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Sulfur Resistance of Ba-Pt/γ-Al_2O_3 Pellets for Carbonyl Sulfide Hydrolysis

(Rintangan Sulfur Pelet Ba-Pt/γ- Al_2O_3 untuk Hidrolisis Karbonil Sulfida)

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ABSTRACT

The catalytic hydrolysis of carbonyl sulfide (COS) was studied using γ-Al_2O_3 pellets promoted with platinum (Pt) and barium (Ba). A series of catalysts, including γ-Al_2O_3, 0.1Pt/γ-Al_2O_3, and Ba-promoted Pt/γ-Al_2O_3 with varying Ba loadings (0.5-3.0 wt%) were evaluated in terms of catalytic activity and sulfur tolerance. Catalyst deactivation after 180 min was quantified and correlated with sulfur retention determined by CHNS analysis. Bare γ-Al_2O_3 resulted in the most severe deactivation (25.56%), whereas the Pt modification markedly improved the catalyst durability, reducing the degree of deactivation to 7.78%. Among the Ba-promoted catalysts, 0.5Ba-0.1Pt/γ-Al_2O_3 exhibited the best performance, showing the lowest deactivation (7.73%) and the lowest sulfur retention (0.0427 wt%). In contrast, higher Ba loadings increased sulfur accumulation (up to 0.1259 wt%) and resulted in moderately higher deactivation (9.14-10.04%). TGA/DTG analysis of fresh and spent catalysts further supported the sulfur retention mechanism. This suggests that Pt improves sulfur tolerance by facilitating a more uniform distribution of sulfur species, whereas Ba enhances resistance by stabilizing and trapping sulfur species on the catalyst surface. These findings demonstrate that an appropriate balance of Pt and Ba loading is essential for improving catalyst durability, with 0.5Ba-0.1Pt/γ-Al_2O_3 identified as the optimal composition for COS hydrolysis.

Keywords: Barium promotion; catalyst deactivation; COS hydrolysis; platinum catalyst; sulfur poisoning; γ-Al_2O_3 pellets

ABSTRAK

Hidrolisis pemangkin karbonil sulfida (COS) telah dikaji menggunakan pelet γ-Al_2O_3 yang dipromosikan dengan platinum (Pt) dan barium (Ba). Satu siri pemangkin, termasuk γ-Al_2O_3, 0.1Pt/γ-Al_2O_3 dan Pt/γ-Al_2O_3 yang dipromosikan oleh Ba dengan pelbagai beban Ba (0.5-3.0 wt%) telah dinilai dari segi aktiviti pemangkin dan toleransi sulfur. Penyahaktifan pemangkin selepas 180 minit telah diukur dan dikaitkan dengan pengekalan sulfur yang ditentukan oleh analisis CHNS. γ-Al_2O_3 kosong menghasilkan penyahaktifan yang paling teruk (25.56%), manakala pengubahsuaian Pt telah meningkatkan ketahanan pemangkin dengan ketara, mengurangkan tahap penyahaktifan kepada 7.78%. Antara mangkin yang digalakkan oleh Ba, 0.5Ba-0.1Pt/γ-Al_2O_3 mempamerkan prestasi terbaik, menunjukkan penyahaktifan terendah (7.73%) dan pengekalan sulfur terendah (0.0427 wt%). Sebaliknya, pemuatan Ba yang lebih tinggi meningkatkan pengumpulan sulfur (sehingga 0.1259 wt%) dan mengakibatkan penyahaktifan yang agak tinggi (9.14-10.04%). Analisis TGA/DTG bagi mangkin segar dan terpakai menyokong lagi mekanisme pengekalan sulfur. Ini menunjukkan bahawa Pt meningkatkan toleransi sulfur dengan memudahkan taburan spesies sulfur yang lebih seragam, manakala Ba meningkatkan rintangan dengan menstabilkan dan memerangkap spesies sulfur pada permukaan mangkin. Penemuan ini menunjukkan bahawa keseimbangan pemuatan Pt dan Ba yang sesuai adalah penting untuk meningkatkan ketahanan mangkin dengan 0.5Ba-0.1Pt/γ-Al_2O_3 dikenal pasti sebagai komposisi optimum untuk hidrolisis COS.

Kata kunci: Hidrolisis COS; keracunan sulfur; mangkin platinum; pelet γ-Al_2O_3; penyahaktifan mangkin; promosi Barium

INTRODUCTION

The integrated gasification combined cycle (IGCC) technique has been introduced for electricity generation because of its higher thermal efficiency than that of conventional pulverized coal-fired systems. The IGCC can also utilize diverse feedstocks, such as biomass and municipal wastes, offering greater flexibility in energy production. Gasification converts carbonaceous materials into valuable gases such as carbon monoxide and hydrogen. However, under high-temperature and oxygen-deficient conditions, carbonyl sulfide (COS) inevitably forms (West et al. 1998). COS is recognized as a toxic compound that poses risks to human health, contributes to environmental pollution, and deactivates downstream catalysts in industrial processes (Lei et al. 2023; Renda, Barba & Palma 2022; Sun et al. 2014; West et al. 1998; Zhao et al. 2013).

To remove COS, several techniques, including hydrogenolysis, hydrolysis, and adsorption, have been investigated (Kim et al. 2018; Nimthuphariyha et al. 2021; Wang et al. 2014). Among these, catalytic hydrolysis is considered one of the most promising methods (Lei et al. 2023; Renda, Barba & Palma 2022; Zi et al. 2024). It is thermodynamically favorable, applicable over a wide temperature range, and does not require molecular hydrogen, thereby reducing operational costs. In addition, catalytic hydrolysis has also been integrated with adsorptive processes to enhance overall sulfur removal efficiency (Wang et al. 2024). However, since sulfur-containing species are directly involved in the reaction, catalyst selection is critical in terms of both activity and long-term stability.

Previous studies have explored various supports and modifications to improve COS hydrolysis performance. For example, pristine coal-based activated carbon (CAC) and alumina (Al_2O_3)-modified CAC were compared, showing that compared with pristine CAC, Al_2O_3/CAC achieved higher COS hydrolysis activity, particularly at temperatures above 50 °C. However, high relative humidity was reported to significantly reduce COS hydrolysis efficiency (Sun et al. 2014). Similarly, Al_2O_3 has been widely reported as an effective support, and its performance can be further enhanced by incorporating transition metals such as Pt, Fe, Cu, Ni, and their mixed oxides (Kim et al. 2012; Song et al. 2020; Wang et al. 2014; West et al. 2001). Another study on low-temperature COS hydrolysis (<100 °C) using modified walnut shell biochar doped with Fe–Cu–KOH mixed oxides reported improved activity, although sulfate formation remained the primary cause of catalyst deactivation (Song et al. 2017). Surface hydroxyl groups (Al–OH) on Al_2O_3, formed via the dissociative adsorption of water on Lewis acid–base sites, are widely recognized as key active sites in COS hydrolysis. These hydroxyl groups act as nucleophilic centers that react with COS to form intermediate species, which subsequently decompose into H_2S and CO_2 (Feng et al. 2025; West et al. 1998). During operation, the availability of surface –OH is dynamically maintained by water in the feed. However, sulfur-containing species can interact with or block these hydroxyl groups, leading to catalyst deactivation. Therefore, the preservation of surface hydroxyl groups is essential for sustaining catalytic activity.

Catalyst deactivation, particularly due to sulfur poisoning, remains among the most critical challenges in COS hydrolysis. Recent studies on poisoning-resistant catalysts based on γ-Al_2O_3 have focused on surface modification and promoter addition to mitigate sulfur accumulation (Nimthuphariyha et al. 2021; Sun et al. 2024). Sulfur species tend to accumulate on active metal sites, blocking catalytic centers and leading to rapid loss of activity. This process not only shortens the catalyst lifetime but also reduces the conversion efficiency, making sulfur resistance a key factor in catalyst design. To enhance catalytic performance and durability, modification strategies such as alkaline-earth metal doping have been introduced. It has been reported that oxygen vacancies and surface basic sites play important roles in sulfur adsorption and subsequent deactivation (Kim et al. 2012). Our previous work demonstrated that Pt/Ba/Al_2O_3 catalysts can significantly enhance COS hydrolysis performance and improve resistance to sulfur poisoning (Nimthuphariyha et al. 2021). In that study, Pt- and Ba-modified γ-Al_2O_3 powder catalysts were synthesized and subsequently pelletized for use in a packed-bed reactor. The results showed that barium acts as an effective promoter; for example, 0.5%Pt/5%Ba/Al_2O_3 achieved complete COS conversion (500-1000 ppm) and exhibited a catalyst lifetime more than four times longer than that of pristine γ-Al_2O_3. Characterization of the spent catalysts using field emission scanning electron microscopy (FE-SEM), Brunauer-Emmett-Teller (BET) specific surface area analysis, and temperature-programmed oxidation (TPO) showed distinct morphological changes, surface area reduction due to pore blockage, and the presence of deposited carbon and sulfur species, confirming that sulfur poisoning and carbon deposition are the primary causes of deactivation.

In this study, we extend our previous work by directly quantifying sulfur retention on spent catalysts, providing further insight into the relationship between sulfur accumulation and catalyst deactivation. During COS hydrolysis, sulfur species can form surface sulfide or sulfate species that interact strongly with catalyst surfaces. In Ba-promoted systems, these species are expected to be preferentially stabilized on Ba-containing sites, thereby limiting their interaction with Pt active sites and enhancing sulfur tolerance.

Building upon this foundation, the present work adopts a different approach: instead of synthesizing catalysts from γ-Al_2O_3 powder followed by shaping, commercially preformed γ-Al_2O_3 pellets were directly impregnated with the Pt and Ba promoters. This strategy better

reflects practical catalyst formulations used in industrial reactors. In this study, the COS hydrolysis performance was systematically evaluated, with a particular emphasis on catalyst stability during operation, to assess sulfur tolerance under representative experimental conditions. By bridging the gap between laboratory-prepared powders and commercially shaped supports, this work provides insight into the practical feasibility of upgrading industrial alumina pellets for COS removal applications. Recent studies have emphasized the importance of surface basicity, hydroxyl-mediated mechanisms, and synergistic catalytic-adsorptive strategies in improving COS removal performance (Feng et al. 2025; Jia et al. 2025; Wang et al. 2024). Unlike previous powder-based studies, this work provides additional mechanistic insight into sulfur tolerance through direct sulfur quantification and TGA/DTG analysis of fresh and spent catalysts.

MATERIALS AND METHODS

MATERIALS

The chemicals used in this study included γ-Al_2O_3, 1/8" pellets (99.9%, Alfa Aesar, USA), $H_2PtCl_6 \cdot xH_2O$ (99.9%, Alfa Aesar, USA), $BaCl_2$ (99.9%, Carlo Erba, Italy), COS in N_2 (1,500 ppm, Linde, Thailand), N_2 (99.9% Linde, Thailand), H_2 (99.9% Linde, Thailand), and He (99.9% Linde, Thailand).

SYNTHESIS OF Ba-Pt/γ-Al_2O_3 PELLETS

To synthesize 0.1Pt/γ-Al_2O_3, 20 mL of $H_2PtCl_6 \cdot xH_2O$ solution corresponding to 1 wt% Pt relative to the γ-Al_2O_3 support was evenly dispersed onto 10 g of γ-Al_2O_3 pellets. The mixture was sonicated in an ultrasonic bath at a frequency of 40 Hz for 30 min and then dried at 105 °C for 6 h to remove moisture. The catalyst was finally calcined at 600 °C for 4 h in air. For Ba-Pt/γ-Al_2O_3 synthesis, 2 mL of $BaCl_2$ solution corresponding to 0.5, 1, and 3 wt% Ba (relative to the catalyst) was evenly dispersed onto 1 g of 0.1Pt/γ-Al_2O_3. The samples were sonicated at 40 Hz for 30 min, dried at 105 °C for 6 h, and subsequently calcined at 600 °C for 4 h in air.

CARBONYL SULFIDE HYDROLYSIS EXPERIMENT

First, 0.5 g of catalyst was placed at the center of a brass column (1-inch inner diameter) and packed with glass fibers at both ends to serve as a catalyst holder and gas distributor. The packed column was then installed in the hydrolysis reactor. Second, the catalyst was reduced under a H_2 flow (100 mL/min) at 350 °C for 2 h to convert the Pt oxide species into their metallic active state. This pretreatment also facilitates the removal of surface oxygen species and residual contaminants. After the reduction step, the H_2 flow was immediately switched to N_2 (100 mL/min), while the reactor temperature was simultaneously decreased to 200 °C. Third, since steam plays a crucial role in COS hydrolysis, a steam generation system was integrated into the reactor setup. The system consisted of a temperature-controlled water bath connected to two glass cylindrical saturators. The first saturator contained deionized water, while the second was packed with 1-mm glass beads to enhance mixing between N_2 and steam. N_2 gas was passed through the first saturator to carry water vapor and then through the second saturator to improve gas-steam mixing. The amount of steam was controlled by adjusting the water bath temperature and N_2 flow rate. Prior to introducing COS, the N_2-steam mixture (100 mL/min) was allowed to flow through the system for 15 min to ensure stable conditions. After stabilization, a 1,500 ppm COS gas stream was introduced and mixed with the N_2-steam flow to obtain a final concentration of 500 ppm COS. The reaction was then carried out at 200 °C for 3 h. Finally, the outlet gas was sampled after COS introduction at specific time intervals to determine the COS concentration. A schematic diagram of the reactor setup is presented in Figure 1.

CARBONYL SULFIDE ANALYSIS

Quantitative analysis of COS gas was carried out using a gas chromatography-a-flame photometric detector (GC-FPD) (Shimadzu, GC-14A, Japan) with helium as the carrier gas and a flow rate of 10 mL/min. A GC packed-column, Gaskuropak, with a diameter of 4 mm and a length of 10 m was used. The initial temperature program was set at 50 °C for 5 min. The temperature was then increased at a heating rate of 20 °C/min to 150 °C, and the temperature was maintained at that temperature for 5 min. The 6-port value was used for automatic sampling for COS concentration analysis.

CATALYST CHARACTERIZATION

Powder X-ray diffraction (XRD) is an analytical technique used to characterize the crystalline structure of materials. The measurements were carried out using an AXS D8 Discover X-ray Diffractometer (Bruker, Germany) under operating conditions of 40 mA and 40 kV. The diffraction patterns were recorded over a 2θ range of 20-80° with a step size of 0.1°. The obtained data are presented as intensity versus diffraction angle (2θ) to identify the crystalline phases and structural characteristics of the modified catalysts.

N_2 adsorption-desorption analysis was used to determine the specific surface area of the catalysts. The measurements were carried out using a 3Flex surface characterization analyzer (Micromeritics, USA). Prior to analysis, both the sample and reference cells were degassed at 150 °C for 3 h to remove physically adsorbed gases and moisture. After degassing, the cells were evacuated under vacuum and immersed in liquid N_2 at 77.318 K. The specific surface area was then determined from the N_2 adsorption-desorption isotherms.

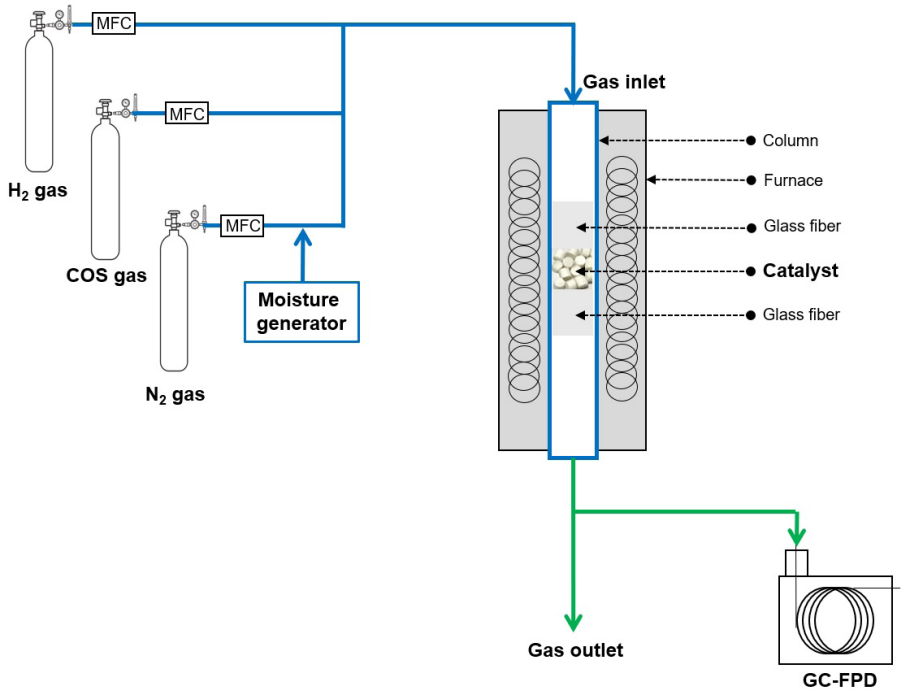

FIGURE 1. Reactor setup for COS hydrolysis

The sulfur content in the spent catalysts was determined using a CHNS elemental analyzer (Elementar, Germany). This analysis was conducted to quantify sulfur accumulation on the catalyst surface, which is a critical factor contributing to sulfur poisoning. The deposition of sulfur species on active sites can block catalytic centers, thereby reducing catalytic activity and leading to catalyst deactivation during operation.

Thermogravimetric analysis (TGA) was conducted to evaluate the thermal behavior and sulfur tolerance of the catalysts before and after COS hydrolysis. The measurements were performed using a TG 209 F3 Tarsus thermogravimetric analyzer (NETZSCH, Germany), which continuously records the mass change of a sample as a function of temperature under controlled atmospheric conditions. Three catalysts were investigated, including γ-Al2O3, 0.1Pt/γ-Al2O3, and 0.5Ba-0.1Pt/γ-Al2O3, in both fresh and spent states. The spent samples were collected after catalytic testing under COS hydrolysis conditions. Approximately 10 mg of each sample was placed in an alumina crucible and heated from 30 to 900 °C at a constant heating rate of 5 °C/min. The analyses were carried out under two different atmospheres: high-purity nitrogen (N2, >99.999%) and air. An inert atmosphere (N2) was used to investigate the thermal desorption and decomposition of physically or weakly bound species, whereas an oxidative atmosphere (air) was employed to assess the behavior of sulfur-containing species under oxidizing conditions. The TGA and differential thermogravimetric (DTG) curves were recorded and compared between fresh and spent catalysts to identify characteristic weight loss regions associated with adsorbed water, surface hydroxyl groups, and sulfur-containing species. Attention was given to the differences in mass loss patterns among the three catalysts, which provided insights into the nature, distribution, and thermal stability of sulfur species, as well as the relative sulfur tolerance of the catalyst systems.

RESULTS AND DISCUSSION

FRESH CATALYST CHARACTERISTICS

The appearance of the catalyst pellets prepared in this study is shown in Figure 2. All the samples exhibit a uniform cylindrical shape with a white color, indicating that the impregnation and calcination procedures did not significantly alter the macroscopic morphology of the commercial γ-Al_2O_3 support, which is consistent with previous reports on the thermal stability of shaped alumina carriers (Sun et al. 2014; West et al. 1998). The parent γ-Al_2O_3 pellets and 0.1Pt/γ-Al_2O_3 maintained their physical integrity after metal loading, in agreement with earlier studies showing that noble metal addition at low loading levels does not induce bulk phase transformation (Song et al. 2020; Wang et al. 2014). Similarly, Ba-promoted samples (0.5-3.0Ba-0.1Pt/γ-Al_2O_3) preserved their shape and mechanical stability without visible cracking or discoloration, which aligns with previous observations that alkaline earth modification primarily affects surface properties rather than pellet morphology (Lei et al. 2023; Nimthuphariyha et al. 2021). The slight variations in the pellet size distribution are attributed to the

commercial support batches rather than the impregnation process. These observations confirm that the addition of the Pt and Ba promoters did not adversely affect the pellet morphology, thereby ensuring their suitability for catalytic hydrolysis performance testing (Renda, Barba & Palma 2022; Zi et al. 2024).

The XRD patterns of 0.1Pt/γ-Al_2O_3 and 3.0Ba-0.1Pt/γ-Al_2O_3 are presented in Figure 3. Both catalysts exhibit broad diffraction peaks at 2θ ≈ 37°, 46°, and 67°, which are characteristic of γ-Al_2O_3 support, confirming that the impregnation and calcination processes did not significantly alter the crystalline phase of alumina (Sun et al. 2014; West et al. 1998). The presence of weak reflections at approximately 39.8°, 46.2°, and 67.5° in the Pt-loaded sample can be assigned to the (111), (200), and (220) planes of metallic Pt, respectively, although their low intensity indicates that the Pt species are highly dispersed on the alumina surface (Song et al. 2020; Wang et al. 2014).

For the Ba-promoted catalyst (3.0Ba-0.1Pt/γ-Al_2O_3), additional peaks appear at 25-28°, 45°, and 55°, which correspond to Ba-containing phases such as $BaCO_3$ or BaO (Kim et al. 2018). Notably, no significant peak shift or new crystalline phase was observed after Ba incorporation, suggesting that the Pt and Ba species are well dispersed without altering the bulk structure of γ-Al_2O_3. The coexistence of highly dispersed Pt species and Ba-containing phases provides complementary functionalities, where Pt acts as the primary active site and Ba contributes to surface basicity and sulfur trapping. This synergistic effect is supported by the preserved alumina structure and the presence of both Pt and Ba diffraction features, which together contribute to enhanced catalytic stability and sulfur resistance (Lei et al. 2023; Nimthuphariyha et al. 2021; Renda, Barba & Palma 2022; Zi et al. 2024).

The BET surface areas of the fresh catalysts are summarized in Table 1. The commercial γ-Al_2O_3 pellets had a surface area of 220 m^2/g. After Pt impregnation (0.1Pt/γ-Al_2O_3), the surface area slightly decreased to 218 m^2/g, indicating that the low loading of Pt had a minimal effect on the porous structure. This finding is consistent with earlier studies showing that noble metal incorporation at low concentrations does not significantly alter the textural properties of alumina (Sun et al. 2014; West et al. 1998). The subsequent incorporation of Ba promoters led to a progressive decrease in surface area. This reduction is attributed to partial pore blockage or coverage of the support surface by Ba species formed during impregnation and calcination. Similar decreases in BET surface area upon Ba addition have been reported previously, where heavier promoter loading induced more significant pore filling and agglomeration effects (Nimthuphariyha et al. 2021; Song et al. 2020; Wang et al. 2014). Despite this decrease, the surface areas remained sufficiently high to allow good dispersion of active components and accessibility of reactant molecules, thereby maintaining their suitability for catalytic hydrolysis applications (Lei et al. 2022; Renda, Barba & Palma 2022).

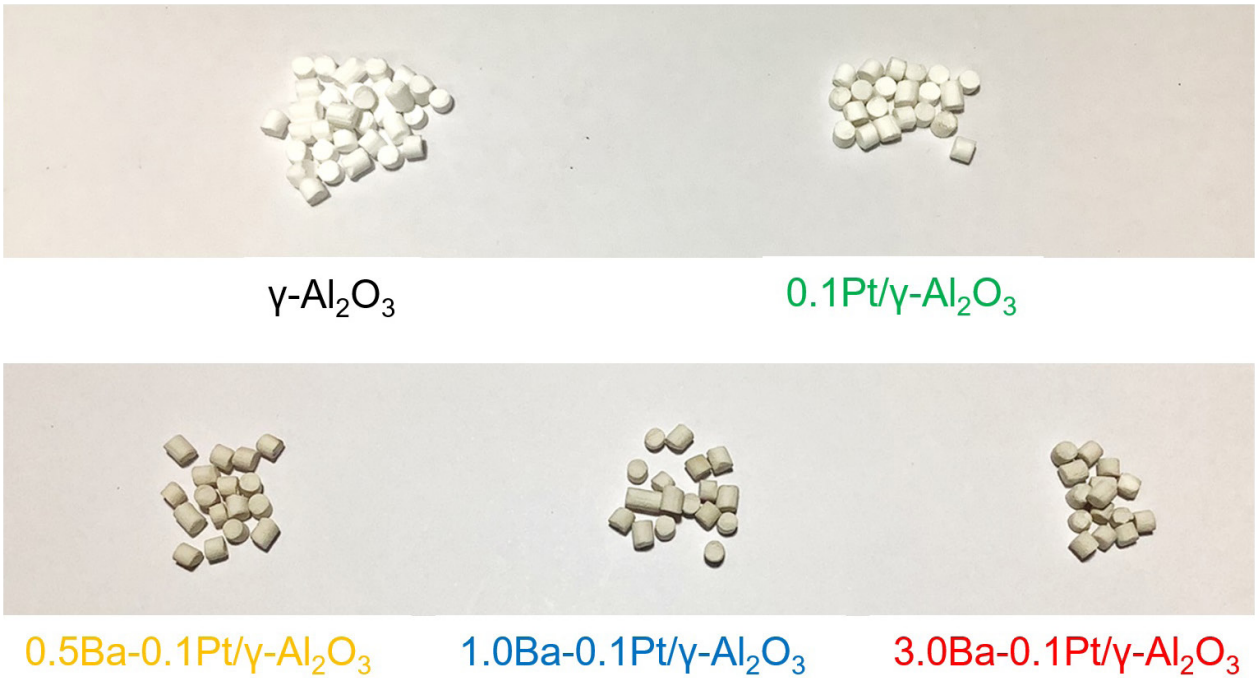

FIGURE 2. Appearance of the γ-Al_2O_3, 0.1Pt/γ-Al_2O_3, and Ba-Pt/γ-Al_2O_3 catalysts

The COS hydrolysis performance of the γ-Al_2O_3 and Pt-Ba/γ-Al_2O_3 catalysts as a function of time on stream is shown in Figure 4. Unpromoted γ-Al_2O_3 exhibited a steady decrease in COS conversion, confirming its limited intrinsic activity and susceptibility to deactivation, which is consistent with the findings of earlier studies highlighting the poor stability of bare alumina in sulfur-containing environments (West et al. 1998; Zhao et al. 2013). Upon loading with Pt (0.1Pt/γ-Al_2O_3), the initial conversion improved, and the stability increased, indicating that Pt provided additional active sites to facilitate the hydrolysis reaction (Song et al. 2020; Wang et al. 2014).

When Ba was introduced as a promoter, distinct trends were observed depending on the Ba loading. Compared with the Pt-only catalyst, the catalyst with 0.5Ba-0.1Pt/γ-Al_2O_3 displayed improved stability, suggesting that a low amount of Ba helps neutralize acidic sites and reduces sulfate deposition on the surface (Kim et al. 2012; Lei et al. 2023; Song et al. 2020). The 1.0Ba-0.1Pt/γ-Al_2O_3 sample, however, showed a more pronounced decrease in activity, which may be attributed to excessive Ba species partially blocking the pore structure, as evidenced by the decrease in the BET surface area (from 214 m^2/g compared to 220 m^2/g for bare γ-Al_2O_3). Interestingly, the 3.0Ba-0.1Pt/γ-Al_2O_3 catalyst maintained relatively high conversion for a

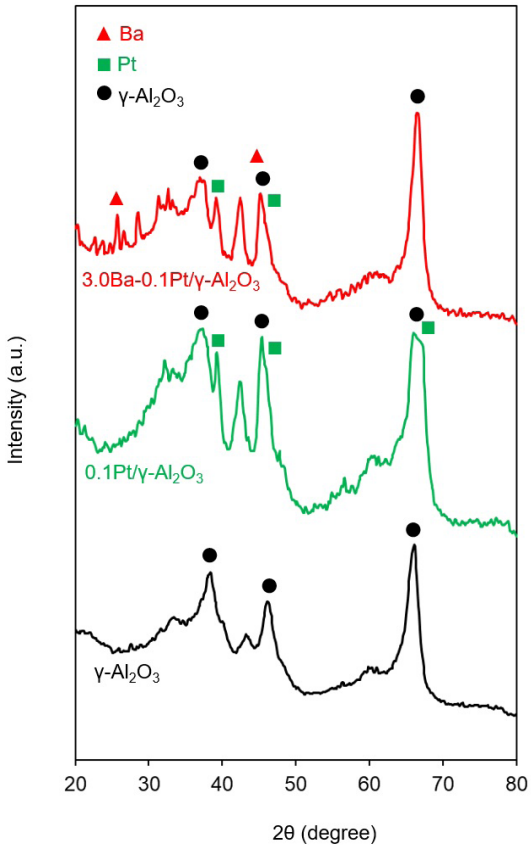

FIGURE 3. XRD patterns of γ-Al_2O_3, 0.1Pt/γ-Al_2O_3, and 3.0Ba-0.1Pt/γ-Al_2O_3

TABLE 1. BET specific surface areas of the γ-Al_2O_3, 0.1Pt/γ-Al_2O_3, and Ba-Pt/γ-Al_2O_3 catalysts

Catalyst	BET specific surface area (m^2/g)
γ-Al_2O_3	220
0.1Pt/γ-Al_2O_3	218
0.5Ba-0.1Pt/γ-Al_2O_3	217
1.0Ba-0.1Pt/γ-Al_2O_3	214
3.0Ba-0.1Pt/γ-Al_2O_3	200

longer period, implying that at higher loadings, Ba species can also act as sulfur traps, improving resistance to sulfur poisoning (Nimthuphariyha et al. 2021; Renda, Barba & Palma 2022).

These results are consistent with the CHNS analysis presented in Table 2, where sulfur accumulation on the spent catalysts correlated with the extent of deactivation. Catalysts with optimized Ba loading adsorbed less sulfur per surface area, thereby maintaining catalytic performance for a longer period (Zi et al. 2024). This highlights the dual role of Ba as both a structural modifier and a sulfur scavenger, which is crucial for prolonging catalyst lifetime under COS hydrolysis conditions (Kim et al. 2018; Nimthuphariyha et al. 2021).

To better evaluate the long-term stability of the catalysts and compare the results with those of Nimthuphariyha et al. (2021), linear extrapolation of COS conversion with respect to time on stream was carried out (Figure 5). The extrapolated trends indicate that the parent γ-Al_2O_3 undergoes the fastest deactivation, as reflected by the steep negative slope (–0.1381), predicting a rapid decrease in COS conversion at extended reaction times. The incorporation of Pt (0.1Pt/γ-Al_2O_3) significantly reduced the deactivation rate (slope –0.0389), suggesting that Pt species effectively provide additional active sites and partially suppress sulfur deposition (Song et al. 2020; Wang et al. 2014). Nimthuphariyha et al. (2021) experimentally demonstrated similar trends, where Pt/Al_2O_3 catalysts maintained >80% conversion for extended periods, while Ba-containing catalysts (particularly 0.5-1% Ba loadings) further suppressed deactivation at higher COS concentrations (750-1000 ppm). Their results confirmed that optimal Ba addition enhances sulfur-trapping ability while preserving accessible Pt active sites, thereby minimizing sulfur poisoning. Notably, excessive Ba loading (≥3–5%) resulted in a slight decrease in performance because of pore blockage and a reduced surface area, in agreement with the extrapolation outcomes in this work (Lei et al. 2023; Song et al. 2017).

As shown in Figure 5, the Ba-promoted catalysts exhibited varying deactivation behaviors depending on the Ba loading. Compared with the Pt-only sample, the 0.5Ba-0.1Pt/γ-Al_2O_3 sample presented the lowest slope (–0.0361), indicating enhanced stability. This can be attributed to the ability of Ba to neutralize surface acidity and reduce sulfate formation, thereby mitigating sulfur poisoning (Lei et al. 2023; Song et al. 2017). In contrast, 1.0Ba-0.1Pt/γ-Al_2O_3 had a higher deactivation rate (slope of –0.0454), which may have resulted from pore blockage and a reduced surface area (214 m^2/g) due to excessive Ba species deposition. Interestingly, the 3.0Ba-0.1Pt/γ-Al_2O_3 catalyst displayed a slope of –0.0508, indicating slightly faster deactivation than the 0.5Ba-promoted sample but still superior to bare γ-Al_2O_3. This observation is consistent with the sulfur content reported in Table 2, where higher Ba loading is associated with increased sulfur accumulation. This suggests that although Ba can act as a sulfur trap and enhance sulfur tolerance, excessive loading may lead to pore blockage and reduced surface accessibility (Nimthuphariyha et al. 2021; Renda, Barba & Palma 2022).

The deterioration of the catalyst activity at 180 min and the corresponding sulfur contents in the spent samples are summarized in Table 2. Catalyst deterioration (%) was calculated on the basis of the relative decrease in COS conversion from the initial value to that at 180 min on stream. γ-Al_2O_3 exhibited the most severe deactivation (25.56%) despite retaining a relatively low sulfur content (0.0517 wt%). This finding indicates that the absence of Pt or Ba promoters renders the support highly vulnerable to poisoning, with rapid loss of active surface functionality (Lei et al. 2023; West et al. 1998; Zhao et al. 2013). In contrast, the deterioration of the Pt-loaded catalysts significantly decreased even when sulfur retention was high. For example, 0.1Pt/γ-Al_2O_3 decreased by only 7.78% despite the accumulation of 0.0693 wt% sulfur, suggesting that Pt provides more robust and resistant active sites for COS hydrolysis (Song et al. 2020; Wang et al. 2014; Wang et al. 2011). The observed sulfur retention behavior can be explained by the interaction between sulfur species and catalyst components. Sulfur generated from COS hydrolysis is retained either on Pt sites or trapped by Ba species. In Ba-promoted catalysts, the formation of stable Ba–S compounds reduces sulfur migration to Pt active sites, thereby mitigating deactivation. In contrast, in the absence of Ba, sulfur species directly accumulate at active sites, leading to rapid loss of catalytic activity.

Among the Ba-Pt-promoted catalysts, the optimal performance was observed for 0.5Ba-0.1Pt/γ-Al_2O_3, which showed the lowest sulfur retention (0.0427 wt%) and the lowest deterioration (7.73%). This result demonstrates the beneficial effect of a low Ba loading in suppressing sulfur poisoning. The incorporation of Ba introduces basic sites (BaO or $BaCO_3$ species) onto the catalyst surface, which can neutralize the intrinsic acidity of γ-Al_2O_3 and enhance the adsorption of acidic sulfur-containing intermediates. This interpretation is consistent with Jia et al. (2025), who showed that surface basicity strongly influences both catalytic performance and the form of retained sulfur species during COS hydrolysis. Such modification may promote a more uniform distribution of sulfur species and lessen their direct interaction with Pt active sites, thereby mitigating catalyst deactivation (Kim et al. 2018; Nimthuphariyha et al. 2021; Song et al. 2017; Zi et al. 2024). However, higher Ba loadings (1.0-3.0 wt%) resulted in increased sulfur retention (0.0639-0.1259 wt%) and moderately greater deterioration (9.14-10.04%), indicating that excessive promoter addition can create strong sulfur binding sites and lead to pore blockage, ultimately accelerating catalyst deactivation (Renda, Barba & Palma 2022; Zi et al. 2024).

The correlation between sulfur retention and deterioration is shown in Figure 6. While a general trend of increasing deterioration with increasing sulfur retention can be observed, notable exceptions (0.1Pt/γ-Al_2O_3 and 3.0Ba-0.1Pt/γ-Al_2O_3) indicate that catalyst deactivation

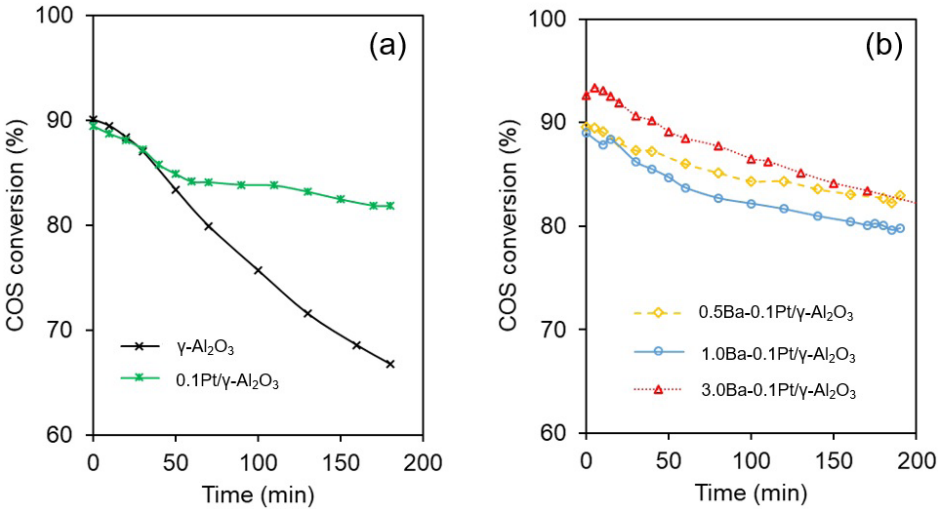

FIGURE 4. COS hydrolysis performance of the γ-Al_2O_3, 0.1Pt/γ-Al_2O_3, and Ba-Pt/γ-Al_2O_3 catalysts as a function of time on stream

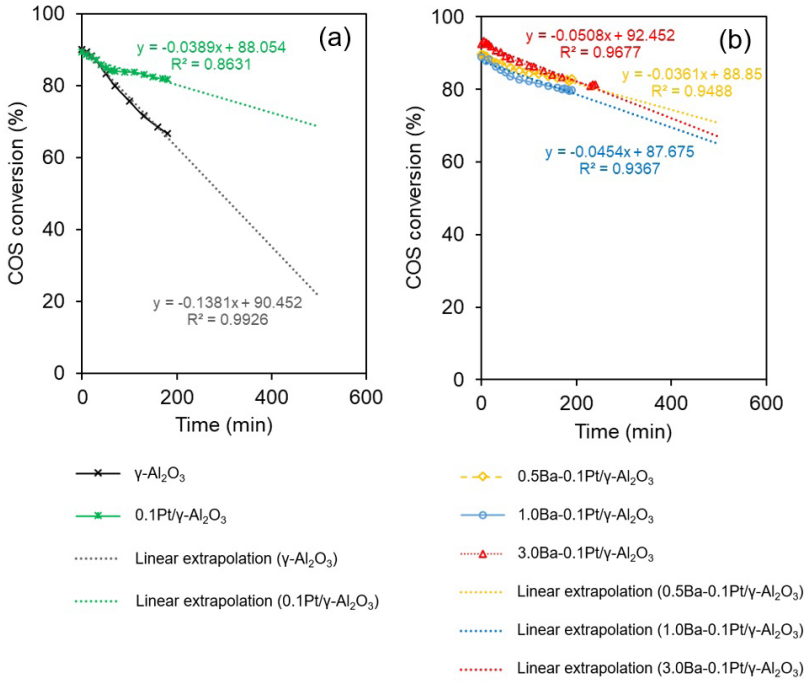

FIGURE 5. Linear extrapolation of COS conversion versus time on stream for γ-Al_2O_3, 0.1Pt/γ-Al_2O_3, and Ba-Pt/γ-Al_2O_3 catalysts

TABLE 2. Catalyst deterioration at 180 min and sulfur content of spent catalysts

Catalyst	Catalyst deterioration at 180 min (%)	Sulfur content (wt%)
γ-Al_2O_3	25.56	0.0517
0.1Pt/γ-Al_2O_3	7.78	0.0693
0.5Ba-0.1Pt/γ-Al_2O_3	7.73	0.0427
1Ba-0.1Pt/γ-Al_2O_3	10.04	0.0639
3Ba-0.1Pt/γ-Al_2O_3	9.14	0.1259

is not solely governed by sulfur loading alone. Instead, sulfur retention originates from the formation of strongly adsorbed sulfur-containing species during COS hydrolysis. COS is first hydrolyzed to H_2S and CO_2, after which H_2S can interact with the catalyst surface to form surface sulfide or sulfate species. These sulfur species may either adsorb weakly and remain reversible or bind strongly to active sites such as Pt, leading to site blockage and irreversible deactivation (Song et al. 2017; Sun et al. 2014). Different sulfur species (sulfide, elemental sulfur, or sulfate) may exhibit distinct stability and deactivation behaviors (Jia et al. 2025).

The presence of Ba further influences this behavior by introducing basic sites that preferentially interact with acidic sulfur species. Ba-containing phases (BaO or $BaCO_3$) can act as sulfur traps by capturing H_2S or sulfate species, thereby reducing direct poisoning of Pt active sites. However, excessive sulfur accumulation at these sites can still contribute to overall deactivation, especially when pore blockage or surface coverage becomes significant. Therefore, the extent of sulfur retention is governed not only by the amount of sulfur formed but also by its distribution, chemical state, and interaction with specific catalytic sites (Gao et al. 2024; Nimthuphariyha et al. 2021; Song et al. 2017; Sun et al. 2014). These findings highlight that an optimal balance between Pt and Ba loading is essential for controlling sulfur retention pathways, minimizing active site poisoning, and enhancing catalyst durability during COS hydrolysis.

SULFUR TOLERANCE OF THE CATALYSTS

The TGA and DTG profiles of fresh and spent catalysts under air and N_2 atmospheres are shown in Figure 7, providing further insight into the nature and thermal stability of sulfur species formed during COS hydrolysis. For the fresh catalysts (Figure 7(a) and 7(c)), all samples exhibit an initial DTG peak in the low-temperature region (~40–60 °C), corresponding to the removal of physically adsorbed water and weakly bound surface species. The similarity in peak positions indicates comparable surface hydration characteristics, while the lower overall mass loss observed for 0.5Ba-0.1Pt/γ-Al_2O_3 suggests improved thermal stability upon Ba incorporation, likely due to modification of surface basicity and reduced hydroxyl density (Gao et al. 2024; Song et al. 2017). For the spent catalysts (Figure 7(b) & 7(d)), more distinct differences are observed. The γ-Al_2O_3 catalyst exhibits an additional DTG feature and a more pronounced mass loss step in the intermediate-temperature region (~200-300 °C), indicating the presence of relatively labile sulfur-containing species, such as surface sulfides or thiocarbonate intermediates. These species are weakly bound and can decompose at moderate temperatures, but their accumulation on active hydroxyl sites leads to severe catalyst deactivation (Sun et al. 2014; West et al. 1998).

In contrast, the spent 0.1Pt/γ-Al_2O_3 catalyst shows a broader and less intense DTG signal without a sharp intermediate-temperature peak, indicating that sulfur species are more evenly distributed and are likely associated with Pt sites, possibly forming Pt–S or Pt–S–O interactions. This can mitigate localized poisoning by redistributing sulfur species away from critical alumina sites, resulting in improved sulfur tolerance (Nimthuphariyha et al. 2021; Song et al. 2017). Further enhancement is observed for 0.5Ba-0.1Pt/γ-Al_2O_3, where both the TGA and the DTG profiles show only minor differences between the fresh and spent samples, with no distinct intermediate-temperature DTG peak observed. This suggests that sulfur species are more thermally stabilized and evenly distributed on the catalyst surface, likely through interactions with Ba-containing sites. In this role, Ba is suggested to act as a

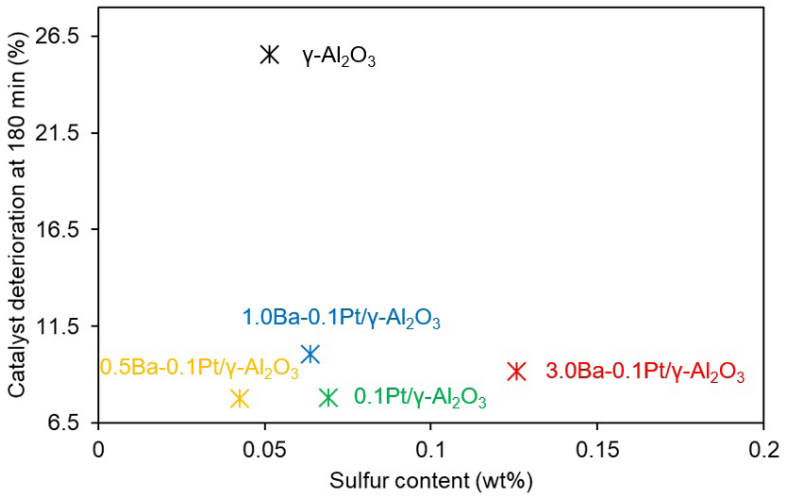

FIGURE 6. Correlation between sulfur retention and catalyst deterioration at 180 min for γ-Al_2O_3, 0.1Pt/γ-Al_2O_3, and Ba-Pt/γ-Al_2O_3 catalysts

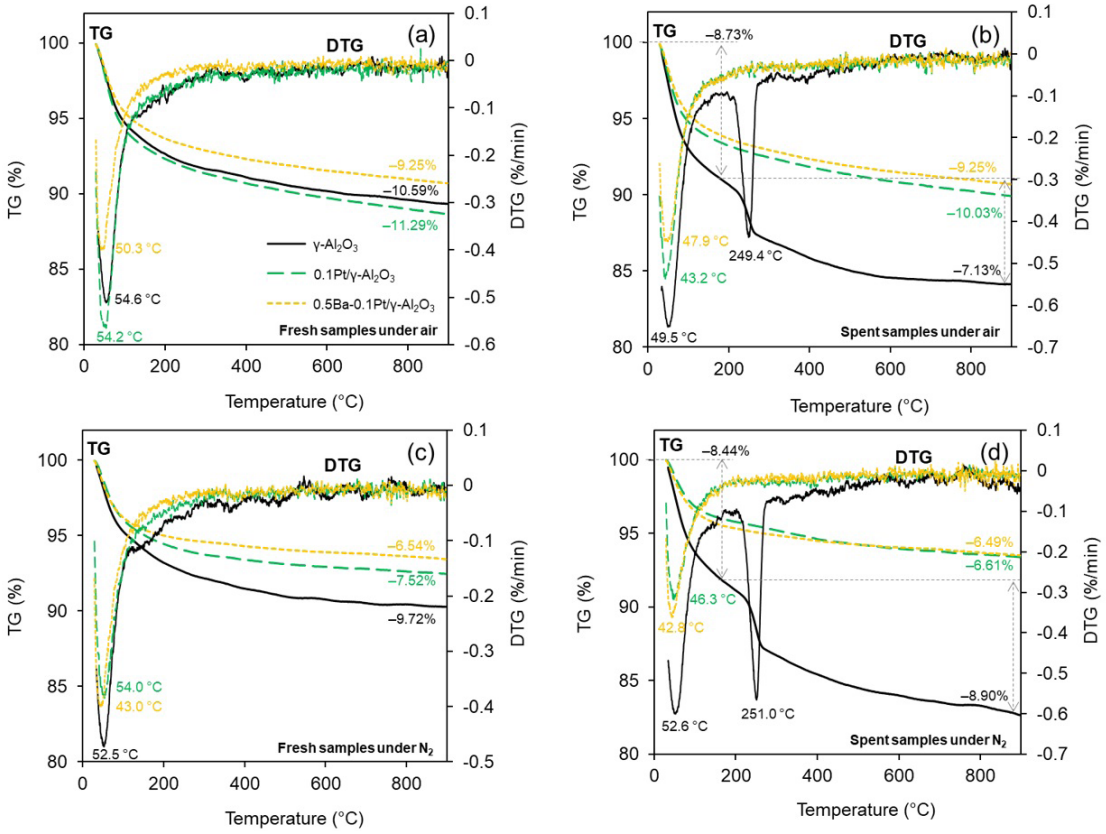

FIGURE 7. Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) profiles of fresh and spent γ-Al_2O_3, 0.1Pt/γ-Al_2O_3, and 0.5Ba-0.1Pt/γ-Al_2O_3 catalysts under (a, b) air and (c, d) N_2 atmospheres

sulfur scavenger, preferentially trapping sulfur species and limiting their accumulation on catalytically active sites, thereby improving sulfur tolerance (Gao et al. 2024; Nimthuphariyha et al. 2021). Additionally, the reduced total mass loss observed for Ba-promoted catalysts under both air and N_2 atmospheres indicates that sulfur species are more strongly retained and thermally stable, further supporting the role of Ba in enhancing sulfur resistance.

Overall, the sulfur resistance inferred from both the TGA and the DTG analyses follows the order of γ-Al_2O_3 < 0.1Pt/γ-Al_2O_3 < 0.5Ba-0.1Pt/γ-Al_2O_3. These TGA/DTG results are in good agreement with the correlation presented in Figure 6, where catalyst deterioration increases with increasing sulfur retention. The reduced mass loss and absence of distinct DTG features in the Ba-promoted catalyst further confirm that sulfur species are stabilized and less likely to deactivate active sites, highlighting the effectiveness of Ba in enhancing sulfur resistance.

CONCLUSIONS

In this study, the catalytic hydrolysis of COS over γ-Al_2O_3 pellets promoted with Pt and Ba was investigated. Bare γ-Al_2O_3 exhibited the most severe deactivation, reaching 25.56% after 180 min, whereas Pt loading significantly improved catalyst stability, reducing deactivation to 7.78%. The incorporation of a small amount of Ba (0.5 wt%) further increased the sulfur resistance, resulting in the lowest degree of deactivation (7.73%) and the lowest degree of sulfur retention (0.0427 wt%). In contrast, higher Ba loadings (1.0-3.0 wt%) led to increased sulfur accumulation (0.0639-0.1259 wt%) and moderately higher deactivation (9.14-10.04%). The combined CHNS, TGA/DTG, and catalytic performance results indicate that sulfur retention plays a key role in catalyst deactivation, while the extent of deactivation also depends on the interaction of sulfur species with the active and promoter sites. These results suggest that Pt may improve sulfur tolerance by facilitating a more uniform distribution of sulfur species, whereas Ba is likely to increase resistance by stabilizing and trapping sulfur species on the catalyst surface. Overall, 0.5Ba-0.1Pt/γ-Al_2O_3 was identified as the optimal catalyst formulation, providing the best balance between catalytic activity and sulfur tolerance for COS hydrolysis.

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REFERENCES

Feng, X., Zhao, C., Chen, Z., Yun, J., Zhao, Y., Zheng, H., Wei, N., Tong, Z. & Chen, Z. 2025. Research on a novel ZSM-5@Al_2O_3 compound catalyst for the hydrolysis of carbonyl sulfide from blast furnace gas and *in situ* reaction mechanism. *Journal of Environmental Chemical Engineering* 13: 116885.

Gao, S., Zhao, S., Tang, X., Wang, Y. & Yi, H. 2024. Mechanics of COS removal by adsorption and catalytic hydrolysis: Recent developments. *Fuel* 359: 130394.

Jia, T., Guan, J., Qin, Z., Wu, M., Chang, L., Zhai, Z., Lin, G. & Du, Z. 2025. Correlation between alkaline characteristics and catalytic performance of K_2CO_3/Al_2O_3 in carbonyl sulfide hydrolysis. *Results in Chemistry* 18: 102755.

Kim, D.H., Kwak, J.H., Szanyi, J. & Peden, C.H.F. 2012. Isothermal desulfation of pre-sulfated Pt–BaO/γ-Al_2O_3 lean NOx trap catalysts with H_2: The effect of H_2 concentration and the roles of CO_2 and H_2O. *Applied Catalysis B: Environmental* 111-112: 342-348.

Kim, J., Do, J.Y., Park, N-K., Hong, J-P. & Kang, M. 2018. Adsorption/desorption behavior of carbonyl sulfide gas on scheelite type MWO_4 adsorbent. *Separation and Purification Technology* 207: 58-67.

Lei, G., Zheng, Y., Cao, Y., Shen, L., Wang, S., Liang, S., Zhan, Y. & Jiang, L. 2023. Deactivation mechanism of COS hydrolysis over potassium modified alumina. *Acta Physico-Chimica Sinica* 39(9): 2210038.

Nimthuphariyha, K., Usamani, A., Grisdanurak, N., Kanchanatip, E., Suthirakune, S., Yan, M. & Tulaphol, S. 2021. Hydrolysis of carbonyl sulfide over modified Al_2O_3 by platinum and barium in a packed-bed reactor. *Chemical Engineering Communications* 208(4): 539-548.

Renda, S., Barba, D. & Palma, V. 2022. Recent solutions for efficient carbonyl sulfide hydrolysis: A review. *Industrial & Engineering Chemistry Research* 61: 5685-5697.

Song, X., Chen, X., Sun, L., Li, K., Sun, X., Wang, C. & Ning, P. 2020. Synergistic effect of Fe_2O_3 and CuO on simultaneous catalytic hydrolysis of COS and CS_2: Experimental and theoretical studies. *Chemical Engineering Journal* 399: 125764.

Song, X., Ning, P., Wang, C., Li, K., Tang, L-H., Sun, X. & Ruan, H-T. 2017. Research on the low temperature catalytic hydrolysis of COS and CS_2 over walnut shell biochar modified by Fe–Cu mixed metal oxides and basic functional groups. *Chemical Engineering Journal* 314: 418-433.

Sun, J., Du, X., Li, Z., Yu, H., Hong, Y., Pan, M., Nie, G., Fan, W., Gao, F., Wu, F., Li, L., Deng, G., Sun, Z. & Duan, L. 2024. Rational design of poisoning-resistant catalyst based on γ-Al_2O_3 for hydrolysis of carbonyl sulfide. *Chemical Engineering Science* 295: 120150.

Sun, X., Ning, P., Tang, X-L., Yi, H-H., Li, K., He, D., Xu, X-M., Huang, B. & Lai, R-Y. 2014. Simultaneous catalytic hydrolysis of carbonyl sulfide and carbon disulfide over Al_2O_3-K/CAC catalyst at low temperature. *Journal of Energy Chemistry* 23(2): 221-226.

Wang, H., Liu, C., Gong, Z., Jiang, H., Gao, W., Guo, G., Yang, F., Wu, Q., Mertsoy, E.Y., Zhao, J., Liu, J., Ling, H., Shen, B., Wu, D. & Sun, H. 2024. CuY@NiAl-Layered double oxides bi-functional composites for "Catalytic–Adsorptive" removal of carbonyl sulfide. *Chemical Engineering Journal* 493: 151992.

Wang, H.Y., Yi, H.H., Ning, P., Tang, X.L., Yu, L.L., He, D. & Zhao, S. 2011. Calcined hydrotalcite-like compounds as catalysts for hydrolysis of carbonyl sulfide at low temperature. *Chemical Engineering Journal* 166(1): 99-104.

Wang, X., Ma, Y., Ning, P., Qiu, J., Ren, X., Li, Z., Chen, W. & Liu, W. 2014. Adsorption of carbonyl sulfide on modified activated carbon under low-oxygen content conditions. *Adsorption* 20(4): 623-630.

West, J., Williams, B.P., Young, N., Rhodes, C. & Hutchings, G.J. 2001. Ni- and Zn-promotion of γ-Al_2O_3 for the hydrolysis of carbonyl sulfide under mild conditions. *Catalysis Communications* 2(3-4): 135-138.

West, J., Williams, B.P., Young, N.C., Rhodes, C. & Hutchings, G.J. 1998. New directions for COS hydrolysis: Low temperature alumina catalysts. *Studies in Surface Science and Catalysis* 119: 373-378.

Zhao, S., Yi, H., Tang, X., Jiang, S., Gao, F., Zhang, B., Zuo, Y. & Wang, Z. 2013. The hydrolysis of carbonyl sulfide at low temperature: A review. *The Scientific World Journal* 2013: 739501.

Zi, S., Li, K., Wang, X., Sun, L., Tian, Y., Huang, B., Zeng, H. & Ma, Y. 2024. Influence of surface basic sites and oxygen vacancies on the performance of metal-modified rod-like ceria catalysts for low-temperature hydrolysis of carbonyl sulfide. *Chemistry – An Asian Journal* 19: e202400235.

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