



Article Ultrasound-Assisted Synthesis of a N-TiO₂/Fe₃O₄@ZnO Complex and Its Catalytic Application for Desulfurization

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Abstract: Ultrasound (US)-assisted synthesis of a N-doped TiO₂ catalyst supported on magnetically separable Fe₃O₄@ZnO particles and its subsequent application for catalytic desulfurization were performed in the present work. The catalyst was also synthesized conventionally to compare the role of acoustic cavitation (US horn working at 20 kHz frequency) in improving the catalyst characteristics. The effects of different ultrasonic (US) power (80 W to 120 W) and duration (15 min to 75 min) were studied to elucidate the best operating conditions for obtaining the minimum particle size of the catalyst. Under optimal conditions of 80 W power and 30 min of time, a minimum particle size of 31.22 μ m was obtained. The particle size for the conventionally synthesized catalyst was 806.4 μ m, confirming that the particles were agglomerated in the absence of ultrasound. The synthesized catalyst was used for the desulfurization of thiophene to assess the performance of the catalyst, along with a comparative study between the conventionally synthesized catalyst and that obtained using the US-assisted approach. It was evident that the performance of the catalyst synthesized sonochemically was superior, as US enhanced the activity of the catalyst by reducing the particle size and achieving homogeneity. The desulfurization achieved using the sonochemically synthesized catalyst was 47% in 100 min at a 2 g/L catalyst dose and a 3 mL/L H₂O₂ dose. The desulfurization was only 25% using the conventionally synthesized catalysts under the same operating conditions. Overall, the present work demonstrates the advantages of US in improving the catalyst characteristics, as well as the successful application of catalyst in desulfurization.

Keywords: ultrasound; heterogeneous catalyst; thiophene desulfurization; intensification; catalyst characteristics

1. Introduction

The ever-increasing population is creating an increasing demand for various means of public and private transport, leading to a rise in fuel consumption and vehicular pollution. Burning of different sulfur compounds that are present in the fuels used in power stations and transportation causes emissions of sulfur oxides (SO_x) to the atmosphere. To counter the environmental concerns, rigid regulations are being imposed on the amounts of sulfur allowed in fuels used in both the transportation sector and for power generation [1]. There are diverse sulfur compounds—e.g., thiols, sulfides, disulfides—that release SO_x into the atmosphere from different fuels [2]. SO_x gases can also react with atmospheric moisture to form sulfates and cause acid rain, which has the potential to damage the ecosystem. Furthermore, particulate matter (PM) formed through sulfur emissions can cause respiratory illnesses, heart disease, and asthma, posing problems for human health. The catalytic converters in automobiles are installed to reduce NO_x emissions and particulate matter. Sulfur compounds poison the catalytic converters by adsorbing on the precious metal catalysts and, hence, reducing the adsorption of NO_x, CO, and hydrocarbon reactions, again contributing to the environmental emissions. Considering all of these issues, desulfurization of



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). liquid fuel is very important so as to reduce its sulfur content to lower than 10 ppm, as per the typical guidelines set by the United States Environmental Protection Agency (USEPA) for diesel and gasoline [3]. Over the years, several catalytic processes have been developed and commercialized targeting the removal of the harmful sulfur compounds from the liquid fuel. Hydrodesulfurization (HDS) is typically used in the petroleum industry for the elimination of sulfur from fuels. In this process, the fuel makes contact with H₂ gas passed over a catalytic bed under extreme conditions (T = $350-400 \degree C$, P = 3-7 MPa) [4]. However, HDS is not effective for eliminating refractory heterocyclic compounds such as dibenzothiophene (DBT) and its derivatives. The steric hindrances of the bulky molecules and the stable S-C bonds make it difficult to treat DBT and its derivatives using the HDS approach. Additionally, high temperature and pressure are required for the HDS, along with 5–15-fold larger processing units [5]. Thus, HDS is neither very cost-effective nor an efficient process for removing the refractory sulfur group compounds.

Adsorptive desulfurization (ADS), extractive desulfurization (EDS), and biodesulfurization (BDS) are other potential desulfurization techniques that operate under mild conditions and produce ultraclean fuels. In the ADS process, adsorbents are used that selectively adsorb the sulfur compounds. The active adsorbent is placed on a porous and non-reactive substrate that allows the greatest surface area for adsorption. However, efficient adsorbents can be costly, and disposal is a problem. Moreover, regeneration of spent adsorbent is a major problem and not cost effective. Extractive desulfurization can be easily carried out under atmospheric conditions using appropriate solvents with higher selectivity for sulfur-containing compounds. However, the effective extraction process comes at a cost of generating huge amounts of liquid waste. Recently, BDS has gained significant attention as it offers a green processing route; however, the sluggish process is a major hindrance in the successful application of the BDS process [6]. Oxidative desulfurization (ODS) is an emerging approach where the sulfur-containing compounds are oxidized to corresponding sulfones by a chemical reaction with an oxidant (e.g., H₂O₂, Fenton). ODS is usually carried out under mild operating conditions and in the absence of hydrogen gas. The formed sulfone compound, which has higher polarity, can be easily extracted from the fuel. Among the different ODS approaches, photocatalytic oxidative desulfurization (PODS) is an emerging technique that is environmentally friendly, given that a suitable photocatalyst and oxidant are used in the process that do not create disposal issues. This process also offers advantages over other processes owing to its low operating costs and the probable free source of radiation in the form of natural sunlight [5]. During PODS, sulfur-containing molecules in the oil phase are oxidized at the catalyst surface, increasing the molecular polarity and, hence, causing extraction into the solvent phase [7]. Different oxidants—including hydrogen peroxide, O₂, and air—are generally applied to increase the rates of oxidation of sulfur compounds, including thiophenes. A typical photocatalytic oxidative reaction can be represented as follows:

Refractory Organosulfur compounds (thiophene and derivatives) $\xrightarrow{\text{Photocatalyst, Oxidant}}_{\text{UV/Visible light irradiation}}$ Sulfoxides Sulfones SO₄²⁻ (1)

Despite the fact that ODS is a low-cost process, its operating temperature (60–80 °C) can lead to oxidation of some parts of alkenes and aromatics, lowering the octane number of the fuel [8]. By replacing the catalyst in the ODS process with a suitable photocatalyst, the process could be accomplished under ambient conditions. Considering this benefit, PODS was selected in the present work. Critical analysis of the literature revealed that the catalytic desulfurization depends on various operating parameters, including pH, agitation speed, reaction temperature, and catalyst loading. For example, Abbas et al. [9] observed that the desulfurization efficiency increased with the decrease in the pH of the solution and the increase in the agitation speed, reaction temperature, and catalyst loading. A similar trend was observed by Yu et al. [10] for oxidative desulfurization of dibenzothiophene (DBT), which increased as the pH of the solution decreased, reaching its maximum at the lowest value of pH 14. Dedual et al. [5] reported that both increasing and decreasing

the pH from the natural pH of the solution (which was 4) decreased the photocatalytic desulfurization process using TiO_2 as photocatalyst.

Titanium dioxide (TiO_2) is a well-established photocatalyst, but it also has some drawbacks, including rapid electron–hole recombination and poor responses in visiblelight irradiation. To obtain a better result in the visible range, non-metal doping is one of the applied methods, as it can shift the edge of the valance band, thereby decreasing the bandgap [11]. N is supposed to be a better dopant among different non-metals, as the size of its anion is close to that of the oxygen present in the catalyst structure [12].

Recently, many researchers have proposed various methods for enhancing the efficacy of photocatalysts by (i) incorporating defects into the crystal lattice by metal/ nonmetal doping, (ii) addition of other semiconductor materials, and (iii) improving the structure/surface area of the photocatalyst. Non-metal doping (e.g., N, C, P, S, O) narrows the bandgap of the photocatalyst and extends the light absorption range from UV to visible light [13]. Kalantari et al. [12] synthesized N-doped TiO₂ for photocatalytic oxidative desulfurization of dibenzothiophene and reported it to be a very efficient catalyst for PODS. Moreover, the photocatalyst showed very good reusability. Khan et al. [14] also observed 5.76% sulfur removal from dibenzothiophene using the Fe-N-TiO₂ photocatalyst. The best performance was observed using the catalyst, 0.2 Fe-30 N-TiO₂, which was synthesized by calcination at 200 °C with the addition of H₂O₂. Although there are reports of the use of N-doped TiO₂ for PODS, the synthesis process has been based on the conventional approach. The present work reports the use of ultrasound-assisted synthesis, while also highlighting the comparison with a conventionally synthesized catalyst for confirming process intensification.

In the context of the reusability of the catalyst, the use of catalysts with magnetic properties in oxidative desulfurization has gained significant importance. Such catalysts usually work as active components loaded on supports, offering magnetic properties and allowing easy separation using an external magnetic field. The major catalyst particles or the active component can be loaded on the magnetic Fe_3O_4 NPs using a simple synthesis process, and the resulting combination achieves higher efficiency and better separation [15]. Fe_3O_4 nanoparticles also offer the distinct advantage of biocompatibility. However, the bare Fe_3O_4 NPs have high surface energy and tend to agglomerate. Moreover, they are susceptible to oxidation due to their high chemical activity, which affects their magnetic properties [16]. Hence, surface modification is required to improve the stability and dispersibility of Fe_3O_4 NPs. Such functionalization of the surface of NPs can be achieved by coating them with a protective shell around the magnetic core. It has been reported that can be easily coated on Fe_3O_4 as a protective layer [17]. ZnO has also been reported to show enhanced activity for desulfurization [18], and it is also a porous nanomaterial as well as a good photocatalytic material. A higher degree of porosity for the supports implies enhanced adsorption of the compound on the surfaces of ZnO-based materials. Improved adsorption is also an important requirement in photodegradation, making ZnO an excellent catalyst owing to its adsorption capabilities [18,19]. For example, Khalafi et al. reported that the application of a synthesized ZnO catalyst at an optimal loading of 0.01 g/L led to an effective degradation of dibenzothiophene (DBT) under ambient conditions [20]. In another study, the performance of ZnO in the degradation of DBT was studied by Hosseini et al., and it was reported that DBT degradation of 45% and 35% was observed under UV and visible light, respectively [21].

As the surface characteristics of catalysts are important in deciding the intensification in desulfurization, the use of ultrasound during the synthesis can be an effective approach to obtain catalysts with higher surface areas. Ultrasonic irradiation leads to the formation of compression and rarefaction cycles that drive different stages of cavitation, including the origination of cavitational bubbles, subsequent growth, and spontaneous collapse when the size reaches equilibrium, depending on the operating conditions [22]. The collapse of cavities is followed by the release of immense amounts of energy. Extreme temperature (~5000 K) and pressure (~1000 atm) pulses are created in the medium, creating local hot spots coupled with turbulence, as well as strong liquid jets [23]. The generated cavitational conditions intensify the chemical and physical processes, leading to beneficial synthesis of various nanostructured materials with desired particle size distribution. The chemical effects caused by acoustic cavitation include generation of reactive free radicals, which can bring about intensification of photocatalytic oxidation reactions [24].

The present work focuses on synthesizing a N-doped TiO₂ catalyst supported on magnetically separable Fe₃O₄@ZnO nanoparticles in the presence of ultrasound to enhance their magnetic separability. Subsequent application of the synthesized catalyst in catalytic desulfurization was studied to demonstrate the efficacy of this catalyst for desulfurization of the model fuel oil under ambient conditions, which can help in maintaining the fuel's characteristics. It was observed from the literature that there are very few research papers available for PODS using magnetically separable catalyst—and none where the process intensification of ultrasound during the synthesis has been demonstrated. Considering this analysis, the novelty of the present work—elucidating an improved synthesis method for a catalyst and its subsequent application for control of harmful emissions such as SO₂ from liquid fuel—is clearly established.

2. Experimental

2.1. Materials

Ethylenediamine (98%) and titanium(IV) isopropoxide (98%) were obtained from AVRA Synthesis Pvt., Ltd. (Hyderabad, India). Ferrous chloride tetrahydrate (FeCl₂·4H₂O) was procured from Molychem Manufacturers of Laboratory Reagents and Fine Chemicals, Mumbai, India. Ferric chloride hexahydrate (FeCl₃·6H₂O) and zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O) were procured from Thomas Baker Pvt., Ltd., Mumbai, India. In this work, the simulated diesel fuel was prepared by mixing thiophene (representative sulfur compound; Spectrochem Pvt., Ltd., Mumbai, India) and n-hexane (representative diesel, 98% pure; obtained from Thomas Baker Pvt., Ltd., Mumbai, India). Hydrogen peroxide (30% v/v), HPLC-grade acetonitrile, and n-octane (AR grade) were also procured from Thomas Baker Pvt., Ltd., Mumbai, India.

2.2. Synthesis of Magnetic Fe₃O₄ Nanoparticles

The synthesis of magnetic Fe_3O_4 NPs was based on the synthesis procedure for polyoxometalate-based magnetic nanocomposites reported in the literature [25]. Figure 1 describes the conventional procedure and the modifications performed in the ultrasound-assisted synthesis approach. Essentially, the conventional process was modified by incorporating ultrasonic irradiation for 10 min at room temperature (ultrasonic horn, M/S Dakshin, Mumbai, operating frequency of 20 kHz) as a source of intensification. During the synthesis, NaOH was added gradually to adjust the pH of the solution to 10, along with continuous stirring until a black precipitate was obtained. The mixture was then sonicated again for 20 min using the same ultrasonic horn. The precipitate was then magnetically separated, followed by washing with deionized water and ethanol. The washed precipitate was then dried at 100 °C for 5 h.



Figure 1. Stepwise methodology for the synthesis of magnetic Fe_3O_4 nanoparticles using conventional and ultrasound-assisted synthesis methods.

2.3. Synthesis of Fe₃O₄@ZnO 'Core-Shell' Nanoparticles

The core–shell magnetic $Fe_3O_4@ZnO$ NPs were prepared using the co-precipitation method [26]. Precursors of Fe_3O_4 and ZnO were taken at a mass ratio of 1:6, which was selected based on the literature results showing that better photocatalytic activity is obtained at this ratio [27]. Figure 2 shows the conventional method of synthesis [27] and the modifications made during the ultrasound-assisted synthesis. In the US-assisted synthesis, zinc acetate was dissolved in ethanol, followed by the addition of Fe_3O_4 , and the resultant solution was sonicated for 10 min. Subsequently, the pH was adjusted to 10 using NaOH, and the mixture was again subjected to sonication for 30 min. The resulting precipitate was magnetically separated, washed with deionized water and ethanol, and then dried at 100 °C for 5 h.



Figure 2. Stepwise methodology for the synthesis of $Fe_3O_4@ZnO$ 'core-shell' nanoparticles using conventional and ultrasound-assisted synthesis methods.

2.4. Synthesis of N-Doped TiO₂ Supported on Magnetic NPs

N-doped TiO₂ was first obtained using ethylenediamine (EDA) as the nitrogen precursor, which has been proven to offer a greater surface area and enhanced photodegradation capability [28]. Subsequently, the N-TiO₂/Fe₃O₄@ZnO complex was synthesized using the sol–gel method. A TiO₂ sol stock solution was prepared using titanium(IV) isopropoxide, ethanol, nitric acid (to maintain a pH of 4), and deionized water, such that the TTIP concentration was 0.4 M. The prepared core–shell Fe₃O₄@ZnO particles were added to this solution and mixed thoroughly. Ethylenediamine (EDA) was added to the resultant solution until the molar ratio of Ti:N became 4. The resulting mixture was sonicated for 30 min, followed by 2 h of aging. The formed gel was dried at 100 °C for 12 h and then calcined at 500 °C for 2.5 h.

During the synthesis, the effects of US power (over the range of 80–120 W) and time (15–75 min) were studied to establish the best synthesis conditions for the photocatalyst complex. Figure 3 shows the flow diagram for better understanding of the catalyst synthesis process. The catalyst was prepared conventionally without being subjected to sonication and with mechanical stirring at 400 rpm for 3 h, using an otherwise similar procedure. A

catalyst complex was also prepared using only Fe_3O_4 as a support under similar conditions in the presence of US for comparison of the activity in the desulfurization.





2.5. Characterization of the Synthesized Catalyst

2.5.1. Particle Size Analysis

The main purpose of using ultrasound in the synthesis is to obtain reduced particle size and achieve uniform distribution of particles. Hence, analyzing the particle size of the obtained catalyst is of utmost importance. A Bettersizer 2600E (Wet) particle size analyzer (M/s Bettersize Instruments Ltd., Liaoning, China), working on the principle of laser diffraction, was used to quantify the mean particle size of all of the catalyst samples, as well as to understand the particle size distribution.

2.5.2. X-ray Diffraction Analysis

X-ray diffraction is an important technique that reveals information about the crystallinity of the samples. The X-ray diffraction patterns of the catalysts were recorded using a Rigaku Smartlab A Series diffractometer (Tokyo, Japan) operating with Cu-K α radiation at $\lambda = 1.5425$ Å and room temperature. The XRD patterns of the catalyst samples were recorded between 5° and 80°, with an increment of 0.01° per step.

2.5.3. Fourier-Transform Infrared (FTIR) Spectroscopy Analysis

FTIR spectroscopy is used for the identification of different functional groups. During the analysis, infrared (IR) radiation is passed over the catalyst sample, part of which is

transmitted through the sample, while the rest is absorbed by the sample. The obtained spectrum shows the various absorbance peaks at different wavelengths, indicating different types of bonds or functional groups (e.g., alkanes, alkyls, alcohols, ketones, etc.) present in the analyzed samples. Typically, the analytical spectrum of an unknown sample is compared with a catalogue of known material spectra to identify the components of the sample. In the present work, the FTIR spectra of the catalysts were recorded on an Alpha instrument from Bruker (Billerica, MA, USA), with the wave number for the analysis ranging from 4000 to 600 cm⁻¹.

2.6. Studies of Desulfurization of Thiophene

2.6.1. Experimental Methodology

The catalysts were screened based on particle size, and the catalyst with optimal size was used for the desulfurization trials. All of the experiments were performed in a 250 mL quartz beaker with a height of 95 mm and diameter of 68 mm. For all of the desulfurization experiments, the US horn was operated at 100 W and a 70% duty cycle. The diameter of the US horn's tip was 1 cm, and it was dipped in the reaction mixture to a depth of 0.5 cm. The reactor assembly (Figure 4) contained the quartz beaker, US horn, and a UV chamber equipped with two 8 W lamps (the generally available configuration locally) placed opposite to one another [28].



Figure 4. Combined ultrasonic horn with UV setup for the photo-oxidative desulfurization.

All experiments were performed at a constant thiophene concentration of 100 ppm in n-hexane used as a model diesel fuel. The catalyst quantum of 2 g/L and oxidant quantity of 3 mL/L were kept constant for all experiments, since the main objective was to compare the activity of the different catalysts in terms of the extent of desulfurization. The desulfurization experiments were carried out using three catalysts: N-TiO₂/Fe₃O₄@ZnO (conventionally obtained), N-TiO₂/Fe₃O₄@ZnO (synthesized using the US-assisted approach), and N-TiO₂/Fe₃O₄ (synthesized using the US-assisted approach). The effectiveness of a combined approach of sonocatalysis and UV photo-oxidation in the presence of H₂O₂ was also studied. The experiments were performed for 100 min of treatment time, and sampling was conducted at 20 min intervals to analyze the progress of desulfurization. The withdrawn samples were analyzed using HPLC to quantify the extent of desulfurization.

2.6.2. Analysis Using HPLC

The thiophene concentration in the model diesel was quantified using HPLC analysis (Thermo Fisher Scientific Ltd., Waltham, MA, USA, model Ultimate 3000). A C18 reversephase column (4.6 mm \times 150 mm) was used for the analysis, and a mixture of acetonitrile and DI water (at a ratio of 80:20) was applied as the mobile phase at a constant flow rate of 1 mL/min. During the analysis performed at a wavelength of 231 nm, the column temperature was maintained at 25 °C. A calibration curve was initially established using known concentrations of thiophene and, subsequently, applied for the measurements of concentrations of the samples withdrawn during the treatment.

3. Results and Discussions

3.1. Effects of US Parameters on Particle Size

The study of the effects of US parameters such as sonication power and US irradiation time on the particle size of the synthesized catalyst was carried out in order to obtain the optimal particle size with uniform distribution. The US parameters were varied during the synthesis of N-doped TiO₂ supported on magnetic NPs.

3.1.1. Effect of US Power

Experiments on the effect of power dissipation over the range of 80 W to 120 W were performed to establish the best power for obtaining the lowest particle size of the catalyst. The experiments were performed under constant conditions of 20 kHz as the frequency, 70% as the duty cycle, and 30 min of sonication time. The obtained results are presented in Table 1. It can be observed from the table that the particle size increased from $31.22 \ \mu m$ to $304.4 \,\mu\text{m}$ as the power increased from 80 to 120 W. The obtained trend indicates that the effective tendency of formation and collapse of cavitation bubbles at lower power causes effective breakage of the particles, rather than the higher power. In addition, higher power may lead to too many cavitation bubbles in the system, leading to agglomeration effects and lower cavitational activity. The physical effects of US irradiation are better seen under lowintensity irradiation [22]. Moreover, higher power input to the reaction medium stimulates increased agglomeration of the particles, as also observed in a previous study [29]. Hence, a power of 80 W was selected for further studies based on the results obtained in the present work over the specific range of power investigated. Still, lower power values below 80 W were not used in the present work due to the expected trend that cavitational activity will be much lower at much lower power dissipation. It is imperative to understand that the trends obtained in the current work cannot be generalized and are dependent on the specific system. Tiple et al. [28] elucidated that particle size decreased from 780 nm to 361.4 nm with an increase in ultrasonic power from 80 W to 110 W. Similarly, the average particle size was reported to decrease from 298 nm to 167 nm when the ultrasonic power was increased from 80 W to 200 W for the studies conducted by Yang et al. [30].

Table 1. Effects of US power on particle size of the catalyst.

Sr. No.	Power Mean Size (µm)		D10 (μm) D50 (μm)		D90 (µm)
1	80	31.22	7.078	25.73	63.37
2	90 52.91		9.134	37.73	121.8
3	100	52.97	11.84	42.2	111.1
4	110	51.89	6.388	32.51	129.7
5	120	304.4	13.42	85.53	1036

3.1.2. Effect of US Irradiation Time

The US irradiation time was varied from 15 min to 75 min during the synthesis of the catalyst at a constant ultrasonic power of 80 W. The obtained results are elucidated in Table 2, where it can be seen that the initial particle size reduced from 38.67 μ m obtained at 15 min of irradiation time to the lowest particle size of 31.22 μ m obtained at 30 min of irradiation time, and beyond 30 min the particle size again increased. It is evident that the particle size initially decreases with the increase in the time of irradiation to 30 min, attributed to higher exposure to the physical effects of cavitation as intense liquid streaming and turbulence. However, after the optimal time of 30 min, it starts to increase again, possibly due to agglomeration based on too much cavitational activity and particle–

particle interactions. Shirsath et al. [31] also reported a similar result, where ultrasound irradiation until an optimal time results in smaller particle size and higher duration of sonication leads to agglomeration of the particles, forming large particles. In another study by Yan **et al**. [32] for the synthesis of ZrO_2 nanoparticles, it was reported that the particle size increased with an increase in the irradiation time to 15 min, after which the particle size was mostly constant. The comparison with the literature clearly illustrates the specificity of the trends on the system investigated. The best ultrasonic time of 30 min was chosen for further investigations based on the results obtained in this work

Sr. No.	Time (min)	Mean Size (µm)	D10 (µm)	D50 (µm)	D90 (µm)
1	15	38.67	0.063	5.268	135.2
2	30	31.22	7.078	25.73	63.37
3	45	40.47	0.068	21.59	112.5
4	60	324.5	0.053	73.86	1101
5	75	78.73	0.051	34.74	228

Table 2. Effect of US irradiation time on the particle size of the catalyst.

3.1.3. Comparison with Particle Size of the Conventionally Synthesized Catalyst

Table 3 gives the particle size data for the conventionally synthesized catalyst in the absence of ultrasound. The obtained size for the conventional approach in the absence of ultrasound was 806.4 μ m, as opposed to the 31.22 μ m achieved in the presence of US irradiation under optimal conditions. It can thus be seen that the conventional process leads to agglomeration and that the use of ultrasound under optimal conditions gives the best results for the particle size, mainly based on the intense turbulence and microscale mixing. In a similar study [33], an Fe-TiO₂ catalyst synthesized without ultrasound irradiation (conventionally) demonstrated a much higher particle size of 348 nm. The results clearly imply that better fragmentation of the catalyst particles into smaller particles is achieved due to the higher degree of turbulence induced in the presence of ultrasound [34–36].

Table 3. Particle size data of the conventionally synthesized catalyst (in the absence of US).

Sr. No.	Sample	Mean Size (µm)	D10 (µm)	D50 (µm)	D90 (µm)
1	Conventional	806.4	403.9	791.3	1229

The particle size distribution data presented in Figure 5A,B also reveal that the size distribution pattern clearly shifted towards the left for the US-assisted method as compared to the conventionally synthesized catalyst, meaning that lower mean sizes were obtained. It was also evident that all of the particles obtained using the synthesis process based on ultrasound were smaller as compared to the conventional synthesis process, clearly elucidating the much greater effectiveness of ultrasound.



Figure 5. Particle size distribution of (**A**) the catalyst synthesized using the US-assisted approach, and (**B**) the conventionally synthesized catalyst.

3.2. Characterization of the Synthesized Catalyst

3.2.1. XRD Analysis

Figure 6 shows the XRD pattern of the synthesized magnetic Fe₃O₄@ZnO NPs. The distinct diffraction peaks of Fe₃O₄ were detected at the angles of $2\theta = 30.48^{\circ}$, 43.2° , and 53.6° . A few peaks of Fe₃O₄ coincided with those of ZnO, resulting in amplified peaks. The distinct peaks of ZnO were observed at the angles $2\theta = 31.76^{\circ}$, 34.43° , 36.26° , 47.5° , 56.65° , 62.91° , 66.4° , 67.96° , and 69.19° . These results are consistent with those reported by Beltran-Huarac et al. [37]. The presence of peaks corresponding to both Fe₃O₄ and ZnO confirms the existence of both of these compounds in the core–shell configuration. The Debye–Scherrer equation was applied for the estimation of crystallite size as follows:

$$L = \frac{K\lambda}{\beta cos\theta}$$
(2)

where *K* is the crystallite shape constant (approximately 0.94), *L* is the mean crystallite size (nm), λ is the wavelength of the X-rays (nm), β is the full width at half-maximum height of the diffraction peak, and θ is the Bragg angle. The average crystallite size for Fe₃O₄@ZnO nanoparticles, estimated using the Debye–Scherrer equation, was 12.46 nm.



Figure 6. XRD analysis of magnetic Fe₃O₄@ZnO NPs.

Figure 7 shows the XRD pattern of the N-TiO₂/Fe₃O₄@ZnO catalyst obtained using the US-assisted approach. The prominent peaks were obtained at $2\theta = 25.3^{\circ}$, 37.8° , 47.9° , 54.1° , 55.1° , 62.9° , 68.9° , and 75.1° , showing the presence of TiO₂ in the anatase phase and predominantly crystalline [38]. The coinciding peaks at 47.5° and 62.9° elucidated the presence of the Fe₃O₄@ZnO support in the catalyst complex. The XRD pattern also indicated that N doping in TiO₂ did not alter its crystalline nature. The average crystallite size for the N-TiO₂/Fe₃O₄@ZnO nanoparticles, estimated using the Debye–Scherrer equation, was 16.69 nm.



Figure 7. XRD analysis of the N-TiO₂/Fe₃O₄@ZnO catalyst.

3.2.2. FTIR Analysis

The FTIR spectral analysis of the sonochemically synthesized N-TiO₂/Fe₃O₄@ZnO catalyst is shown in Figure 8. From the figure, it is evident that the observed absorption band between 3420 cm⁻¹ and 3450 cm⁻¹ is assigned to stretched vibrations, the absorption band between 1620 cm⁻¹ and 1640 cm⁻¹ is assigned to bending vibrations, and the absorption band between 520 cm⁻¹ to 580 cm⁻¹ is assigned to stretched vibrations of Ti–O [39,40]. The anatase phase of TiO₂ showed a strong FTIR absorption band over the 800 cm⁻¹ to

 650 cm^{-1} region [41]. The N–H stretching and the N–H bending vibration were seen at 3458 cm⁻¹ and 1646 cm⁻¹, respectively, which also indicates the attachment of N atoms to the TiO₂ lattice in the form of NH₄⁺. The peaks confirmed the doping of TiO₂ with nitrogen atoms from the source as EDA (ethylenediamine). The peaks at 571 cm⁻¹ and 480 cm⁻¹ attributed to the Fe-O bond in Fe₃O₄ and the Zn-O bond in ZnO [26], respectively, clearly elucidate the presence of Fe₃O₄ and ZnO in the catalyst synthesized in the present work.



Figure 8. FTIR analysis of the N-TiO_{2/}Fe₃O₄@ZnO catalyst.

3.3. Catalytic Activity of the Synthesized Catalyst for Desulfurization

The N-TiO₂/Fe₃O₄@ZnO complex catalyst with optimal particle size was selected for all of the desulfurization experiments. The activity of the catalyst was examined for desulfurization of thiophene using both UV and US irradiation in the presence of the catalyst and oxidant. A US horn (conditions of 20 kHz frequency, 70% duty cycle, and 100 W power) was used for the study, and two 8 W lights located on the opposite sides of reactor (at a distance of 20 mm each side) were used as sources of UV light. H₂O₂ was used as an oxidant for the combination studies.

3.3.1. Comparative Study of the Activity of Ultrasonically and Conventionally Synthesized Catalysts

Experiments were performed using the catalysts obtained using both ultrasonic and conventional approaches at 2 g/L of catalyst loading and 3 mL/L of H_2O_2 loading to compare their activity in the desulfurization of diesel oil. The results shown in Figure 9 confirm that desulfurization obtained using the sonochemically synthesized catalyst was 47% in 100 min, while only 25% desulfurization in same 100 min was obtained for the conventional catalyst. This result can be explained on the basis that sonochemically synthesized catalysts have a lower particle size and higher surface area, offering better catalytic action for desulfurization of thiophene, as also established in the literature, albeit for different catalysts. Tiple et al. [28] reported 29% extent of desulfurization of thiophene using conventionally synthesized TiO₂, while US-assisted TiO₂ showed 43% desulfurization. Amiri et al. [42] reported excellent photocatalytic activity of magnetically driven Ag/Fe₃O₄/graphene nanocomposites, with 95% desulfurization activity in 2 h and effective reuse of the catalysts for 10 cycles. Similarly, 91% desulfurization of dibenzothiophene and 64% desulfurization of benzothiophene were observed by Dedual et al. [5] using TiO₂ as a catalyst under the



optimal operating conditions of 40 °C as the temperature, pH of 4, 6 g/L as the TiO₂ dose, and 0.7% v/v as the H₂O₂ loading.

Figure 9. Comparative study of ultrasonically and conventionally synthesized catalysts (2 g/L of catalyst loading, 3 mL/L of H_2O_2 dosage, 100 min time).

3.3.2. Comparative Study of the Activity of Catalysts with and without ZnO in the Support Matrix

A comparative study was performed between the catalysts containing ZnO (NTFZ-US) in the support matrix along with Fe_3O_4 and the one without ZnO (NTF-US), at a constant catalyst loading of 2 g/L and 3 mL/L as the H_2O_2 dosage. The results illustrated in Figure 10 establish that desulfurization as high as 47% in 100 min was obtained for NTFZ-US, whereas much lower desulfurization (as low as 14%) was obtained in the same treatment time for the NTF-US catalyst. The obtained results prove that the presence of ZnO, along with the TiO₂ photocatalyst, provides a synergistic effect and enhances the photocatalytic activity of the complex attributed to the interactions of the two oxides, lowering the bandgap energy and driving enhanced generation of the oxidizing species. This trend is similar to that reported by Khaki et al. [43], where remarkably improved characteristics were demonstrated for the Cu-TiO₂/ZnO catalyst compared to individual TiO_2 and ZnO. The major governing mechanism was the reduction in the bandgap level of Cu-TiO₂/ZnO (2.2 eV) compared to TiO₂ and ZnO (3.2 eV and 3.37 eV, respectively), which resulted in higher photodegradation of methylene blue. Another study by Fatimah and Novitasari [44] also explained the complimentary behavior of TiO₂ and ZnO during the degradation of phenol using sonophotocatalysis; 99.99% degradation was observed when the TiO₂-ZnO complex was used, while 90.99% and 80.99% degradation was obtained for TiO_2 and ZnO, respectively.

A comparative study of the results of the present work with previous literature, as presented in Table 4, reveals that the activity of the complexes varies depending on the active compound and the model sulfur compound used. It can be said, based on analyzed literature, that significant results were achieved in the visible light range, paving the way for a greener and more cost-effective treatment of the liquid fuel.



Figure 10. Comparative study of catalyst matrices containing ZnO (NTFZ-US) and without ZnO (NTF-US) (2 g/L of catalyst loading, 3 mL/L of H₂O₂ dosage, 100 min time).

r. No.	TiO ₂ Complex	Target Compound	Conversion (%)	Time (h)	Photo-Irradiation	Reference
1	TiO ₂ -P25	Thiophene	91	3	UV	[5]
2	CuW/TiO ₂ -GO	FCC gasoline model oil	100	1	UV	[1]
3	RuO ₂ /SO ₄ ²⁻ -TiO ₂	Thiophene	88	3	UV	[45]
4	TiO ₂ powder	Diesel sample	97	0.83	UV	[4]
5	Ag-TiO ₂ /MWCNTs	Thiophene	100	0.5	Visible light	[46]
6	N-doped TiO ₂	Dibenzothiophene	40.3	4	Visible light	[12]
7	Dye-sensitized TiO ₂ @SBA-15	Dibenzothiophene Benzothiophene Thiophene	96.1 87.5 79	1.5	Visible light	[47]
8	N-doped CeO ₂ -TiO ₂ nanosheets	Dibenzothiophene	93.7	3	Visible light	[11]
9	RGO/TiO ₂	Thiophene	94.3	1.67	Visible light	[48]
10	N-TiO ₂ /Fe ₃ O ₄ @ZnO	Thiophene	47	1.67	UV	Current work

Table 4. Summary of photo-oxidative desulfurization studies using TiO₂ complexes.

4. Conclusions

Synthesis of a novel catalyst complex (N-TiO₂/Fe₃O₄@ZnO) was performed by conventional and US-assisted methods. The experimental findings showed that the catalyst prepared using US irradiation had a lower particle size (31.22 μ m) than the conventionally prepared catalyst (806.4 μ m). The best particle size was obtained at 80 W of sonication power applied for 30 min during synthesis. The results from the various characterization methods confirmed the presence of individual components of the catalyst. XRD and FTIR analyses established the anatase form of TiO₂. The crystallite size of Fe₃O₄@ZnO was obtained as 12.46 nm, while that of N-TiO₂/Fe₃O₄@ZnO was obtained as 16.69 nm. The FTIR spectra also verified the efficient N doping in the TiO₂ lattice.

The desulfurization of thiophene in the model fuel (n-hexane) was also studied with a combined approach of UV and US irradiation, along with H_2O_2 as an oxidant. The initial concentration of 100 ppm of thiophene was reduced by 47% in 100 min in the presence of the US/UV/ H_2O_2 /NTFZ-US catalyst. The conventionally prepared catalyst, when used with

the US/UV/H₂O₂ combination, resulted in only 25% desulfurization. The results clearly demonstrated that the catalyst prepared using US showed better activity in degrading thiophene. The extent of desulfurization was found to be only 14% for the case of the US/UV/H₂O₂/NTF-US catalyst, establishing the importance of the presence of ZnO in the catalyst complex, which provides overall synergistic photocatalytic activity of the catalyst. Overall, this work clearly establishes the role of ultrasound in obtaining lower particle size of the catalyst, as well as ZnO support, both of which resulted in a higher photoactivity of the catalyst, as demonstrated in terms of oxidative desulfurization of thiophene.

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