Mercury Chemisorption by Sulfur Adsorbed in Porous Materials

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The sorption of mercury vapor by adsorbed sulfur in the zeolites CaA (=5A) and NaX (=13X) and two types of active carbon has been measured at a temperature of 50°C. With increasing degree of micropore filling by sulfur the fraction of sulfur accessible to mercury atoms decreased for CaA and NaX. The sulfur chemisorbed on carbon (only less than 0.05 g sulfur per g) is not very active for mercury chemisorption. The mercury uptake shows a sharp maximum as a function of the amount of sorbed sulfur in the case of CaA, NaX and activated sugar charcoal. The oxidation rate of H_2S with oxygen on NaX and activated sugar charcoal correlates with the capacity for mercury chemisorption, both as a function of the amount of sorbed sulfur. From the amount of sorbed mercury an estimate of the specific sulfur surface area may be given. When sulfur impregnated CaA, NaX or activated sugar charcoal are used as adsorbents for mercury traces out of gas streams, the mercury sorption capacity may be maximized by using materials with a micropore volume approximately half filled with sulfur.

INTRODUCTION

Studying the selective oxidation of hydrogen sulfide we found that the product sulfur catalyses the reaction (1). This sulfur deposits during the reaction in the pores of a material and it may possess a high surface area, causing autocatalysis.

From the literature (2) it is known that sulfur containing active carbons are effective for the removal of mercury from gas streams. For this reason we studied the possibility of using mercury chemisorption as a method for the determination of the sulfur surface area. If the reaction of mercury is limited to the surface layer of sulfur, then the chemisorption of mercury will be a suitable method for the determination of the specific sulfur surface area.

The aim of this paper is to report on the sorption of mercury by some porous materials with a variable sulfur content. The measurement of the accessibility of the adsorbed sulfur to mercury vapor may yield additional in-formation on the structure of the adsorbed phase and also on the structure of the adsorbent. The results will be compared with previous investigations on the oxidation rates of H_2S on sulfurized materials.

EXPERIMENTAL

Materials. Sulfur was adsorbed by the materials from the vapor phase. The procedure is described in the preceding paper (3). The amount of sorbed sulfur could be varied by variation of the adsorber temperature and relative pressure. The particle diameter was always between 0.3 and 0.6 mm. The amount of sample may vary from 0.5 to 2 g.

Apparatus and procedure for the sorption of mercury. The apparatus, which is very simple, is depicted in Fig. 1. It consists of a mercury containing device mounted on top of an ordinary dessicator. The apparatus is placed in a furnace which is kept at a constant temperature of 50°C. The liquid mercury is, however, kept at 40°C. In this way the relative vapor
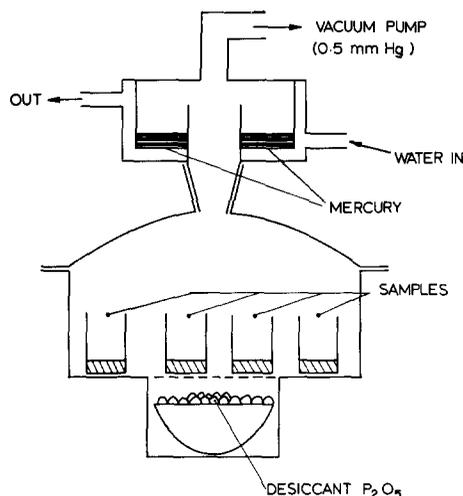
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FIG. 1. Mercury chemisorption apparatus.

pressure of mercury around the samples is lowered to about 0.5, which prevents condensation of mercury. The total pressure is lowered to below 1 mm Hg. This is done to increase the diffusion constant of mercury which accelerates the sorption process.

The chemisorption temperature of 50°C is a maximum temperature for samples which are highly charged with sulfur. At higher temperatures sulfur desorbs and forms a HgS-layer on top of the mercury. For microporous materials which have a micropore volume only partially filled with sulfur, the chemisorption temperature may be taken as high as 100°C.

The time needed to reach a constant weight was 1–2 weeks for NaX and 2–4 weeks for CaA and activated sugar charcoal. As a criterion for a constant weight we took that the relative increase in mercury uptake was less than 1% in 3 days. The samples were weighed every 3 or 4 days and a weight change as small as 0.5 mg could be determined. Before and during the mercury chemisorption procedure the samples were dried over P_2O_5 (Fig. 1) to prevent sorption of water.

RESULTS AND DISCUSSION

1. Physical adsorption on pure porous materials and on HgS. Our experiments with pure

materials, i.e., zeolites CaA and NaX and active carbons showed that the amount of physisorbed mercury is negligible at 50°C even at a relative mercury pressure of 0.5. Barrer and Whiteman (4) studied also the physical adsorption of mercury by NaX; at 261°C and a relative pressure of 0.5 only 4 mg mercury are sorbed per gram of zeolite. The transfer of mercury from liquid mercury into the zeolite is endothermal by 5.3 kcal (mole)$^{-1}$ and sorption would decrease with decreasing temperature at a constant relative pressure. By extrapolation to our conditions (50°C and $P_{rel} = 0.5$) it can be calculated that mercury adsorption should be neglible. As mentioned before this was indeed observed in our experiments.

Barrer and Whiteman (4) also studied the sorption of mercury by the zeolite HgX. Here they found that the mercury chemisorbs on the Hg^{2+} ion sites:

$$Hg^{2+} + Hg \rightarrow Hg_2^{2+}.$$
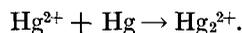
Further mercury may be sorbed by this Hg_2^{2+} and clusters of mercury are formed in the zeolite crystals:

$$Hg_2^{2+} + xHg \rightarrow Hg_{x+2}^{2+}.$$

The mercury atoms desorb on lowering the partial pressure of mercury. This desorption does not occur from our samples which is a proof for the absence of mercury clusters and mercury chemisorbed on mercuric sulfide. According to Gmelin (5) the compound Hg_2S is not stable at room temperature.

2. The chemisorption of mercury as a function of the amount of sorbed sulfur. Figures 2, 3a, 4a, and 5 give the results of the mercury sorption measurements on some porous materials. The straight lines drawn in these figures give the amount of mercury required to convert all the adsorbed sulfur into HgS. The zeolites and the activated sugar charcoal show a clear maximum in the mercury uptake as a function of the amount of sorbed sulfur. For every experiment we calculated the fraction of sulfur which reacted with mercury to form HgS. In Table I
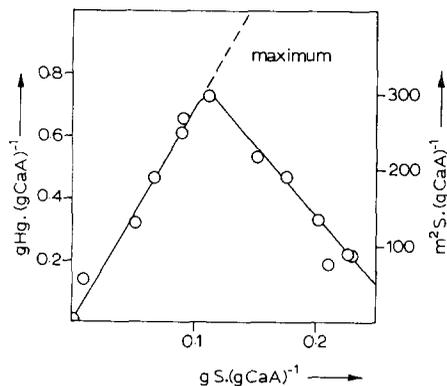
FIG. 2. Mercury chemisorption by sulfurized zeolite CaA.

we give these fractions which were obtained by interpolation in Figs. 2–5. Table I shows that generally the part of the sulfur accessible to mercury decreases with the S-load; for the active carbons, however, the first amount of S adsorbed seems hardly reactive. From desorption experiments we got evidence that this
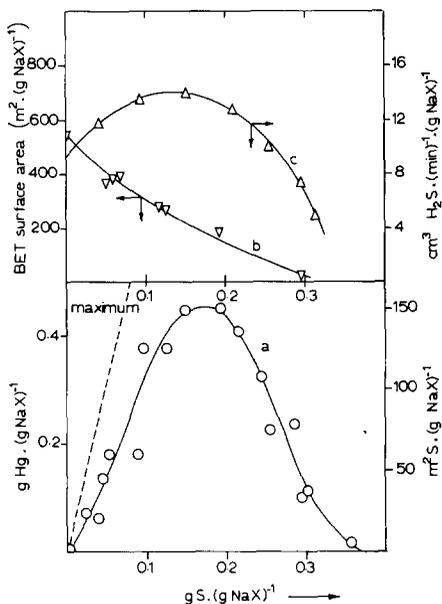

FIG. 3. As a function of the amount of sorbed sulfur in zeolite NaX are given: (a) amount of chemisorbed mercury and specific sulfur surface area ($\odot$); (b) BET-surface area ($\bigtriangledown$); (c) H₂S oxidation rate ($\triangle$); conditions: 0.1 g NaX at 130°C, feed: 1.27 vol% H₂S and 0.29 vol% O₂ in N₂.
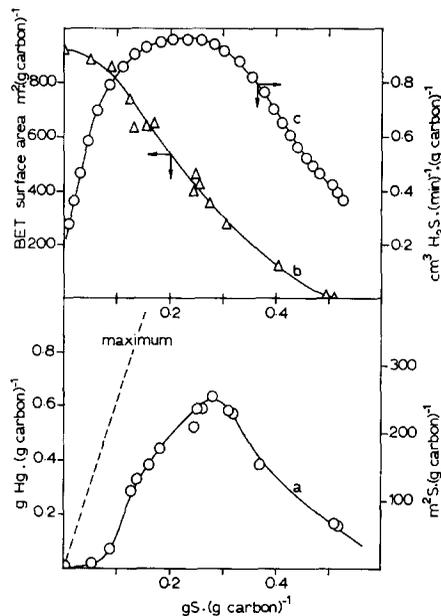

FIG. 4. As a function of the amount of sorbed sulfur in activated sugar charcoal are given: (a) amount of chemisorbed mercury and specific sulfur surface area ($\odot$); (b) BET–surface area ($\triangle$); (c) H₂S oxidation rate ($\odot$); conditions: 1.547 g carbon at 150°C, feed: 1.05 vol% H₂S and 0.5 vol% O₂ in N₂.

quantity of sulfur (0.05 g S (g carbon)$^{-1}$) is chemisorbed. According to Puri and Hazra (6) a chemical fixation of sulfur by active carbon may occur. This sulfur is fixed by addition to unsaturated bonds and by substitution of certain oxygen groups.

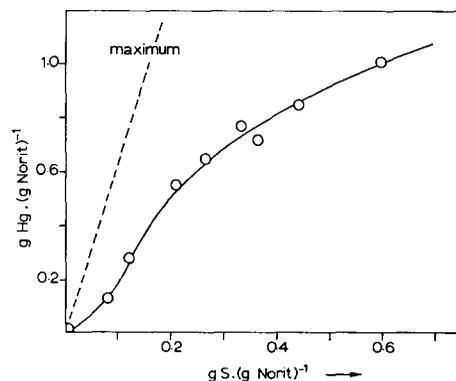The amount of chemisorbed mercury is very

FIG. 5. Mercury chemisorption by sulfurized Norit RBW1 carbon.

TABLE I

Fraction of Adsorbed Sulfur which Reacted with Mercury as a Function of the Amount of Sorbed Sulfur in Various Materials

gS (g sample)$^{-1}$	$S_{reacted}/S_{total}$			
	CaA	NaX	sugar carbon	Norit RBW
0.05	1.00	0.51	0.06	0.23
0.10	1.00	0.50	0.16	0.23
0.15	0.58	0.47	0.37	0.38
0.20	0.28	0.34	0.37	0.42
0.25	0.06	0.14	0.37	0.38
0.30	—	0.05	0.31	0.37
0.35	—	0.005	0.21	0.37
0.40	—	—	0.15	0.35
0.45	—	—	0.10	0.31
0.50	—	—	0.05	0.30
0.55	—	—	—	0.29
0.60	—	—	—	0.27

small when the micropore volume of a zeolite is completely filled with sulfur. For the activated sugar charcoal this is also true, but the Norit carbon shows a different behavior. Here the amount of sorbed mercury increases with the amount of sorbed sulfur, although the fraction of sulfur which reacts with mercury decreases (see Table I). From X-ray diffraction measurements we derived that bulk HgS was present in samples Norit carbon containing more than 0.5 g S (g carbon)$^{-1}$. The diffraction pattern of HgS was also observed after mercury sorption in sulfur containing alumina catalysts. Obviously a migration of sulfur and/or mercuric sulfide occurs in materials which contain pores in the range $20 < \bar{d}p < 100$ Å, this results in the formation of mercuric sulfide crystallites. In materials which contain only micropores we never observed HgS in the X-ray diffractogram. When the HgS lines are not visible it is still possible that for instance the upper two or three sulfur layers react with mercury.

Very interesting are the differences in the mercury chemisorption behavior between CaA (channel diameter: 4.3 Å) and NaX (channel diameter: 8.5 Å). When 0.1 g sulfur is adsorbed per gram zeolite, all the sulfur

in CaA is accessible to mercury but in NaX only 50% of the sulfur reacts with mercury (see Table I). This difference must be related to the much stronger interaction between the adsorbed sulfur in the NaX zeolite (3). This interaction leads to a decrease of the accessibility of adsorbed sulfur.

3. Estimation of the specific sulfur surface area. For an accurate determination of the sulfur surface area it is necessary to have a sample of elemental sulfur with a known surface area of some m^2 g^{-1}. This in order to obtain a measurable chemisorption of mercury of some milligrams. Th issample can be used as a standard for the mercury chemisorption method. We did not succeed in the preparation of such a sulfur sample. Even the method of Gwiazdowski (7) and Golyland *et al.* (8) for the preparation of a high surface area sulfur was not successful.

An experiment with flowers of sulfur at 25°C showed that the mercury chemisorption by this pure elemental sulfur was less than 0.001 g (g sulfur)$^{-1}$, compared to values of the order of 1 g (g sulfur)$^{-1}$ for adsorbed sulfur. The reason for this tremendous difference is of course the value of the sulfur surface area.

From the amount of sorbed mercury it is possible to give an estimate of the specific sulfur surface area. One possible assumption is that the mercuric sulfide forms a continuous monolayer, with a closest packing of S^{2-} ions. Now it can be calculated that 2.5 mg mercury may cover 1 m^2 sulfur surface. In Figs. 2–4, the estimated sulfur surface area is plotted on the right ordinate. We feel, however, that the values calculated for the sulfur surface area are somewhat arbitrary.

It should be interesting to compare the values of the sulfur area with the total surface area (BET). In Figs. 3b and 4b the total surface areas of respectively NaX and activated sugar charcoal are given as a function of sulfur load. The surface area was calculated from the argon isotherm measured at −196°C. The BET method may give, however, unrealistic values for the surface area of a micro-

porous material because for instance penetration of the adsorbate may be restricted. Remarkable is that for the active sugar charcoal the sulfur surface area is much higher than the BET area when the pore volume is near the saturation with sulfur (0.5 g S (g carbon)$^{-1}$; compare Figs. 4a and 4b). An explanation might be a porenarrowing effect upon sulfur adsorption in carbon. If there are pores with a diameter between 3 and 4 Å, then argon (diameter 3.5 Å) will not penetrate at $-196°C$ but mercury (diameter 3 Å) could penetrate these pores at 50°C. Sinha and Walker (2) observed that the surface area measured with nitrogen at $-196°C$ shows a much larger decrease upon sulfur adsorption than that calculated from the CO_2 isotherm at 25°C.

4. Comparison of the mercury chemisorption with the activity for H_2S oxidation. The oxidation rate of H_2S shows a maximum as a function of the amount of sorbed sulfur in the case of zeolite NaX (Fig. 3c) and activated sugar charcoal (Fig. 4c). By comparison of these figures with respectively 3a and 4a it may be concluded that the maximum oxidation rate occurs at the same sulfur content where maximum chemisorption of mercury occurs. Furthermore both oxidation rate and amount of chemisorbed mercury approach zero when the micropore volume is near the saturation with sulfur.

If the oxidation rate per m² sulfur surface area is considered it may be concluded:

(a) The activity of sulfur adsorbed in NaX is by one order of magnitude higher than for activated sugar charcoal.

(b) The activity of sulfur decreases with increasing sulfur load in NaX and activated sugar charcoal.

In a previous paper (1) we demonstrated that the sulfur radicals are the active sites for the H_2S oxidation. A possible explanation for the observations mentioned above, might be that the concentration of radicals per volume of sulfur is dependent on the type of microporous material and the degree of filling of the micropore volume of a material with sulfur. The high initial oxidation rates are probably caused by impurities like ironoxide (1) (Figs. 3c and 4c). This may explain the high activity per m² sulfur at a low sulfur load.

CaA with a micropore volume half filled with sulfur shows a high maximum mercury uptake of about 0.8 g Hg (g CaA)$^{-1}$ (see Fig. 2). This value is nearly twice as much as observed for NaX, the activity of CaA at 175°C is, however, by a factor 35 lower than for NaX under the same conditions. In a U. S. A. patent (9), the activities of some zeolites for H_2S oxidation are compared and here also a lower activity for CaA compared with NaX is reported. Zeolite NaA, which has still smaller apertures between the supercages, showed no catalytic activity at 175°C. It is remarkable because the diffusion of the reactants, hydrogen sulfide (diameter 3.6 Å) and oxygen (diameter 3.5 Å), into the supercages is not restricted by the diameter of the apertures in the zeolites (NaX: 9 Å, CaA: 4.5 Å, and NaA: 3.8 Å).

The differences in catalytic activity of the different types of zeolites are probably connected with the state of the adsorbed sulfur. As we pointed out in the preceding paper (3) there exist differences in the sulfur adsorption behavior of NaX, CaA, and NaA.

In this paper we demonstrate that for the removal of mercury from gas streams the sulfur content of an adsorbent may be optimized. For the zeolites and the microporous carbon a degree of micropore filling of about 50% yields the best adsorbents for mercury. Active carbons which possess besides micropores also meso- and macropores (Norit RBW1 for example) are still good adsorbents when the micropore volume is near the saturation with sulfur.

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