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ADSORPTION ON INORGANIC MATERIALS

VII.* HYDROUS TIN OXIDE AND SnO₂-FILLED CARBON

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SUMMARY

An adsorbent based on "filling" the macropores of activated carbon with tin oxide was prepared and characterized. This material, as well as hydrous tin oxide, has an unusually high selectivity for lithium permitting its separation from the other alkali metals. This selectivity is not shown by a number of other hydrous oxides, such as those of Al(III), Fe(III), Zr(IV), and Nb(V).

INTRODUCTION

In several earlier publications[2,3], we attempted to show that "filling" the macropores of activated carbons with inorganic adsorbents such as hydrous oxides and sulfides yields materials which combine the controllable hydraulic properties of activated carbon with the particular adsorptive properties of the inorganic materials. The earlier work dealt with carbons filled with various iron oxides and some sulfides, particularly ZnS. We have now prepared activated carbon filled with hydrous tin oxide and the present paper describes its preparation and some of its properties. We chose hydrous tin oxide because it has attractive ion-exchange properties[4-8], but under many conditions of ionic strength and ion composition, tends to disperse or peptize making some column experiments difficult and some "shaking" (equilibrium) experiments often impossible. During a preliminary examination of the adsorptive properties of carbons filled with SnO₂, a striking selectivity for lithium was noted. We confirmed that this is a relatively unique property of hydrous tin oxide and is not a property of the carbon–oxide mixture. This selectivity is not shown by some other hydrous oxides [Al(III), Fe(III), Zr(IV), Nb(V)] which we examined.

PREPARATION OF SnO₂-FILLED CARBONS

Three methods were tested for incorporating SnO₂ into activated carbon. In all of them, Sn(IV) was adsorbed on the carbon from HCl–SnCl₄ solutions. The

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carbon phase containing $SnCl_4$ was exposed to NH_3 vapor to form the hydrous oxide and the final material was washed with water and dried.

A granular coconut charcoal (100–170 mesh, Fisher Scientific) was used as support for the hydrous SnO_2. Since this activated carbon has a high ash content, the carbon was pretreated with mineral acids. It was soaked at room temperature for several days in 11 M HCl–0.5 M HF, filtered, washed extensively with 1 M HCl and distilled water. The ash content of the acid-treated carbon, based on its weight dried at 110°, was 1.2 %.

We first hoped to fill the carbon by a technique similar to the one we used to incorporate large amounts of Fe_2O_3 into coconut charcoal[2]. In that case we took advantage of the fact that Fe(III) is extremely strongly adsorbed by activated carbon from concentrated chloride solutions and obtained a material with finely divided iron oxide in the macropores of the carbon. Adsorption of Sn(IV) by activated carbon is extensive[9]. Adsorbability of Sn(IV) tends to decrease with HCl concentration; optimum adsorbabilities apparently are obtained near 1 M HCl. We determined adsorbability of Sn(IV) by the coconut charcoal in 1 M HCl as a function of tin concentration. As also shown by Taushkanov *et al.*[9], distribution coefficients of Sn(IV) decrease rapidly with increasing Sn(IV) concentration. With our activated carbon D was *ca.* 200 in 10^{-3} M Sn(IV) and *ca.* 5 in 0.1 M Sn(IV): the latter corresponds to a loading of 0.5 moles Sn(IV) per kg C which we considered unsatisfactorily low. Adsorbabilities are expected to vary widely with the type of activated carbon chosen. We illustrated this well-known effect earlier[2] with adsorption of Fe(III) from concentrated HCl solutions and a variety of activated carbons. Thus, this technique of filling activated carbons with Sn(IV) might yet prove satisfactory if in a systematic search a more selective carbon can be identified. In any case, repetitive adsorption, precipitation, and drying sequences might allow utilization of the technique for preparation of activated carbons containing sufficient amounts of hydrous SnO_2.

In the second method, we attempted incorporation of Sn(IV) by contacting the carbon with 1 M HCl–2 M $SnCl_4$ and carrying out a low temperature (40°) evaporation in a rotary evaporator under reduced pressure. This yielded obviously unsatisfactory products with Sn(IV)/C ratios of 8 and 5 moles per kg C. The particles tended to stick together and much of the oxide was on the outside of the particles rather than on the inside. This method might have yielded a satisfactory product if less concentrated Sn(IV) solutions or lower Sn(IV)/C ratios had been used. In that case, repetitive contacting might again be required to have a final product with a satisfactory tin loading.

The method finally selected is essentially an extension of the first one. Since $SnCl_4$ is very soluble in water or dilute HCl, contacting the carbon with a very concentrated $SnCl_4$ solution "fills" the carbon pores with a large amount of Sn(IV) even if the distribution coefficients are of the order of unity. This method has the disadvantage that separation of the carbon from the viscous concentrated Sn(IV) solution by filtration or other methods is difficult. Thus, on subsequent treatment with NH_3 vapor, a large amount of SnO_2 precipitates externally and is lost (or would need to be recovered) on washing.

In a typical preparation, 100–170 mesh activated coconut charcoal was added to a 5.75 M $SnCl_4$–1 M HCl solution prepared from $SnCl_4 \cdot 5\ H_2O$. The solution was heated to near boiling to hasten displacement of air from the pores of the carbon. The

mixture was poured on blotting paper to facilitate removal of the excess $SnCl_4$ solution and dried in air several hours. The material was then contacted with NH_3 vapor (in a desiccator containing 17 M NH_3) and then washed with ca. 0.1 M NH_3. While the substantial amounts of SnO_2 which precipitated externally to the carbon particles could be removed by decantation, several wash-decantation steps were needed before a clear wash solution was obtained. The final product was dried in an oven at 60°. From a residue analysis (ashing at 1000°), it was determined that the material contained 2.19 moles SnO_2 per kg adsorbent, or 33% SnO_2. The bed density was 0.75 kg (air-dry) adsorbent per 1 bed or 1.64 moles Sn(IV) per 1 bed. The bed density is consistent with the assumption that the bed volume of the filled carbon (2.2 to 2.3 l per kg C) does not differ greatly from that of the original activated carbon.

This material was used in all the experiments described here involving SnO_2-filled carbon. It was used for both shaking and column experiments. We noted no peptization of SnO_2 or loss of it from the particles. Thus, this procedure, though somewhat cumbersome, is suitable for preparing carbons filled with (hydrous) SnO_2.

ADSORPTIVE CAPACITY OF FILLED CARBON

We determined the cation-exchange capacity of the filled carbon and compared it with that of the untreated carbon under the same conditions of pH and electrolyte concentration (capacities of both materials, of course, are strongly dependent on pH since both the carbon and the oxide behave as weak acid exchangers). The capacity can conveniently be established by a column tracer–breakthrough technique in which the column is first pre-equilibrated with the electrolyte solution in which the capacity is to be determined. The column is then treated with an identical electrolyte solution containing tracer (here, [22]Na). The product of column volumes (c.v.) at 50% breakthrough and cation concentration of the solution (corrected for interstitial volume) gives the cation content (cation-exchange capacity) of the bed if there are no major kinetic difficulties. Kinetic difficulties are usually less severe with this method than when capacities are established by replacing one adsorbed ion by another. With complex materials like these, this latter method, of course, also suffers from the fact that capacity at a given pH depends on the relative selectivity of the materials for the ions.

Typical capacity measurements for the filled carbon and the untreated carbon are summarized in Fig. 1 which displays the breakthrough curves in terms of c.v. passed through the columns. The electrolyte solution was 0.02 M Na_2CO_3. Filling with SnO_2 clearly causes a large increase in the adsorptive properties of the carbon from 0.08 moles per l bed (untreated carbon) to 0.30 moles per l bed (filled carbon). The difference in capacities corresponds to adsorption of approximately 1.2 moles Na^+ per kg SnO_2 which seems consistent with the value 0.75 moles Na^+ per kg which we earlier reported[4] for the pure hydrous tin oxide at a somewhat lower pH (pH 10).

ADSORPTION OF ALKALI METALS BY SnO₂-FILLED CARBON

We had earlier demonstrated that hydrous tin oxide[4] and activated carbon[2] are cation exchangers in basic solutions with cation-exchange capacity increasing with increasing pH (in addition, of course, tin oxide is an anion exchanger in acidic solutions). Since adsorptive capacity of the filled carbon seems largely determined by the
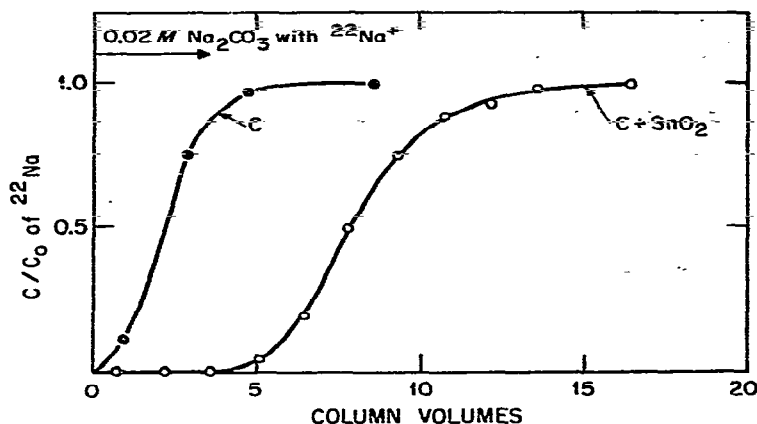
Fig. 1. Cation uptake by tracer self-exchange method. Coconut charcoal with and without SnO$_2$ at room temperature.

incorporated tin oxide, it was of interest to explore possible application of the material to the separation of alkali metals. Fig. 2 gives the results obtained by atomic absorption analyses of a typical column experiment involving all the alkali metals Li$^+$ to Cs$^+$. In this experiment a small column (*ca.* 2 cm high, 0.25 cm^2 cross-sectional area) was pretreated with 0.05 M (NH$_4$)$_2$SO$_4$–0.5 M NH$_3$. A small aliquot of the same solution containing 10^{-3} M salts of the various alkali metals was added and elution continued with the same supporting electrolyte. This caused elution of Cs$^+$, Rb$^+$, and K$^+$ with little separation from each other followed by a partially separated Na$^+$. Lithium remained on the column but could be eluted with 1 M HNO$_3$ in which medium the oxide is converted from a cation exchanger to an anion exchanger. This material, thus has a striking selectivity for lithium. While activated carbon permits some separation of alkali metals[2], the elution order is either Li$^+$, K$^+$, Rb$^+$, Cs$^+$, or K$^+$, Rb$^+$, Li$^+$,
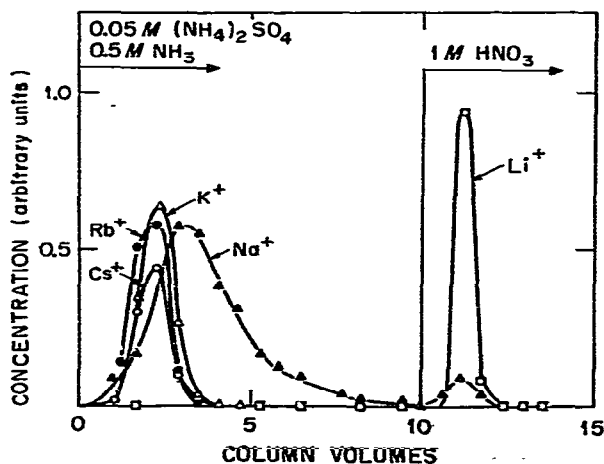

Fig. 2. Separation of alkali metals by activated carbon filled with SnO$_2$. Coconut charcoal 100–230 mesh, 2.2 moles SnO$_2$ per kg adsorbent. Flow-rate, 0.9 cm/min; room temperature.

Cs$^+$ depending on the pH. Presumably, the unusual lithium selectivity is a property of the incorporated tin oxide.

This was confirmed by similar column elution experiments, illustrated in Fig. 3, where hydrous SnO$_2$ was the adsorbent. With this "pure" oxide, Cs$^+$, Rb$^+$, and K$^+$ could be eluted and partially separated with 0.05 M (NH$_4$)$_2$SO$_4$–1 M NH$_3$. These three elements were well separated from Na$^+$ which was eluted with 0.5 M (NH$_4$)$_2$ SO$_4$–1 M NH$_3$. Even after 20 column volumes Li$^+$ was still retained by the oxide; it was removed in a sharp band on elution with 1 M HNO$_3$ the elution peak coinciding with appearance of acid in the effluent.
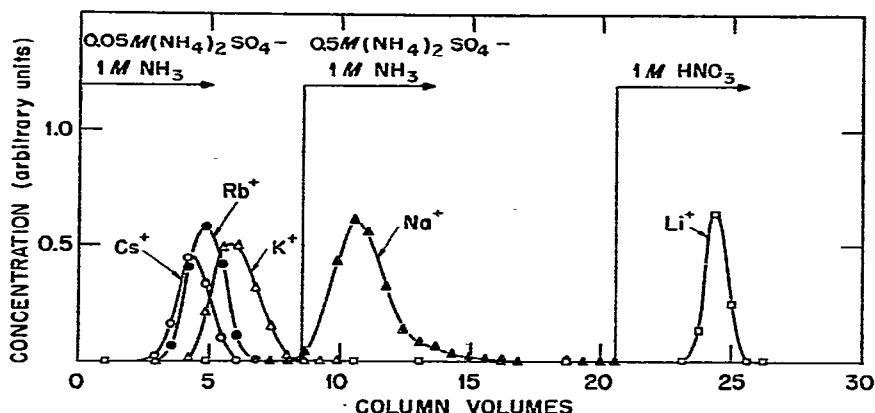

Fig. 3. Separation of alkali metals by hydrous SnO$_2$ (80–170 mesh). Flow-rate, 0.9 cm/min; room temperature.

Adsorption of lithium by hydrous SnO$_2$ or the filled carbon is not a "trace" effect. Fig. 4 shows the comparative uptake of lithium by our filled carbon from 0.05 M Na$_2$CO$_3$–0.005 M LiCl, using our usual small columns. The Li$^+$ breakthrough curve here was established at 75° for the filled carbon; lower temperature operation yields a much more drawn out breakthrough curve implying significant kinetic difficulties in the adsorption-conversion. Fifty percent breakthrough occurred near 24 c.v. corresponding to uptake of 0.12 moles Li$^+$ per 1 bed. This is approximately half its cation-exchange capacity. Presumably under these conditions, the adsorbent is approximately 50% in the Na$^+$ and 50% in the Li$^+$ forms. Fig. 4 includes a corresponding Li$^+$ breakthrough curve for the activated carbon; while it shows some retention of Li$^+$, it is obviously very much less than for the filled carbon.

Included in Fig. 4 is a lithium breakthrough curve, also obtained at 75°, for an Fe$_2$O$_3$ filled carbon (6.9 moles Fe(III) per kg C) described earlier[2,3]. Its lithium retention is somewhat larger than of the untreated carbon but still very much smaller than of the SnO$_2$-filled carbon implying that selectivity for lithium is not a general property of hydrous oxides.

Indeed, we have demonstrated this in a series of comparative experiments with the hydrous oxides of Al(III), Fe(III), Zr(IV), Nb(V), and Sn(IV). The materials used were prepared some time ago by H. O. Phillips by our usual precipitation–drying–sieving technique; they were similar to the materials we used in our earlier studies of
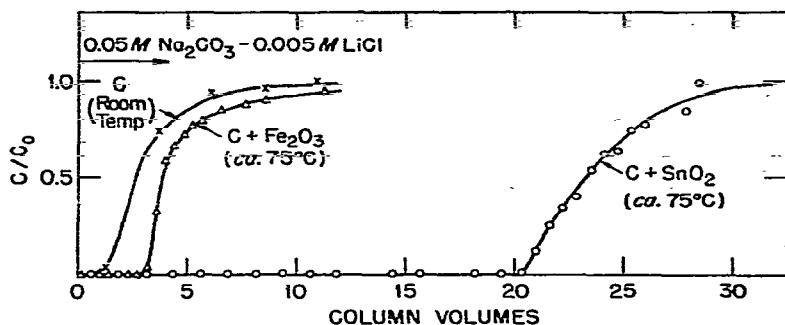
Fig. 4. Comparative uptake of Li(I) by carbon and filled carbons.

hydrous oxides. Some of these materials had been dried at room temperature (Al_2O_3, Fe_2O_3, Nb_2O_5); others were dried at 200° (ZrO_2, SnO_2). Using small columns (2 cm $\times$ 0.25 cm^2) and 0.05 M Na_2CO_3–0.05 M LiCl solutions, breakthrough curves were established at room temperature. The results are displayed in Fig. 5. Lithium uptake by hydrous SnO_2 is clearly much larger than for the other oxides. For SnO_2 50 % breakthrough occurs at ca. 25 c.v. corresponding to a lithium loading of 1.25 moles per l of bed. For the other oxides 50 % breakthrough occurs at less than 5 c.v. We also checked hydrous ZrO_2 for possible intrinsic selectivity between the alkali metals with elution experiments similar to the one described for hydrous SnO_2 in Fig. 3 (0.05 M $(NH_4)_2$ SO_4–0.5 M NH_3). With hydrous ZrO_2 all five alkali metals showed peak elution at less than 2 c.v. without any significant separation.
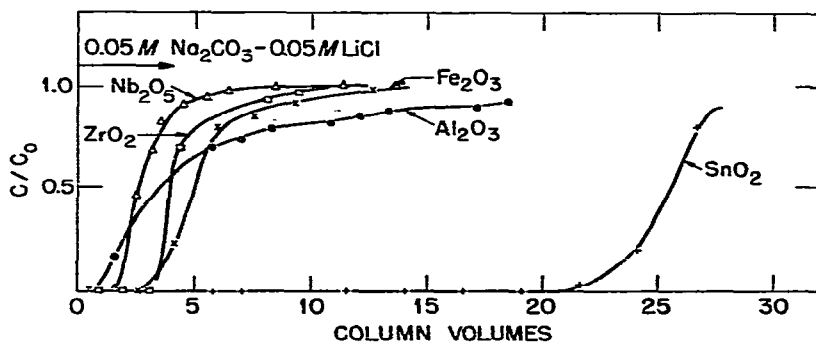

Fig. 5. Comparative uptake of Li(I) by hydrous metal oxides. Flow-rate, ca. 0.25 cm/min; room temperature.

We have no explanation why hydrous SnO_2 shows an unusual selectivity for lithium. Such special selectivity of hydrous oxides seems rare; in a sense this selectivity is reminiscent of the relatively unique selectivity for Na^+ that we found for zirconium antimonate[10], or the lithium selectivity of thorium arsenate[11]. In the latter case the selectivity has been attributed to steric reasons typical of a crystalline material. This explanation almost certainly would not apply here. From line broadening in X-ray diffraction patterns the conclusion was reached that the "pure" tin-oxide was composed of crystallites (cassiterite) of approximately 50-Å diameter and that the SnO_2

included in the carbon was of significantly smaller size. One surely does not expect steric effects with such essentially amorphous materials.

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