



Full Length Article

Effect of preparation conditions on $\text{Mn}_x\text{O}_y/\text{Al}_2\text{O}_3$ sorbent for H_2S removal from high-temperature synthesis gasHaifeng Li^{a,b}, Sheng Su^{a,*}, Song Hu^a, Kai Xu^a, Long Jiang^a, Yi Wang^a, Jun Xu^a, Jun Xiang^{a,*}^a State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, China^b JiangHan University, Wuhan 430056, China

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ABSTRACT

A series of $\text{Mn}_x\text{O}_y/\text{Al}_2\text{O}_3$ sorbents with different tissue and chemical structures were prepared by repeated incipient wet impregnation method with different calcination conditions, including calcination temperature from 500 °C to 900 °C and calcination time from 3 h to 9 h. The H_2S absorption performances of the prepared sorbents were investigated by a model synthesis gas containing 2000 mg/m³ H_2S at 850 °C. The chemical and physical structures of the samples were characterized by Brunauer–Emmett–Teller, X-ray diffraction and scanning electron microscopy techniques to obtain fundamental information about the deactivation of $\text{Mn}_x\text{O}_y/\text{Al}_2\text{O}_3$ sorbents during desulfurization–regeneration cycles. Results showed that the structural features of the sorbents at high reaction temperature played an important role in the stability of desulfurization performance. The analysis of the characteristics of the sorbents indicated that the sorbents obtained stabilized chemical and physical structures during desulfurization–regeneration cycles when the calcination temperature was 900 °C and the calcination time was above 6 h. The sorbent suffered serious deactivation during five successive desulfurization–regeneration cycles when the calcination temperature of sorbents was below 850 °C. The sulfur capacity decreasing of $\text{Mn}_x\text{O}_y/\text{Al}_2\text{O}_3$ sorbents may probably be attributed to a part of Mn_xO_y covered by Al_2O_3 , which can un-sulfide during adsorption process. The coverage of active phase Mn_xO_y may be caused by the shrinking and disappearing of some micropores, and phase transformation of Al_2O_3 , as well as the transformation of MnAl_2O_4 lead to a part of Mn_xO_y on the sorbents being covered by alumina.

1. Introduction

Integrated gasification combined cycle (IGCC) is considered to be one of the most promising and competitive technologies in the field of clean coal-fired power generation [1–2]. In the IGCC system, coal-derived synthesis gas contains certain harmful impurities, especially H_2S [3]. Synthesis gas from coal contains almost all of the sulfur in coal, a typical H_2S composition is 0.1–1.5% [4], H_2S not only fails to fulfill the safety requirement of the gas turbine but also causes environmental problem [5]. Therefore, removing H_2S and limiting its concentration to less than 20 ppm in the synthesis gas is necessary [6,7]. The wet desulfurization process has been used in the IGCC, but the synthesis gas must be cooled from approximately 1123 K to room temperature with a large syngas cooler, thereby leading to low energy efficiency in this technology [8,9]. High-temperature coal gas desulfurization (HGD) has attracted many researchers because it can avoid the heat exchange and enhance the process efficiency (compared to the wet desulfurization process, the energy efficiency improves by 0.7–2%) [10–12]. At exit of a typical gasifier the temperature is about 800–900 °C, if the fuel gas

can be purified at such a high temperature, the heat efficiency of the whole IGCC system will be greatly improved, so the reaction temperature to investigate the desulfurization performance in this work was selected at 850 °C [13].

Prospecting the suitable sorbent for the desulfurization is important for the HGD technology. Metal oxides are the main active materials in the HGD process, and the thermodynamics of H_2S absorption on Ba, Ca, Co, Cu, Fe, Mn, Mo, Sr, W, V, and Zn oxides are reported to be favorable for desulfurization at high temperature [14]. A number of metal oxides and their mixtures have been investigated for H_2S removal; however, a few metal oxides can be easily reduced to metallic states at high temperature under reducing atmosphere, or form the lower sulfur capacity and mechanical strength of the sorbent [15,16]. In recent years, Mn-based sorbents have attracted a considerable amount of research attentions not only due to their high sulfur capacity, high mechanical stability, and fast initial reaction rate for H_2S removal in the range of 400–1000 °C, but also due to their reduction capability to MnO when the temperature is below 1200 °C [17–22]. A high temperature was beneficial for the S/O exchange rate of the manganese-based acceptor,

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and the sulfur capacity of the sorbent was proportional to the manganese content for H_2S removal from high-temperature synthesis gas [23–29]. For achieving a more even distribution of active components with high manganese content (for high sulfur capacity), $\text{Mn}_x\text{O}_y/\text{Al}_2\text{O}_3$ was prepared by different methods, such as repeated impregnation and co-precipitation methods [30–32]. If metal oxides were loaded on a suitable support, then the sorbents would present high breakthrough sulfur capacity and utilization, strong mechanism strength, and reliable regenerability due to the high dispersion of active particles. The Mn-based sorbents were synthesized by various sorbent supports with good tissue structures, such as Al_2O_3 [33,34], mesoporous silica, and TiO_2 [35–39]. Compared to SiO_2 and TiO_2 , the Al_2O_3 -supported manganese sorbent exhibits the best sorption capability [39]. Compared to silica, alumina is more stable and Al_2O_3 has a better catalytic effect for high-temperature H_2S decomposition [36]. Therefore, Al_2O_3 was applied as the support along with manganese in this work.

As the desulfurization sorbent, the stability and durability of such sorbents under successive sulfuration–regeneration cycles were considered important factors. In many studies committed to examining the desulfurization performance of Mn-based oxides, the deactivation problem of sulfur capacity during several desulfurization–regeneration cycles were observed [26,27]. According to the investigation on Mn-based oxide sorbents, the deactivation of sorbents during desulfurization–regeneration cycles may be attributed to a few factors. The desulfurization of hot coal gas is a kind of gas–solid contacting reaction process. Generally, a sorbent with a larger surface area exhibits more active sites on its surface. Thus, some studies speculated that the decrease in breakthrough time after the first desulfurization–regeneration cycle was attributed to the reduction in the surface area and pore volume of sorbents. The desulfurization and regeneration processes of HGD are conducted under high temperature for a long time. Particularly, the regeneration process with high O_2 content can release strong heat, and such phenomenon can create pore blockage and decrease in surface area during desulfurization–regeneration cycles, there by leading to the loss of the sulfur capacity [36,37,40]. However, the report of Svatopluk [41] showed that the high surface area of a material will not necessarily mean a high sorption activity, and the deactivation rate is not directly proportional to the loss of surface area. The side reaction on the formation of manganese (II) sulfate was also regarded as another factor that can lead to the loss of desulfurization performance because the sulfate is inert with respect to the desulfurization process [42,43]. However, the deactivation of the desulfurization performance aroused by the formation of MnSO_4 during multiple desulfurization–regeneration cycles was reported to be unconfirmed, and the formation of sulfate did not cause the significant reduction in the H_2S sorption capacity at several desulfurization–regeneration cycles [44]. As mentioned, many unconfirmed questions regarding the deactivation mechanism in the desulfurization of the sorbents still exist. Moreover, the system can become more complicated at high temperature with the possible interaction of Al_2O_3 with Mn oxides, which can further affect the stability of the desulfurization performance of the sorbent [45]. Therefore, the deactivation mechanism of the sorbents needs further work to provide significant guidance for the industrialization of HGD technology.

In this work, a series of $\text{Mn}_x\text{O}_y/\text{Al}_2\text{O}_3$ sorbents with various tissue and chemical structures were prepared using repeated incipient wet impregnation method with different calcination conditions. The chemical and physical structures of the samples were characterized by Nitrogen Isothermal Adsorption, X-ray powder diffraction (XRD), and scanning electron microscopy (SEM), and the desulfurization performances of the sorbents at high temperature (850 °C) were investigated. The deactivation of sorbents during the successive desulfurization–regeneration cycles were discussed by analyzing the relationship between characterization results and desulfurization performance.

2. Experimental

2.1. Preparation of sorbents

The support Al_2O_3 (Alumina, Aladdin Industrial Cor., USA) presents itself with the particle shape. The $\text{Mn}_x\text{O}_y/\text{Al}_2\text{O}_3$ sorbents were prepared by repeated incipient wet impregnation method using $\text{Mn}(\text{NO}_3)_2$ (50% $\text{Mn}(\text{NO}_3)_2$, Sinopharm Chemical Reagent Co., Ltd, China) as the metal precursors. This impregnated slurry was conducted in the Vapour-bathing Constant Temperature Vibrator for 24 h at 40 °C. The sample was dried in a drying oven at 80 °C for 24 h. The dried sample was used for second impregnation and drying without intermediate calcination. Finally, samples were calcined at a certain temperature ranging from 500 °C to 900 °C for 6 h. The final amount of Mn doping was approximately 30 wt% (The sorbent underwent chemical digestion, and the amount of Mn ion was measured by WSY2000 Atom Adsorption Spectrometer, Wayneal, China). The samples were denoted as MA500, MA600, MA700, MA800, and MA900 according to the calcination temperature. Other samples were calcined at certain times (3, 6, and 9 h) with 900 °C, which were denoted as MA-T3, MA-T6, and MA-T9, respectively, according to the calcination time.

2.2. Characterization

The pore structure of fresh sorbents, the fourth regenerated sorbents was determined via nitrogen adsorption at low temperature (−196 °C) with the ASAP 2020 analyzer (Micrometrics Instrument Cor., America). Prior to the BET measurement, the sorbents were degassed in a vacuum at 350 °C for 4 h. BET surface area, pore volume, and average pore diameter were calculated using adsorption isotherm while pore size distribution was estimated by Barrett–Joyner–Halenda method. The surface area was measured by the BET equation [32].

The XRD measurements were performed on the Bruker AXS D8 (Bruker, Germany) Advance X-ray diffractometer (Cu K α , $k = 0.15406$ nm, 40 kV, 40 mA) in the step scanning mode with 2 θ between 20° and 80°. A step size of 0.02° (0.24 s per step) and wide-angle XRD patterns were recorded with PANalytical Automatic. The crystalline phases were identified with reference to powder diffraction file (PDF).

The morphological characteristics of the fresh sorbents, the first sulfide sorbents and the fourth regenerated sorbents were observed by the SU8010 (Hitachi Limited, Japan) field emission scanning electron microscopy, with an accelerating voltage of 15 Kv and a resolution of 1 nm.

2.3. Desulfurization and regeneration tests for the sorbents

The schematic diagram of desulfurization–regeneration apparatus is shown in Fig. 1. The Mn-based sorbents were subjected to sulfuration–regeneration tests in a vertically oriented quartz tube reactor, with an inner diameter of 6 mm. In every case, 0.5 g of the sorbent (50–80 mesh) was packed to a height of approximately 2 cm. The reactor was heated with an electrical furnace, and the packed sorbents were placed in a constant temperature zone. The temperature was monitored using a K-type thermocouple inserted into the middle of the reactor. A typical test comprised several repeated cycles. Every cycle included sulfuration, flushing, regeneration, and flushing processes.

The synthesis gas is composed dominantly of H_2 and CO with small quantities CO_2 , CH_4 and other harmful components. CO has reducing property and may leading to the formation of coke at high temperature, which may affect the desulfurization of sorbent. However, according to the former work [30], the reducing intensity of CO was weaker than H_2 , the reducing property of CO during desulfurization process can be replaced by H_2 in experiment. The desulfurization process of this paper was conducted at 850 °C, no coke formation was observed at such high desulfurization temperature [29]. The former work [23,46] also found

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