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TiO_2-ZnO Catalyst: A New Composite For Selective Catalytic Reduction of NO_x with NH_3

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Abstract

Investigations have underscored the pivotal role of NO_x gases in the formation of smog and acid rain, posing threats to human health and ecosystems. Selective Catalytic Reduction (SCR) has emerged as a promising strategy for curtailing NOx emissions. SCR involves the catalytic conversion of nitrogen oxides into benign nitrogen and water vapour, thereby offering a viable approach. In this study, a new composite of low-temperature selective catalytic reduction (LT-SCR) catalyst is synthesized by impregnating ZnO onto TiO_2 ceramic substrate. The introduction of ZnO not only provides a high surface area but also results in the formation of a catalyst. This research presents the outcomes of an investigation involving a range of catalysts employed in SCR, including a composite catalyst composed of titanium dioxide and zinc oxide. The objective is to evaluate the composite catalyst's capacity to reduce pollutants characterized by observable NO_x content. The catalysts, synthesized through the sol-gel processing technique, are characterized by XRD and SEM to ascertain their suitability for catalytic applications. A comprehensive analysis concludes that the laboratory-synthesized samples exhibit acceptable purity, possess a crystalline structure, and hold potential as catalysts.

Keywords: *Composite Catalysts, Environmental Mitigation, Nitrogen Oxides, Power Plant Emissions, Selective Catalytic Reduction, Sol-Gel Processing*

1.0 Introduction

Nitrogen oxides (NO_x), encompassing a group of reactive gases primarily consisting of nitric oxide (NO) and nitrogen dioxide (NO_2), have emerged as pivotal contributors to environmental pollution, with far-reaching implications for human health, the ozone layer, and the ecosystem[1]. Arising predominantly from the combustion of fossil fuels, including coal, diesel, petroleum, natural gas, and various others, NO_x emissions are marked by their adverse effects on both the atmospheric composition and its interaction with the biosphere. The implications of NO_x emissions are multifaceted and multifarious[2]. NO_x has detrimental effects on human well-being, acting as respiratory irritants that threaten respiratory health and overall air quality. Moreover, these emissions contribute to environmental degradation by precipitating smog formation, fine particulate matter generation, acid rain occurrence, ozone layer depletion, and the release of greenhouse gases[3]. The complex interplay between NO_x and environmental components underscores the urgency of addressing this pollution phenomenon. The NO_x emissions matrix is primarily constituted by NO and NO_2, where NO often constitutes a significant fraction, at

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times accounting for up to ninety per cent (90%) of the NOx mixture. While NO_2 is relatively water-soluble and can be efficiently removed from emissions, NO presents a distinct challenge. Due to its unique behaviour resembling that of supercritical fluid at room temperature, NO is notably resistant to conventional atmospheric dispersion and removal mechanisms. This peculiarity renders NO one of the most challenging pollutant gases to eliminate from the atmosphere[4].

The adverse consequences of NO_x emissions have motivated governments, researchers, and industries worldwide to seek effective strategies for reducing their impact. In response to escalating concerns, particularly in the last decade, diverse reduction technologies have been systematically introduced in industries reliant on fuel combustion. Notable among these are industrial boilers and power plants, which are major contributors to NO_x emissions. Among the available technologies, Selective Catalytic Reduction (SCR) has garnered significant attention due to its demonstrated potential to achieve substantial NO_x reduction, often exceeding ninety percent[5]. SCR's effectiveness hinges on the judicious choice and application of catalysts, coupled with a wide operating temperature range that enhances its applicability. Independent studies have investigated the efficacy of reducing agents in SCR, particularly the use of ammonia (NH_3) and urea at temperatures of 200°C-300°C. These reducing agents have exhibited robust potential in facilitating the breakdown of NO_x into nitrogen and water vapour, thereby mitigating their impact on the environment. The catalyst-reducing agent interaction takes place within a catalytic chamber, where NO_x-laden gases meet the catalyst, promoting the desired transformation[6]. The application of both aqueous and anhydrous ammonia in SCR underscores the versatility and adaptability of this technique in diverse industrial settings. The reaction can now be represented by the chemical equations:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (1)$$

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \quad (2)$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \quad (3)$$

The fundamental equation (1) is the cornerstone, outlining the central reaction that drives SCR. Nitric oxide (NO) is a dominant component of NO_X emissions, making up more than 90% of this group. As such, controlling the reaction involving NO is pivotal in NO_X reduction strategies. Equation (1) provides a comprehensive view of the SCR mechanism, where a precise interaction occurs between a nitrous oxide (NO) molecule and an ammonia (NH_3) molecule. This intricate interaction takes place within an environment rich in oxygen (O_2), which plays a crucial role in facilitating the reaction. Under these conditions, the reduction of NO_x emissions is effectively achieved[7]. However, it is essential to note that in situations where oxygen is scarce or absent, the reaction dynamics take a different route, as described in equation (2). In such cases, understanding this alternate pathway becomes crucial for comprehensive SCR process management. However, the narrative embraces further complexity, as rapid SCR events also manifest even in the presence of oxygen. In this context, both NO and NO_2 partake as active participants in the gaseous effusion. As oxygen engages with NO_x gases, the manifestation of NO_2 is realized, orchestrated by their oxidative conversion. The intricate interplay of oxygen in the milieu engenders the evolution of NO_2, an essential intermediary. The differentiation between rapid and standard SCR methods hinges on the formation of nitrogen dioxide (NO_2). In the context of rapid SCR, NO_2 plays a transformative role, giving rise to nitric acid (HNO_3) and nitrous acid (HNO_2) as its byproducts following the breakdown of NO_2. This sequence of transformations eventually leads to the creation of ammonium nitrate (NH_4NO_3), a transient compound formed through the combination of NH_3 and HNO_3. As the temperature increases, ammonium nitrate undergoes gradual decomposition, yielding NO_2 and water vapour (H_2O) as the end products. This transition highlights the pivotal role of NO_2 in accelerating the rapid SCR process due to its unique capacity as a powerful oxidizing agent, surpassing even oxygen (O_2) in this respect. A significant aspect of this phenomenon emerges when considering the interaction between NO and HNO_3. This interaction assumes a central role in governing the rate-controlling phase within the rapid SCR mechanism. The intricate dance of reactions in this focal area underscores its profound importance in orchestrating the kinetic characteristics of the rapid selective catalytic reduction process[8].

In contrast to the frequently employed TiO_2 support, ZnO shares comparable characteristics, including an approximate band gap of 3.0–3.3 eV, excellent thermal stability, and the ease of generating diverse nanostructure morphologies. These attributes make it a promising choice for use as a catalyst support[9,10]. Moreover, both Lewis and Brønsted acid sites can coexist simultaneously on the ZnO surface[11]. This can be ascribed to the improved distribution of active components across the high-surface-area array structure. Furthermore, it's worth noting that in the NO oxidation process using LSMO/ZnO catalysts, no N_2O or any other by-products were detected[12]. This necessarily suggests that ZnO nanostructures on a substrate could be a promising choice as a support for low-temperature selective catalytic reduction (LT-SCR). The objectives of the current research are i) To obtain the composite of TiO_2-ZnO through the Sol-gel process. ii) To characterize the obtained TiO_2-ZnO composite.

1.1 Selection of Catalysts

Within the purview of this investigative study, the process of selecting the catalyst material encompassed two quintessential contenders: titanium dioxide (TiO_2) and zinc oxide (ZnO). The ensuing deliberation probes the ramifications of this selection. Titanium dioxide (TiO_2), a preeminent choice, owes its prominence to its multifaceted attributes, combining remarkable catalytic efficacy with an inherent resilience against sulphur-induced poisoning. This salient property, underpinning its extensive usage as a support material, finds empirical corroboration in a spate of independent studies[13].

Notably, zinc oxide (ZnO) emerges as a formidable candidate for catalyst deployment, distinguished by its dual role as a proficient semiconductor and catalyst. These attributes come to fruition in the context of its application as a catalyst in SCR processes aimed at mitigating NO_x emissions. Expanding on this facet, the amalgamation of manganese oxide (MnO) with zinc oxide (ZnO) nanorods yields intriguing outcomes. The ensuing catalytic assembly exhibits superior efficacy in low-temperature reduction vis-à-vis its titanium dioxide (TiO_2) counterparts, further complemented by an expansive surface area conducive to the absorption of NO_x species[14].

A thorough examination of existing literature highlights the widespread prevalence and universal acceptance of the sol-gel technique in the preparation of catalysts. The inclination towards this method is founded on its ability to create catalysts that possess exceptional physicochemical properties, which align closely with the requirements of the Selective Catalytic Reduction (SCR) field[15,16]. The ascendancy of the sol-gel method in the realm of catalyst synthesis is further reinforced by its capacity to produce materials distinguished by heightened reactivity, uniform structure, and customizable surface characteristics. This, in turn, amplifies their efficiency and utility within the context of SCR applications.

2.0 Preparation of Catalysts

In this research study, we utilized the versatile Sol-gel method for the preparation of our catalyst materials. This wet chemical technique comprises a sequence of steps that lead to the creation of catalyst particles with specific properties. Let us break down the process to gain a more comprehensive understanding:

1. ***Chemical Solution Preparation*****:** The process initiates with the formulation of a chemical solution. We blend the chosen catalyst material with a forming agent, which can be a precursor compound that aids in the conversion of the catalyst into its desired solid form. The mixing is performed meticulously to ensure an even distribution of the catalyst throughout the solution.

2. ***Stirring*****:** The chemical solution is placed within a controlled environment, in our case, a laboratory with a room temperature of 25°C and a relative humidity of 55 per cent. In this setting, the solution is vigorously stirred using a magnetic stirrer. The purpose of this stirring is to promote the interaction between the catalyst and the forming agent, guaranteeing a homogeneous mixture. Achieving homogeneity is crucial because it significantly influences the catalyst's properties and its subsequent performance.

Subsequently, centrifugal force is employed to eliminate any remnants of the residual solution. The resulting amalgamation is then promptly subjected to crushing, closely followed by a precisely timed calcination process. This calcination process is carefully tailored to occur at the specified temperature and under prevailing atmospheric conditions. The application of heat is orchestrated at an exact temperature, primarily to enhance reaction kinetics, thereby facilitating the removal of excess liquids and residual moisture. The meticulous execution of these steps is critical to the successful preparation of our catalyst materials, ensuring that they possess the desired characteristics and performance qualities for their intended application.

2.1 Titanium Dioxide

Approximately 40 ml of titanium isopropoxide was dissolved in 20 ml of distilled water. This amalgamation took place within a beaker. Subsequently, a magnetic stirrer was employed, setting it to operate within the range of 1200 to 1300 rpm, with the specific objective of thoroughly mixing the contents within the beaker. During the stirring process, nitric acid (HNO_3) was introduced gradually, in small and incremental quantities, to the amalgamated solution within the beaker. The stirring continued for a continuous duration of one hour, ensuring a complete and uniform dispersion of the components. Following this one-hour stirring period, “sonification” was initiated, which involves subjecting the mixture to high-frequency ultrasonic waves, within the frequency range of 20 to 40 kilohertz (kHz), with the primary aim of purifying and cleansing the mixture. The sonication step was executed for 30 minutes. Upon completion of sonication, the mixture was carefully transferred into centrifuge tubes. The first round of centrifugation was carried out for 30 mins using distilled water, followed by a second round of centrifugation for another 30 mins, this time employing ethanol. These centrifugation steps were instrumental in separating and isolating the wet mixture, which was subsequently transferred to a dish. the dish was introduced into an oven set at a constant temperature of 70^{o}C. This operation was sustained for three hours with the primary objective of eliminating any remaining moisture content from the mixture. The resultant mixture was meticulously placed into a crucible, which was subsequently inserted into a muffle furnace for calcination. The calcination procedure was executed at elevated temperatures, specifically within the range of 550^{o}C to 600^{o}C for an exposure duration of six hours, inducing the transformation of the dry powder into crystalline nanoparticles.

2.2 Zinc oxide

To initiate the preparation process, a 1M solution of zinc sulfate ($ZnSO_4$) and a 2M solution of sodium hydroxide (NaOH) were created by dissolving them separately in distilled water. The sodium hydroxide solution was added drop by drop into the zinc sulfate solution while maintaining constant stirring, employing a magnetic stirrer. The stirring was continued over a 12-hour duration, with the stirrer operating within a range of 900 to 1000 rpm. This extended stirring period ensured the thorough homogenization of the two solutions. Following the prolonged stirring, the mixture underwent a “sonication” treatment for 30 mins, with the conditions remaining the same as mentioned before. After the sonication process, the mixture was carefully transferred into a centrifuge for further processing. The centrifugation procedure consisted of two rounds, like the process for Titanium dioxide: the first round, lasting 30 minutes performed using distilled water, and the second round, also lasting 30 minutes, utilizing ethanol as the medium. The centrifuged wet mixture was subsequently transferred into a dish, which was then positioned inside an oven set to maintain a constant temperature of 70^{o}C, sustained for 3 hours. After the meticulous drying process, the resulting mixture was transferred into a crucible. The crucible, containing the dry mixture, was then inserted into a muffle furnace for the calcination process, which involves subjecting the mixture to high temperatures, specifically at 650^{o}C for an extended period of 6 hrs.

2.3 Titanium Dioxide and Zinc Oxide Composite

To create the composite catalyst, finely ground crystalline nanoparticles of titanium dioxide (TiO_2) and zinc oxide (ZnO) were carefully blended. The blending process was carried out in a stone crucible, and a pestle was employed to ensure a thorough and homogeneous mixture of these two compounds. This meticulous blending was essential to achieve the desired composite structure. Subsequently, the prepared mixture was subjected to the calcination process at a controlled temperature of 450^{o}C for 3 hrs.

The formulation process of the TiO_2-ZnO composite catalyst is represented in Figure 1.

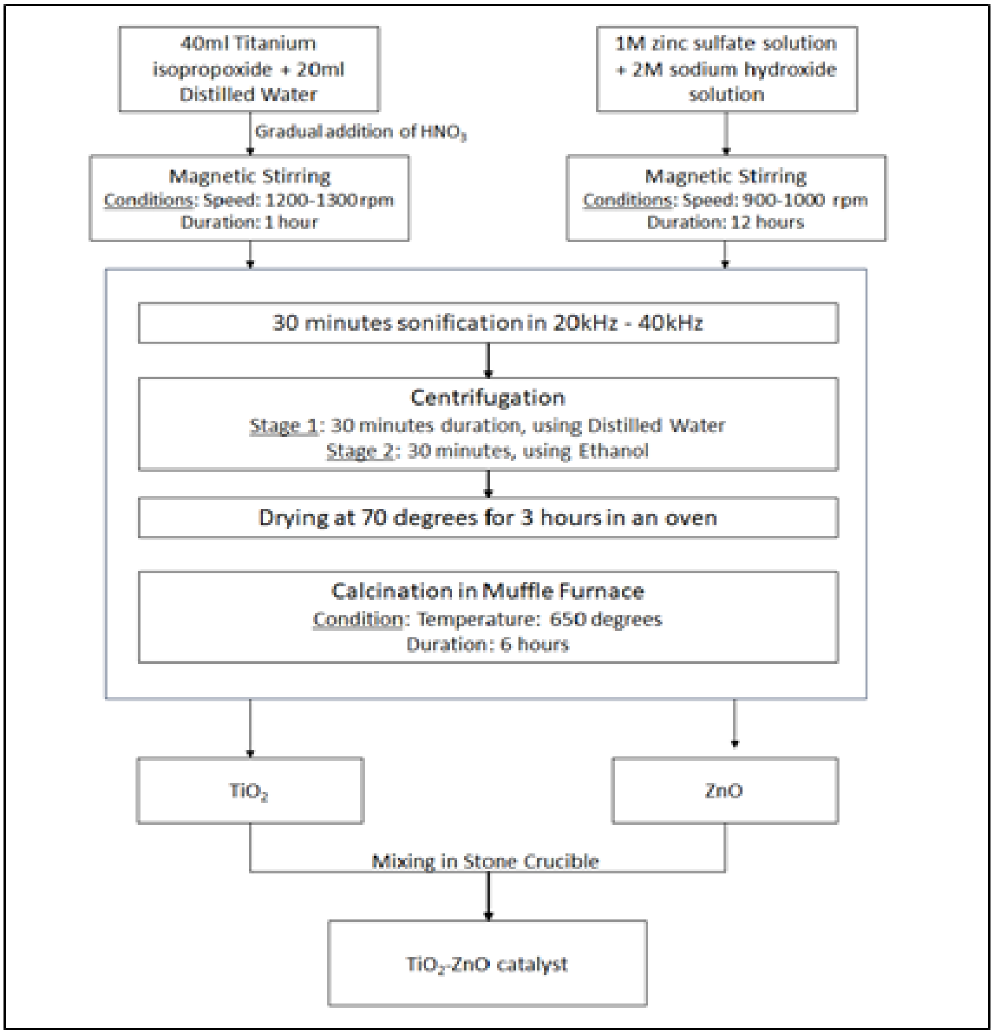


Figure 1. TiO_2 - ZnO formulation process.

3.0 Results and Discussion

3.1 X-ray Diffraction

The X-ray Diffraction (XRD) pattern obtained for the three chosen samples is shown in Figures 1 to 3. Following are the key observations specific to each catalyst:

(a) In Figure 2(a), the diffraction pattern obtained for the titanium dioxide (TiO_2) nanoparticles agrees well with the presence of the anatase phase of Titania [JCPDS card no.21-1272]. A strong diffraction peak around 27.50 and 440 confirms the anatase phase to form from the as-synthesized nanoparticles. The absence of other observable and/or spurious peaks reveals an overall purity of the as-synthesized sample. The intense and broad diffraction peaks suggest the formation of nano-sized crystalline particles.

(b) In Figure 2(b). the x-ray diffraction (XRD) studies carried out on the ZnO nanoparticles confirm a hexagonal "wurtzite" structure. The diffraction peaks are located at 31.780, 34.570, 36.340, 47.620, 56.650, 63.050, 66.600, 68.100 and 69.190. These peaks confirm the presence of the "wurtzite" phase of the ZnO nanoparticles [JCPDS Card no.36-1451]. No other additional peaks were noticed, which confirms the overall purity of the sample prepared.

(c) In Figure 3 formation of the composite is evident from the X-ray diffraction (XRD) pattern obtained for the TiO_2-ZnO sample. The presence of peaks corresponding to

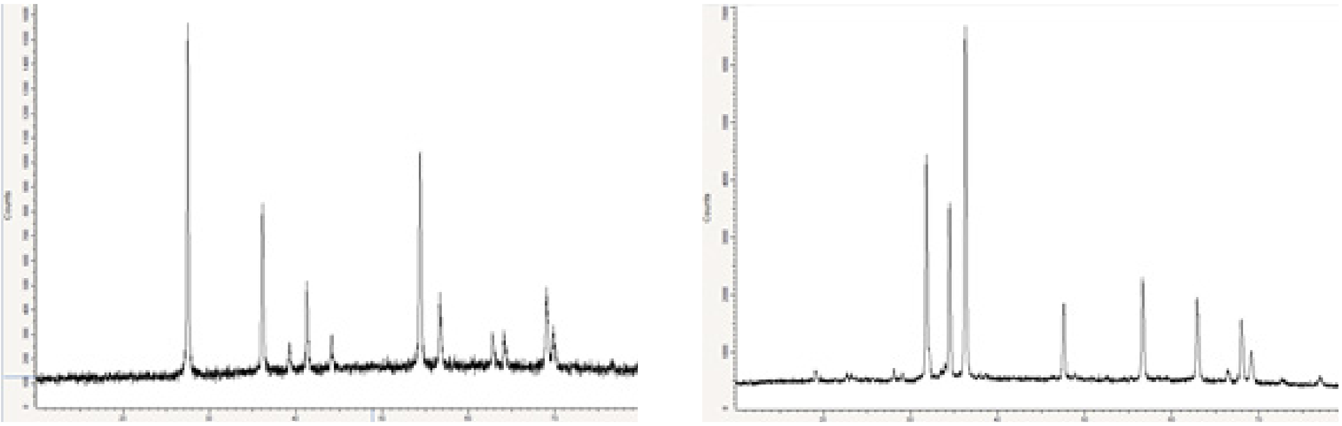


Figure 2. X-ray diffraction (XRD) pattern of (a) titanium dioxide (TiO_2), (b) zinc oxide (ZnO).

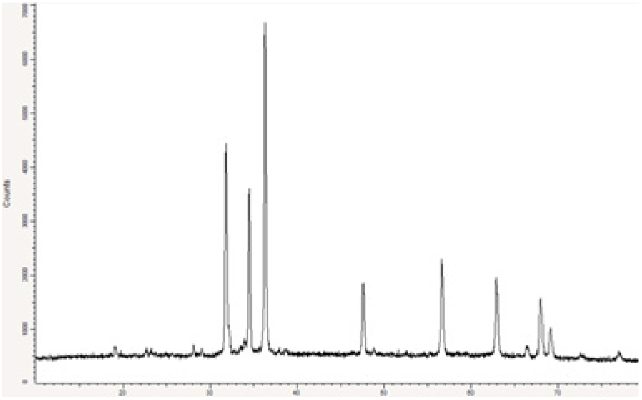


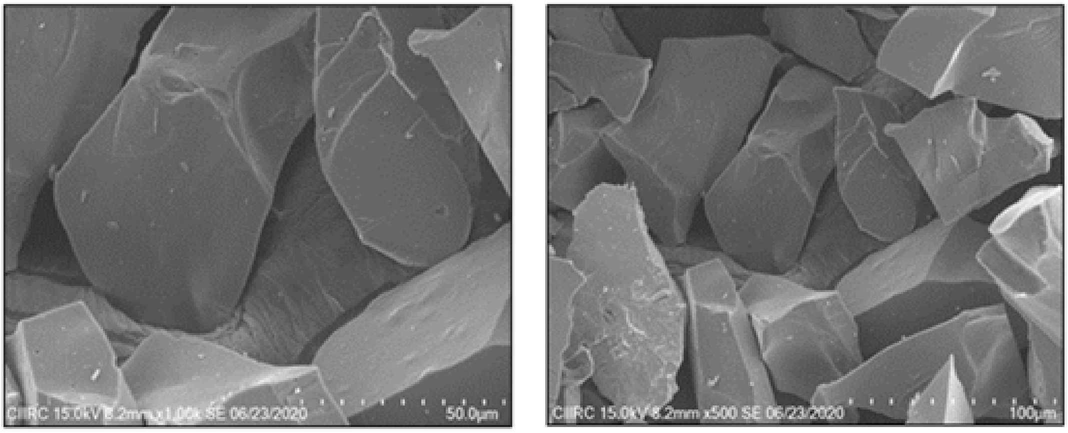
Figure 3. X-ray Diffraction (XRD) pattern of the composite TiO_2-ZnO.

both the 'anatase' phase of Titania as well as the hexagonal 'wurtzite' phase of zinc oxide (ZnO) was observed in the X-ray diffraction study, which confirms the formation of the composite. The broad and intense peaks suggest the size to be in nano-regime.

The size of the nanoparticles was calculated using the Debye-Scherer formula. D = 0.89 λ / β Cos θ, where 0.89 is Scherer's constant, λ is the wavelength of the X-ray and β is full width at half maximum corresponding to the most intense peak. The size obtained for the titanium dioxide (TiO_2) nanoparticles was 62 nm, it was 51 nm for the zinc oxide (ZnO) and for the composite (TiO_2-ZnO) nanoparticles it was 45 nm.

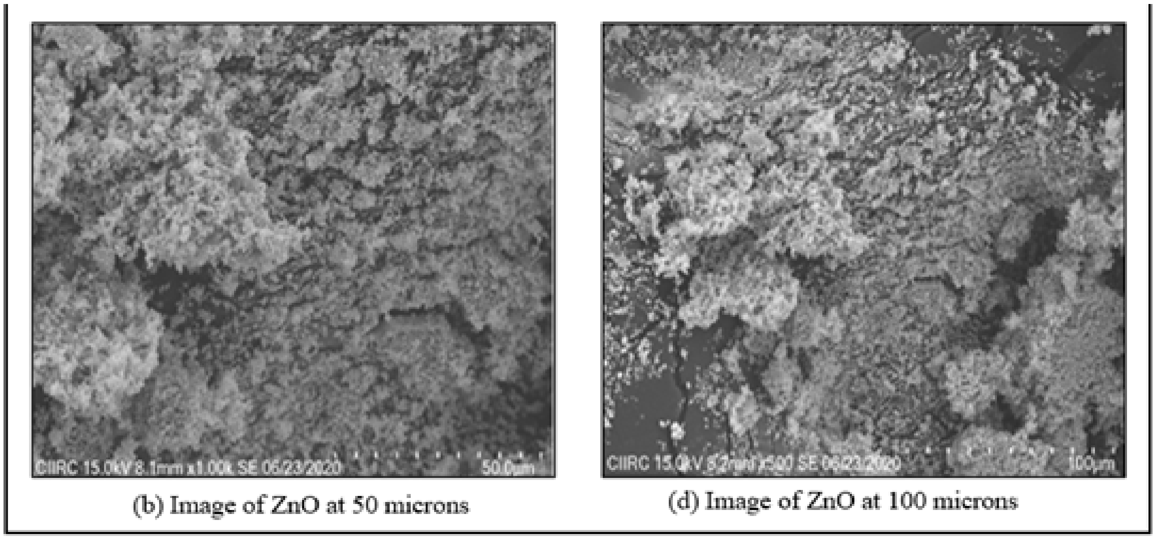
3.2 Scanning Electron Microscopy [SEM] Observations

All three samples synthesized were examined in a scanning electron microscope as shown in Figures 4



(a) Image of TiO_2 at 50 microns

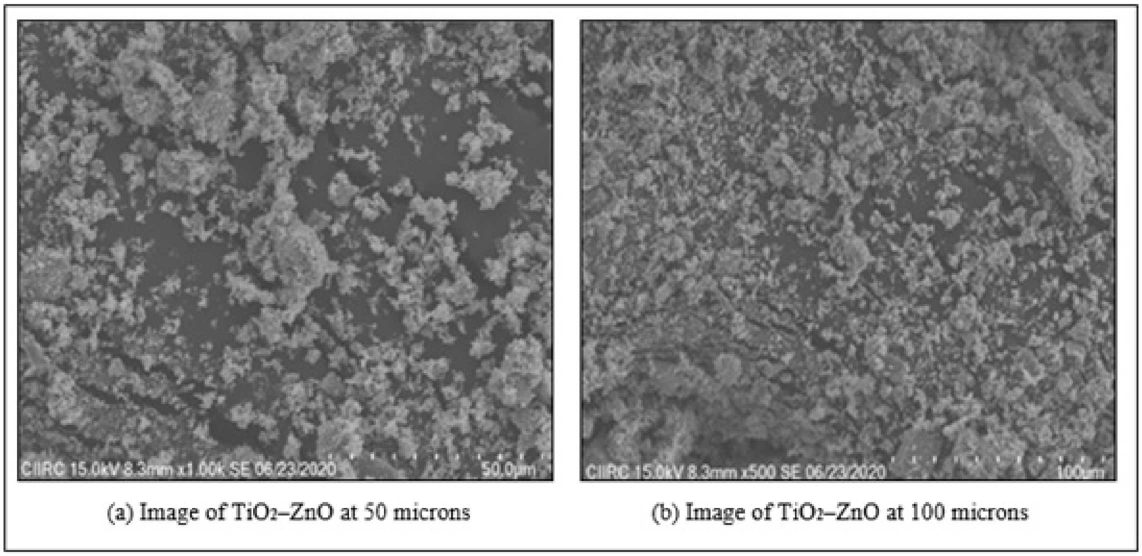
(c) Image of TiO_2 at 100 microns



(b) Image of ZnO at 50 microns

(d) Image of ZnO at 100 microns

Figure 4. Scanning electron micrographs at two different magnifications of the as-processed (a) titanium dioxide (TiO_2) at 50 microns (b) titanium dioxide (TiO_2) at 100 microns (c) zinc oxide (ZnO) at 50 microns (d) zinc oxide (ZnO) at 100 microns.



(a) Image of TiO_2–ZnO at 50 microns

(b) Image of TiO_2–ZnO at 100 microns

Figure 5. Scanning electron micrographs showing the catalyst TiO_2-ZnO at 50 and 100 microns.

and 5, to analyze the morphology of the particles along with other key intrinsic features in the microstructure. The titanium dioxide (TiO_2) nanoparticles revealed a polished nano-flake-like morphology with trace evidence of facets (Figure 4(a) and 4(b)). The facets may be the result of the temperature chosen for calcination. Both zinc oxide (ZnO) (Figure 4(c) and 4(d)) and the TiO_2-ZnO composite (Figure 5) revealed a near-spherical morphology with traces of agglomeration. The particle size agrees reasonably well with the value obtained using the Debye equation.

4.0 Conclusions

This pioneering experimental research study has unveiled a range of pivotal findings that carry substantial significance for the field.

1. The synthesis of zinc oxide (ZnO) and titanium dioxide (TiO_2) nanoparticles through the meticulous sol-gel technique, followed by their subsequent amalgamation, grinding, and calcination, culminated in the successful production of TiO_2-ZnO composite nanoparticles.
2. The peaks in the XRD graph of all the samples match reasonably well with the peaks of the reference nanoparticles of the same material thereby confirming the samples synthesized to be relatively pure.
3. The size of the nanoparticles was calculated using the Debye-Scherer formula. The size obtained for the TiO_2 nanoparticles was 62 nm, for the ZnO nanoparticles it was 51 nm and for the TiO_2 -ZnO composite nanoparticles it was 45 nm.
4. This is supported by the scanning electron micrographs, which show relatively good dispersion and less clustering of the nanoparticles, despite the titanium dioxide TiO_2 nanoparticles having a flaky structure.
5. Using the chosen parameters, the compounds synthesized can be catalysts suitable for Selective Catalytic Reduction (SCR). This opens new avenues for catalytic applications, thereby augmenting our understanding of how nanomaterials address complex challenges.

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