

Removal of SO₂ from gases on carbon materials

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The aim of the work is to describe a capability of the active carbon CARBON L-2-4 (AC) and of the nanocarbon (NC) materials containing iron nanoparticles to continuously remove SO₂ from air. The carbon nanomaterials (NC) containing iron nanoparticles were synthesised using a chemical vapor deposition method – through catalytic decomposition of ethylene on nanocrystalline iron.

The process of SO₂ removal was carried out on dry and wet with water carbon catalyst (AC or NC) and was studied for inlet SO₂ concentration 0.3 vol.% in the presence of O₂, N₂ and H₂O, in the temperature range of 40–80°C.

Keywords: sulphur dioxide removal, nanocarbon materials.

INTRODUCTION

The emission of SO₂ is mainly due to the combustion of natural fuels containing sulphur – as coals (brown and black) and crude oil.

Sulphur dioxide is also emitted as a result of various industrial processes. To decrease the level of emission various absorption, adsorption or catalytic methods are used. Absorption in alkali solutions results in production of solid products (sulphates), which are not always commercially demanded. The application of adsorption and catalysis on one bed is possible when carbon materials are used. In this case SO₂ is catalytically oxidised to SO₃ and sulphuric acid is formed. The reported carbon materials applied in this method are: coke, porous active carbon¹⁻⁴, carbon fibres^{5,6} or carbon nanomaterials.

The removal of SO₂ on activated carbons (ACs) and activated carbon fibres (ACFs) in presence of oxygen at room temperature was described in¹. The adsorption of sulphur dioxide and its oxidation to trioxide was impeded by the presence of surface oxygen. An optimum pore size (0.7 nm) was determined for which the oxidation of SO₂ to SO₃ was favoured.

Lizzio and DeBarr² studied the effect of surface area and the presence of oxygen on SO₂ adsorption carried out on activated char, prepared from bituminous Illinois coal. No correlation was found between SO₂ adsorption capacity and surface area of active char. As in the previous paper, the authors concluded that the SO₂ adsorption capacity was inversely proportional to the amount of oxygen stable surface complexes C(O). The fleeting C(O) surface complexes were supposed to be reaction intermediates necessary for the conversion of SO₂ to H₂SO₄.

Martin *et al.*³ used 2 kinds of activated carbons: a granulated activated carbon (CN) and a PAN fiber (CF) under SO₂ concentrations lower than 100 ppm. Carbon CN used 'as received' is able to trap SO₂ in air at concentrations as low as 2.5 ppm, but the amounts of SO₂ adsorbed per gram of carbon are much smaller than in the case of high SO₂ contents in air (>1000 ppm) The adsorption of SO₂ can be irreversible (and then the oxidation occurs) or reversible – in the case of physisorbed sulphur dioxide.

In the paper of Bandosz⁴ an ability of carbonaceous

materials to efficiently adsorb various sulphur containing species (as hydrogen sulphide, sulphur dioxide, methyl mercaptans, etc.) from gas phase is discussed. The role of oxygen and nitrogen containing groups and catalytic metals as iron or calcium is taken into account. The presence of water film enables to create conditions necessary to for dissociation, providing that the local pH of the surface is greater than pK_a of the adsorbate.

Gaur, Asthana and Verman⁵ studied a removal of SO₂ by activated carbon fibers in the presence of O₂ and H₂O. The aim was to perform the process without catalyst regeneration. The steady-state SO₂ concentration levels at the reactor exit increased with increasing inlet SO₂ concentration and decreased with increasing concentration levels of O₂ as well as H₂O. Increase in the reaction temperature was moderately unfavourable for SO₂ removal. The best results were obtained at 40°C in the presence of O₂ and H₂O with concentration of 20% and 30% (v/v), respectively. Above this temperature a gradual degradation of catalytic activity was observed. The overall removal process was diffusion or kinetics controlled and the limit value was D_{eff} = 5.2 × 10⁻¹⁰ m²/s. Diffusion was controlling below this value and kinetics – above it. In the kinetic area the limiting step was the desorption of product – sulphuric acid from the surface. The catalytic activity (as well as mechanical integrity) of ACFs remained constant for long duration – 120 h. To predict the gas concentration profiles along the reactor, the authors developed a mathematical model.

Daley *et al.*⁶ studied the adsorption of sulphur dioxide on pristine and heat-treated ACFs. The initial rate of SO₂ adsorption from flue gas was shown to be inversely related to pore size. At longer times, the amount of SO₂ adsorbed from flue gas was dependent on both the pore size and pore volume. Oxidation of the ACFs, using an aqueous oxidant, decreased their adsorption capacity for SO₂ from flue gas due to a decrease in pore volume and repulsion of the SO₂ from acidic surface groups. On the contrary, the heating caused the increase of ACFs activity, due to the removal of surface oxygen.

This work is devoted to a removal of sulphur dioxide from gases on a traditional adsorbent – active carbon and in parallel – on a new kind of adsorbent – multi-

wall carbon nanotubes (MWCNTs). Carbon nanotubes can be used as adsorbents for volatile impurities in gases, because of their significant specific surface area. Additionally, in the case of the carbon nanomaterials presented in this work, a positive catalytic effect of iron can be expected, because the tubes were synthesised on nanocrystalline iron.

EXPERIMENTAL

The traditional adsorbent used in the studies, granulated active carbon CARBON L-2-4 (AC) has a density of 443 g/dm^3 and humidity of about 3%. The specific surface area of AC reaches $925 \text{ m}^2/\text{g}$ (BET – Brunauer-Emmett-Taylor, low-temperature nitrogen adsorption), the volume of micropores – $0.26 \text{ cm}^3/\text{g}$, and the surface area of pores – $567 \text{ m}^2/\text{g}$. A mean pore diameter determined using BET was 2.13 nm.

Apart from AC, the multiwall carbon nanotubes, synthesised using chemical vapour deposition (CVD) method were used in the studies. The material obtained through the decomposition of ethylene in nanocrystalline iron, contained multiwall carbon nanotubes (with some small amount of single wall carbon nanotubes) as well some amount of amorphous carbon. The crystallites of iron carbide having a diameter of about 40 nm were located at the end of the tubes. The synthesis method was described in our previous papers^{7–10}. The specific surface area of the nanocarbons material (NC) measured using BET method was of about $42.5 \text{ m}^2/\text{g}$ (BET), then more than 20 times lower than that of commercial AC used in the study. The relatively low value of specific surface area in the case of nanocarbons is due to the content of iron in this material, and then, its higher density.

The gas mixture containing O_2 , N_2 and 0.3 vol% of SO_2 was passed through a catalyst bed in a temperature range of 40–80°C and gas flow of $10.6 \text{ dm}^3/\text{h}$.

The schema of the laboratory equipment used for carbon material testing is shown in Fig. 1. The process was carried out in a glass flow reactor, filled with 10 ml of carbon material. The height of the bed amounted to

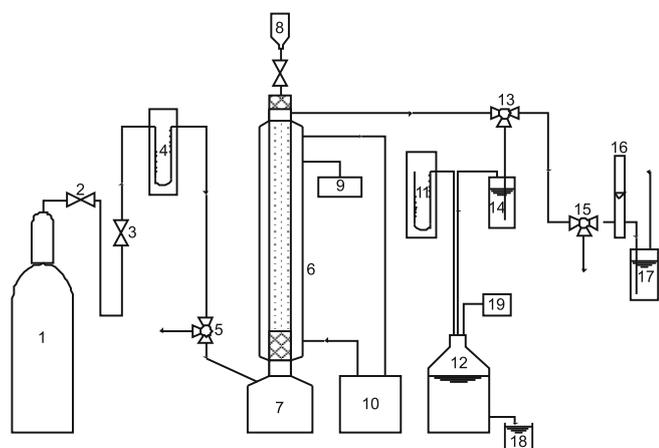


Figure 1. Testing equipment: 1 – bottle with gas mixture, 2 – reduction valve, 3 – regulating valve, 4 – flowmeter, 5,13,15 – three-way valves, 6 – reactor, 7 – container for acidic water, 8 – dropping funnel, 9 – temperature control, 10 – thermostat, 11 – mercure manometer, 12 – aspirator, 14 – analytical washer, 16 – rotameter, 17 – absorption washer, measuring jar, 18 – measuring cylinder, 19 – thermometer

140 mm.

The reactor was placed inside a water jacket, in which a temperature was stabilised using a thermostat 10. A stable temperature in the range of 40–80°C was kept during the process. A gas mixture was stocked in the bottle 1 and came to the reactor through mass flow regulators 3.

A concentration of sulphur dioxide at the inlet and outlet of the reactor was measured using iodimetric titration. The measurements were carried out until the outlet concentration was equal to the inlet one.

After a series of measurements the catalyst bed was regenerated through washing for 60 min in a temperature range of 40 to 80°C with distilled water (1 dm^3) from a dropping funnel (8) placed above the reactor. After washing the sorption of the sulphur dioxide was repeated.

It can be supposed that SO_2 adsorbed on the wet catalyst undergoes a catalytic conversion according to the reaction:



RESULTS AND DISCUSSION

Fig. 2 and 3 show changes of an outlet concentration of SO_2 in time on dry and wet AC, respectively. An inlet concentration of sulphur dioxide was equal to 0.26 vol.%.

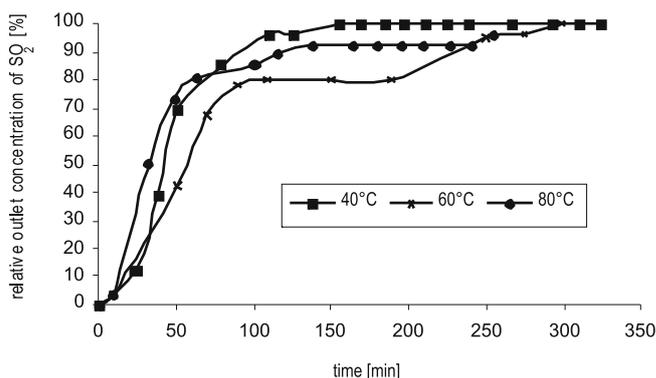


Figure 2. Changes of outlet SO_2 concentration in a temperature range of 40–80°C for dry Carbon L-2-4 catalyst

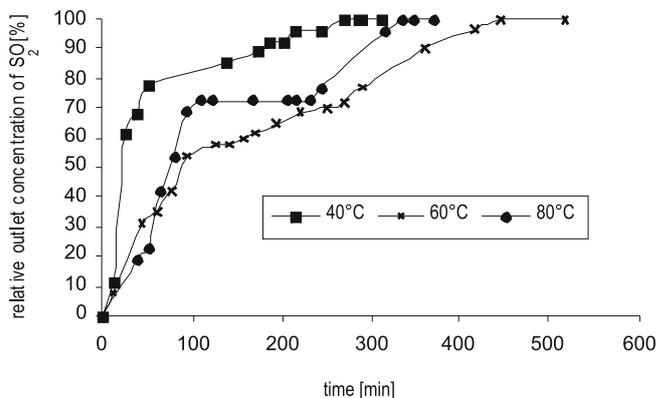


Figure 3. Changes of outlet SO_2 concentration in a temperature range of 40–80°C for wet Carbon L-2-4 catalyst

The bed of active carbon L-2-4 becomes saturated after about 150 min. The best results were obtained for lower temperatures

The work period of the catalyst bed increased significantly after the washing with water, mainly at the temperature of 60°C to 80°C.

The results of adsorption tests carried out on the ac-

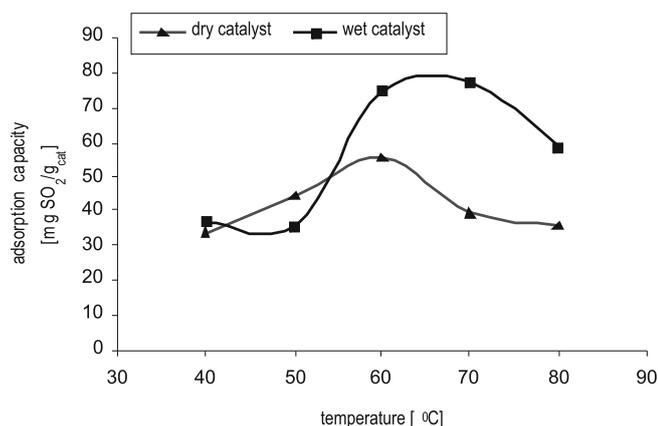


Figure 4. Dependence of the adsorption capacity of active carbon on temperature

tive carbon L-2-4 are summarised in Fig. 4, where the dependence of the adsorption capacity (defined as a ratio of the mass (in mg) of sulphur dioxide trapped on the catalyst bed, referred to the mass (in g) of this catalyst bed, in the unit of time) on temperature is shown. For the dry bed the maximum of adsorption capacity is reached at 60°C and on the wet bed the maximum is higher and reached at 70°C.

To answer a question, if the same catalyst can be regenerated and used many times, the catalyst after the experiment was washed with hot water and then dried at 110°C for 24 h. After that, the activity measurements were repeated. No changes in the amount of the removed sulphur dioxide were observed. The same simple regeneration procedure was repeated 2 times, without any effect on the activity.

The adsorption lines for the nanocarbon bed (NC) are shown in Fig. 5 and 6 for dry and wet catalyst, respectively.

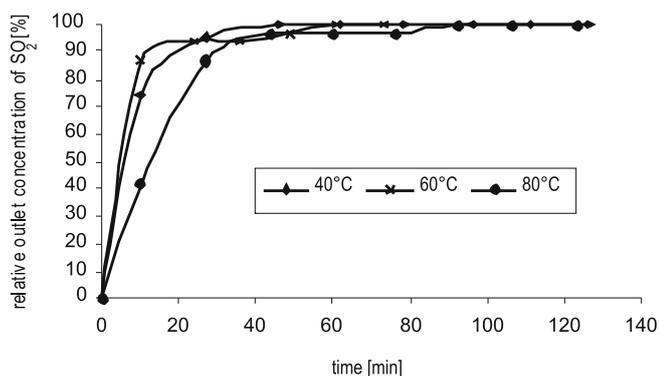


Figure 5. Changes of outlet SO₂ concentration in a temperature range of 40–80°C for dry NC catalyst

On the dry bed of carbon nanotubes the adsorption of SO₂ (inlet concentration 0.31 vol.%) in a temperature range of 40°C–80°C is rather low and increases with temperature – the best results are obtained at 80°C. The bed becomes saturated after 50 min. The adsorption capacity was larger after the regeneration of the bed with water (Fig. 6).

The results of adsorption tests carried out on the nanocarbon bed are summarised in Fig. 7, where the dependence of the adsorption capacity on temperature is shown. For both dry and wet bed the maximum of adsorption capacity is reached at 60°C, however on the wet bed it is four times higher. In the latter case, the adsorption capacity is 1.5 higher than that of the wet

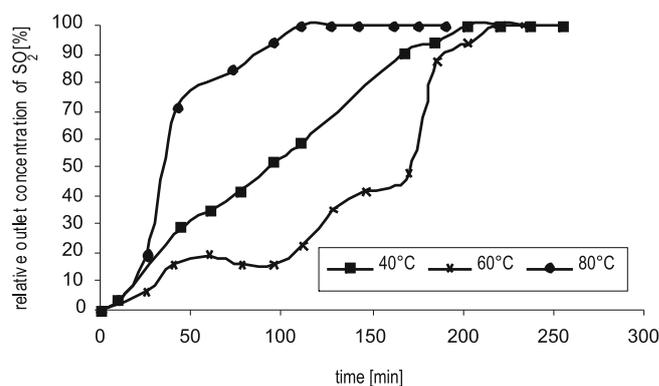


Figure 6. Changes of outlet SO₂ concentration in a temperature range of 40–80°C for wet NC catalyst

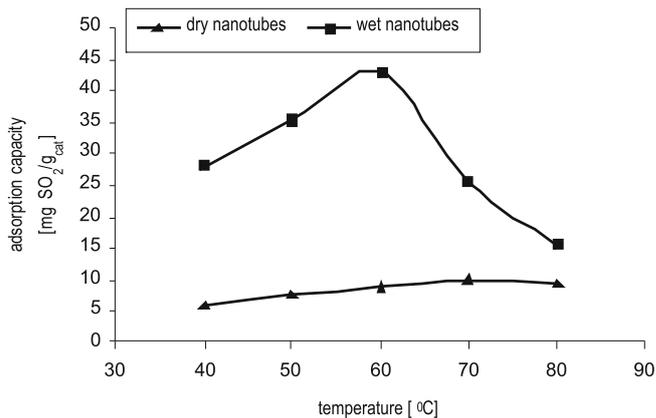


Figure 7. Dependence of the adsorption capacity of nanocarbon on temperature

bed of active carbon. However, comparing the adsorption capacity of dry beds, this is the opposite case – that of AC is roughly twice higher than that of NC.

The situation changes if we compare the adsorption capacity of both catalysts referred to their specific surface area (not to mass of the bed). The results are shown in Fig. 8 a) and b). The catalyst based on nanocarbon reveals better adsorption capacity than AC. Of course, the adsorption capacity related to the specific surface area in case of NC materials is over-estimated, because their S_{BET} is lowered due to the iron content.

In all cases the adsorption on a catalyst bed regenerated with water is more effective. It can suggest, that in a two-phase system SO₃ formed as a result of SO₂ oxidation on the catalyst bed desorbs too slowly from the surface and in the three-phase system SO₃ is removed after transformation into sulphuric acid. The differences between two- and three-phase system are shown in Fig. 9 a) and b).

In the two-phase system sulphur dioxide and oxygen diffuse from the gas stream to the active surface of carbon catalyst, where both gases chemisorb and then react to form SO₃, which desorbs from the surface. In the three phase system the situation becomes more complicated – in this case sulphur dioxide and oxygen from the gas phase have to diffuse additionally through a thin water layer at the catalyst surface. The reaction occurs, as in the two phase system, on the catalyst surface, but substrates and products of the reaction are absorbed in the liquid. The above observations are in accord with the paper of Bandosz, in which the presence of thin water film on the surface of carbonaceous species enhances the ability of dissociation of sulphur-containing species.

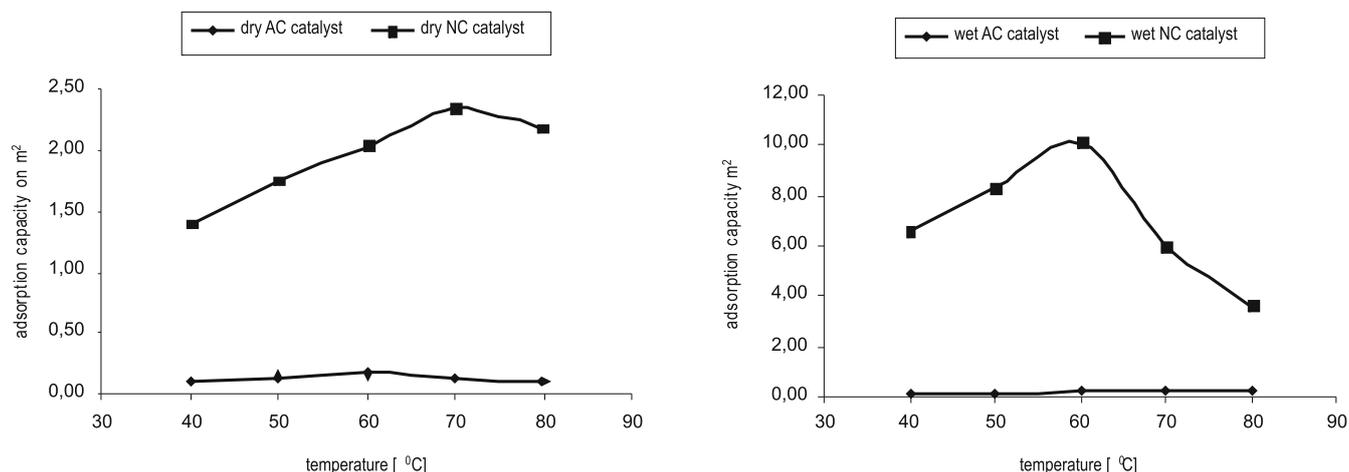


Figure 8. Dependence of the adsorption capacity (referred to the specific surface area of the catalyst bed) on temperature: a) dry AC and NC bed, b) wet AC and NC bed

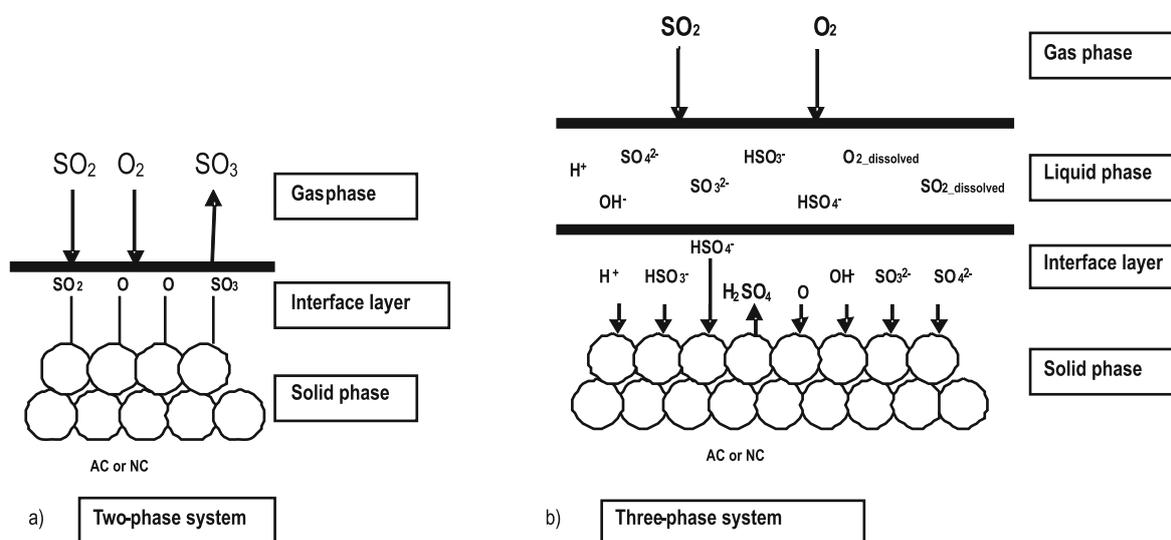


Figure 9. Schema of the SO₂ sorption on a) dry, b) wet catalyst bed

Nevertheless, the occurrence of the mechanism shown here above depends on temperature and in case of our experiments the desorption of sulphur dioxides from catalyst surface is very low, as catalyst beds become saturated and the outlet sulphur dioxide concentration reaches the level of the inlet one.

CONCLUSIONS

Sulphur dioxide can be removed from gases using various types of carbon, among them active carbons and nanocarbons. For both kinds of carbon the adsorption effectiveness is improved after a regeneration of catalyst by washing with water. It can suggest, that in a two-phase system SO₃ formed as a result of SO₂ oxidation on the catalyst bed desorbs slowly from the surface and in the three-phase system SO₃ is removed after transformation into sulphuric acid.

In the case of nanocarbons, for both dry and wet bed the maximum of adsorption capacity is reached at 60°C, however on the wet bed it is four times higher and 1.5 higher than that of the wet bed of active carbon. Comparing the capacity of dry beds, that of AC is roughly twice higher than that of NC. If the adsorption capacity is referred to the specific surface area of catalysts, the catalyst based on nanocarbon has better adsorption capacity than active carbon.

In all cases the adsorption on a catalyst bed regenerated with water is more effective. The regeneration procedure can be repeated several times without a drop in activity.

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