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Pyrolytic Sulfurization Gas Chromatography. IV. Removal of Trace Amounts of Organic Compounds in Sulfur by Refluxing with Oxides

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Synopsis. Oxides of aluminium, silicon, and titanium, instead of the magnesium oxide used in the Bacon-Fanelli method, were found to be effective for the elimination of trace amounts of organic compounds in sulfur. Prolonged refluxing in an inert gas atmosphere were especially favorable for the removal of organic compounds

The atomic ratio between C, H, O, and N in a sample can be simultaneously determined by pyrolytic sulfurization gas chromatography.[1] Since the high purity of sulfur was indispensable for the analysis, various purification methods such as distillation,[2] recrystallization, refluxing, decomposition of sodium thiosulfate, vacuum sublimation were investigated. The Bacon-Fanelli method[3] was found to be most promising for the present purpose. Sulfur was refluxed with several kinds of oxides including the magnesium oxide (MgO) in the Bacon-Fanelli method, its purity being examined gas chromatographically. Aluminium oxide(Al_2O_3), silicon oxide(SiO_2), and titanium oxide(TiO_2), which do not react with sulfur under the reaction conditions in a sealed quartz tube, were found to be effective for the elimination of carbonaceous impurities similarly to MgO. However, calcium oxide(CaO) and zinc oxide (ZnO), which react with sulfur to evolve sulfur dioxide (SO_2) under the same conditions as above, were unfavorable. Since the amounts of H, O, and N in the sulfur obtained by the present method, in which sulfur is refluxed with one of Al_2O_3, SiO_2, and TiO_2, were almost definite and small in comparison with those of carbonaceous impurities, the removal of carbonaceous impurities was exclusively investigated for the purification of sulfur.

Experimental

Reagents. Of the oxides, Al_2O_3 and SiO_2 were of GC-grade and MgO, TiO_2, ZnO, and CaO were of guaranteed grade. They were ignited at 950 °C for 1 h in the air before use. By this treatment, magnesium and calcium carbonates were expected to decompose with evolution of carbon dioxide (CO_2). Practically no CO_2 was detected in the gas chromatogram for the analysis of MgO. Sulfur as a starting material was of chemical grade.

Standard Procedure. About 100 g of sulfur was placed in a 300 ml four-hole flask with a reflux condenser and fused with an electric furnace, followed by addition of 1% (wt) MgO to sulfur. The contents were refluxed for about 24 h, and then the melts were filtered through the cylindrical glass filter held at 125 °C with a ribbon-heater. To the filtrate was added about 1% (wt) MgO and the same operation as above was repeated. About 75 g of sulfur was recovered after filtration. The oxides such as Al_2O_3, SiO_2, TiO_2, ZnO, and CaO were also used instead of MgO.

Analysis. The sulfur obtained in each purification step was analyzed by the same procedure as that given in the previous paper.[1] Twenty milligrams of sulfur was used for analysis. Carbonaceous impurities were determined as follows: A definite volume of a dilute glycine solution was taken in a reaction tube (a transparent quartz tube with one end closed) and evaporated to dryness in an oven at 65 °C, followed by addition of 20 mg of purified sulfur. The reaction tube was closed at the other end and the contents were analyzed. A calibration curve obtained on the basis of chromatograms was used for the determination of carbonaceous impurities.

Results and Discussion

Choice of Oxides. Since MgO did not react with sulfur, no SO_2 was evolved from MgO used in the Bacon-Fanelli method. The reaction between sulfur and oxides other than MgO was examined. Al_2O_3, SiO_2, and TiO_2 were found to be non-reactive with sulfur. Sulfur was purified by use of these oxides and the sulfur obtained was analyzed. The peaks of CO_2, carbonyl sulfide (COS), and carbon disulfide (CS_2) coming from carbon in the sample are shown in the gas chromatogram. The carbon content in the sulfur sample obtained in each purification step was determined by multiplying the correction factors[4] of CO_2, COS, and CS_2 by their peak areas and summing up the products. As seen from the relationship between the number of filtration and the content of carbonaceous impurities (Fig. 1), Al_2O_3, SiO_2, and TiO_2 are effective for the purification of sulfur similarly to the case of MgO, but not ZnO and CaO. Since the reaction

$$2AgNO_3 + 2S_2 \longrightarrow Ag_2S + 3SO_2 + N_2 \qquad (1)$$

reached completion, the relative conversion of the reaction between an oxide and sulfur was calculated from the amount of SO_2, based on the conversion of $1 = 1.0$. There is a good correlation between the efficiency of the oxides (Fig. 1) and the relative conversion (Table 1). According to Bacon and Fanelli the effectiveness of MgO for the purification of sulfur is attributed to the basicity of MgO which shows an affinity to organic and inorganic acids in sulfur.[3] However, the reactivity of oxides to sulfur was concluded, on the basis of experimental results, to be more predominant than the basicity of the oxides.

Determination. The content of carbonaceous impurities in several sulfur samples was determined by means of the curve: 30—50 ppm in chemical grade sulfur, 3—6 ppm in sulfur purified with Al_2O_3, SiO_2, TiO_2, and MgO, and >100 ppm in commercial high purity sulfur (purity 99.9999%).

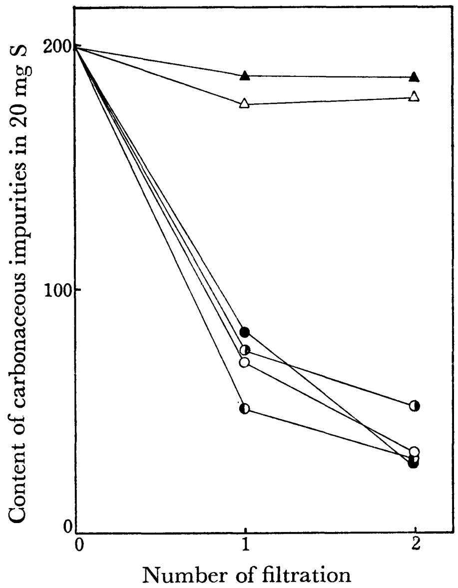

Fig. 1. The relationship between the number of filtration and the content of carbonaceous impurities.
○: MgO, ●: Al_2O_3, ◑: SiO_2, ◐: TiO_2, ▲: ZnO, △: CaO.

Table 1. Relative conversion in the reaction between an oxide and sulfur

Metal oxide	Relative conversion
MgO	0
Al_2O_3	0
SiO_2	0
TiO_2	0
CaO	0.67
ZnO	1.1

Organic Test. The spot test[3] to detect an organic substance in sulfur was applied to the sulfur obtained by refluxing with MgO, Al_2O_3, SiO_2, and TiO_2, but no black spot was hardly ever confirmed. However, a black spot appeared distinctly in the sulfur obtained by treatment with ZnO and CaO. This is in line with the results shown in Fig. 1. A fraction of the black spot was isolated and analyzed. Since the presence of carbonaceous impurities was confirmed gas chromatographically, the appearance of black color being attributed to the presence of an organic substance.

Reaction Time. Bacon and Fanelli pointed out that the organic substance in sulfur is isolated as a black cake during the course of refluxing and removed by filtration, a similar phenomenon to that above being also observed.[3] That is, sulfur was purified by refluxing for some time and by filtering a sludge in the absence of oxides. The effect of refluxing times 6 and 24 h on the removal of carbonaceous impurities was investigated by use of Al_2O_3 and the content of carbonaceous impurities was found to decrease with increase in refluxing time.

Effect of Oxygen. It was also found by use of Al_2O_3 that carbonaceous impurities are removed more effectively in nitrogen atmosphere than in the air. The result is contrary to what we expected. The reason remains unknown. A dark gray sludge sample obtained by refluxing sulfur with MgO in the air and by filtering the melts was analyzed and the peak area of CO_2 was found to be abnormally large.

From the results, it can be concluded that the purification of sulfur is mainly achieved by the adsorption of organic substances on the oxide, but not by the atmospheric oxidation of organic substances.

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