CHAPTER- 7

Conclusions and Recommendations

7.1. Conclusions

With the increasing severity of air pollution and the increase in the public's awareness of the role for protecting the environment, the treatment of air pollutants is imminent. Nitrous oxides (NO_x) emitted by both mobile and stationary sources have been considered as one of the main causes of air pollution, which could harm environment and human health. In recent years, researchers are working on developing suitable catalyst for NO_x removal emitted from various industries. The current research focuses on developing a suitable post-treatment catalyst to reduce the nitrogen oxide emissions from stationary sources through NH_3-SCR technique. The following significant conclusions were drawn based on the experimental results performed on fixed bed reactor in various conditions.

7.1.1. Effect of different support morphology on NO reduction

The different morphologies of CeO_2 (nanorod, nanocube, and nanopolyhedral) were synthesized using the hydrothermal technique. The synthesized supports were thoroughly investigated by *Brunauer–Emmett–Teller* (BET), Raman, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), Scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX), temperature-programmed reduction (TPR), and Raman spectroscopy. The objective of synthesizing different morphologies is to expose different crystal facet which affects the redox and acidic properties of ceria. The oxygen vacancies on CeO_2 plays an important role in improving surface acidity and redox ability, which are considered as adsorption sites of NH_3, NO_x and surface oxygen species. The different ceria morphologies were tested for NO reduction and results showed that CeO_2-NR catalyst exhibited maximum NO conversion of 46% and more than 75% N_2 selectivity at 250℃ due to the significantly high surface area, oxygen sites and oxygen vacancies. The main accomplishment of work based on support morphology can be summarized as follows:

- The crystal size of CeO_2-NR is less than that of CeO_2-NC and CeO_2-NP. The CeO_2-NR catalyst's particle sizes were also small compared to the others, and these properties enhanced the surface area, pore volume, and pore diameter
- The H_2-TPR profile demonstrates that a wide range of H_2 consumption correlates to lattice oxygen, resulting in maximal conversion. Among the three morphologies of ceria, it was observed that the CeO_2-nanorod morphology showed the highest H_2 consumption
- The NH_3-SCR activities for different morphologies were found in the following sequence: CeO_2-NR > CeO_2-NC> CeO_2-NP. The highest activity of CeO_2-NR is due to low crystallinity, high reducibility, and presence of abundant surface adsorbed oxygen

7.1.2. Effect of different oxides of manganese in the MnO_x/CeO_2 catalyst

In first phase, it was observed that CeO_2-NR showed the highest activity among other morphologies, therefore it was selected as a support for loading of MnO for further evaluation for NO reduction. The different oxides of MnO were supported on CeO_2-NR through wet-impregnation technique. The different oxidation states of manganese on CeO_2 support significantly impacted the SCR performance. The MnO_2/CeO_2-NR catalysts showed the highest NO reduction compared to MnO/CeO_2-NR and Mn_2O_3/CeO_2-NR catalysts. The highest activity of MnO_2/CeO_2-NR catalyst is due to significant amount of Ce^{3+} content and adsorbed oxygen which enhanced the NO reduction activity of the catalyst. The following points are concluded:

- The MnO_2/CeO_2-NR catalyst reported highest Ce^{3+} content (31.5%) which is due to the larger amount of oxygen vacancy at the interface of CeO_2
- The crystallite size of the MnO_2/CeO_2-NR catalyst is smaller than other catalysts which could be due to the entry of Mn^{n+} into the CeO_2 lattice
- At higher temperatures (350°C < T <450°C), the catalysts were less active for NO reduction whereas N_2 selectivity remained constant. The MnO_2/CeO_2-NR catalyst showed 65% NO conversion and 85% N_2 selectivity with significant temperature windows (100-350°C)
- MnO_2 loading was varied from 3-20 wt.% and maximum NO conversion (90%) was obtained between 300-350°C when MnO_2 loading reached to 17 wt.% due to higher dispersion of MnO_2

7.1.3. Effect of MnO_2 crystal phases in the MnO_2/CeO_2 catalyst

In second phase, MnO_2 oxide supported on CeO_2-NR showed the best performance for NO conversion. Therefore, we further evaluate the effect of different crystal phases (α, β, γ, δ) of MnO_2 for the NO reduction using the NH_3-SCR process. These different phases of MnO_2 were synthesized by hydrothermal method and were supported on CeO_2-NR through wet-impregnation process. Among all the catalysts, α-MnO_2/CeO_2-NR catalyst showed maximum NO conversion of 65% at 350°C due to significant oxygen sites and strong interaction of Mn^{4+} with the support. The main accomplishments of work based on different phases of MnO_2 can be summarized as follows:

- According to the Rietveld analysis, the inclusion of α-MnO_2/CeO_2-NR has a higher strain of ceria than CeO_2-NR. The α-MnO_2/CeO_2-NR catalyst's particle sizes and crystal sizes were small compared to the other catalysts, which enhanced the catalysts' BET properties and improved the catalysts' performance.

- According to XPS data, the combination of MnO_2 and CeO_2 creates oxygen vacancies, promoting NO elimination and providing more active sites for NO dissociation. The XPS analysis shows that adding Mn^{n+} enhanced the lattice oxygen contents of mixed oxide catalysts, which is favourable for the NH_3-SCR reaction.
- According to Raman spectroscopy, the maximum shift is not entirely dependent on adding MnO_2. It could be related to creating an oxygen vacancy due to the partial reduction of surface Ce^{4+} to Ce^{3+}, which changes the geometrical characteristics and shifts the vibrational frequency of adsorbed oxygen. The broadening of Raman peaks primarily depends on the catalyst's oxygen vacancy, which corresponds to the amount of adsorbed oxygen.
- The activity and selectivity were the two variables most affected by temperature. Based on textural characteristics, it was established that there was no systematic tendency for NO reduction. NO_x conversion plots show the highest NO reduction for α-MnO_2/CeO_2-NR catalyst due to better dispersion of Mn metal over support, high surface area, and pore volume.
- The α-MnO_2/CeO_2-NR catalyst had the highest BET surface area, pore volume, and larger pore diameter than other catalysts. This may be the reason which provided more active sites for the reaction.

7.2. Suggestions for Future Work

NH_3-SCR is the most promising deNO_x technology to minimize the NO_x emission. A substantial amount of work was carried out to improve the operation of the SCR system for low temperature reactions. Although lot of work has been carried out to evaluate the performance of SCR catalysts under different conditions, but there are still some research directions which should be focused on:

- Ce-based catalyst is highly resistant to SO_2 and H_2O in a part of the temperature range (150–300°C), it is still required to expand the temperature window
- The morphology effect of Mn catalysts can be study to further enhance the activity and stability of Mn based catalysts
- Effect of promotors can be study to enhance the catalyst activity and life cycle
- Improving catalyst poisoning-resistance and regeneration technology is essential for the practical industrial application of catalysts for the elimination of NO_x. With proper understanding of catalyst deactivation mechanisms, effective regeneration techniques should be developed to enhance their industrial application
- The reaction mechanism needs to be addressed in detail for further investigation of catalysts