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Characterization of southern Taiwan red soils as a regenerable sorbent for sorption of hydrogen sulfide from coal gas with spectroscopic techniques

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Abstract

The purpose of this research is to use red soils as a high-temperature regenerable sorbent for sorption of hydrogen sulfide from coal gas and collocates with a series of spectroscopic apparatuses in order to investigate the structure changes after multiple sorption/regeneration processes. Results indicate that red soils could be reused after 10 multiple sorption/regeneration cycles and maintain approximately 80% sorption efficiency. With EDS and EA analyses, residual sulfur species are detected in the 10th regenerated red soils and exist with values of 0.6 and 0.33%, respectively. Undesired sulfur species including sulfide, sulfate and elemental sulfur are further identified by XPS spectroscopy. With the best regression fitting results, sulfate species is the dominative sulfur species, which occupies approximately 71% of residual sulfur. It is believed that these residual sulfur species are the major cause to result in red soils' deterioration after regeneration and reduce the sorption efficiency. Appreciable amounts of regeneration gases CO, CO_2 and SO_2 are detected by on-line FTIR spectroscopy. Their formation mechanisms are attributed to the different gas–solid reaction, one is the reaction of carbon and oxygen, and the other is FeS and oxygen. From the analysis of solid-state nuclear magnetic resonance spectroscopy (SSNMR), a significant change for ^{27}Al and ^{29}Si and it is established that a portion of aluminum is reformed into pentacoordinated structure. Formation of aluminosilicate is maybe another reason to result in deterioration as a result of the loss of surface area.

Keywords: Red soils; Hydrogen sulfide; Residual sulfur; Deterioration; Pentacoordinated

1. Introduction

Hydrogen sulfide (H_2S) is one of the most common compounds and can be easily found in the integrated gasification combined cycle (IGCC) and molten-carbonate fuel cell (MCFC) plants [1–3]. Generally, in these systems hydrogen sulfide accompanies a great quantity of reductive gases at high temperature, including CO, H_2, CH_4 and N_2, etc. This mixture gas is so-called coal gas or syngas. Coal gas is a valuable resource for generating electronic power. Prior to using, H_2S needs to be removed because of its harmful effect. In addition, H_2S is not only a malodorous and corrosive gas but also is the source of acid rain when it is oxidized into SO_2 and reacts with water.

The traditional methods for removal of H_2S are centered on activated carbon adsorption and chemical wet absorption. However, the bigger barrier for these traditional methods is that they must be operated under ambient temperature or slightly above, which diminishes the thermal efficiency of the IGCC/MCFC system significantly.

To the points of thermal efficiency and energy saving, high-temperature desulfurization techniques have received a great deal of much attention in recent years due to its higher thermal efficiency and environmental predominance [4,5]. Recently, we have reported that red soils could remove effectively H_2S under high temperature and identified the major sorption mechanism and the products analysis via spectroscopic techniques [6,7].

In this study, we further investigate the feasibility of red soils on sorption of H_2S with multiple sorption/regeneration cycles. In addition, a series of spectroscopic techniques,

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such as X-ray photoelectron spectroscopy (XPS), scanning electronic microscopy/energy dispersive X-ray spectroscopy (SEM/EDS), Fourier transform infrared spectrometer (FTIR) and solid-state nuclear magnetic resonance spectroscopy (SS-NMR) are used to examine the characterization of the regenerated red soils. Moreover, the qualitative analysis of gas phases is monitored and recorded by FTIR during the regeneration process.

2. Experimental

2.1. Materials

Owing to plenty distribution and easy availability in Taiwan, 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 the ambient temperature for a week. Prior to using, red soils were ground with an agate mortar and sieved to the acquired particle size to pass through a 2-mm sieve. The basic chemical and physical properties of the red soils and their chemical compositions were reported in our previous study [6].

2.2. Procedure

The sorption and regeneration experiments were carried out using a continuous flow fixed-reactor under atmosphere pressure 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 equipped with a PID controller. The quartz fibers were set in the reactor to support the red soil. A sufficient quality of red soil was loaded in 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 correctly. The gaseous mixture was composed of 1% H_2S, 25% CO, 15% H_2 and a balance of N_2 from regulation cylinders. All mass flow meters were calibrated using an IR soap bubble meter and the concentrations of all species were calculated at the STP condition. Prior to entering the reactor, the gases were conducted into a mixing pipe to establish that the mixture gases were in turbulence.

The overall experiment consisted of a sequence sorption and regeneration runs. In the sorption run, the mixture gases were introduced into the reactor and were terminated when the outlet concentration of H_2S reached 1500 ppm. Following the sorption run, the reactor was purged with nitrogen gas for 30 min, and then regeneration was commenced by passing 1% O_2. The weight hourly space velocity (WHSV) for both sorption and regeneration was set at 2000 ml h^{-1} g^{-1}. The inlet and outlet gases (H_2S) 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. The outlet concentration of H_2S was calculated using 1% standard H_2S with greater than $r^2 = 0.995$ of calibration curves fitting.

2.3. Characterization of the red soils

2.3.1. X-ray photoelectron spectroscopy

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

2.3.2. Scanning electronic microscopy/energy dispersive spectroscopy

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

2.3.3. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy was used to identify the gas phase composition during the regeneration process and the major clay minerals in the red soils. The infrared spectra were recorded on a Perkin-Elmer One B model FTIR spectrometer with fully computerized data storage and data handing capability. To provide adequate characterization of the red soils, the spectrum was set from a range of 400–4000 cm^{-1}. For solid and gas phases, a 100-scan data accumulation was carried out at 4 cm^{-1} resolution.

For the solid-state analysis, a blank test was first performed with a thin disk of pure potassium bromide. The red soil powder was ground with potassium bromide at a weight ratio of 1:300 and then pressed into a thin disk shape. The sample was placed on an aluminum-made holder to be analyzed using the transmittance model.

For the gas phase analysis, a 30 cm length gas cell chamber was used as the gas storage tool. Prior to analysis, the gas cell chamber was purged with highly pure dry nitrogen gas until a flat baseline with minimum noise was obtained.