New Generation Novel Hybrid Perovskite Catalysts For De-NOx Applications

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Abstract: Air pollution due to the emission of toxic gases is a serious threat for human health. Recently, it was reported that perovskite based De-NO_x catalysts can be used as an alternative to the high-cost Pt oxidation catalysts [1,2]. In this work, a new generation of hybrid perovskites were designed in the form of $LaCo_xMn_{1-x}O_3$ by varying Co and Mn loadings (x=0.1-0.9) in an attempt to fine-tune the thermal stability and catalytic activity of the catalysts.

Keywords: Perovskite, NO_x, Hybrid

1. Introduction

The toxicity levels of air (*e.g.* CO, NO_x, SO_x and unburned hydrocarbons) have recently become a serious threat for human health. Thus, there are intense efforts to develop novel, affordable and superior materials for catalytic exhaust emission control technologies. Recently, it was reported that low-cost perovskite-based DeNO_x catalysts could be potentially feasible candidates that can replace Pt-based conventional exhaust emission control catalysts [1-2]. La-based simple perovskites such as $LaMnO_3$ and $LaCoO_3$ can reveal either high thermal stability or high NO oxidation capability but cannot possess both of these merits at the same time [1]. Based on this fact, catalytic activity and thermal stability of La-based perovskites can be optimized by designing $LaCo_xMn_{1-x}O_3$ perovskite structures (Figure 1). In the current work, mixed perovskite structures were synthesized by varying Co and Mn loadings (x=0.1-0.9). These mixed perovskites were also structurally characterized via XPS, *XRD*, *BET*, and *TEM* techniques. Also, interaction of mixed perovskites with SO_x and NO_x species were spectroscopically investigated via *in-situ FTIR, TPD, TPR, TPO and XANES* techniques under oxidizing, reducing and ambient conditions.

2. Experimental

Detailed description of synthesis protocol of $LaCoO_3$ and $LaMnO_3$ has been reported in one of our former publications [1]. The synthesis of simple and hybrid perovskites were achieved by co-precipitation of La-Co, La-Mn or La-Co-Mn based nitrate precursors via citrate method. Perovskite based De-NO_x catalysts were synthesized in the form of $LaCoO_3$, $LaMnO_3$ and $LaCo_xMn_{1-x}O_3$ (x=0.1-0.9). NO_x uptake and release capacity of simple and hybrid perovskites was investigated via in-situ FTIR and TPD. Reduction characteristic of perovskites was also studied by TPR method.

3. Results and discussion

As illustrated in Figure 2, former studies reported that Co based perovskites show a high NO oxidation capability [1] which is also supported by the current TPD results (Fig.2). On the other hand, NO_x storage capacity can be fine-tuned by changing Mn/Co ratio in the perovskite structure. Low loadings of Mn in the structure increases NO_x storage capacity (Fig.2). In Fig. 4, relative amount of oxygen release from $LaCo_{0.8}Mn_{0.2}O_3$ and $LaCo_{0.7}Mn_{0.3}O_3$ indicates that low loadings of Mn enhances the oxygen enrichment on the catalyst surface/subsurface. Oxygen release (Fig 4.) at low temperatures indicates that the majority of oxygen enhancement occurs at the perovskite surface. Based on these facts, pretreated (*i.e.* pre-reduced in the presence of H_2(g)) perovskites have different surface oxygen vacancy coverages/concentrations which are titrated with NO_x during NO_x adsorption and storage. XANES experiments were also performed at DESY Synchrotron facility in Hamburg in order to investigate the oxidation states of Co and Mn sites in the perovskites (Fig 3.) XANES results indicate that addition of Mn enhances Mn^{+4} formation in the perovskite structure. XANES results are in line with the oxygen enhancements on $LaCo_{0.8}Mn_{0.2}O_3$ and $LaCo_{0.7}Mn_{0.3}O_3$ perovskites. Thermal stability of perovskites is an important step of this study. Reduction profiles of simple and hybrid perovskites were investigated as a function of Co/Mn ratio (Figure 5). Reduction peaks of perovskites are attributed to $Co3^{+} + e^{-} \rightarrow Co^{2+}$ (280-370 °C), $Co2^{+} + 2e^{-} \rightarrow Co^{0}$ (400-700 °C) for cobalt enriched perovskites [3]. On the other hand, reduction of Mn enriched perovskites are assigned to $Mn^{+4}+e^- \rightarrow Mn^{+3}$ (280-390 °C) and $Mn^{+3} + e^- \rightarrow Mn^{+2}$ (700-800 °C).

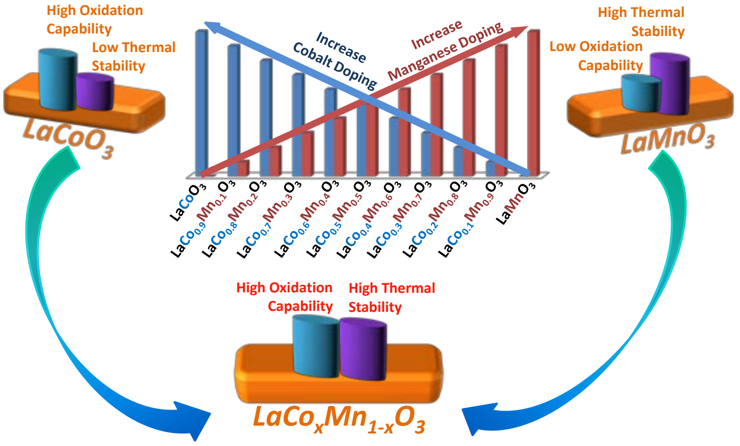

Figure 1. Schematic description of the functionality of simple and hybrid perovskites.

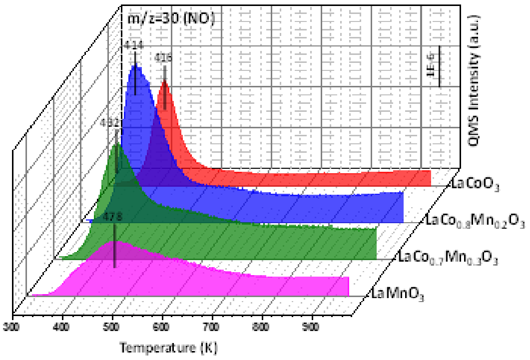

Figure 2. NO TPD of perovskites

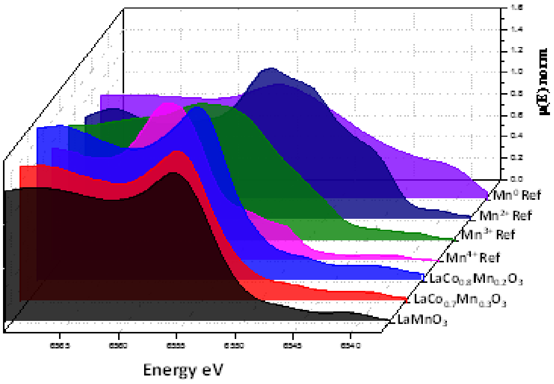

Figure3. XANES spectra comparison of perovskites.

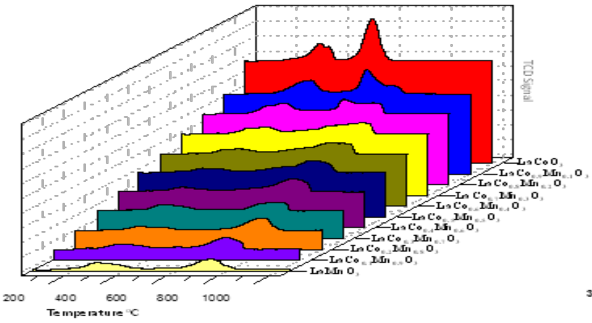

Figure 4. TPR profiles in the presence of H_2

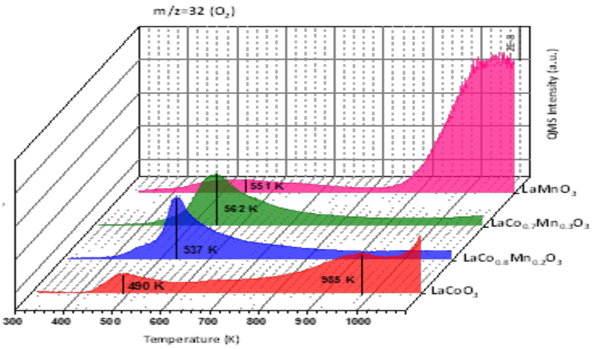

Figure 5. O_2 TPD profiles of perovskites.

4. Conclusions

A new generation of hybrid perovskites with high thermal stability and high NO_x oxidation capability were designed, synthesized and characterized. It was demonstrated that surface properties of hybrid perovskites can be fine-tuned to optimize their thermal stability and NO_x oxidation performance.

References

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