

USE OF PURE AND SULPHUR DOPED TiO₂ NANOPARTICLES FOR HIGH TEMPERATURE CATALYTIC DESTRUCTION OF H₂S GAS

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H₂S reduction over Pure and Sulphur doped TiO₂ nanoparticles was studied in this work. The parameter was catalytic destruction of H₂S gas under high temperature of 450°C using fixed bed catalytic system under laboratory conditions. Under these conditions 99.97% reduction was achieved using S-doped TiO₂. 2.89% Sulphur was adsorbed on S-doped TiO₂ nanoparticles to form Ti(SO₄)₂. Comparatively, no significant reduction in the H₂S gas concentration was observed using Pure TiO₂. The XRD, SEM and EDX techniques were performed to characterize the nanoparticles and gas reduction analysis was done using GC-MS for gas samples. FTIR analysis was carried out to investigate the byproducts of the experiments.

(Received November 14, 2012; Accepted January 25, 2013)

Keywords: TiO₂ nanoparticles, H₂S gas

1. Introduction

More stringent regulations are being imposed by the Environmental Protection agencies for the control of air pollution because of growing environmental concerns in the 21st century. In addition to NO_x and SO_x, malodorous H₂S gas with a characteristic rotten egg smell and having extremely low odour threshold (0.0004 ppm) and high toxicity [1] is also important and the removal of this gas is of great environmental concern. 300 ppm concentrations of H₂S in air can result in death for long term exposures and concentrations up to 2000 ppm for few minutes only may be fatal for humans [2].

It has been found in many research studies that 90% of the H₂S is found in the coal-derived gaseous products containing sulphur [3]. Many H₂S reduction techniques like Claus process [4], catalytic wet oxidation [5] have been employed. Activated Carbon adsorption has also been used as non-destructive process, while destructive processes like incineration involve oxidation of toxic compounds resulting in by products which may be more hazardous than the original compounds. Oxidizing agents (Na/CaOCl, Cl₂, H₂O₂, KMnO₄, etc.) or ferrous/ferric sulphate for removal by precipitation has been used as alternatives [2, 6, 7]. Packed-towers scrubbers, biofilters and activated carbon adsorption are most commonly used processes in gas phase [6, 8- 11].

Quite a number of studies have been carried out using pure and mixed sorbents including Fe₂O₃, FeO, CuO, ZnO etc. for removal of H₂S gas at high temperatures [12-17]. Jardim and Huang used TiO₂/UV-VIS to study the gas phase destruction of H₂S [18] and observed 97.2% H₂S degradation at low concentrations of 300 ppmv. In another study carried out by Maria and co authors, photocatalytic destruction of H₂S gas phase was investigated [19], but both these studies were carried out at room temperature and ambient pressure. Keeping in view the catalytic properties of TiO₂ nanoparticles, the destruction of H₂S at high temperatures was investigated in this study so that simultaneous destruction of H₂S gas could be investigated for power generation and gasification processes which are carried out at high temperatures.

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Different studies were conducted using pure and varying concentrations of S-doped TiO₂ nanoparticles and TiO₂ nanotubes [20, 21]. Pure TiO₂ nanoparticles and S-doped TiO₂ nanoparticles with a minute concentration of 0.05% were used in this study to investigate the effect of S-doping if any. The nanoparticles were synthesized using co-precipitation method [22]. The nanoparticles were characterized using XRD, SEM and EDX techniques and final product of the sample (spent sample) after passing the gas was analysed using the same characterization techniques. Gas analysis was done using GC-MS. FTIR analysis was carried out to investigate the final byproducts. The experiments were conducted using fixed bed catalytic system under laboratory conditions.

2. Experimental

2.1. Materials

H₂S gas (8%) used in this experiment was supplied from gas cylinder which was procured from BOC specialist gases Ltd, UK. All analytical grade reagents were used. Titanium tetrachloride 98.0% (Fluka), sodium hydroxide (Merck) and sulphuric acid 98.2% (J.T.Baker) were used for synthesis of Pure and S-doped TiO₂ nanoparticles.

2.2. Catalyst Preparation

Pure and S-doped TiO₂ nanoparticles were synthesized using the co-precipitation method [22]. The nanoparticles were prepared at room temperature and atmospheric pressure.

2.3 Characterization

X-ray diffraction (XRD) patterns of samples were recorded using Scintag XDS 2000 diffractometer with Cu *K* α radiation having 1.5406 Å wavelength. To assess the crystallinity and confirmation of structure and phase, analysis was carried out from 0° to 70° (2θ) with a step size of 0.05° and step time of 3 seconds. Scherrer's equation was used to estimate the crystallite size of the samples.

XRF spectra were obtained from Energy Dispersive X-ray Fluorescence Spectrometer (JEOL Model JSX-3202 M). Applied tube voltage and current were 30 kV and 0.54 mA, respectively. Scan energy range was 0-41 keV and collimator was of 4mm diameter. Three readings were taken and its average was taken for each sample.

To generate high resolution images of the nano materials, samples were imaged on JEOL JSM 6490-A, Scanning Electron Microscope.

2.4. FTIR analysis

Infrared (IR) studies were carried out using KBr disks in the region of 4000-450 cm⁻¹ on a Perkin Elmer Spectrum 100 FTIR.

2.5 Catalytic reactions

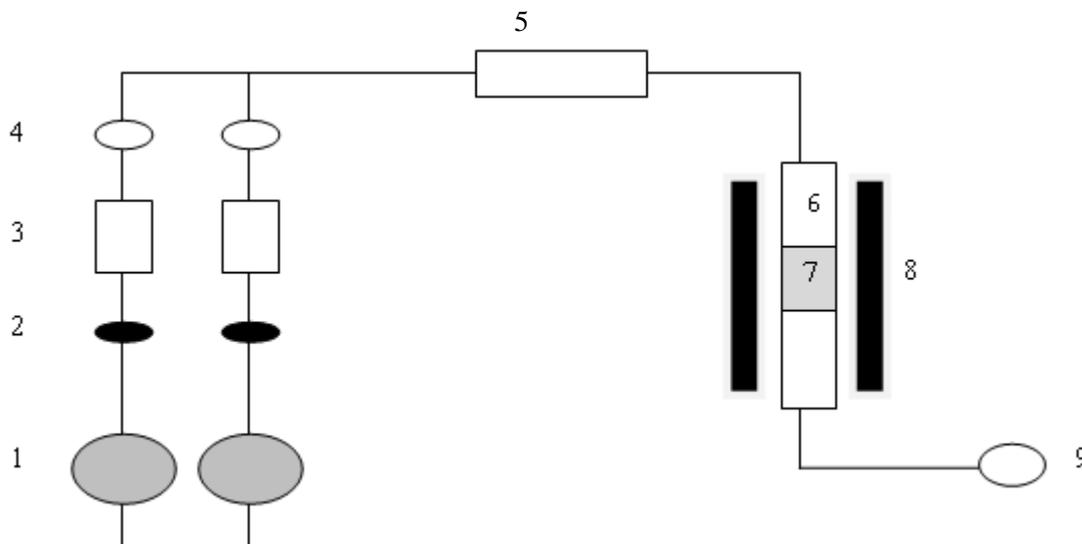


Fig. 1. Experimental Setup. (1) Gas Cylinders, (2) Flow Controllers, (3) Flow Meters, (4) Greaseless Stopcocks, (5) Wash Bottles, (6) Glass Tube Reactor, (7) Loaded Catalyst, (8) Furnace, (9) Sampling Port.

The degradation of H_2S was carried out in fixed bed catalytic system as shown in Figure 1. The whole system was flushed using Ar gas before running the experiment so that no residual was present. In Experiment no.1, 1gm of pure TiO_2 catalyst was packed in the centre of a glass tube with quartz wool at both ends and the tube was placed in the furnace along with the thermocouple to control the temperature. H_2S cylinder was then connected to the experimental set up and gas was passed through the sample at a flow rate of 45 ml/minute. A sample of the gas was collected in gas collecting bottle to be used as reference. The temperature of the furnace was gradually raised to 450°C and after 1 hour, 1st sample was collected. Similarly, 2 more samples were taken after every hour. In Experiment no.2, the same procedure was used replacing pure TiO_2 nanoparticles with the S-doped nanoparticles. All the gas samples were analyzed using GC-MS. The degradation of H_2S was determined through difference in peak areas of H_2S gas from all these samples. The results were then compared with the reference to calculate the net degradation separately for pure and S-doped nanoparticles.

3. Results and discussion

3.1 Physical Properties

The XRD spectrum of the synthesized Pure and S-doped TiO_2 nanoparticles are shown in Figure 2(a) and 3(a), respectively. The peaks correspond to anatase phase which was confirmed by JCPDS standard files no. 21-1272. Using Scherrer's equation, the crystallite sizes of Pure TiO_2 nanoparticles and S-doped nanoparticles were found to be 4 and 11 nm respectively. By observing the FWHM of the S-doped nanoparticles, we find that it was slightly broadened than observed for undoped TiO_2 nanoparticles which is a consequent of S- doping [22]. This clearly reflects the modification of TiO_2 properties due to addition of sulphur. XRD spectrum of the spent samples for pure and S-doped nanoparticles are as shown in Figure 2(b) and 3(b), respectively. Both the spectra showed considerable noise owing to the chemical reactions following the experiment.

Some peaks in the spectrum of the S-doped spent sample matched $\text{Ti}(\text{SO}_4)_2$ showing that TiO_2 might have been converted to $\text{Ti}(\text{SO}_4)_2$ after the experiment.

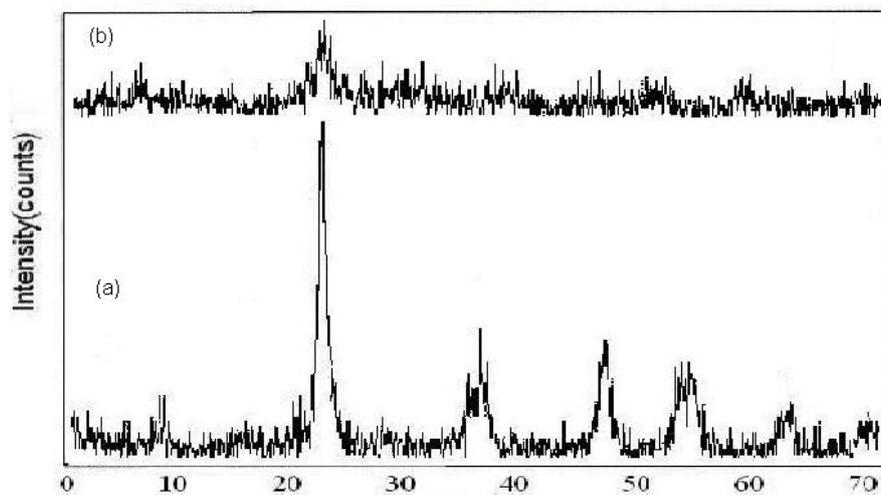


Fig. 2. XRD Spectra of Pure TiO_2 nanoparticles (a) fresh samples, (b) spent samples

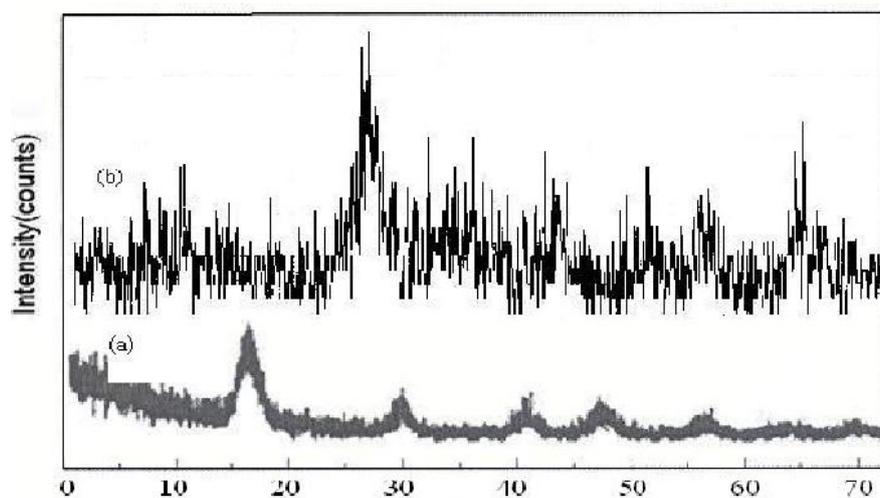


Fig. 3: XRD spectra of S-doped TiO_2 nanoparticles (a) fresh samples, (b) spent samples

SEM images of the Pure and S-doped TiO_2 nanoparticles are as shown in Figures 4 and 5. There is no significant change on the surface of Pure TiO_2 as shown in Figure 4 but by observing Figure 5, we find that sulphur seems to have been adsorbed on the surface of the spent sample.

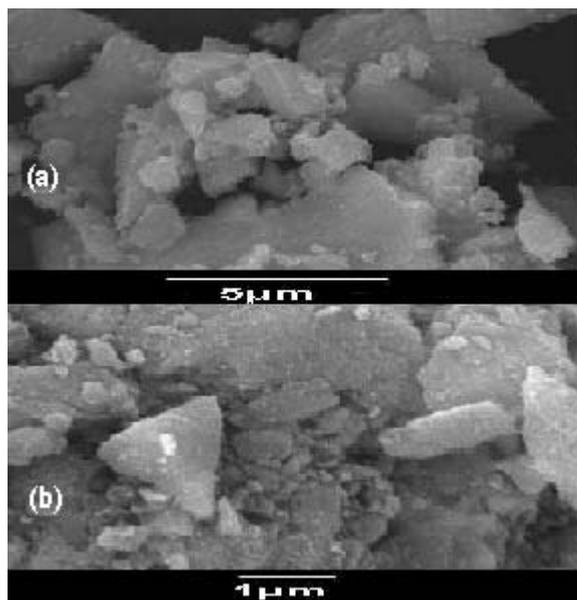


Fig. 4: SEM images of Pure TiO₂ nanoparticles (a) fresh samples, (b) spent samples

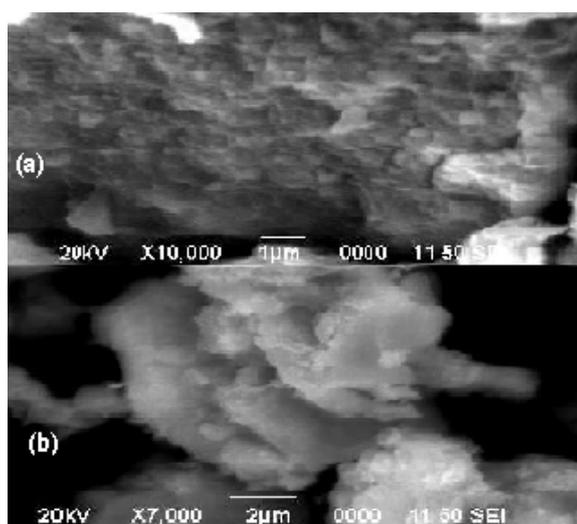


Fig. 5: SEM images of S-doped nanoparticles (a) fresh samples, (b) spent samples.

Table 1 contains the energy dispersive elemental analyses of the Pure and S-doped samples. In Pure TiO₂, sulphur percentage has slightly increased from zero to 0.196% in the spent sample as compared to the percentage of sulphur in the S-doped sample which increased from 0.0506% to 2.942% in the spent sample, showing that 2.89 % sulphur has been adsorbed on the surface of doped TiO₂ nanoparticles.

Table 1: Quantitative Analysis –XRF

Sample	Ti (ms%)	S (ms%)
Pure TiO ₂	100	0
Spent	99.80	0.2
S-doped TiO ₂	99.95	0.05
Spent	97.05	2.95

3.2 Effect of Sulphur doping

The GC-MS analysis of the gas samples is shown in the tabulated form in Table 2. In Experiment no.1, we find that initially there is a drastic reduction in the 1st sample but afterwards the peak areas start increasing which shows that probably deactivation of the catalyst has occurred and therefore, instead of decreasing, H₂S gas peak area started increasing. On the contrary, by observing the H₂S gas peak areas in Experiment no. 2, we find that after a gradual reduction in the 1st and 2nd sample, considerable reduction of 99.97% was observed in the 3rd sample. This shows that S-doping had a renowned effect on H₂S gas reduction and H₂S gas peak almost completely disappeared in the experiment using S-doped TiO₂ which was not the case with Pure TiO₂ nanoparticles.

Table 2: H₂S gas peak areas-GC MS

Gas Sample	Experiment no.1 using pure TiO ₂ nanoparticles)	Experiment no.2 (using S-doped TiO ₂ nanoparticles)
Reference	624256	624256
1 st	23435	167552
2 nd	30823	720448
3 rd	31252	1896
% reduction	Increasing	99.7%

3.3 Byproduct adsorption onto the catalyst surface

FTIR analysis was used to investigate the adsorption of byproducts onto the surface of pure and doped TiO₂ nanoparticles. IR spectra of Pure TiO₂ before and after the experiment are shown in Figure 6 (a) and (b), respectively. Figure 6 (a) shows the appearance of bands at 2355 cm⁻¹ and 1620 cm⁻¹. The band at 2355 cm⁻¹ corresponds to the presence of TiOH₂ (masked by CO₂) [23], while the band at 1620 cm⁻¹ is due to the presence of TiO₂ [24]. IR spectrum of the spent sample in Figure 6 (b) indicates a slight change showing the appearance of a very weak band at 1548 cm⁻¹ which corresponds to alkyl sulfonates [25] showing that no significant sulfate adsorption had occurred on the TiO₂ surface. In both Figures 6 (a) and 6 (b), presence of bands 3400-3500 cm⁻¹ indicates a number of OH stretching bands from water molecules [19].

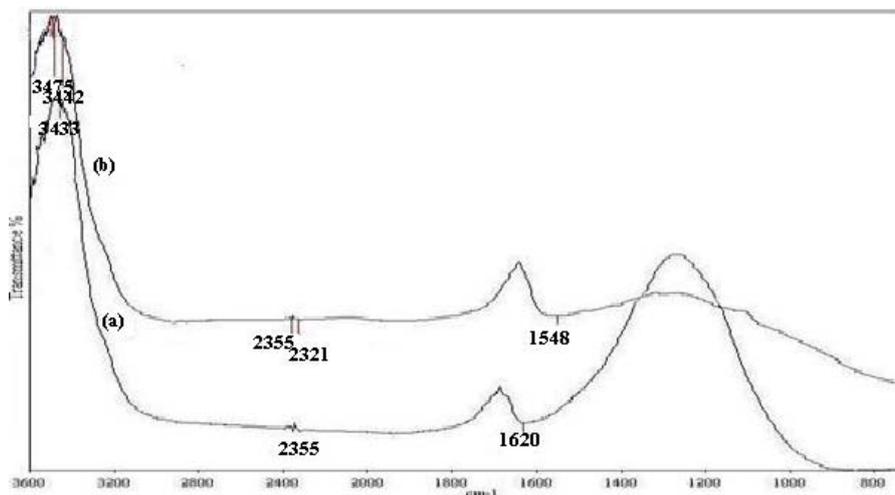


Fig. 6. FT-IR Spectra of the Pure TiO_2 nanoparticles (a) fresh samples, (b) spent samples

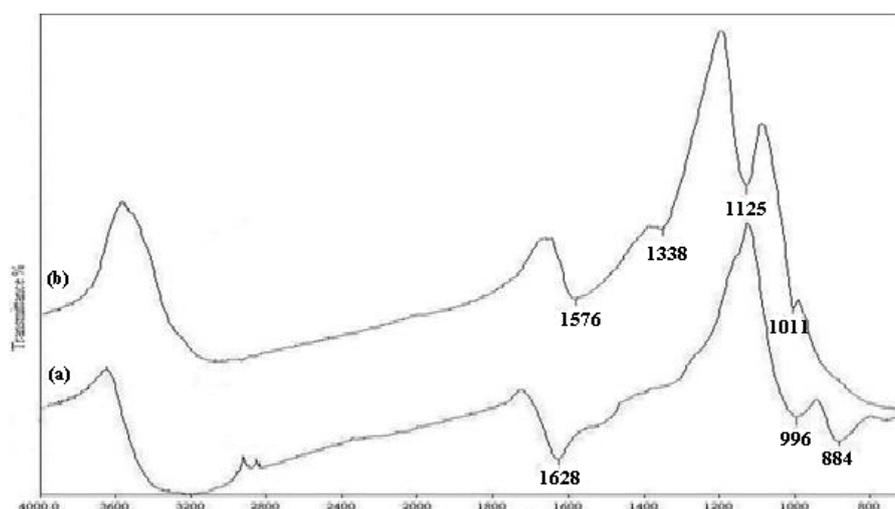


Fig. 7: FT-IR Spectra of the S-doped TiO_2 nanoparticles (a) fresh samples, (b) spent samples

Figure 7(a) and (b) shows the IR spectra of S-doped TiO_2 before and after the experiment, respectively. IR spectrum of the sample before the experiment shows bands at 1628 cm^{-1} , 996 cm^{-1} , 884 cm^{-1} . The presence of strong band at 1628 cm^{-1} is due to presence of TiO_2 [24] while bands at 996 cm^{-1} and 884 cm^{-1} indicate that Ti-S is present [23], which is not the case in pure TiO_2 as shown in Figure 6. IR of the spent sample shows the presence of bands at 1576 cm^{-1} , 1338 cm^{-1} , 1125 cm^{-1} and 1011 cm^{-1} . Band at 1338 cm^{-1} indicates S=O induced from titanium sulphate [26], while the band at 1125 cm^{-1} represents sulphates [27]. Presence of 1338 cm^{-1} and 1125 cm^{-1} bands indicate that the reduction of H_2S gas resulted in adsorption of sulphates on to the TiO_2 surface which is also shown in XRD spectrum of the S-doped TiO_2 spent sample.

4. Conclusion

The gas-phase catalytic process using Pure and S-doped TiO_2 at 450°C was studied. S-doped TiO_2 showed very high efficiency in the destruction of H_2S gas, and reached a degradation yield of 99.97% which was not observed in the case of Pure TiO_2 nanoparticles in which case H_2S

peak started rising after prominent initial decrease. This study shows that S-doping effects the degradation of H₂S and further studies are in process by varying the concentration of S-doping and evaluating its effects on H₂S destruction. In addition, the catalytic deactivation also requires further evaluation. This process could be a viable option for the in situ treatment of H₂S gas in high temperature processes especially coal-derived gaseous products.

Acknowledgements

The author gratefully thanks the National Centre for Physics, Islamabad, Nanoscience lab for allowing access to the fixed bed catalyst system.

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