Further Use of Spent Co-Based Macroporous Adsorbent for Low-Temperature Hydrodesulfurization

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Abstract
Spent cobalt-based macroporous adsorbents are considered to be used for the hydrotreating process. Herein, cobalt-based spent materials from the low-temperature desulfurization process were used as organic sulfur hydrotreating catalysts. Physicochemical properties of waste adsorbents were characterized and the performance for COS conversion was evaluated at different conditions. The spent Co-containing adsorbents exhibit considerable organic sulfur hydrogenation performance at low temperature, the residual cobalt oxide in sulfided samples will absorb part of hydrogen sulfide and generate new active phase Co9S8. By further characterization, it can be found that the unstable Co-S bond on the surface of the sample played a key role in hydrogenation catalysis. Results indicated that the sulfidation degree of the waste adsorbents played a key role in the hydrotreating process. With the temperature increasing from 150 ~ 250 °C, the conversion rate and H2S selectivity were increased. It is hoped that this paper will provide significant suggestions in waste adsorbents treatment for future work.

Graphical Abstract

Keywords Transition metal · Catalysis · Low-temperature desulfurization · Adsorption · Solid waste

1 Introduction
Sulfur removal from industry gas streams has been an important issue since sulfur contaminants, especially hydrogen sulfide, contribute mainly to the formation of acid rain, and poisoning the catalysts used in industry [1–4]. Hence, many
techniques are in use for sulfur removal. Out of them adsorbing by metal oxide-based adsorbents is a commonly used method as it is simple and reliable for sulfide removal [5, 6]. Typically, cobalt oxide can be used as a perfect adsorbent for \( \text{H}_2\text{S} \) removal at room temperature, but it is overpriced and hard for regeneration [7, 8]. In addition, the used adsorbents have to be treated as solid waste before disposal with further management problems of environmental transition metal and sulfur emission. These facts have grown interested in the search for adsorbents whose spent one could also be useful avoiding the second pollution as the solid waste [9].

Sulfides of transition metals (Co, Ni, Mo or W) are of great interest as industrial catalysts and have been used in petroleum refining for hydro-processing applications like hydrodesulfurization (HDS) [10–12]. \( \text{Co(Ni)}-\text{Mo/Al}_2\text{O}_3 \) based catalyst systems are mostly used for HDS catalysis. Commercially used \( \text{Co(Ni)}-\text{Mo/Al}_2\text{O}_3 \) have good performance and economic advantage [13]. Generally, cobalt/nickel is commonly considered as the promoter of the catalyst, since the additional small amount of Co can dramatically improve the HDS activity of Mo. However, the use of monometallic cobalt catalysts is also described in literature [14, 15]. A report from Hussain and Ihm showed an experimental observation that Co/CMK catalysts exhibited higher HDS activities than Mo/CMK catalysts due to its higher metal dispersion [14]. The catalytic performance is highly related to the preparation method, the type of support, and presulfidation temperature since they influence the final dispersion and the reducibility of the metal. In other words, they affected the morphology and the electronic structure of the active species [16, 17].

As known, commercial hydrodesulfurization catalysts are in the form of oxides, they need to be totally converted into sulfide phase by complicated and time-consuming presulfidation process before use. A recent study, from this laboratory, has shown that the breakthrough sulfur capacity of macroporous cobalt oxide could reach as high as 189 mg/g with \( \text{Co}_3\text{O}_4 \) utilization of 63% under room temperature [7]. We speculated that the spent adsorbents with a high cobalt sulfide content can be further used in HDS. With which, the hard regeneration process as \( \text{H}_2\text{S} \) adsorbent, and the time-consuming and environmental unfriendly presulfidation process as hydrodesulfurization catalyst can be avoided.

The HDS activity of the spent adsorbents were explored in a micro-reaction device and the samples were analyzed by means of XRD, nitrogen adsorption–desorption, HRTEM, TG-MS, TPR, and other characterization methods. The experimental results indicate that spent cobalt-based adsorbents exhibit great performance for COS hydrodesulfurization. \( \text{CoS} \) formed during the \( \text{H}_2\text{S} \) adsorption process and spread over the surface of spent cobalt adsorbent, and subsequently transferred into active sites to use for efficient hydrogenation. Moreover, the generated hydrogen sulfide from the catalytic process partially reacts with \( \text{Co}_3\text{O}_4 \) which is unreacted during the sulfidization process and then transformed into a new cobalt sulfide species (\( \text{Co}_3\text{S}_8 \)), and the catalytic activity of spent adsorbents hence enhanced. This work establishes a new, simple and efficient means of reusing spent cobalt-based adsorbents for low temperature hydrodesulfurization.

## 2 Experimental Section

### 2.1 Catalyst Preparation

Macropores cobalt-silica oxide composites were synthesized by the colloidal crystal template method and described elsewhere in detail [7, 18]. Typically, macropores cobalt oxide-silica composites can be synthesized in two steps. The synthesis process is shown in Scheme 1. First, mix tetraethyl orthosilicate (TEOS), distilled water, anhydrous ethanol (EtOH) and hydrochloric acid at a molar ratio of 1: 1.8: 3.9: 0.3 together to form silicon sol, then dissolve cobalt nitrate hexahydrate in methanol and ethylene glycol (volumetric ratio 60%) mixed solvent to achieve cobalt nitrate solution (1.5 M). The precursor was prepared by mixing silica sol and cobalt nitrate solution, and then soak 5 g polystyrene spheres (PS) hard template in the above precursor for 7 h. After soaking, remove excessive liquid by vacuum filtration and dry precursor/PS composites under room temperature overnight. The dried materials were calcined in muffle furnace at a heating rate of 1 °C/min from 25 to 300 °C and maintained at 300 °C for 1 h, then ramping to 500 °C and maintained for 4 h. The typical macropores cobalt oxide-silica composite adsorbents with the weight ratio of \( \text{Co}_3\text{O}_4 \) of 57% was chosen on the biases of the previous study showing the positive effect of such adsorbent deserve the highest sulfur capacity of \( \text{H}_2\text{S} \) under ambient condition, and labeled as SC in this work, where S, C are simplified form of silica and cobalt oxide [7]. SC-S denoted the sample which was obtained after SC was used for breakthrough test at ambient temperature with outlet \( \text{H}_2\text{S} \) concentration less than 0.1 ppm (The detailed description of breakthrough test can referred to ref. 7)). Continuing sulfiding SC-S until the outlet \( \text{H}_2\text{S} \) concentration is equal to the inlet, then SC-E could be obtained. SC-E-X means the samples after SC-E were used for COS hydrogenation, where X means catalysis reaction temperature. For convenient comparison, sample SC-E only pretreated at 200 °C under Ar was named as SC-E–H to see the effect of pretreatment. A commercial catalyst (\( \text{CoMo/Al}_2\text{O}_3 \)) containing 11 wt.% Co and Mo was provided by Shanxi Clean Company for comparison. The name of commercial \( \text{CoMo/Al}_2\text{O}_3 \) catalyst is shortened to be CM. Commercial \( \text{CoMo/Al}_2\text{O}_3 \) were presulfided before catalytic reaction by 1000 ppm...
H₂S in the mixture of 10% H₂ and 90% Ar feed gas at 300 °C for 2 h.

2.2 Hydrogenation Performance Tests

The performance tests of spent adsorbents for hydrodesulfurization were carried out in a continuous-flow fixed-bed glass microreactor (i.d. = 6 mm). Typically, an amount of 10 mg of fresh adsorbent (SC, 60-80mesh), diluted with inert particles of silicon dioxide and a bed height of 2 cm. Prior to the experiments, samples in bed were prehumidified by passing moist N₂ (ca. 3% moisture) for 1 h at room temperature. Then the sample was sulfided in a moisture atmosphere containing 500 mg/m³ H₂S under room temperature (30 °C) with a flowing rate of 100 ml/min. With this sulfidation process, SC-S and SC-E could be obtained. Then the sulfided sample was heated in argon atmosphere to a specified test temperature at a heating rate of 5 °C/min, and maintained at this temperature for 1 h. The feed gas was then switched to an Ar atmosphere containing 1000 mg/m³ COS and 10 vol.% H₂ to start HDS test. The gas hourly space velocity (GHSV) is 21333 h⁻¹ (10% H₂). The outlet reaction products were monitored using a gas chromatography (Haixin, GC-920) equipped with a photometric detector (FPD). The COS conversion and corresponding H₂S selectivity of materials were calculated according to Eqs. 1 and 2.

\[
\text{COS Conversion (\%)} = \frac{C_i - C_o}{C_i} \times 100\% \tag{1}
\]

\[
\text{H₂S Selectivity (\%)} = \frac{C_{H₂S,Out}}{C_i - C_o} \times 100\% \tag{2}
\]

where \(C_i\) and \(C_o\) are the inlet and outlet COS concentration, \(C_{H₂S,Out}\) is outlet H₂S concentration.

2.3 Characterization Methods

X-ray diffraction analysis was carried out to evaluate the crystallinity of samples, materials were determined on Rigaku D/max-2500 diffractometer with Cu Kα radiation. Diffraction patterns were obtained in the range of 5–85° at a scan rate of 8° min⁻¹. Nitrogen adsorption–desorption isotherms were measured using an Micromeritics 3H-2000PS2 apparatus. Pore size distribution and the total pore volumes were calculated by Barrett-Joyner-Halenda modal, Specific surface areas were determined by the Brunauer–Emmett–Teller method. Thermogravimetric–mass spectroscopy (TG-MS) curves were taken on Setaram SETSYS Evolution TGA-Hiden HPR20 QIC R&D instrument. Samples were tested at a heating rate of 10 °C/min under constant air flow (100 ml/min) from room temperature to 1000 °C. The morphology of catalysts was observed by high-resolution transmission electron microscopy (HRTEM), and it was performed on Nanosem430 and JEM 2100F electron microscopy. Temperature programmed reduction (TPR) was conducted using Quantachrome Chambert 3000 equipped with TCD detector, using mixed H₂ (10%) and Ar gas with a flow rate of 100 ml/min.

3 Results and Discussion

3.1 Characterization of Synthesized Adsorbents

Figure 1 shows the X-ray diffraction (XRD) of the samples. Fresh adsorbent is also present for comparison. XRD results...
of all the samples show diffractograms resembling that of Co$_3$O$_4$ indexed crystal faces (220, 311, 400, 511 and 440), although the peaks are very weak in SC-S and SC-E [19, 20]. Even in the sample of SC-E, which was saturated with H$_2$S at room temperature, no cobalt sulfide was found. This finding suggested that, in the spent adsorbents, cobalt sulfide species are either in the form of amorphous or in smaller nanosize less than 4 nm (detection limit). In addition, it can be indicated that the Co$_3$O$_4$ in adsorbent may be so difficult to convert completely to sulfide. It is also possible that some surface cobalt sulfide may easily convert back to oxide even at room temperature during the process of treating the sample for XRD measurement. Furthermore, compared with SC-S sample, SC-E shows a very weak diffraction peak of Co$_3$O$_4$ at 2θ = 38.5°, indicating a greater conversion of Co$_3$O$_4$ due to a longer adsorbing time. It is also noted that SC-E–H presents stronger intensities than SC-E suggesting that heating treatment might cause the aggregation of Co$_3$O$_4$ nanoparticles.

Figure 2 shows the nitrogen adsorption–desorption isotherms and pore size distribution of as-synthesized samples, the textural parameters are listed in Table 1. For the commercial Co/Mo-Al$_2$O$_3$ catalyst, a type IV adsorption isotherm was observed, indicating the existence of mesoporous structures [21]. In addition, as the N$_2$ physisorption analysis indicates that the SC-based adsorbents have a type II physisorption isotherm with a type H3 hysteresis loop in the relative pressure (p/p$_0$) of 0.8–1.0, which is typical for macroporous materials [22, 23]. Moreover, the hysteresis loop in the relative pressure range of 0.2–0.8, indicating the textural mesopores existed [21]. The hysteresis loops in the high p/p$_0$ ranges of the spent SC-based samples were slightly different from that of the fresh samples, indicative of the discrepancy in pore-size distribution (insert of Fig. 2).

Table 1 summarizes the textural parameters of the fresh and spent samples. It can be seen that specific surface area of SC-E greatly dropped off after sulfidation (SC-E), and a slightly further decrease after stepped heating process (SC-E–H). The catalytic process almost has no significant effect on the surface area. However, the pore volume of samples is typically increased after hydrogenating of COS with shrinkage of average pore size, demonstrating new pores could be generated during this process.

To further investigate composition of spent adsorbents, TG-MS analysis of SC-E sample was performed from room temperature to 1000 °C at a heating rate of 10 °C/min in 100 ml/min of Ar atmosphere. The TG-MS curves of SC-E is presented in Fig. 3. DTG curve shows that there are four remarkable weight loss accompanying gas release during the heating process. The first weight loss below 150 °C can be ascribed to the liberation of water molecules physically absorbed and chemical bonded [8]. The second noteworthy weight loss showed up around 150–210 °C, and was accomplished by the evolution of H$_2$O (MS-H$_2$O signal) and SO$_2$ (MS-SO$_2$ signal), which are thought to be the thermal decomposition of CoSOH [7, 24]. As we mentioned in our previous study, CoSOH can be easily formed when CoS...
directly contact with O₂ and H₂O. The decomposition of CoSOH would release O₂ which might lead to the oxidation of CoS at this temperature range, besides, the surface hydroxyl groups could be also applied in this case and result in CoO oxidation [7].

The third weight loss occurring at around 660–780 °C was very sharp and was accomplished by the elution of SO₂. It was considered to be caused by the thermal decomposition of CoSO₄, which was formed during the desulfurization process as well as the oxidation of CoS during the TG test [25].

The final imperceptible weight loss ranged from 780 to 860 °C without MS signal is explained by decomposition of Co₃O₄ to CoO [26]. Obviously, the weight loss of Co₃O₄ with a fraction of the total weight loss, which further illustrates that Co₃O₄ mainly converted into sulfide phase during the desulfurization process.

High-resolution transmission electron microscopy (HRTEM) investigations were carried out to analyze the microstructure of the saturated sulfided samples and the evolution due to the influences of heat treatment and hydrogenation reaction. Figure 4a–c shows that SC-E displayed an ordered macropores structure and no lattice fingers could be found in the nanoparticles. The corresponding selected-area electron diffraction (SAED) shows no evidence of crystallinity with only diffuse rings present. The phenomenon presented a consistent conclusion with the XRD result and our previous study, that cobalt sulfide obtained at room temperature is in amorphous form [7].

Parts d, e, and f of Fig. 4 show the morphology of sample SC-E–H. The figures show that SC-E, after heat treatment at 200 °C for 1 h, still retained its macropores structure, but a slight break of the walls in macropores structure was observed, which is considered to be due to the agglomeration of nano-sized crystallite. A larger version image (Fig. 4f) shows that the nanocrystals displayed an irregular morphological with particle size ranges of 15–40 nm. The lattice spacing of the exposed planes were 0.467, 0.15, 0.24 nm, corresponding to the crystal faces of (111), (220), (311) of Co₃O₄, 0.26 nm and 0.4 nm were that of (101) and (001) of CoS [27, 28], indicating phase transformation occurs during the process of heat treatment. Both of them exhibited well-defined lattice fringes and multiple bright electron diffraction rings in the SAED pattern (insert of Fig. 4f), revealing the polycrystalline nature of the SC-E–H samples [7].

Parts g, h, i, of Fig. 4 show different magnification HRTEM images of the sample after catalytic reaction (SC-E-200). The figures show that after using for the catalysis of COS under 200 °C for 10 h, the ordered macropores structure collapsed but the walls were preserved to some extent. The nanocrystals are still well spread and the particle size are significantly smaller than before hydrogenation. Part i of Fig. 4 reveals that the exposed planes attribute to (311) and (220) (lattice spacing 0.28 nm and 0.33 nm) of CoS, and (311) (lattice spacing of 0.299 nm) for Co₉S₈ [7, 29]. No lattice fringes could be found for cobalt oxide. As the XRD results indicated that no crystallite cobalt sulfide was detected and the bulk of SC-E-200 remains as Co₃O₄ structure, we speculate that the cobalt oxide in bulk counterpart was entirely covered by accumulated CoS and newly formed Co₉S₈.

Figure 5 is the X-ray photoelectron spectroscopy (XPS) images of SC-E and SC-E-200 samples. As shown in Fig. 5a, the characteristic peaks of Co 2p1/2 and Co 2p3/2 centered at 782.2 and 798.0 eV indicated the presence of CoS in the catalysts [7, 30]. Interestingly is that a new peak positioned at 778.9 eV is found in Co 2p XPS spectrum in SC-E-200, which suggested the formation of Co₉S₈ during hydrogenation process [31]. The S 2p XPS spectra in Fig. 5b
Fig. 4 HRTEM images of SC-E (a, b, c), SC-E–H (d, e, f), SC-E-200 (g, h, i).

Fig. 5 XPS spectra of Co 2p (a) and S 2p (b) for SC-E and SC-E-200.
indicated that besides metal sulfides (162.2 eV), some sulfates (169 eV) were also presented in both samples [32, 33]. These results were consistent with the results obtained from TG-MS and HRTEM.

Reduction patterns of SC-E under investigation are presented in Fig. 6. Three typical regions of $\text{H}_2$ consumption on increasing temperature are found in the patterns. The broad peak with high intensity centered at 240 °C accompanied with a well-defined shoulder at higher temperature (290 °C) can be ascribed to the reduction of CoS to Co$^0$. This reduction temperature is much lower than the literature report, which means the surface Co-S bonds are more unstable and easier to be reduced [34]. The shoulder observed at 290 °C can imply the reduction of Co$^{3+}$ to Co$^{2+}$. The hydrogen consumption peak at slightly higher temperature (400 °C) is ascribed to the reduction of Co$^{2+}$ to Co$^0$ [35]. The higher reduction temperature of Co$_3$O$_4$ in this research is mainly because it is covered by surface sulfide phases. The last $\text{H}_2$ consumption peak around 500 °C is corresponding to the reduction of CoSO$_4$ [36].

Combining all the above mentioned characterization results, the components on the samples are clearly presented in Table 2.

### 3.2 Evaluation of HDS Performance of Spent Adsorbents

The prepared adsorbents and commercial catalyst were tested at low temperatures (200 °C) in the presence of 10% $\text{H}_2$ for COS conversion. The measured COS conversion and $\text{H}_2$S selectivity curves are shown in Fig. 7. Figure 7a shows that COS conversion follows a sequence of Silica < Commerical catalyst < SC < SC-S < SC-E. It can be clearly seen that in the presence of only pure silica without any active phase, a very slight conversion is observed and no $\text{H}_2$S was detected in outlet during the reaction. This conversion of COS can be explained by the thermal decompose of COS, and we believe that the contribution of silica to COS conversion could be ignored [37]. The COS conversion curve of the fresh sample SC showed a fluctuating rise, and the release of hydrogen sulfide was detected at the outlet after 7 h of reaction, which was attributed to the hydrolysis of COS. As for adsorbents presulfided at room temperature, adsorbents SC-S and SC-E displayed COS conversion rate reached as high as 90% and lasted for 10 h. Regard to SC-S adsorbent, the COS conversion curve increases slowly than saturated sulfide SC-E adsorbent, owing to the lower sulfidation degree at the initial stage. SC-E showed higher COS conversion than SC-S after stabilized. Additionally, we found that the release of $\text{H}_2$S in the SC-E catalyst evaluation experiments can be detected from the start and takes a shorter time to reach its stabilization, which means sulfidation degree of fresh adsorbents has played an important role in catalytic activity. Combined with HRTEM results, the formation of Co$_9$S$_8$ new phase is attributed to the reaction between unreacted Co$_3$O$_4$ and catalytic product hydrogen sulfide during the catalytic process. Adsorbents with higher sulfidation degree might show less exposed Co$_3$O$_4$ phase and easily to be stabilized during the catalytic process. The CoS active site formed by adsorption at room temperature shows higher activity than Co$_9$S$_8$ formed by the catalytic process. Therefore, when the catalytic performance is stabilized, the catalytic active center should be provided by CoS and Co$_9$S$_8$. For comparison, commercial Co-Mo/Al$_2$O$_3$ catalyst (CM) was tested under the same conditions, a low conversion rate (15%) is observed. This poor activity of the commercial catalyst compared with the spent absorbent is supposed to be caused by the fewer active components, as the former is a supported catalyst whereas the latter is almost bulk.

Table 3 summarized the performance of different catalysts for COS hydrogenation and compared their performance with the results of this paper. As shown in Table 3, SC-E catalyst shows a similar COS conversion with that reported results, which indicated that the Co-containing

![Fig. 6 $\text{H}_2$-TPR profile of SC-E](image-url)
adsorbents after H₂S removal have great potential to be reused as hydrogenation catalysts realizing their high value reutilization.

### 3.3 Influence of Temperature on Hydrogenation Performance of Spent Adsorbents

The catalytic activity of SC-E was also evaluated for COS hydrogenation at different temperatures, and the COS conversion as well as H₂S selectivity curves were shown in Fig. 8. Figure 8a shows that increasing the reaction temperature from 150 to 250 °C increased the COS conversion rate. The maximum (99.9%) conversion of COS can be reached at 250 °C. At lower temperatures (200 °C), COS conversion can also stabilize at 92%. These results indicate that the catalytic activity of the spent adsorbents could be greatly dependent on the reaction kinetics [38]. Figure 8b shows a quite remarkable difference in H₂S selectivity owing to the temperature effect. The H₂S selectivity can be stabilized around 80% at different short running time. Combining with HRTEM results, it is thought that on the surface could totally be transformed into Co₉S₈, or we can say that Co₉S₈ originates from the surface Co₃O₄ transformation during the catalysis process. The equation can be described as follows:

\[
\text{COS} + \text{H}_2 \rightarrow \text{H}_2\text{S} + \text{CO} \tag{3}
\]

\[
\text{Co}_3\text{O}_4 + \text{H}_2\text{S} \rightarrow \text{Co}_9\text{S}_8 + \text{H}_2\text{O} \tag{4}
\]

According to the corresponding H₂S selectivity curve, the higher the reaction temperature, the faster the hydrogen sulfide concentration at the outlet reaches equilibrium, and the adsorption reaction of Co₃O₄ with H₂S is less effective at lower temperature, it takes a longer time to surface sulfur equilibrium. When the reaction temperature is as low as 150 °C, the COS conversion and the adsorption of H₂S slow down, and thus results in a poor catalysis performance.

### 3.4 Influence of Water Vapor on Hydrogenation Performance of Spent Adsorbents

In the industry gas streams, the reformate gases in the steam contain considerable amounts of water vapor, which may affect COS hydrodesulfurization characteristics and lead to produce SOₓ species [39]. In order to investigate the water tolerance of spent adsorbents, we carried out experiments as 3 vol.% water vapor and/or 10% H₂ can be added to the feed (Ar contains 1000 ppm COS) automatically. The results obtained over SC-E are summarized in Fig. 9. From these

![Fig. 7](image-url)  
Fig. 7  a COS conversion curves for different samples and b corresponding H₂S selectivity curves

**Table 3** Comparison of the COS hydrogenation performance of SC-E and the reported catalysts

| Catalyst               | Feed                          | GHSV (h⁻¹) | Temp (°C) | COS Conversion (%) | Time (min) | References |
|------------------------|-------------------------------|------------|-----------|--------------------|------------|------------|
| SC-E                   | 1000 mg/m³ COS, 10% H₂       | 21,333     | 200       | 92                 | 600        | This work  |
| Sulfided Co₃O₄ nanorods | 0.1%COS, 10%H₂               | 8000       | 200       | 90                 | 400        | [40]       |
| ML-MoS₂/RGO            | 50 ppm COS, 10%H₂, balance N₂| 32,000     | 200       | 93.8               | 480        | [41]       |
| 5% 2Ni-1Co/GS          | 0.05%COS, 10%H₂, balance N₂ | 10,000     | 200       | 96                 | 300        | [15]       |
results, the activity was shown to be around 10% after 10 h exposure to water vapor but without H₂, and the conversion of COS can be explained by the hydrolysis of COS. The catalytic activity of SC-E for conversion of COS is around 92% in the presence of H₂ only. However, when water vapor was switched in or off, the COS conversion changed accordingly. As seen, when water vapor was switched in the feed, the COS conversion rate decreased from ca. 92% to ca. 35% gradually, whereas the conversion rate restored to about 80% while water vapor was cut off from the inlet. Therefore, it is suggested that the presence of water in the feed gas has a negative effect on COS hydrosulfurization over the SC-E system. The negative effect was possibly due to the competitive adsorption of water and COS. Moreover, it was reported that water vapor can significantly accelerate the rate of CoS oxidation and enhance the sintering of the sample, thus affecting the performance of the catalyst and leading to the reduction of the conversion rate of CoS [7].

4 Conclusion

In the present work, the spent Co-containing adsorbents were used as a catalyst for COS hydrosulfurization, experiments were performed at atmospheric pressure over the temperature range of 150 ~ 250 °C. The data shows that the spent cobalt-based macroporous adsorbent after the room temperature desulfurization process has 92% COS conversion at lower temperature (200 °C), which is about 6 times as commercial Co-Mo/Al₂O₃ displayed under the same conditions. The excellent catalytic performance could be related to enriched Co-S active sites with unstable Co-S bonds on the surface, and its content is a key factor affecting its catalytic performance. The H₂S formed during the catalytic reaction also reacts with the unreacted Co oxides during the sulfidation process to form Co₉S₈, which is also conducive to improve the catalytic performance. Temperature played a great role on the conversion rate and H₂S selectivity, with temperature increasing from 150 ~ 250 °C, the conversion rate and H₂S selectivity were increased. In addition, the study also found the presence of water vapor will compete with COS for adsorption, resulting in a decrease in catalytic performance during the catalytic process. The results indicated that there is a strong potential to use spent cobalt-based macroporous adsorbent as catalysts for the hydrotreating process.

Author Contributions All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by [YF], [JW], [CY], [ZS] and [HF]. The first draft of the manuscript was written by [YF] and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data Availability  The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of Interest  The authors have no relevant financial or non-financial interests to disclose.

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