

Reactions of sulphur mustard on impregnated carbons

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Abstract

Activated carbon of surface area 1100 m²/gm is impregnated with 4% sodium hydroxide plus 3% Cr(VI) as CrO₃ with and without 5% ethylene diamine (EDA), 4% magnesium nitrate and 5% ruthenium chloride by using their aqueous solutions. These carbons are characterized for surface area analysis by BET conventional method and exposed to the vapours of sulphur mustard (HD) at room temperature (30 °C). After 24 h, the reaction products are extracted in dichloromethane and analyzed using gas chromatography and mass spectrometry (GC–MS). Hemisulphur mustard, thiodiglycol, 1,4-oxathiane are observed to be the products of reaction between sulphur mustard and NaOH/CrO₃/C system, whereas on NaOH/CrO₃/EDA/C system HD reacted to give 1,4-thiazane. On Mg(NO₃)₂/C system it gave hemisulphur mustard and thiodiglycol. On RuCl₃/C system it degraded to divinyl sulphone. Residual sulphur mustard is observed along with reaction products in all systems studied. Reaction mechanisms are also proposed for these interesting surface reactions. Above-mentioned carbons can be used in filtration systems for protection against hazardous gases such as sulphur mustard.

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Keywords: Activated carbon; Adsorption; Hazardous chemical; Impregnation and Sulphur mustard

1. Introduction

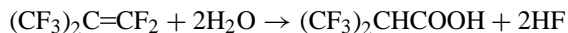
Adsorption being the process of choice for the removal of hazardous chemicals from contaminated environment [1], adsorbent such as activated carbon is most widely used in filtration systems for the purification of polluted air and water streams [2,3]. Air purification includes mainly physical adsorption, chemical detoxification/degradation and chemisorption. Involvement of these processes depends upon physical and chemical properties of toxic chemicals to be removed. For example, physical adsorption is the operating principle for high molecular weight, low volatile chemicals, in filtration systems. For the non-persistent chemical warfare gases (CW agents), a reactive carbon is needed, which can perform two activities; one is physical adsorption of the noxious chemicals and second one is the degradation of the ph-

ysisorbed vapours by chemical reactions [4]. In order to make the carbon reactive towards non-persistent CW agents, metal salts are impregnated and impregnated carbons are obtained. ASC whetlerite [5] is one such impregnated carbon which is used in NBC filtration systems for the reactive removal of hydrogen cyanide, cyanogen chloride and phosgene, etc, [6]. This impregnated carbon contains Cu(II), Cr(VI) and Ag(I) metal ions in the form of their salts on its surface. These metal ions play important role in chemical degradation of HCN, CNCl, COCl₂, etc. [7–21]. Of these toxic chemicals, the degradation of cyanogen chloride depends upon the amount of chromium present as Cr(VI) on impregnated carbon. Due to weathering, aging, exposure to high temperatures and storage for long time, chromium(VI) reduces to Cr(III), and obviously efficiency of the adsorbent diminishes [22–24]. Further reasons for this may be deactivation of the active catalyst ingredient and the drastic reduction in surface area due to the formation of large crystallites which further causes deactivation of catalyst due to the dissolution of active species in water present in the adsorbent surface. However, the effective surface area is available on the carbon for physical

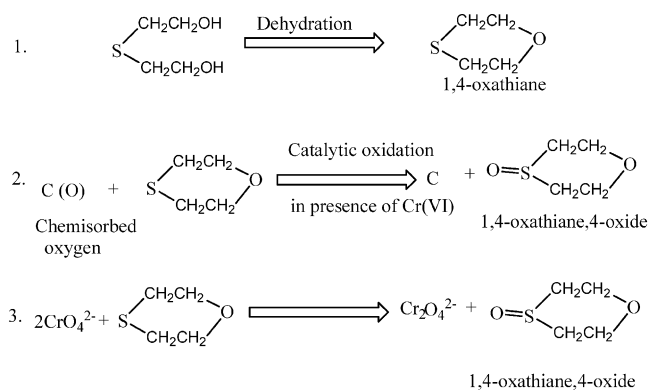
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adsorption. Nevertheless, the reactions of many gases on impregnated carbons are strongly influenced by the presence of water [25]. Hall et al. [26] studied the hydrolysis reaction of perfluoro isobutylene on charcoal. Perfluoroisobutylene [27] is hydrolysed as per the following reaction to hexafluoro isobutyric acid and hydrofluoric acid.



Recently, Gall Robin Damico reported [28] the detoxification reactions of thioether (mustard analogue) with polyoxometallate on carbon supports. Singh et al. [29] also studied the reaction of thiodiglycol (a hydrolysis product of sulphur mustard) on impregnated carbon. 1,4-Oxathiane and 1,4-oxathiane, 4-oxide were characterized as reaction products and proposed reactions are as follows:



Karwacki et al. [30] also studied thermal desorption of sulphur mustard from active carbon. It is evident that the chemical degradation, of toxic chemical on carbon is receiving renewed interest and attention of chemists and opens a new field for the development of adsorbent suitable for in situ degradation of persistent chemical warfare agents.

It is also interesting to note that an effective protection is achieved against the blood and choking agents by chemically destroying them on impregnated carbons. On the other hand protection against persistent CW agents such as blister agents and nerve agents is achieved based on physical adsorption. It is felt that these physisorbed CW agents may desorb and cross contaminate the environment if the used filtration systems (NBC canisters and filters) are left/thrown carelessly or are not disposed off properly. This situation needs a reactive carbon which can degrade persistent agents, in situ in filtration systems. It, therefore, requires the development of suitable impregnated carbon which can degrade such persistent chem-

ical warfare agents. Attempts are, therefore, made to prepare such carbons by impregnating active carbon of high surface area with NaOH plus CrO₃, NaOH plus CrO₃ plus ethylenediamine (EDA), Mg(NO₃)₂·6H₂O, RuCl₃·3H₂O. These impregnated carbons are used for studying detoxification reactions of sulphur mustard on their surface.

2. Experimental

2.1. Materials

Activated carbon of surface area 1100 m²/g of coconut shell origin, particle size 12 × 30 CSS was procured from Active Carbon India Ltd., Hyderabad. Sulphur mustard of purity more than 99% was obtained from process technology development division of our establishment. Dichloromethane, AR grade, NaOH, RuCl₃·3H₂O, CrO₃, Mg(NO₃)₂·6H₂O and ethylenediamine were obtained from E. Merck, India.

2.2. Impregnated carbon

Activated carbon was impregnated with aqueous solutions of NaOH (4%), Cr(VI) oxide (3% Cr(VI)), EDA (5%), Mg(NO₃)₂·6H₂O (4%) and RuCl₃·3H₂O (5%) (Table 1). Incipient wetness technique was used for impregnation. These impregnation experiments on active carbon were carried out at room temperature by slowly mixing above solutions and activated carbon. Obtained metal impregnated carbons were dried at 110 °C for 6 h and stored in air tight bottles.

2.3. Estimation of impregnants

Chromium was extracted in basic media from carbons and estimated iodometrically [31]. Magnesium was extracted as MgCl₂ using hydrochloric acid and estimated by EDTA titration [32]. NaOH was extracted by boiling carbon in distilled water and estimated by titrating with dilute hydrochloric acid, whereas, RuCl₃ was extracted by using hydrochloric acid and estimated by spectrophotometric method [32].

2.4. Surface area analysis

Impregnated carbon and unimpregnated carbons were characterized for surface area (N₂ BET) using Gemini 2765 surface area analyzer (Micrometrics, USA). Micropore

Table 1
Recipe of impregnants and systems prepared

S.no	Amount of impregnant loaded on carbon (wt.%)	Impregnated carbon	Surface area (m ² /g) (N ₂ BET)	Micropore volume (ml/g)
1	NaOH (4%) CrO ₃ (3% Cr(VI))	NaOH/CrO ₃ /C	912	0.53
2	NaOH (4%) CrO ₃ (3% Cr(VI)) EDA (5%)	NaOH/CrO ₃ /EDA/C	855	0.50
3	Mg (NO ₃) ₂ ·6H ₂ O (4%)	Mg(NO ₃) ₂ /C	866	0.50
4	RuCl ₃ ·3H ₂ O (5%)	RuCl ₃ /C	950	0.52

Table 2
Reaction products and GC–MS data

System	Reaction products	<i>m/z</i> values
NaOH/CrO ₃ /C	Hemisulphur mustard	140/142, 109/111, 73, 45
	Thiodiglycol	122, 104, 61, 43
	1,4-oxathiane	104, 74, 46, 15
NaOH/CrO ₃ /EDA/C	1,4-thiazane	117, 103, 88, 75, 57, 45
Mg(NO ₃) ₂ /C	Hemisulphur mustard	140/142, 109/111, 73, 45
	Thiodiglycol	122, 104, 61, 43
RuCl ₃ ·3H ₂ O	Divinyl sulphone	75, 47, 27

volume was determined using Dubinin equation. The results are described in Table 1.

2.5. Apparatus for adsorption of sulphur mustard

Impregnated carbons were exposed to the vapours of HD under static conditions. For these adsorption experiments, 0.5 g of carbons were taken in gooch crucibles and placed in an atmosphere of HD, which was created in a desiccator. The desiccator was kept at room temperature (30 °C) under the sorption conditions (partial pressure of HD was not measured in these experiments). Moisture free air was not used for this purpose. The samples were taken out after 24 h of exposure to HD at ambient temperature.

2.6. Characterization of reaction products

Reaction products were extracted from impregnated carbons using dichloromethane and analyzed by GC–MS of Hewlett Packard 5739 equipped with BP5 column of 30 feet length 0.33 mm i.d. using a temperature program. The GC–MS data are given in Table 2.

3. Results and discussion

The impregnated carbons are characterized for surface area and micropore volume (Table 1). The results show that the surface area and micropore volume decrease after impregnation. This observation can be attributed to the fact that the N₂ molecules could not enter the pores as some pores are blocked by the impregnant material.

3.1. Reaction products

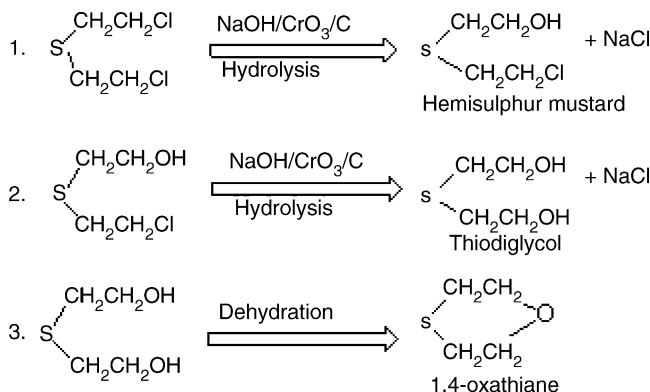
The reaction products and mass-to-charge (*m/z*) ratio values of the molecular ions produced when the reaction products were subjected to GC–MS analysis are illustrated in Table 2. All the prepared systems (Table 1) were found to be giving the reaction products.

3.2. Reaction mechanisms

3.2.1. (a) Reaction of HD with NaOH/CrO₃/C system

Sulphur mustard reacted with NaOH/CrO₃/C system to give hemisulphur mustard, thiodiglycol and 1,4-oxathiane.

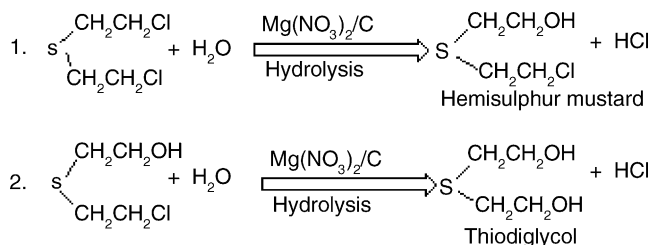
Probable reactions are given below.



Probably reaction proceeds as described above where HD hydrolyzed first and then the resulted product converted into its cyclic product, i.e., 1,4-oxathiane, due to dehydration on the surface of impregnated carbon.

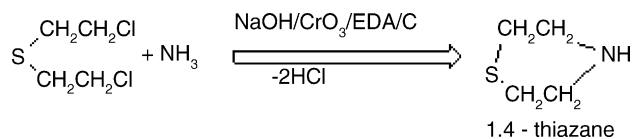
3.2.2. (b) Reaction of HD with Mg(NO₃)₂/C carbon system

Mg(NO₃)₂/C system reacts with HD to give two reaction products, i.e., hemisulphur mustard and thiodiglycol. Probably, HD molecules are expected to be chemisorbed on impregnated inside the porous structure. The chemisorbed HD reacted with water molecules that were present surrounding the impregnant in adsorbent and hydrolyzed to give hemisulphur mustard and thiodiglycol.



3.2.3. (c) Reaction of HD with NaOH/CrO₃/EDA/C systems

NaOH/CrO₃/EDA/C system reacts with HD to give 1,4-thiazane. Probably, reaction follows as given below.

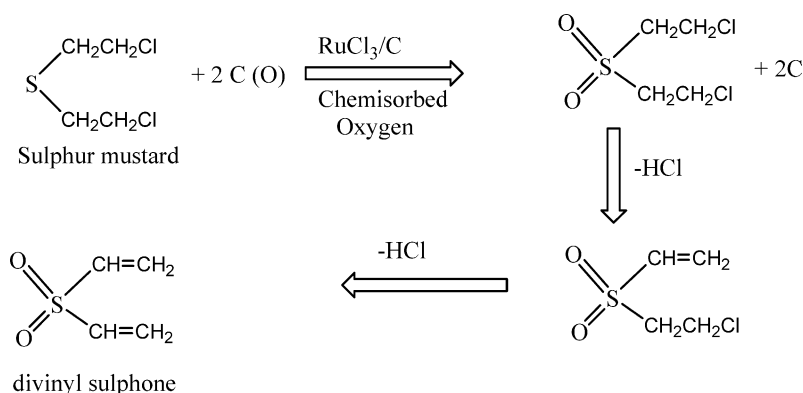


Continuous ammonia evolution was observed from the system studied indicating that the system decomposes on storage. This evolved ammonia probably reacted with HD to give 1,4-thiazane.

3.2.4. (d) Reaction of HD on RuCl₃·3H₂O/C systems

RuCl₃·3H₂O/C system reacted typically to oxidize the HD to give divinyl sulphone. Probably, HD molecules in the presence of chemisorbed oxygen oxidized to sulfoxide, which further converted into divinyl sulphone. Proposed reaction is

described as follows:



Moreover, no reaction product however was extracted from HD exposed active carbon.

4. Conclusion

Impregnated carbons such as NaOH/CrO₃/C, NaOH/CrO₃/EDA/C, Mg(NO₃)₂/C and RuCl₃/C reacted with HD to give various reaction products such as hemisulphur mustard, thiodiglycol, 1,4-oxathiane, 1,4-thiazane and divinyl sulphone. The system RuCl₃/C only seems to be the suitable adsorbent for in situ degradation of HD in filters as the reaction product is non-toxic. System NaOH/CrO₃/EDA/C could also be utilized but it decomposes and loses its efficiency for HD degradation. The other two systems gave the toxic hemisulphur mustard as reaction product thereby making them not suitable for HD degradation. More works needs to be done to evolve and develop for in situ degradation of persistent chemical warfare agents as in all the studied systems residual HD was observed.

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