

# REACTIVE ADSORPTION OF ARSINE ON SULFUR-CONTAINING CARBONS: ROLE OF SURFACE CHEMISTRY IN THE OXIDATION PROCESS AT AMBIENT CONDITIONS

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## Introduction

Arsine is widely involved in the field of semiconductor synthesis as a doping material [1]. Because of its high toxicity, any excess of this gas in the preparation process should be removed. Moreover, arsine appears as a trace contaminant of the syngas used in methanol synthesis and its presence is associated with catalyst poisoning [2]. Considering these two aspects, efficient technologies to separate arsine from air or syngas are needed.

Toward this purpose, several adsorbents such as alumina and activated carbon have been tested [3, 4]. Whereas some studies report the use of virgin adsorbents, the modification of these materials with metal oxides, such as copper oxide, is also presented as a promising method to remove arsine [3, 4]. The active sites for arsine binding are provided by both the oxide and the carbon support [4]. It was shown that water can bind to these active sites faster than arsine and thus decreases the removal efficiency [5]. Nevertheless, the nature and role of these active centers were not explored.

The objective of this study is to investigate the role of oxygen and sulfur-containing groups on the surface of microporous carbon in the removal of arsine.

## Experimental

Two series of polymer-based carbon were prepared based on poly(4-styrene sulfonic acid co-maleic acid) sodium salt and poly(sodium 4-styrene sulfonate) via a method described elsewhere [6]. The two carbons obtained are referred to as C-1 and C-2, respectively. The initial samples were oxidized either using ammonium persulfate (method A) or hot air at 350 °C (method B). The four carbons obtained are referred to as C-1A, C-1B, C-2A and C-2B where “A” and “B” state for the method of oxidation.

The materials were tested for arsine adsorption at room temperature. A small amount of adsorbent was packed into a fritted glass tube and exposed to a flow of arsine (4% in nitrogen). Experiments were conducted both in dry conditions (-ED) and moist conditions (-EM).

In order to derive the adsorption mechanism(s), the samples were analyzed before and after exposure to arsine by various techniques including energy dispersive X-ray spectroscopy (EDX), Fourier Transform infrared spectroscopy (FT-IR), thermal analysis (TG), and sorption of nitrogen.

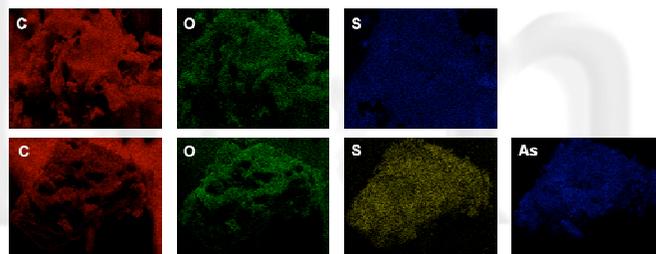
## Results and Discussion

The arsine adsorption capacities of all samples are listed in Table 1. The materials run in dry air exhibit the best performance, especially the samples oxidized in air. On the contrary, when water is present, no or only small amount of arsine is retained, which is in agreement with a previous study [5]. EDX analysis (Table 1) indicates the strong retention of arsine on our materials. The content of arsine measured follows the same trend as does the adsorption capacity.

**Table 1. Arsine removal capacities for the samples studied and arsine surface content from EDX analysis.**

Sample	Removal capacity [mg/g]	As [wt%]
C-1A-ED	66	12.5
C-1A-EM	0	-
C-1B-ED	539	22.3
C-1B-EM	0	-
C-2A-ED	331	16.5
C-2A-EM	16	-
C-2B-ED	444	19.0
C-2B-EM	0	-

Analysis of EDX maps (Fig. 1) indicates that both arsenic oxides and arsenic sulfides are formed as a result of arsine adsorption on the C-2A and C-2B samples.

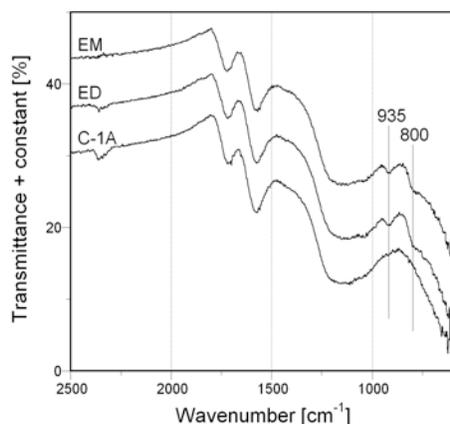


**Fig. 1** Example of EDX maps of C-2B sample before (top) and after (bottom) exposure to arsine in dry conditions.

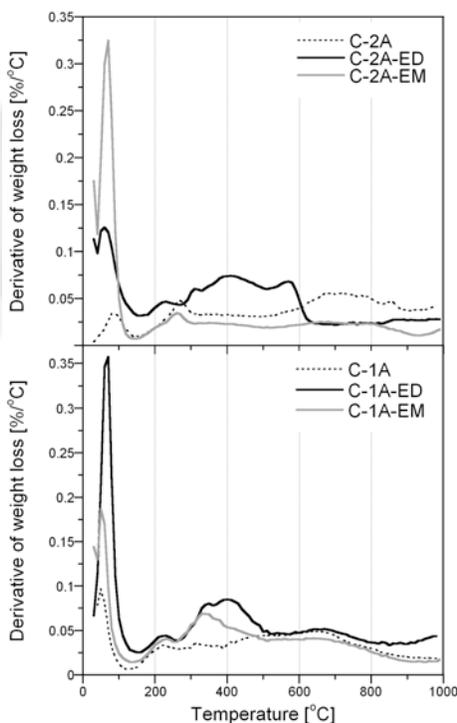
Additional information on the products of arsine reactive adsorption is provided by FT-IR (Fig. 2). New bands at 935 and 800  $\text{cm}^{-1}$  are observed after exposure to arsine and they are attributed to As(V) and As(III) species, respectively [7]. Although similar features are observed for all the exhausted samples, only the results for the C-1A series are presented here for the sake of clarity.

Thermal analysis can be also used to identify the products of arsine reactive adsorption (Fig. 3). For the C-1A-EM sample, two new broad peaks are observed compared to the initial sample. The first one at ~200 °C is assigned to arsenic acid  $\text{H}_3\text{AsO}_4$ , while the one at ~350 °C corresponds to  $\text{As}_2\text{O}_3$  [8]. The presence of the acid is also detected on C-1A-ED and the peaks at ~350 °C and ~400 °C are assigned to  $\text{As}_2\text{O}_3$  present in pores of different sizes. While no new species is detected on the surface of C-2A-EM, the DTG curve for C-2A-ED exhibits complex features which suggest the presence of other species than arsenic oxides. At ~200 °C,  $\text{H}_4\text{AsO}_7$  is

detected [8]. The peak at  $\sim 400$  °C is attributed to  $\text{As}_2\text{O}_5$  [8]. Sulfur-containing species are observed at  $\sim 300$  °C with the decomposition of  $\text{As}_2\text{S}_2$  at  $\sim 600$ °C with the release of  $\text{As}_2\text{S}_2$  and/or  $\text{As}_2\text{S}_5$ . However the latter peak can also be linked to the sublimation of  $\text{As}^0$  [8].



**Fig. 2** FT-IR spectra for C-1A sample before and after exposure to arsine in dry and moist conditions.



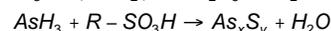
**Fig. 3** DTG curves in nitrogen for the C-1A and C-2A series of samples before and after exposure to arsine.

The presence of arsenic acids ( $\text{H}_3\text{AsO}_4$  and  $\text{H}_4\text{AsO}_7$ ) even in dry conditions is related to the high hydrophilicity of the materials (water adsorption isotherms not shown here). It likely enhances the adsorption in the so-called “dry conditions”. On the other hand, in the presence of humidity, water is adsorbed in a significant quantity and thus blocks the access of arsine to the binding sites of carbon (oxygen and

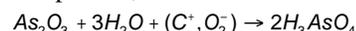
sulfur-containing groups). This can explain the negligible amount of arsine retained in moist conditions.

The oxidizing ability of our carbons can be related to the presence of oxygen superoxide ions formed in presence of oxygen species [6] and likely sulfur-containing groups.

Considering the above discussion, a summary of the reactions taking place on the surface of the materials studied is proposed. In dry conditions, arsenic oxides are formed by action of superoxide ions. Reduction of the sulfonic groups leads to the formation of arsenic sulfides.



When water is present, arsenic acids are formed:



## Conclusions

The above results indicate that oxygen and sulfur-containing groups on carbon lead to the reactive adsorption of arsine with the subsequent formation of arsenic oxides and arsenic sulfides. Oxygen superoxide ions can be involved in the former processes. The highly hydrophilic character of the adsorbents enhances the retention of  $\text{AsH}_3$  when tests are run in dry conditions. On the contrary, in the presence of humidity, water is adsorbed in a significant quantity. It blocks the pores (and thus the binding sites of arsine, oxygen and sulfur groups) and limits the arsine retention.

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