

## Adsorption/oxidation of sulfur-containing gases on nitrogen-doped activated carbon

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**Abstract.** Coconut shell-based activated carbon (CAC) was used for the removal of methyl mercaptan (MM). CAC was modified by urea impregnation and calcined at 450°C and 950°C. The desulfurization activity was determined in a fixed bed reactor under room temperature. The results showed that the methyl mercaptan adsorption/oxidation capacity of modified carbon calcined at 950°C is more than 3 times the capacity of original samples. On the other hand, the modified carbon calcined at 950°C also has a high capacity for the simultaneous adsorption/oxidation of methyl mercaptan and hydrogen sulfide. The introduction of basic nitrogen groups significantly increases the desulfurization since it can facilitate the electron transfer process between sulfur and oxygen. The structure and chemical properties are characterized using Boehm titration, N<sub>2</sub> adsorption-desorption method, thermal analysis and elemental analysis. The results showed that the major oxidation products were dimethyl disulfide and methanesulfonic acid which adsorbed in the activated carbon.

### 1 Introduction

Methyl mercaptan (CH<sub>3</sub>SH) and hydrogen sulfide (H<sub>2</sub>S), which exist in the chemical gas from crude oil, petroleum, coal, natural gas and many other industrial gases, are the major compositions of sulfur compounds [1-3]. Release of the sulfur-containing gases into the atmosphere will cause environmental problems since they can be oxidated into sulfate and sulfonic species. However, a small amount of methyl mercaptan and hydrogen sulfide can poison the catalyst in many industrial processes such as the synthesis of ammonia and Fischer-Tropsch. In few decades, there are many efforts for the deep removal of hydrogen sulfide and methyl mercaptan. The main processes for the removal of methyl mercaptan and hydrogen sulfide include adsorption, biological degradation, incineration and adsorption/oxidation, et al [4-5]. Among the above technologies, adsorption/oxidation is recognized as a promising method due to the high efficiency, low investment and mild operating conditions.

Activated carbons are widely used in the gas purification process due to the well-developed porous structure, large removal capacity and easy regeneration property. The removal capacity for methyl mercaptan and hydrogen sulfide also depends on the surface chemistry, such as nitrogen groups and metal oxides. The purpose of the paper is to study the introduction of nitrogen through the impregnation and calcination method and its effect on the adsorption/oxidation of methyl mercaptan in the existence of hydrogen sulfide. In order to study the reaction mechanism, the original and modified carbons

were determined by Boehm titration, N<sub>2</sub> adsorption-desorption method, thermal analysis and elemental analysis.

### 2 Experimental

#### 2.1 Materials

The original coconut shell-based activated carbon was obtained from Beijing Kecheng Guanghua New Technology Co, LTD. The size of the original activated carbon was 40-60 mesh. The activated carbon was washed with distilled water and dried at 115°C for 12h. This coconut shell-based activated carbon was designed as CAC.

Firstly, CAC was oxidated using 30 wt.% HNO<sub>3</sub> solution at 60°C and stirred for 2h. Then, the oxidative activated carbon was washed using distilled water until neutral pH and dried at 115°C for 12h. Secondly, 3g oxidated sample was mixed with a saturated urea solution and stirred for 24h at 25°C. Then the mixture was heated to accelerate the evaporation process and the carbon was dried at 115°C. Thirdly, the impregnation activated carbon was heated in nitrogen from room temperature to 450°C or 950°C at 10°C/min and kept at this temperature for half an hour. Then boiling water was used to wash the carbon. At last, the samples were heated at 115°C for 12h. The samples were designated as CAC-450(450°C) and CAC-950(950°C). A supernumerary letter E was added to represent the exhausted samples after the desulfurization test.

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## 2.2 Methods

### 2.2.1 Breakthrough capacity

Dynamic tests were performed to evaluate the removal capacity of CH<sub>3</sub>SH under atmospheric pressure. Before the test, moist air was used to moisten the adsorbents and the time was 1h. Then the moist gas mixture was used to test the desulfurization activity. The inlet concentration of CH<sub>3</sub>SH was 0.3% in volume. The reactor condition was as follows: reaction temperature 25°C, relative humidity 80% (25°C), overall gas hourly space velocity (GHSV) 5000h<sup>-1</sup>. The test was stopped when the outlet concentration of CH<sub>3</sub>SH was 50ppm. To study the simultaneous removal capacity of CH<sub>3</sub>SH and H<sub>2</sub>S, the mixture air containing 0.3% CH<sub>3</sub>SH and 0.03% H<sub>2</sub>S was also used. The concentrations of CH<sub>3</sub>SH and H<sub>2</sub>S were analysed using GC-6890 gas chromatography with a PFPD detector. The adsorption capacity was calculated by integration of the area above the breakthrough curves.

### 2.2.2 pH of carbon surface

0.4g carbon powder was mixed with 20 ml water and the mixture was kept at room temperature for 12h. Then the pH of the suspension liquid was denoted as pH of the carbon surface. For the exhausted samples, the pH was designated as pHE.

### 2.2.3 Sorption of nitrogen

Nitrogen isotherms were measured at 77K using a NOVA2000e (Quantachrome instruments) surface area analyzer. The samples were heated at 120°C and outgassed at the temperature for 12h. The specific surface area was determined using Brauner-Emmett-Teller measurements (BET) method. Nonlocal Density Functional Theory (NLDFT) was used to calculate the micropore volume (V<sub>mic</sub>) and pore size distribution. The total pore volume (V<sub>t</sub>) was obtained by the amount of N<sub>2</sub> adsorbed when p/p<sub>0</sub>=0.99.

### 2.2.4 Boehm titration

The method of Boehm was used to determine the acidic and basic surface groups. The numbers of acidic sites and basic sites were calculated according to the corresponding amounts of NaOH and HCl.

### 2.2.5 Thermal analysis

Thermal analysis was performed using a TGA/DSC1 (Mettler Toledo) instruments thermal analyzer. The settings were as follows: heating rate, 10°C /min, argon atmosphere with 50ml/min.

### 2.2.6 Elemental analysis

The content of carbon, hydrogen and nitrogen was determined using Vario EL elementary analyzer.

## 3 Results and discussion

Elemental analysis results are shown in Table 1. The nitrogen content was significantly increased after modifying with urea and calcining at certain temperature. Since the calcination temperature is important for the dissociation of nitrogen-containing species, the nitrogen content in CAC-450 is highest due to the incomplete decomposition of nitrogen-containing compounds. When the calcination temperature reaches at 950°C, many nitrogen-containing groups decompose thus resulting in a decrease in the nitrogen content. After the calcination at 950°C, the majority of nitrogen incorporated into the sample matrix. The nitrogen mainly existed in the form of pyridine-like or quaternary configuration.

The surface chemistry of the activated carbon was studied and the results were shown in Table 2. The pH of the sample surface increased after introduction of nitrogen. The Boehm titration results were also shown in Table 2. Since the nitrogen-containing species and oxygen-based species can have similar pK<sub>a</sub>, so the results include only acidic and basic groups. The amount of basic groups increased after modification with urea. The results were in agreement with the changes in the surface pH.

Table 1. Elemental analysis of the carbon samples

Sample	C	H	N
CAC	81.15	0.75	0.13
CAC-450	87.38	1.38	2.25
CAC-950	90.92	0.91	1.16

Table 2. pH and surface chemistry from Boehm titration (number of groups in mmol/g)

Sample	pH	Acidic	Basic	Basic/Total
CAC	7.51	0.35	0.43	0.55
CAC-450	8.47	0.39	0.57	0.59
CAC-950	9.43	0.31	0.65	0.68

The surface area and pore structure are important in the removal process. N<sub>2</sub> adsorption isotherms and micropore size distribution curves are shown in Figure 1 and Figure 2. The textural parameters were calculated based on the nitrogen isotherms and the results were shown in Table 3. The pore < 2nm is called micropore based on the IUPAC classification. For the different samples, the adsorption isotherms were all similar and the results show that they were micropore materials. For the sample treated at 450°C, the surface area and pore volume decreased compared with the original sample. Otherwise, for the sample treated at 950°C, the surface area and pore volume slightly increased. For the exhaustion samples, the decrease in the total pore volume might be due to the reaction products adsorbed on the carbon surface. For the

exhaustion sample CAC-950E, the relative large decrease in the pore volume, especially the micropore volume, suggested that the existence of more strongly adsorbed productions after the breakthrough test. This will be discussed in the later part of the paper.

Table3. Structural parameters of carbon samples from sorption of nitrogen

Sample	$S_{BET}(m^2/g)$	$V_{mic}(cm^3/g)$	$V_t(cm^3/g)$	$V_{mic}/V_t$
CAC	772	0.279	0.390	0.72
CAC-450	738	0.258	0.419	0.62
CAC-950	783	0.279	0.421	0.66
CAC-450E	717	0.256	0.415	0.62
CAC-950E	695	0.242	0.407	0.59

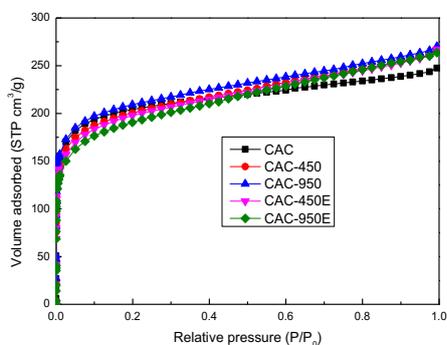


Figure1. Nitrogen adsorption isotherms of the initial and exhausted samples

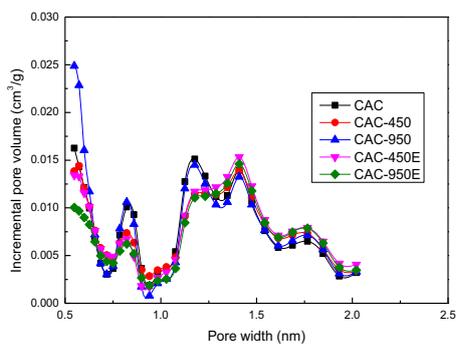


Figure2. Micropore size distributions of the initial and exhausted samples

The breakthrough results were shown in Figure3 and Table4. After modification with urea, the  $CH_3SH$  capacity increased. For the carbon treated at 950°C, the  $CH_3SH$  capacity exceeds more than 3 times of the CAC sample. The reason maybe that the nitrogen incorporated into the carbon matrix can catalysis the oxidation reaction through improving the electron transfer rates from sulfur to oxygen. The interesting behavior is that the sample treated at 950°C shows good simultaneous adsorption/oxidation of methyl mercaptan and hydrogen sulfide. Since the content of hydrogen sulfide is much

lower than methyl mercaptan, hydrogen sulfide can not be detected in the outlet gas. The results show that the modified sample can be used for the simultaneous adsorption/oxidation of methyl mercaptan and hydrogen sulfide. For all the samples, pH of the carbon surface decreased after the breakthrough test. For the modified samples, the large decrease in the pH indicated that some acid species were part of the oxidation products. The results can be explained in the later DTG results.

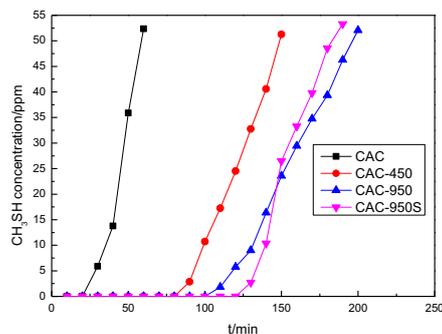


Figure3.  $CH_3SH$  breakthrough curves

Table4. pH of exhausted samples, their  $CH_3SH$  breakthrough capacity and the amount of water preadsorbed on the carbon surface

Sample	Water preadsorbed (mg/g)	$CH_3SH$ breakthrough capacity (mg/g)	pHE
CACE	81.2	71.8	6.25
CAC-450E	89.5	169.5	7.38
CAC-950E	78.6	232.6	4.85
CAC-950SE	78.6	230.2	4.71

Thermal analysis (TA) can be used to evaluate the adsorbed species on the carbon surface. The differential thermogravimetry (DTG) results are shown in Fig4. For all the samples, there are two main peaks. The first peak centered at about 80 °C which means desorption of water. According to the results reported by many researchers, the second peak which centered between 80°C and 300°C may represent desorption of dimethyl disulfide [6]. An interesting behavior was found for the sample treated at 950°C. There is another peak centered between 300°C to 350°C. According to the previous research, the peak centered between 300°C to 350°C may represent the strongly adsorbed species [7]. Based on the pH decrease and the literature, the peak centered between 300°C to 350°C may represent strongly adsorbed sulfonic acid species. The DTG results also were in accordance with the breakthrough tests.

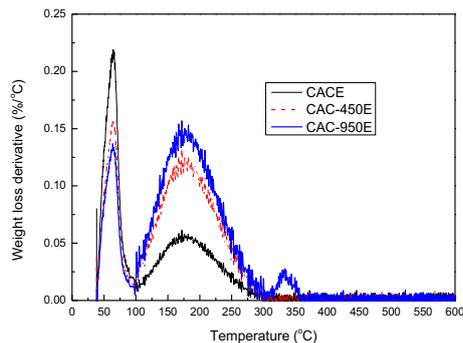


Figure4. DTG curves for the exhausted samples

## 4 Conclusions

The coconut shell-based activated carbon can be used as good materies for the adsorption/oxidation of sulfur-containing gases in many industrial processes. The sample modified by urea and calcined at 950°C indicates high adsorption/oxidation capacity for methyl mercaptan and the adsorption capacity is more than 3 times the capacity of original sample. On the other hand, the modified sample also shows high efficiency for the simultaneous adsorption/oxidation of methyl mercaptan and hydrogen sulfide. The basic nitrogen groups are highly dispersed on the carbon surface and act as catalytic sites for the oxidation of sulfur-containing gases. Dimethyl disulfide and sulfonic acid species are the major oxidation productions.

## References

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