

H₂S EMISSIONS CONTROL IN INDUSTRIAL EXHAUSTS USING TiO₂ NANOPARTICLES

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ABSTRACT

The response from the industrialists in Pakistan towards environmental laws and regulations regarding air pollution is very poor. This study focuses on developing a technique for in-situ treatment of H₂S gas at high temperatures by using TiO₂ nanoparticles, so that simultaneous destruction of H₂S gas could be investigated for power generation and gasification processes and brick kilns, which are carried out at high temperatures. Initial experimental results at lab scale have shown a decrease of 95-99% in the H₂S gas concentrations. This technique is likely to help in the in-situ treatment of this malodourous toxic gas resulting in considerable abatement of air pollution in Pakistan without installing any new device or changing the existing practices of exhaust gases by the industrialists making it easy for them to comply with the environmental laws and regulations.

Keywords: TiO₂ nanoparticles, gas destruction, high temperatures, fixed bed catalyst systems

INTRODUCTION

Awareness regarding the harmful effects of air pollution is minimal in Pakistan. The industrialists and factory owners are adding to air pollution every day as they have no control on their industrial emissions which is the main cause of deteriorating air quality in our country. The magnitude of industrial air pollution cannot be assessed since there is hardly any air pollution data available in Pakistan and that too is also limited to provincial capitals only. Our country has responded well to these environmental problems by establishing environmental protection institutions, passing laws and developing human resources and technical capabilities through local and foreign assistance, but despite of all these measures many aspects of the environmental degradation have remained under regulated and uncontrolled.

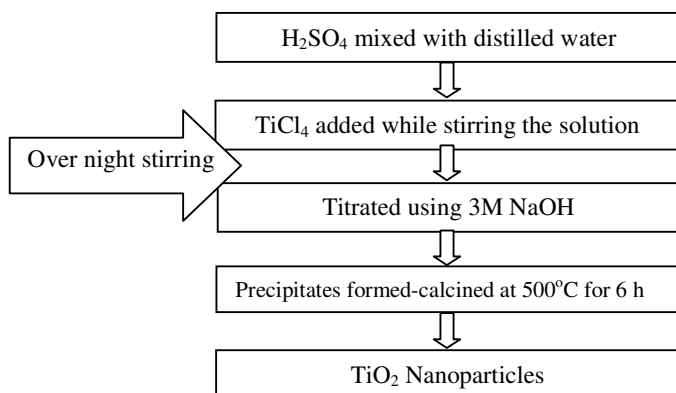
It is well known that NO_x and SO_x are the major air pollutants. A lot of research is underway for the abatement of these pollutants through out the world. Another pollutant gas that requires attention and is also of a great environmental concern is H₂S gas because of its characteristic rotten egg smell, extremely low odour threshold (0.0004 ppm) and high toxicity (Mills, 1995). 300 ppm concentrations of H₂S in air can result in death for long term exposures and concentrations upto 2000 ppm for few minutes only, may be fatal for humans (Tomar and Abdullah, 1994). H₂S levels have been found to exceed 300 ppm in 1360 wells out of the 10,652 producible oil wells in Michigan, USA (H₂S Q&A, DEQ, Michigan). If this could be the state in USA, where there are very stringent environmental protection regulations, the H₂S gas concentrations in our country near such wells could be well imagined.

Quite a number of techniques are in use for the destruction and control of H_2S gas. Some authors have investigated the photocatalytic potential of TiO_2 nanoparticles for carrying out H_2S gas phase destruction (Jardim and Huang, 1996; Maria et al., 1998). This study encompasses exploring the catalytic potential of pure and doped TiO_2 nanoparticles. The nanoparticles have been synthesized using co-precipitation method (Tajammul et al., 2009). These nanoparticles were characterized using XRD and EDX techniques and the gas samples were analyzed using GC-MS.

MATERIALS AND METHODS

Synthesis of nanoparticles

Pure and doped TiO_2 nanoparticles (sulphur doped) were synthesized using co-precipitation method (Tajammul et al., 2009) using standard chemicals and reagents. The flow chart for the synthesis process is as follows:



Characterization of nanoparticles

X-ray diffraction (XRD)

XRD patterns of the nanoparticles were recorded using Scintag XDS 2000 diffractometer having a wavelength of 1.54056 \AA . XRD analysis was carried out from 0° to 70° with a step size of 2 seconds.

Energy dispersive X-ray spectroscopy (EDX)

XRF spectra of the nanoparticles were obtained through JEOL Model JSX-3202 M energy dispersive x-ray fluorescence spectrometer.

Experiments

The catalytic reactions were carried out using fixed bed catalyst system for evaluating the H_2S gas destruction. Ar gas was used to flush the whole system before running the experiments so that residuals if any may be removed. The experimental arrangement is as shown in figure 1. The nanocatalysts (0.5 gm) were loaded in the center of the quartz tube and placed in the furnace along with the thermocouple. The 1st sample was taken immediately after connecting the H_2S gas cylinder, later to be used as reference.

The temperature of the furnace was gradually raised to $450^\circ C$ and after one hour, another sample was taken in gas sampling tubes, which was followed by two more samples after every hour. These samples were then analysed using GC-MS. By calculating the difference in peak areas of the reference and the other three gas samples, the percentage destruction of H_2S gas is calculated.

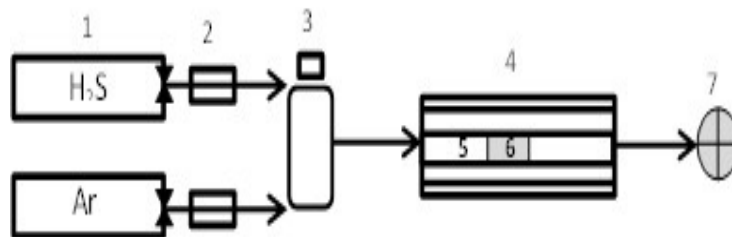


Figure 1. Experimental Set up. 1. Gas Cylinders, 2. Flow meters, 3. Wash bottle, 4. Furnace, 5. Quartz tube, 6. Catalyst, 7. Sampling port

RESULTS AND DISCUSSIONS

XRD analysis

XRD spectra of the pure and doped nanoparticles showed presence of anatase phase after confirming from the JCPDS standard files no. 21-1272. The size of the nanoparticles was found out to be 5-11nm using Scherrer's equation.

EDX analysis

EDX analysis showed that sulphur had been adsorbed on the surface of the doped TiO_2 nanoparticles and sulphur concentration increased from 0.1-3.5% showing sulphur adsorption of 2.5% on the doped nanoparticles surface but it was negligible in the case of pure TiO_2 nanoparticles as shown in table 1 below.

Table 1. Elemental analysis

Element	Ti (ms%)	S (ms%)
Pure TiO_2 nanoparticles	100	0
Spent Sample	99.81	0.19
Doped TiO_2 nanoparticles	99.0	0.1
Spent Sample	96.5	3.5

GC-MS analysis

The destruction of H_2S gas was found out by comparing the peak areas which correspond to the gas concentrations present in the gas sampling tubes. By calculating the difference in peak areas of the reference and subsequent three gas samples for each experiment, the net destruction of H_2S gas was calculated. The H_2S gas concentrations decreased upto 95-99% in the case of the doped TiO_2 nanoparticles but it was otherwise in the case of pure nanoparticles. This was also shown by the negligible sulphur adsorption on the surface of the pure nanoparticles as well, which was not the case for doped TiO_2 nanoparticles.

The increase in H_2S peak areas in the case of pure nanoparticles could be explained as a result of catalyst deactivation. Considerable decrease in the gas peak areas for doped TiO_2 nanoparticles may have resulted due to affinity of the dopant for sulphur, which in our case was sulphur as well.

CONCLUSIONS

This study shows that there is a great potential for the destruction of H₂S gas by using doped TiO₂ nanoparticles. 95-99% destruction of H₂S gas was observed in this study, but further studies need to be carried out by varying the temperature and dopant concentrations to find out the maximum degradation efficiency using optimum dopant concentration of sulphur doped TiO₂ nanoparticles at a particular temperature. In addition, other dopants having large diameters for better adsorption of sulphur should also be explored. This study can provide a viable option for in-situ destruction of H₂S gas in the processes which are carried out at high temperatures and also, it does not require any UV or special arrangements for its reactions to proceed as explored by some of the authors for photocatalytic gas phase destruction of H₂S gas.

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REFERENCES

1. H₂S Q&A, department of environmental quality, Michigan USA. http://www.michigan.gov/deq/0,1607,7-135-3311_4111_4231-9162--00.html#3. How does H₂S occur in oil and gas well (accessed 6 July 2011)
2. Jardim, W. F., Huang, C.P. (1996). *Gas phase destruction of VOCs by Heterogeneous Photocatalysis*, Proceedings of the 6th International Symposium of Chemical Oxidation, Technology for the Nineties, Vanderbilt University, Nashville, USA.
3. Maria, C. C., Rosana, M. A., Jardim, W. F. (1998). Gas-phase destruction of H₂S using TiO₂/UV-VIS. *Journal of Photochemistry and Photobiology A: Chemistry*, 112, 73-80.
4. Mills B. (1995). Review of methods of odour control. *J. Filtration and Separation*, 32(02), 147-152.
5. Tajammul, H., Khaiber, K., and Hussain, R. (2009). Size control synthesis of sulfur doped titanium dioxide (anatase) nanoparticles, its optical property and its photo catalytic reactivity for CO₂ + H₂O conversion and phenol degradation. *Journal of Natural Gas Chemistry*, 18, 383-391.
6. Tomar M., Abdullah T.H.A. (1994). Evaluation of chemicals to control the generation of malodorous hydrogen sulfide in waste water. *J. Water Res.*, 28(12), 2545-2552