Performance of Cerium Oxides from Different Preparation Methods for Desulfurizing Hot Coal Gas

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ABSTRACT: Four CeO$_2$ samples were prepared by pyrolysis of cerium hydroxide, cerium nitrate, cerium oxalate, and cerium perchlorate. The structures of CeO$_2$ samples were characterized by means of X-ray diffraction and nitrogen adsorption–desorption. Temperature-programmed reduction and thermogravimetry tests were carried out to evaluate the reduction and sulfurization behaviors of the CeO$_2$ samples. The results indicate that the samples, prepared from different precursors, have larger surface areas and pore specific volumes, smaller average crystallite sizes, and better reducibilities (except the sample from cerium perchlorate) than the CeO$_2$ reagent. The sulfurization performances of CeO$_2$ samples are directly correlated with the reduction degrees of CeO$_2$ samples. Compared with fresh CeO$_2$ samples, reduced ones have better sulfurization performances. Among the four CeO$_2$ samples, the one prepared from cerium nitrate, with the best reducibility, exhibits the best performance in sulfurization.

1. INTRODUCTION

Hot gas desulfurization of coal-derived fuel gases is an essential process in emerging power generation technologies, such as the integrated gasification combined cycle and the coal-based polygeneration system (an advance technology for clean and efficient utilization of coal with the advantages of low cost, high efficiency, and environmental friendliness). Cerium oxide based sorbents have been developed in recent years for the removal of H$_2$S from coal-derived gas and natural gas and SO$_2$ from flue gas. CeO$_2$ shows very good promise. There are several advantages of cerium oxide based sorbents including their usability at high temperature (>700 °C), the favorable sulfurization equilibrium in reducing gas environments, and the potential to be regenerated via a route that directly produces elemental sulfur, which reduces the complexity of the regeneration step.$^{1-10}$

In the work of Zhang et al.$^{11}$ the kinetics of reaction between CeO$_2$ and SO$_2$ was affected by the preparation method of CeO$_2$. The precursors of cerium oxides can result in different CeO$_2$ microlitic structures and then influence both the reduction and the sulfurization of CeO$_2$. However, there are very few studies on either the structure or the surface properties of the cerium oxide samples from different precursors or their effect on desulfurization in hot gas.

In this study, cerium oxide samples were prepared by pyrolysis of cerium hydroxide, cerium nitrate, cerium oxalate, and cerium perchlorate. Nitrogen adsorption–desorption (BET) and X-ray diffraction (XRD) were conducted to characterize the structural properties of the cerium oxide samples prepared from different precursors. Temperature-programmed reduction (TPR) and thermogravimetric (TG) tests were carried out to investigate their reduction and sulfurization behavior, respectively.

2. RESULTS AND DISCUSSION

2.1. Characterization of the Prepared CeO$_2$ Samples.

The surface areas, pore specific volumes, and pore size distributions of the prepared CeO$_2$ samples and chemical reagent CeO$_2$ were measured by nitrogen adsorption and desorption. The characteristic results of all samples are shown in Table 1.

It can be seen that the surface areas and pore specific volumes of all the prepared CeO$_2$ samples are larger than those of the CeO$_2$ reagent. The sample of cerium oxalate with the largest fraction of micropores ($R < 20$ Å) has the largest BET surface area (101.91 m$^2$/g). The sample from cerium nitrate has the largest pore specific volume (0.208 cm$^3$/g) with most of the pores in the range of 20–200 Å. All the samples prepared in this work were identified by XRD, and the results are shown in Figure 1.

The crystallite sizes of CeO$_2$ samples were estimated by the half-height width of diffraction peaks,$^{12}$ and the results are shown in Table 2.

CeO$_2$ crystallized in the face-centered cubic system has a characteristic fluorite oxide type structure. The diffraction pattern of CeO$_2$ from Ce$_2$(C$_2$O$_4$)$_3$ is broader than those of the other samples, indicating a small crystallite size of the oxide phase. The prepared CeO$_2$ samples, except the one from Ce(ClO$_4$)$_3$, have smaller average crystallite sizes than the CeO$_2$ reagent. The average particle size of CeO$_2$ from Ce$_2$(C$_2$O$_4$)$_3$ is 7.1 nm, and it grows to 10.9 and 13.4 nm in the sample from Ce(NO$_3$)$_3$ and Ce(OH)$_3$, respectively.
2.2. TPR Tests of the Prepared CeO₂ Samples. TPR tests were performed from 200 to 850 °C in the gases of 40 vol% H₂/N₂ at a heating rate of 10 °C/min. The H₂-TPR profiles of the prepared CeO₂ samples and chemical reagent CeO₂ are shown in Figure 2. Appreciable reduction capacity can be found at temperatures above 400 °C. A large and broad reduction peak in the temperature range of 400−550 °C and a shoulder around 580 °C appear for all samples in the TPR profiles of CeO₂. The main and shoulder peaks correspond to the reduction of surface oxygen and bulk oxygen, respectively.13 Compared with the CeO₂ reagent, the prepared CeO₂ samples have larger main peak areas except the CeO₂ sample from Ce(ClO₄)₃. It indicates that the amount of surface oxygen in these prepared samples is more than that in the CeO₂ reagent. The surface oxygen change of the structure, as revealed by BET and XRD studies, could contribute to this change of reduction patterns. As shown in Table 2, the reduction peak areas of the CeO₂ samples from Ce(NO₃)₃, Ce(OH)₃, and Ce₂(C₂O₄)₃ are about 94, 46, and 3% larger than that of the CeO₂ reagent, respectively. It indicates that these CeO₂ samples have better reducibility than the CeO₂ reagent, especially the one from Ce(NO₃)₃.

2.3. Sulfurization Tests of the Prepared CeO₂ Samples. Sulfurization experiments of the CeO₂ samples were performed in the TG apparatus at 700 °C. In this experiment, a ceramic crucible containing 10 mg of the sample was placed on the platinum pan suspended from a thin quartz rod attached to one arm of the microbalance, and then the apparatus was purged by N₂ carrier gas for cleaning the air in it. The reactor system containing a sorbent was heated from room temperature up to 700 °C in nitrogen at a rate of 10 °C/min, and then the reducing gas containing H₂S was introduced. The sulfurization experimental results are shown in Figure 3. According to the phase stability diagrams for the Ce−O−S system, Ce₂O₃ can be produced from ceria (reaction 1) in a very reducing atmosphere, and cerium oxysulfide and cerous sulfide can be derived from both cerium(IV) oxide (reactions 2 and 3) and cerium(III) oxide (reactions 4 and 5), respectively.14−17

The reduction reaction equation of cerium(IV) oxide is

\[
\text{CeO}_2 + \frac{1}{2}\text{H}_2 \rightarrow \frac{1}{2}\text{Ce}_2\text{O}_3 + \frac{1}{2}\text{H}_2\text{O}
\]  

(1)

Sulfurization reaction equations of cerium oxide are

\[
\text{CeO}_2 + \frac{1}{2}\text{H}_2\text{S} + \frac{1}{2}\text{H}_2 \rightarrow \frac{1}{2}\text{Ce}_2\text{O}_3 + \text{H}_2\text{O}
\]

(2)
Cerium oxide in its higher oxidation state (+4) has low sulfurization equilibria; however, the reduced oxide Ce2O3 is a superior sorbent to remove H2S.18,19 As shown in Figure 3, a slight weight loss is initially observed followed by a rapid weight gain at about 10 min, and afterward, the weight gain proceeds but at a gentle pace. It should be noted that reduction and sulfurization both contributed to the weight change.20,21 At the beginning time of the experimental process, a slight weight loss indicates that the reduction rate is a bit faster than the sulfurization rate. The rapid weight increase shows the high sulfurization rate due to the increase of reduced cerium oxide. It is not possible to specify the sulfurization products of ceria from the weight increase due to the combination of reactions 3–5. However, at the given reaction conditions, the most plausible reactant on the basis of thermodynamics is Ce2O3, not CeO2. Thus, the stable sulfurization product is considered to be Ce2S3 on the basis of the phase diagram.14,17

Figures 4 and 5 show the profiles of estimated sulfurization conversion of fresh and reduced CeO2 samples in the same sulfurization conditions. The conversion Xs was calculated assuming formation of Ce2S3. As shown in Figure 4, combining the effects of reduction and sulfurization, the value of Xs increases rapidly after about 5 min of reaction, achieving about 81, 79, and 69% for CeO2 samples from Ce(NO3)3, Ce(OH)3, and Ce(ClO4)3, respectively, at the latter 10 min of reaction. However, the rapid increase of Xs for the CeO2 sample from Ce2(C2O4)3 begins at 10 min of reaction, and the conversion Xs achieves only 58% at 20 min of reaction.

As shown in Figure 5, Xs of the reduced CeO2 samples (after 30 min pre-reduction in 40% H2/N2 reductant gas) enhanced, especially for the CeO2 sample from Ce2(C2O4)3. The value of Xs increases rapidly in the first 10 min, achieving about 92, 87, 83, and 73% for CeO2 samples from Ce(NO3)3, Ce(OH)3, Ce(ClO4)3, and Ce2(C2O4)3, respectively. Xs of the reduced CeO2 samples, except the sample from Ce(ClO4)3, is above 90% after 20 min of reaction. Xs of the CeO2 sample from Ce2(C2O4)3 improves greatly from 58 (without pre-reduction) to 91% (with pre-reduction) at 20 min of sulfurization.

From Figures 4 and 5 and Table 2, it can be seen that the sulfurization performance is directly correlated with the reduction degree of CeO2 samples. The CeO2 sample from cerium nitrate, with the largest TPR reduction peak area, exhibits the best behavior in sulfurization among the four prepared CeO2 samples.

3. CONCLUSIONS
In this paper, CeO2 samples were prepared by pyrolysis of cerium hydroxide, cerium nitrate, cerium oxalate, and cerium perchlorate. To evaluate the effects of different preparation methods on the structure and the reactivity of CeO2 samples, XRD and BET techniques were used to characterize the structural properties, and the tests of H2-TPR and TG were carried out to investigate the reduction and sulfurization, respectively. It is found that the microlitic structures of CeO2 samples are different obviously, which influences the reduction and sulfurization performances of CeO2 samples. The prepared CeO2 samples, except the sample from Ce(ClO4)3, have better...
reduction performances than the CeO₂ reagent. The sulfuration performances of CeO₂ samples are directly correlated with the reduction degree of CeO₂ samples. Compared with fresh CeO₂ samples, reduced ones have better sulfuration performances. The CeO₂ sample from cerium nitrate, with the largest TPR reduction peak area, exhibits the best behavior in sulfuration.

4. EXPERIMENTAL SECTION

4.1. Preparation of Cerium Oxide Samples. Four cerium oxide samples were prepared by pyrolysis of cerium hydroxide, cerium nitrate, cerium oxalate, and cerium perchlorate. The raw materials were A. R. grade chemical agent Ce(NO₃)₂·6H₂O (purity 99.95%). Cerium hydroxide, cerium oxalate, and cerium perchlorate were prepared by precipitation. First, cerium nitrate was dissolved in deionized water. Oxalic acid and perchloric acid were then added to prepare cerium oxalate and cerium perchlorate, respectively. Ammonia water was added to prepare cerium hydroxide. Each solution was subjected to the precipitation reaction, and the solution in the flask was continuously stirred with a magnetic stirrer on a hot plate so that the solution was kept at 60°–70°C. The precipitate was then filtered, washed in deionized water twice, dried at 110°C, and crushed to a powder before pyrolysis. Cerium hydroxide, cerium oxalate, cerium nitrate, and cerium perchlorate were pyrolyzed in a muffle furnace at 340°C for 15 h, 300°C for 20 h, 340°C for 15 h, and 260°C for 10 h, respectively.

4.2. Characterization of Cerium Oxide Samples. Specific surface areas and the pore size distributions of the prepared samples were determined by nitrogen adsorption and desorption using a BET instrument (CE Sorptomatic 1990, Italy). The crystal structure was determined from the diffraction pattern obtained with an X-ray diffractometer (Rigaku D/max-2500, Japan).

4.3. TPR and TG Tests of Cerium Oxide Samples. Temperature-programmed reduction (TPR) tests were performed using a TP-5000-II adsorber manufactured by Tianjin Xianquan Co. Ltd., China. A 40% H₂/N₂ gas mixture was used as the reducing gas. The cerium oxide sample powder of 100 mg and 180–200 mesh was placed in a quartz tube reactor and surrounded with quartz chips. The sample was first heated in N₂ gas flow at 200°C for 2 h to remove the adsorbed gases, and then TPR was carried out under H₂/N₂ flow at a heating rate of 10°C/min up to 850°C. All gases were of analytical grade (H₂, N₂ from cylinder and with purity of 99.99%).

The TG tests were conducted in a thermogravimetric analysis apparatus manufactured by the Netzsch Company, Germany. A gas flow rate of 200 mL/min and a sample powder of 180–200 mesh were used to prevent or minimize the gas-phase mass-transfer resistance and the effects of pore diffusion. In a TG test run, 10 mg of cerium oxide sample powder was uniformly spread on a circular pan. Before starting the experiment, pure nitrogen was introduced to replace the oxygen atmosphere, and the sample was heated from ambient temperature to 700°C. Then the isothermal experiments were carried out to study the sulfuration with and without pre-reduction in a gaseous mixture consisting of 1% H₂S, 40% H₂, and nitrogen balance. All these gases are stored in cylinders, and their purity reach 99.99%.

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