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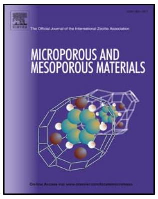

# Chemical trapping of gaseous $H_2S$ at high and low partial pressures by an iron complex immobilized inside the montmorillonite interlayer

Daniele Malferrari[a], Elena Castellini[a,*], Fabrizio Bernini[a], Aida Serrano Rubio[b,c], German Rafael Castro[b,c], Claro Ignacio Sainz-Díaz[d], Matteo Caleffi[a], Maria Franca Brigatti[a], Marco Borsari[a]

[a] Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, Via Campi 103, I-41125 Modena, Italy
[b] SpLine, Spanish CRG BM25 Beamline at the ESRF, 6 Jules Horowitz, F-38043 Grenoble, France
[c] Instituto de Ciencia de Materiales de Madrid (ICMM), CSIC, Sor Juana Inés de la Cruz 3, E-28049 Madrid, Spain
[d] Instituto Andaluz de Ciencias de la Tierra (IACT) CSIC, Universidad de Granada, Av. de Las Palmeras 4, 18100 Granada, Spain

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## ABSTRACT

A stable hybrid material (Mt-Fe(III)Phen) formed by intercalation of the μ-oxo Fe(III)-phenanthroline complex $[(OH_2)_3(Phen)FeOFe(Phen)(OH_2)_3]^{4+}$ (Fe(III)Phen) in montmorillonite (Mt) is able to immobilize $H_2S$ in gaseous phase with high efficiency even at extremely low pressures. DR UV–vis and I.R. spectroscopies, elemental analysis, X-ray powder diffraction, thermal analysis coupled with evolved gas mass spectrometry, and X-ray absorption spectroscopy show that the material has high adsorption capacity, performs fast $H_2S$ trapping and is long-lasting. Moreover, even extremely low levels of $H_2S$ can be removed easily and quickly from gaseous phase using a suitable amount of the trapping material. The immobilization mechanism likely involves a redox reaction between iron (III) and one $S^{2-}$ ion, followed by the binding of a second $S^{2-}$ ion to the metal centre. The process takes place at room temperature, is reversible for several cycles, and does not require pre-treatment of neither gaseous $H_2S$ nor the adsorbent material. Therefore, this modified montmorillonite is a promising material to get rid of $H_2S$ in processes of environmental interest and to obtain gaseous (and gasifiable) high quality hydrocarbons in fuels refineries.

## 1. Introduction

Sulphur-containing compounds, such as $H_2S$ and thiols, are commonly found in most hydrogen rich gaseous fuels including natural gas, associated petroleum gas, bio-gas, landfill gas, synthesis gas, and coke-oven gas. Removal of $H_2S$ is an obliged process in industry because $H_2S$ is toxic, even low amounts of it are highly corrosive for the refinery equipment and transport lines, and lead to poisoning of many catalysts. Furthermore, $H_2S$ (oxidized to $SO_2$) originates acid rains and is disliked in all private and public environments because of its bad smell [1]. $H_2S$ therefore represents a serious problem for people living or working close to industrial plants [2]. Several technologies are available for $H_2S$ removal from industrial waste gas streams which can be grouped into several main classes. A first group of technologies involves the multi-step Claus process [3,4], a highly energy intensive industrial procedure which converts $H_2S$ into elemental sulphur through two process steps, *i.e.*, a thermal step (at temperatures above 850 °C) and a catalytic step (using activated aluminium(III) or titanium(IV)oxides). A second group includes chemical treatments in aqueous solutions. These processes can be divided into two categories: those based on oxidation of $S^{2-}$ to $S^0$, by using iron-chelated solutions, and those involving the trapping of $S^{2-}$ through precipitation of its metallic salts [5]. A third group implicates adsorption on solid adsorbents at various pressures and temperatures. Subcategories of these processes are defined by adsorbent type e.g., oxides such as FeO, ZnO, CuO, MnO, $TiO_2$, $Al_2O_3$, Au (110), Ag (111), GaAs (001), $ZrO_2$ (110) and ceria (110) crystal surfaces; graphene-nanotube hybrid structures, activated carbons and doped activated carbons [6–11]. A forth group, mostly suitable for $H_2S$ removal from biogas, exploits biofiltration [12]. Biofiltration is performed in a multiphase system in which the contaminated gas is dissolved and adsorbed on a biofilm and then degraded by microorganisms that are immobilized on a packing material forming a thin layer (biofilm). The packing material in the biofilter may be either natural or synthetic and must fulfil the requirements of high surface area, high permeability, and high adsorption capacity [13–15]. A fifth group of technologies consists of adsorption on silica gels, adsorbent rocks (e.g., moisturized

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[*] Corresponding author. Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, Via Campi, 103, 41125 Modena, Italy.
*E-mail address:* elena.castellini@unimore.it (E. Castellini).

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**Abbreviations**

| | |
|---|---|
| Mt | Montmorillonite STx-1a |
| Phen | 1,10-phenanthroline ($C_{12}H_8N_2$) |
| Fe(III)Phen | $[(OH_2)_3(Phen)FeOFe(Phen)(OH_2)_3]^{+4}$ |
| Mt-Fe(III)Phen | solid hybrid material made by montmor illonite STx-1a intercalated with Fe(III)Phen complex in saturation conditions |
| Mt-FePhen-$H_2S$ | Mt-Fe(III)Phen exposed to $H_2S$ gas |

pumices, dolomite and limestones) and minerals (e.g., zeolites, clays and maghemite) [16–19].

Recently, Ozekmekci et al. [20] summarized experimental and theoretical reports for removal of $H_2S$ by using zeolites. They concluded that the best results in terms of selectivity were obtained with zeolites with faujasite-like structures, whereas synthetic zeolite-A and ZSM-5 type structures did not performed well. However, Bülow [21] replied that studies of sorption of binary $H_2S$–$CO_2$ gas mixtures on zeolites (zeolite-A and faujasite) demonstrated a dual function of these materials. These zeolites may act as both selective sorbents and catalysts for converting $H_2S$ and $CO_2$ into COS and $H_2O$, according to the reaction $H_2S + CO_2 \leftrightarrows COS + H_2O$. Eventually, zeolite-A, due to its large specific surface area, reduces the carbonyl sulfide content [22].

In this work we propose an innovative and efficient method for $H_2S$ capture in gaseous phase working even at extremely low pressures using the layer silicate montmorillonite (Mt) intercalated with a μ-oxo Fe(III) phenanthroline complex $[(OH_2)_3(Phen)FeOFe(Phen)(OH_2)_3]^{4+}$, Fe(III)Phen hereafter [23]. Moreover, we review the recent literature on the $H_2S$ capture mechanism and removal performance of swelling clays. Montmorillonite is a 2:1 layer aluminosilicate, in which one sheet of octahedrally coordinated cations (M) is sandwiched between two sheets of tetrahedrally coordinated cations (T) to form a TMT layer. Isomorphic substitutions, mostly in the M sites (e.g., $Mg^{2+}$ and $Fe^{2+}$ for $Al^{3+}$), induce a permanent negative layer charge, which is compensated by the presence of hydrated cations in the interlayer. Hydroxyl groups complete the coordination of each octahedron. Most of the technological uses of smectite are related to reactions taking place in the interlayer space where the hydrated cations can be easily exchanged [24].

The proposed trapping material (Mt-Fe(III)Phen), which proved to be effective in adsorbing thiols [25], is able to immobilize gaseous $H_2S$ through a redox process involving the oxidation of $S^{2-}$ to $S^0$ and a subsequent formation of covalent bond between another $S^{2-}$ and the iron centre, providing an efficient and strong retention. In this work, the trapping capacity of this material was determined along with the chemical speciation of the absorbent and adsorbate after interaction. We also demonstrated that the process is reversible: the adsorbent can be easily regenerated and reused several times before exhaustion. In addition, since many civil and industrial contexts produce very low, but prolonged, emissions of gaseous $H_2S$ resulting in latent dangerous accumulation in the environment, specific attention was paid to the exploitation of Mt-Fe(III)Phen as a long-lasting trap immobilizing $H_2S$ also at extremely low levels. This fact, together with a high capacity and rate of $H_2S$ trapping, makes the proposed modified montmorillonite a promising material for applications in industrial and environmental field and for the treatment of the fossil fuels. In addition, although innovative materials demonstrated to selectively adsorb thiols from an $H_2S$ containing gas stream [26,27], for some applicative contexts, like the treatment of fossil fuels or the treatment of gaseous emissions from waste landfills and composting plants, the possibility to simultaneously (and economically) remove all these sulphur compounds even at very low levels results a priority need.

## 2. Experimental

### 2.1. Materials

Montmorillonite used in this work is STx-1a (Mt), a source clay from the County of Gonzales, State of Texas, USA, provided by the Clay Minerals Society (The Clay Minerals Society, Source Clays Repository, University of Missouri, Columbia, MO). Mt characterization is reported on the Clay Minerals Society web-page (http://www.clays.org/Sourceclays.html).

$Fe_2(SO_4)_3 \cdot 8H_2O$, acetic acid and NaOH pellets (> 99% purity) are Carlo Erba products. 1,10-Phenanthroline ($C_{12}H_8N_2$, Phen), ferroin Fe(II)$Phen_3SO_4$ (> 99% purity) are purchased by Sigma-Aldrich. $H_2S$ is supplied by Alpha gas, Air Liquide.

Details of material preparation, already reported in previous works [23,25], are extensively described in SM1. Final adsorbent material, Mt-Fe(III)Phen, is Mt saturated in Fe(III)Phen complex, *i.e.* it contains equivalents of complex which are the double with respect to the CEC of Mt. As already found for other iron-pillared montmorillonite, the exceeding positive charge is neutralized by anions, sulphate in our case [23,28]. The separated solid was washed several times with distilled water to remove residual Fe(III)Phen and dried at 30 °C. This was exactly the material used for investigating the $H_2S$ immobilization.

Reference compounds for X-ray Absorption Spectroscopy (XAS) measurements were: $Fe_2(SO_4)_3 \cdot 8H_2O$, ferroin (see above), $FeSO_4 \cdot 7H_2O$ (Carlo Erba, RPE), and the minerals hematite ($Fe_2O_3$), pyrite ($FeS_2$), and magnetite ($FeOFe_2O_3$) are used as reference.

### 2.2. Immobilization of $H_2S$ on Mt-Fe(III)Phen

The immobilization of $H_2S$ on Mt-Fe(III)Phen yields the samples hereafter indicated as Mt-FePhen-$H_2S$. The reaction was performed in a glass box covered by a layer of aluminium foil. 100 mg of Mt-Fe(III)Phen is dispersed on the bottom of a 5 cm-diameter glass Petri dish. The glass box hosts an inner and outer gas hose. The gas supplied to the glass box is a mixture of $H_2S$/Ar whose composition was accurately tuned by means of calibrated mass flow controllers (Alltech Digital Flow Check-HR) and gas mixing valves. The flow was set as to yield a constant partial pressure of $H_2S$ of 250 Pa. Adsorption tests were performed at different times (i.e., from 1 to 166 h). The corresponding S content of the Mt-Fe(III)Phen samples was determined by elemental analysis (Carlo Erba Model 1106 Elemental Analyser).

In the recovery experiments, the Mt-FePhen-$H_2S$ samples were heated at 210 or 295 °C for about 30 min before undergoing each cycle of adsorption/desorption. This time ensures the complete desorption of the adsorbed $H_2S$. Elemental analyses were performed before and after each thermal cycle.

#### 2.2.1. Immobilization performance at extremely low $H_2S$ pressures

Additional experiments were specifically addressed to investigate the lowest limit value of $H_2S$ vapour pressure for which Mt-Fe(III)Phen is still efficient as a gas trap. The selected values of vapour pressure were 10, 5, 1, 0.3 and 0.15 Pa. These values are not reliable using the calibrated mass flow controller. For this reason, $H_2S$ was produced *in situ* by evaporation of proper volumes of water saturated with $H_2S$ inside a closed glass box (Volume = 1 $dm^3$; $H_2S$ solubility in water: 4 g $dm^{-3}$ [29]; volumes: 34.38, 17.19, 3.44, 1.03, 0.52 μL for vapour pressure 10, 5, 1, 0.3, 0.15 Pa, respectively; Gilson mod. Pipetman P200 and Gilson mod. Pipetman P20 pipettes were used). The immobilization of $H_2S$ at extremely low levels on Mt-Fe(III)Phen was performed at room temperature (T = 298 K) in a glass box of 1 $dm^3$ of volume covered by a layer of aluminium foil; different amounts of Mt-Fe(III)Phen (10, 20 and 50 mg) in a glass Petri dish (Φ = 10 cm) and a proper volume of $H_2S$ saturated water in a small beaker were placed inside the glass box. Exposure time ranged between 0.1 and 100 h.