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Modified clinoptilolite catalysts for seawater flue gas desulfurization application: Preparation, characterization and kinetic evaluation

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ARTICLE INFO

Article history:

Received 17 March 2015

Received in revised form 29 October 2015

Accepted 30 October 2015

Available online 10 November 2015

Keywords:

Flue gas desulfurization

Seawater

Catalytic packing

Kinetics

Clinoptilolite

SO₂ desorption

ABSTRACT

Seawater flue gas desulfurization (FGD) process has been adopted by a number of coastal power plants for its lower operation cost. Natural clinoptilolite (clin) was modified by Fe²⁺ ion exchange, drying, and calcination to prepare a catalytic packing for improving desulfurization efficiency of the adsorption tower. Compared with natural clin, the most active 350-Fe-clin (Fe²⁺ exchanged clin, calcined at 350 °C) catalyst kept 6–12% higher SO₂ removal efficiency at the operation temperature regime 45–85 °C. The acidic effluent of the adsorption tower was below pH 3.0, and S(IV) oxidation efficiency was above 80%. This confirmed that the modified clin catalytic packing played a crucial role on seawater FGD process. Mechanistic and kinetic studies were carried out on the seawater SO₂ removal over prepared catalytic packings. XRD, SEM and temperature programmed desorption (TPD) were employed to characterize the catalysts. Kinetic and TPD experiments showed that SO₂ desorption energy on 350-Fe-clin was 19.85 kJ/mol, apparent reaction activation energy of seawater FGD on 350-Fe-clin in the scrubber was 20.27 kJ/mol, and liquid phase S(IV) oxidation rate constant in liquid phase was much higher than that of overall reaction. It could be deduced that the reaction rate determining step existed in gas phase reactions.

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1. Introduction

Seawater flue gas desulfurization (FGD) process is a kind of wet FGD technology. It takes advantages of inherent alkalinity of seawater to absorb and neutralize sulfur dioxide in exhaust gases (Wang et al., 2013; Feng et al., 2014; Andreasen and Mayer, 2007). In power plants' application, seawater is obtained from the condenser outlet of steam turbine, and the acidic effluent of the scrubber is treated with air to reduce its chemical oxygen demand (COD) and acidity before it is discharged. The main commercialized SWFGD processes were Norway ABB, Lentjes Bischoff (Germany), and Fujikasui (Japan). In ABB's seawater scrubbing process (the Flakt-Hydro process), adsorption tower was filled with patented random

packing (Falcone Miller and Miller, 2010; Xia, 1999). The packings provided high specific surface area to improve the interaction of flue gas and seawater, and the desulfurization efficiency was determined by the adsorption equilibrium of liquid and gas. The SO₂ removal efficiency would be greatly improved when catalytic packing was loaded, and the about 5 vol% oxygen in flue gases was used as oxidant for S(IV) to S(VI), the latter has higher solubility. Recently, carbon-based catalytic packings were employed by Vidal Barrero to promote the desulfurization efficiency (Vidal Barrero et al., 2009; Zhou et al., 2015). Our research group designed and prepared the structured catalytic packing and used it in a pilot plant experiment (Bian et al., 2012). This structured packing performed higher desulfurization efficiency, lower pressure drop, and

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<http://dx.doi.org/10.1016/j.psep.2015.10.018>

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SO₂ catalytic removal, compared with the tested random ones (Zhang et al., 2011; Li et al., 2009).

The novel, catalytic properties of zeolites created new commercial applications, while environmental legislation created market pull to use catalysis to meet the new regulatory standards. Natural clinoptilolite is widely available, low cost, and characterized with high mechanical strength. Thermal and chemical treatment could improve the industrial applicability of clinoptilolite due to changes in their composition, structure and properties. Natural Laixi clinoptilolite is highly siliceous zeolite with a mole ratio SiO₂/Al₂O₃ of about 10 (Table S-1), and its high acid stability allows it to work as a catalyst in acidic seawater in which a large amount of SO₂ had been adsorbed. In this paper, modified clinoptilolite was prepared and employed as the catalytic packing in an adsorption tower. It provided the active sites for S(IV) oxidation both in gas phase and in liquid phase (Fu et al., 2007; Guo et al., 2015). At the near bottom of the packing bed where the pH was below 4.0 and non-catalytic oxidation rate was nearly zero, the modified clinoptilolite was stable and would performed well for S(IV) catalytic oxidation. The main unit operations of seawater FGD consisting of adsorption, oxidation and neutralization, the oxidation unite burden would be reduced when the catalytic packing was loaded in adsorption tower (Lan et al., 2012).

The aim of this study is to investigate the preparation, characterization and kinetic evaluation of the modified clinoptilolite catalysts. Through the compare of the apparent activation energy of flue gas desulfurization in the adsorption tower with the activation energy of SO₂ oxidation in gas phase, the possible desulfurization mechanism would be proposed. Pursuit of a better understanding of S(IV) catalytic oxidation in seawater buffering system, led to the application of this zeolite based catalyst to a packed scrubber in seawater FGD process.

2. Material and methods

2.1. Catalyst preparation

The material used in this study is Laixi clinoptilolite taken from the Laixi, Shangdong, China with mineral purity of 90%. These zeolites were ion-exchanged twice in a 1.0 M FeCl₂·4H₂O at 60 °C for 24 h, dried at 120 °C for 10 h, and calcined at 250, 350 or 450 °C for 6 h, prepared 250-Fe-Clin, 350-Fe-Clin, and

450-Fe-Clin, respectively. The zeolite gained about 5% more weight, and its surface color turned to dark brown.

2.2. Catalyst characterization

X-ray diffraction analysis (XRD) was conducted for phase identification of modified clinoptilolite catalysts on a D/Max-rB diffractometer with a CuKα radiation in the 2θ range from 10° to 70° at 0.02° steps.

Scanning electron microscopy (SEM) was performed on a JSM-6700F with a detector INCA Energy for EDS. The samples were not coated with gold.

Temperature-programmed desorption of SO₂ was employed to monitor the desorption behavior of the modified clinoptilolite catalysts from 30 to 350 °C. TPD profiles were measured by using a lab-built temperature programmed apparatus. 200 mg of the catalyst was dried at 120 °C for 2 h, and 5% SO₂/N₂ (99.99% purity) was used as an adsorption gas. Temperature ramp rate was 10 K/min and total flow rate was 100 mL/min. The changes in SO₂ flow were followed using a thermal conductivity detector.

2.3. Catalyst activity evaluation

The lab seawater FGD process was illustrated in Fig. 1. The simulated flue gas was prepared by balancing of SO₂ with diluted pure nitrogen, and adding certain amount of O₂ and CO₂. Seawater was obtained from the seaside of Laoshan Dist, Qingdao. The mineral clinoptilolite was crushed, sieved and modified to produce the catalytic random packing. The 2.5 g, 20–40 mesh granules was mixed with certain amount of 10–20 mesh silica beads, and packed into the column. The total packing volume was 4.5 cm³, and the column φ12 × 350 mm (110 mm length for constant temperature part) was equipped electric heating system, and the thermocouples were placed at the center of the reactor. There is a liquid distributor in the top of the column. Flue gas was contacted with the injected seawater in a cocurrent flow. The SO₂ concentration of inlet and outlet simulate flue gas were determined by Flue Gas Analyzer (model: Laoying 3022) with a measuring range 0–0.57% (mass fraction). The desulfurization efficiency η of absorption tower is defined as: $\eta = (C_i - C_o/C_i) \times 100\%$, where C_i and C_o refer to the inlet and outlet SO₂ concentration. In the lab seawater SO₂ adsorption system, non-isothermal fixed bed adsorption column was

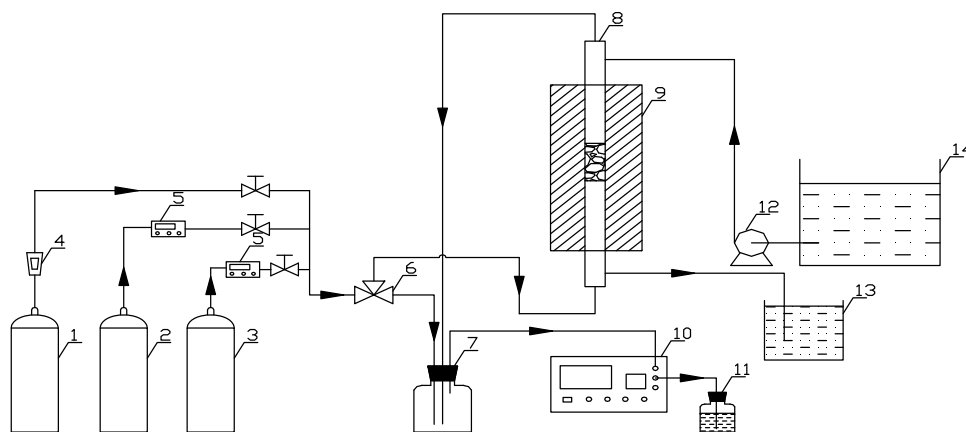


Fig. 1 – Schematic diagram of the lab seawater FGD process: modified clinoptilolite catalyst was packed in the tubular reactor, and flue gas was contacted with seawater in a cocurrent flow. (1) N₂; (2) SO₂; (3) O₂; (4) Glass rotameter; (5) mass flow meter; (6) tee valve; (7) mixing tank; (8) tubular furnace; (9) heat; (10) flue gas analyzing apparatus; (11) Exhausted gas absorption; (12) pump; (13) acidic effluent seawater; (14) fresh seawater.

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