Modified Silica Gels as Selective Adsorbents for Sulphur Dioxide

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Summary Silica gel modified by $-CH_2CH_2CH_2NH_3X$ where X is chloride, bromide, or iodide adsorbs sulphur dioxide selectively to form the halogenosulphinate ion SO_2X^-; the process reverses upon warming.

We report here an unusual chemisorption reaction of sulphur dioxide which is selective, reversible, and of potential analytical utility and one in which, because of close molecular analogies, the identity and nature of the adsorption site and of the adsorption complex are much clearer than is usual in chemisorption.

Silica gel, chemically modified by conversion into σ-CH_2-$CH_2CH_2NH_2$, where σ represents a silicon atom at the surface of silica gel, selectively adsorbs carbon dioxide.[1] In this and in the present work, helium of high purity is passed through the adsorbent and then through a thermal conductivity cell. Adsorbed gas is liberated by temperature programmed desorption (t.p.d.) and its quantity measured by the output of the thermal conductivity cell. Carbon dioxide (or, for example, a sample of air) injected ahead of σ-$CH_2CH_2CH_2NH_2$, is completely adsorbed at 25° and liberated by t.p.d. at about 100°. The amine gel, converted into a co-ordination complex by treatment with aqueous $CuSO_4$ and activated at 180°, does not adsorb carbon dioxide but adsorbs carbon monoxide and ethylene and liberates them at about 100°.

The modified gel is prepared by refluxing wide-pore silica gel, Davison Grade 59, in *meta*-xylene with removal of water to dry the gel and the system, adding freshly distilled $(C_2H_5O)_3SiCH_2CH_2CH_2NH_2$ and the refluxing continued for about one day. The gel is then washed with xylene in the absence of moisture and dried. Coverages of about two $-CH_2CH_2CH_2NH_2$ groups per nm^2 result.

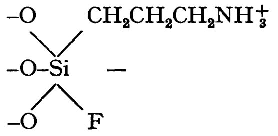
The amine gel adsorbs sulphur dioxide strongly but it does not release it on t.p.d. However, if the gel is converted into σ-$CH_2CH_2CH_2NH_3^+Br^-$ by adding it to an excess of aqueous HBr followed by washing and drying, a selective and reversible adsorbent for sulphur dioxide results. The hydrobromide gel (0·58 g, 0·93 mmol N per g) was first activated at 190° in helium flowing at 60 cm^3 per min. Sulphur dioxide (0·3 cm^3) injected ahead of the adsorbent at 25° was fully adsorbed and released after 30 min by t.p.d. at 30° per min as a peak centring at 92°. No sulphur dioxide was lost in 3 h but the temperature for the peak had fallen to 86°. The capacity of the gel before immediate break-through was 2·4 cm^3. This corresponds to the reaction of about one-fifth of the bromide ions.

We suggest that sulphur dioxide is adsorbed by reaction with bromide ion to form bromosulphinate ion, SO_2Br^-. In acetonitrile solution[2] the equilibrium constants for formation of halogenosulphinate ions from tetraethylammonium halides and sulphur dioxide decrease in the sequence $F^- > Cl^- > Br^- > I^-$. The halogenosulphinate ions are also formed in liquid sulphur dioxide.[2,3]

Carbon dioxide is not adsorbed by the amine hydrobromide gel nor is nitrogen, oxygen, carbon monoxide, ethylene, ethane, nitric oxide, or nitrogen dioxide. Since these silica based adsorbents adsorb water vapour and release it as a broad peak which at rather large water loadings starts at 90°, the presence of much water would interfere with the analytical use of these gels.

The amine hydroiodide gel adsorbs sulphur dioxide distinctly more weakly. Thus, if 0·2 cm^3 of sulphur dioxide is injected ahead of 0·8 g of the hydroiodide gel, a sharp yellow band appears when the pulse of sulphur dioxide reaches the adsorbent. The band spreads and reaches the end of the adsorbent bed in 17 min. The width of the initial yellow band should give a rough measure of the amount of sulphur dioxide. The adsorption spectrum of the hydroiodide gel saturated with sulphur dioxide and immersed in carbon tetrachloride[4] shows an adsorption maximum at 370 nm *vs.* 378 for SO_2I^- in acetonitrile.[2] A gel which behaves like σ-$CH_2CH_2CH_2NH_3^+I^-$ but which seemed to adsorb sulphur dioxide somewhat more strongly was prepared by alkylating σ-$CH_2CH_2CH_2NH_2$ with methyl iodide presumably to give σ-$CH_2CH_2CH_2NH_2CH_3^+I^-$. The hydroiodide gels appear to undergo slow oxidation in air but this matter has not been investigated in detail.

The amine hydrochloride gel binds sulphur dioxide with a strength intermediate between that of the hydrobromide and the hydroiodide gels. The amine hydrofluoride gel does not adsorb sulphur dioxide under the conditions described perhaps because the fluoride ion is involved in a five-co-ordinate surface silicon complex.[4]



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