

Spectroscopic study on sorption of hydrogen sulfide by means of red soil

T.H. Ko, H. Chu*

Department of Environmental Engineering, National Cheng Kung University, Tainan City 70101, Taiwan

Received 15 July 2004; accepted 1 September 2004

Abstract

This paper reports the results of the characterization of red soils in relation to the sorption of H_2S from coal gas at 500°C by spectroscopic techniques in order to provide more information on red soils' structural change both before and after reaction. In addition, by-products analysis has also been studied using Fourier transform infrared (FTIR) spectroscopy. Before and after the experiments the red soils were characterized with X-ray powder diffraction (XRPD), energy dispersion spectrum (EDS), X-ray photoelectron spectroscopy (XPS) and FTIR spectroscopy. XRPD results indicate that iron oxide species disappear from the original to reacted red soil. EDS analysis shows that a significant amount of sulfur is present in the reacted red soil, which is in agreement with the results of the elemental analysis and the calculated value based on breakthrough curve. XPS regression fitting results further indicate that sulfur retention may be associated with the iron oxides. S 2p XPS fittings point out that the major sulfur species present in the reacted red soil are composed of S^{-2} , elemental sulfur, polysulfide, sulfite and sulfate. Additionally, the binding energy of iron shifts to a lower position for the reacted red soil, which indicates that iron oxides in the original red soil have been converted into iron sulfide. Appreciable amounts of the by-products CO_2 , SO_2 and COS are detected by on-line FTIR spectroscopy during the initial and later stages of the sorption process. The formation of CO_2 is related to the water-shift reaction, and SO_2 is probably attributable to the reaction of organic matters and H_2S . The concentration of COS is quantified by GC/FPD and found it to be about 350 ppm, which is close to the equilibrium concentration of the reaction of inlet CO and H_2S at a temperature of 500°C .

© 2004 Elsevier B.V. All rights reserved.

Keywords: Red soil; H_2S ; Spectroscopy techniques; Sulfur; By-products

1. Introduction

It has been known for many years that certain soils have the ability to absorb reductive sulfur-containing species such as hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbon disulfide (CS_2), dimethyl sulfide (CH_3SCH_3) and dimethyl disulfide (CH_3SSCH_3) at room temperature [1–4]. Therefore, soils could act as an important sorption media for the removal of waste gases before they are released into the atmosphere. Among all reductive sulfur-containing species, H_2S has received the most attention because it is a toxic and malodorous gas. Generally, H_2S can be found in petrochemical plants, semiconductor plants, wastewater treatment plants and coal

gasification plants [5,6]. H_2S present in gasified coal gas involves other inorganic reduction gases, carbon monoxide and hydrogen, making coal gasification plants different from others. The exit temperature of the gasified coal gas is usually at temperatures of approximately 500°C . So far, few papers have been reported on the sorption of H_2S using red soils at high temperature.

In previous researches, experiments mainly focused on the performance of H_2S sorption, however, less information and analysis were investigated on the by-products formation and the structure of red soils after the sorption of H_2S . Therefore, X-ray powder diffraction (XRPD), X-ray photoelectron spectroscopy (XPS), Energy dispersive X-ray spectroscopy (EDS) are used in this study to characterize red soils before and after H_2S sorption at 500°C . Meanwhile, the by-products are simultaneously monitored with Fourier transform infrared spectroscopy (FTIR).

* Corresponding author. Tel.: +886 6 2080108; fax: +886 6 2752790.
E-mail address: chuhsin@mail.ncku.edu.tw (H. Chu).

Table 1
Selected physical and chemical properties of original Loupi red soil

	Depth (cm)	Sand (%) 2000–50 μm	Silt (%) 50–2 μm	Clay (%) < 2 μm	Texture ^b	CEC ^c (cmol/kg)	OM ^d (g/kg)	pH (H ₂ O) ^e	CBD- Fe oxides ^f (g/kg)
Original red soil	0–10	14.3	34.2	51.5	Clay	8.4	32.3	4.0	53.1

^a By pipette method [13].

^b According to U.S. soil survey staff.

^c Ammonium acetate method [14].

^d Organic matters, by Walkley–Black wet oxidation method [15].

^e By glass electrode [16].

^f CBD is citrate–bicarbonate dithionite extraction [17].

2. Experimental

2.1. Materials

The Loupi red soils investigated in this study were collected from a field at the National Pingtung University of Science and Technology, located in the southern Taiwan. Unwanted materials such as leaves, tree roots and pebbles were removed from samples and then dried at ambient temperature for a week. Prior to use, red soils were ground with an agate mortar and sieved to the acquired particle size to pass through 2-mm sieve. The chemical and physical properties of the red soil and its chemical compositions are given in Tables 1 and 2, respectively.

2.2. Procedure

The sorption experiment was carried out in a bench scale fixed-reactor at 500 °C. The reactor consisted of a quartz tube, 1.6 cm i.d., 2.0 cm o.d., and 150 cm long, located inside an electric furnace. The quartz fibers were set in the reactor to support the red soil. A sufficient quantity of red soil was loaded into the center of the reactor. Two K-type thermocouples were inserted into the reactor to the positions at the top and bottom of the red soils to enable the inlet and outlet temperatures to be measured and controlled. The gaseous mixture was composed of 1% H₂S, 25% CO, 15% H₂ and a balance of N₂ from regulation cylinders. All mass flow meters were calibrated using an IR soap bubble meter and the concentrations of all species were calculated at STP condition. The weight hourly space velocity (WHSV) was set at 2000 ml h⁻¹ g⁻¹. The inlet and

outlet gases (H₂S) were analyzed by a gas chromatograph (Shimadzu, GC-14B) equipped with a flame photometry detector (FPD). A six-port sampling valve with a 500 μl sampling loop was used to sample the gases for analysis.

2.3. Characterization of the red soils

2.3.1. X-ray powder diffraction spectroscopy (XRPD)

The crystalline structure of the red soils was determined by X-ray powder diffraction spectroscopy (Rigaku D/max IIIV XRPD) by using a Cu K α radiation (40 kV and 30 mA) with a nickel filter. Samples were scanned from 4° to 80° (2 θ). The peaks were recorded and identified by a computer library system.

2.3.2. X-ray photoelectron spectroscopy (XPS)

The XPS chemical analyzing instrument is a VG Micro Lab. MKIII XPS analyzing instrument with a Mg K α X-ray radiation source (1253.6 eV). The sample was initially tapped on a sample supporting plate. The plate was then placed in a pre-treatment chamber attached to the instrument. The chamber pressure was then decreased from 100 to 1.33 $\times 10^{-10}$ kPa via a turbo pump. The time needed to reach the final pressure was approximately 4 h. A gate valve between the pre-treatment chamber and a vacuum chamber was then opened after the pre-treatment. The sample was moved to the vacuum chamber for analysis. The pressure in the vacuum chamber was maintained at 1.33 $\times 10^{-10}$ kPa via an ion pump. The following analyzing conditions were a resolution of 0.1 eV and the number of scans = 100. The binding energy spectra were obtained under the above-mentioned conditions within a pre-determined scanning range.

2.3.3. Energy dispersive X-ray spectroscopy (EDS) and X-ray fluorescence (XRF)

Surface distribution of elements in red soils was obtained by using an EDS technique which employs a Phillip XL-40FEG scanning electron microscope. Red soil was mounted on the copper holder and was platinum-coated prior to EDS analysis.

The chemical compositions of red soils were obtained by X-ray fluorescence (XRF) on a semi-automated Philips PW 1410 X-ray spectrometer.

Table 2
Chemical compositions (wt%) of original Loupi red soil analyzed by X-ray fluorescence

	Original red soil
SiO ₂	65.48
Al ₂ O ₃	23.50
Fe ₂ O ₃	6.61
K ₂ O	2.60
TiO ₂	0.94
CaO	0.51
MnO ₂	0.21
SO ₃	0.15

Download English Version:

<https://daneshyari.com/en/article/1238920>

Download Persian Version:

<https://daneshyari.com/article/1238920>

[Daneshyari.com](https://daneshyari.com)