Research on preparation of low bulk density Claus tail gas hydrogenation catalyst

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Abstract. With the continuous improvement of national energy conservation and emission reduction requirements, oil and natural gas production industry has increasingly strict requirements for SO₂ emission from tail gas. Nowadays, most of large and medium-sized natural gas purification plants and refineries adopt hydrogenation reduction tail gas treatment process to achieve ultra-low SO₂ emission, which puts forward high requirements for the activity, stability and economy of tail gas hydrogenation catalyst. In recent years, due to the high price of hydrogenation catalyst, it has become a research hot spot to reduce the cost of catalyst by reducing the bulk density. Traditional catalyst preparation process focused on the types and properties of support and active components, while the influence of alumina powder properties and preparation conditions have not been paid enough attention. With the extensive application of fine characterization methods and the further understanding of catalyst micro-structure, the influence of alumina powder properties and preparation conditions on the performance of catalyst are more and more obvious. In this paper, the Pseudo boehmite was investigated. TG, SEM, XRD and other characterization methods were used to study the preparation method of low bulk density Claus tail gas hydrogenation catalyst.

1. Background
The national standard GB31570-2015 “emission standard of pollutants for petroleum refining industry” has been issued and implemented, which puts forward strict requirements for SO₂ emission limit of tail gas from sulfur recovery unit, in which the emission limit for general areas is less than 400mg/m³, and that for key environmentally sensitive areas is less than 100mg/m³. According to the national standard GB39728-2020 "emission standard of air pollutants for onshore oil and gas exploitation industry", it is required that the SO₂ emission concentration of sulfur recovery unit with a total scale of more than 200t/d is less than 400mg/m³, and that of sulfur recovery unit with a total scale of less than 200t/d is less than 800mg/m³, which means natural gas purification plants will also face severe pressure to meet the production standards. Nowadays, most of large-scale natural gas purification plants and refineries use hydrogenation reduction tail gas treatment process to achieve ultra-low emissions, which puts forward higher requirements for the performance and cost of hydrogenation catalyst.

In recent years, due to the high price of hydrogenation catalyst, it has become a research hot spot to reduce the cost of catalyst by reducing the bulk density. Traditional catalyst preparation process focused on the types and properties of support and active components, while the influence of alumina powder properties and preparation conditions have not been paid enough attention. With the extensive application of fine characterization methods and the further understanding of catalyst micro-structure, the influence of alumina powder properties and preparation conditions on the performance of catalyst...
are more and more obvious. The pore distribution and phase structure of alumina powder, catalyst impregnation time, temperature, pH value, calcination temperature and atmosphere all have great influence on the final morphology and dispersion of the catalyst. For the calcination process, krijn P. de Jong \cite{1} pointed out that great importance should be attached to some side reactions, such as the oxidation reaction of organic compounds, the combination reaction of ammonium salt and nitrate, etc. Jelle.r.a\cite{2,3} found that the Co-Ni catalyst with smaller particle size and uniform distribution can be obtained by calcining in dilute nitrogen oxide atmosphere with the same carrier and the same impregnation and drying steps. For the impregnation methods, R. Nava\cite{4} found that the co-impregnation usually lead to high dispersion of Co and Mo in the hydrogenation catalyst than the step-by-step method;Mohans.Rana\cite{5} found that the hyrodesulfurization activity of Co-impregnation catalyst was higher than that of step-by-step impregnation catalyst. Kyriakos bourikas\cite{6} summarized the advantages and influencing factors of interfacial deposition in catalyst preparation.

In this paper, the Pseudo boehmite was investigated. the preparation method of low bulk density Claus tail gas hydrogenation catalyst was studied, and the optimal control conditions were selected to improve the comprehensive performance of the catalyst.

2. Experimental principle and methods

2.1. Experimental materials and instruments

The types/specifications of main reagents and instruments used in the preparation experiment of catalyst carriers and tail gas hydrogenation catalysts, as well as the manufacturers are shown in Table 1.

Table 1. Main reagents and instruments.

| Main reagents and instruments | type /specifications |
|---|---|
| Pseudo boehmite | 1#, 2#, 3#, 4#, 5# |
| Sesbania powder | Food-grade |
| Cobalt salt | AR |
| Molybdate salt | AR |
| Ammonia | AR |
| Electronic scale | T-000 type |
| Twin screw extruder | F-26 type |
| Electric blast drying oven | 101-3 |
| Microwave ashing furnace | PYRO-260 |

2.2. Experimental process

Carrier preparation: a certain quality of raw materials, pore expanding agent and adhesive solvent were mixed evenly, then kneaded, extruded, dried and finally calcinated to prepare the clover shaped alumina carrier.

Catalyst preparation: the solution containing active components was prepared, then the active components were loaded on the above-mentioned alumina support by impregnation method. The support was dried and calcined to prepare Claus hydrogenation catalyst.
2.3. Characterization methods

Dtg-60 TGA produced by Shimadzu company of Japan was used to determine the decomposition temperature of catalyst precursor. (1) The crystal structure analysis of the carrier was carried out on XRD produced by panalyomechanical. (2) The morphology of the catalyst was observed by jsm-6510 SEM produced by Japanese electronics company. (3) The specific surface area and pore structure were characterized by low temperature nitrogen adsorption method, and the instrument was ASAP2020 plush88 automatic adsorption instrument produced by American micromeritics company. (4) The bulk density and strength tests were carried out on the strength tester and bulk density tester produced by Deyi precision instrument company respectively. (5) The evaluation method of catalyst performance is shown in figure 1.

![Figure 1](image.png)

**Figure 1.** Process flow of Claus tail gas micro reactor (1-valve; 2-flowmeter; 3-water booster; 4-mixer; 5-pressure gauge; 6-preheater; 7-heater; 8-sampling point; 9-temperature measurement point; 10 reactor; 11 catalyst; 12 separator; 13 vessel; 14 condenser; 15 wet flowmeter; 16-cs2 bottle; 17 burning place).

3. Results and discussion

3.1. Investigation of alumina powder

Different pseudo boehmite materials were investigated and screened to meet the preparation requirements of low bulk density Claus hydrogenation catalyst. The specific surface area and pore structure of five typical materials of pseudo boehmite were determined by low temperature nitrogen adsorption desorption method. The results are shown in Table 2. The corresponding isotherms and pore size distribution of nitrogen adsorption desorption are shown in Figure 2 and Figure 3 respectively. It can be seen from the figures that 1#, 3#, 4#, and 5# have large specific surface areas, which are all above 400m²/g; the pore volume is also large, which are all above 1.0cm³/g. The average pore size of 1# is the largest, but its specific surface area and pore volume are smaller than those of 3#, 4# and 5#. The crystal phases of the five pseudo boehmite materials were determined by XRD. The results are shown in Figure 4. It can be seen from the figure that the pseudo boehmite 1# and 2# contain impurity peaks, while the other three kinds of raw materials are relatively pure without impurity crystalline phase. They are all γ-Al2O3 crystalline phase, and their crystallinity is not good, which also shows that the raw materials have large pore volume and specific surface area.
Table 2. Specific surface area and pore structure parameters of pseudo boehmite.

| Pseudo boehmite | Specific surface area m²/g | Pore volume cm³/g | Average pore diameters nm |
|-----------------|---------------------------|-------------------|--------------------------|
| 1#              | 405                       | 1.11              | 9.9                      |
| 2#              | 323                       | 0.87              | 9.0                      |
| 3#              | 424                       | 1.08              | 9.35                     |
| 4#              | 475                       | 1.22              | 9.27                     |
| 5#              | 464                       | 1.24              | 9.56                     |

Figure 2. Nitrogen adsorption and desorption isotherms of pseudo boehmite.
Based on the above experimental results, considering the specific surface area, pore structure, phase and price of the five pseudo boehmite, pseudo boehmite 5# was selected as the raw material to prepare low bulk density hydrogenation catalyst carrier.

3.2. Determination of calcination temperature of precursor by TGA

The decomposition temperature of catalyst support precursor was determined by TGA. The results of TGA are shown in Figure 5. It can be seen from the figure that there is a small exothermic peak near 115°C, where water is decomposed; there is a very large exothermic peak at 260°C, which should be the decomposition of a large amount of organic matter such as pore expanding agent and binder; there is also a small exothermic peak near 430°C, where the decomposition of some impurities should take place. Therefore, the calcination temperature was determined at 450°C.
3.3. Characterization of carrier performance

The physical and chemical properties of the carrier are analyzed. The test results of strength, bulk density and specific surface area are shown in Table 3, and the results of SEM are shown in Figure 6. It can be seen from the SEM that there are many macropores above micron level, which provides a large number of interfaces for the next impregnation of active components, and is helpful to improve the catalytic activity.

| Sample          | Strength, N/cm | Bulk density, g/cm³ | Specific surface area, m²/g |
|-----------------|----------------|---------------------|----------------------------|
| Catalyst carrier| 181            | 0.49                | 310                        |

Figure 5. TGA analysis.

Table 3. Strength, bulk density and specific surface area of catalyst carrier

Figure 6. SEM photograph.
3.4. Investigation of catalyst performance

The catalyst sample was prepared by impregnation method, and its activity was evaluated. The results are shown in Figure 7 and Figure 8. It can be seen from the figures that: with the decrease of catalyst operation temperature from 280 °C to 230 °C, the SO₂ hydrogenation conversion rate decreases from 99.8% to 99.5%, which has little effect on the total sulfur of tail gas; the hydrolysis rate of organic sulfur decreases from 98.5% to 88.4%, which has a great decrease, and the total sulfur of tail gas increases from 21ppm to 119ppm. However, the temperature of industrial tail gas hydro-hydrolysis is generally above 240 °C. At this temperature, the catalyst has very good activity of SO₂ hydrogenation and organic sulfur hydrolysis.

![Figure 7. Function of the relationship between catalyst operating temperature and SO₂ conversion rate.](image)

![Figure 8. The relationship between catalyst operating temperature and organic sulfur conversion rate.](image)

4. Conclusion

(1) Screening of alumina powder. Through the characterization of specific surface area, pore volume and XRD, the pseudo boehmite powder with specific surface area of 464m²/g, pore volume of 1.24cm³/g and average pore size of 9.56nm was selected.

(2) Preparation of catalyst carrier. The catalyst carrier with strength of 181 N/cm, bulk density of 0.49g/cm³ and specific surface area of 310m²/g was prepared.

(3) Investigation of catalyst activity. The catalyst was prepared by impregnation method, and its activity was investigated. The catalyst has very good SO₂ hydrogenation and organic sulfur hydrolysis activity.
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