was an excellent catalyst for the oxidation of primary aromatic alcohols to corresponding aldehydes with molecular O_2. In the present report we extend the study further with respect to the oxidation of secondary alcohols. Herein, we report the synthesis of $X\%$ ZrO_x–$MnCO_3$ (where $X = 0, 1, 3, 5,$ and 7), followed by calcination at elevated temperatures, which yielded 1% ZrO_x–MnO_2 and 1% ZrO_x–Mn_2O_3. A comparative study of the catalysts towards the oxidation of secondary benzylic alcohols to the corresponding ketones was carried out employing molecular O_2 as green oxidizing agent and the results obtained were also compared with the results of the oxidation of primary alcohols and based on this detailed investigation some inferences have been drawn. The oxidation of 1-phenylethanol to acetophenone was selected as a model reaction for optimization of the process. The present procedure is simple, straightforward, mild, and environment-friendly and water is the only by-product in this reaction. It was found that all alcohols used in this study were completely oxidized to corresponding aldehydes and ketones without using any additives or base. Furthermore, the synthesized catalysts have characterized by several types of techniques such as SEM, EDX, TEM, XRD, TGA, and BET.

2. Materials and Methods

2.1. Materials. Manganese(II) nitrate-tetrahydrate (97%), zirconium nitrate (99%), sodium bicarbonate (99%), toluene (98%), benzyl alcohol (99.5%), biphenyl-4-methanol (98%), 2-phenylethanol (98%), furfuryl alcohol (98%), cinnamyl alcohol (98%), diphenylmethanol (99%), 4-chlorobenzhydrol (98%), 1-phenylethanol (98%), 1-(4-chlorophenyl)ethanol (98%), 1-phenyl-2-propanol (98%), 4-phenyl-2-butanol (97%), cyclohexanemethanol (99%), 1-octanol (99%), 5-hexen-1-ol (98%), β-citronellol (98%), cyclohexanol (99%),

Mn$_x$Zr$_y$(CO$_3$)$_{x+y}$ ZrO$_x$–MnCO$_3$

ZrO$_x$–Mn$_2$O$_3$ ZrO$_x$–MnO$_2$

● Mn(NO$_3$)$_2$
● Zr(NO$_3$)$_4$

SCHEME 1: Graphical representation of the preparation of ZrO_x–Mn carbonate and oxides.

3-buten-2-ol (97%), and 2-octanol (99%) were purchased from Sigma Aldrich, St. Louis, MO 63118, USA.

2.2. Catalyst Preparation. ZrO_x nanoparticles doped $MnCO_3$ catalysts of the type $X\%$ ZrO_x–$MnCO_3$ (where $X = 0, 1, 3, 5,$ and 7) were prepared via coprecipitation method where $X\%$ denotes w/w%. Stoichiometric amounts of manganese (II) nitrate-tetrahydrate ($Mn(NO_3)_2 \cdot 4H_2O$) and zirconium nitrate ($Zr(NO_3)_2$) were dissolved in distilled water. About 100 mL of the stoichiometric mixture of solutions was taken in a round bottomed flask. The solution was heated to 100°C, while stirring was carried on a mechanical stirrer and 0.5 M solution of sodium hydrogen carbonate ($NaHCO_3$) was added dropwise until the solution attained pH = 9. The solution was continuously stirred at the same temperature for about 3 hours and then left on stirring overnight at room temperature. The solution was filtered using a Buchner funnel under vacuum and the product obtained was dried at 70°C overnight and calcined at different temperatures (Scheme 1).

2.3. Catalyst Characterization. The morphology of the as-synthesized nanocomposite was examined by SEM (Jeol SEM model JSM 6360A (Japan)). Quantitative analysis of the nanocomposite was performed by energy-dispersive X-ray spectroscopy (EDX). Transmission electron microscopy (TEM) was carried out using Jeol TEM model JEM–1101 (Japan), which was castoff to identify the size and shape of nanoparticles. Powder X-ray diffraction studies were carried out using Altima IV [Make: Regaku] X-ray diffractometer. BET surface area was investigated on NOVA 4200e surface area and pore size analyzer. The thermal stabilities of the nanoparticles were characterized by thermogravimetric analysis (TGA), using a Pyris 1 TGA instrument (PerkinElmer, USA), with a heating rate of 10°C/min under a nitrogen gas flow at 20 mL/min. The temperature range was maintained from room temperature to 800°C using a ceramic pan.
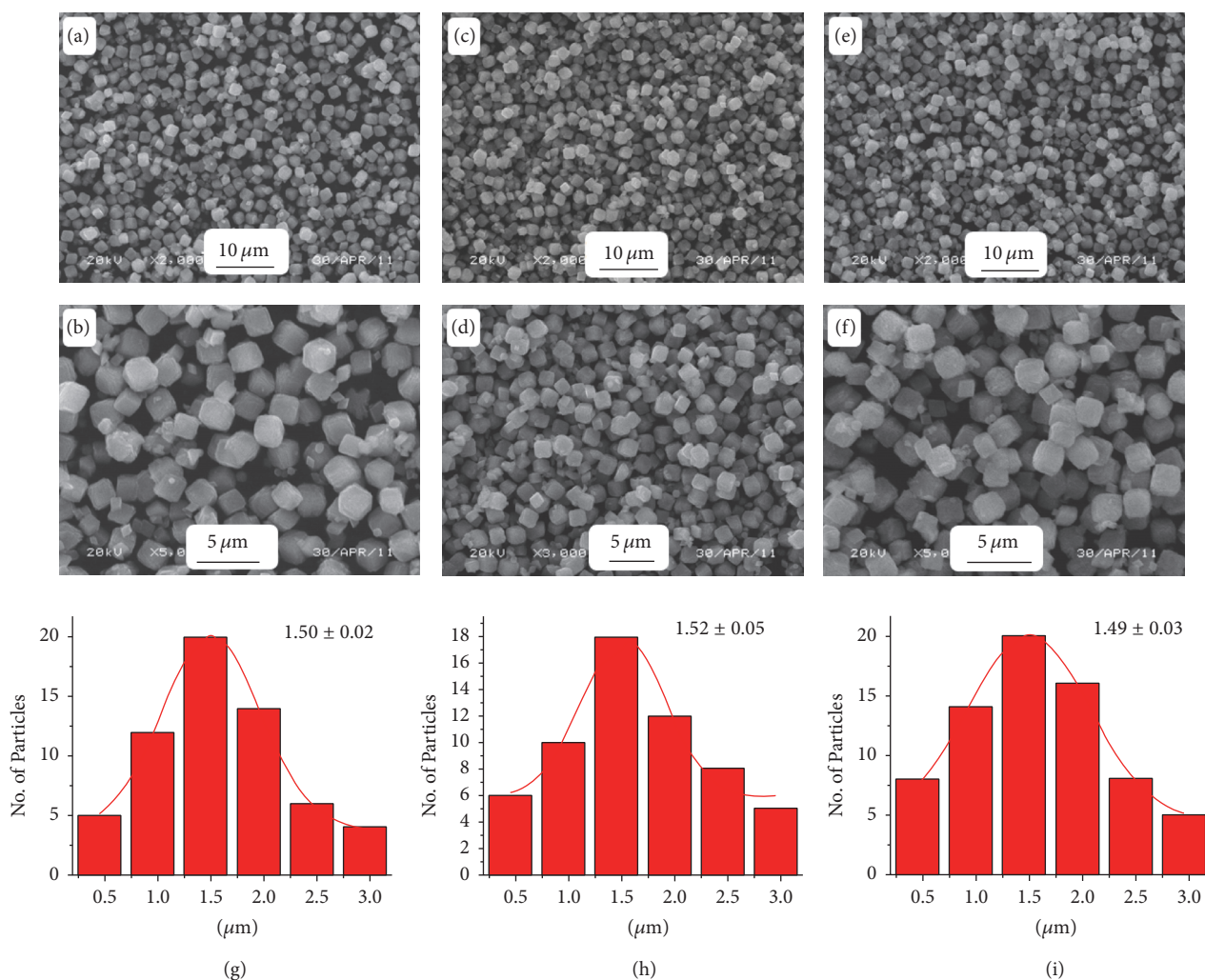
FIGURE 1: SEM analysis of the as-synthesized catalysts calcined at (a-b) 300°C; (c-d) 400°C; (e-f) 500°C. (a-b) Overview image for as-synthesized 1% ZrO_x–$MnCO_3$; (c-d) overview image of 1% ZrO_x–MnO_2; (e-f) overview image of 1% ZrO_x–Mn_2O_3; (g) particle size distribution of 1% ZrO_x–$MnCO_3$; (h) particle size distribution of 1% ZrO_x–MnO_2; (i) particle size distribution of 1% ZrO_x–Mn_2O_3.

2.4. General Procedure of Oxidation of Alcohols. The protocol followed for the oxidation of alcohols is as previously reported [66].

3. Results and Discussion

3.1. Characterization of the Catalysts

3.1.1. Morphology and Phase Structure. The prepared catalyst by coprecipitation technique was calcined at 300°C, 400°C, and 500°C. The scanning electron microscopy (SEM) micrographs of the as-synthesized catalyst 1% ZrO_x–$MnCO_3$ and the product 1% ZrO_x–$MnCO_3$ calcined at temperature 300°C, 1% ZrO_x–MnO_2 at 400°C, and 1% ZrO_x–Mn_2O_3 at 500°C are displayed in Figure 1. The SEM micrographs exhibit particles with a well-defined cuboidal morphology. The particle size distribution graph was obtained by using Image J software program (Figures 1(g), 1(h), and 1(i)) and exhibits merely small differences in the particle sizes with

changes in calcination temperature. The elemental composition of the catalyst is examined using energy-dispersive X-ray spectroscopy (EDX) and stays within experimental error to the theoretical composition.

3.1.2. Energy-Dispersive X-Ray Spectroscopy (EDX) Analysis. Moreover, the elemental composition of the zirconia/manganese carbonate nanocomposite was also investigated by energy-dispersive X-ray spectroscopy (EDX), which discloses the elemental composition summary of the catalyst prepared as displayed in Figure 2. The intense signal at 5.5–6 keV strongly indicates that "Mn" was the major element, which has an optical absorption in this range due to the surface plasmon resonance (SPR). The mass % ratio of Mn found to be 98.41% which are almost close to theoretical value 99% as shown in Figure 2. A signal at 2 keV strongly corresponds to the presence of "Zr" element. It was also eminent that the other signals were also found in the range
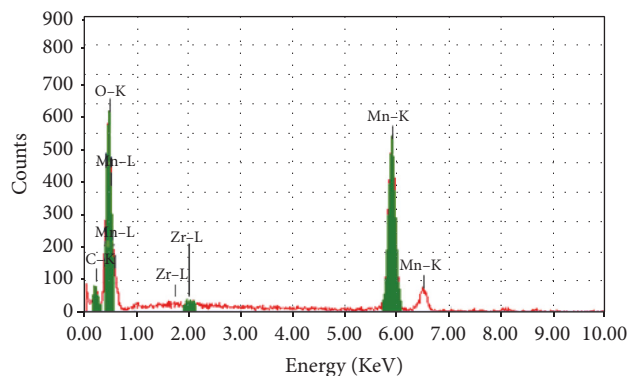
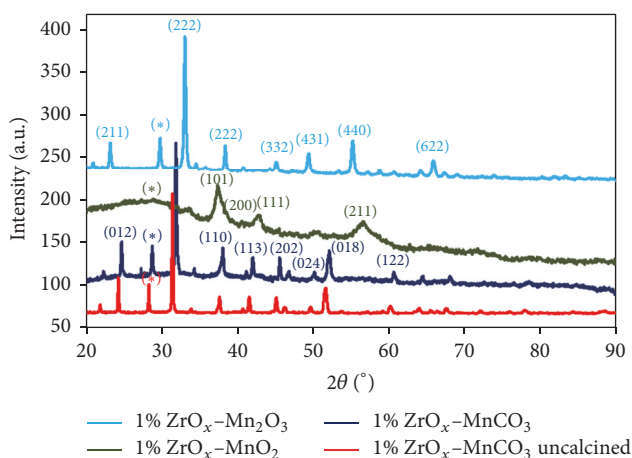FIGURE 2: Elemental composition from the EDX analysis of the as-synthesized catalysts calcined 1% ZrO_x–$MnCO_3$.

FIGURE 4: The HRTEM images of 1% ZrO_x–$MnCO_3$ nanocomposite.

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

FIGURE 5: Thermogravimetric analysis of catalyst calcined at different temperatures 300°C, 400°C, and 500°C; 1% ZrO_x–$MnCO_3$; 1% ZrO_x–MnO_2; and 1% ZrO_x–Mn_2O_3.

0.0–0.5 keV, which signifies the typical absorption of carbon and oxygen.

3.1.3. XRD Analysis. XRD analysis was used to determine the crystal structure of the nanosized ZrO_x doped $MnCO_3$ catalyst uncalcined (1% ZrO_x–$MnCO_3$) and calcined at 300, 400, and 500°C. Figure 3 displays the existence of rhodochrosite and syn manganese carbonate (JCPDS number 00–007–0268) with space group R–3c (167) which upon calcination at 300°C transformed to rhodochrosite manganese carbonate oxides (JCPDS number 00–001–0981) (space group R–3c (167)) (Figure 3). Calcination at 400°C leads to the formation of MnO_2 (JCPDS–ICDD number 00–44–0141). In case of calcination at 400°C as shown in Figure 3 the X-ray diffraction pattern exhibits an amorphous form. Calcination at 500°C leads to the formation of bixbyite Mn_2O_3 (JCPDS number 00–002–0909) (Figure 3). The reflections marked with asterisk (∗) could be due to the presence of ZrO_x. The synthesized nanocomposite catalysts have been compared with known compounds stated in the literature.
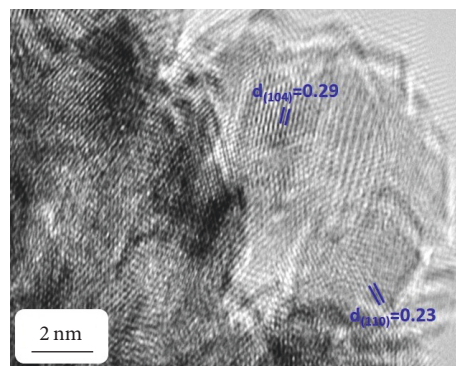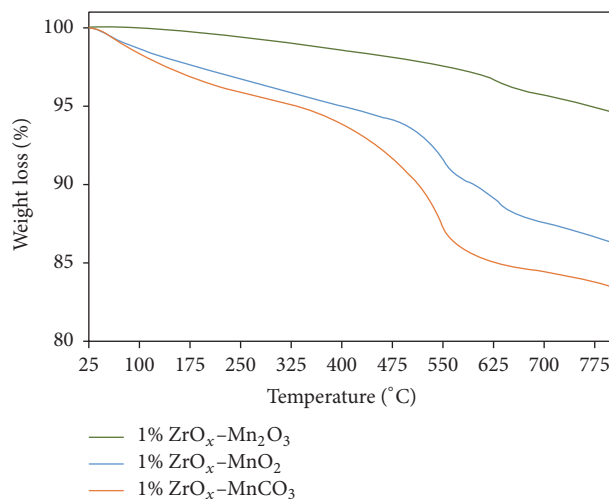
3.1.4. High-Resolution Transmission Electron Microscopy (HRTEM) Analysis. The HRTEM images of 1% ZrO_x–$MnCO_3$ nanocomposite obtained after calcination at 300°C (Figure 4) exhibit polycrystalline particles with clear lattice fringes. The interplanar distance calculated from the HRTEM image of the sample calcined at 300°C (Figure 4) revealed d-spacing 0.29 nm and 0.23 nm corresponding to the (104) and the (110) planes of rhombohedral $MnCO_3$ and the similar type of polycrystalline particles with clear lattice fringes structures was noticed from the samples 1% ZrO_x–MnO_2 calcined at 400°C and 1% ZrO_x–Mn_2O_3 at 500°C.

3.1.5. Thermogravimetric Analysis. Thermogravimetric analysis is a sensitive method that measures mass changes in a sample as it is heated. This method is particularly advantageous for determining degradation of samples at different temperatures. The thermogravimetric analysis was accompanied to notice the change in the weight of the synthesized doped and ZrO_x/$MnCO_3$ nanocomposite catalysts. Figure 5 displays that a gradual weight loss occurred from room temperature to 800°C. Figure 5 shows typical TGA

TABLE 1: Effect of the calcination temperature on the catalytic activities of 1% ZrO_x–$MnCO_3$ for the selective oxidation of 1-phenylethanol.[a]

Entry	Catalyst	T (°C)	SA (m^2g^{-1})	Conv. (%)	Sp. activity (mmol·g^{-1}·h^{-1})	Sel. (%)
1	1% ZrO_x–$MnCO_3$	300	133.58	100.00	20.0	>99
2	1% ZrO_x–MnO_2	400	53.19	70.13	14.03	>99
3	1% ZrO_x–Mn_2O_3	500	17.48	61.34	12.27	>99

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

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

Entry	Catalyst	Conversion (%)	Sp. activity (mmol·g^{-1}·h^{-1})	Sel. (%)
1	0% ZrO_x–$MnCO_3$	80.36	16.07	>99
2	1% ZrO_x–$MnCO_3$	100.00	20.00	>99
3	3% ZrO_x–$MnCO_3$	95.41	19.08	>99
4	5% ZrO_x–$MnCO_3$	63.97	12.80	>99
5	7% ZrO_x–$MnCO_3$	42.46	8.49	>99

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

thermogram of the synthesized 1% ZrO_x–$MnCO_3$ catalyst in nitrogen environment. The thermal stability of the 1% ZrO_x–$MnCO_3$ calcined at 300°C, 1% ZrO_x–MnO_2 calcined at 400°C, and 1% ZrO_x–Mn_2O_3 attained after calcining at 500°C catalysts was determined using TGA (Figure 5). The catalyst calcined at 300°C was stable up to 410°C with a slight weight loss of <8% ascribed to loss of physisorbed moisture. Increasing the temperature leads to a further weight loss of 15% in the temperature range between 405 and 605°C, which appears to be due to the loss of CO_2 of $MnCO_3$ to form MnO_2 and further oxidation of MnO_2 to Mn_2O_3 as stated from the literature by Zhu et al. [81]. These findings are in agreement with the results (5% weight loss) obtained for heating the catalysts calcined at 500°C.

3.1.6. BET Analysis. The surface area of the synthesized catalysts was investigated using BET sorption measurements, in order to determine the surface area and deduce the relationship between surface area and catalytic activity of the as-synthesized catalyst for the present study of oxidation of secondary alcohols. Table 1 exhibited that the specific surface area of the synthesized catalyst calcined at different temperatures such as 300°C, 400°C, and 500°C, that is, 1% ZrO_x–$MnCO_3$, 1% ZrO_x–MnO_2, and 1% ZrO_x–Mn_2O_3, respectively, was about 133.58, 53.19, and 17.48 m^2·g^{-1}, respectively. It can be observed that the 1% ZrO_x–$MnCO_3$ (i.e., the synthesized material calcined at 300°C temperature) have higher specific surface area when compared to the catalysts 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 sintering. Thus, this may partially be responsible for high catalytic efficiency in case of the catalyst calcined at 300°C, whereas, in case of 400 and 500°C calcination temperature, there is a considerable decrease in the specific surface area, possibly due to the agglomeration of ZrO_x NPs, which has adverse effect on the
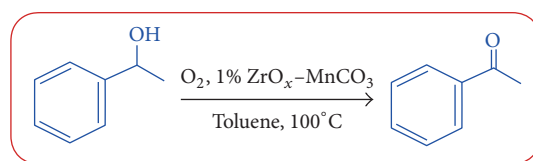
SCHEME 2: Aerobic oxidation of 1-phenylethanol to acetophenone.

catalyst functioning, which leads to poor alcohol conversion. From the above findings, it can be said that calcination treatment of the catalysts plays a significant role in changing the surface area of the as-prepared catalysts, which in turn affects the functioning of the catalyst.

3.2. Catalytic Performances. In order to evaluate the catalytic performance of the prepared material, the aerobic oxidation of secondary alcohol using 1-phenylethanol was used as the model reactant (Scheme 2). This particular reaction was also used as an ideal reaction for optimizing the reaction conditions for other reactions. The effects of several parameters such as effect of % loading of promoter ZrO_x, reaction time, calcination temperature of the catalyst, catalyst dosage employed, and reaction temperature were studied in detail and the results are presented in Tables 1–4.

3.2.1. Effect of Calcination Temperature on the Catalytic Performance. The catalytic activity of the prepared catalyst calcined at various temperatures 300°C, 400°C, and 500°C, that is, 1% ZrO_x–$MnCO_3$, 1% ZrO_x–MnO_2, and ZrO_x–Mn_2O_3, respectively, was studied. It was found that the catalysts studied exhibited a variation in catalytic performance indicating the effect of calcination temperature [13]; nevertheless all the catalysts displayed high selectivity towards acetophenone (>99%). For instance, the catalyst calcined at 300°C, that is, 1% ZrO_x–$MnCO_3$, exhibited the highest catalytic conversion

TABLE 3: Effect of reaction temperature on the catalytic performance.[a]

Entry	Reaction temp. ($^\circ$C)	Conv. (%)	Sp. activity (mmol·g^{-1}·h^{-1})	Sel. (%)
1	20	44.82	8.96	>99
2	40	60.05	12.01	>99
3	60	74.53	14.91	>99
4	80	87.96	17.59	>99
5	100	100	20.0	>99

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

TABLE 4: Effect of catalyst amount in oxidation of 1-phenylethanol.[a]

Entry	Catalyst amount (mg)	Conv. (%)	Sp. activity (mmol·g^{-1}·h^{-1})	Sel. (%)
1	100	41.81	83.62	>99
2	200	57.66	57.66	>99
3	300	72.43	48.29	>99
4	400	86.75	43.38	>99
5	500	100	40.0	>99

[a] Reaction conditions: 2 mmol of 1-phenylethanol, calcination temperature at 300°C, oxygen with rate 20 mL min^{-1}, reaction temperature at 100°C, 10 mL of toluene, and 6 min of reaction time.

yielding 100% conversion of 1-phenylethanol within 20 min and the specific activity calculated was found to be about 20.0 mmol·g^{-1}·h^{-1} (Table 1, entry 1). Further, similar studies employing the other catalysts, obtained by calcining the as-prepared material at different temperatures such as 400°C and 500°C, that is, 1% ZrO$_x$–MnO$_2$ and 1% ZrO$_x$–Mn$_2$O$_3$, were carried out; it was found that the catalyst calcined at 400°C, that is, 1% ZrO$_x$–MnO$_2$, yielded ~70% alcohol conversion, while the catalyst calcined at 500°C, that is, 1% ZrO$_x$–Mn$_2$O$_3$, yielded ~61% conversion. Moreover, as the calcination temperature has evident effect on the surface area of the catalyst, this in turn has an effect on the catalytic performance of the catalyst. Hence, in order to draw a correlation between the calcination temperature and surface area, the surface area of the prepared catalysts was determined employing BET; the results are tabulated in Table 1. It was observed that the specific surface area of the prepared catalyst calcined at various temperatures, that is, 1% ZrO$_x$–MnCO$_3$, 1% ZrO$_x$–MnO$_2$, and ZrO$_x$–Mn$_2$O$_3$, was 133.58, 53.19, and 17.48 m^2·g^{-1}, respectively. The catalyst 1% ZrO$_x$–MnCO$_3$ calcined at 300°C was found to possess the highest surface area among all other catalysts obtained after calcination at different temperatures. Interestingly, the catalyst calcined at 300°C, that is, 1% ZrO$_x$–MnCO$_3$, possesses highest surface area and gave a 100% conversion product, while the catalyst calcined at 400 and 500°C, that is, 1% ZrO$_x$–MnO$_2$ and ZrO$_x$–Mn$_2$O$_3$, was found to possess lower surface area also showing lower 1-phenylethanol conversion. Hence, it can be concluded that the catalytic performance was strongly affected by calcination treatments of the catalyst. Therefore, we chose to use 300°C as the best calcination temperature to optimize other parameters. The results including alcohol conversion, surface area, specific activity, and acetophenone selectivity over the catalyst was listed in Table 1 and plotted in Figure 6.
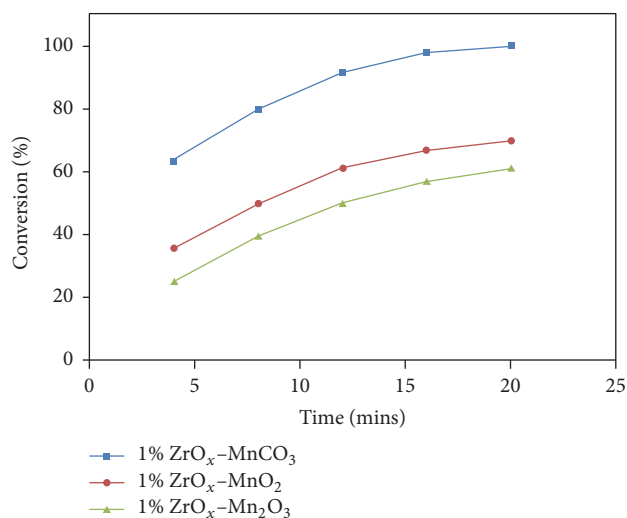

FIGURE 6: Graphical representation of 1-phenylethanol oxidation using catalyst calcined at different calcination temperatures.

3.2.2. Effect of % of ZrO$_x$ on the Catalytic Performance.

As implied by the literature, the presence of a promoter in a catalytic system enhances the catalytic performance of the catalyst many folds. In the present study in order to study the effect of the presence of ZrO$_x$ as promoter and to assess the optimum % of ZrO$_x$ doping on MnCO$_3$ for best catalytic activity as catalyst for secondary alcohol oxidation, we examined the effect of % ZrO$_x$ in the catalytic system by varying load of ZrO$_x$ on MnCO$_3$ supports from 0 to 7% in the catalyst MnCO$_3$, that is, calcined at 300°C and the obtained catalysts were tested for their catalytic activity. It was found that undoped manganese carbonate catalyst (0% ZrO$_x$–MnCO$_3$) gave about 80.36%
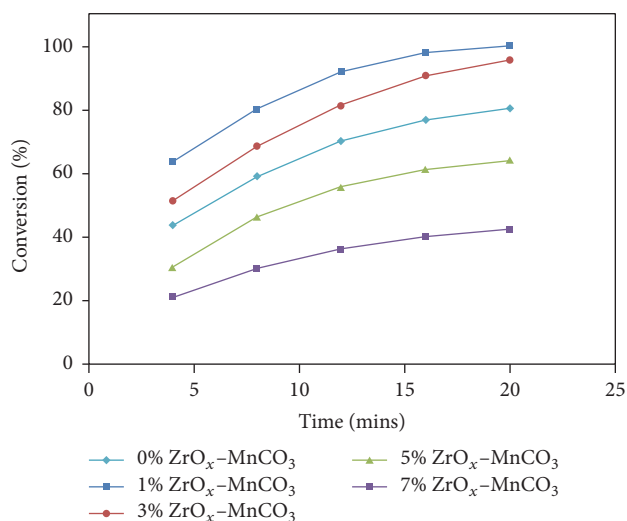
FIGURE 7: The effect of different weight % ZrO_x on the oxidation of 1-phenylethanol.

FIGURE 8: Catalytic performance of 1% ZrO_x–$MnCO_3$ catalyst as a function of reaction temperature.

conversion of 1-phenylethanol within 20 min of reaction time, and the calculated specific activity was found to be 16.07 mmol·g^{-1}·h^{-1} (Table 2, entry 1). However, after doping ZrO_x nanoparticles on $MnCO_3$, the catalytic performance remarkably improved, and the resultant catalyst yielded a 100% conversion of 1-phenylethanol within 20 min with a specific activity of 20.0 mmol·g^{-1}·h^{-1} (Table 2, entry 2), while, the other catalysts with higher % of ZrO_x nanoparticles doping, that is, 3% ZrO_x–$MnCO_3$, 5% ZrO_x–$MnCO_3$, and 7% ZrO_x–$MnCO_3$, yielded lower percentage of alcohol conversion with 95.41, 63.97, and 42.46%, respectively, resulting in the decrease in the specific activity of the catalyst from 19.08 to 8.49 mmol·g^{-1}·h^{-1} (Table 2, entries 3–5). In addition, the selectivity towards acetophenone remains almost constant (<99) throughout all experiments. From the results obtained it can be concluded that ZrO_x nanoparticles play a crucial role in enhancing the catalytic efficiency for the aerobic oxidation of 1-phenylethanol into acetophenone, however as the % of ZrO_x increases beyond 1%, a negative impact on the catalytic performance of the catalyst was observed, which may be due to the agglomeration of ZrO_x nanoparticles. Therefore, the 1% ZrO_x–$MnCO_3$ catalyst was the best catalyst among all catalysts synthesized. Consequently, we choose to use 1% ZrO_x–$MnCO_3$ for further optimization studies. Graphical representation of the results is plotted in Figure 7 and is listed in Table 2.

3.2.3. Effect of Reaction Temperature on the Catalytic Performance. Further studies towards evaluating the influence of reaction temperature on the selective oxidation of 1-phenylethanol was carried out in presence the 1% ZrO_x–$MnCO_3$ catalyst. The temperature of the reaction was altered from 20°C to 100°C and the results include alcohol conversion, specific activity, and selectivity to acetophenone which was monitored. The results obtained by carrying out the reaction at temperatures such as 20, 40, 60, 80, and 100°C
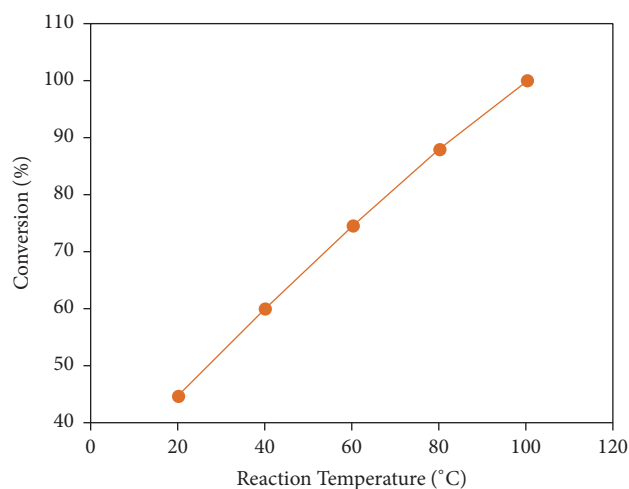
are summarized in Table 3 and plotted in Figure 8. It was found that the rate of oxidation reaction of 1-phenylethanol to acetophenone is very much dependent on the reaction temperature. From the results obtained it was found that the optimum temperature for the complete conversion of 1-phenylethanol to acetophenone is 100°C with the specific activity of 20.0 mmol·g^{-1}·h^{-1}. At lower reaction temperatures it was found that the same catalyst yields a conversion of 1-phenylethanol ranging from 44.82% obtained at 20°C (Table 3, entry 1) to 87.96% obtained at 80°C (Table 3, entry 4). However, the selectivity towards acetophenone remained unchanged with >99% while the reaction temperature was varied. Therefore, it was realized that the optimum reaction temperature for this conversion is 100°C, which was used for all the further studies carried out.

3.2.4. Effect of Catalyst Amount on the Catalytic Performance. The catalyst quantity also has significant effect on the catalytic performance for any conversion reaction; hence a study was carried out to optimize the amount of catalyst required for the oxidation of 1-phenylethanol. The oxidation process was carried out using 100, 200, 300, 400, and 500 mg of catalyst calcined at 300°C, that is, 1% ZrO_x–$MnCO_3$ under the conditions optimized from the earlier study. The selectivity towards acetophenone was almost constant throughout all oxidation experiments (<99%), whereas the 1-phenylethanol conversion increases with catalyst amount increasing. The results revealed that, in presence of a low catalyst concentration (100 mg), a low conversion of 41.81% was obtained, which may be owing to the occurrence of fewer catalytic active sites (Table 4, entry 1). As expected, by increasing the catalyst amount to 200 mg, the alcohol conversion also increases to 57.66% (Table 4, entry 2). When the catalyst amount was increased to 500 mg the complete conversion product was obtained within a short reaction time (6 min), with the specific activity of 40.0 mmol·g^{-1}·h^{-1} (Table 4,

TABLE 5: Comparison between our work and earlier publications for the selective oxidation of 1-phenylethanol into acetophenone.

Catalyst	Conv. (%)	Sel. (%)	T (°C)	Time (h)	Sp. activity (mmol·g^{-1}·h^{-1})	Ref.
1% ZrO$_x$–MnCO$_3$	100	>99	100	0.1	40.0	This work
NbP–S2	72	100	90	24	2.74	[3]
VOPO$_4$	38.5	89	80	6	8.02	[8]
Pd/GC	18.9	>99.9	110	6	0.50	[15]
Ru/Mg–LaO	96	>99	80	4	2.4	[9]
FeAPO	56.2	100	70	6	7.45	[67]
CoAl$_2$O$_4$	63.45	83.25	80	8	0.79	[36]
POM/ZrO$_2$	88	>99	RT	3	11.73	[68]
Fe(NO$_3$)$_3$·9H$_2$O	92	>99	RT	48	1.92	[69]
Ru/CaO–ZrO$_2$	>99	>98	40	6	1.67	[70]
CuZnO	>99	>99	RT	3	33.33	[50]
NG900	1.8	>98	70	3	0.02	[51]
Oxo–V SB/G	89	>99	65	0.33	13.35	[71]
Cu(II)–Zn(II)	78	>99	100	14	16.39	[52]
Fe$_3$O$_4$	76	>99	80	18	1.4	[72]
UiO–66–Sal–CuCl$_2$	45	99	60	24	4.34	[73]
Co(II)/ZnO	95	100	70	13	1.45	[74]
CeCrO$_3$	100	100	90	6	15.15	[75]
Co(acac)$_2$	94	100	40	7	6.1	[76]
Na/CoCl$_3$	99	100	RT	46	0.43	[77]
Au/HT	99	99	RT	6	416	[78]
Au/CeO$_2$	>99	>99	100	5	173	[79]
Pd/HAP	>99	>99	90	1	208	[80]

entry 5). From this study, it can be said that the complete oxidation of 1-phenylethanol into acetophenone can be attained within 6 min with 500 mg of the catalyst. A linear relationship was found between the catalyst amount and alcohol conversion as shown in Figure 9. Under the optimum conditions, a blank reaction was also examined in the absence of the catalyst. No formation of acetophenone was observed in this case which indicates that the prepared catalyst plays a fundamental role in the aerial oxidation of 1-phenylethanol.

In order to recognize the performance of the catalyst in comparison to the previously reported studies, a list of reported catalysts has been compiled as shown in Table 5, which demonstrates the results of 1-phenylethanol oxidation by molecular O$_2$ in the presence of various catalysts [3, 8, 9, 15, 36, 52, 67–80, 82]. It was found that the prepared 1% ZrO$_x$–MnCO$_3$ catalyst is the utmost effective catalyst among all the mentioned catalysts. In present work, the prepared 1% ZrO$_x$–MnCO$_3$ catalyst is used for the selective oxidation of 1-phenylethanol to acetophenone and exhibited a complete conversion and good selectivity within extremely short reaction time of 6 min at 100°C and highest specific activity (40.0 mmol·g^{-1}·h^{-1}) when compared to the other catalysts for the same oxidation reaction, since the other catalysts reported require a longer reaction time to complete oxidation of 1-phenylethanol, higher reaction temperature, or lower specific activity. For example, Du et al. [8] reported liquid phase selective oxidation of 1-phenylethanol to acetophenone
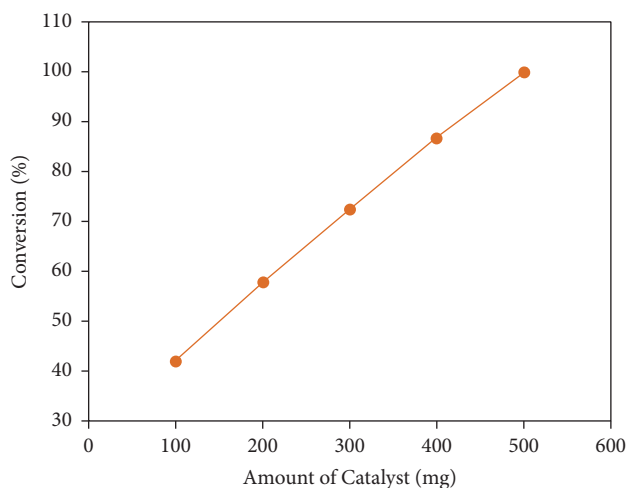

FIGURE 9: Catalytic activity of 1% ZrO$_x$–MnCO$_3$ catalyst as a function of catalyst amount.

using VOPO$_4$ catalyst in combination with TEMPO with molecular O$_2$ using water as a solvent. The VOPO$_4$ catalyst exhibits relatively low alcohol conversion of 38.5%, selectivity to acetophenone about 89%, and the specific activity of this conversion around 8.02 mmol·g^{-1}·h^{-1} within long reaction time of 6 h at 80°C. In another example, Farhadi
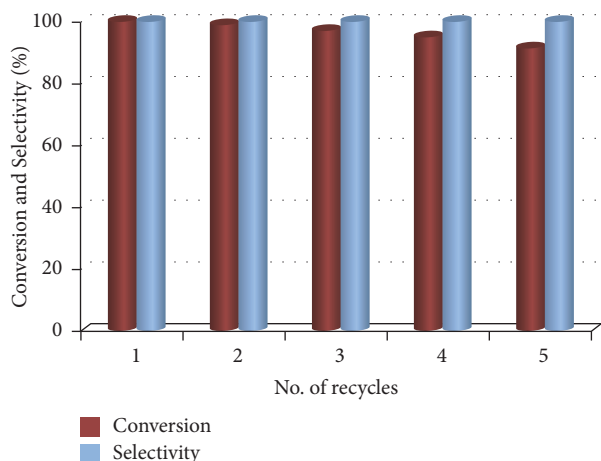
FIGURE 10: The reusability of 1% ZrO_x–$MnCO_3$ catalyst in the oxidation of 1-phenylethanol. (Reaction conditions: 2 mmol of 1-phenylethanol, calcination temperature at 300°C, oxygen with rate 20 mL min^{-1}, 0.5 g of catalyst, reaction temperature at 100°C, 10 mL of toluene, and 6 min of reaction time.)

and Zaidi [68] have synthesized a polyoxometalate-zirconia (POM/ZrO_2) nanocomposite by sol-gel technique used for aerobic oxidation of 1-phenylethanol to acetophenone. The POM/ZrO_2 nanocomposite exhibited 88% alcohol conversion and more than 99% acetophenone selectivity along with 11.3 mmol·g^{-1}·h^{-1} specific activity after relatively long reaction time 3 h at room temperature. From the above findings, it can be deduced that the synthesized 1% ZrO_x–$MnCO_3$ catalyst was found to be the best choice for this oxidation reaction.

3.3. Catalyst Recovery. The catalyst reusability has significant importance from both economic and academic point of view; hence the recyclability of 1% ZrO_x–$MnCO_3$ for the selective oxidation of 1-phenylethanol was evaluated under optimal circumstances and the results are shown in Figure 10. During this study after the completion of oxidation reaction, the solvent toluene was evaporated, and to the recovered catalyst toluene was added, and the mixture was filtered by simple filtration. The filtered catalyst is washed with toluene again to assure that the remnant from the previous reaction is completely washed off; then the recovered catalyst was dried at 100°C for 4 h. This process was repeated for five cycles and it was found that apparently there is no appreciable decrease in the activity of the catalyst. During the five recycling reactions, the alcohol conversion decreased from 100% to 91.4%, probably due to the catalyst loss during the filtration method [83]. Moreover, the selectivity of the catalyst towards acetophenone is intact even after subsequent reuse. Thus, the results indicate that the catalyst, that is, 1% ZrO_x–$MnCO_3$, has a perfect recyclability and stability.

3.4. Oxidation of a Variety of Alcohols with Molecular Oxygen Catalyzed by 1% ZrO_x–$MnCO_3$ Catalyst. Using the optimized conditions including 2 mmol of alcohol in 10 mL toluene with 20 mL min^{-1} oxygen flow rate and 100°C reaction temperature in presence of 1% ZrO_x–$MnCO_3$ catalyst (0.5 g) calcined at 300°C, the conversion of a wide range of alcohols including secondary, primary, benzylic, aliphatic, heteroatomic, and allylic alcohols was carried out to understand the catalytic performance of the catalyst against various substrates. It was observed that the alcohols were oxidized into their corresponding carbonyl derivatives in different reaction times (Table 6, entries 1–18). According to Table 6, all secondary benzylic alcohols have completely converted into their corresponding ketones in extremely short reaction times (Table 6, entries 1–6). An excellent selectivity towards ketones (<99) has been achieved in most of oxidation reactions and no by-products were detected in the reaction mixture. Benzhydrol was the most reactive among all secondary benzylic alcohol and gave 100% conversion within only 5 min (Table 6, entry 3). It can be noted that the 4-chlorobenzhydrol required longer reaction time than benzhydrol to complete the conversion, possibly due to the presence of electron-withdrawing chloro group, that deactivates the aromatic ring by decreasing the electron density (Table 6, entry 4). Moreover, 1-phenylethanol and its derivatives also exhibited complete conversion and more than 99% selectivity in relatively short reaction times (Table 6, entries 1 and 2). Commonly, the oxidation of aromatic alcohols is much easier than aliphatic counterparts [84–86]. Besides, compared to secondary aromatic alcohols the oxidation of secondary aliphatic alcohols to their corresponding ketones exhibited relatively low reactivity towards oxidation process (Table 6, entries 7–9). For instance, the secondary aliphatic alcohols such as cyclohexanol (Table 6, entry 7) require longer reaction times than that of the secondary aromatic alcohols as reported in the case of various other catalysts; hence it can be said that the catalyst is selective towards aromatic alcohols. As expected, it was necessary to increase reaction period, owing to the fact that oxidation of aliphatic alcohols is more difficult than that of secondary aromatic alcohols.

When the other primary, benzylic, allylic, heteroaromatic, and aliphatic alcohols were subjected to oxidation using the similar catalyst, the corresponding aldehydes were formed with varying reaction times under optimum conditions (Table 6, entries 10–18). Thus, the catalyst 1% ZrO_x–$MnCO_3$ demonstrates excellent catalytic activity against aromatic alcohols (primary and secondary aromatic, allylic, and heteroatomic) when compared to the aliphatic alcohols. Although, in case of aliphatic alcohols, 100% conversion was obtained, the reactions require a longer time. Clearly, the studied catalyst demonstrates the selectivity towards aromatic alcohols. Furthermore, it can be concluded that the catalytic performance is affected by the electronic and steric factors.

4. Conclusions

In conclusion, ZrO_x nanoparticles doped $MnCO_3$ was introduced as an efficient, cheap, and recyclable catalyst for the selective oxidation of secondary alcohol into their corresponding carbonyl compounds with O_2 as a green oxidant under base-free condition. Interestingly, the catalytic performance $MnCO_3$ as oxidation catalyst was enhanced

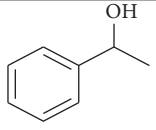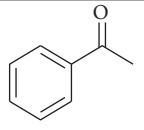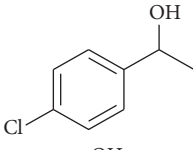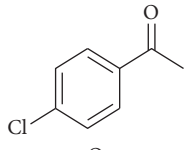TABLE 6: Oxidation of a variety of alcohols catalyzed by 1% ZrO$_x$–MnCO$_3$.[a]
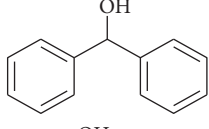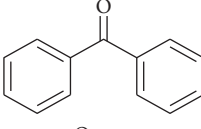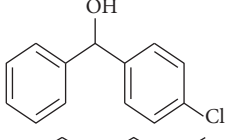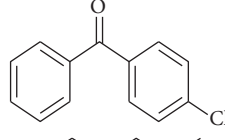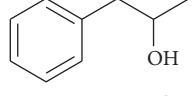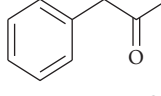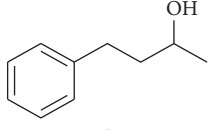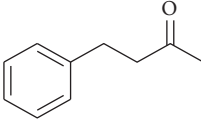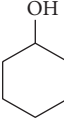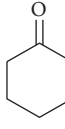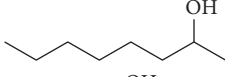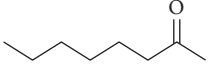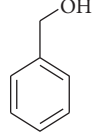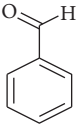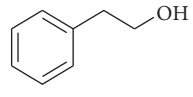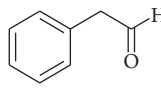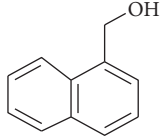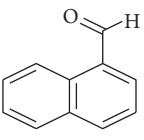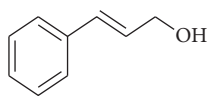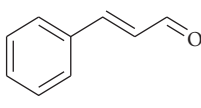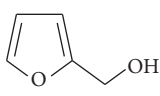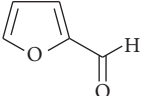
Entry	Substrate	Product	Time (min)	Conv. (%)	Sel. (%)
1			6	100	>99
2			9	100	>99
3			5	100	>99
4			7	100	>99
5			11	100	>99
6			15	100	>99
7			30	100	>99
8			75	100	>99
9			90	100	>99
10			5	100	>99
11			9	100	>99
12			20	100	>99
13			8	100	>99
14			18	100	>99

Table 6: Continued.

Entry	Substrate	Product	Time (min)	Conv. (%)	Sel. (%)
15			25	100	>99
16			75	100	>99
17			80	100	>99
18			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^{-1}, 10 mL of toluene, and reaction temperature at 100°C.

remarkably after doping ZrO_x NPs on $MnCO_3$ and it exhibited superior catalytic efficiency in the aerial oxidation of 1-phenylethanol to acetophenone compared to the results reported earlier. An extremely high specific activity of 40.0 mmol·g^{-1}·h^{-1} and complete alcohol conversion with more than 99% selectivity towards acetophenone has been achieved in short reaction time (6 min). In addition, wide range of benzylic, aliphatic, and allylic alcohols was also studied for selective oxidation into their corresponding carbonyl compounds, which yielded complete convertibility within short reaction times under mild reaction conditions. This catalytic system was found to possess several advantages such as 100% conversion within very short reaction times with very high specific activities and excellent selectivities. Therefore, the catalyst developed and the optimized reactions can be applicable for aerobic oxidation of other alcohols.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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