Soot Oxidation Studies on SrMn$_{0.98}$B$_{0.02}$O$_3$ (B – Fe, Ni) Perovskites

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Abstract. In this paper, the performance of SrMn$_{0.98}$B$_{0.02}$O$_3$ (B = Fe, Ni) perovskites was evaluated for catalytic soot oxidation applications. All the samples exhibited a nano-crystalline hexagonal structure (XRD analysis) with the crystal sizes ranging 30 to 46 nm. XPS analysis reveals the presence of multiple valence states of Ni cations (Ni$^{2+}$/Ni$^{3+}$) and Mn cations (Mn$^{4+}$/Mn$^{3+}$) cations with the divalent strontium and trivalent iron cation on the surface of the perovskites. O$_2$-TPD analysis infers that the sample SrMn$_{0.98}$Ni$_{0.02}$O$_3$ showed the highest quantity of surface adsorbed oxygen molecules (78.87 µmol.g$^{-1}$) followed by SrMnO$_3$ sample (72.16 µmol.g$^{-1}$). Furthermore, the soot-TPR analysis confirms that the sample SrMn$_{0.98}$Ni$_{0.02}$O$_3$ shown the higher catalytic activity than SrMn$_{0.98}$Fe$_{0.02}$O$_3$ due to synergetic effect between Mn - Ni cations, the higher reducibility tendency of the metal ions and the higher quantity of active oxygen species initiated the structural defects in the catalysts. The superior catalytic activity of soot oxidation of the as-synthesized samples was observed in the order of SrMn$_{0.98}$Ni$_{0.02}$O$_3$ > SrMn$_{0.98}$Fe$_{0.02}$O$_3$ > SrMnO$_3$ > bare soot.

1. Introduction

Diesel engines hold higher fuel efficiency when compared to petrol engines but these engines contribute emissions of hydrocarbons, NOx and particulate matter. The particulate matter poses a serious threat to the environment and living beings [1]. Actually, the emitted soot from diesel engines oxidizes at above 600°C, but the operating engines (light to heavy-duty) are 150 – 350°C. Therefore, various catalytic processes such as diesel oxidation catalyst (DOC) [2] and diesel particulate filters (DPF) [3] have used to control the emissions. To operate within, the researchers need to explore novel catalysts to hold good thermal stability, chemically resistant and good catalytic properties. So far, many catalysts such as noble metal-based [4], ceria-based [5], and perovskite oxides [6] have studied for soot oxidation. However, the parameters like thermal stability, sensitive to be chemical poisoning and economic viability remain open [7]. Perovskites have used as a substitute for noble metal-based catalysts, which has the structure (ABO$_3$) and flexible in their structure. Perovskites have extensively explored because of their excellent oxidation activity. This is due to the creation of oxygen vacancies because of doping/substituting with other metals [8]. These oxygen vacancies allow more amount of gaseous oxygen to adsorb results in the enhancement of soot oxidation.

Doroftei et al [9] investigated properties of SrMnO$_3$ and applied for combustion of propane. The authors examined that 50% and 90% conversion of propane have observed at around 240°C and 350°C.
respectively. The superior catalytic behaviour of SrMnO$_3$ was due to redox properties of Mn (+4 and +3) and generation of a larger quantity of oxygen vacancy density (O$^-$ and O$^{2-}$). Zhang et al [10] reported complete oxidation of CO over microspheres of binary oxides of CeO$_2$-MnO$_2$ composite at around 206°C. The superior catalytic performance of Ce-Mn oxide was due to higher surface area, more oxygen storage capacity and easy redox properties. Rezlescu et al [11] reported SrMn$_{1-x}$Ce$_x$O$_3$ (x = 0-0.2) perovskite, studied the surface properties of the samples and tested for combustion of dilute acetone. They examined that SrMn$_{0.9}$Ce$_{0.1}$O$_3$ took advantage over SrMn$_3$ because of the formation of larger active species (O$^-$, O$^{2-}$), generated due to redox properties of Ce ions. In the current work, the SrMn$_{0.9}$B$_{0.02}$O$_3$ (B = Fe, Ni) perovskites were synthesized and applied for soot oxidation applications. The physio-chemical properties were examined using XRD, BET surface area, SEM, XPS, O$_2$-TPD, and Soot-TPR. The soot oxidation experiments on SrMn$_{0.9}$B$_{0.02}$O$_3$ (B = Fe, Ni) were carried out in a TGA instrument. The detailed soot oxidation studies on these samples have not studied and this prompted to undertake the soot oxidation investigations.

2. Experimentation

2.1 Preparation of perovskites

The three perovskites SrMnO$_3$ (SM), SrMn$_{0.98}$Fe$_{0.02}$O$_{3\pm\delta}$ (SMFe2%), SrMn$_{0.98}$Ni$_{0.02}$O$_{3\pm\delta}$ (SMNi2%) were prepared using the ultra-sonicated sol-gel method. All the materials are of analytical grade. The dissolved metal nitrates in distilled water were ultra-sonicated for 60 min, followed by addition of ammonia solution to metal nitrates mixture to maintain the pH ~10 and kept for constant stirring at 500 rpm and 90°C. The combustible agent citric acid was added to the resultant mixture, maintaining the molar ratio of nitrates and citric acid as 1:1.5. The final mixture has kept for constant stirring at 90°C until it forms the gel. The formed gel transferred into the oven at 120°C for overnight. Thus, the combusted sample kept for calcination in a furnace at 950°C for 24 h.

2.2. Characterization and performance of catalytic studies

The structural analysis of the as-synthesized samples were done using XRD technique (Rigaku) with Cu Kα radiation (λ =1.54 Å, 40 kV, 20 mA). The BET surface area of the samples was examined using SmartSorb 92/93 BET surface area analyzer. SEM analysis was performed on Carl Zeiss (Germany) to understand the surface morphological properties of the samples. O$_2$-TPD experiments were performed on Micromeritics Auto Chem II 2920 instrument to examine the active oxygen species available on the surface of catalysts. XPS analysis was carried on XPS microprobe (ESCALAB Xi$^+$) equipped with (Mono 900 μm and Al-Kα (1486.6 eV)). Soot-TPR experiments were carried out in the TGA instrument in the temperature range of 100 to 800°C in the absence of bulk oxygen species, performed in Ar medium (99.99% UHP). In soot oxidation experiments, typically 15 mg of the tightly contacted catalyst/Printex carbon black mixture (1:10) in TGA instrument. All the catalysts have tested for soot oxidation reactions in the temperature range of 50 to 700°C at the ramp input of 10°C per min. The CO$_2$ gas at the outlet of TA instrument have recorded using ACCURA CO$_2$ analyzer.

3. Results and Discussion

3.1 Structural and surface morphological studies:

The structural analysis of as-prepared perovskites are studied using XRD technique, and the spectra are depicted in figure 1 (i) which exhibits hexagonal phase and the characteristic peaks are well accord with standard data ICDD: 00-024-1213 (space group - P63/mmc). The introduction of the foreign metal cation (B$^{3+}$) into the crystal lattice of SM sample, contributes a slight shift in (110) peak towards higher angles, which confirms the contraction of the crystal lattice of the samples. In addition, the lattice parameters of these doped samples (shown in Table 1) is smaller than the SrMnO$_3$, which might be associated with the partial replacement of foreign metal cation (B$^{3+}$) at the B-site of SrMnO$_3$ (the ionic radii are Sr$^{2+}$ (1.18 Å), Mn$^{4+}$ (0.65 Å), Mn$^{3+}$ (0.53 Å), Fe$^{3+}$ (0.645 Å), Ni$^{3+}$ (0.69 Å), Ni$^{2+}$ (0.56 Å) respectively) [12]. An extra weak signal was observed for the sample SMNi2% at around 32.16°, indicated slightly perturb the crystallinity of the sample or reached the maximum solubility of the
dopant. The BET surface area of all the catalysts is observed in the range of 1.58 to 3.06 m$^2$/g. SEM images of the perovskites are shown in figure 1 (ii). All the prepared catalysts exhibited nano-crystals with non-uniform distribution of particles sizes.

**Table 1:** Structural parameters estimated from XRD analysis.

| Perovskite | Crystal Size, L (nm) | Lattice Parameters | Volume (Å$^3$) |
|------------|----------------------|--------------------|---------------|
|            |                      | a (Å)              | b (Å)         | c (Å)         |                |
| SM         | 46.6                 | 5.468              | 5.468         | 9.105         | 235.82         |
| SMFe2%     | 29.9                 | 5.467              | 5.467         | 9.099         | 234.90         |
| SMNi2%     | 35.8                 | 5.446              | 5.446         | 9.066         | 232.96         |

**Figure 1.** (i) XRD pattern (ii) SEM images (a) SM, (b) SMFe2% and (c) SMNi2%.

### 3.2 XPS analysis

Fe2p spectra is depicted in figure 2 (1-6). The peaks of Fe2p of the sample SMFe2%, cornered at around 711.9 eV and 725.8 eV are ascribed to Fe$^{3+}$ 2p3/2 and Fe$^{3+}$ 2p1/2 with the spin-orbital energy difference of 13.9 eV [13]. A very small super-imposed shoulder peak of Fe$^{4+}$ cation is also observed at around ~712 eV. In addition, the shake-up satellite peaks of Fe$^{3+}$ spin orbitals are also observed at around 719.1 eV and 733.3 eV. The Ni2p peaks (SMNi2%) are shown in figure 2 (7-12). The two spin-orbital doublets are observed on the surface of the catalyst. The first doublet binding energies (850.0 eV, 869.5 eV) and the second doublet energies (855.7 eV, 873.3 eV) are related to Ni$^{2+}$ and Ni$^{3+}$ cations respectively [14]. Furthermore, the two shake-up satellite peaks are also observed at 860.97 eV is related to Ni$^{2+}$ and the peak cornered at 865.6 eV is ascribed to Ni$^{3+}$ cation respectively, these peaks are consistent with the reported literature [15]. In this study, the sample SMNi2% showed more predominant Ni$^{3+}$ cations on the surface.

For the undoped SM sample, there are two main peaks observed at ~641.3 eV and ~643.2 eV with the corresponding spin-orbital split at around ~652.8 eV and ~654.6 eV is related to Mn$^{3+}$ and Mn$^{4+}$ respectively, and these B.E’s are well-matched with the literature [9, 16, 17]. Furthermore, the Mn2p peaks for the doped samples are analyzed and reported Mn$^{3+}$ at (SMFe2% - 642.1 eV, 653.6 eV; SMNi2% - 642.3 eV, 653.8 eV) and Mn$^{4+}$ at (SMFe2% - 643.9 eV, 655.5 eV; SMNi2% - 644.2 eV, 655.7 eV) respectively. For the doped sample, the peaks are shifted towards higher B.E’s when compared with the un-doped sample because of partial substitution of more electronegative elements (Fe-1.83, Ni-1.91) with the less electronegative element (Mn-1.55). Figure 2(17-19) shows the O1s peaks of the as-prepared samples. It can be noted that the release of $\text{C}_2\text{O}_4^{2-}$ is more crucial to carry out the soot oxidation reactions at lesser temperatures [18]. As summarized in Table 2, the binding energies of the surface adsorbed oxygen species ($\text{C}_2\text{O}_4^{2-}$/O$^{-}$) of the samples SM, SMFe2% and SMNi2% are cornered at around 530.0, 530.7 and 531.0 eV respectively and the corresponding calculated percentages of surface adsorbed oxygen species are 48.1%, 42.6%, and 48.2% respectively. Thus, the
sample SM and SMNi2% exhibited the almost the same quantity of active oxygen species, indicating both the sample might exhibit better soot oxidation rate when compared with the SMFe2% sample.

Figure 2. XPS peaks of the samples (a) SM, (b) SMFe2% and (c) SMNi2%. [Note: 1 – Fe(III)2p3/2, 2 – Fe(IV)2p3/2, 3 – Fe(III)sat, 4 – Fe(III)2p1/2, 5 – Fe(IV)2p1/2, 6 – Fe(IV)sat, 7 – Ni (II) 2p3/2, 8 – Ni (III) 2p3/2, 9 – Ni (II)sat, 10 – Ni (III)sat, 11 – Ni (II) 2p1/2, 12 – Ni (III) 2p1/2, 13 – Mn(III) 2p3/2, 14 – Mn(IV) 2p3/2, 15 – Mn(III) 2p1/2, 16 – Mn(IV) 2p1/2, 17 - O2, 18 - O/O2−, 19 - Ohyd]

3.3 $O_2$-TPD and soot-TPR analysis:
$O_2$-TPD peaks are divided into three regions and the corresponding graphs are shown in figure 3 (i). The three peaks at below 200°C, 200-600°C and at above 600°C are ascribed to weakly adsorbed oxygen, surface adsorbed ($\alpha_S$ - O, $\alpha_O$) and lattice oxygen species ($\beta_L$ - O$^2$) respectively. For the SM sample, the two detected desorption peaks (331°C and 572°C) are ascribed to $\alpha_S$ - species with the calculated amount of desorbed oxygen is 72.16 µmol.g$^{-1}$. Similarly, the detected $\alpha_S$ desorbed oxygen species for the SMNi2% sample is at around 593°C, with the corresponding amount of oxygen species is 78.87 µmol.g$^{-1}$. However, the $\alpha_L$ - desorbed oxygen species is not detected for SMFe2% sample. Moreover, the calculated amount of $\beta_L$ desorbed oxygen molecules for the samples SM, SMFe2% and SMNi2% are 6.57, 53.63 and 57.64 µmol.g$^{-1}$ respectively. The sample SMNi2% showed the highest quantity of ‘$\alpha_S$’ when compared with the other samples, the results are consistent with the O1s analysis (figure 2 (17–19)). Figure 3 (ii) depicts the soot-TPR analysis, to further investigate the presence of active species and the reducibility of the catalysts in the presence of soot. In the Soot-TPR experiments, the soot can only be oxidized because of reduction of catalysts which successively enhances the release of the surface adsorbed oxygen species ($O_2^-$/O) [19]. The catalysts reduction by soot at low temperatures observed the sequence as follows SMNi2%>SMFe2%>SM, the trend of the catalytic property of these catalysts is well consistent with the XPS analysis.

Figure 3. (i) $O_2$-TPD analysis (ii) Soot-TPR analysis (a) SM, (b) SMFe2%, and (c) SMNi2%.
3.4 Catalytic activity studies:

Figure 4 (i) depicts the conversion profiles of un-catalyzed and catalyzed soot in a temperature range of 150 to 700°C, the corresponding soot conversion temperatures are displayed in table 2. The T_{50\%} values of the samples un-catalyzed soot, SM, SMFe2% and SMNi2% are found to be 614, 458, 445, 438°C respectively. The T_{50\%} conversion of the un-catalyzed soot is at the temperature of around 614°C, whereas for the pure perovskite sample SrMnO_3 takes place at around 458°C which means calculated decrement of temperature is around 156°C. Further decrement of soot conversion temperature is observed for doping of Ni and Fe (2 mole %) at B-site of SrMnO_3. The T_{50\%} of the corresponding SMFe2% and SMNi2% catalysts is lowered by ca. 169°C and 176°C respectively when compared with the un-catalyzed soot (614°C). It is very interesting to note that SMNi2% exhibited highest soot oxidation rate compared with the SMFe2% and SM sample. And the results are consistent with the soot-TPR analysis as noticed earlier, due to the creation of more oxygen defects in the perovskite. The soot conversion results are further confirmed by recording CO_2 concentration at the exit of the TGA instrument, the CO_2 concentration (%) v/s temperature as depicted in figure 4 (ii). The maximum soot conversion was observed at 628°C, 477°C, 458°C, 447°C for the samples bare soot, SM, SMFe2% and SMNi2% respectively. Thus, the CO_2 conversion profile is also consistent with the results obtained from soot-TPR and the soot conversion profiles.

![Figure 4. (i) Soot oxidation activity (ii) the CO_2 conversions (%) (a) SM, (b) SMFe2% and (c) SMNi2%.

Table 2. XPS – B.E’s of O1s, surface metal ions and surface oxygen species from O_2-TPD and the corresponding soot conversion temperatures.

| Sample     | Binding Energies (eV) | aOs (%) | Atomic (%) Mn^{4+}/(Total) | bαS (µ mol. g^{-1}) | cβL (µ mol. g^{-1}) | T_{50\%} | T_{max} |
|------------|-----------------------|---------|----------------------------|---------------------|---------------------|----------|---------|
| SM         | O_L 528.1 O_S 530.0 O_{hyd} 531.8 | 48.1    | 52.7                       | 72.16               | 6.57                | 456      | 477     |
| SMFe2%     | O_L 528.9 O_S 530.7 O_{hyd} 532.7 | 42.6    | 61.5                       | d_{nd} 53.63        | 445                 | 458      |         |
| SMNi2%     | O_L 529.1 O_S 531.0 O_{hyd} 532.9 | 48.2    | 55.9                       | 78.87               | 57.64               | 438      | 447     |

aSurface adsorbed oxygen (%) = \frac{O_L + O_S + O_{hyd}}{O_{hyd}}.

bAmount of surface adsorbed oxygen species from O_2-TPD analysis in between 200-600°C.

cAmount of lattice oxygen molecules desorption from O_2-TPD at above 600°C; d_{nd} no detection.
4. Conclusions
SrMn_{0.98}B_{0.02}O_{3} \ (B = \text{Fe, Ni}) \ perovskite-type \ catalysts \ have \ successfully \ synthesized \ and \ applied \ for \ the \ soot \ oxidation \ applications. \ The \ XRD \ patterns \ showed \ hexagonal \ structure. \ XPS \ results \ evidenced \ the \ Sr^{2+}, \ Fe^{3+} \ and \ redox \ coupling \ properties \ of \ Mn^{4+}/Mn^{3+} \ and \ Ni^{3+}/Ni^{2+} \ respective \ cations \ on \ the \ surface. \ Besides, \ the \ calculated \ quantity \ of \ release \ of \ surface \ adsorbed \ oxygen \ species \ from \ the \ surface \ of \ SM, \ SMFe2% \ and \ SMNi2% \ are \ 48.1, \ 42.6 \ and \ 48.2\% \ respectively. \ Furthermore, \ the \ O_2^{-}\ TPD \ experiments \ evidenced \ that \ the \ mobility \ of \ surface \ adsorbed \ oxygen \ molecules \ is \ highest \ for \ SMNi2% \ (78.87 \ \mu \text{mol.g}^{-1}). \ From \ soot-\ TPR \ experiments, \ SMNi2% \ exhibited \ a \ lesser \ soot-catalyst \ reduction \ temperature \ compared \ with \ the \ other \ perovskites. \ Moreover, \ the \ sample \ SMNi2% \ showed \ more \ oxygen \ vacancy \ density \ than \ the \ SMFe2%. \ Thus, \ the \ sample \ SMNi2% \ exhibited superior \ catalytic \ activity \ (T_{50\%}=438^\circ \text{C}).

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5. References
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