# Unveiling the Morphology and Composition of Heterogeneous Co, Zn and ferrite Catalysts for Efficient Catalysis

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**Highlights**

- All catalysts form irregular nanocrystalline particles with great surface area because of their sheet-like shapes, according to FE-SEM images.
- EDS verifies catalyst purity and stoichiometry by confirming the presence and appropriate ratios of Co, Zn, Fe, and O.
- The polydispersity of the catalysts is demonstrated by HR-TEM micrographs, which exhibit quasi-spherical, octahedral, and cubic-shaped particles with wide size variations.

**Abstract:** In order to explore the possible catalytic activity of Co, Zn ferrite catalysts, the current work explores their morphological and compositional features. The extraordinary surface area was attributed to the development of irregular nanocrystalline particles with sheet-like shapes, as indicated by field emission scanning electron microscopy (FE-SEM) study. The presence and appropriate ratios of Co, Zn, Fe, and O were verified by energy-dispersive X-ray spectroscopy (EDS), reflecting catalyst stoichiometry and purity. The polydispersity of the catalysts was further revealed by high-resolution transmission electron microscopy (HR-TEM) micrographs, which showed a wide range of particle sizes shaped as quasi-spherical, octahedral, and cubic. These results offer insightful information about the catalysts' structural properties and point to their possible utility in a range of catalytic applications particularly for the volatile organic compounds (VOC).

**Keywords:** catalysts; catalysis; ferrites

## 1. Introduction

Air pollution due to anthropogenic activities has become a foremost concern for public health because it is the cause of many diseases that may lead to death, both for humans and living beings [1]. As a result, environmental regulations are constantly rising and becoming more stringent, which demands more efficient methods to clean up gas streams [2,3] . The cause of air pollution is hazardous materials in the atmosphere. The world's large population is still exposed to excessive concentrations of air pollutants, particularly volatile organic compounds (VOC). The adverse consequences on flora, the environment, human health, and property are the basis for categorizing certain substances as air pollutants.

Due to potential health risks associated with exposure to VOC and increasing awareness, the treatment of VOC has become an important research area that is receiving much attention. Many international and national organizations formulated rules and extended directives for industries to mitigate and limit VOC emissions and to implement emission reduction measures. Therefore, effective treatment and control of VOC are crucial for protecting human health and the environment. This requires carrying out research and development of innovative solutions. Consequently, it is imperative to take swift and practical actions to address the issue and control VOC emissions.

The traditional technologies used to degrade the VOC are inefficient and unable to handle low-concentration VOC emissions [4,5] . However, recent research has focused on developing more effective methods for VOC degradation. For this purpose, non-thermal plasma (NTP) has drawn considerable attention among researchers. The Dielectric barrier discharge plasma (DBD) plasma, a type of NTP, is considered a prospective approach for treating VOC emitted with low concentrations, as it offers low energy consumption and is easy to operate. The limitation of this technology is low energy efficiency and the potential generation of byproducts that are also harmful to health and the environment . This limitation can addressed by choosing catalyst(s) in combination with DBD to affect the transformation of byproducts and the overall efficiency of the degradation process. The DBD plasma can operate at room temperature to convert air pollutants, giving the best performance and stable plasma region with easy connection with the catalytic system [8]. However, the practical application of NTP on VOC abatement is limited by three reasons, incomplete oxidation and emissions with harmful compounds (CO, NOx, other VOC), low energy efficiency, and low mineralization rate. NTP coupled with the catalytic systems termed "plasma catalysis" have attracted research in recent years. Catalyst-combined NTP processes allow enhanced efficiency by generating highly oxidizing substances. Our previous work has been done with the catalysts Co and Zn ferrite catalysts exploring excellent performance in degradation of toluene as target VOC pollutant with the plasma-catalysis system [9–13]. In the current study, exploration of their morphological characterization has been studied who play a vital role in selecting the catalysts for degradation of toluene in plasma-catalytic system has been investigated.

## 2. Materials and Methods

Cobalt nitrate hexahydrate $Co(NO_3)_2{\cdot}6H_2O$, zinc nitrate hexahydrate $Zn(NO_3)_2.6H_2O$, and iron nitrate nonahydrate $Fe(NO_3)_3.9H_2O$ of the needed molar solution were dissolved in deionized water with continuous stirring for 30 minutes in order to create Co-Zn ferrite using the co-precipitation method. With constant stirring, the produced NaOH solution was added to the nitrate solution as a precipitating agent, keeping the pH between 12 and 13. The solution was heated to 70 °C for 60 minutes while being stirred. After that, the solution was allowed to cool and was left overnight without being stirred. After washing and drying the mixture, the pH level approached seven. Following two hours of drying in an air oven, the solution was calcined for three hours at 800 °C. The sample was designated as C-Z-F catalysts. The same procedure was used to prepare the Zn and Co ferrites for comparison [9] and designated as Z-F and C-F catalysts, respectively. The molar ratios of the Co and Zn was taken 1 with ferrites of 2 catalysts were synthesized as follows: 1:1:2, 1:2, and 1:2.

### 2.1 Morphological Characterizations of Catalysts

Figure 1 and Figure 3 show the morphological characteristics of the prepared catalysts studied by scanning electron microscopy (SEM, JSM-630LV, Tokyo, Japan), and transmission electron microscopy (TEM) images obtained with a JEM-2100CX microscope (JEOL Ltd., Japan) at 200 kV, respectively. The produced catalysts' stoichiometric concentrations were confirmed by Energy Dispersive Spectroscopy (EDS) using an AMETEX instrument equipped with a Silicon Drift Detector (SDD), as illustrated in Figure 2.

## 3. Results and discussion

The Field emission scanning electron microscopy (FE-SEM) obtains the morphological properties. The main idea behind this is that the grating is scanned across the sample surface by the upper stage focusing mirror of the scanning electron beam.

SEM analysis offers valuable insights into the surface structural characteristics and distribution of the metal oxides of C-Z-F, Z-Fe, and C-Fe catalysts and sheds light on their potential catalytic activity. Figure. 1 shows the formation of irregular nanocrystalline particles at 500 µm. Figure. 2 (a-c) displays that particles are well-dispersed and distributed homogeneously in all the catalysts with a wide range of sizes of irregular shapes, dominant in nanometers that substantiate the excellent surface area. All the catalysts show mostly the sheet-like

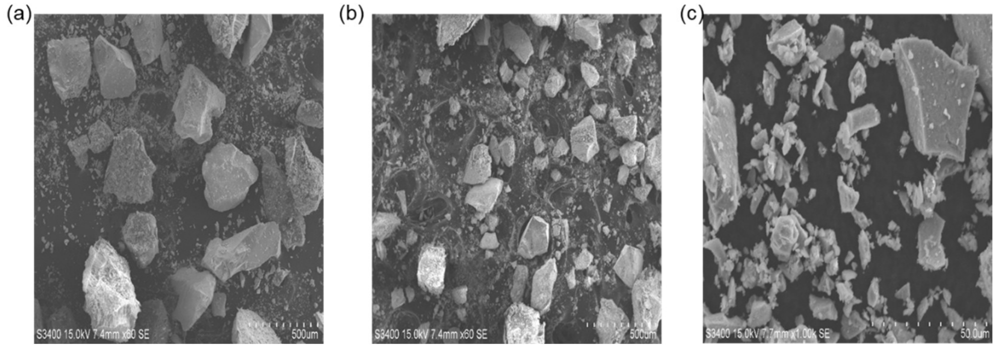

Figure. 1 FE-SEM images of (a) C-Z-F (b) Z-F (c) C-F catalysts.

structure of most of their particles. Accompanying the SEM analysis with EDS spectroscopy provides elemental information by quantifying the presence and distribution of Co, Zn, Fe, and other constituent elements and ensures that the desired metal ratios for effective catalytic performance have been achieved. The EDS spectra of all the catalysts C-Z-F, Z-F, and C-F with the respective inset tables are demonstrated in Figure 2 (a – c), respectively, which clearly illustrate elemental spectra of O, Zn, Fe, and Co. this assure the purity of all the catalysts as no other element peak is observed in the EDS spectrum. The stoichiometric proportion of elements in synthesized nanoparticles is shown in the inset table of the respective catalyst in Figure 2 (a – c), which is aligned closely to the anticipated values [14].

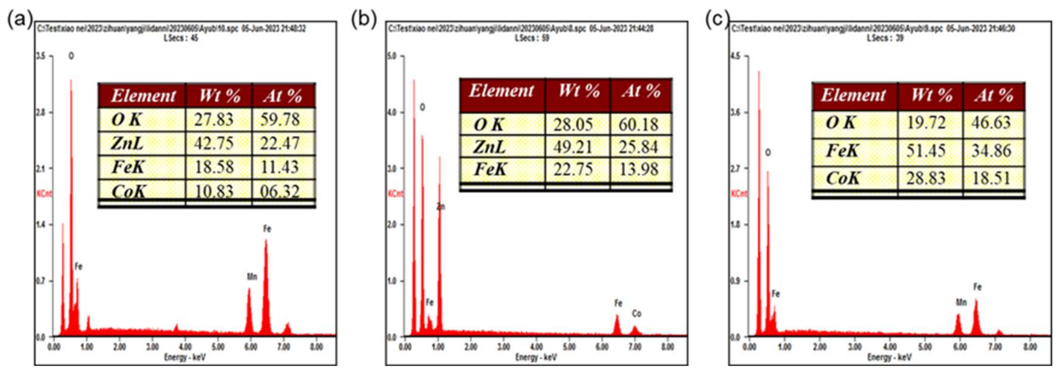

Figure. 2 EDS with inset tables of the elemental composition of (d) C-Z-F (e) Z-F (f) C-F catalysts

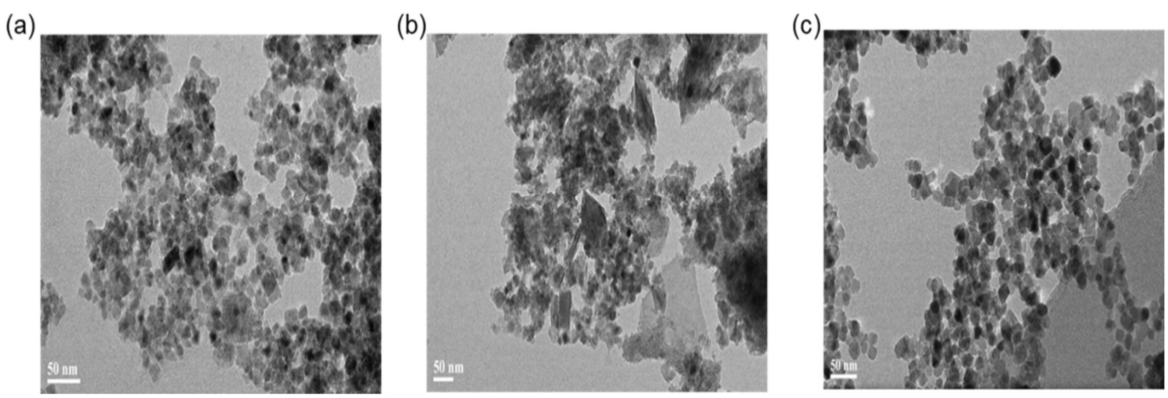

Figure.3 TEM images of (a) C-Z-F (b) Z-F (c) C-F catalysts.

For the high-resolution transmission electron microscope (HR-TEM) to gain an excellent resolution of the morphological structure, the sample must be the conductor for the electrons to be transmitted to the bottom of the sample to generate a signal.

TEM micrographs are displayed in Figure. 3 (a- b) for all the catalysts. The TEM images show that the particles' shape is quasi-spherical, octahedral, or cubic-shaped and polydispersed in all the catalysts. The particles having irregular shapes have a broad distribution range.

## 4. Conclusions

In order to clarify the morphological and compositional features of the C-Z-F, Z-F, and C-F catalysts, this study effectively synthesized them and used sophisticated characterization techniques. The catalyst purity and potential effectiveness were confirmed by FE-SEM and EDS investigations, which also revealed the presence of irregular nanocrystalline particles with excellent surface area and confirmed the appropriate stoichiometric ratios of constituent elements. The catalysts' polydispersity with a range of particle sizes and shapes was further revealed by HR-TEM. These results open the door to the catalysts' effective use in a variety of catalytic processes by offering insightful information about their structural properties.

**Author Contributions:** All authors contributed to the study. Khurram Shahzad Ayub contributed to the study conception, design, experiments, and data collection and wrote the paper. Umair Mushtaq and Saqlain Abbas also analyzed the results and investigated under the supervision of Yang Ji. Asad Ali with Homely Isaya Mtui helped to analyze the EDS. The manuscript was revised through discussion and comments of all the authors. All authors read and approved the final manuscript**.**

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## References

[1] S.H.H. Al-Taai, W.A. Mohammed al-Dulaimi, Air Pollution: A Study of Its Concept, Causes, Sources and Effects, Asian J. Water, Environ. Pollut. 19 (2022) 17–22. https://doi.org/10.3233/AJW220003.

[2] Q. Liu, Y. Zhu, W. Yang, X. Wang, Research on the Impact of Environmental Regulation on Green Technology Innovation from the Perspective of Regional Differences: A Quasi-Natural Experiment Based on China's New Environmental Protection Law, Sustainability. 14 (2022) 1714. https://doi.org/10.3390/su14031714.

[3] D. Noh, E. Lee, The Effects of Environmental Regulations on Technology Innovation: Focusing on the Technology Intensity and Firm Size, J. Environ. Policy Adm. 30 (2022) 87–122. https://doi.org/10.15301/jepa.2022.30.3.87.

[4] B. KVSS, D. Ray, P. Chawdhury, B.S. Rajanikanth, S. Thatikonda, S. Challapalli, Catalytic non-thermal plasma reactor for oxidative degradation of toluene present in low concentration, Catal. Today. 423 (2023) 113998. https://doi.org/10.1016/j.cattod.2023.01.005.

[5] Y. Ding, W. Liu, W. Huang, G. Gao, Z. Liu, H. Xu, Z. Qu, N. Yan, Enhancement of Flue Gas Low-Concentration Toluene Removal in Pulsed Plasma Coupling with Porous Ceramic Modified Catalyst Reactor, Ind. Eng. Chem. Res. 62 (2022) 3249–3258. https://doi.org/10.1021/acs.iecr.2c04086.

[6] X. Yu, S. Li, X. Dang, Y. Zhang, Q. Zhang, H. Zheng, A highly efficient multi-stage dielectric barrier discharge (DBD)-catalytic system for simultaneous toluene degradation and O3 elimination, J. Ind. Eng. Chem. 105 (2022) 393–404. https://doi.org/10.1016/j.jiec.2021.09.040.

[7] M. Xu, Y. Mori, M. Aoki, T. Umemura, A. Okino, Decomposition of Large Flow Toluene Using Multilayer Dielectric Barrier Discharge, in: 2022 IEEE Int. Conf. Plasma Sci., IEEE, 2022: pp. 1–2. https://doi.org/10.1109/ICOPS45751.2022.9813226.

[8] H. Guo, X. Liu, H. Hojo, X. Yao, H. Einaga, W. Shangguan, Removal of benzene by non-thermal plasma catalysis over manganese oxides through a facile synthesis method, Environ. Sci. Pollut. Res. 26 (2019) 8237–8247. https://doi.org/10.1007/s11356-019-04264-5.

[9] K.S. Ayub, Z. Abbas, W.Q. Zaman, Nonthermal plasma catalysis using ferrites as an efficient catalyst for toluene degradation, Res. Chem. Intermed. (2023). https://doi.org/10.1007/s11164-023-05010-w.

[10] Z. Abbas, W.Q. Zaman, M. Danish, A. Shan, C. Ma, K.S. Ayub, M. Tariq, Q. Shen, L. Cao, J. Yang, Catalytic nonthermal plasma using efficient cobalt oxide catalyst for complete mineralization of toluene, Res. Chem. Intermed. 47 (2021) 2407–2420. https://doi.org/10.1007/s11164-021-04406-w.

[11] Z. Abbas, K.S. Ayub, W.Q. Zaman, A. Shan, A. Idrees, H. Khalid, M.U. Mushtaq, S. Abbas, L. Cao, J. Yang, Efficient toluene oxidation by post plasma catalysis over hollow Co3O4 nanospheres, Res. Chem. Intermed. (2022). https://doi.org/10.1007/s11164-022-04930-3.

[12] Z. Abbas, K.S. Ayub, W.Q. Zaman, A. Shan, A. Idrees, M. Abbas, M.U. Mushtaq, S. Abbas, L. Cao, J. Yang, Enhanced toluene degradation using Co3O4 nanorods in post plasma catalysis, Res. Chem. Intermed. 49 (2023) 2843–2853. https://doi.org/10.1007/s11164-023-05025-3.

[13] K.S. Ayub, W.Q. Zaman, W. Miran, M. Ali, Z. Abbas, U. Mushtaq, A. Shahzad, J. Yang, Efficient post-plasma catalytic degradation of toluene via series of Co–Cu/TiO2 catalysts, Res. Chem. Intermed. 48 (2022) 4227–4248. https://doi.org/10.1007/s11164-022-04805-7.

[14] M. Shafaee, E.K. Goharshadi, M. Mashreghi, M. Sadeghinia, TiO2 nanoparticles and TiO2@graphene quantum dots nancomposites as effective visible/solar light photocatalysts, J. Photochem. Photobiol. A Chem. 357 (2018) 90–102. https://doi.org/10.1016/j.jphotochem.2018.02.019.