Chapter 7

7. CONCLUSION AND FUTURE SCOPES

One of the primary objectives of this thesis was to synthesize and characterize metal oxide-based nanostructures with evaluation of their activity for organic transformation such as Friedel-Crafts (FC) acylation reaction. Another major objective was to employ the synthesized metal oxide-based nanostructures for wastewater treatment as adsorbent and photocatalyst towards the efficient removal of organic dye pollutants from aqueous solution. Inspired by published literatures, such applications were selected for activity measurements of the metal oxide-based nanostructures in this thesis work.

This chapter coalesces the major findings drawn from each chapter of the thesis. The potential future scopes of the present work have also been highlighted in this chapter.

7.1 Concluding remarks and outlook

In context of the objectives of the present investigation, this thesis comprised of total seven chapters.

Chapter 1: This chapter presents an overview on metal oxide-based nanostructures. The suitable synthesis protocols and key properties of metal-oxide based nanostructures are highlighted to achieve material's property for specified applications: organic transformation and wastewater treatment. Extensive literature survey in perspective of the applications of metal oxide-based nanostructures are included in this chapter. Furthermore, the objectives of the present investigation were outlined at the end of the chapter.

Chapter 2: All the details of materials and characterization techniques that have been used in this entire thesis work are included in this chapter. The experimental procedures adopted for each reaction are also described in this chapter.

Chapter 3: This chapter deals with the results and discussion part describing the characterization of bare zinc oxide (ZnO) hierarchical nanostructures (HNs) and tin dioxide (SnO_2) nanostructures that correlate with the catalytic activities for Friedel-Crafts acylation reaction. This chapter is divided into three sections depending on the metal/method employed in the syntheses of respective oxides. Some major findings of this chapter are highlighted below:

(i) The hydrothermal reaction time is a decisive factor for controlling morphology of the ZnO HNs (Chapter 3A).

(ii) Nanoflake-assembled ZnO HNs exhibit better catalytic activity towards the FC acylation reaction compared to the rod-like HNs which is attributable to higher surface area and acidity of the nanostructures.

(iii) Comprehensive catalytic investigations in Chapters 3B and 3C reveal that the SnO_2 nanosheet assembly outperforms SnO_2 nanoparticles in terms of activity and recyclability in solvent-free reaction conditions.

(iv) Overall, both ZnO and SnO_2 samples have their own advantages and disadvantages. While ZnO is quite active for FC acylation compared to SnO_2, some leaching occurs in the case of ZnO. On the other hand, leaching of the catalyst is negligible in case of SnO_2 implying better stability of SnO_2 samples compared to ZnO.

Chapter 4: This chapter deals with the complete characterization of ZnO and SnO_2 supported on mesoporous silica SBA-15 modified by using trimethylbenzene as swelling agent. Furthermore, the synthesized nanocatalysts are employed for the FC acylation of anisole with benzoic anhydride. Some significant findings derived from this chapter are listed below:

(i) Mesoporous silica (modified SBA-15) plays a crucial role in enhancing the activity of the metal oxide loaded samples owing to its enhanced surface area, efficient mass transport, and chemical stability regardless of the location of metal oxide loading. The interaction between the metal oxide and the modified SBA-15 support may contribute to changes in the electron density within the metal oxide phases, leading to the generation of acidic sites or stabilization of the existing acidic sites. This property may have resulted in the active participation of benzoic anhydride in FC reaction which is otherwise inactive with pure metal oxide particles.

(ii) SnO_2 supported on SBA-15 exhibits better SnO_2 loading and higher acidity compared to ZnO supported on SBA-15.

(iii) SnO_2 supported on modified SBA-15 shows better catalytic activity towards FC acylation of anisole with benzoic anhydride compared to ZnO supported on SBA-15 which is attributed to better loading and higher acidity of the former catalyst.

(iv) The catalyst is recycled up to four consecutive cycles with minimal loss of catalytic activity.

Chapter 5: In this chapter, we have employed SnO_2 nanoparticles (NPs) and SnO_2 nanosheets (NSs) synthesized via simple template-free solvothermal route for the selective adsorption of organic dye pollutants such as Congo red (CR) and rhodamine B (RhB) from their mixed aqueous solution. The characterizations of the synthesized oxides are already discussed in Chapters 3A and 3B. Some of the major findings related to this chapter are mentioned below:

(i) The adsorption capacities of the SnO_2 nanostructures are dependent on the pH of the dye solution.

(ii) At pH 3.0, SnO_2 nanostructures can significantly remove CR due to the interactions between the base hydroxyl group of SnO_2 and $R–SO_3^-$ ions of CR from the mixture of CR−RhB solution.

(iii) At pH 7.0, SnO_2 nanostructures can selectively remove RhB pertaining to the electrostatic interaction and π−π electron donor-acceptor interaction between the acid hydroxyl group of SnO_2 and $R–N^+$ ions of RhB.

(iv) The SnO_2 nanostructures retain their effectiveness even after repeated regeneration and usage for adsorption-desorption cycles.

Chapter 6: This chapter of the thesis deals with the complete characterization of reduced graphene oxide supported Cu-doped ZnO (Cu-doped ZnO/rGO) nanocatalyst. This chapter also presents the photocatalytic degradation studies of the synthesized catalyst for methylene blue (MB) in aqueous solution under UV light and sunlight irradiation. The salient findings of this chapter are as follows:

(i) The combination of copper and rGO with ZnO expanded the material's response to visible light.

(ii) A significant increase in photocatalytic degradation for MB using Cu-doped ZnO/rGO is achieved compared to ZnO and ZnO/rGO which are ascribable to the combined effects of rGO and copper doping into the ZnO crystal lattice.

(iii) The photodegradation process follows first order kinetics with recyclability up to five cycles.

Chapter 7: This chapter of the thesis depicts the concluding remarks and major findings of the present work as well as highlights the future scopes which can be further explored.

7.2 Future scopes

This thesis documented a systematic and comprehensive study on metal oxide-based nanostructures and their application in FC acylation reaction as well as wastewater treatment. However, there remains room for further studies in this domain and henceforth the following points may be considered as future scopes of the present investigation:

(i) The effect of different reaction parameters such as pH, concentration of starting materials, temperature etc. in the syntheses of nanostructures for controlling their morphologies which can significantly alter their activities can be further investigated.

(ii) The impact of other bare and supported metal oxides on catalytic reactions may be explored.

(iii) The catalytic studies can be performed for other acid-catalyzed organic transformations.

(iv) Wastewater treatment can be further extended for various other organic contaminants.

(v) Studies can be attempted for the photocatalytic degradation of dyes with other dopants such as Fe, Ce, N etc. and supports such as graphene, CNTs etc.

(vi) Detail analysis of the products of degradation process which remained untouched in this limited period can be done.

(vii) An in-depth understanding of the complete reaction mechanisms is necessary using theoretical studies.

LIST OF PUBLICATIONS

[1] Deka, R. C., Deka, A., Deka, P., **Saikia, S.**, Baruah, J., and Sarma, P. J. Recent advances in nanoarchitectonics of SnO_2 clusters and their applications in catalysis. Journal of Nanoscience and Nanotechnology, 20(8):5153–5161, 2020.

[2] **Saikia, S.**, Deka, P., Saikia, L., and Deka, R. C. Influence of solvent on morphological texture and catalytic activity of SnO_2 nanoparticles. *International Journal of Nanotechnology*, 18(5–8):358–373, 2021.

[3] **Saikia, S.**, Devi, R., Gogoi, P., Saikia, L., Choudary B. M., Raja, T., Deka, P., and Deka, R. C. Regioselective Friedel-Crafts acylation reaction using single crystalline and ultrathin nanosheet assembly of scrutinyite-SnO_2. *ACS Omega*, 7(36):32225–32237, 2022.

[4] Bharali, D.†, **Saikia, S.**†, Devi, R., Choudary, B. M., Gour, N. K., and Deka, R. C. Photocatalytic degradation of phenol and its derivatives over ZnFe layered double hydroxide. *Journal of Photochemistry and Photobiology A: Chemistry*, 438:114509, 2023.

†equally contributed

[5] **Saikia, S.**, Gogoi, P., Saikia, L., Bharali, P., Raja, T., Deka, P., and Deka, R. C. Insights into hydrothermal time-driven morphology evolution and catalytic activity of ZnO hierarchical nanostructures. (To be communicated)

LIST OF CONFERENCES ATTENDED

[1] **Participated** in "National Conference on Sustainability, Medicine and Clean Energy" at Tezpur University, Tezpur, Assam, India on 1st March, 2022.

[2] **Poster Presentation** in "International Conference on Emerging Trends in Chemical Sciences 2020 (ETCS-2020)" at Gauhati University, Guwahati, Assam, India, 13th-15th February, 2020.

[3] **Oral Presentation** in "2nd International Conference on Nanoscience and Nanotechnology (ICNAN'19)" at Vellore Institute of Technology, Chennai, Tamil Nadu, India, 29th November-1st December, 2019.

[4] **Poster Presentation** in "SAIS Symposium 2019" at Indian Association for the Cultivation of Science, Kolkata, West Bengal, India, 8-9th March, 2019.

[5] **Poster Presentation** in "OrganiX-2018" an International Conference in Chemistry at Tezpur University, Tezpur, Assam, India, 20th-21st December, 2018.

[6] **Poster Presentation** in "International Conference on Recent Trends in Materials Science and Technology 2018 (ICMST 2018)" at Indian Institute of Space Science and Technology (IIST), Trivandrum, Kerala, India, 10th-13th October, 2018.

[7] **Poster Presentation** in "International Conference on Advancement in Science and Technology 2018 (ICAST-2018)" at Visva-Bharati University, Santiniketan, West Bengal, India, 3rd-4th September, 2018.