Research article

Development and industrial application of catalyzer for low-temperature hydrogenation hydrolysis of Claus tail gas

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Abstract

With the implementation of more strict national environmental protection laws, energy conservation, emission reduction and clean production will present higher requirements for sulfur recovery tail gas processing techniques and catalyzers. As for Claus tail gas, conventional hydrogenation catalyzers are gradually being replaced by low-temperature hydrogenation catalyzers. This paper concentrates on the development of technologies for low-temperature hydrogenation hydrolysis catalyzers, preparation of such catalyzers and their industrial application. In view of the specific features of SO_2 hydrogenation and organic sulfur hydrolysis during low-temperature hydrogenation, a new technical process involving joint application of hydrogenation catalyzers and hydrolysis catalyzers was proposed. In addition, low-temperature hydrogenation catalyzers and low-temperature hydrolysis catalyzers suitable for low-temperature conditions were developed. Joint application of these two kinds of catalyzers may reduce the inlet temperatures in the conventional hydrogenation reactors from 280 °C to 220 °C, at the same time, hydrogenation conversion rates of SO_2 can be enhanced to over 99%. To further accelerate the hydrolysis rate of organic sulfur, the catalyzers for hydrolysis of low-temperature organic sulfur were developed. In lab tests, the volume ratio of the total sulfur content in tail gas can be as low as 131×10^{-6} when these two kinds of catalyzers were used in a proportion of 5:5 in volumes. Industrial application of these catalyzers was implemented in 17 sulfur recovery tail gas processing facilities of 15 companies. As a result, Sinopec Jinling Petrochemical Company had outstanding application performances with a tail gas discharging rate lower than 77.9 mg/m³ and a total sulfur recovery of 99.97%.
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Keywords: High-sulfur natural gas; Claus; Tail gas; Low-temperature; Hydrogenation; Hydrolyzation; Catalyzer; Industrial application

1. Introduction

As the requirements in China on clean production, energy conservation and emission reduction, and environmental protection get higher, the requirement on SO_2 emission for refinery plants and natural gas purification plants becomes increasingly strict. Sulfur recovery and tail gas treatment are the primary technologies to treat sulfur acid gas. The reduction—absorption procedure widely used in large-scale facilities is the key technology to ensure SO_2 emission in tail gas to meet the standard [1].

Since the 1970s, a major progress has been made in reduction—absorption procedure for sulfur recovery and tail gas treatment, greatly reducing the SO_2 emission in tail gas. Traditional reduction—absorption procedure requires high inlet temperature of reactor, which can only be achieved by electric heating or online combustion. In order to meet the requirement of clean production and energy saving, the reactivity of catalyzers has been raised and the activity energy of catalyzers decreased to realize low-temperature hydrogenation reduction; the surplus medium-pressure steam in equipment is used for heat transfer to save energy [2,3].

Low-temperature hydrogenation catalyzer is the key to low-temperature hydrogenation reduction procedure. Co–Mo/γ-Al_2O_3 is the most widely used catalyzer in industrial application at present, which can simultaneously hydrogenate SO_2 and hydrolyze organic sulfur at the reactor inlet temperature of 230–250 °C. Therefore, the available low-temperature hydrogenation catalyzer is only a transitional catalyzer between high-temperature hydrogenation catalyzers and low-temperature hydrogenation catalyzers. The application of the catalyzer at low temperature could result in Claus side reaction, which will lead to the rapid decrease of organic sulfur hydrolyzing efficiency and the increase of SO_2 concentration in tail gas [4–7].

Based on the SO_2 hydrogenation and organic sulfur hydrolyzation in low-temperature hydrogenation reaction, a new procedure using hydrogenation and hydrolyzation catalyzer jointly is proposed in this study. Low-temperature hydrogenation and low-temperature hydrolyzation catalyzers applicable to low-temperature condition have been developed respectively, and the inlet temperature of traditional hydrogenation reactor was reduced from 280 °C to 220 °C by joint application of the two catalyzers. In addition, the hydrogenating and hydrolyzing efficiency has also been improved. The Sinopec Jinling Petrochemical Company is taken as an example to demonstrate the effect of the industrial application of the two catalyzers.

2. Laboratory experiment

2.1. Preparation of catalyzers

A low-temperature hydrogenation catalyzer and a low-temperature hydrolyzation catalyzer were developed respectively for hydrogenation and hydrolyzation reactions, hereinafter referred to as Catalyzer A and Catalyzer B. The preparation of Catalyzer A involves preparing a new carrier by band extrusion firstly, impregnating the new carrier with active components, and then drying and calcinating the new carrier to get the final product. The preparation of Catalyzer B involves impregnating spherical carrier γ-Al_2O_3 with active component, and then drying and calcinating to get the final catalyzer. In order to compare the reactivity of the catalyzers, a low-temperature hydrogenation catalyzer made by a foreign company (referred to as Catalyzer C) was selected to do comparison experiment.

2.2. Laboratory reactivity evaluation equipment

A fixed bed reactor was used to evaluate the reactivity of different catalyzers, and the specific process is shown in Fig. 1. H_2S, SO_2, H_2, CO_2 and N_2 were provided by gas steel cylinders, CS_2 and steam were carried by CO_2 and N_2 bubbling respectively.

2.3. Reactivity evaluation and characterization of catalyzers

The air speed and reaction temperature are 1500 m^3/h and 220 °C respectively in the catalyzer reactivity evaluation if not
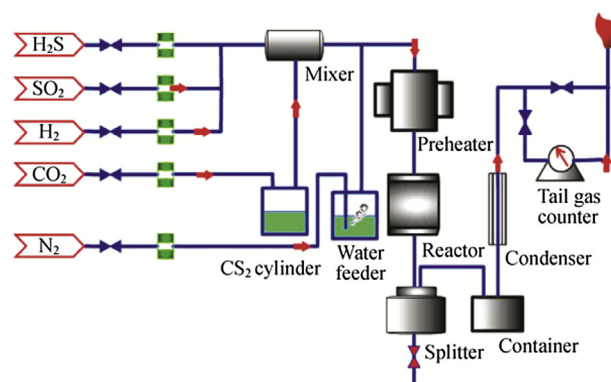

Fig. 1. Flow of laboratory catalyzer reactivity evaluation.

noted specifically. The gas composition used in evaluating catalyzer hydrogenating, hydrolyzing, and hydrogenating-hydrolyzing performances is listed in Table 1. The composition of feed gas and tail gas were tested by Agilent 7890 gas chromatography with TCD detector. The total sulfur content except H_2S (hereinafter referred to as total sulfur content of tail gas) was tested by trace sulfur analyzer.

Catalyzer bulk density, attrition rate, crush strength and specific surface area were tested according to the standards of GB/T 6286-1986, HG/T 2976-1999, HG/T 2782-1996 and GB/T 5816-1995. JEOL JSM6501 SEM was used in the catalyzer characterization.

3. Experimental results

3.1. Physico-chemical properties of catalyzers

Table 2 shows the physic-chemical properties of the catalyzers, including bulk density, attrition rate, crush strength and specific surface area. This indicates that the catalyzers are applicable to industrial application.

3.2. Evaluation of hydrogenation catalyzers

Fig. 2 shows the SO_2 hydrogenating performance of Catalyzer A and Catalyzer B at different reaction temperatures. This figure demonstrates that, when the reaction temperature is 280 °C, the SO_2 hydrogenating rate of Catalyzer A is 99.7%, which is slightly higher than that of Catalyzer C; SO_2 hydrogenating rate decreases with the decrease of reaction temperature, when the reaction temperature reduces to 210 °C, the SO_2 hydrogenating rate of Catalyzer A reduces to 98.3%. In contrast, the SO_2 hydrogenating rate of Catalyzer C couldn't be accurately tested due to the production of massive sulfur in tail gas as a result of Claus side reaction at this temperature.

Fig. 3 shows the SEM image of Catalyzer A and Catalyzer C. It can be seen from this figure that the crystals of Catalyzer A are smaller in size, allowing even distribution of active components on the catalyzer surface. In comparison, crystals on Catalyzer C are large in size (at micron scale), and