

EFFECT OF OXYGEN ON THE ADSORPTION OF SO₂ ON ACTIVATED CARBON

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Introduction

Sulfur dioxide, an important atmospheric pollutant, is generated in most combustion processes involving carbonaceous fuels. Oxidative adsorption of SO₂ on activated carbon presents a potential interest for flue gas desulfurization due to the high adsorption capacity of activated carbons and the additional possibility of NO_x removal in the same process [1]. Several studies have been carried out dealing with the removal of SO₂ by activated carbon [2-6]. It has been reported that the presence of oxygen (and water) increases the SO₂ adsorption on activated carbon [7-9] and that certain surface oxygen groups, which increase the surface basicity of the carbons, play an important role on the SO₂ adsorption [2,4]. However, the nature of the interaction between SO₂ and carbon surface (whether physical or chemical) is far from being understood yet.

In the present work, the influence of oxygen on the SO₂ adsorption on activated carbon has been studied.

Experimental

Saran polymer was the precursor of the carbon char used in this study. This copolymer of vinylidene chloride and vinyl chloride (mol ratio of 9:1) was heated to 900 °C and held at this temperature for 4 h in a flowing stream of high purity N₂. Adsorption of SO₂ was carried out gravimetrically (CI Electronics TGA system) at 25 °C. Different SO₂ concentrations (0.25 to 4% molar in He) in the absence and presence of oxygen were used. For a total flow rate of 100 cm³/min and a total pressure of 1 atm., an inlet O₂ concentration of 5% was used. Approximately 10 mg of saran char with 54-63 μm particle size was always used. Desorption experiments were also performed in the TGA system at 25 °C under He atmosphere (100 cm³/min).

Temperature programmed desorption (TPD) experiments (He, 25-900 °C, 10 °C/min) have been carried out in a fixed-bed reactor (5 mm ID) to study and analyze the behavior of surface oxygen complexes formed during adsorption and desorption of SO₂ in the absence and presence of O₂ on saran char. Quadrupole mass spectrometer was used for continuously monitoring the concentrations of CO, CO₂ and SO₂ in the outlet gas.

Prior to each run, the char sample (approximately 150 mg) was subjected to outgassing for surface cleaning by heating the char in He at 30 °C/min to 900 °C and maintaining this temperature for 15 min. Subsequently, the temperature was decreased to the desired value and the feed mixture was introduced. Adsorption and desorption on saran char were carried out, at identical conditions of SO₂ and O₂ concentration and temperature as in the TGA system, in the fixed-bed reactor prior to the TPD experiments. In some cases, before SO₂ or SO₂/O₂ adsorption, O₂ was chemisorbed on saran char at 160 °C overnight, in order to increase the oxygenated surface groups on the surface of the carbon.

Results and Discussion

Analysis of the N₂ and CO₂ adsorption isotherms (-196 °C and 0 °C, respectively) of the saran char indicate that this char presents a narrow microporous structure with an apparent surface area (BET, N₂) of 1200 m²/g. SO₂ was adsorbed on saran char at 25 °C and the amount adsorbed increased with the SO₂ concentration from 50 to 225 mg SO₂/g carbon for 0.25 and 4% SO₂, respectively [7]. The removal of oxygen surface complex by heat treatment of saran char at 900 °C in He increased the adsorption of SO₂ on the char, suggesting that the free carbon sites control the uptake of SO₂ [9].

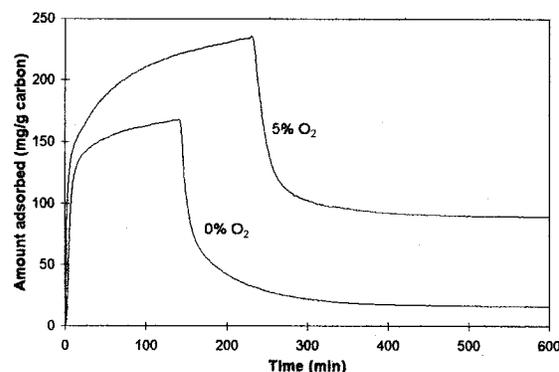


Figure 1. Amount adsorbed as a function of time for SO₂ (1% molar) adsorption on saran char at 25 °C in the absence and presence of O₂.

Addition of oxygen (5%) to the inlet gas stream increased the rate of adsorption and amount adsorbed on the char, as it is illustrated in Fig.1 for a concentration of 1% SO₂. Adsorption of oxygen on the saran char was not observed when only 5% of O₂ in He was fed to the system at 25 °C. In both absence and presence of O₂, desorption took place only partially at the adsorption temperature and a significant amount of adsorbate (larger in the case that O₂ was present in the adsorption step) remains adsorbed on the carbon. This effect may be produced by strong (physical) interactions between adsorbate molecules and narrow micropore walls or by chemisorption of adsorbate molecules on very energetic adsorption sites of the carbon. Gravimetric analysis is not a suitable technique to discriminate whether adsorption of SO₂ is, actually, enhanced by the presence of O₂ or just competitive adsorption of O₂ and SO₂ (or reaction between them) is taken place on the surface of the carbon, with the corresponding increase of weight gain.

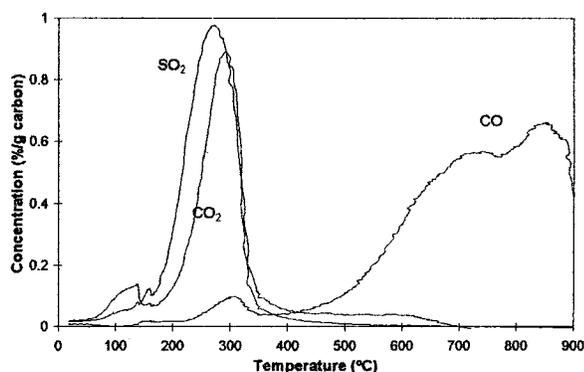


Figure 2. TPD profiles of saran char after adsorption of SO₂ (1% molar) in the presence of O₂ (5% molar) for 5 h and desorption in He overnight at 25 °C

TPD profiles of thermally desorbed saran char after adsorption of SO₂ in the presence of O₂ and desorption in He atmosphere at 25 °C, represented in Fig. 2, indicate the presence of two desorption peaks for a temperature range between 150 and 350 °C, corresponding to SO₂ and CO₂ with a maximum at 270 and 295 °C, respectively. CO becomes appreciable above 500 °C, with a small amount desorbed around 300 °C. Similar results were found for the adsorption of SO₂ in the absence of O₂ on saran char at 25 °C, although in this case, lower amount of SO₂ and, especially, of CO₂ were desorbed at the temperature range between 150 and 350 °C. Davini [2], based on TGA adsorption experiments, reported that SO₂ adsorbed on activated carbon at ambient temperature could be weakly bonded to the carbon surface and desorbs easily at 120 °C, and strongly bonded to the carbon surface, which is only desorbable at higher temperature. Moreno-Castilla et al. [4] observed,

after adsorption of SO₂ in a dry air stream on activated carbon in a TGA system at 85 °C, two desorption peaks at 100 °C and 270 °C, respectively. They related the desorption of SO₂ at two different temperatures to physisorbed SO₂ into wider and narrower micropores, respectively. In our case, CO₂ was not observed in the isothermal desorption of SO₂ at 25 °C after adsorption of SO₂ in the presence of O₂. In this regard, the desorption of SO₂ at 25 °C may be related to physisorption of SO₂ on wide (and in some extent narrow) micropores. Part of the SO₂ desorbed in the temperature range between 150 and 350 °C may be related to physisorption on narrow micropores. However, the presence of CO₂ at the same temperature range as SO₂ desorption takes place suggests some interaction between oxygen and surface carbon atoms, which seems to be possible only when adsorption of SO₂ occurs in the presence of molecular oxygen or C-O complex exist on the surface of the carbon prior to the adsorption of SO₂.

These results seem to suggest that SO₂ is adsorbed on the free sites of the char surface, producing a C-O₂S complex weakly bonded that can be desorbed, as SO₂, at low temperatures. When O₂ is present, this complex can react directly with molecular oxygen in the vicinity of a free site to form strongly bonded C-O₂S-O₂-C complexes, which are desorbed only at higher temperatures. This mechanism would explain the increase in adsorbed amount on the saran char when SO₂ is adsorbed in the presence of O₂ and the release of CO₂ (and CO) during the TPD experiments.

References

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