

Short communication

Impregnated carbon for degradation of diethyl sulphide

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Abstract

Activated carbon of surface area $1100\text{ m}^2/\text{g}$ was impregnated with 5 wt.% ruthenium chloride by using its aqueous solution. Obtained carbon was exposed to the vapors of diethyl sulphide at room temperature ($30 \pm 1^\circ\text{C}$). Thereafter, the reaction products were extracted in dichloromethane and analyzed using gas chromatography and mass spectrometry. The data revealed that, the impregnated carbon reacted with diethyl sulphide producing the diethyl sulphone. In addition to the above reaction product, residual reactant was also observed. Reaction mechanisms have also been proposed for these interesting surface reactions.

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1. Introduction

Activated carbon is well known for its capacity to physisorb various toxic chemicals from air [1–3]. Impregnation of this carbon with various metal salts adds reactivity to the surface and helps in in situ degradation of the toxic chemicals [4]. One such reactive carbon developed long back is the Whetlerite carbon, i.e., activated carbon impregnated with Cu(II), Cr(VI) and Ag(I) [5]. This carbon is being used effectively for the reactive removal of the non-persistent chemical warfare (CW) agents like cyanogen chloride, hydrogen cyanide and phosgene [6–12]. However, in the case of persistent CW agents such as sulphur mustard (HD) and its analogues, a suitable reactive carbon is to be used in filtration systems for in situ degradation [13]. In this regard, we studied recently the reactions of HD on impregnated carbons such as NaOH/CrO₃/C, NaOH/CrO₃/EDA/C and RuCl₃/C and found that HD reacted to give hemisulphur mustard, thiodiglycol, 1,4-oxathiane, 1,4-thiazane and divinyl sulphone [14–15].

On the other hand, persistent CW agents such as HD, is highly toxic and difficult to handle [16]. Hence, it is preferable to use the analogues of HD which are less toxic than it to study

their reactivity on carbon beds. Diethyl sulphide (DES) is one of such chemicals which has similar structure as HD and also has bad smell and eye irritating nature. Hence, reaction of diethyl sulphide vapor on carbons is worth studying.

Hence, we have attempted to study the degradation reaction of DES on the RuCl₃/C system as this carbon seemed [15] to be the suitable one for developing a next generation filters capable of degrading the adsorbed toxic chemicals/CW agents in in situ manner.

2. Experimental

2.1. Materials

Activated carbon of surface area $1100\text{ m}^2/\text{g}$ of coconut shell origin, particle size $12 \times 30\text{ BSS}$ was procured from Active Carbon India Ltd., Hyderabad. Diethyl sulphide (of 98% purity) was obtained from Fluka Corporation, USA. Dichloromethane of AR grade and RuCl₃·3H₂O were obtained from E. Merck, India.

2.2. Impregnated carbon

Activated carbon was impregnated with an aqueous solution of RuCl₃·3H₂O (5 wt.%). The impregnation experiment

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on active carbon was carried out at room temperature by slowly mixing above solution and activated carbon. Obtained metal impregnated carbon was dried at 110 °C (in air) for 6 h and stored in air tight bottle. The metal impregnant content was determined after extracting the carbon in acidic media by using the recently reported titrimetric method [14].

2.3. Surface area analysis

Impregnated and unimpregnated carbons were characterized for surface area (N_2 BET) using Gemini 2765 surface area analyzer (Micrometrics, USA) and the results are described in Table 1.

2.4. Apparatus for adsorption of diethyl sulphide

Impregnated carbon and unimpregnated carbon were exposed to the vapors of DES under static conditions. For these adsorption experiments, 0.5 g of carbon was taken in gooch crucibles and placed in an atmosphere of DES which was created in a desiccator. The desiccator was kept at room temperature (30 °C) under the sorption condition and partial pressure of DES was not measured in these experiments. Presumably it was 97.5 mmHg and the remaining 662.5 mmHg inside was due to atmospheric air and the moisture free air was not used for this purpose. The samples were taken out after 24 h of exposure to DES at ambient temperature.

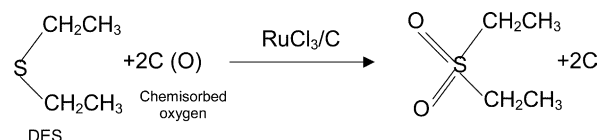
2.5. Characterization of reaction products

Reaction products were extracted from impregnated carbon using dichloromethane. For this purpose, the impregnated carbon (which was exposed to DES) was shaken with 5 ml of dichloromethane for 30 min. Subsequently, the mixture was centrifuged and the supernatant solution was retrieved and analyzed by GC–MS of Hewlett Packard 5739 equipped with BP 1 column of 30 ft length, 0.33 mm i.d. using a temperature programme. The GC–MS data are given in Table 2.

3. Results and discussion

The $RuCl_3/C$ system and the activated carbon were characterized for surface area and micropore volume and the results are shown in Table 1. The results show that the surface area and micropore volume decrease after impregnation which can be attributed to the fact that the N_2 molecules could not enter the pores as some of them are blocked by the impregnant material and the results are in agreement with the recently reported [14] ones by us. Afterwards, the impregnated carbon system ($RuCl_3/C$) and the activated carbon were subjected to react with diethyl sulphide. Reaction of diethyl sulphide (DES) on the surface of $RuCl_3/C$ system was studied by using GC–MS technique. The analysis of the extracted product obtained from DES exposed activated carbon (unimpregnated) shows only one peak eluted at 2.84 min and this can be attributed to unreacted diethyl sulphide. Whereas, the analysis of the extracted product obtained from DES exposed $RuCl_3/C$ shows two GC peaks at 2.84 and 6.28 min. The GC peak which is appeared at 2.84 min is attributed to the presence of unreacted DES, whereas the peak at 6.28 min is attributed to the presence of diethyl sulphone. In order to confirm the formation of diethyl sulphone further, we have subjected the above mixture to GC–MS analysis. The mass spectra (Fig. 1a and b) show peaks at 90 and 122 (m/z values in the mass spectra) confirming the formation diethyl sulphone and also the presence of unreacted DES (Table 2). Moreover, the mass spectral analysis has also confirmed that there is no such reaction product (diethyl sulphone) formation on the surface of activated carbon when exposed to diethyl sulphide.

Based on the above results, we tried to represent the scheme of reaction between DES and $RuCl_3/C$ as shown below:



From the GC–MS data and the reaction scheme it seems that, in the presence of chemisorbed oxygen, $RuCl_3/C$ oxi-

Table 1
Surface characteristics of $RuCl_3/C$ and activated carbon

S. no.	Amount of impregnant loaded on carbon (wt.%)	Carbon system	Surface area (N_2 BET) (m^2/g)	Micropore volume (ml/g)
1	$RuCl_3 \cdot 3H_2O$ (5%)	$RuCl_3/C$	950	0.52
2	–	Activated carbon (unimpregnated)	1100	0.62

Table 2
Reaction products and GC–MS data

System	Reaction products or unreacted reactants	GC retention time (min)	m/z values (MS data)
$RuCl_3/C$	Diethyl sulphide	2.49	477590
	Diethyl sulphone	6.28	296694122
Activated carbon (unimpregnated)	Diethyl sulphide	2.49	477590

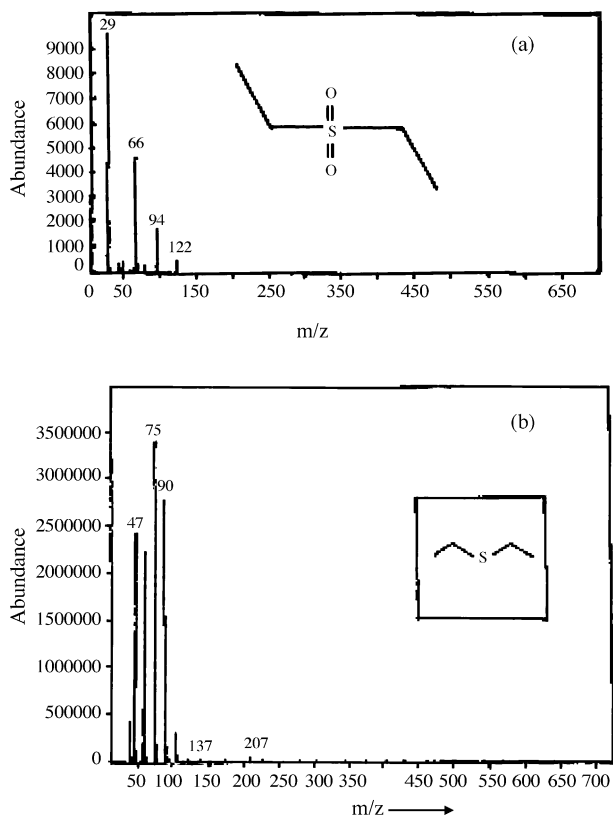


Fig. 1. (a) Mass spectrum of compound extracted from carbon exposed to diethyl sulphide (diethyl sulphone). (b) Mass spectrum of compound extracted from carbon exposed to diethyl sulphide (unreacted DES).

dizes diethyl sulphide to diethyl sulphone. Further, the chances that air present in the desiccator oxidizes the diethyl sulphide are ruled out as there is no formation of reaction product (diethyl sulphone) in the case of unimpregnated carbon when exposed to DES. These results suggest that Ru(III) plays the role of catalyst or oxygen carrier in the above reaction. Presumably, the oxygen is supplied to Ru(III) from chemical functional groups or chemisorbed oxygen present on the surface of carbon.

On the other hand, the carbon system containing oxidizing agent such as Cr(VI) oxidized DES to diethyl sulphone which is consistent with the presently observed result [16]. By these reports, it appears that the oxidation is one of the potential reactions which can be employed for the development of reactive carbons for the reactive removal of persistent CW agents for the use in futuristic NBC filtration systems. Suchlike filtration systems will not leave any scope for cross contamination when they are disposed off without proper care after their use.

4. Conclusion

Impregnated carbon RuCl_3/C reacts with DES to give diethyl sulphone which is non-toxic. In addition to the reaction product, residual reactant (DES) is also observed. The RuCl_3/C seems to be the suitable adsorbent for in situ degradation of non-persistent CW agents such as HD and its analogues such as DES as the reaction product is non-toxic. More work needs to be done to develop suitable carbon for in situ degradation of persistent CW agents.

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