Study on the removal of hydrogen sulfide from natural gas by titanosilicate zeolite

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Abstract: The presence of hydrogen sulfide in natural gas will reduce the calorific value of natural gas, so hydrogen sulfide in natural gas needs to be removed. Titanosilicate zeolite is a stable porous material with good catalytic effect and has attracted much attention due to its excellent catalytic oxidation performance in the system composed of it and hydrogen peroxide. Therefore, in this paper, the removal of hydrogen sulfide in natural gas was studied by using titanosilicate zeolite as catalyst and hydrogen peroxide as oxidant, and the mixture of hydrogen sulfide and nitrogen gas was used as the simulated gas of natural gas. The experimental results show that the titanosilicate zeolite has a good catalytic effect on hydrogen sulfide. The influence of the concentration of hydrogen peroxide, reaction temperature and pH of the initial solution in the process of removing hydrogen sulfide by titanosilicate zeolite was studied.

1. Introduction

Natural gas is a kind of clean energy with high calorific value and low air pollution[1], which occupies an important position in industry and civil use. Hydrogen sulfide (H₂S) is often present in natural gas production, in the development process of natural gas containing hydrogen sulfide, due to its extremely strong corrosion, under the conditions of oxygen and heat and humidity, it seriously corrodes the transport pipeline and equipment, which reduces the pipeline life and is also one of the culprits of acid rain. Therefore, the removal of acidic gases from natural gas, especially hydrogen sulfide, is particularly important.

At present, the methods of natural gas desulfurization include Claus method, activated carbon method and alcohol amine method, etc.[2]. The Claus method involves burning hydrogen sulfide to remove it[3]. Its disadvantage is that the combustion temperature should be kept above 920 °C, which requires higher fire resistance of the equipment. Activated carbon method is also one of the commonly used gas desulfurizer, its internal has a huge specific surface area and developed pore structure, has a good adsorption of a variety of gases, can be used to remove hydrogen sulfide adsorption[2]. However only using activated carbon to remove hydrogen sulfide can not meet the requirement of natural gas.

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alcohol amine method uses alkanolamine solution to react with hydrogen sulfide to achieve the purpose of removing hydrogen sulfide\textsuperscript{[4]}. In the process of alcohol amine desulfurization, the solvent regeneration is difficult, corrosive, easy to bubble and so on.

In consequence, in order to find an efficient and environmentally friendly method to remove hydrogen sulfide from natural gas, in this paper uses titanosilicalite zeolite (TS-1) as catalyst and low concentration hydrogen peroxide as oxidant to remove trace hydrogen sulfide from natural gas by catalytic oxidation. Its advantages are that the TS-1 has high catalytic activity, stable performance in the environment of weak acid, the combined system with hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) under normal temperature and pressure for desulfurization, operational safety, and the catalyst is easy to recover without secondary pollution.

2. Materials and Methods

2.1. Main instruments and reagents

The mixture of hydrogen sulfide and nitrogen gas is used as the simulated gas of natural gas containing hydrogen sulfide, 1g/L (CH\textsubscript{3}COO)\textsubscript{2}Zn, 1% H\textsubscript{2}O\textsubscript{2}, 0.01mol/L Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}, 0.025mol/L iodine liquor, starch indicator, diluted hydrochloric acid and dilute sulphuric acid.

2.2. Experimental methods

Nitrogen and hydrogen sulfide gas were uniformly mixed and sealed with a three-mouth flask containing catalyst TS-1 and H\textsubscript{2}O\textsubscript{2}. H\textsubscript{2}S removal reaction was mainly carried out in a three-mouth flask with a volume of 100 ml. The tail gas after the reaction was absorbed by zinc acetate, after absorption for 30min, zinc acetate was transferred to 250 ml conical flask, and add 0.025mol/L iodine solution 10 ml, diluted hydrochloric acid 5 ml, the reaction took about 5 min in an environment away from light.

After the reaction, the removal rate of H\textsubscript{2}S was titrated by iodine content method. Titration was performed with sodium thiosulfate with a concentration of 0.01 mol/L, and until the solution turned pale yellow. Then add 3-4 drops of starch indicator, and the solution was dark blue. The titration continued until the blue just disappeared, and the recorded data was V\textsubscript{1}. At the same time, do the blank experiment and write the reading as V\textsubscript{0}. The chemical equation of the reaction is:

\begin{align}
H\textsubscript{2}S + (CH\textsubscript{3}COO)\textsubscript{2}Zn &= ZnS \downarrow + 2CH\textsubscript{3}COOH \\
ZnS + 2HCl &= H\textsubscript{2}S + ZnCl\textsubscript{2} \\
H\textsubscript{2}S + I\textsubscript{2} &= 2HI + S \downarrow \\
I\textsubscript{2} + 2Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} &= 2NaI + Na\textsubscript{2}S\textsubscript{4}O\textsubscript{6}
\end{align}

2.3. Calculation method of removal rate of H\textsubscript{2}S

The concentration of hydrogen sulfide in tail gas is calculated as follows:

\[ C_{H_2S}(mg/m^3) = \frac{(V_0 - V_1) \cdot C \times 34.076/2}{V} \]  

\( V_0 \) is the amount of sodium thiosulfate consumed by the blank titration (mL); \( V_1 \) is the dosage of sodium thiosulfate in the experimental (mL); \( V \) is the volume of the mixture in 30 min under standard conditions(m\textsuperscript{3}); \( C \) is the concentration of sodium thiosulfate.

3. Results and Discussion

This research intends to use a mixture of H\textsubscript{2}S standard gas and N\textsubscript{2} to simulate natural gas containing hydrogen sulfide, and to change the different concentrations of H\textsubscript{2}S by separately controlling the inlet flow of H\textsubscript{2}S and N\textsubscript{2}. In this experiment, H\textsubscript{2}O\textsubscript{2} was used as the oxidant and TS-1 was used as the catalyst to remove hydrogen sulfide. There are many variable factors in the process of catalytic oxidation and removal of H\textsubscript{2}S. Such as: H\textsubscript{2}O\textsubscript{2} concentration, reaction temperature, initial solution pH. These factors have a great influence on the desulfurization process.
3.1. Influence of H₂O₂ concentration on H₂S removal

Keep other factors unchanged, and investigate the effect on the removal of hydrogen sulfide by changing the concentration of H₂O₂. Adjust the flow of H₂S and N₂ to stabilize the concentration of H₂S in the feed gas at 250 mg/m³, the reaction temperature is 20 °C, the addition amount of the catalyst TS-1 is 0.5 g, and the pH is 4.6. The concentration of H₂O₂ is 0 %, 0.5 %, 1 %, 2 %, 3 % and 5 %, respectively. The influence of a single H₂O₂ system and a combined system of H₂O₂ and TS-1 on the removal of H₂S were investigated, respectively. The results are shown in Fig. 1 and Fig. 2.

![Fig. 1 The influence of a single H₂O₂ system on desulfurization](image1)

![Fig. 2 The influence of the combined system of H₂O₂ and TS-1 on desulfurization](image2)

As can be seen from Fig. 1, when the concentration of H₂O₂ in the reaction system is 0 %, the removal rate in 30 minutes is 2.33 %, and when the reaction is 90 minutes, the conversion rate is 0. Since the absorption of H₂S by water is minimal, it can be ignored. After adding 0.5%, 1%, 2%, 3%, 5% concentration of H₂O₂, the removal rate of H₂S at 30min reaction was 7.45%, 20.44%, 27.45%, 41.91%, 55.55%, respectively. After 3 hours of reaction, it is basically in an equilibrium and stable state. At this time, the removal rate of H₂S is 0, 9.16%, 13.45%, 18.91%, and 25.11%, respectively. It is concluded that as the concentration of H₂O₂ increases, the removal rate of H₂S also increases, but as the reaction time continues to extend, the removal rate of H₂S gradually decreases. Therefore, different concentrations of H₂O₂ can oxidize and remove a certain amount of H₂S.

As shown in Fig. 2, Under the combined system of TS-1 and H₂O₂, as the concentration of H₂O₂ increases, the removal rate of H₂S also increases. When the H₂O₂ concentration is 0.5%, 1%, 2%, 3%,
5%, the removal rate of H\textsubscript{2}S after 30 minutes of reaction is 86.64%, 88.39%, 89.22%, 97.16%, 98.26%. After 180 minutes of reaction, the removal rate of H\textsubscript{2}S has dropped to a certain extent. At this time, the removal rate of H\textsubscript{2}S is 79.45%, 84.41%, 85.25%, 92.69%, and 94.79%. Therefore, From the perspective of economic cost and safety, 1 % H\textsubscript{2}O\textsubscript{2} was selected as the oxidant in this experiment.

3.2. Effect of TS-1 on removal of H\textsubscript{2}S

In order to investigate the removal effect of TS-1 on H\textsubscript{2}S, the reaction conditions were 1% H\textsubscript{2}O\textsubscript{2}, 0.5 g TS-1, temperature 20 ℃, pH 4.6, H\textsubscript{2}S concentration is 250 mg/m\textsuperscript{3}, and H\textsubscript{2}S removal experiment was carried out. The result is shown in Fig. 3.

![Fig. 3 The catalytic performance of TS-1 to H\textsubscript{2}S](image)

Reaction conditions: TS-1 0.5 g, 20℃, H\textsubscript{2}S 250mg/m\textsuperscript{3}, 1% H\textsubscript{2}O\textsubscript{2}, pH=4.6

The results show that, when only TS-1 catalyst was present in the reaction system, the removal rate of H\textsubscript{2}S at 30min was 43.52%. After 4 hours of adsorption, the removal rate of H\textsubscript{2}S gradually reached equilibrium and stable, at which time the removal rate was only 7.51%, TS-1 has certain adsorption capacity to hydrogen sulfide; When only 1% H\textsubscript{2}O\textsubscript{2} is present in the reaction system, the removal rate of H\textsubscript{2}S at 30min is 20.44%. With the increase of time, H\textsubscript{2}O\textsubscript{2} is gradually consumed and its decomposition is ineffective\textsuperscript{[5]}. After 4 hours of reaction, the removal rate of H\textsubscript{2}S decreases to 6.31%. H\textsubscript{2}O\textsubscript{2} can oxidize a certain amount of H\textsubscript{2}S.

When H\textsubscript{2}O\textsubscript{2} and TS-1 were present in the reaction system, it could be seen that the removal rate of H\textsubscript{2}S reached 88.39% after 30min of reaction, and remained at 82.84% after 4 hours of reaction. Compared with the above two system available: when H\textsubscript{2}O\textsubscript{2} and TS-1 exist alone, response 4 hours for the combined removal of H\textsubscript{2}S are both 28.07%, while H\textsubscript{2}O\textsubscript{2} with TS-1 exist at the same time, the reaction for 4 hours, the H\textsubscript{2}S removal rate of 82.84%, much higher than the sum of both individual exists H\textsubscript{2}S removal rate. It can be seen that TS-1 has synergistic effect with H\textsubscript{2}O\textsubscript{2} and has good desulfurization effect.

3.3. The effect of reaction temperature on the removal of H\textsubscript{2}S

In the desulfurization reaction, the reaction temperature has a great influence on the entire desulfurization system. In order to investigate the effect of reaction temperature on the removal of H\textsubscript{2}S, keep other conditions unchanged, the temperature was controlled at 10 ℃, 20 ℃ and 30 ℃ respectively to conduct experiments, and the removal effect of TS-1 on H\textsubscript{2}S at three temperatures was investigated. The result is shown in Fig. 4.
Fig. 4 Influence of different reaction temperature on desulfurization effect

Reaction conditions: TS-1 0.5 g, H2S 250 mg/m^3, 1% H2O2, pH=4.6

It can be seen from Fig. 4 that in the reaction system where H2O2 alone exists, the temperature increases from 10 °C to 30 °C, and the removal rate of H2S also increases. When the TS-1 exists alone, the removal rate of H2S at elevated temperature is also increased. Similarly, when both H2O2 and TS-1 exist simultaneously, the removal rate of H2S also increases with the increase of temperature.

When H2O2 and TS-1 coexist and react for 30 min at a temperature of 10 °C, the removal rate of H2S is 78.60%; When the temperature is 20 °C, the removal rate of H2S is 85.62%; When the temperature is 30 °C, the removal rate of H2S by the reaction system increases by about 5 percentage points to 90.74%. However as the reaction time progressed, the removal rate of H2S at the three temperatures decreased. After 4 hours of reaction, when the temperature is 10 °C, the removal rate of H2S is 75.90%; When the temperature is 20 °C, the removal rate of H2S is 79.67%; When the temperature is 30 °C, the removal rate of H2S is 80.34%. It can be concluded that when H2O2 and TS-1 exist alone, they are greatly affected by temperature, while the system composed of them is less affected by temperature. The reason may be that when H2O2 and TS-1 exist at the same time, the two will interact, thereby promoting the removal of H2S.

3.4. Effect of initial pH of solution on removal of H2S

The pH of the initial solution has a certain effect on the desulfurization of the TS-1/H2O2 reaction system. Study the catalytic oxidation ability of TS-1 on H2S under different pH. Since H2O2 is weakly acidic, in order to eliminate the influence of other chemical substances, especially alkaline substances, on the desulfurization experiment, when adjusting the pH of the solution, only dilute sulfuric acid was used to adjust the pH of the initial solution of the reaction system. In this paper, three reaction systems with different pH are selected for desulfurization experiments, and the pH is 1.45, 2, 4.6, respectively. The experimental results are shown in Fig. 5.
It can be seen from Fig. 5 that when pH is 4.6, the removal rate of H$_2$S was 88.39% after 30 minutes of reaction, and the removal rate of H$_2$S did not decrease basically after 3 hours of reaction; When pH is 2, the removal rate of H$_2$S in 30 minutes of reaction was 87.51%, and after three hours, the removal rate was 79.21%, which was a decrease of 8.3%; When pH is 1.45, the removal rate of H$_2$S in 30 minutes of reaction was 76.81%. After 3 hour, the removal rate of H$_2$S was 56.02%, a decrease of 20.79%. Compared with the above two conditions, the removal rate of H$_2$S is significantly reduced. It can be seen that, TS-1 has a certain degree of acid resistance. The TS-1/H$_2$O$_2$ system has a better catalytic oxidation effect on H$_2$S in a weakly acidic environment, but in a strong acid environment, the removal effect of H$_2$S is reduced.

4. Conclusions
In this paper, the influence of the concentration of H$_2$O$_2$, the reaction temperature and the initial pH of the solution on the desulfurization effect in the process of removing H$_2$S by TS-1 is studied. The experimental results show that the TS-1 has a good desulfurization effect and excellent catalytic performance in the catalytic oxidation of H$_2$S. Under the TS-1/H$_2$O$_2$ system, the removal rate of H$_2$S increases with the increase in the concentration of H$_2$O$_2$ and the increase in temperature. As the pH decreases, the acidity of the initial solution increases and the removal rate of H$_2$S decreases. TS-1 has a certain degree of acid resistance, and has a high catalytic effect on hydrogen sulfide in a weak acid environment, but the catalytic effect decreases with the increase of acidity.

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