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Adsorption of Sulphur Dioxide on Zirconium Vanadophosphate for Flue Gas Clean Up

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The scrubbing of sulphur dioxide from the flue gas by adsorption reaction between the gas and synthetic mineral, zirconium vanadophosphate (Zr.V.P.), was investigated by passing simulated flue gas through a fixed bed reactor of fully swelled exchanger material. The influence of carbon dioxide and water vapour present in the flue gas was studied in the temperature range of 40° to 100°C. The adsorption of sulphur dioxide on Zr.V.P. is reversible and can be desorbed by eluting with 0.1% hydrogen peroxide, collecting the sulphuric acid in the effluent. The scrubber has been designed to remove the SO_2 gas from flue gas; the capacity was measured 70 mg SO_2 per gram of exchanger material. The infrared studies confirm the adsorption of SO_2 in the frequency range 1500–1600 cm^{-1} on the O–H bond of which the bending frequency appeared as 1630 cm^{-1} in the molecular structure of pure Zr.V.P.

INTRODUCTION

The sulphur dioxide is quantitatively a modest air pollutant compared to the oxide of nitrogen and carbon, particulate matter and other organic and inorganic gases. Nevertheless, it is indeed an undesirable species in the atmosphere due to its high solubility and corrosive nature. Emission of sulphur dioxide occurs mainly from the exhausts of burning fossil fuels, coals and sulphur-bearing materials. The concentration in the flue gas may vary from a few hundred to several thousand ppm. A considerable option for control cf sulphur dioxide is wet-dry scrubbing with lime slurry[1]. The reaction can be regarded as irreversible since the equilibrium is strongly shifted to the right. This process requires subsequent removal of dry product so obtained and the waste disposal. Thus the study of gas-solid adsorption has excited interest in the scrubbing of gases which have the ability to be adsorbed on the solid particles of higher porosity, permeability and with the matrix of capillaries, crevices and cracks[2] of higher capacity adsorbent. The material ion exchangers have been tested in this laboratory[3, 4] with a special attention to zirconium vanadophosphate as an efficient adsorbent.[5, 6] The present study was undertaken to obtain kinetic data for the adsorption reaction between sulphur dioxide and zirconium vanadophosphate (Zr.V.P.) to have sulphur dioxide flue gas.

EXPERIMENTAL

Chemical kinetics

Experiments were performed in a small fixed bed reactor under controlled conditions and a typical flue gas was simulated by mixing gases produced from the respective reactions.

The ion exchanger material, zirconium vanadophosphate utilized, has the following properties.:

1. Solubility	Nil in almost all solvents and in 1 N mineral acids
2. Ion exchanger capacity	1.75 m.eq. of M^+ gm^{-1}
3. Basicity	Monobasic
4. Swelling	28%
5. Interstelial volume	27%
6. Apparent density of the dry material	3.04 gm cm^{-3}
7. Water of crystallization	36%
8. Particle size of the material	100 ± 10 mesh
9. Composition	Zr.V.P. Zr 21.21% V 11.87% P 11.92%
10. Apparent density of the swelled wet material	2.37 gm cm^{-3}

The compound Zr.V.P. was pasted on the surface of glass balls of 1 cm diameter with the help of water insoluble adhessives. The amount of the material adsorbed on the spherical surface of the balls was 90 mg to 110 mg per ball. These balls were packed as close as possible in the 10 cm internal diameter glass column with the help of water supported on fibrous plug in the bottom; the water was drained off from the bottom. However, the approach is the best option from an engineering point of view since lumped data are obtained which do not have to be recalculated for redesigning the scrubber. The adsorbed gas was driven off the adsorbent by passing 0.1% hydrogen peroxide solution through the column, which is exhausted and the effluent collected as sulphuric acid. Though the adsorbed gas may be driven off by heat but it was not tried because the arresting of the SO_2 gas in the form of dilute sulphuric acid is the best option so as to give a byeproduct. The capacity to retain sulphur dioxide in such a designed column comes to be 70 mg SO_2 per gram of the material packed. A total of 20 experiments were performed utilizing the different experimental conditions and each test run lasted for 2 to 5 hrs depending upon the reaction temperature, quantity and the information required from the break-through curves.

The equipment used in this study, consisted of a gas mixing chamber, column bed reactor and analysis system comprising of several analytical instruments. The temperature was controlled by thermal heater. The gas was passed from the bottom of the reactor operated with a mild suction at the top which is connected with the analysis system for the unadsorbed sulphur dioxide gas. The IR spectra were taken on Backman IR–8 spectrophotometer using KBr disc technique.

Unless otherwise stated, the reagents used were of analytical grade, water used was bidistilled.

RESULTS AND DISCUSSION

A term scrubbing efficiency, defined as

$$SE = \frac{\text{Quantity of gas adsorbed gm}^{-1}}{\text{Total gas adsorption capacity gm}^{-1}} \times 100,$$

was studied in various adsorption isotherms, where the total gas adsorption capacity was measured by repeating the experiment and an excess gas was passed through the material. The adsorbed gas was analysed in isolated ideal conditions which are most suitable for the adsorption. The following isotherms were studied.

1. Scrubbing efficiency of Zr.V.P. for SO_2 with concentration of SO_2 in flue gas at 60° ± 5°C, 0.5 kg cm^{-2} pressure.
2. Scrubbing efficiency of Zr.V.P. for SO_2 with various temperatures of the flue gas at 45 mg gm^{-1} conc. and 0.5 kg cm^{-2} pressure.
3. Scrubbing efficiency of Zr.V.P. towards SO_2 with gas flow pressure at 45 mg gm^{-1} conc. and 60 ± 5°C temp.

The mechanism of sorption of sulphur dioxide on Zr.V.P. is as follows:

(i) The osmosis developed on the surface of the swelled Zr.V.P. helps in the sorption of the gas on the surface. Therefore pressure exerted by the gas on fibrous packing of the column pertains to the retention of the gas.

(ii) In the matrix of Zr.V.P. there is one group $>O^-$ which is the actual group which characterises the material Zr.V.P. as an inorganic ion exchanger.[5, 6]

(iii) The surface tensional forces in the water film adhering on the swelled exchanger material operate to pull down the gaseous molecules together with the orientation. Thus the cohesional forces attain their maximum intensity throughout the whole network for adsorption of the gas. Further, the graph of scrubbing efficiency of Zr.V.P. with different concentration, of SO_2 is indicative of 99 to 100% efficiency of Zr.V.P. towards SO_2 when it is alone. The reduction in the efficiency, 95 to 90%, in the presence of 10% CO_2 and 10% water vapour and mixture of both is due to the partial adsorption of these gases and sealing of the free sites meant for adsorption in the matrix of Zr.V.P.

The isotherms of scrubbing efficiency of Zr.V.P. at various temperatures confirm that Zr.V.P. is an efficient adsorption agent at higher temperatures and holds the sulphur dioxide concentration to a maximum without the interference of carbon dioxide and water vapour.

In graphs of scrubbing efficiency of Zr.V.P. vs. pressure of the flue gas, the velocity of gas passing through the reactor has been correlated with the adsorption in terms of pressure. Due to rise of pressure the efficiency of Zr.V.P. towards SO_2 adsorption decreases due to insufficient time of contact required for adsorption. However, at low pressure the efficiency is equally good.

Infrared: IR spectrum of Zr.V.P. in the H^+ form shows a bending frequency of the O–H bond at 1630 cm^{-1} which shifts to the lower frequency in the range of 1500–1600 cm^{-1} as a bunch of peaks in the SO_2 adsorbed Zr.V.P. complex IR spectrum. This confirms that the $>O^- - H^+$ is the only group in the matrix of the exchanger reponsible for the adsorption of the gas. In addition to the peaks of interest mentioned above other peaks were identical in both the pure exchanger and its SO_2 adsorbed species.

Advantages

The adsorption of sulphur dioxide with ion exchanger method can be proved to be a good method in gaseous pollution control from both scientific and economic points of view, as there will be no extra burden on the cost of the plant for waste disposal as well as the recovery of the byproduct. When one column is exhausted, second one can be operated and the exhausted column can be regenerated within a short time. Size of the column can be increased, otherwise two or more than two columns can be operated simultaneously to control higher concentration of sulphur dioxide.

Disadvantages

The flue gas should be free from dust (ash) particles as there always remains a fear of plugging the column. However, it may be made free from dust by any mechanism before passing through the column.

REFERENCES

1. H.T. Karlson, J. Klngspor and B. Ingemar, *J. Air Pollution Control Association (JAPCA)*, **31**, 1177 (1981).
2. C.B. Amphiette, Inorganic Ion Exchanger, Elsevier, Amsterdam, p. 69 (1984).
3. H.O. Gupta and H.D Tayal, *Acta Cienca Indica*, **12**, 15 (1986).
4. A.P. Gupta, M. Qureshi, R.C. Kaushik, V. Sharma and H.O. Gupta, *J.Indian Chem. Soc.*, **63**, 206 (1986).
5. H.O. Gupta and H.D. Tayal, *Ind. J. Env. and Agri.*, **4**, 81 (1989).
6. ________, *Analyt. Chemica Acta*, **235**, 435 (1990).

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