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程序升温表面反应技术研究氧化铈上 H_2S 的吸附和转化

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摘要: 采用程序升温表面反应技术研究了 H_2S 在 CeO_2, TiO_2 和 Al_2O_3 三种载体上的吸附和反应行为. 结果表明, CeO_2 具有最强的脱硫能力. 系统研究了预处理气氛对 H_2S 在 CeO_2 上吸附和反应行为. 发现 CeO_2 的脱硫能力在惰性气氛、还原性气氛、氧化性气氛中依次增强. H_2S 首先吸附在经预处理的 CeO_2 表面, 进一步在 Ar 氛围下升温脱附时, 一部分 H_2S 在 673 K 以下脱附, 部分则与 CeO_2 表面氧反应, 在 473 K 下产生硫和水, 而在 473~673 K 温度范围内, 生成 SO_2. 在 673 K 以上, 所生成的 SO_2 进一步与晶格氧反应, 转化成硫酸盐. 后者在 873 K 再次分解为 SO_2. 因此, CeO_2 表面脱硫过程应控制在 673 K 以下, 可避免复杂的再生过程.

关键词: 氧化铈; 硫化氢; 吸附; 程序升温表面反应

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Temperature-Programmed Surface Reaction Study of Adsorption and Reaction of H_2S on Ceria

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Abstract: H_2S adsorption and reaction on CeO_2, TiO_2, and γ-Al_2O_3 were studied by temperature programmed surface reaction (TPSR). Ceria had the best desulfidation ability. The pretreatment atmosphere affected H_2S adsorption and reaction on ceria, and desulfidation efficiency increased in the order of inert atmosphere, reducing atmosphere, oxidizing atmosphere. H_2S was first adsorbed on pretreated ceria at room temperature. On increasing the temperature in an Ar (99.99%) atmosphere, part of the H_2S desorbed below 673 K, and another part reacted with the surface oxygen on ceria to produce sulfur and water below 473 K, and SO_2 between 473 and 673 K, which further reacted with lattice oxygen and was transformed into sulfate above 673 K. The sulfate decomposed into SO_2 again at 873 K. To avoid the complex regeneration, it is advisable to carry out desulfidation below 673 K when using ceria as adsorbent.

Key words: ceria; hydrogen sulfide; adsorption; temperature-programmed surface reaction

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The production of hydrogen from a heavy oil for a solid oxide fuel cell is a clean and efficient way to generate renewable energy. However, heavy oils usually contain sulfur species. H_2S is often produced during the gasification of heavy oils and would exist in the syngas [1]. For instance, 0.002% H_2S is still present in syngas from the integrated gasification combined cycle (IGCC) process [2]. This H_2S should be removed because it is a corrosive gas and it will deactivate most catalysts [3,4].

Many methods have been developed to remove H_2S, including physical adsorption, chemical adsorption, chemical oxidation, and catalytic combustion [5,6]. Among these methods, physical adsorption and chemical adsorption are the preferred methods. Rare earth oxides, especially ceria, have excellent desulfidation ability and are thermodynamically favorable [7]. Zheng et al. [8] have reported an efficient method for the removal of H_2S by reduced cerium oxide (CeO_n, $n < 2$). The adsorption reactions were

$$CeO_2(s) + (2–n)H_2(g) \leftrightarrow CeO_n(s) + (2–n)H_2O$$

$$2CeO_n(s) + H_2S(g) + (2n–3)H_2 \leftrightarrow Ce_2O_2S(s) + 2(n–1)H_2O$$

If the bulk ceria adsorbent gets deeply sulfided, Ce_2O_2S is formed in a reducing atmosphere. Then the adsorption is quickly degraded, and a regeneration step is needed to reproduce CeO_2 as follows:

$$Ce_2O_2S(s) + SO_2(s) \leftrightarrow 2CeO_2(s) + 2S(s)$$

This complex regeneration step usually causes a structural change of the adsorbent during the transformation from the sulfide to oxide phase [9,10]. However, the structural change of the adsorbent can be avoided by controlling the sulfidation and regeneration processes using a low temperature and high gas velocity [7]. On the other hand, it is important to understand the interaction between H_2S and ceria in different gas atmospheres because ceria is a common support or catalyst for many reactions. Ma et al. [11] studied a sulfur-tolerant CeO_2 supported Pd (Pd/CeO_2) catalyst for methanol synthesis. A bifunctional reaction mechanism on Pd/CeO_2 was proposed. Methanol was formed at the active Pd site. H_2S was first adsorbed on the ceria surface, and then it reacted with surface oxygen to form SO_2. A small amount of oxygen was added into the syngas to fill the oxygen vacancies, which were formed on the surface of ceria. In our previous work, it was shown that Pt/CeO_2 showed good sulfur tolerance in the water gas shift reaction (WGS) in the presence of 0.002% H_2S [12]. However, all of the adsorbed H_2S desorbed in the form of H_2S in the WGS reaction, which was different from the methanol synthesis reaction. It was suggested that H_2S adsorbed competitively with water on oxygen vacancies on the ceria surface in the presence of water vapor, and the SH species produced was desorbed in the form of H_2S by H_2 spillover from platinum.

In this study, the adsorption and reaction of H_2S on CeO_2, TiO_2, and γ-Al_2O_3 were studied by temperature programmed surface reaction (TPSR) experiments, and the desulfidation conditions were optimized for different gas atmospheres. The study of H_2S adsorption and conversion would be helpful for understanding sulfur-tolerance mechanisms for ceria supported catalysts.

1 Experimental

1.1 Catalyst preparation

Ceria was prepared by co-deposition. An aqueous solution of $(NH_4)_2CO_3$ and $(NH_4)_2Ce(NO_3)_6$ was added dropwise to deionized water at 328 K while keeping the pH at 8–9. The slurry mixture was aged at 328 K for 2 h with constant stirring. The precipitate was washed with deionized water several times, then dried at 393 K overnight, and finally calcined at 773 K for 4 h to obtain ceria. TiO_2 was prepared by the hydrolysis of $TiO(C_4H_9)_4$. $TiO(C_4H_9)_4$ was first dissolved in ethanol, and then added dropwise to an aqueous solution of $(NH_4)_2CO_3$. The following steps were the same as those for the preparation of ceria. Commercial γ-Al_2O_3 was purchased from Degussa Co., Ltd (Germany), and was calcined at 773 K for 4 h before use.

1.2 Catalyst characterization

A Quantachrome NOVA-4000 automated adsorption instrument was used to measure N_2 adsorption isotherms at liquid N_2 temperature (77 K). The samples were degassed in vacuum at 623 K for 3 h to remove physically adsorbed components prior to the measurements. The specific surface area was determined from the linear portion of the BET plot. The pore size distribution was calculated from the desorption branch of the N_2 adsorption isotherm using the Barrett-Joyner-Halenda (BJH) formula.

In the TPSR experiments, 100 mg sample (γ-Al_2O_3, TiO_2 or CeO_2) was first treated in pure Ar (99.99%) from room temperature to 673 K at a rate of 10 K/min and held for 1 h at 673 K, then cooled down to room temperature (RT) in the same atmosphere. After pretreatment, 1% H_2S/N_2 (30 ml/min) was passed over the surface of ceria at RT for 20 min to get saturated adsorption. The sample was swept by Ar (50 ml/min) until the gas chromatograph (GC) signal was stable, then the temperature was increased from RT to 673 K at a rate of 10 K/min. For ceria, besides the pretreatment in pure Ar (99.99%), 5% H_2/Ar and 5% O_2/Ar were also used as the pretreatment atmosphere. The flow rate was 30 ml/min. The other steps were the same as in the pretreatment in pure Ar (99.99%) except that a mass spectrometer (MS) was the detector.

In the recycle adsorption experiment, the sample was first

treated with 5% O_2/Ar from RT to 873 K at a rate of 10 K/min and held for 1 h at 873 K, then cooled to RT in the same atmosphere. After pretreatment, 1% H_2S/N_2 (30 ml/min) was passed over the surface of the ceria at RT for 20 min to get saturated adsorption. Before the desorption, the sample was swept by Ar (30 ml/min) until the MS signal was stable, then the temperature was increased from RT to 873 K at a rate of 10 K/min and it was kept at 873 K for 4 h until the MS signal was flat for the first desorption process. This process was named the first cycle. After the first cycle, the ceria sample was cooled down to RT in Ar (99.99%), and H_2S adsorption was carried out at RT for 20 min. The temperature was increased from RT to 873 K at a rate of 10 K/min and it was kept at 873 K for 4 h until the MS signal was flat during the second desorption process. This process was named the second cycle. For the third cycle, the ceria sample was again treated with 5% O_2/Ar from RT to 873 K at a rate of 10 K/min and held for 1 h at 873 K then cooled down to RT in the same atmosphere. The desorption process was the same as in the first and the second cycles. For the fourth cycle, the treatment process and desorption process were the same as for the second cycle. All of the desorption processes used Ar (99.99%) as the carrier gas.

2 Results and discussion

The physical properties of the three samples were characterized using the physical adsorption of N_2. As shown in Table 1, the surface area, pore volume, and average pore diameter of ceria were smaller than those of the other two samples.

Table 1 Physical properties of CeO_2, TiO_2, and γ-Al_2O_3

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
CeO_2	68.3	0.108	6.34
TiO_2	100.5	0.252	10.0
γ-Al_2O_3	204.6	0.423	8.26

γ-Al_2O_3, TiO_2, and CeO_2 were studied by H_2S-TPSR experiment. The GC signals are shown in Fig. 1. Only one desorption peak was observed at 370 K for γ-Al_2O_3. Two desorption peaks were present for TiO_2. The peak area of the low temperature peak at 340 K was much smaller than that at 580 K. Chen et al. [13] also observed this phenomenon with γ-Al_2O_3 and TiO_2 samples, and they assigned the peak at low temperature to H_2S and the other peak at high temperature to SO_2. TiO_2 has more active surface oxygen than γ-Al_2O_3, which favored the conversion of adsorbed H_2S to SO_2. There was also one desorption peak for ceria but the temperature was increased to 480 K. The desorption peak area on ceria was the highest of the three samples. Since GC

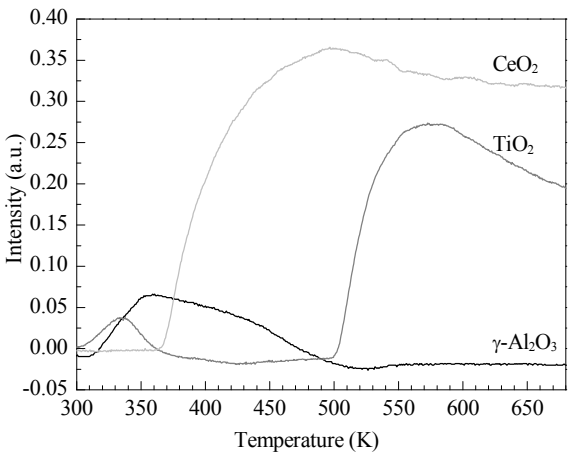

Fig. 1. H_2S-TPSR spectra from γ-Al_2O_3, TiO_2, and CeO_2.

is not a good detector for different sulfur species, the H_2S-TPSR signals were detected by MS in the following experiments.

The adsorption and reaction of H_2S on ceria were further studied by TPSR experiments in which the samples were pretreated in three different gas atmospheres. The H_2S and SO_2 MS signals are shown in Figs. 2 and 3, respectively. The H_2S and SO_2 signals were recorded from 373 to 573 K and had a center at 453 K. The H_2S and SO_2 desorption peak areas after the three different gas atmosphere pretreatments are summarized in Table 2. The desorbed H_2S peak area from ceria after different pretreatment decreased in the order of O_2 > Ar > H_2. The desorbed SO_2 peak area decreased in the order of O_2 > H_2 > Ar. The SO_2 formed after the O_2 pretreatment was mainly from the reaction of H_2S with the surface oxygen of ceria. On the other hand, SO_2 formed after the H_2 pretreatment was from the reaction $CeO_n + H_2S \rightarrow Ce_2O_2S + SO_2 + H_2O$, which was similar to the sulfidation process with reduced ceria as the adsorbent [8]. H_2S tended to react with reduced ceria, and did not just directly desorb from the reduced ceria. The H_2S conversion was

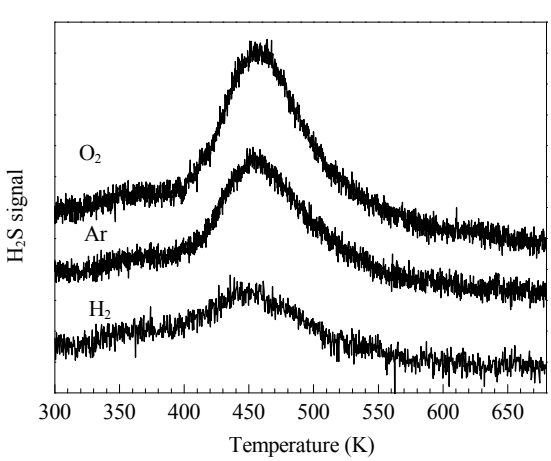

Fig. 2. TPSR H_2S signals from ceria after O_2, Ar, or H_2 pretreatment.

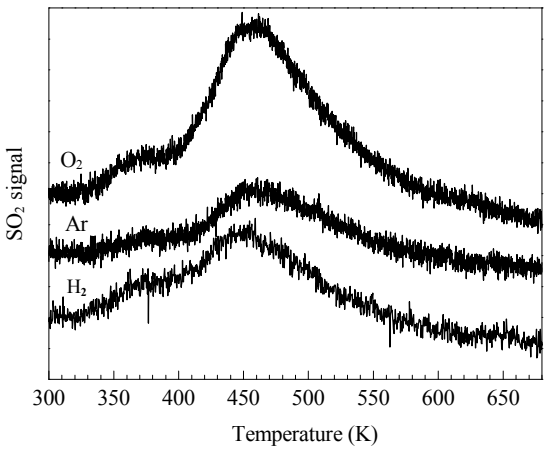

Fig. 3. SO_2 signals during H_2S-TPSR on ceria after O_2, Ar, or H_2 pretreatment.

Table 2 Adsorption and conversion of H_2S on ceria

Pretreatment condition	Peak area*			$X(H_2S)$/%
	H_2S	SO_2	Total	
Ar	1	1	2	46.8
H_2	0.56	1.58	2.14	71.2
O_2	1.59	2.66	4.25	59.5

*Defined as 1 from the Ar pretreatment.

calculated as $X(H_2S) = [SO_2]/([H_2S] + [SO_2]) \times 100\%$. The results are also shown in Table 2.

The total peak areas from H_2S and SO_2 desorption were much higher for the sample pretreatment with O_2 than with the other pretreatments with H_2 and Ar. The active oxygen species formed during O_2 pretreatment can oxidize part of adsorbed H_2S to SO_2, and SO_2 was desorbed together with unreacted H_2S between 473 and 673 K. In addition, water and sulfur were observed on the outside of the quartz reactor below 473 K. Water and sulfur may form by two possible ways. One possible way was the reaction of H_2S with oxygen species (O*) at a relative low temperature, by the reaction $H_2S + O^* \leftrightarrow S + H_2O$. This had been reported in the H_2S-TPSR experiments with a reducible TiO_2 support [13]. The other possible way was the Claus reaction ($H_2S + SO_2 = S + H_2O$).

Other than H_2S and SO_2, no other sulfur species were detected in the MS signal until 673 K. However, Ce_2O_2S was formed in the sulfidation process following the H_2 pretreatment and a complex regeneration step was required to recover the adsorbent [14]. From the above discussion, it is preferred to carry out the sulfidation process below 673 K after an O_2 pretreatment to avoid the complex regeneration process.

In order to characterize the reversibility of desulfidation on ceria, recycle experiments were carried out. The H_2S and SO_2 signals in the recycle experiments are shown in Figs. 4 and 5, respectively, and the four cycles were assigned as 1, 2, 3, and 4. The H_2S and SO_2 peak areas below 673 K in the first cycle were similar as those with the sample pretreated in an O_2 atmosphere at 673 K in the TPSR experiments. During the temperature increase, a sharp SO_2 desorption peak was present near 673 K. The signal increased with the temperature and did not reach a maximum at 873 K. When the desorption temperature was kept at 873 K, it required 40 min to get the desorption signal to decrease to the baseline. The SO_2 desorption peak at high temperature was much larger than that below 673 K, and it was not accompanied by H_2S desorption. The SO_2 desorption peak at 873 K was from the decomposition of $Ce(SO_4)_2$, which was formed by the reaction of SO_2 with the lattice oxygen of ceria at high temperature. $Ce(SO_4)_2$ is thermodynamically stable at low temperature and is decomposed to Ce_2O_2S and SO_2 at around 873 K [15].

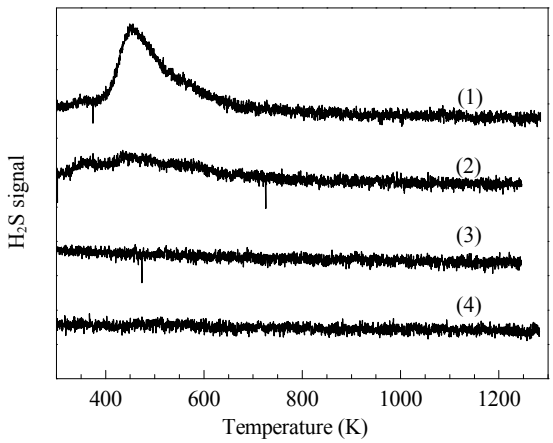

Fig. 4. H_2S signals of the H_2S-TPSR cycle experiments with O_2 pretreatment. (1) First cycle; (2) Second circle; (3) Third cycle; (4) Forth cycle.

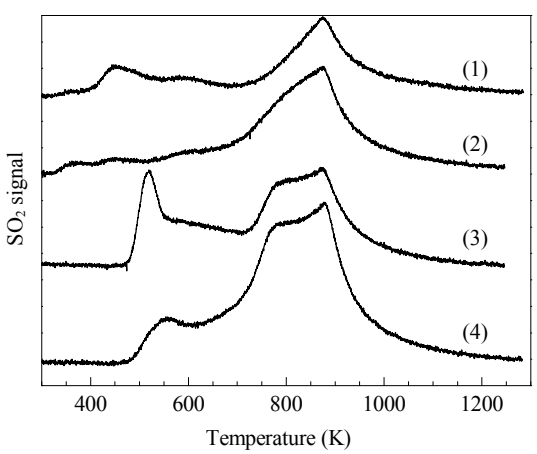

Fig. 5. SO_2 signals of H_2S-TPSR cycle experiments in O_2 pretreatment. (1) First cycle; (2) Second circle; (3) Third cycle; (4) Forth cycle.

In the second cycle, the sample after the first cycle was first cooled to 298 K in Ar (99.99%), and then it was used again to adsorb H_2S at 298 K. For the second cycle, most of the surface oxygen had been consumed during the first cycle, therefore, the reaction of H_2S with surface oxygen to form SO_2 was negligible, and this desorbed below 673 K as compared with the first cycle. Thus adsorbed H_2S can only react with the lattice oxygen of ceria to form SO_2, and then SO_2 reacted with lattice oxygen to form sulfate, resulting in more sulfate species as compared with the first cycle. The sulfate species formed was decomposed to release SO_2 at 873 K, which was more than in the first cycle. After the second cycle, the third cycle was carried out, and the process was the same as the first cycle. First, the sample was regenerated in an O_2 atmosphere, and then it was used to adsorb H_2S at 298 K. Finally the adsorption was characterized by TPSR. As shown in Fig. 5, all of the adsorbed H_2S was converted into SO_2 and it desorbed in a wide temperature range between 473 and 873 K. During the regeneration process, active oxygen species were formed on the surface of ceria, such as O^{2-} and O^{-}, which readily reacted with H_2S to form SO_2, and the SO_2 produced desorbed at 523 K. There was also a high temperature desorption peak, which was also attributed to the decomposition of sulfate.

After the third cycle, the fourth cycle was carried out, and the details of the process were the same as in the second cycle. It was surprising to note that there was still no desorption peak of H_2S in a full range of the temperature tested, and the SO_2 desorption peak area above 673 K was much larger than the one below 673 K. The reason why there was no H_2S desorption may be due to the presence of excess active oxygen species provided during the previous oxygen regeneration step. From the above H_2S-TPSR experiments, it can be concluded that more sulfate was formed at the high temperature above 673 K. It is preferred to carry out the sulfidation with ceria as adsorbent below 673 K in order to avoid the complex regeneration process.

3 Conclusions

Ceria showed the best desulfidation ability for H_2S among the CeO_2, TiO_2 and γ-Al_2O_3 tested. TPSR experiments demonstrated that H_2S was first adsorbed on the pretreated ceria at room temperature, then part of the H_2S desorbed below 673 K during the temperature increase in an Ar atmosphere. The other part of H_2S reacted with the surface oxygen of ceria to form different sulfur species at different temperatures. Sulfur and water were formed below 473 K, and SO_2 was formed between 473 and 673 K. SO_2 further reacted with lattice oxygen and was transformed into sulfate above 673 K, which decomposed into SO_2 again around 873 K. Sulfidation with ceria as the adsorbent should be performed below 673 K in order to avoid the complex regeneration process.

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