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A dsorption of H₂S or SO₂ on an activated carbon cloth modified by ammonia treatment

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Abstract

The aim of this research is to investigate how ammonia treatment of the surface can influence the activity of a viscose-based activated carbon cloth (ACC) for the oxidative retention of H₂S and SO₂ in humid air at 25 °C. Surface basic nitrogen groups were introduced either by treatment with ammonia/air at 300 °C or with ammonia/steam at 800 °C. The pore structure of the samples so prepared was examined by adsorption measurements. Changes in the surface chemistry were assessed by X-ray photoelectron spectroscopy, X-ray absorption spectroscopy and temperature programmed desorption (TPD). The change of ACC activity could not be merely attributed to surface nitrogen groups but to other changes in the support. Ammonia/steam treatment improved ACC performance the most, not only by introducing nitrogen surface groups, but also by extending the microporosity and by modifying the distribution of surface oxygen groups. Successive adsorption–regeneration cycles showed important differences between oxidative retention of H₂S and SO₂ and the subsequent catalyst/support regeneration process.

Keywords: A. Activated carbon; Carbon cloth; B. Surface treatment; D. Catalytic properties; Surface properties

1. Introduction

Recent studies have reported that activated carbon fibers, such as PAN-ACF [1] or Nomex-ACF [2], have relatively high flue gas desulfurization capacities at low temperature. ACF shows a great rate of transfer of matter, compared to granular activated carbon, due to the fact that more of its micropores are open directly to its outer surface. Hence ACF provides a higher rate of SO₂ oxidation and retention than granular activated carbons with similar pore size distribution [3]. However, the cost of ACFs makes the improvement of their activity for sulfur removal necessary. In this respect, a few works have been reported to demonstrate how ammonia treatment affects the porous structure and the activity of ACFs for SO₂ [4-7]. Li et al. [7] found that ammonia treatment enhanced both adsorption and oxidation activity of ACF. They replaced the thermal regeneration method by a continuous regeneration by SO₂ recovery as H₂SO₄ at room temperature by the humidity within the reactant gas. They found that ACF is more suitable for the recovery of sulfuric acid compared to granular activated carbon because the diffusion of sulfuric acid is much easier in the pores of the fiber.

From the literature, it appears that ammonia/air reaction at low temperature [4,8], less complicated than ammonia reaction at high temperature or ammonia activation, has rarely been investigated to improve the performance of activated carbon fibers for the removal of SO₂. In addition, ammonia treatment, whatever the form, has never been used to modify ACF for the removal of H₂S. Therefore, in this work, a commercial activated carbon fiber in the form of
of cloth has been subjected to an ammonia/steam treatment at 800 °C or to two types of ammoxidation treatment with ammonia/air at 300 °C (one on the precursor cloth and the other one directly on the activated carbon cloth). The modified activated carbon cloths (ACCs) have been investigated for their activity in the removal of H2S or SO2 in wet air at room temperature.

2. Experimental

2.1. Samples

The commercial activated carbon cloth used in this study was provided by Actitex (Ref.: WKL20). The sample was selected among a set of Actitex activated carbon cloths for its good mechanical properties and high resistance towards air oxidation at 300 °C. It was prepared from a viscose rayon cloth (precursor) using a classified method which involves carbonization followed by CO2 activation. For convenience, the commercial Actitex sample was noted as Ac (see Scheme 1).

Ammonia/steam treatment was performed by placing a 0.5 to 1 g sample in a quartz tube under flowing nitrogen (100 ml min⁻¹) at 800 °C. The reactor temperature was ramped (30 °C min⁻¹) to 800 °C, then the input nitrogen line was directed by valve switching to a saturator containing an aqueous solution of 28% NH3. The carrier gas line and the saturator were kept at ambient temperature. Isothermal treatment was performed during 40 min. After treatment, the sample was cooled down in a stream of N2. The loss of weight during this process was ca. 13 wt% daf. The obtained sample was designated by the code Ac-NH3/H2O. In this study, ammonia-steam was preferred to pure ammonia because ammonia treatment using an aqueous solution of ammonia is more straightforward. Yet, this experimental option is not optimal because addition of steam increases pore development and thus micropore widening [9].

Ammoxidation treatments of the samples Pr (precursor cloth) and Ac were performed in a vertical glass tube reactor, 34 mm i.d. A mixture of ammonia and air was passed through the substrate bed placed on a sintered glass inside the reactor. The flow rates of gases were adjusted by rotameters. The reaction temperature was controlled by an external oven equipped with a temperature control system. The reaction conditions were as follows: mass of sample: 5.0 g, rate of ammonia flow: 3.0 l h⁻¹, rate of air flow: 3.0 l h⁻¹, temperature: 300 °C, time: 6 h. The samples Pr and Ac after ammoxidation were named as PrAm or AcAm, correspondingly.

Samples of the precursor cloth (Pr) and of the precursor treated by ammoxidation (PrAm) were submitted to pyrolysis in a thermogravimetric apparatus under the flow

![Scheme 1. Scheme of modification methods and codes.](image-url)
of a neutral gas (Ar) at the rate of 10 °C min⁻¹ up to 850 °C, with a soaking time of 30 min. The process of steam activation was carried out in one run, directly after the pyrolysis at 700°C. After achieving the final burn-off (close to 20%), steam was changed for argon, and the activated samples were cooled down to room temperature. The codes of the steam activated samples from the precursor cloth are Pr-H₂O and PrAm-H₂O from the precursor cloth modified by ammonia/air treatment.

2.2. Porosity and surface area

The N₂ adsorption isotherm at 77 K and the benzene and carbon dioxide adsorption isotherms at 298 K were determined gravimetrically [10–12]. Micropore half-width (ξ) of treated and untreated ACC was calculated from the experimental isotherms using the Dubinin–Radushkevich (DR) equation.

2.3. Temperature programmed desorption mass spectrometry (TPD-MS)

The sample (5 to 10 mg) was thermally treated in He: 1% Ne from 40 to 1400 °C at 30 °C min⁻¹. Evolved gases were continuously detected with a quadrupole mass spectrometer. N₂ was detected after selective oxidation of CO to CO₂ on MnO₂ at 120 °C. External calibration was done with mixtures of the gas to calibrate and pure helium containing 1% neon—used as an internal standard. After normalization to neon, integration of the signal was computed by using points on either side of a given desorption peak for which the mass spectrometer was at its base line value.

2.4. X-ray photoelectron spectrometry (XPS)

X-ray photoelectron spectra were measured using a Surface Science Instrument SSX 100 spectrometer with a monochromated Al Kα X-ray source (hν=1486.6 eV), a hemispherical electron analyzer and a multichannel detector. Carbon fibers were placed in an especially designed support ensuring that no signal was observed from the sample holder. Before each XPS analysis, the samples were dried under vacuum at 80 °C. Samples were then outgassed in the pretreatment chamber at 10⁻³ Torr prior to transfer to the analysis chamber. The vacuum applied during the measurements was typically less than 5 x 10⁻⁸ Torr and data were accumulated in separate regions. The C1s peak of the ‘graphitic’ carbon (binding energy, BE= 284.6 eV) was taken as reference in calculating BEs and accounting for charging effects. Data processing was achieved with a Winspec software using a nonlinear, least-square fitting algorithm and a Shirley baseline. High resolution envelopes were fitted using mixed Lorentzian–Gaussian curves. For all elements, atomic concentrations were estimated based on comparisons of integrated peak intensities normalized by the atomic sensitivity factors. BEs were reproducible to within 0.2 eV.

2.5. X-ray absorption spectrometry (XANES)

Nitrogen K-edge measurements were performed at the Laboratoire pour l’Utilisation du Rayonnement Electromagnétique (LURE, Orsay, France) on the NUV Super-Acro storage ring. They were carried out on the Sacemor beam line equipped with a high-energy TGM monochromator (resolution of about 0.2 eV at the N K edge). The spectra were recorded in total electron-yield detection, by dividing the signal by that normalized from the fluctuations in the X-ray intensity of a copper grid freshly coated with gold, simultaneously recorded. They were recorded at normal X-ray incidence (E parallel to the surface). The samples were ground to a very fine particle size, dispersed in acetone, and applied dropwise to high-purity tungsten plates, and the solvent was allowed to evaporate. All measurements were made at room temperature under ultra high vacuum 10⁻¹⁰ Torr. Calibration of the monochromator at the N 1s edge was made setting the N1s* transition of the cyano group in polycrylonitrile (PAN, Aldrich) at 401.4 eV.

2.6. Fixed bed experiments

Sulfur removal was carried out in a fixed bed contained in a micro-column (i.d. 4 mm) surrounded by a tube furnace. An air stream flowing through the fixed bed (inlet at the lower end of the vertical micro-column) contained H₂S (5000 ppmv) or SO₂ (3000 ppmv) with 75% water saturation at 25 °C. The mass of ACC and the total flow rate were about 20 mg and 35 ml min⁻¹ respectively (contact time in weight of sample per gas flow rate was about 0.4 mg min ml⁻¹ and average residence time in the bed: 0.1 s). The H₂S or SO₂ concentrations in the inlet (C₀) and outlet (C) gases were continuously detected with a flame photometric detector (FPD). After a protocol recommended by Bagreev et al. [13], before each adsorption experiment the samples were prehumidified for 2 h in flowing air with 75% humidity at room temperature. Each adsorption experiment was carried out at room temperature (25 °C) and continued until the H₂S or SO₂ concentration in the effluent gas (C) equaled that in the feed stream (C₀). The first adsorption experiment was performed with the sample as received (without any conditioning). After H₂S or SO₂ adsorption, regeneration of the bed was carried out by heating for 10 min in flowing N₂ at 500 °C. Four subsequent adsorption–regeneration experiments were carried out to determine how completely the capacity of the bed could be restored following the regeneration step. The amount of sulfur retained by the active carbon was computed by integration of the breakthrough curve until the breakthrough point corresponding to a de-SO₂ ratio (C/C₀) of about 0.005. Retention rate
(loading) was expressed in mg of SO$_2$ or H$_2$S per gram of dry sample. The relationship between intensity of photon emission from sulfur ($i(E)$) detected by FPD and the amount of sulfur ($M$) is given by $i(E) = k(E$)$^n$, where $n$ is close to 1 with experimental conditions used in this study (high S concentration, low hydrogen flow rate). After desorption under vacuum at 80 °C of gases physically adsorbed, the amount of thermal-desorbed SO$_2$ or H$_2$S was determined on the loaded sample for $C/C_0 - 1$ (steady state) by integration of the TPD-MS signal of the $m/z$ 64 and $m/z$ 34 fragments. The signal was normalized to $m/z$ 20 (1% neon in helium) and calibrated with external gas standards containing SO$_2$ or H$_2$S in helium with 1% neon.

### 3. Results and discussion

#### 3.1. Modification of porosity related to ammonia treatment

The porous system of the commercial activated cloth (Ac) is mainly composed of a well developed micropore volume, resulting in a BET surface area close to 800 m$^2$. This volume of mesopores is low (Table 1). It appeared possible to create, under laboratory conditions, a very similar development of porosity in the samples based on the precursor (Pr): Pr-H$_2$O.

In Table 1, it can also be noticed that in case of the two initial samples—Ac and Pr—their different treatments (ammoxidation, pyrolysis, gaseous activation with different agents including ammonia and steam together) brought about specific changes in the structure of their porous system. The influence of ammoxidation preceding gaseous activation of the precursor is visible by comparing the porosity of Pr-H$_2$O with the porosity developed in PrAm-H$_2$O. It can be perceived that ammoxidation causes in the sample PrAm-H$_2$O a pronounced increase in the mesopore and micropore volumes (the corresponding BET surface area decreases by ca. 26%).

Furthermore, it is only in this sample that submicropores have been created. It is known that during carbonization, an excess of oxygen groups forming radicals able to stabilize fragment radicals would lead to less bond breaking, to more radical recombination and to thermal condensation forming cross-links with micropores in between. Ammoxidation of the precursor cloth (Pr) removes a good part of oxygen functional groups which otherwise would have triggered more crosslinking reactions during the course of carbonization and, as a consequence, produces a less microporous char less reactive toward steam gasification. Contrary to carbonization-activation of a precursor modified by ammoxidation, post-activation treatment of the commercial activated cloth (Ac), either by ammonia-steam activation or ammoxidation followed by pyrolysis, increases the development of porosity as a result of further activation by ammonia and steam, or ammonia and air. The highest development of porosity (Gurvich volume over 0.5 cm$^3$ g$^{-1}$, close to 1200 m$^2$ g$^{-1}$) has been obtained in the case of the ammonia-steam activated commercial cloth (Ac-NH$_3$/H$_2$O). This sample is also characterized by the largest average micropore width ($2\lambda$) among the samples investigated, i.e. 1.24 nm. The rather low pore enlargement and burn-off (ca. 13%) obtained after ammonia-steam activation at 800°C during 40 min would be due to ammonia inhibition of steam activation. NH$_2$ and NH radicals formed by NH$_3$ decomposition would quench the active sites formed by reaction of steam with the carbon matrix [7]. A possible explanation for the limited burn-off obtained with ammonia, which may also explain the activation degree of PrAm, may be ‘deactivation’ of active sites by formation of the stable pyridine like nitrogen groups [9].

#### 3.2. Surface groups characterization after modification with ammonia

Fig. 1 shows survey and narrow N1s regions for the untreated (Ac) and ammonia treated carbon cloth. The survey scan of ammonia treated Ac indicates qualitatively that ammonia treatment was effective in introducing surface nitrogen groups readily detected by the N1s peak centred at ca. 400 eV. N1s XPS spectra were fitted according to Stanczyk et al.’s work [14] on N-model compounds with 4 components having mixed Gaussian–

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**Table 1**

<table>
<thead>
<tr>
<th>NH$_3$ treatment (cf. Scheme 1)</th>
<th>Volume</th>
<th>Surface area</th>
<th>Micropore width</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda = 0.4$ nm</td>
<td>$\lambda = 0.4-2$ nm</td>
<td>$\lambda = 2-50$ nm</td>
</tr>
<tr>
<td>Ac</td>
<td>0.000</td>
<td>0.317</td>
<td>0.036</td>
</tr>
<tr>
<td>Ac-NH$_3$/H$_2$O</td>
<td>0.000</td>
<td>0.472</td>
<td>0.046</td>
</tr>
<tr>
<td>AcAm-Py</td>
<td>0.000</td>
<td>0.351</td>
<td>0.038</td>
</tr>
<tr>
<td>Pr-H$_2$O</td>
<td>0.000</td>
<td>0.316</td>
<td>0.056</td>
</tr>
<tr>
<td>PrAm-H$_2$O</td>
<td>0.021</td>
<td>0.230</td>
<td>0.033</td>
</tr>
</tbody>
</table>
Fig. 1. Overall (I), N1s (II) XPS, and N1s XANES (III) spectra obtained for the untreated and ammonia treated activated carbon cloth (Note: XANES was not used to characterize the nitrogen forms in Ac).

Lorentzian peaks (75% Gaussian) with FWHM of 1.8 eV: pyridinic N at ca. 398.3 eV (N6), pyrrolic N at ca. 400.1 eV (N5), quaternary N at ca. 401.3 eV (NQ) and N-oxide at ca. 403.1 eV (NX). To take into account pyridone species, a fifth peak at ca. 399.5 eV (N6') was added and pyridinic N was set at ca. 398.1 eV. N5, N6, NQ and NX codes are from Pels et al. [15]. As confirmed by N K-XANES measurements, N1s XPS of Ac-NH3/H2O displays a dominant zone of 'pyridinic' N. Similar N1s XPS spectra were reported by several authors, including Stohr et al. [16], for a peat-based activated carbon treated by ammonia or HCN at high temperature, and Mangun et al. [5,6] for ACFs produced by steam/CO2 activation of woven phenolic fibers treated with dry ammonia above 700 °C. In the case of ACC samples produced by ammoxidation (AcAmPy and PrAm-H2O), the relative amount of pyridinic N is significantly lower, and N1s XPS displays additive peaks at higher binding energy. Similar results have been reported for a peat-based activated carbon modified by ammoxidation [17], and for activated carbons prepared from precursors modified by treatment with ammonia/air and with several other N-reagents [18–21]. XANES work in the literature showed the presence of pyridinic, pyridone and pyrrolic functionalities in an activated carbon prepared from polyacrylonitrile and after treatment of an oxidized activated carbon with ammonia at 800 °C [22]. These data support the conclusions from XPS and TPD experiments described in this paper.

TPD N2 profiles presented in Fig. 2 are similar to those obtained by Stanczyk and Boudou [23] for acridine or carbazole coals. Thermal treatments during Ac preparation or modification would have removed in Ac-NH3/H2O and PrAm-H2O the small temperature shoulder observed at ca. 500 °C.

Fig. 2. TPD profiles (from 313 to 1673 K at 30 K min−1) obtained for the untreated and ammonia treated activated carbon cloth.
1050 K with the model cokes and in the AcAm-Py. The increase of nitrogen emission and the corresponding reduction of hydrogen emission, occurring in two peaks centred at 1200 and 1500 K during the TPD of Ac-NH$_3$/H$_2$O, suggest that N atoms could have replaced CH aromatic groups during attack by N radicals generated from ammonia at high temperature.

Table 2 gives the integrated amounts of thermally desorbed CO$_2$ and CO, expressed as mmol per gram of dry sample. Excepted for PrAm-H$_2$O, H$_2$O was essentially physisorbed. In contrast to the untreated sample (Ac) and samples prepared by ammoxidation, TPD of the sample produced by ammonia-steam activation (Ac-NH$_3$/H$_2$O) released a minute amount of CO$_2$—ascribed to acidic groups: below 675 K (carboxylic groups) and above 675 K (anhydrides, lactones), and a small amount of CO below 1250 K (weakly acidic CO groups). In contrast, ammonia treatment increased the evolution rate of CO above 1250 K—ascribed to basic groups (pyrrole-type oxygen). Such an increase of CO evolution has already been reported after high temperature heat treatment of pre-oxidized carbon [24,25,26]. Singoredo et al. [26] found that impregnation of an activated carbon with glucosamine and heating at 1173 K results in an increase of extremely stable oxygen-containing groups, which can only be desorbed above 1400 K. Glucosamine gives a larger increase in stable O-groups than glucose.

The distribution of nitrogen and oxygen functional groups is clearly influenced by the type of ammonia treatment, but one does not accurately know by which mechanisms and what is the role of these particular groups for the surface catalytic oxidation of sulfur species [6]. In contrast to the activated carbon modified by ammonia/steam at 800°C, activated carbon modified by ammonia/air at 300°C presents more surface acidic oxygen groups, which are deleterious for H$_2$S [27] or SO$_2$ [28] adsorption. In addition, due to a more pronounced ‘amphoteric’ character [29], nitrogen enriched-activated carbon produced by ammoxidation should be less selective for the adsorption of sulfur species from gas mixtures. Pyridinic groups, more abundant in Ac-NH$_3$/H$_2$O, are much more basic than pyrrolic groups—more readily generated by N introduction into a non-aromatic substrate, such as cellulose material. After Cagniant et al. [21], ammoxidation of cellulose material leads to fixation of 60% of nitrogen as imine which gives pyridinic nuclei, while the synthesis of pyrrolic nucleus occurs also by reaction of ammonia with dicarbonyl moieties. After Thomas et al. [30,31], formation of pyrrole, pyridinic and pyridine N-oxide functions at the edge and in the interior of the poly-aromatic systems (graphene layers) would depend on the isotropic/anisotropic character of the carbon and on the fact that the ammonia treatment is performed during or after carbonization.

### Table 2

<table>
<thead>
<tr>
<th>NH$_3$ treatment (cf. Scheme 1)</th>
<th>XPS N/C (3100)</th>
<th>TPD (mmol g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CO$_2$ (.675 K)</td>
</tr>
<tr>
<td>Ac</td>
<td>1.59</td>
<td>0.29</td>
</tr>
<tr>
<td>Ac-NH$_3$/H$_2$O</td>
<td>5.69</td>
<td>0.01</td>
</tr>
<tr>
<td>AcAm-Py</td>
<td>5.86</td>
<td>0.25</td>
</tr>
<tr>
<td>Pr-H$_2$O</td>
<td>n.d.</td>
<td>0.11</td>
</tr>
<tr>
<td>PrAm-H$_2$O</td>
<td>7.03</td>
<td>0.17</td>
</tr>
</tbody>
</table>

*Atomic N/C ratio $\times$100 (N1s/C1s ratio $\times$instrumental sensitivity factor).

CO$_2$ as free carboxylic-type (.675 K).

CO$_2$ as lactone-type (.675 K).

CO as ketone or hydroxyl-type (.1250 K).

CO as pyrone-type (.1250 K).

n.d. ‘not determined.

3.3. Successive adsorption–regeneration cycles

In Fig. 3, experimental time is expressed as the cumulative amount of H$_2$S or SO$_2$ introduced into the column at constant inlet/outlet pressures, flow rates and inlet concentration ($C_C$: 5000 ppmv for H$_2$S and 3000 ppmv for SO$_2$). To compare H$_2$S and SO$_2$ adsorption, experimental conditions were taken (vertical reactor, low W/F ratio) to avoid any elution of H$_2$SO$_4$ out of the fixed bed, as in the Mochida’s experimental setup [32]. Breakthrough curves level off at $C/C_C$ | 1 — where $C$ is the outlet concentration. Small overshoots, probably due to hydrophilicity of the carbon surface, can be observed for the sample designated by the code PrAm-H$_2$O. These normalized breakthrough curves for H$_2$S and SO$_2$ on the as received samples and on the thermally regenerated samples in three subsequent adsorption–thermal regeneration cycles show significant differences. Breakthrough curves of the as received samples (the corresponding cycle number designation is 1 in Fig. 3) show an enhancement of the
ammonia and steam at 800°C (Ac-NH₃/H₂O) and by ACC ammoxidation treatment followed by pyrolysis (AcAm-Py). No activity enhancement can be observed for the sample produced by ammoxidation of the precursor cloth before activation (PrAm-H₂O)—the same negative result was obtained if the PrAm sample was activated with CO₂ using adjusted experimental conditions to get optimal pore structure and surface area. As shown in Fig. 3 and Table 3, after the first thermal-regeneration, the activity of the untreated sample and of the two samples prepared by ammoxidation (AcAm-Py and PrAm-H₂O) either increased or remained the same, while a quick activity decrease is observed for the sample obtained by ammonia-steam activation (Ac-NH₃/H₂O). In all cases, breakthrough curves can be fairly well reproduced after the second thermal generation, but in contrast to H₂S, SO₂ adsorption capacity of the Ac-NH₃/H₂O sample continues to decrease (even if more slowly) with the successive adsorption–desorption cycles (the corresponding cycle number designations are 2, 3 and 4 in Fig. 3). In a previous work [33], we showed that this strong activity decrease, due to a carbon surface and nitrogen site oxidation caused by SO₂ to SO₃ conversion occurring during thermal regeneration, can be avoided if regeneration is performed by washing in a solution of ammonia (28% in water) at room temperature.

4. Conclusions

In this study, we found that ammonia treatments can markedly change the desulfurization ability of a commercial activated carbon fiber (Actitex WKL20 ACC). There is a relationship between H₂S or SO₂ retention rates in wet air at room temperature with either porous properties or surface functional groups, but there is an obvious preponderant role of the surface chemistry. The sulphur removal activity can be related with the pore structure of the ACC modified by introduction of nitrogen functional groups as follows:

- As a result of an induced decrease of the char reactivity toward steam gasification, precursor cloth modified by ammoxidation produced an activated carbon cloth with low pore volume and surface area and low sulfur removal capacity.
- Ammoxidation of the commercial ACF, followed by a carbonization at 600 °C, slightly increases the porosity parameters presumably due to opposite effects between

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Cycle No.</th>
<th>Ammonia treatment (cf. Scheme 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ac-NH₃/H₂O</td>
</tr>
<tr>
<td>H₂S</td>
<td>1</td>
<td>30</td>
</tr>
<tr>
<td>H₂S</td>
<td>2</td>
<td>223</td>
</tr>
<tr>
<td>H₂S</td>
<td>3</td>
<td>223</td>
</tr>
<tr>
<td>H₂S</td>
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<td>202</td>
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<tr>
<td>SO₂</td>
<td>1</td>
<td>61</td>
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<td>SO₂</td>
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<td>69</td>
</tr>
<tr>
<td>SO₂</td>
<td>4</td>
<td>76</td>
</tr>
</tbody>
</table>
oxidative micropore ‘constriction’ and steam, ammonia, air activation and further carbonization. The treatment hardly improves the removal performance.

- Modification of AC by ammonia/steam at 800 °C further activates the carbon cloth by extending the ACC microporosity and most improves the sulfur retention activity of the commercial activated carbon cloth. The treatment selectively transformed the surface map of functional groups by introducing a high density of pyridinic-type nitrogen and by desorbing the largest part of acidic oxygen groups, leaving behind some residual basic oxygen groups which generate CO at high temperature.

In contrast to ammonia/steam treatment at 800 °C, ammoxidation did not bring any noteworthy improvement of the pore structure and introduced basic surface nitrogen groups together with new acidic oxygen surface groups. Based on the results obtained by cyclic adsorption–regeneration on a fixed bed, it has been stated that the ability of the AC-NH₃/H₂O sample to remove SO₂ or H₂S from wet air at room temperature is clearly enhanced by the following factors affecting its porosity parameters and chemical properties:

- An increase in micropore volume (expressed also by a high BET surface area) without too large widening of micropores—leading to a decrease of the adsorption energy.
- An increase in nitrogen content as surface pyridinic groups which behave as basic and polar surface sites on the internal surface of the final material.
- A removal of most surface acidic groups.

Acknowledgements

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