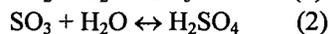


TRANSIENT KINETICS STUDY ON THE MECHANISM OF SO₂ OXIDATION BY ACTIVE CARBON AND ACTIVE CARBON FIBRES

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Introduction

One interesting characteristic of active carbons (AC) and active carbon fibres (ACF) for SO₂ removal from flue gases, is their ability to catalyze SO₂ oxidation to H₂SO₄ even at room temperature [1]. The main reactions involved in the process are [2-4]:



To improve SO₂ removal efficiency by AC and ACF is necessary to understand the mechanism of the reaction. Previous studies for reaction (1) suggested a Langmuir-Hinshelwood mechanism in which all the species taking part in the reaction are adsorbed on the surface [2-4]. The first step of reaction (1) is SO₂ adsorption, but there is not agreement in the state of oxygen. It has been suggested that it adsorbs molecularly [2] or dissociatively [3]. However, other authors postulate the formation of carbon-oxygen complexes at the carbon surface during SO₂ adsorption as intermediate for reaction conversion of SO₂ to SO₃ [4].

At the present study, TPD experiments after SO₂ adsorption at room temperature and in-situ FTIR experiments during the adsorption and the subsequent desorption are carried out over a wide variety of samples with different porosity and surface oxygen content. Thus, the aim of this work is analyse the nature of the SO₂-O₂-carbon interaction to deepen into the SO₂ oxidation mechanism.

Experimental

Two series of ACF obtained by activation of pitch based carbon fibres with CO₂ (CFC series) and steam (CFS series), activated carbon prepared by chemical activation of an anthracite with KOH (KUA1), a char of a phenolformaldehyde resin (A) and two commercial carbon molecular sieves (Takeda 3A, Takeda 5A) were used in this study.

Temperature programmed desorption (TPD) experiments, after SO₂ adsorption experiments at 313K in presence or absence of O₂, were carried out in a fixed bed reactor in a vertical furnace. The gas flow rate used was 60 ml/min

(STP) with a composition of 4500 ppm SO₂, 5% O₂ in N₂. Gas phase composition (SO₂, O₂, CO and CO₂) was analysed with a mass spectrometer (VG-Quadrupoles).

In-situ FTIR experiments of SO₂ adsorption (15 ml/min, 2000ppm SO₂, 5% O₂, He) at room temperature and desorption (15 ml/min, He) up to 773K were done by diffuse reflectance in a FTIR (Mattson Series Infinity) with a controlled ambient chamber.

Results and Discussion

Figure 1 shows an example of TPD after SO₂ adsorption in the presence of O₂ for an ACF (previously heat treated up to 1193K, He). Two different types of SO₂ adsorbed were observed by TPD after SO₂ adsorption. The first peak is related with physically adsorbed SO₂, while the peak desorbed at higher temperature is assigned to strongly adsorbed SO₂ or being oxidised to SO₃. CO and CO₂ are also evolved during the TPD from thermal decomposition of carbon-oxygen surface complexes.

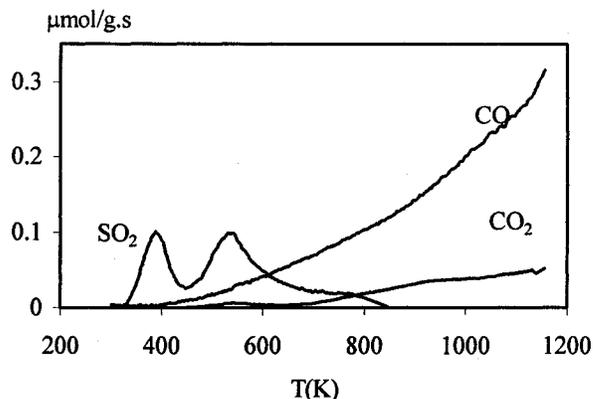


Figure 1. Example of TPD after SO₂ adsorption.

Figure 2 contains TPD profiles for SO₂ at different experimental condition (i.e. SO₂/O₂ and SO₂ atmosphere) for samples heat treated before SO₂ adsorption. The figure shows that for the SO₃ related peak to appear in a considerable extent both a heat treatment at high temperature before SO₂ adsorption (to remove most of oxygen surface groups) and the presence of O₂ in the gas phase are needed. These results seems to indicate that

oxygen groups at the carbon surface inhibit SO₂ oxidation even in the presence of O₂.

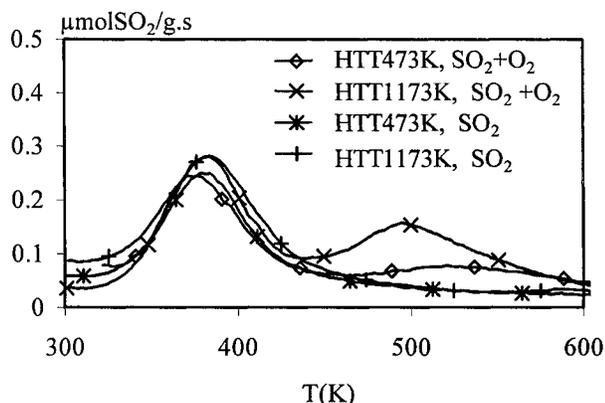


Figure 2. SO₂ TPD profiles at different experimental conditions.

Figure 3 shows SO₂ TPD profiles after consecutive adsorption of SO₂ and O₂ over heat-treated samples (1173K, N₂). An important observation is that if SO₂ adsorption is done after O₂ adsorption at room temperature, the SO₃ related peak does not appear, indicating that oxidation does not happen. O₂ adsorption at higher temperature has been also tested with similar results. So, the formation of a hypothetical carbon-oxygen complex that oxidises the SO₂ seems to be not reasonable. However, if over SO₂ preadsorbed sample O₂ is flowed through, the physically adsorbed SO₂ is oxidised to SO₃.

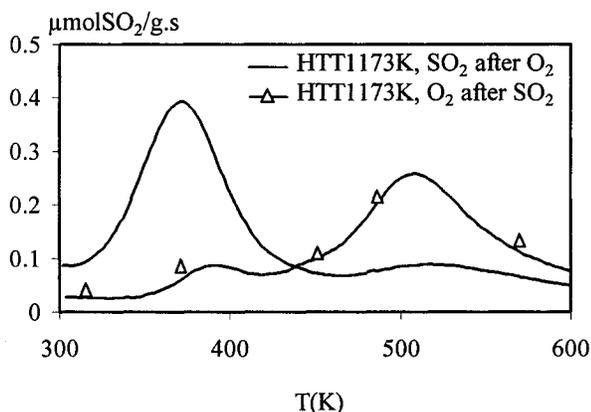


Figure 3. SO₂ TPD profiles after consecutive adsorption of SO₂ and O₂.

CO and CO₂ evolution during TPD after SO₂ adsorption also depends on the experimental conditions. If the sample is not heat treated before SO₂ adsorption step, the amounts

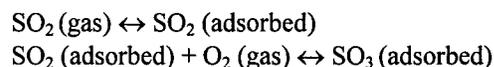
of CO and CO₂ evolved during the TPD after SO₂ adsorption are almost the same than the amounts evolved during TPD of the fresh sample. However, if a heat treatment of the sample up to 1173K in He is done before SO₂/O₂ adsorption at 313K, CO and CO₂ evolution is observed during the subsequent TPD. The amount of oxygen released as CO and CO₂ correspond quantitatively to the oxygen left by the reduction of adsorbed SO₃ into SO₂ during TPD. In this case in-situ FTIR studies shows the formation at the carbon surface of C-O complexes, identified like ethers, because carbon gasification by SO₃.

Conclusions

Carbon oxygen complexes at the carbon surface inhibits SO₂ oxidation into SO₃. A heat treatment before SO₂ adsorption enhances SO₂ oxidation.

The presence of O₂ at the gas phase is needed for the SO₂ oxidation. Oxygen does not interact with the carbon surface at the adsorption temperature.

A more plausible mechanisms for SO₂ oxidation step seems to be:



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