



High-temperature H₂S removal performance over ordered mesoporous La-Mn-supported Al₂O₃-CaO sorbents



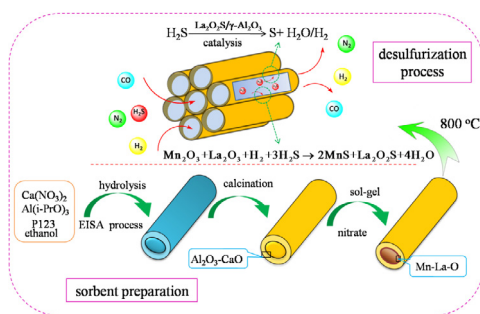
Hong Xia, Xiaoqian Chang, Bingsi Liu *

Department of Chemistry, School of Science, Tianjin University and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

HIGHLIGHTS

- Novel Mn-La/OMA-2Ca exhibited excellent desulfurization performance.
- Mesoporous structure and basic modifier promoted dispersion of particles and adsorption of acidic H₂S.
- Ordered mesoporous γ -Al₂O₃ possessed high thermal stability.
- Abundant elemental sulfur was produced due to synergistic catalysis of γ -Al₂O₃ and La₂O₂S.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 10 January 2017

Received in revised form 14 March 2017

Accepted 16 March 2017

Available online 19 March 2017

Keywords:

Ordered mesoporous alumina

Mn-La sorbents

High stability

H₂S removal

ABSTRACT

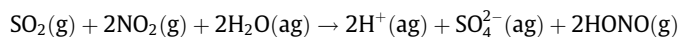
A series of La-Mn supported on ordered mesoporous Al₂O₃-CaO (OMA-2Ca) sorbents with various Mn/La molar ratio were first designed and synthesized for removal of H₂S at 650–850 °C. 40% 98Mn2La/OMA-2Ca exhibited satisfactory desulfurization performance at 800 °C with a breakthrough sulfur capacity (BSC) of 16.15 g S/100 g sorbent. Elemental sulfur was formed during desulfurization as a result of synergistic catalysis of γ -Al₂O₃ and lanthanum oxysulfide at high temperature. The existence of high content steam in hot coal gas obviously reduced the sulfur capacity because of the formation of MnAl₂O₄. After five successive sulfidation-regeneration cycles, high BSC (about 90% of the initial BSC) was maintained. In addition, the characterization results indicated that the mesostructure of OMA-2Ca remained intact during sulfidation and regeneration except that the amorphous wall was converted to γ -Al₂O₃ phase, and active species were still well dispersed on support, which indicated the stability of Mn-La/OMA-2Ca sorbent.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

In recent decades, there were high pollutant emissions (such as sulfur and nitrogen oxides) from combustion of coal and petroleum products in developing countries spurred on by fast economic development, which exerted profound impacts on human health, ecosystem and climate [1]. Recently, severe haze occurs frequently in China. A major fraction of Chinese haze is attributed to the

outstanding sulfur problem. Sulfate is a key particulate matter (PM) constituent, which derives from aqueous oxidation of SO₂ by NO₂ under suitable atmospheric conditions [2].



Under the circumstances, clean coal utilization in China is particularly important. H₂S contained in hot coal gas not only can be oxidized into SO₂ in atmospheric environment, exacerbating severe haze development, but it also causes equipment corrosion. Thus, H₂S needs to be removed prior to coal gas use. In view of thermal efficiency, hot gas desulfurization (HGD) is more attractive

* Corresponding author.

E-mail address: bingsiliu@tju.edu.cn (B. Liu).

than cold gas desulfurization due to the fact that HGD avoids the procedure of coal gas cooling and heating [3]. In general, coal gasification typically operates at temperature higher than 1000 °C, and the temperature of hot coal gas is between 800 and 900 °C. Therefore, the desulfurization temperature should be around 800 °C. However, so far, it is difficult to establish this industrial practice, mainly due to the absence of an effective and economic sorbent that can withstand such a high temperature.

Numerous sorbents have been extensively investigated with the aim to remove hydrogen sulfide more effectively [4–9]. Transition metal oxides, such as zinc, ferric, manganese, molybdenum, vanadium, calcium, copper etc [5,7,10–13] and rare earth oxides [14,15] have showed good desulfurization behavior. However, the fatal drawback of zinc, ferric and copper-based sorbents, rapid degradation deriving from metal evaporation and the reduction of oxides in reducing atmosphere, limits their applications at high temperature. Westmoreland et al. [13] claimed that MnO was stable and possessed high sulfur capacity, fast sulfidation rate and enduring regeneration ability in the range of 800–1000 °C. Low desulfurization precision is the shortcoming of Mn-based sorbents, which can be improved remarkably by the doping of other metal oxides, for instance, Zn, Cu, Fe, La and Ce oxides [14,16–20]. Among these additives, rare earth oxides were stable at higher than 800 °C as reported by Flytzani-Stephanopoulos [8].

Sorbent deactivations caused by sintering and aggregation of active particles at high temperature are very common. Supported sorbent is a feasible solution to address these tough problems. So far, many materials were used as supports for desulfurization, such as zeolites, activated carbon, fly ash, TiO₂, ZrO₂, γ -Al₂O₃, mesoporous silica and so on [7,10,17,21,22]. Among them, mesoporous silica materials as support have attracted world-wide attention due to their large surface areas, large pore volume and tunable pore structure. The influence of textural types of mesoporous silica on desulfurization performance also has been researched [23,24]. Despite obvious virtues, mesoporous silica is composed of amorphous silica, which is very unstable at high temperature. The deterioration of mesoporous framework at high temperature largely restricts their large scale applications. Compared to silica, alumina is more stable. Unfortunately, the common γ -Al₂O₃ has low surface area and disordered structure, which is unfavorable for the dispersion of particles and gas diffusion. However, alumina with ordered mesostructure maintains the advantages of both mesoporous silica and common γ -Al₂O₃. In particular, ordered mesoporous γ -alumina is stable up to 900 °C [25]. Moreover, γ -Al₂O₃ has a better catalytic effect for high temperature H₂S decomposition. At present, the ordered mesoporous alumina (OMA) has been proved to possess wide applications in catalysis [26,27]. Nevertheless, to the best of our knowledge, there were few reports on OMA using as a support in hot coal gas desulfurization. It is proposed to be a good candidate for the fabrication of sorbents with high thermal stability.

Herein, a group of La-Mn/Al₂O₃-CaO sorbents with ordered mesostructure were originally designed and synthesized for H₂S removal. A small amount of CaO was added to mesoporous Al₂O₃ via a one-pot synthesis strategy and the formed composite oxide was directly used as support. The mesoporous framework and basic modifier promoted gas diffusion and the adsorption of acidic H₂S. Moreover, the nanochannels could confine the La-Mn active sites within a nanometer size, which effectively assured high dispersion of active phase and inhibited the thermal sintering of particles during multiple sulfidation-regeneration cycles. Elemental sulfur was obtained during desulfurization due to synergistic catalysis of γ -Al₂O₃ and lanthanum oxysulfide. Furthermore, the effects of composition, reaction temperature, loading and steam on the desulfurization performance were also investigated. Particularly,

the reasons for the negative effect of steam on desulfurization behavior were discussed.

2. Experimental section

2.1. Synthesis and characterization of sorbent materials

Ordered mesoporous Al₂O₃-CaO composite oxide (denoted as OMA-2Ca) was prepared via a one-pot evaporation-induced self-assembly (EISA) strategy based on previous literatures [25,28]. Approximately 2.0 g pluronic P123 was dissolved in 40 mL ethanol in a 100-mL beaker at room temperature (RT). Then, 3.2 mL of 67 wt% nitric acid, 20 mmol of aluminum iso-propoxide and 0.4 mmol of Ca(NO₃)₂·4H₂O were added into the above solution with vigorous stirring (400 rpm). The solution was allowed to continue stirring for 6 h, and then put into a drying oven at 60 °C to undergo the solvent evaporation in static air. After 2 days of aging, the final gel was calcined at 550 °C for 6 h in flowing air (120 mL/min) in muffle furnace with a heating rate of 1 °C min⁻¹.

In contrast, Al₂O₃-CaO composite oxide without ordered mesoporous structure (denoted as NMA-2Ca) was also prepared by similar method to that of OMA-2Ca, just without the addition of pluronic P123 template.

A series of sorbents with various Mn/La molar ratio (98:2, 95:5, 90:10) were synthesized by a sol-gel method [18]. Taking the preparation of 40 wt% 98Mn2La/OMA-2Ca as an example, 2.91 g of Mn(NO₃)₂ aqueous solution and 0.07 g of La(NO₃)₃·6H₂O were added into 50 mL deionized water (DW) in a 100-mL beaker. 2.62 g of citric acid (a molar amount of 1.5 times of the total metal ions) was added to above solution, and the resultant mixture was vigorously stirred (450 rpm) for 15 min. Then, 1.0g OMA-2Ca was slowly added into the aforementioned solution and the mixture was further stirred for 2 h. The obtained sol was continuously stirred at 60 °C until a viscous gel was formed. The gel was aged at AT for 3 days and finally calcined at 550 °C for 6 h with a heating rate of 1 °C min⁻¹. The loading of metal oxides was set as 20, 40 and 50 wt%. The obtained sorbents were pressed, crushed and sieved through 20–40 meshes.

Nitrogen adsorption isotherms were carried out on a domestic adsorption system at 77 K [29]. The specific surface area, pore volume and average pore diameter were calculated from isotherm adsorption branch by applying Barrett-Joyner-Halenda (BJH) model. Small-angle X-ray diffraction (XRD) patterns were recorded with a Rigaku automatic diffractometer equipped with a Ni filtered Cu K_α radiation ($\lambda = 0.15406$ nm) source at settings of 20 kV and 30 mA. Wide-angle XRD patterns were conducted on a PANalytical automatic diffractometer using Ni filtered Cu K_α radiation source (40 kV, 50 mA). The diffuse reflectance spectra of sorbents were recorded in the range 200–800 nm using a UV-vis spectrophotometer (Shimadzu UV-2101) equipped with an integration sphere. The spectra were analyzed using Kubelka-Munk theory. Absorbance was converted to F(R) according to Kubelk-Munk function ($A = -\lg(R)$, $F(R) = (1 - R)^2/2R$).

The temperature-programmed reduction (TPR) was conducted in a domestic system using gas chromatography (GC) with thermal conductivity detector (TCD) for monitoring H₂ consumption. More details regarding the operation have been described elsewhere [18].

2.2. Sulfidation-regeneration test

The desulfurization tests were performed in a fixed-bed reactor (10 mm i.d.) using simulated hot coal gas with composition of 0.33% H₂S, 10.5% H₂, 18% CO and N₂ balance. The gas flow rate

Download English Version:

<https://daneshyari.com/en/article/6465795>

Download Persian Version:

<https://daneshyari.com/article/6465795>

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