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## ORIGINAL ARTICLE

# Ceria doped mixed metal oxide nanoparticles as oxidation catalysts: Synthesis and their characterization



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**Abstract** Mixed metal nanoparticles (NPs) have attracted significant attention as catalysts for various organic transformations. In this study, we have demonstrated the preparation of nickel–manganese mixed metal oxide NPs doped with  $X\%$  nano cerium oxide ( $X = 1, 3, 5 \text{ mol}\%$ ) by a facile co-precipitation technique using surfactant and surfactant free methodologies. The as-synthesized materials were calcined at different temperatures (300 °C, 400 °C, and 500 °C), and were characterized using various spectroscopic techniques, including, FTIR and XRD. SEM analysis, TEM analysis and TGA were employed to evaluate the structural properties of the as-prepared catalyst. These were evaluated for their catalytic behaviour towards the conversion of benzyl alcohol to benzaldehyde, which was used as a model reaction with molecular oxygen as oxidant. Furthermore, the effect of the variation of the percentage of nano ceria doping and the calcination temperature on the performance of as-prepared mixed metal catalysts was also evaluated. The kinetic studies of the reactions performed employing gas chromatographic technique have revealed that the mixed metal oxide catalyst doped with 5% nano ceria displayed excellent catalytic activity, among various catalysts synthesized.

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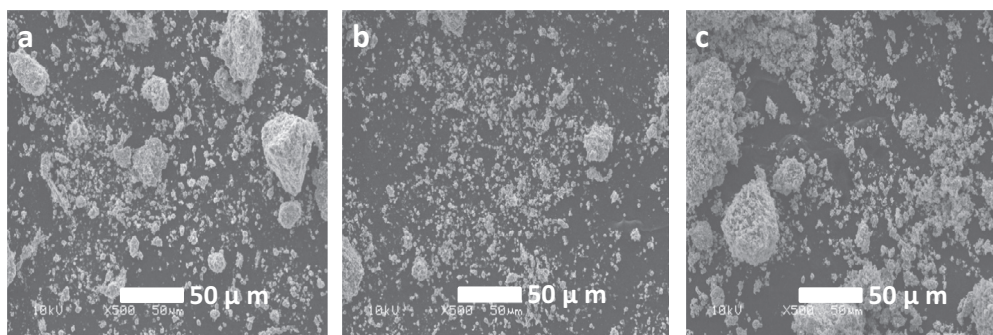
## 1. Introduction

Oxidation catalysis is one of the most important subjects for the scientists around the world due to its evident role played in the industrial process for the production of high value chemicals. Among various oxidation reactions, oxidation of alcohols has been studied extensively, which commonly leads

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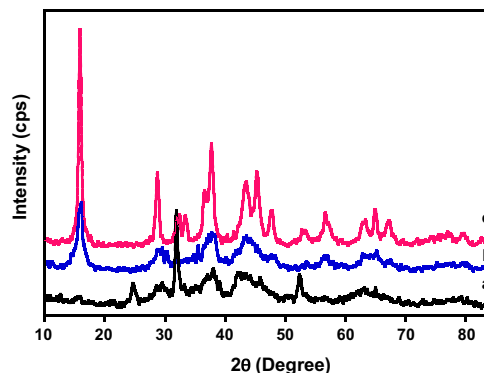
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**Figure 1** SEM images of CeO<sub>2</sub> (5%)–NiMnO calcined at different temperatures (a) 300 °C, (b) 400 °C and (c) 500 °C.

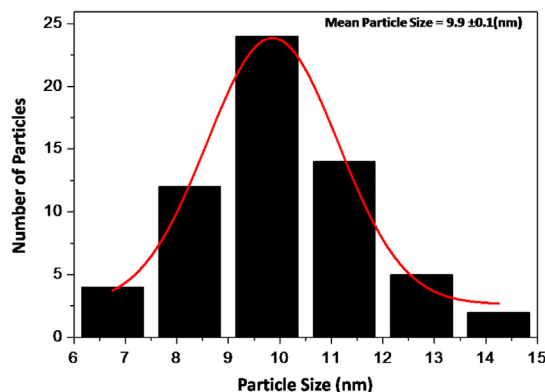
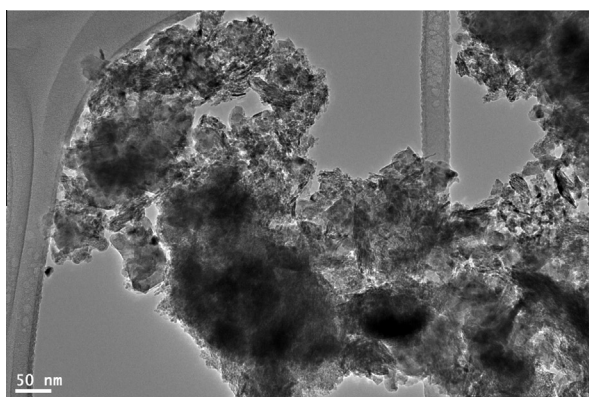
to the formation of industrially important starting materials, including aldehydes and ketones. A variety of transition metals and metal oxides based catalysts have been reported for the catalytic oxidation of alcohols, among them mixed metal oxide nanocatalysts were found to be very effective, which have exhibited excellent catalytic activities for such reactions. Furthermore, it has been widely reported that the catalytic activity of mixed metal oxide nanocatalysts enhanced significantly upon doping with other elements (Fu et al., 2003; Siddiqui et al., 2012; Adil et al., 2015; Alabbad et al., 2013).

Variety of elements have been applied as dopants, among them cerium doped compounds have also been found in the literature. For instance, ceria doped Mn/TiO<sub>2</sub> nanocatalyst was used for the selective catalytic reduction of NO with NH<sub>3</sub>. The as-prepared catalyst was found to be resistant to SO<sub>2</sub> poisoning (Wu et al., 2009). In other example, Ce-doped SnO<sub>2</sub> thin films have been used for the photoluminescence studies, which were found to be highly sensitive toward the selective sensing of butanone (Chen et al., 2012; Jiang et al., 2010). Similarly, CeO<sub>2</sub> based catalyst was found to be fast degradation agents of pesticides such as parathion methyl and other organophosphates (Janos et al., 2014). Apart from this, the ceria doped mixed metal oxide nanocatalysts have also been applied for various organic transformations. For instance, Pt/ceria-doped catalysts were employed for the partial oxidation of methane (Salazar et al., 2006), and Au/doped-ceria catalysts for the preferential CO oxidation reaction (Avgouropoulos et al., 2008), for WGS reaction (Andreeva et al., 2009) and also for the total oxidation of methane and light hydrocarbons (Terribile et al., 1999).

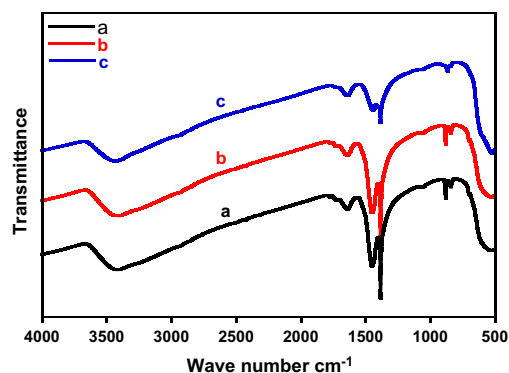


**Figure 3** XRD spectra of the catalyst CeO<sub>2</sub> (5%)–NiMnO calcined at different temperatures (a) 300 °C, (b) 400 °C and (c) 500 °C.

In our previous study, we have reported the use of nickel manganese mixed metal oxide based catalysts for the catalytic oxidation of benzyl alcohol, using various dopants (Siddiqui et al., 2012; Adil et al., 2015; Alabbad et al., 2013). In the continuation of our work in the area of selective alcohol oxidation to aldehydes using mixed metal oxides, herein, we report the synthesis of nano ceria doped nickel manganese mixed oxide nanocatalysts and their application toward the oxidation of benzyl alcohol as a model compound. For this purpose, various catalysts were prepared by altering the w/w% of ceria doping on nickel manganese mixed oxide, which were characterized by SEM, TEM, XRD, FTIR and TGA. The catalytic



**Figure 2** TEM images of CeO<sub>2</sub> (5%)–NiMnO calcined at 400 °C and particle size distribution graph.



**Figure 4** FTIR spectra of the catalyst  $\text{CeO}_2$  (5%)–NiMnO calcined at different temperatures (a) 300 °C, (b) 400 °C and (c) 500 °C.

activities of as-prepared catalysts were evaluated and the conversions were monitored by gas chromatography.

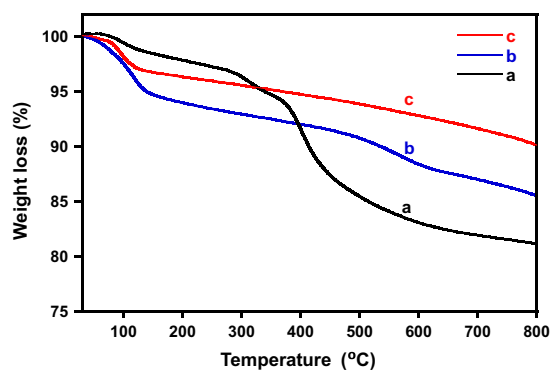
## 2. Material and method

### 2.1. Materials used

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Nickel Nitrate),  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Manganese Nitrate),  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Cerium Nitrate hexahydrate),  $\text{NaHCO}_3$  (Sodium bicarbonate),  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  (Benzyl alcohol),  $\text{C}_6\text{H}_5\text{CHO}$  (Benzaldehyde) and  $\text{C}_6\text{H}_5\text{CH}_3$  (Toluene) [Merck grade] were purchased from Sigma Aldrich Pure Chemical Industries Co., Ltd. They were used as received without further purification.

### 2.2. Synthesis of ceria doped on nickel manganese mixed oxide [ $\text{CeO}_2$ (X%)–NiMnO]

In a typical approach to synthesize the X% ( $X = 1, 3, 5$  mol%) ceria doped nickel–manganese mixed oxide stoichiometric volume of 0.2 M solution of nickel nitrate and manganese nitrate were mixed in a round bottom flask, then it was added with desired volume of 0.2 M solution of cerium nitrate solution. The resulting solution was heated to 90 °C, while stirring using a mechanical stirrer. To this solution,



**Figure 5** Thermal stability pattern of the  $\text{CeO}_2$  (5%)–NiMnO catalyst calcined at different temperatures (a) 300 °C, (b) 400 °C and (c) 500 °C.

1 M solution of  $\text{NaHCO}_3$  was added dropwise until the solution attained a pH of 9. The solution was continued to stir at the same temperature for about 3 h and then left for stirring over night at room temperature. The solution was filtered using a Buchner funnel under vacuum and then dried at 70 °C overnight. The resulting product obtained was then calcined at different temperatures i.e. 300 °C, 400 °C, 500 °C which were characterized by various analytical techniques including, SEM, TEM, FTIR, and XRD in order to obtain structural information of the product.

### 2.3. Catalyst testing

In a typical reaction run, 300 mg of calcined catalyst was loaded in a glass flask pre-charged with 0.2 ml (2 mmol) benzyl alcohol with 10 ml toluene as solvent; the mixture was then refluxed at 100 °C along with vigorous stirring. Oxygen was bubbled at a flow rate of 20 ml  $\text{min}^{-1}$  into the mixture once the reaction temperature was attained. After reaction, the solid catalyst was separated by centrifugation and the liquid samples were analyzed by gas chromatography to evaluate the conversion of the desired product by (GC, 7890A) Agilent Technologies Inc., equipped with a flame ionization detector (FID) and a 19019S-001 HP-PONA capillary column.

## 3. Result and discussion

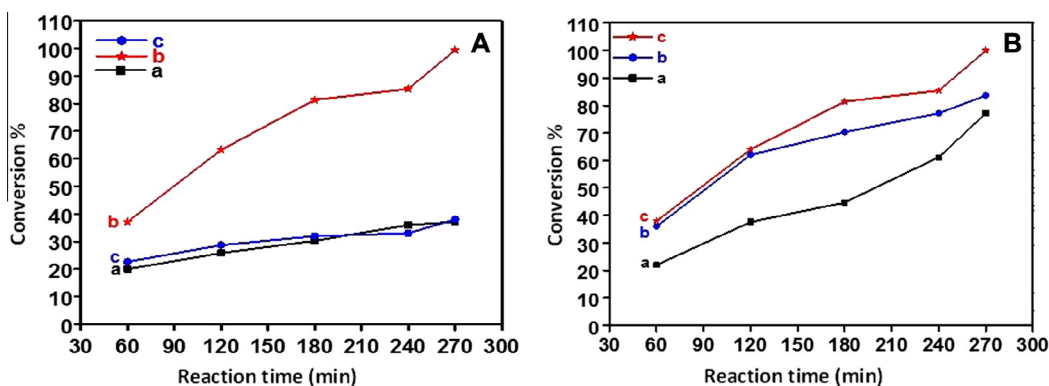
### 3.1. Catalyst characterization

The morphology of nanoparticles and elemental analysis was determined using Scanning Electron Microscopy (SEM) Jeol SEM model JSM 6360A (Japan). 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 a D2 phaser (Bruker) X-ray diffractometer. Thermogravimetric Analysis (TGA) was carried out using Perkin–Elmer Thermogravimetric Analyzer 7. Fourier transform infrared spectroscopy (FT-IR) was used to see the presence of functional groups.

#### 3.1.1. Microscopic and spectroscopic characterization of the catalysts

**3.1.1.1. Scanning Electron Microscopy (SEM).** The SEM images of all the synthesized catalysts were measured and it was revealed that the catalysts were devoid of distinct features, pointing to the absence of well-defined morphology. There is no change in the surface morphology when calcined at different temperatures i.e. 300 °C, 400 °C, 500 °C as observed in Fig. 1.

**3.1.1.2. Transmission Electron Microscopy (TEM).** The as prepared catalyst calcined at different temperatures was subjected to transmission electron microscopy in order to ascertain the nanoparticle size formed. It was found that the particles formed were in varying sizes from 6 to 12 nm. However there was no correlation found between the particle size and conversion rate, signifying that there must be other factors governing the catalytic performance of the catalyst. The TEM image for the catalyst  $\text{CeO}_2$  (5%)–NiMnO calcined at temperature 400 °C is given in Fig. 2.



**Figure 6** Graphical representation of time vs conversion (%) [A] for the catalyst CeO<sub>2</sub> (5%)–NiMnO catalyst calcined at different temperatures (a) 300 °C, (b) 400 °C and (c) 500 °C [B] CeO<sub>2</sub> (X%)–NiMnO catalyst calcined at 400 °C wherein X = (a) 1%, (b) 3% and (c) 5%.

**3.1.1.3. X-ray Diffraction (XRD).** The XRD analysis of the prepared catalyst was carried out and it confirmed that the mixed metal oxides formed were crystalline in nature. Different patterns of the diffractograms have been obtained which indicates the formation of different phases of the mixed metal oxides. The XRD patterns obtained are given in Fig. 3. The phase identification and crystallite size calculation will be carried out and shall be reported later.

**3.1.1.4. FT-IR.** Fig. 4 shows FT-IR spectra of the synthesized catalysts at different calcination temperatures (300, 400 and 500 °C). High wave number region reveals stretching vibrations of the hydroxyl groups. The characteristic bands of  $\nu$  OH, located at approximately  $3450\text{ cm}^{-1}$  were found to be present in all prepared catalyst. The decrease in the intensity of these bands with an increase of the calcination temperature depicts the decrease of hydroxyl group on the catalyst. Similar trends are visible for the bands located at around  $1650\text{ cm}^{-1}$ , identified as fingerprint region for bending vibrations of the hydroxyl groups (Gac, 2007). Significant peaks are observed in the range of  $400\text{--}700\text{ cm}^{-1}$  typical of different oxides of manganese (Dubal et al., 2010; Maslen et al., 1995).

**3.1.1.5. TGA.** The degradation pattern obtained from the thermogravimetric analysis of the catalyst, displayed varied thermal stability. The catalyst calcined at 300 °C displayed a  $\sim 20\%$  weight loss, while the 400 °C showed a weight loss of  $\sim 15\%$ . The catalyst with 500 °C displayed best thermal stability with  $< 10\%$  weight loss. The degradation pattern is given in Fig. 5.

### 3.2. Catalytic evaluation as oxidation catalysts

In order to determine the catalytic oxidation properties of synthesized catalysts, oxidation of benzyl alcohol was used as a model reaction and the reaction was carried out in the presence of the as prepared catalyst. The percentage of ceria doping and the calcination temperature was varied, in order to confirm the optimum % of ceria doping required and the calcination temperature for the best catalytic performance of the synthesized catalyst. The reaction was carried out for 5 h and different results were obtained as mentioned below. A graphical illustration of the results obtained is given in Fig. 6.

#### 3.2.1. CeO<sub>2</sub> (1%)–NiMnO catalyst

When 1% CeO<sub>2</sub> doped NiMnO catalyst calcined at different temperatures was used, a 33% and 30% conversion product was obtained by using the catalyst calcined at 300 °C and 500 °C respectively. The 400 °C calcined catalyst yielded a 77% conversion product.

#### 3.2.2. CeO<sub>2</sub> (3%)–NiMnO catalyst

When 3% CeO<sub>2</sub> doped NiMnO catalyst calcined at different temperatures was used, 35%, 83% and 33% conversion product was obtained by using catalyst calcined at 300 °C, 400 °C and 500 °C respectively.

#### 3.2.3. CeO<sub>2</sub> (5%)–NiMnO catalyst

When 5% CeO<sub>2</sub> doped NiMnO catalyst calcined at 400 °C was used, a 100% conversion product was obtained while using catalyst calcined at 300 °C and 500 °C yielded 37% and 35% to the conversion product respectively.

From the above mentioned results it was evident that the calcination temperature played an important role in the catalytic performance of prepared catalyst and a direct relation between percentage of ceria in the catalyst and its catalytic performance could be observed, thus confirming that ceria nanoparticles play the role of a promoter. It can be concluded that the 400 °C calcination temperature and 5% doping of ceria nanoparticles is the best combination for the highest catalytic performance.

## 4. Conclusions

Ceria doped nickel manganese oxide exhibits high activity and stability for the oxidation of benzyl alcohol using molecular oxygen as a source of oxygen. A synergistic effect between calcination temperatures and the chemical kinetics of the reaction was observed and it was confirmed that calcination temperature plays a vital role forming an active and durable catalyst. Among different percentages of ceria doped catalyst, CeO<sub>2</sub> (5%)–NiMnO gave the 100% conversion from benzyl alcohol to benzaldehyde at 400 °C. Hence, this catalyst can be considered the best among the synthesized catalysts and its performance toward various aromatic and aliphatic alcohols is being explored and shall be reported later as a full paper.

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