

Table V. Comparison of Lead Surface Enrichments Observed by XPS vs SIMS for the Adsorbed Samples

sample no. ^a	extent of lead surface enrichment	
	XPS ^b	SIMS ^c
3	45	13
4	9	10

^a See Table II for sample descriptions. ^b Ratio of surface weight percent (XPS) to bulk weight percent (AAS). ^c Ratio of surface and interior ²⁰⁶Pb⁺ intensities normalized to the steady state ⁴⁰Ca²⁺ signals (SIMS).

estimate of the immediate surface region Pb concentration for sample 3. A much greater fraction of the total adsorbed Pb apparently is in the outermost surface layers of sample 3 vs sample 4 on the basis of the XPS results shown in Table V. This again suggests that the higher concentration adsorbed sample (sample 4) has more extensive Pb penetration and adsorption in internal pores of the carbonate particles. The higher concentration of Pb in sample 4 also may allow for the formation and precipitation of a Pb-Ca solid solution, as has recently been illustrated for Cd and calcite (14). No attempt was made to distinguish between surface precipitation and adsorption in this study.

Acknowledgments

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Registry No. CaCO₃, 13397-26-7; Pb, 7439-92-1.

Literature Cited

- (1) Tessier, A.; Campbell, P. G. C.; Bisson, M. *Anal. Chem.* 1979, 51, 844.
- (2) Kheboian, C.; Bauer, C. F. *Anal. Chem.* 1987, 59, 1417.
- (3) Linton, R. W.; Loh, A.; Natusch, D. F. S.; Evans, C. A., Jr. *Science (Washington, D.C.)* 1976, 191, 852.
- (4) Cox, X. B.; Bryan, S. R.; Linton, R. W.; Griffis, D. P. *Anal. Chem.* 1987, 59, 2018.
- (5) Farmer, M. E.; Linton, R. W. *Environ. Sci. Technol.* 1984, 18, 319.
- (6) Harvey, D. T.; Linton, R. W. *Colloids Surf.* 1984, 11, 81.
- (7) Riggs, M. W.; Parker, M. J. in *Methods of Surface Analysis*; Czanderna, A. W., Ed.; Elsevier: Amsterdam, 1975; pp 103-158.
- (8) Lepareur, J. *Rev. Tech. Thomson-CSF* 1980, 12, 225.
- (9) Blaise, G. *Surf. Sci.* 1976, 60, 65.
- (10) Wagner, C. D.; Davis, L. E.; Zeller, M. V.; Raymond, R. H.; Gale, L. H. *SIA, Surf. Interface Anal.* 1981, 3, 211.
- (11) Turnbull, A. G. *Geochim. Cosmochim. Acta* 1973, 37, 1593.
- (12) Seah, M. P.; Dench, W. A. *SIA, Surf. Interface Anal.* 1979, 1, 2.
- (13) Pederson, L. R. *J. Electron Spectrosc. Relat. Phenom.* 1982, 28, 203.
- (14) Davis, J. A.; Fuller, C. C.; Cook, A. D. *Geochim. Cosmochim. Acta* 1987, 51, 1477.

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NOTES

Hydrogen Sulfide Removal by Supported Vanadium Oxide

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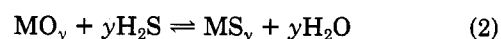
■ The retention of hydrogen sulfide by alumina-supported vanadium oxide at 650–700 °C is studied with flow reactor experiments. The effects of sorbent prereduction and gas-phase composition (H₂ and H₂O content) are discussed. It is found that hydrogen sulfide is chemisorbed reversibly on a nonstoichiometric vanadium oxide. Bulk sulfide is not formed.

Introduction

In efforts to develop a process for the removal of H₂S from coal-derived fuel gas at high temperatures (500–800

°C), various transition metal oxides have been considered as potential sorbents. Comparative evaluation of various oxide sorbents have been published in U.S. Department of Energy reports (1) and in journals (2, 3).

In a fuel gas atmosphere most metal oxides are first reduced to lower oxides or even metals, which in turn react with H₂S. Thus, in general, the reactions can be represented as



The level of H₂S in the purified gas and the sulfur loading of the sorbent at H₂S breakthrough are governed by the kinetic as well as the thermodynamic parameters of these reactions. In the case of V₂O₅, thermodynamic data

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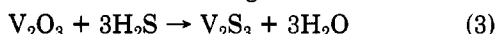
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Table I. Properties of Supported Vanadium Oxides

property	UCI alumina	NV1	NV2
source	United Catalysts, T-2432	UCI alumina impregnation	UCI alumina impregnation
bulk density	40		
particle size, mesh	-35+45	-35+45	-35+45
surface area, m ² /g	85 ^a	93	93
pore vol, cm ³ /g	0.6-0.7 ^b		
vanadium, wt %		2.24	1.88

^a After stabilization process. ^b Manufacturer data.

[JANAF tables (4)] predict reduction to V₂O₃, which has been considered to react according to



This reaction was regarded as thermodynamically favorable (1, 5) in the temperature range of interest resulting in equilibrium H₂S levels of less than 10 parts per million (ppm). In view of the presumed favorable thermodynamics of reaction 3, V₂O₅ appeared to be a very promising sorbent. The reaction rate, however, was much slower compared to sulfidation reactions of other metal oxides (3). Moreover, even when V₂O₅ was supported on high surface area alumina or zeolites, the sulfur capacity was much lower than that expected from the stoichiometry of reaction 3 (5).

In the studies mentioned above, the free energy of reaction 3 was calculated with the thermodynamic data for V₂S₃ published in a NBS report (6) and other conventional sources. Subsequently, Mills (7) found these data to be in great error. The revised values of the heat of formation and the free energy of formation for V₂S₃ estimated by Mills (7) imply that reaction 3 has unfavorable equilibrium under conditions of practical interest.

In apparent contradiction with the unfavorable equilibrium suggested by the recent data, Jalan et al. (5) consistently observed a finite H₂S uptake by various vanadium oxide sorbents. To explain this finding, Jalan et al. (8) postulated formation of a surface complex V(HS)₃, which, however, was not substantiated by direct means. In this study, simple packed-bed flow experiments were used to show that at 650-700 °C, H₂S is strongly but reversibly adsorbed on a nonstoichiometric reduced form of vanadium oxide, which is being formed ahead of the sulfidation front or during a separate prereluction step. A similar study on adsorption of H₂S on MoO₃-TiO₂ was reported by Matsuda et al. (9).

Experimental Section

Sorbent Preparation. A high surface area alumina (γ-Al₂O₃) support in the form of 1/8 in. pellets was obtained from United Catalysts, Inc. (UCI). The pellets were crushed, and a -35+45 mesh size fraction was collected. The alumina was thermally stabilized by heating in air at 800 °C for 2-5 h. With this thermal treatment, the original surface area of 100 m²/g was reduced to 85 m²/g. After being cooled, the alumina was washed a few times in concentrated NH₄OH to remove fines and then dried slowly to 200 °C. After this treatment, the surface area remained unchanged.

The stabilized alumina was impregnated with a solution of ammonium meta-vanadate in concentrated NH₄OH. The impregnated particles were quickly washed, slowly dried, and then calcined at 350 °C to obtain V₂O₅ supported on alumina (V₂O₅/Al₂O₃). The sorbent properties are listed in Table I.

Since these experiments were conducted in a reducing atmosphere, resembling that of fuel gas, a preliminary

study of the reducibility of the sorbent in the presence of H₂ was performed. A small sample of NV1 was heated in a thermogravimetric analyzer, and when the temperature reached 700 °C, flow of 9% of H₂ in N₂ was introduced. A rapid weight loss occurred within the first minute, approximately equivalent to the removal of one atom of oxygen from each V₂O₅ molecule. The weight continued to decrease slowly, and after 10 min the equivalent of an additional 0.25 atom of oxygen was removed. At this point, the rate of weight loss had declined to an almost undetectable level, in the time range of the experiment. On the basis of these results it is assumed that a nonstoichiometric vanadium oxide of approximate composition V₂O_{3.75} is acting as substrate for H₂S chemisorption.

Apparatus and Procedure. The experiments were performed with a reactor consisting of a quartz tube, 1 cm i.d. and 41 cm length, mounted vertically inside an electric furnace and instrumented with a K-type thermocouple moving inside a quartz thermowell (0.3 cm i.d.) concentric to the reactor, as described elsewhere (10). Different gases from cylinders passed through calibrated flowmeters into a common gas line leading to the reactor. The gas mixture could be flown through the reactor in the upward or downward direction, as desired. The lines leading to the reactor were heated and insulated. Nitrogen bubbling through water maintained at a constant temperature in a 3-neck flask assembly was used to introduce known amounts of water vapor into the feed gas stream. Temperatures at various locations in the system were monitored by K-type thermocouples connected to a multichannel digital readout. In all experiments the reactor pressure was slightly above atmospheric.

The experiments generally consisted of adsorption, desorption, and regeneration periods, carried out at the same temperature in the range 500-700 °C. Typically 3-6 g of sorbent was loaded into the reactor, which was brought to the desired temperature under flow of nitrogen. In adsorption runs, the feed gas contained H₂ (0-20%), H₂S (150-2000 ppm), and N₂ (balance). Desorption was carried out by a N₂ purge, while regeneration was carried out with a N₂-air mixture (O₂, 1-5%).

The product gas was passed through ice traps to condense any elemental sulfur formed and was analyzed for H₂S and SO₂ by a gas chromatograph equipped with a flame photometric detector. The column was Teflon tubing 6 ft long and 1/8 in. o.d. packed with Chromosil 310 (Supelco Inc.) and was operated isothermally at 50 °C. By using an automated valve system, samples could be analyzed every 2-3 min to provide time-resolved composition. The tubing downstream of the reactor consisted of Teflon-coated stainless steel to avoid H₂S adsorption. An absorber loop containing iodine solution in the exit line from the gas-sampling valve was used to analyze total sulfur gases (H₂S, SO₂) eluted from the bed or produced during any period. The amount of sulfur gases absorbed was determined by titrating the excess iodine with a solution of sodium thiosulfate. Elemental sulfur collected in the traps was dissolved in a solution of sodium sulfite and analyzed by a standard iodometric titration method.

Results and Discussion

The first set of experiments carried out at 700 °C with sorbent NV1 included a sequence of six adsorption periods C1-C6 with N₂ purge and/or regeneration by air between successive adsorptions. The results are presented in Figure 1 in the form of plots of outlet H₂S concentration versus time. In the first two adsorption periods, C1 and C2, the breakthrough of H₂S takes place at about 6 min. Beyond the breakthrough, H₂S continued to be partially retained

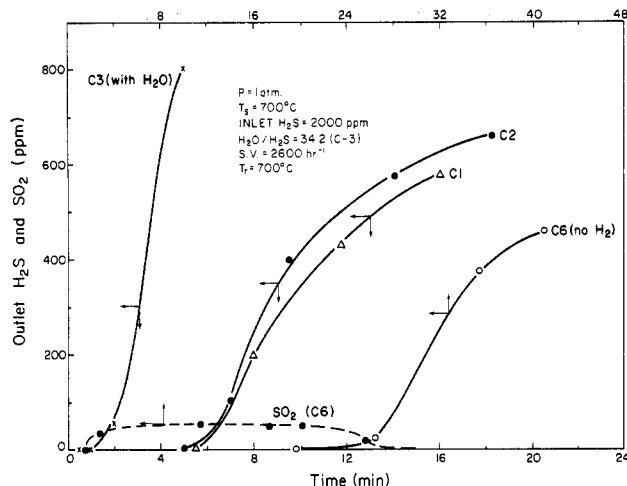


Figure 1. Breakthrough curves in successive sulfidation cycles of NV1 sorbent.

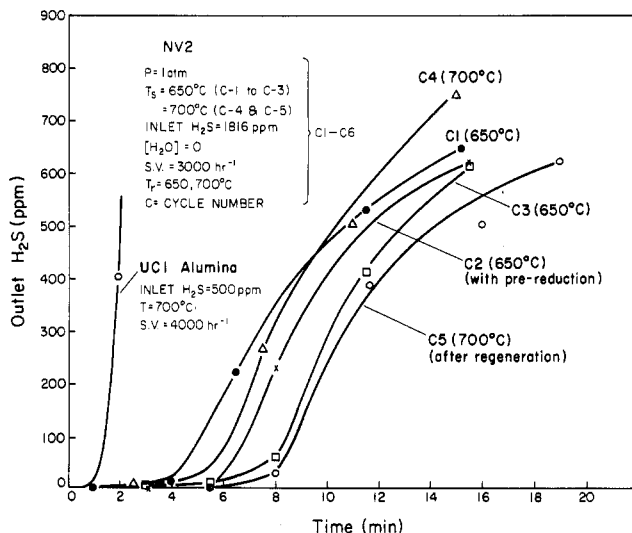


Figure 2. Breakthrough curves in successive sulfidation cycles of NV2 sorbent and UCI alumina.

in the bed as indicated by the slow rise in H_2S concentration. Similar sulfidation runs shown in Figure 2 were conducted with sorbent NV2.

A nitrogen purge followed cycles C1, C2, and C3 of sorbent NV1, as well as all cycles done with sorbent NV2. During those purging periods, H_2S and elemental sulfur were detected at the bed outlet. The amount of H_2S collected in the iodine absorbers together with the sulfur captured in the trap was equivalent, within experimental error, to the amount of H_2S retained in the bed during the sulfidation step. The amount of H_2S retained per mol of V_2O_5 originally present varies from cycle to cycle, especially because complete saturation of the bed was not achieved. Values as high as 0.42 mol of H_2S /mol of V_2O_5 were observed.

After each nitrogen purge, the sorbent was regenerated by flow of a nitrogen-air mixture, except after cycles C2 and C3 of sorbent NV2 where this step was omitted. In all cases only traces of SO_2 were detected during this period. This provides clear evidence that no bulk sulfide is being formed and that H_2S is chemisorbed reversibly.

In the set of experiments with sorbent NV2, five consecutive cycles of adsorption-desorption were carried out. The adsorption breakthrough curves are shown in Figure 2. Two parameters, viz., pretreatment with a nitrogen-hydrogen mixture and temperature, were changed in the adsorption cycles. The effects of these changes on the

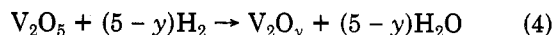
adsorption breakthrough curves are not too significant, and the total amount of H_2S retained at the end of each cycle did not vary greatly. However, some subtle differences are apparent. Thus, in the first cycle, since the reduced form of V_2O_5 was not present from the beginning but was formed in situ, an early breakthrough is seen. Following adsorption periods C1, C2, and C3, the bed was not regenerated but simply purged with nitrogen. With the bed prerduced, the breakthrough time in C2 and C3 is somewhat larger than in C1. The amount retained in period C4 at 700 °C was somewhat lower than in C2 and C3, perhaps because of less favorable equilibrium at 700 °C compared to 650 °C and the possible loss of surface area in repeated high-temperature operation without regeneration. On regeneration V_2O_5 is reformed at 700 °C, and consequently, the adsorption performance in cycle C5 is substantially better than in cycle C4.

To study the contribution of alumina to the sorbent adsorption capacity a separate run was performed. A 2.0-g sample of UCI alumina was placed inside the reactor, and a sulfidation run was performed at 700 °C, with a 20% H_2 concentration and 5000 ppm of H_2S . The amount retained was 80×10^{-8} mol/ m^2 compared with values of 10^{-6} mol/ m^2 obtained with the vanadium-containing sorbents. The adsorptive contribution of alumina in vanadium-containing sorbents would be even smaller, in view of the blocking effect of the vanadium oxide at the values of loading employed.

During the nitrogen purge following various sulfidations, as much as 26% of the total H_2S retained in the bed desorbed as elemental sulfur and was collected at the bed outlet. Since H_2 is not present in the purging gas, decomposition of H_2S takes place and, as reported by Fukuda et al. (11), is catalyzed by the solid substrate. The amount of elemental sulfur collected was lower than the equilibrium amount corresponding to the measured H_2S concentration at the reactor outlet.

The above results can be described by the following reaction sequence:

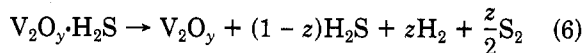
reduction



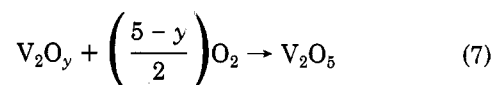
adsorption



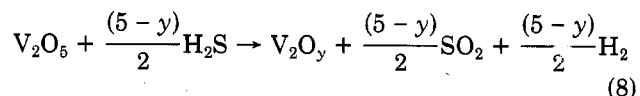
desorption



regeneration



An additional reaction that is important in the absence of H_2 from the input gas is the direct reduction of V_2O_5 by H_2S :



In the presence of H_2 , reaction 8 is ineffective since V_2O_5 is reduced ahead of the sulfidation front. Nevertheless at the beginning of sulfidation of fresh or regenerated sorbents, SO_2 in amounts of 1-5 ppm levels was observed. These small peaks of SO_2 , which are not shown in the figures, fade away as sulfidation proceeds, evidently due to the conversion of V_2O_5 to a lower oxide by reduction

with H₂. When sulfidation was carried out in the absence of H₂, as in period C6 (Figure 1), H₂S consumption was much higher and SO₂ was formed in larger amounts. The constant level of SO₂ observed before breakthrough is an indication that reduction of V₂O₅ is performed by means of reaction 8.

An important aspect in relation to the desulfurization of a coal-derived fuel gas is the effect of H₂O on the interaction of H₂S with V₂O₅ or the reduced vanadium oxides present. In sulfidation period C3 in the above batch of experiments, 7 mol% H₂O was added to the reaction gas. The resulting H₂S retention was found to be much lower (Figure 1) and the breakthrough sharper, suggesting that H₂O and H₂S compete for the same adsorption sites. Because of its low sulfur capacity in the presence of water vapor, vanadium oxide is not a practical sorbent for desulfurization of coal-derived fuel gas, which usually contains 10-30% water. It could be of some utility for desulfurization of fuel gas of very low water content.

Registry No. H₂S, 7783-06-4; V₂O₅, 1314-62-1; V₂O_{3.75}, 12165-50-3.

Literature Cited

(1) MERC Hot Gas Cleanup Task Force *MERC/SP-78/2*; 1978.

(2) Westmoreland, P. R.; Harrison, D. P. *Environ. Sci. Technol.* 1976, 10, 659.
 (3) Westmoreland, P. R.; Gibson, J. B.; Harrison, D. P. *Environ. Sci. Technol.* 1977, 11, 488.
 (4) *JANAF Thermochemical Tables*; Stull, D. R., Prophet, H., et al., Eds.; U.S. Government Printing Office: Washington, DC, 1971; NSRDS-NBS 37; Supplement, *J. Phys. Chem. Ref. Data* 1974, 4, 1.
 (5) Jalan, V.; Desai, M.; Frost, D.; Wu, D. "Final Report to DOE on Contract 31-109-38-5804"; Giner Inc.: Waltham, MA, 1981.
 (6) *NBS Technical Note (U.S.)* 1971, No. 270-5.
 (7) Mills, K. C. *Thermodynamic Data for Inorganic Sulfides, Selenides and Tellurides*; Butterworth: London, 1974.
 (8) Jalan, V.; Desai, M.; Brooks, C.; Waterhouse, R. *Proceedings of the Third Annual DOE Contractors' Meeting on Contaminant Control in Hot Coal Derived Gas Streams*; DOE/METC: Morgantown, WV, 1983; DE64000216.
 (9) Matsuda, S.; Kamo, T.; Imahashi, J.; Nakajima, F. *Ind. Eng. Chem. Fundam.* 1982, 21, 18.
 (10) Tamhankar, S. S.; Bagajewicz, M. J.; Gavalas, G. R.; Sharma, P. K.; Flytzani-Stephanopoulos, M. *Ind. Eng. Chem. Process Des. Dev.* 1986, 25, 429.
 (11) Fukuda, K.; Dokiya, M.; Kameyama, T.; Kotera, Y. *Ind. Eng. Chem. Fundam.* 1978, 17, 4.

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Adsorptive Displacement Analysis of Many-Component Priority Pollutants on Activated Carbon. 2. Extension to Low Parts per Million (Based on Carbon)

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■ An earlier paper described the analysis of multiple trace contaminants on activated carbons that are extracted by adsorptive displacement, i.e., equilibration in a solvent (e.g., dichloromethane) containing a large excess of a strongly adsorbing solute/displacer (e.g., benz[a]anthracene-7,12-dione). The method was previously applied to the simultaneous determination of 25 base-neutral priority pollutants, including such strongly adsorbed pollutants as benz[a]anthracene, at loadings less than 0.1 mg/g. The lower limits for detection and analysis have been extended downward to the low-ppm range based on carbon. The method should be applicable to the analysis of strongly adsorbed organic impurities in water at levels that are too low for solvent extraction methods and to the monitoring of carbon beds in water purification plants.

Introduction

A preceding paper (1) described the simultaneous determination of multiple trace contaminants on activated carbon by the application of adsorptive displacement, a process in which the carbon sample is equilibrated in a good solvent (e.g., dichloromethane) with a high concentration of a strongly adsorbed compound ("displacer"), e.g., benz[a]anthracene-7,12-dione. Under these circumstances, many of the trace contaminants go completely into solution; most of the others exhibit isotherms that are linear, with slopes that are mutually independent (1, 2) and with zero intercept. The principal exceptions are phenolic compounds, which exhibit nonlinear isotherms at low capacities (fractions of a milligram per gram); these com-

pounds also exhibit linear isotherms with zero intercepts when equilibrated with phenolic displacers. For contaminants that are not completely extracted into the solvent, the amount of each unextracted compound is readily calculated from the (predetermined) slope of its isotherm (2).

The previous paper (1) described the application of adsorptive displacement to the simultaneous determination of some 25 base-neutral priority pollutants at loadings down to about 0.1 mg/g carbon, even for such strongly adsorbed ("refractory") compounds as anthracene, phenanthrene, and benz[a]anthracene. Although these levels were considered sufficiently low to suggest the potential power of the method for the analyses of pollutants in drinking waters at extremely low concentrations, it seemed likely that these already low limits could be extended downward by at least an order of magnitude by the application of relatively simple techniques. This paper describes the improvements in sensitivity that were attained.

Experimental Section

Except as noted, the materials and experimental conditions were essentially the same as in the previous paper (1), except that the solvent here was dichloromethane (without methanol addition).

Attempts were first made to improve the sensitivity of the analysis by concentrating the filtered equilibrium solutions by solvent evaporation under ambient conditions. These attempts were unsatisfactory, partly because of loss of some of the more volatile components, even at only tenfold concentration, but also because of the appearance of new impurity peaks with increasing concentration. The desired improvement came about from adjustments in the gas chromatographic technique that made it possible to

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