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Comparison of Sulphur and Zirconium Doped TiO_2 Nanoparticles for H_2S Gas Destruction

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Abstract—**This study draws a comparison between destruction potential of TiO_2 nano particles when its doped with Sulphur and Zirconium. When TiO_2 gets excited, it induces into electron pairs and holes and due to the presence of Sulfur in the nanoparticles, the energy of these pairs of electrons will be enhanced since S donates additional electrons during the reaction. While Zr has been found to improve the thermal stabilization of TiO_2 and it also increases its surface area. Fixed bed catalysis system was used to assess the destruction potential of H_2S gas using S and Zr doped TiO_2 nanoparticles. The gas samples obtained were analysed using Gas Chromatography-Mass Spectroscopy to ascertain the percentage destruction of H_2S gas before and after passing the gas samples from the doped TiO_2 nanoparticles. The results showed around 90% destruction of H_2S gas using S-doped TiO_2 nanoparticles while doping with Zr proved to be very less effective for degradation of H_2S gas as compared to S doped nanoparticles.**

Index Terms—**S doped, TiO_2, H_2S, nanoparticles.**

I. INTRODUCTION

US EPA list of extremely hazardous substances contains Hydrogen Sulfide and is also included in another category under US Clean Air Act which regulates the substances “known or may be anticipated to cause death, injury or serious adverse effects to human health or the environment upon accidental release’’ [1]. Even lower concentrations of H_2S gas can be dangerous. One of the studies carried out in Iceland, revealed how H_2S gas exposure at a concentration of around 7.00 μg/m^3 were related to increased hospital visits were associated as shown in Fig. 1 [2]. Owing to the considerable environmental concerns, the removal of H_2S gas is very important. Lot of research has been carried out for the removal of this toxic gas. Numerous techniques are being used world over to degrade H_2S gas, including Claus and Super Claus processes, incineration of the toxic compounds, activated carbon catalytic wet oxidation and many more [3]. In addition to different H_2S removal techniques, catalysis and photocatalysis has a lot of potential for the destruction of numerous pollutant gases including H_2S gas.

In different studies carried by our research group, we used pure and doped TiO_2 nanoparticles for assessing the destruction potential of H_2S gas. Dopants used were Sulphur and Zirconium. Reasons for using the Sulphur doping being that energy of TiO_2 is enhanced when it gets excited due to presence of Sulphur which induces into electron pairs and results into creation of holes thereby providing mechanism for H_2S gas to be adsorbed on its surface [4]. Sulfur-doped TiO_2 has been studied quite extensively owing to its highest photoacatalytic efficiencies and hence proved to be a good photocatalyst [5]-[7].While Zr has been found to improve the thermal stabilization of TiO_2 and it also increases its surface area [8], [9]. In another study, the photocatalytic decomposition efficiency of Zr-doped TiO_2 films, measured with stearic acid coating was increased by 50% as compared to undoped TiO_2 films [10]. Moreover, many studies have explored Zirconium Dioxide (ZrO_2) due to its wide band gap (ca. 5.0 eV) and extra-positive (4.0 V vs NHE) and added-negative (-1.0 V vs NHE) reducing potentials in its valence and conduction bands, respectively, corresponding to those of TiO_2, and found it as a promising alternative photocatalyst for the degradation of large variety of pollutants [11]-[14].

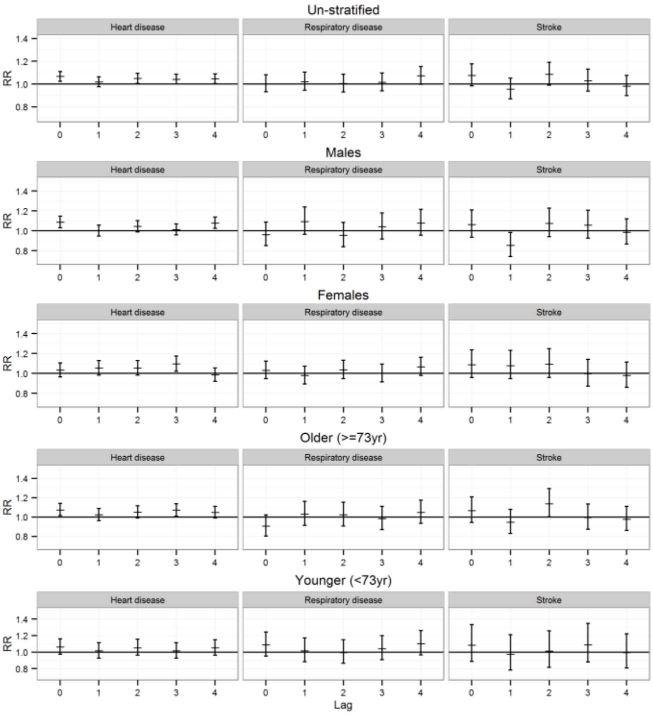

Fig. 1. Associations between daily emergency hospital visits with heart diseases, respiratory diseases, and stroke as primary diagnosis and H_2S concentrations exceeding 7.00 μg/m^3 in fully adjusted models for lags 0–4, un-stratified, and gender and age stratification [2].

Fixed bed catalysis system was used to assess the destruction of H_2S gas in our studies. It was observed that doping with Sulphur increased the destruction efficiency of TiO_2 considerably as compared to Zirconium doped nanoparticles.

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II. METHODOLOGY

A. Materials

All reagents used were of analytical grade. All the solutions were prepared in distilled water (E.C. 2.8 µS/cm) which was obtained from the distillation apparatus (Model WSB/4, Hamilton Laboratory Glass Ltd.). Argon (Ar) gas (98%) and H_2S gas (8%) used were acquired from OC specialist gases Ltd. UK. Chemicals used for synthesis of nanoparticles included Titanium Tetrachloride ($TiCl_4$, 98.0%) from Fluka, Hydrochloric acid (HCl, 98.0%) and Sulfuric acid (H_2SO_4, 98.2%) from J. T. Bakers and Sodium Hydroxide (NaOH) from Merck, while Zirconium Oxychloride ($ZrOCl_2.8H_2O$) Merck was used as a precursor for Zr doping.

B. Synthesis of Nanoparticles

Co precipitation method was used to synthesize the pure and doped TiO_2 nanoparticles at atmospheric pressure and room temperature [15].

1) S-doped TiO_2 nanoparticles

Sulfur doped (S-doped) TiO_2 nanoparticles were synthesized by method described in another study as stated above [15]. In this case, H_2SO_4 percentage of was increased from 15 to 25% in order to control the concentration of sulfur in the doped TiO_2 nanoparticles to get 1, 1.5, 2, 2.5 and 3% sulfur doping of the nanoparticles.

2) Zr-doped TiO_2 nanoparticles

The same process was used for Zirconium (Zr) doping of TiO_2 nanoparticles synthesis with minor modification. Molar ratio was used to determine the weight of Zr salt required to achieve equivalent Zr dopant percentage in the TiO_2 nanoparticles. Zr doped TiO_2 nanoparticles were synthesized by adding required amount of Zirconium Chlorated solution into the TiO_2 suspension. The solution was then titrated with 3M NaOH to raise the pH to 4. The precipitates formed were thus collected and washed with distilled water. The precipitates were then dried at 105°C, overnight and calcined at 500°C for 6 hrs to get Zr-doped TiO_2 nanoparticles [16].

C. Characterization

Scintag XDS 2000 diffractometer with Cu *Kα* radiation having 1.5406 A ° wavelength was used for recording the X-ray Diffraction (XRD) patterns of samples at a voltage and current of 40 kV and 30mA, respectively. XRD analysis was carried out from 0° to 70° (2θ) with a step time of 3-6 seconds for different results and step size of 0.05° to confirm the structure and phase and assessing the crystallinity.

Energy Dispersive X-ray Florescence Spectrometer (JEOL Model JSX-3202 M) was used to get the XRF spectra of the samples. 30 kV and 0.54 mA tube voltage and current were applied, respectively. Scan energy range was 0-41 keV and collimator was of 4mm diameter.

SEM model JEOL JSM 6490-A was used to generate high resolution images of the nanoparticles.

D. Experimental Settings

Fixed bed catalysis system was used to carry out experiments for evaluating the net destruction of H_2S gas. The experimental arrangement is shown in Fig. 2. Before running the experiment, the whole system was flushed with Ar gas to remove any residuals in the system. 0.1 gm of the catalyst was loaded in the centre of the glass tube with quartz wool at both ends. This tube was placed in the centre of the furnace along with the thermocouple to control the temperature. All the experiments were carried out at 450°C. H_2S gas was passed through these catalyst samples and three gas samples were collected after every hour in wash bottles. These samples were then analyzed using GC-MS [16].

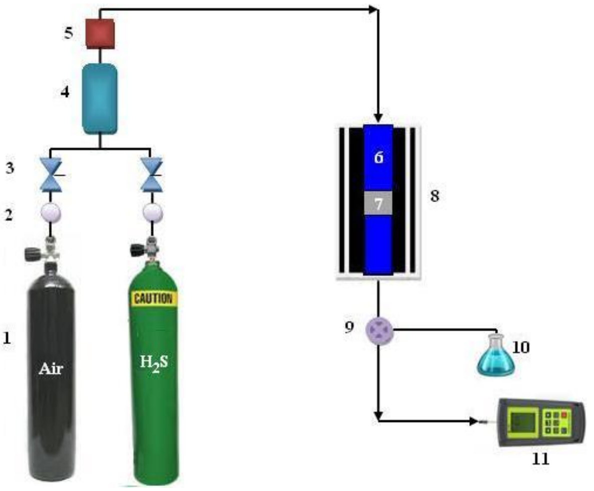

Fig. 2. Fixed Bed Catalyst System used for the catalytic gas phase destruction of H_2S gas using TiO_2 nanoparticles (1-gas cylinders, 2-gas flow controllers, 3-flow meters, 4-greaseless stopcocks, 5-wash bottles, 6-glass tube, 7-loaded sample, 8-furnace, 9-multi flow controller, 10-gas sampling port, 11-exhaust).

E. H_2S Gas Analysis

The H_2S gas analysis was carried out by using the Gas-Chromatography-Mass Spectroscopy (GC-MS) for the gas samples collected after the catalytic experiments. In addition to GC-MS, Biogas analyzer was also used for detection of H2S gas after passing it through the nanocatalyts. H_2S concentrations were measured using the GPA 1.8 Gas Pod which was fitted with the analyzer. The detection limit of 2S gas using this gas pod is 0-10000 ppm.

III. RESULTS AND DISCUSSIONS

All the gas samples obtained from the experiments were analyzed using GC-MS. The net reduction in the H_2S gas peak areas was calculated by difference in the peak areas of the reference samples and the samples collected after an interval of one hour. Three samples were collected in all the experiments. The different peak areas obtained from the GC-MS analysis of the gas samples after passing H_2S gas through TiO_2 nanoparticles are presented graphically in Fig. 3 [16].

0P, 1P and so on shows the samples with percentage of dopant concentration, e.g., 0P means pure TiO_2, 1P means 1% S doped nanoparticles and so on. Similarly, 1 ZrP means 1% Zr doped nanoparticles.

The results of the GC-MS analysis show that the highest reduction in concentrations of H_2S gas after 3 hours of the experiments, have been observed for the TiO_2 nanoparticles doped with 2% Sulfur. The destruction efficiency of 91.71% achieved after three hours of the experiment using pure TiO_2 nanoparticles is quite significant [15]. It was observed that the efficiency increased with increase in S-dopant concentration initially till it reached 2 % where the highest efficiency of 93.84% was achieved after 3 hrs of the experiment. But as the S concentration increased further, there was a slight decrease in the H_2S destruction percentage. The initial gradual increase in the destruction efficiency can be explained that the destruction efficiency is increased due to S-S affinity [17] between S-doped TiO_2 nanoparticles and S of H_2S being passed through it.

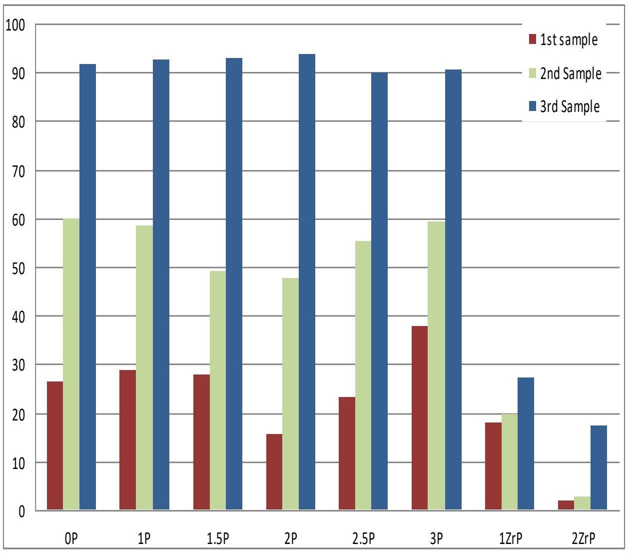

Fig. 3. GC-MS analysis-percentage reduction in H_2S gas peak areas.

This increase in destruction efficiency did not seem to be consistent probably due to the fact that by increasing the S concentration, presumably the TiO_2 surface becomes saturated with S preventing further S adsorption. Another reason could be due to decrease in the amount of surface hydroxyl groups because of increase in S-dopant concentrations as found in another study [18]. This resulted in decrease in the H_2S destruction efficiency by the doped TiO_2 nanoparticles.

However, this shows that S-doping plays a positive role in the higher destruction efficiency of H_2S gas at a high temperature of 450°C, despite of the fact that the destruction efficiency of the pure TiO_2 nanoparticles is also quite significant [16].

Because of the large diameter of the Zr, 1% and 2% Zr-doped TiO_2 nanoparticles were also prepared to check H_2S destruction efficiency of the metal Zr when it was doped on TiO_2 nanoparticles, since in another study, it was found that photocatalytic activity of the Zr-doped TiO_2 increased by 50% when compared with undoped TiO_2 films [10]. The destruction efficieincy of Zr doped TiO_2 was found to be comparatively very low as compared to pure and doped TiO_2 nanoparticles, which was found to be 27% and 17% for 1% and 2% doped nanoparticles, respectively. The results were somewhat similar using the biogas analyzer for the detection of H_2S gas, before and after passing through the nanocatalysts (spent samples). It was observed that by increasing the Zr dopant concentration, the H_2S destruction efficiency decreased. In this study, due to very low (18-30%) H_2S destruction efficiency achieved in the initial two experiments as compared to the efficiency using pure and S-doped nanoparticles, further experiments were not carried out by varying the Zr dopant concentrations. Besides, Energy Dispersive XRF was performed for all the nanoparticles before (fresh samples) and after the experiments (spent samples). From the analysis of the spent samples, it was found that the average amount of S adsorbed on the surface of the TiO_2 nanoparticles for all the S-doped nanoparticles showed slight variation from 2.59 and 2.72 % for all the samples. The S adsorption on the Zr-doped TiO_2 nanoparticles was quite low ranging from 0.5-0.8% only and showing that S was not favourably being adsorbed on the surface of the Zr-doped TiO_2 nanoparticles and it was therefore likely that the H_2S destruction efficiency was not going to be quite noticeable in this case. These results are tabulated as Table I.

The results clearly indicate that the doping of Sulphur played a very positive role towards enhancement of H_2S gas destruction, while Zirconium doping further decreased the TiO_2 efficiency than observed using pure TiO_2 nanoparticles. It was also revealed that further increase in Zr dopant concentration, decreased the H_2S destruction, so additional experiments using higher Zr dopant concentration were not carried out as done for S doped nanoparticles. The reduction in destruction efficiency of Zr doped TiO_2 nanoparticles can be attributed to less affinity of Zr towards S. However, the results obtained from these findings were not found to be in agreement with another study in which photocatalytic efficiency of Zr doped TiO_2 increased by 50% under visible light irradiation [9]. In another study, it was observed that the photoreactivities of the Zr doped TiO_2 materials were associated with the amounts of dopants and the shapes of the nanorods. Probably, in our Zr-doped TiO_2 nanoparticles were lacking optimal Zirconium to Titanium ratio and regular shapes which exhibited highest photoreactivities [19].

TABLE I: QUANTITATIVE ELEMENTAL ANALYSIS OF TiO_2 NANOPARTICLES

Sample ID	**Titanium (Ti)**		**Sulfur (S)**		
	Mass %	**Mol %**	**Mass %**	**Mol %**	**% Increase**
0P	100	100	-	-	
0PS	*99.09*	*99.23*	*0.91*	*0.77*	***0.91***
1P	99.04	98.57	0.96	1.43	
1PS	*96.32*	*95.86*	*3.68*	*4.14*	***2.72***
1.5P	98.56	98.87	1.44	1.13	
1.5PS	*95.87*	*96.17*	*4.13*	*3.83*	***2.69***
2P	97.83	97.78	2.17	2.22	
2PS	*95.24*	*95.09*	*4.76*	*4.81*	***2.59***
2.5P	97.34	97.08	2.66	2.92	
2.5PS	*94.72*	*94.47*	*5.28*	*5.53*	***2.62***
3P	97.03	96.62	2.97	3.38	
3PS	*94.4*	*94.01*	*5.6*	*5.99*	***2.63***
1ZrP	98.81	99.32	1.19*Zr	0. 68*Zr	
1ZrPS	*98.03*	*98.53*	*1.19*Zr & 0.78*S*	*0.68*Zr*	***0.78***
2ZrP	97.83	98.63	2.17*Zr	1.37*Zr	
2ZrPS	*97.33*	*98.12*	*2.17*Zr & 0.5*S*	*1.37*Zr*	***0.5***

IV. CONCLUSIONS

Different results obtained by the passing H_2S gas over different concentrations of Sulphur and Zirconium dopants were compared in this study. It was observed that the 2% S-doped nanoparticle (2P) showed the maximum destruction of H_2S gas after 3 hours using fixed bed catalysis reactions at a high temperature of 450^o C. However, doping of Zr was not found to be favourable for the destruction of H_2S gas. It was revealed in one of the study that the by increasing the Zr concentration in the precursor solution and increasing the reaction temperatures, promotes regular shapes of the nano materials which further enhances the Zr photocatalytic efficiencies [19]. But this was not the case in our study as very low H_2S gas destruction efficiencies were achieved. Therefore, further studies need to be carried out in order to ascertain this fact as to why the efficiency of Zr doped TiO_2 nanoparticles reduced at high temperatures contrary to the findings of another study in which the efficiency increased even under visible light photocatalysis. Probably, this could be attributed to different experimental conditions in this case; the conditions were evaluated under high temperatures. It can therefore be concluded that the best H_2S destruction efficiency could be achieved by using S-doped nanoparticles in catalytic experiments at a high temperature, while TiO_2 doping with Zr is not a feasible option for destruction of H_2S gas as compared to S-doped nanoparticles.

Conflict of Interest

The author's declare no conflict of interest.

Authors Contribution

NS was involved in setting up and carrying out the experimental analysis and results compilation, where as RWA was involved in formatting and vetting the draft of manuscript.

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