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A Review of the Performance and Application of Catalysts for Sulfuric Acid Production

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Abstract. As one of the most widely used basic chemical raw materials globally, the sulfuric acid production process plays an irreplaceable role in chemical, metallurgical, and agricultural fields. The core link of its production process is the catalytic oxidation of sulfur dioxide (SO_2) to sulfur trioxide (SO_3). Catalysts directly determine production efficiency, energy consumption, and product quality. This paper employs case analysis and literature review to systematically summarize the mainstream catalyst types in sulfuric acid production, including vanadium-based, iron-based, platinum-based, and novel composite oxide catalysts. A comparison is conducted from the perspectives of catalytic activity, selectivity, and stability, summarizing the technical characteristics and application boundaries of each type. Meanwhile, in light of the current challenges faced by the sulfuric acid industry, such as high-toxic flue gas treatment, the development trends of catalyst technology are highlighted, providing references for optimizing industrial catalyst selection and novel catalyst research and development.

Keywords: Sulfuric acid production, Contact Process, Catalysts, Performance Comparison, Fe_2O_3

1. Introduction

The global annual output of sulfuric acid has exceeded 300 million tons, with applications in chemical fertilizers, metallurgy, the chemical industry, medicine, and other fields. Relevant data show that over 90% of sulfuric acid is produced via the contact process. This process consists of three core steps: roasting raw materials to generate SO_2, catalytic oxidation of SO_2 to SO_3, and subsequent absorption of SO_3 to produce sulfuric acid. Among these steps, the catalytic oxidation of SO_2 has the slowest reaction rate, becoming the rate-limiting step of the entire production process. As the core functional material of this step, the performance of catalysts directly determines the production capacity ceiling, energy consumption level, and environmental protection of sulfuric acid production [1]. Since vanadium-based catalysts replaced platinum-based catalysts as the mainstream in the early 20th century, catalysts for sulfuric acid production have undergone multiple generations of iteration. In recent years, the production environment of the sulfuric acid industry has undergone significant changes. Environmental requirements such as low sulfur emissions and changes in raw material structure caused by the utilization of low-grade pyrite and high-arsenic flue gas have continuously driven traditional catalysts to adapt to new challenges [2].

Currently, there is a lack of systematic and comprehensive comparative analysis of the performance of various existing sulfuric acid production catalysts within the industry. Therefore, this paper explores various catalysts to clarify their applications, core advantages and disadvantages, and performance limitations. This paper aims to provide theoretical guidance for breaking through the bottlenecks in sulfuric acid production and promoting the industry's transformation towards higher efficiency, lower carbon emissions, and greener practices.

2. Mainstream catalyst types

2.1. Vanadium-based catalysts

Vanadium-based catalysts are one of the types widely used in the current sulfuric acid production industry. The core active component is V_2O_5, the carrier is SiO_2 (or diatomite), and the promoter is K_2O (or Na_2O, Cs_2O), with a typical formula of V_2O_5-K_2O-SiO_2 [3]. These catalysts are characterized by high technical maturity. Their catalytic performance has been continuously improved by optimizing the ratio (e.g., introducing Cs_2O to enhance low-temperature activity) and adopting porous SiO_2 to increase the specific surface area of the carrier. Current mainstream models (such as S101, VK-38) have been industrially applied for more than 50 years [4].

The vanadium content, potassium-vanadium ratio, and sodium-vanadium ratio are key factors affecting the low-temperature activity of the catalyst. Studies have shown that the catalyst exhibits the highest activity when the component contents are as follows: vanadium content 6.3%, potassium-vanadium ratio of 2.7, and sodium-vanadium ratio of 2.2 [4]. Under these conditions, the low-temperature activity of the catalyst can reach 44.8% at 410°C, which is much higher than the standard of $\geq 35\%$ specified in Experimental Methods for Vanadium Catalysts Used in Sulfuric Acid Production [3].

2.2. Iron-based catalysts

Iron-based catalysts are among the earliest used for SO_2 oxidation, with Fe_2O_3 as the core active component. To improve catalytic activity and structural stability, promoters such as CuO, MnO_2, and Cr_2O_3 are typically added, with a typical formula of Fe_2O_3-CuO-MnO_2. The significant advantages of iron-based catalysts are low raw material cost and excellent low-temperature activity. Their critical drawback lies in inadequate high-temperature stability. Owing to this limitation, iron-based catalysts were replaced by vanadium-based catalysts in the mid-20th century and are currently limited to small-scale, low-temperature processes, such as the treatment of low-temperature roasting flue gas from low-grade pyrite [3].

2.3. Platinum-based catalysts

Platinum-based catalysts use Pt as the core active component, while certain modified formulations substitute Pt with palladium (Pd) or rhodium (Rh), with Al_2O_3 as the carrier. They possess extremely high low-temperature activity and selectivity, achieving over 99% conversion at 300°C. However, they have two intractable shortcomings that restrict large-scale industrial application. Extremely high cost due to theexpensive price and large dosage of platinum. Poor toxicity resistance, trace amounts of As_2O_3 and SeO_2 in the feed gas can cause permanent poisoning of the catalyst. Currently, they are only occasionally used in laboratory research or special high-purity sulfuric acid production scenarios [3].

2.4. Novel composite oxide catalysts

Novel composite oxide catalysts have been a research hotspot over the past decade, with the "active component-composite carrier" as the core structure. Currently, two technically mature mainstream series have been developed.

2.4.1. CeO_2-ZrO_2-V_2O_5 series

Catalysts of this series adopt a CeO_2-ZrO_2 solid solution as the carrier and V_2O_5 as the active component, with the active component loading controlled between 3% and 8%. Their core advantage are in the synergy between dual functions: oxygen storage capacity and toxicity resistance. On one hand, the valence cycle between Ce^{3+} and Ce^{4+} enables rapid transfer of oxygen species, improving the oxidation kinetics of SO_2. On the other hand, the introduction of Zr^{4+} can inhibit the growth of CeO_2 grains, enhancing carrier stability. Meanwhile, the adsorption capacity of CeO_2 for arsenic trioxide (As_2O_3) reaches 80-120 mg/g, much higher than that of traditional SiO_2 carriers (5-10 mg/g). Specifically, stable Ce-As-O compounds form to fix toxins, avoiding poisoning of active sites [5].

Currently, the HC-1 model in this series has completed a 10,000-hour pilot test in an arsenic-containing pyrite-based sulfuric acid enterprise in Yunnan. The results show that under the condition of 0.12% As_2O_3 in the feed gas, the conversion rate of SO_2 remains stable above 98.5%, which is 12%-15% higher than that of traditional vanadium-based catalysts [5].

2.4.2. TiO_2-WO_3-V_2O_5 series

The TiO_2-WO_3-V_2O_5 series refers to catalysts with perovskite-type TiO_2 as the matrix, WO_3 as the promoter, and V_2O_5 as the active component. The typical mass ratio of the three components is 2:10:88, with WO_3 loading between 8% and 12% and V_2O_5 loading between 1% and 3%. Its typical feature is excellent low-temperature activity. The semiconductor properties of TiO_2 can enhance electron transfer between V^{4+} and the carrier, reducing the active temperature to 380-400°C, at which the conversion rate of sulfur dioxide reaches 98.5%. Compared with the 97% conversion rate of traditional vanadium-based catalysts at 400°C, the active temperature is reduced by 20°C, making it suitable for the low-temperature roasting flue gas treatment process of low-grade pyrite. Meanwhile, WO_3 can form Ti-O-W bonds with TiO_2, inhibiting the agglomeration of V_2O_5 and improving catalyst stability.

This series has undergone a pilot test in a low-grade pyrite-based sulfuric acid plant in Guizhou. Relevant data show that the catalytic cost per ton of sulfuric acid is controlled at 2.2 yuan, which is slightly higher than traditional catalysts, but the energy consumption of the low-temperature process is reduced by 15%, and the comprehensive benefit is increased by 8% [5]. In general, novel composite oxide catalysts aim to solve the problems of poor toxicity resistance of traditional vanadium-based catalysts and weak stability of iron-based catalysts [5].

3. Horizontal comparison of mainstream catalyst performances

3.1. Basic catalytic performance

3.1.1. Catalytic activity

Catalytic activity is the core indicator for valuating catalyst efficiency, mainly assessed by two key parameters: active temperature (the minimum temperature at which SO_2 conversion rate reaches 99%) and conversion rate in the full temperature range.

Vanadium-based catalysts: The active temperature range is from 400-420°C. The catalyst exhibits a conversion rate of about 80%-85% at 350°C and over 99.5% at 500°C. Its temperature adaptability covers the industrial three-stage conversion process of 400-550° C range required for the industrial three-stage conversion process, making them the catalysts with the widest temperature adaptability for sulfuric acid production to date [4].

Iron-based catalysts: Active temperature 350-370°C, optimal low-temperature activity (85%-90% conversion at 350°C) but significant high-temperature activity attenuation (conversion rate drops below 98% at 500°C), only suitable for low-temperature processes.

Platinum-based catalysts: Lowest active temperature (300-320°C), achieving 99% conversion at 300°C, but prone to sintering at high temperatures (activity drops sharply above 450°C) with a narrow temperature window.

Novel composite oxide catalysts: The active temperature varies greatly with formulas. The CeO_2-ZrO_2-V_2O_5 series has an active temperature of about 420-450°C (high-temperature activity close to vanadium-based catalysts), and the TiO_2-WO_3-V_2O_5 series has an active temperature of about 380-400°C (low-temperature activity superior to traditional vanadium-based catalysts) [5].

The excellent low-temperature activity of iron-based and platinum-based catalysts stems from Fe^{3+}'s ability to rapidly adsorb SO_2 molecules, form bonds through oxygen atoms, and promote the conversion of O_2 to O^{2-}. The excellent low-temperature activity of iron-based and platinum-based catalysts enables efficient SO_2 oxidation at relatively low temperatures [2].

3.1.2. Selectivity and stability

Catalyst selectivity refers to the ability of a catalyst to preferentially increase the rate of a specific reaction while inhibiting other reactions (such as the overoxidation of SO_2 to form H_2SO_4 mist and sulfates) in multiple reactions, directly affecting product purity and raw material utilization rate.

Among the three types of industrial catalysts, platinum-based catalysts have the highest selectivity (99.9%) but no industrial value due to cost constraints. Vanadium-based catalysts have a selectivity of 99.7%-99.8% with minimal by-products (such as sulfates), meeting the requirements of industrial high-purity sulfuric acid production [4]. Iron-based catalysts have the lowest selectivity (98.5%-99.0%), and side reactions between SO_2 and O_2 are prone to occur at low temperatures. Novel composite oxide catalysts have a selectivity of 99.5%-99.7%, comparable to vanadium-based catalysts. The CeO_2-ZrO_2 or TiO_2-WO_3 composite carrier can inhibit the agglomeration of active components and reduce side reaction active sites [5].

3.2. Environmental adaptability

3.2.1. Stability

Stability is measured by the conversion rate change after 1000 hours of continuous operation. Vanadium-based catalysts have a change rate of only 2%-3% and a service life of 5-8 years [3]. Iron-based catalysts have a change rate of 8%-10% and a service life of only 2-3 years (due to the loss of active sites caused by Fe_2O_3 crystal agglomeration). Novel composite oxide catalysts have better stability than iron-based catalysts (change rate 3%-5%), but their long-term industrial stability still needs verification (current pilot test life is about 4 years) [5].

3.3. Toxicity resistance

Common toxins in the feed gas of sulfuric acid production include As_2O_3 (product of pyrite roasting), SeO_2 (flue gas from non-ferrous metal smelting), and dust in the feed gas necessitates catalysts with robust poison resistance, which is a critical factor determining their practical application.

Vanadium-based catalysts have a moderate tolerance to As_2O_3, suffering a conversion rate decline of $\leq 10\%$ when As_2O_3 content in the feed gas is $\leq 0.05\%$. However, significant poisoning occurs under high-toxic flue gas ($As_2O_3 \geq 0.1\%$) [4]. Iron-based catalysts possess the poorest toxicity resistance. Trace amounts of As_2O_3 ($\geq 0.02\%$) can reduce activity by 20% or more. Platinum-based catalysts are highly susceptible to permanent poisoning even by trace (ppm-level) toxins, resulting in extremely poor practical tolerance. Novel composite oxide catalysts (e.g., the CeO_2-ZrO_2-V_2O_5 series) demonstrate optimal toxicity resistance. The CeO_2 component cant effectively immobilizes As_2O_3 through the adsorption of CeO_2, with a conversion rate drop of only 5%-8% when As_2O_3 content is 0.1%, suitable for high-toxic flue gas scenarios [5].

3.4. Economy and industrial applicability

Economy is evaluated based on three dimensions: initial cost per unit mass, service life, and the resultant catalytic cost per ton of sulfuric acid produced, as summarized in Table 1.

Table 1. Economic comparison and core applications of sulfuric acid catalysts [2,4,5]

Catalyst type	Unit cost (CNY/kg)	Service life (years)	Catalytic cost per Ton H_2SO_4 (CNY/ton)	Core application scenarios
Vanadium-based	80 - 100	5 - 8	1.0 - 1.5	Large-scale conventional production (from sulfur or high-grade pyrite) [4].
Iron-based	30 - 50	2 - 3	1.5 - 2.0	Small-scale, cost-sensitive, or low-temperature processes (e.g., low-grade pyrite) [2].
Platinum-based	5000 - 8000	1 - 2	50 - 80	Laboratory research or ultra-small-scale, high-purity production [2].
Novel composite oxides	150 - 200	4 - 5 (est.)	1.8 - 2.5	Production from high-toxicity feed gas (e.g., As-containing pyrite, smelting flue gas) [5].

As shown in table 1, vanadium-based catalysts is the optimal choice for conventional large-scale production for the balanced efficiency, long service life, and low overall cost [4]. Iron-based catalysts are suitable for cost-sensitive scenarios where initial investment is a primary constraint.

Novel composite oxide catalysts (particularly the CeO_2-ZrO_2-V_2O_5 series), despite a higher initial cost, offer the best technical solution for processing high-toxicity feed gases, owing to their superior poison resistance [4]. Platinum-based catalysts are confined to laboratory at most of the time.

In addition to initial catalyst cost and service life, end-of-life management—particularly the recovery and regeneration of spent catalysts—contributes to overall economic performance. Established recovery processes for vanadium-based catalysts have achieved vanadium recovery rates exceeding 95%, reducing both raw material consumption and waste disposal costs [6].

4. Development trends of catalyst technology

4.1. Performance optimization of traditional catalysts

For vanadium-based catalysts, future research should focus on introducing new promoters (such as Rb_2O, Cs_2O) to reduce the active temperature and improve the carrier structure. By adopting mesoporous SiO_2 and honeycomb carriers, it can enhance toxin adsorption capacity and toxicity resistance [4]. For iron-based catalysts, the core is to address the problem of poor stability. For example, nano-scale iron trioxide (Fe_2O_3) can be used to improve structural stability; anti-agglomeration promoters such as aluminum oxide (Al_2O_3) can be added to inhibit the crystal agglomeration of active components, thereby extending the service life and expanding its application scope in low-temperature processes.

4.2. Future directions

The development of High-efficiency and toxin-resistant catalysts is the core direction. The focus will be on further optimizing the composition and structure of composite carriers such as CeO_2-ZrO_2 and TiO_2-WO_3, enhancing the adsorption and fixation capacity of toxins such as As and Se, thereby enabling them to handle more complex feedstock gas compositions [5].

Driven by environmental concerns, the direction of low-vanadiumvanadium-free catalysts will become an important trend. Future efforts will focus on developing low-vanadium catalysts (containing $\leq 1\%$ V_2O_5) or vanadium-free alternatives (e.g., the Cu-Mn-O series) to reduce both environmental risk and raw material cost without compromising catalytic performance. Additionally, the use of stimuli-responsive materials (e.g., to temperature or toxin concentration) will be explored to achieve dynamic modulation of catalyst active sites, maintaining optimal performance across varying process conditions.

4.3. Catalyst recovery and recycling

With the tightening of environmental protection requirements, the recovery and regeneration technology of vanadium-based catalysts will receive greater focus. As a toxic heavy metal, vanadium in waste catalysts will cause soil and water pollution if directly discharged. Recovery can not only reduce environmental risks but also realize the resource reuse of valuable metals such as V and K. Recovery technologies for waste vanadium-based catalysts have been developed, with reported vanadium recovery rates exceeding 95% [7]. Future development in this field will focus on optimizing the leaching process to reduce energy consumption and reagent costs during recovery.

In summary, the future of sulfuric acid catalyst technology will develop towards greater efficiency, a low carbon footprint, enhanced toxin resistance, and improved environmental sustainability. Through the optimization of traditional catalyst performance, development of novel catalytic materials, and advances in recovery and recycling technologies, the industry will adapt to the needs of diversified raw material structures and green processes in the sulfuric acid industry.

5. Conclusion

This paper systematically summarizes the technical background of mainstream catalysts for sulfuric acid production, clarifying the application boundaries and technical characteristics of each type of catalyst. Research shows that vanadium-based catalysts have balanced comprehensive performance, dominate conventional large-scale production, and will remain the industrial first choice in the short term. Iron-based catalysts, with the advantages of low cost and excellent low-temperature activity, are suitable for small-scale low-temperature processes. Novel composite oxide catalysts (especially the CeO_2-ZrO_2-V_2O_5 series) have made breakthroughs in toxicity resistance, becoming the core development direction for sulfuric acid production from high-toxic flue gas. It further points out that through the optimization of traditional catalyst performance, the research and development of novel catalysts, and the upgrading of recovery and recycling technology, it will adapt to the needs of diversified raw material structures and green processes.

This paper also has certain limitations. The performance comparison data are mainly based on published literature and pilot test reports, lacking long-term verification data from industrial large-scale applications under different working conditions; the discussion on the preparation process optimization of novel composite oxide catalysts is insufficient. In the future, further research can be carried out on the optimization analysis of catalyst performance and process parameters.

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