Selenium uptake and simultaneous catalysis of sulfite oxidation in ammonia-based desulfurization

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Abstract
Accelerating the (NH₄)₂SO₃ oxidation gives rise to the reclaiming of byproduct, while there are secondary environmental risks from reduction of the coexisted selenium species by sulfite. In this study, a bi-functional Co-SBA-15-SH, were synthesized through Co impregnation and sulhydryl (-SH) decoration, which can simultaneously uptake Se and accelerate sulfite oxidation efficiently. Meanwhile, the adsorption kinetics and migration mechanism of Se species were revealed through characterization and density functional calculations, with maximum adsorption capacity of 223 mg/g. The inhibition of Se re-emission and poisonous effect of Se on sulfite oxidation was also investigated. Using the findings of this study, the ammonia desulfurization can be improved by enabling purification of the byproduct and lowering the toxicity of effluent by removing toxic pollutants.

Keywords:
Selenium
Adsorption
Re-emission
Sulfite oxidation
Catalyst

Introduction
The coal-fired flue gas comprises various hazardous pollutants—including SO₂, NOₓ, particles, toxic non-metals and heavy metals—that are harmful to human health (George et al., 2020; Li et al., 2019; Liu et al., 2019; Yang et al., 2020; Yao et al., 2019). Ammonia-based desulfurization is a promising technology for SO₂ treatment owing to its high desulfurization efficiency, small footprint, and the small investment required. The byproduct (NH₄)₂SO₃ can be oxidized into (NH₄)₂SO₄, which is a plant fertilizer, leading to valuable economic benefits (Zhu et al., 2015). In practice, however, overabundant (NH₄)₂SO₃ consumes dissolved oxygen because of its inadequate oxidation and decomposes into NH₃ and SO₂; this can pose a high risk to the atmosphere and water in the environment. To address this issue, we prepared a series of cobalt-based catalysts for use in sulfite oxidation (Li et al., 2017; Wang et al., 2018a, 2017, 2018b). The active cobalt species were evenly dispersed on the surface of porous supports and could increase the oxidation rate by a factor of three to eight. Consequently, the desulfurization efficiency was increased and the decomposition of sulfite was markedly suppressed.

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Desulfurization slurry is enriched with volatile toxic pollutants derived from flue gas, including mercury, selenium, and arsenic (Chang et al., 2019; Chen et al., 2016; Lei et al., 2019; Sun et al., 2019; Zhong et al., 2011). These pollutants can be reduced by (NH₄)₂SO₃, resulting in considerable re-emissions and secondary environmental risks (Liu et al., 2014; Ma et al., 2019; Xu et al., 2018). Therefore, efficient separation of volatile toxic pollutants from desulfurization slurry is another large challenge, in which Se is increasingly attracting attention because of its potential toxicity (Dai et al., 2020; He et al., 2018; Liang et al., 2019; Liu et al., 2013). Se has been found in desulfurization slurry in selenite (SeO₂⁻) and selenate (SeO₄²⁻) forms, which, through the reduction of sulfite, can be converted into insoluble gaseous Se⁰ and escape through flue gas. Because the porous cobalt-based catalyst for ammonium sulfate oxidation can be decorated with functional groups, it can simultaneously serve as an excellent adsorbent of Se species, minimizing the risk to the atmosphere and water in the environment.

The commonly used adsorbents for Se species include active carbon, metal oxides, and nano-TiO₂ (Chan et al., 2009; Sun et al., 2015; Yin et al., 2018; Zhang et al., 2009, 2008). Zhang et al. (2008) developed iron-coated granular activated carbon to adsorb selenite, and the adsorption capacity was discovered to reach 2.5 mg/g in the equilibrium state for an initial selenite concentration of 2 mg/L. Zhang et al. (2009) discovered that nano-TiO₂ with a large specific surface area and small particle size had a maximum selenite adsorption capacity of 8.46 mg/g. To further improve their capacity to adsorb Se species by maximizing their adsorption selectivity, the traditional adsorbents were decorated with organic functional groups. Bleiman and Mishael (2010) designed a composite of chitosan with clay (i.e. montmorillonite) of which the Se(VI) adsorption capacity was 18.4 mg/g. Sharrad et al. (2012) prepared FeOOH to achieve a Se(IV) adsorption capacity of 26.3 mg/g. In addition, some novel adsorbents—such as metal organic frameworks, ligand immobilized conjugate adsorbent, and MS-δ-Bi₂O₃—have been used to capture hypertoxic SeO₂⁻ anions from aqueous solutions due to their unique structural advantages (Howarth et al., 2015; Liu et al., 2018; Rabiiul Awual et al., 2014). The results indicated that Se adsorption performance is highly dependent on the specific surface area, pore structure, and active adsorption site distribution on the surface of the adsorbents.

In view of the potential absorbents that can be used for uptake of toxic pollutants from aqueous solution, the silica-based mesoporous SBA-15 is attracting increasing attention due to its excellent thermal stability, large surface area, tunable pores, and easy surface functionalization (Chandra Mouli et al., 2011; Falcón et al., 2016; Jo et al., 2005). It has been widely used as a catalyst and absorbent for the removal of pollutants (Hernández-Morales et al., 2012; Marcoux et al., 2015). Its capacity to adsorb heavy metals can be greatly improved by grafting on functional groups—such as amino, sulfydryl, and sulfonic acids—resulting from chelation with heavy metals (Dindar et al., 2015; Lee et al., 2015; Yang et al., 2004). McManamon et al. (2012) synthesized amino-functionalized SBA-15 at different pore sizes through controlled thermal treatment. The results demonstrated that the maximum adsorption capacity was 39 and 41 mg/g for Pb²⁺ and Cd²⁺, respectively. Shen et al. (2018) discovered that the sulfhydryl (SH)-functionalized mesoporous material SBA-15, prepared using a post-grafting method, has favorable selective adsorption for mercury ions. Its high Hg(II) removal efficiency was attributed to the covalent bonding and electrostatic attraction between thiol and Hg(II). Kim et al. (2017) prepared SUP-SBA-15 functionalized with melamine sulfonic acid through a two-step post-modification process. The material exhibited excellent efficiency for adsorbing Li⁺, achieving a removal efficiency of 95% and 89% in artificial seawater and wastewater respectively.

In this study, a bi-functional catalyst-absorbent, Co-SBA-15-SH, was synthesized through wet impregnation with Co and decoration with SH. Its performance in simultaneous enhancing the oxidation of (NH₄)₂SO₃ and removing Se species was investigated. The chemical speciation of Se in advanced ammonia desulfurization—including re-emission of Se⁰, aqueous Se⁴⁺ and Se⁶⁺, and adsorbed Se (Seₘ)—was quantitatively analyzed. The effect of Seₘ on the catalysis activity of Co species in sulfite oxidation was discussed as well as its inhibition effect on the re-emission of Se⁰. Our novel insight into the migration behavior of Se species can advance ammonia desulfurization by enabling purification of the desulfurization byproduct and lowering the toxicity of effluent through toxic pollutants removal.

1. Materials and methods

1.1. Chemicals

The reagents used, all of analytical grade, included Co(NO₃)₂·6H₂O from Tianjin Kernel Reagent Corporation, absolute CH₃CH₂OH from Tianjin Fengchuan Reagent Corporation, (NH₄)₂SO₃·H₂O from Alfa Aesar Chemical Corporation, HCl from 3rd Tianjin Chemical Reagent Corporation, and (3-mercaptopropyl) trimethoxysilane (MPTMS) from Shanghai Aladdin Biochemical Technology Corporation.

SBA-15 of length 6–11 nm was purchased from Nanjing XFNano Material Technology Corporation. Standard selenium solution was obtained from the National Analysis and Testing Center for Nonferrous Metals and Electronic Materials, China.

1.2. Synthesis of Co-SBA-15-SH catalyst-adsorbent

Cobalt-loaded SBA-15, with theoretical cobalt loading of 2%, was prepared through impregnation (Wang et al., 2017). In a typical synthesis process, 0.20 g of Co(NO₃)₂·6H₂O was dissolved in 100 mL of absolute CH₃CH₂OH. Subsequently, 2.0 g of SBA-15 was added to the mixture, which was then stirred for 5 hr at 25 °C, after which it was aged at room temperature for 1 day. The pretreated mixture was then dried for 2 hr at 60 °C in a vacuum rotary evaporator, after which it was calcined for 5 hr at 450 °C at a heating rate of 2 °C/min under air in a muffle furnace. The product was named Co-SBA-15.

Subsequently, 40 mL of absolute CH₃CH₂OH, 10 mL of H₂O, and 10 mL of MPTMS were mixed in a 100 mL Erlenmeyer flask. Then, 0.20 g of Co-SBA-15 was fed into the mixture, which was then condensed and refluxed at 120 °C for 4 hr. Subsequently, the brick red precipitate was collected through centrifugation
at 4500 r/min for 5 min and then washed twice—once using absolute CH$_3$CH$_2$OH and once using H$_2$O. Finally, the washed sample was dried for 2 hr at 100 °C. The product was denoted Co-SBA-15-SH. The characterization conditions are detailed in the Supporting Information.

1.3. Catalyst–adsorbent characterization

The morphology and crystallization structure of the Co-SBA-15-SH were identified using scanning electron microscopy (SEM, HitachiS-4800) and transmission electron microscopy (TEM, JEM-2100). Elemental mapping of the adsorbent was conducted using energy-dispersive X-ray spectroscopy (EDS, Bruker Quantax 400). The specific surface area, pore size, and pore volume of the adsorbent were calculated using the Brunauer–Emmett–Teller (BET) equation and Barrett–Joyner–Halenda method from processes N$_2$ adsorption–desorption. Fourier transform infrared spectroscopy (FT-IR-200, JASCO, Japan) was used to identify functional groups on the surface of the adsorbent; the wavelength range used was 4000–400 cm$^{-1}$ and the wavenumber accuracy was 0.01 cm$^{-1}$. A Bruker D8 advance-type X-ray diffractometer was used to qualitatively and quantitatively analyze the crystalline substance of the samples under the following conditions, with varying small angle from 0.5° to 5°, step length of 0.02°, tube voltage of 40 kV, and tube current of 40 mA. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) was employed to analyze the surface elemental composition and valence of the adsorbent; it has resolution of 0.48 eV (Ag 3d5/2) and 0.68 eV (C 1 s).

1.4. Experimental procedure

The kinetics and isotherm of Se adsorption were investigated by feeding 0.05 g of Co-SBA-15-SH into a 100 mL centrifuge tube in a temperature-controlled shaker. The pH was adjusted using 1 mol/L HCl and NaOH. An aqueous sample of size 1.0 mL was collected and filtered at the desired intervals, and these samples were then analyzed using an atomic fluorescence spectrometer to obtain the residual Se concentration.

The catalytic oxidation of (NH$_4$)$_2$SO$_3$ and the simultaneous uptake of Se were performed in a bubbling tank at 45 °C. In a typical process, 10.0 g of (NH$_4$)$_2$SO$_3$·H$_2$O, 2 mL of standard selenium solution at a concentration of 1000 mg/L, and 0.2 g of Co-SBA-15-SH were blended in a reactor with a total volume of 200 mL. During Se adsorption and catalysis of sulfate oxidation, the reaction solution was filtered and sampled at intervals. Barium sulfate spectrophotometry (Wang et al., 2016) was used to determine the sulfate concentration. The (NH$_4$)$_2$SO$_3$ oxidation rate was obtained by plotting the sulfate concentration versus time. The total removal efficiency ($\eta$) and equilibrium Se adsorption capacity ($q_e$, mg/g) of Co-SBA-15-SH were calculated as follows:

$$\eta = \frac{[C_0 - C_e]/C_0}{\times 100\%}$$  \hspace{1cm} (1)

$$q_e = \frac{V(C_0 - C_e)}{m}$$  \hspace{1cm} (2)

Where, $C_0$ (mg/L) is initial concentration in solution, $C_e$ (mg/L) is equilibrium concentration, $V$ (L) is solution volume, and $m$ (g) is mass of the dry sorbent.

1.5. Methodology

Two classical isothermal adsorption models, the Langmuir and Freundlich models, were used to obtain the Se$^{2+}$ adsorption capacity of Co-SBA-15-SH, which can be expressed by Eqs. (3) and (4), respectively:

$$\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{C_e}{q_m}$$  \hspace{1cm} (3)

$$\ln q_e = \ln k_F + \frac{1}{n_F} \ln C_e$$  \hspace{1cm} (4)

Where, $q_m$ (mg/g) is the maximum adsorption capacity of adsorbent, $k_L$ (L/mg) is Langmuir equilibrium adsorption constant, $k_F$ (mg/g) and $n_F$ (L/mg) are Freundlich empirical constant.

Furthermore, the pseudo-first-order and pseudo-second-order models were employed to analyze the adsorption kinetics, which were described using the following equations, respectively:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$  \hspace{1cm} (5)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (6)

Where, $q_t$ (mg/g) is adsorption capacity at time $t$ (min), $k_1$ (min$^{-1}$) is equilibrium rate constant of the pseudo 1st order adsorption, and $k_2$ (g/(mg·min)) is equilibrium rate constant of the pseudo 2nd order adsorption.

1.6. Theoretical calculations

From first principles, the projector augmented wave method and Perdew–Burke–Ernzerhof functional were implemented using VASP (v. 5.4.1). The cutoff energy was defined as 400 eV with a plane-wave basis to ensure accurate results. The k points in the Brillouin zone were of size $3 \times 1 \times 1$ within the Monkhorst–Pack grid for both structural optimization and electronic structural calculations. All structures and energies were converged to less than $10^{-4}$ eV. The width of the vacuum slab was set at 10 Å, and the slab position was 1 Å to prevent interaction errors.

The adsorption energy, $E_{ads}$, is defined as:

$$E_{ads} = E_{total} - E_{SBA-15} - E_{SeO_2^-}$$  \hspace{1cm} (7)

Where $E_{total}$, $E_{SBA-15}$ and $E_{SeO_2^-}$ denote the total energy of the adsorption structures, SBA-15 structures, and isolated molecules, respectively.

2. Results

2.1. Simultaneous removal of Se and SO$_3^{2-}$ by the SBA-15 catalyst–adsorbent

Compared with that of the noncatalyzed reaction, the catalyzed rate of (NH$_4$)$_2$SO$_3$ oxidation was approximately 80% higher when the dosage of neat SBA-15 was 1 g/L (Fig. 1a). SBA-15 may have offered more opportunities for the reactants to come into contact. A similar result was obtained by
However, in addition to these species, even more poisonous selenium oxyanions—such as selenite and selenate—are formed, which can be adsorbed to the SBA-15 catalyst surface. When the SBA-15 was further decorated with a thiol group, the (NH$_4$)$_2$SO$_3$ oxidation rate decreased by 23%, probably because that cobalt active sites were partially covered by thiol functional groups. With the addition of selenium at a concentration of 1 mg/L, a slight descent of the oxidation rate was observed, indicating that the catalytic activity of Co was prohibited by the adsorption of SeO$_3^{2-}$ and SeO$_2^{2-}$. This can be ascribed to the shingling or even poisonous effect of selenite and selenate on active cobalt sites. When the selenium concentration was increased to 10 mg/L, a greater amount of active cobalt may have been covered by adsorbed selenium species, resulting in a 28% decrease in the catalytic activity of Co-SBA-15-SH in sulfite oxidation. However, the concentration of selenium in real desulfurization slurry is lower than 1.2 mg/L. Hence, the inhibition effect of adsorbed selenium on catalyzed sulfite oxidation would be considerably smaller than that observed in this study.

Fig. 1b illustrates the effect of functional groups on the proportion of residual Se in a solution of modified Co-SBA-15 and implies that the neat SBA-15 lacks active sites and thus has little capacity for Se adsorption despite having high specific surface area. The presence of Co, the predominant active species in sulfite oxidation, is beneficial for Se adsorption, leading to a decrease in the proportion of residual Se in solution from 93.6% to 86.3%. This may have been because Co combined with selenium oxyanions through electrostatic interaction (Luo et al., 2018). Once Co-SBA-15 was further decorated with organic functional groups—such as amino, carboxyl, and thiol groups—the Se removal efficiency was substantially improved. This was attributed to the chelate interaction between the functional groups and Se species, resulting in a stably coordinated compound. The proportion of residual Se in the solution was less than 2% when thiol groups were grafted, showing the active adsorption sites role of -SH in Se adsorption by Co-SBA-15-SH. However, the proportion of residual Se in solution in the presence of sulfite was increased.
by 11.3%, because sulfite competed for active -SH adsorption sites against selenium oxyanions and formed new S-S covalent bonds (Córdoba, 2017). Hence, sulfite hindered the adsorption of selenium in the solution and inhibited the rerelease of Se$^{0}$.

In Fig. 1c, the green line represents the greater than 80% removal efficiency of aqueous Se, existing as SeO$_4^{2-}$ and SeO$_3^{3-}$, in presence of ammonium sulfite. However, this efficient removal was caused by the reduction of sulfite, which was responsible for the strong re-emission of gaseous Se$^0$, as illustrated in Fig. 1d. Hence, we inferred that the majority of aqueous Se species in real desulfurization slurry will escape due to the presence of sulfite. By contrast, the red line in Fig. 1c indicates that Co-SBA-15-SH can efficiently adsorb aqueous Se species. The removal efficiency was greater than 95%, contributing to substantial prevention of Se$^{0}$ re-emission. When ammonia sulfite oxidation and Se adsorption were simultaneously controlled by Co-SBA-15-SH, the Se removal efficiency decreased slightly, as shown by the blue line in Fig. 1c. Therefore, the catalytic activity in sulfite oxidation and the Se adsorption ability of Co-SBA-15-SH competed with each other to an extent. Regarding the advanced ammonia desulfurization slurry, the amount of Se$^{0}$ re-emission caused by the reduction in sulfite (blue line in Fig. 1c) was 28% lower in Fig. 1d because of the adsorption ability of Co-SBA-15-SH, resulting in a further increase of the aqueous Se removal efficiency from 81% to 87.8%.

Fig. 1d plots the chemical speciation content of Se under different catalyst conditions, including re-emission of Se$^{0}$, aqueous Se$^{4+}$ and Se$^{6+}$, and Se$_{aq}$. Compared with the SBA-15 and Co-SBA-15 materials, Co-SBA-15-SH significantly inhibited re-emission of Se$^{0}$, which was attributed to the effective adsorption of selenium oxyanions by Co-SBA-15-SH. The presence of -SH groups had a substantial impact on the adsorption of selenium from the desulfurization solution.

### 2.2. Effect of operation parameters on aqueous Se adsorption by Co-SBA-15-SH

The equilibration state for the maximum Se uptake was approached after 10 mg/L selenium solution containing 0.05 g (1 g/L) adsorbent was shaken for 120 min. Fig. 2a indicates that the adsorption proceeded quickly during the first 20 min and then approached the adsorption equilibrium within 40 min. The red line in Fig. 2b illustrates the Se removal efficiency of Co-SBA-15-SH for Se concentrations between 5 and 800 mg/L. The Se concentration at equilibrium ($C_e$) increased from 0.025 to 577 mg/L. The Se adsorption capacity at equilibrium increased sharply as the initial Se concentration was increased from 5 to 400 mg/L. Accordingly, the maximum adsorption capacity of Co-SBA-15-SH was discovered to be 223 mg/g. It was compared with other adsorbents in the literature, shown in Appendix A Table S1. The material’s excellent Se adsorption performance may have been caused by the numerous adsorption sites on the surface of SBA-15. Therefore, when the solution was more concentrated, an increasing number of selenium ions could interact with adsorption sites.

The adsorption isotherm obtained through linear regression according to Eqs. (3) and (4) is presented in Fig. 2b. Fig. 2c and d shows that a higher correlation coefficient ($R^2 = 0.995$) was obtained when data were fitted using the Freundlich model, indicating that Se adsorption occurred at a multi-molecular layer or the heterogeneous interface between selenium and Co-SBA-15-SH (Guo et al., 2014). The $n$ value between 1 and 10 in Fig. 2d indicates that the adsorption intensity was higher at greater Se concentrations. The high value of the intercept, $k_r$, demonstrates the high Se adsorption capacity of Co-SBA-15-SH (McKay et al., 1980).

The adsorption kinetics was obtained using Eqs. (5) and (6). As illustrated in Fig. 2e and f, the Se adsorption kinetics conforms to the pseudo-second-order model, with $R^2 = 0.997$. The adsorption capacity ($q_{e,cal} = 10.7$ mg/g) calculated from the pseudo-second-order model was in favorable agreement with the experimental result ($q_{e,cal} = 9.9$ mg/g). Hence, the rate-limiting step of selenium adsorption by Co-SBA-15-SH was confirmed to be chemical adsorption.

### 2.3. Characterizations

Fig. 3a indicates that the neat SBA-15 comprised rod-like clusters with uniform particle size and a smooth surface. Loading the SBA-15 with cobalt through impregnation did not cause much change in appearance, as shown in Fig. 3b, except for some small Co particles appearing on the SBA-15 carrier. Further decorating the Co-SBA-15 with thiol groups resulted in a much rougher surface than that of the pure SBA-15 (Fig. 3c), which may have contributed to the successful introduction of SH functional groups. However, the overall appearance and structure of the SBA-15 cluster did not change substantially, implying the excellent stability of the Co-SBA-15-SH catalyst-adsorbent. The TEM image presented in Fig. 3d indicates that the neat SBA-15 had a 2D 6 nm hexagonal structure. This orderly channel structure was maintained once Co and thiol groups had been introduced, as illustrated in Fig. 3e,f, in favorable agreement with the results presented in Fig. 3a–c. However, with the grafting of Co and thiol groups, the channel spacing decreased from 9.09 nm for neat SBA-15 to 5.71 nm for the modified catalyst, proving that cobalt and thiol functional groups were successfully introduced into the SBA-15 channels.

The adsorption peaks of Co and SH in Fig. 3d and e indicate that some Co and SH remained on the SBA surface. TEM elemental mapping further demonstrated the distribution of all elements (Fig. 3g), and Si, O, S, and Co species were discovered to all be uniformly dispersed on the SBA-15 carrier. Fig. 3h displays the EDS mapping of Si, O, S, Co, and Se on Co-SBA-15-SH after adsorption. Little morphological difference was observed in the SEM images between the Co-SBA-15-SH before and after Se adsorption. According to Fig. 3h, Si, O, S, Co, and Se were uniformly dispersed on the Co-SBA-15-SH, confirming that the Se species were well adsorbed on the Co-SBA-15-SH support.

The N2 adsorption and desorption isotherms and pore size distribution of SBA-15, before and after decoration with cobalt and -SH, are presented in Fig. 4a and b. Both SBA-15 and Co-SBA-15 had Langmuir IV adsorption isotherms with the typical H1 hysteresis loop, indicating uniform mesopores and favorable connectivity in the 2D hexagonally ordered mesoporous structure (Gao et al., 2014). However, a hysteresis loop from H1 to H2 was obtained for Co-SBA-15-SH, implying a certain irregular channel inside Co-SBA-15-SH. Moreover, the
slopes of curves in Fig. 4a fall at low relative pressure ($P/P_0 < 0.6$), suggesting the existence of a few micropores in the raw SBA-15, Co-SBA-15 catalyst, and bi-functional Co-SBA-15-SH. This may have been caused by adsorption condensation on the channel. The slope of the isotherm increased greatly as $P/P_0$ was increased, indicating that the sharp capillary condensation step in the adsorption and desorption curve (Tang et al., 2014). The specific area of Co-SBA-15 was slightly lower than that of neat SBA-15 because of the distribution of Co species on the SBA-15 support. The hysteresis loop was smaller when thiol groups were grafted on Co-SBA-15, resulting in an even smaller specific area, as illustrated in Fig. 4b.

Fig. 4c presents the small-angle X-ray diffraction (XRD) patterns of the raw SBA-15, Co-SBA-15 catalyst, and bi-functional Co-SBA-15-SH before and after Se adsorption. The well-resolved diffraction peaks in the spectrum of SBA-15 at 0.9, 1.5, and 1.8 were ascribed to reflections at the (100), (110), and (200) lattice planes, respectively. This indicated further improved 2D hexagonal $p6m$ symmetry and a well-ordered structure in the SBA-15-type materials (Lee et al., 2015). Moreover, the diffraction peaks in the spectra of Co-SBA-15 and Co-SBA-15-SH had slightly lower intensity than those in the spectrum of neat SBA-15. This observation implied that Co and thiol groups may have dispersed along the SBA-15 channels and occupied little space in the pores of SBA-15, having little effect on the ordered 2D hexagonal mesostructure. These findings are in favorable agreement with the SEM and TEM images presented in Fig. 3a–f. Furthermore, Fig. 4c shows that the peak position in the spectrum of the modified SBA-15 was shifted slightly to a higher angle. This suggested a pore size decrease in the presence of cobalt oxide and a thiol group, which is consistent with the BET data. These results revealed that the modification of Co-SBA-15-SH by thiol doping was successfully achieved without destroying the material's pore

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**Fig. 2** – Selenium adsorption by Co-SBA-15-SH for different (a) contact times; (b) initial Se concentrations; (c) Langmuir isotherms; (d) Freundlich isotherms; (e) pseudo zero order model; and (f) pseudo 2nd order model.
structure. In addition, the diffraction peaks according to reflections at the (100), (110), and (200) lattice planes with the hexagonal space group in p6mm were observed in the spectrum of the bi-functional Co-SBA-15-SH after Se adsorption. However, the intensity of these peaks was slightly lower after Se adsorption because the inner pores were partially occupied, but the 2D hexagonal mesoporous structure remained. Moreover, the Co species inside Co-SBA-15-SH were in the amorphous form due to the -SH decoration, as illustrated in Appendix A Fig. S1.

Fig. 4d verifies the existence of SiO₂ in the catalyst with and without -SH doping; the absorbance peaks at 805 and 1087 cm⁻¹ were ascribed to the symmetric stretching vibration and asymmetric stretching vibration about Si-O-Si, respectively. The vibration peak at 1635 cm⁻¹ was attributed to the stretching vibration of Si-OH (Sathishkumar et al., 2013), and the peak at 465 cm⁻¹ corresponded to the Si-O-Si bending vibration (Zhu et al., 2017). The wide peak at approximately 3439 cm⁻¹ confirmed the stretching vibration of -OH (Dash et al., 2017). By contrast, the S-H stretching band was too weak to be detected in the spectra of dilute solutions; the same phenomenon was reported elsewhere (Silverstein et al., 2005). In addition, the weak bands observed at approximately 2857 and 2935 cm⁻¹ were ascribed to stretching of C-C from MPTMS after thiol functionalization (Tang et al., 2014). This indirectly verified the existence of -SH grafted onto Co-SBA-15.

To further verify the findings from the XRD patterns, Fig. 5a shows that the peaks at the binding energies of 780.8 and 796.6 eV corresponded to Co 2P½ and Co 2P½, respectively. Additionally, the satellite peak at 786.2 eV was 5.4 eV higher than the main peak, implying the presence of bivalent Co. The Co 2P½ peak was fitted into subbands centered at 780 and 781.6 eV, which were attributed to the surficial bivalent Co and trivalent Co, respectively (Castro and Gervasi, 2000). According
As research; \(^{15}\)tively, \(^{15}\)tivity Co-SBA-15-SH displayed in Fig. 4, the peaks of Se \(3d_{5/2}\) and \(3d_{3/2}\) were centered at 54.1 and 56.0 eV with a spin-orbit splitting of 1.96 eV. This was attributed to the homopolar bond of Se–Se being detected in Co-SBA-15-SH-Se. Besides the Se–Se bond, the doublet peaks at binding energies of 55.6 and 56.4 eV, corresponding to the Se–S heteropolar bond, were deconvoluted and curve-fitted for Co-SBA-15-SH-Se. The results clearly demonstrated that Se had successfully adsorbed onto Co-SBA-15-SH, which is in accordance with the SEM-EDS mapping results.

### 3. Discussion

The migration pathway of Se species in the simulated desulfurization slurry was speculated to be as follows:

\[
\text{SO}_3^{2-} + \text{SeO}_3^{2-} \rightarrow \text{SO}_2^{2-} + \text{SeO}_2^{2-} \quad (8)
\]

\[
2\text{H}^+ + 2\text{SO}_3^{2-} + \text{SeO}_3^{2-} \rightarrow \text{Se}^0 + 2\text{SO}_4^{2-} + \text{H}_2\text{O} \quad (9)
\]

\[
\text{Co-SBA-15} + \text{SeO}_3^{2-} \rightarrow \text{Co-SBA-15-SeO}_3^{2-} \quad (ads) \quad (10)
\]
Co-SBA-15 + SeO$_4^{2−}$ → Co-SBA-15-SeO$_4^{2−}$ (ads) \hspace{1cm} (11)

3RSH + SeO$_3^{2−}$ → RS=Se=SR + 2OH$^−$ + RSOH \hspace{1cm} (12)

R: Co-SBA-15-(OH)$_2$Si(CH$_3$)$_3$

Under noncatalyzed conditions, selenite can be reduced to sulfite in desulfurization slurry, as shown in Reaction (8). Reaction (9) indicates that the main Se species, selenite, is converted into Se$^0$ by sulfite. The species are then carried by bubbles and released into the atmosphere, accounting for 80% of the total Se in Fig. 1d. The doping of Co onto SBA-15 aided Se adsorbance, as illustrated in Fig. 1b, and that may have been due to a simple adsorption reaction between Co-SBA-15 and selenium oxyanions as indicated by Reactions (10) and (11). However, the weak binding force between Se and Co-SBA-15 was unable to markedly inhibit the reduction of Se by sulfite, resulting in limited adsorption ability for Se species. With the aid of silane coupling agent, -SH functional groups were successfully grafted onto the surface of the Co-SBA-15 carrier. Because of the presence of the catalytic-adsorbent Co-SBA-15-SH, selenate remained in the desulfurization slurry instead of being reduced by sulfite. According to Reactions (12) and (13), the thiol functional groups in the prepared Co-SBA-15-SH combine with the selenate and selenite to produce strong Se-S covalent bonds. Consequently, grafting with thiol functional groups resulted in a greatly higher Se removal efficiency of more than 95%.

The sulfite oxidation rate in the presence of bi-functional Co-SBA-15-SH was discovered to be approximately 23% lower than that illustrated in Fig. 1a. This can be ascribed to the active catalysis sites of cobalt for sulfite oxidation being partially covered by thiol functional groups. For the simulated desulfurization slurry used to obtain Fig. 1a, the sulfite oxidation rate might have been further decreased by 6.6% because more active sites were covered with doped thiol groups, preventing Se adsorption. Even at a much higher Se concentration of 10 mg/L, the catalysis activity was maintained at approximately 3.07-fold higher than the activity of the noncatalyzed reaction, which ensures the feasibility of applying Co-SBA-15-SH to the simultaneous catalysis of sulfite oxidation and Se removal.

Integrating with the characterization and experiment results, density functional theory (DFT) calculations were conducted to validate the adsorption of SeO$_4^{2−}$ by S-functionalized Co-SBA-15 catalysts. The structural geometry of Co-SBA-15-SH was determined as a point of comparison.
and $\text{SeO}_3^{2-}$ adsorption on Co and S sites and $\text{SO}_4^{2-}$ adsorption on Co sites was investigated in this sample. In Fig. 6a, the adsorption energy ($E_{\text{ads}}$) of $\text{SeO}_3^{2-}$ on the Co sites in Co-SBA-15-SH ($-0.97 \text{ eV}$) indicates that the Co species have strong Se adsorption capacity. Additionally, Co-SBA-15 has stronger Se adsorption capacity when -S-functional groups are grafted onto the material, as confirmed by the more favorable $E_{\text{ads}}$ ($-1.06 \text{ eV}$) of S-Se in Co-SBA-15-SH. Moreover, the inset image in Fig. 6a and b presents the electronic location function of Co-SBA-15-SH. The covalent interaction between $\text{SeO}_3^{2-}$ and S sites in Co-SBA-15-SH was much stronger than that with Co sites in Co-SBA-15-SH, indicating the higher ability of -S-functional groups to adsorb $\text{SeO}_3^{2-}$. The adsorption of Se species was efficiently promoted by grafting -S onto Co-SBA-15.

The feasibility of $\text{SO}_4^{2-}$ adsorption by Co-SBA-15-SH is illustrated in Fig. 6c. Adsorption and activation of $\text{SO}_4^{2-}$ occurred mainly at Co sites. Notably, the $E_{\text{ads}}$ of $\text{SO}_4^{2-}$ on Co sites was much less than that of $\text{SeO}_3^{2-}$. Therefore, simultaneous removal of Se and catalysis of sulfite oxidation by Co sites was also proved in the DFT calculations. Consequently, adsorbed $\text{SeO}_3^{2-}$ can occupy the adsorption sites of $\text{SO}_4^{2-}$, leading to lower catalytic performance. The calculation result was in favorable agreement with the observations presented in Fig. 1, further validating the feasibility of the bi-functional absorbent-catalyst for ammonia-based desulfurization.

4. Conclusions

In this paper, bi-functional Co-SBA-15-SH was fabricated to simultaneously adsorb Se and accelerate sulfite oxidation in advanced ammonia desulfurization. The kinetics of Se adsorption and the inhibitory effect of Co-SBA-15-SH on Se$^0$ re-emission were revealed. The mechanism of Se migration and the poisonous effect of Se on sulfite catalytic oxidation were demonstrated through characterization and DFT calculations, and the findings can be used as a reference for simultaneous sulfite oxidation catalysis and heavy metal uptake to improve the wet desulfurization process.

Appendix A Supplementary data


REFERENCES


