Enhanced selective catalytic wet oxidation of H_2S to S over Ce–Fe/MgO catalysts at ambient temperature

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ABSTRACT

In the study we prepare novel MgO supported magnetic Ce–Fe catalysts for selective catalytic wet oxidation of H_2S to elemental sulfur at ambient temperature. Characterization of the MgO supported Ce–Fe catalysts and the corresponding catalytic activity for H_2S removal were analyzed and evaluated. Compared to the MgO supported Fe catalysts, the Ce incorporation increases significantly catalytic activity for H_2S removal due to the oxidation of Fe^{2+} to Fe^{3+} improved by the redox couple Ce^{4+}/Ce^{3+}. Besides, we also found that the Ce incorporation reduced sulfates and sulfur deposited on the surface of the catalysts. Under high oxygen atmosphere, contaminants are almost not formed on the surface of the Mg supported Ce–Fe catalysts, extending their lifetime.

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1. Introduction

Hydrogen Sulfide (H_2S) is usually generated from bio landfill, vehicles, and chemical industries with respect to the use of coal, petroleum, and nature gas, which is malodorous and harmful to human health, leads to acid rain, corrodes pipe/equipment, and poisons the catalysts used in industrial process. In large plants, the effluent gas is treated using the Claus process to recover H_2S to elemental sulfur [1]. Due to the thermodynamic limitation, the tail gas emitted from the Claus process still contains some H_2S; additional purification treatments are needed for the tail gas. Based on the mechanisms of adsorption, absorption, chemical oxidation, or catalytic oxidation, various technologies have been developed extensively for H_2S removal [2–8]. In practical applications, Mobil direct oxidation process, super-Claus process, and euro-Claus process involving H_2S-selective catalytic oxidation have been developed commercially [9–11]. Unfortunately, these processes are restricted to the existence of water vapor, concentration of H_2S, or oxygen content [12]. Recently, H_2S-selective catalytic oxidative catalysts made from carbon, metal oxides, clay, or their combinations have been studied extensively [10]. Most of these catalysts feature high performance, wide applications, and few limitations on operative conditions. However, the catalysts operated at catalytic dry (gaseous) oxidation have inevitable drawbacks – low stability and low selectivity at high reaction temperature [13–19].

Compared to dry oxidation, the wet (solution) oxidation features simpler process, smaller apparatus, less labor cost, and higher sulfur recovery. The Fe-chelating homogeneous catalysis has been investigated for H_2S removal through the redox mechanism [20–24]. Unlike Co^{3+}/Co^{2+} ($E = 1.82$) [25], the Fe^{3+}/Fe^{2+} couple can avoid mostly to over-oxide the H_2S to SO_4^{2-} because the reduction potential ($E = 0.77$ V) of Fe^{3+}/Fe^{2+} is higher than oxidation potential ($E = -0.14$ V) of H_2S/S but lower than that ($E = -0.81$ V) of H_2S/SO_4^{2-}. However, the homogeneous catalytic system needs to control the pH of the reaction media to stabilize the Fe-chelating catalysts, increasing operational complexity. Few studies have reported the wet catalytic oxidation for the H_2S removal in a heterogeneous catalytic system. Jung et al. [26,27] discovered a supported Fe catalyst for the wet selective catalytic oxidation of H_2S to S. Due to the strongly basic characteristic [28], it was also found that MgO as supports for iron oxide catalysts shows superior catalytic activity compared to other metal oxides such as Al_2O_3, SiO_2, and ZrO_2 [29]. Unlike the homogeneous catalysis, the MgO supported Fe catalyst needs not control the pH of the reaction media due to the basic property of MgO [30–32]. The MgO supported Fe catalyst reveals quite high conversion and large H_2S-removal capacity at room temperature [33].

During the Fe^{3+}/Fe^{2+} catalytic process, the Fe^{3+} is reduced fast to the Fe^{2+} by H_2S but the Fe^{2+} is oxidized slowly to Fe^{3+} by O_2 [27]. As a result, the catalyst operated at a high-concentration oxygen atmosphere has superior activity compared to that at low-concentration one. Recently, ceria (CeO_2) has been regarded as a promoter on the selective catalytic reduction catalysts as a result of its oxygen storage and redox couple Ce^{4+}/Ce^{3+} [34]. Because

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oxygen can be released from CeO_2 via the redox shift between Ce^{4+} and Ce^{3+}, the performance of the H_2S selective catalytic oxidation is also improved by incorporating Ce into the catalyst structure. The (iron oxide)–(cerium oxide) catalysts have exhibited high conversion and sulfur selectivity for H_2S removal at 250 °C [17]. In this study, we developed a new-type ferromagnetic Ce–Fe/MgO catalyst for the wet catalytic oxidation of H_2S to S at room temperature. By virtue of the ceria incorporation, the Ce–Fe/MgO catalyst shows superior activity and low deactivation compared to the Fe/MgO catalyst. Through magnetic separation, the catalysts are applied easily in practical applications. Characterization of the catalysts and influence of operating parameters were analyzed and discussed.

2. Experimental

2.1. Catalyst preparation

The MgO supported Ce–Fe catalysts were prepared by a wetness impregnation method as reported elsewhere. Briefly, 1 g of MgO (>96%, Showa) was added into the aqueous solution of iron trinitrate nonahydrate ($Fe(NO_3)_3\cdot9H_2O$, >98%, J.T. Baker) and cerium nitrate hexahydrate ($Ce(NO_3)_3\cdot6H_2O$, 99.5%, Acros) with various concentrations. The slurry was mixed and then dried at 100 °C for 24 h. The dried powders were ground and calcined at 600 °C for 2 h under air atmosphere, resulting in xCe–yFe/MgO, where x and y are the weight percent of Ce and Fe to MgO used in the preparation of the catalysts, respectively. For the case of only Fe loading in the catalysts (without Ce), the catalyst was denoted degenerately as yFe/MgO.

2.2. Characterization of catalysts

The morphologies of the as-prepared catalysts were examined using a field-emission scanning electron microscope (JSM-7401F, JEOL). The dispersion of the Fe, Ce, and S on the surface of MgO support was examined using a high-resolution transmission electron microscope (JEM-2010, JEOL) and characterized through X-ray diffraction (XRD) using an X-ray diffractometer (Miniflex II, Rigaku) and Cu Kα radiation. The elemental analysis and binding energy of the surface of catalysts were determined by X-ray photoelectron spectroscopy (XPS) (PHI 5000 VersaProbe, ULVAC-PHI) at a take-off angle of 90°. All XPS spectra were calibrated using Au $4f_{7/2}$ (BE = 84 eV) as internal reference. The concentration of sulfate ions and that of metal ions in the solution were analyzed by an ion chromatography (IC, ICS-1100, Dionex) and an inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent 725), respectively.

2.3. Measurement of catalytic activity

The activity tests for the selective catalytic oxidation of H_2S were performed with a semi-batch reactor at ambient temperature. Different kinds of catalysts (0.1 g) were dispersed into 250 ml of deionized water in the reactor. A gas mixture of H_2S, O_2, and N_2 was conducted into the reactor at a rate of 250 ml/min, bubbling the catalyst solution through a gas distributor. The H_2S concentration in the gaseous stream was analyzed using an electrochemical detector (XAM-5000, Drager). The inlet H_2S and O_2 concentrations were fixed normally at 300 ppm and 16%, respectively, but the values might be varied for further analyses.

3. Results and discussion

Fig. 1 shows XRD patterns for various yFe/MgO and xCe–yFe/MgO catalysts. All of the XRD patterns indicate peaks with
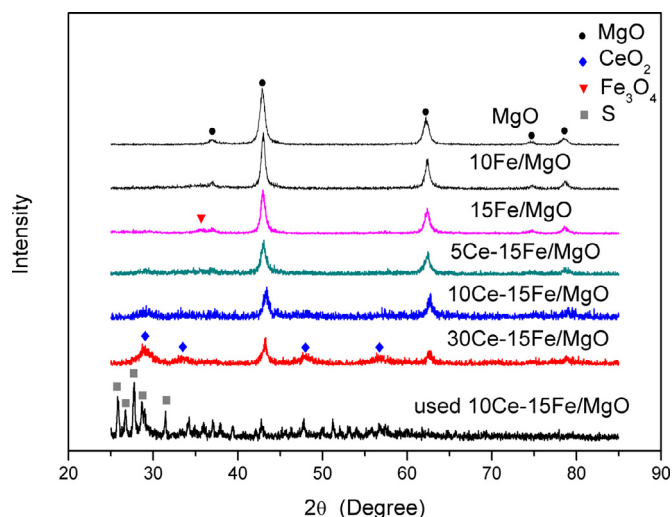
Fig. 1. XRD patterns of xCe–yFe/MgO catalysts.

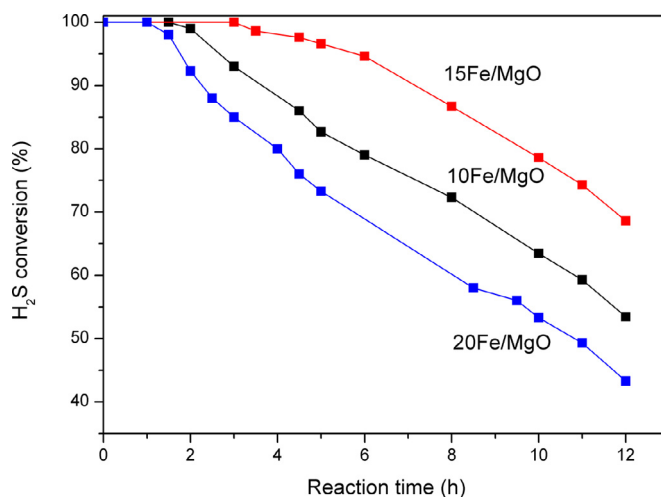**Fig. 2.** H_2S conversion for the Fe/MgO catalysts with various Fe contents. Test conditions: inlet H_2S concentration = 250 ppm.

values of 2θ located at 37.0, 42.9, 62.2, 74.6, and 78.5°, corresponding to the planes (111), (200), (220), (311), and (222), respectively, of MgO (JCPDS #65-0476). For low Fe loading (10Fe/MgO) or low Ce loading (5Ce–15Fe/MgO), no corresponding peak for Fe and Ce can be observed in the XRD patterns of MgO supported catalysts. The result implies that iron oxides and ceria are highly dispersed small crystallites (<5 nm) or amorphous phase formed on the surface of MgO in a low-loading condition [17,35]. When metal loading increases, extra peaks occur in the XRD patterns, revealing that the crystallites are aggregated or formed. In the case of 30Ce–15Fe/MgO, the peak at 2θ = 28.7, 33.4, 47.7, and 56.9° are ascribed to CeO_2 (JCPDS#65-2975). The XRD pattern of the 15Fe/MgO catalyst showed a peak at 2θ value of 35.6°, attributed to α-Fe_2O_3 (JCPDS#33-0664) or Fe_3O_4 (JCPDS#19-0629). Under high-resolution observation, a weak peak at 2θ = 30.0° is indexed to the plane (220) of Fe_3O_4 (Fig. S1). We infer that high metal-loading yFe/MgO or xCe–yFe/MgO catalysts feature α-Fe_2O_3 and Fe_3O_4 crystal structures, displaying ferromagnetic behavior. Actually, the catalysts can be attracted by a magnet (Fig. S2).

The catalytic wet oxidation of H_2S was tested in an aqueous solution. The solution was stirred to keep catalyst powders suspension and avoid their settlement. A gas mixture of $H_2S/N_2/O_2$ with constant H_2S concentration was conducted into the solution at room temperature. Fig. 2 shows that the H_2S conversion