Catalytic Conversion for Hydrogen Sulfide

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ABSTRACT

In this study, a series of transition metal mono-substituted heteropoly compounds $H_7PMo_{11}MO_{39}$ ($M = Co^{2+}$, Mn^{2+} , Ni^{2+} and Zn^{2+}) ($HPMo_{11}M$) and single-absent heteropoly compounds $H_3PMo_{11}O_{39}$ ($HPMo_{11}$) were prepared for highly effective removal of hydrogen sulfide (H_2S) from gas stream. The heteropoly compounds were characterized Fourier transform infrared spectroscopy (FT-IR), elemental analysis and scanning electron microscopy (SEM). The results confirmed that the transition metal ions successfully replaced the Mo atom. $H_7PMo_{11}CoO_{39}$ showed that the outstanding desulfurization capacity and the H_2S removal efficiency can reach more than 90% for 3 h. Besides, after regeneration, the desulfurization capacity of $H_7PMo_{11}CoO_{39}$ towards H_2S only a drop of 5.11% of the initial desulfurization capacity. Optimization experiments demonstrated that $H_7PMo_{11}CoO_{39}$ had the ideal desulfurization performance under the condition of low H_2S concentration or high dosage of $H_7PMo_{11}CoO_{39}$. An appropriate temperature of 25°C is necessary for high removal efficiency. The optimum pH value for desulfurization is 5. The kinetic data can be well described by pseudo-first-order kinetic model. The desulfurization products were proved to be S and SO_4^{2-} based on X-ray photoelectron spectroscopy (XPS) characterization results.

Keywords: Transition metal ions, Heteropoly compounds, H_2S , Desulfurization

1 INTRODUCTION

Heteropoly compounds (HPCs) have been widely used in various organic and catalytic synthesis reactions. This is because the HPCs have high catalytic activity, stable structure, redox and redox reversibility, excellent selectivity, and can be used as homogeneous and heterogeneous catalysts. When the central heteroatoms in the HPCs are replaced by transition metal ions, a wide variety of substituted HPCs can be generated. This expands the field of catalytic reduction of HPCs. In recent years, transition metal-substituted heteropoly compounds have attracted the attention of researchers at home and abroad and become a hot research field (Weakley and Malik, 1967). The vacant heteropoly compound anions are similar to multidentate ligands, with two or more atoms that can provide lone electron pairs. Therefore, people can synthesize substituted heteropoly compounds with transition metal ions (Bi *et al.*, 2004; Proust *et al.*, 2008). The transition metal-substituted heteropoly compound has the same crystal water as the heteropoly compound, and at the same time, there is stable structural water directly connected to the skeleton structure inside the anion. Therefore, the transition metal-substituted heteropoly compounds have a stable structure and strong thermal stability. In addition, they can also store a large number of electrons, thereby increasing the conductivity and enhancing the catalytic activity and are more widely used in various catalytic oxidation reactions (Santos *et al.*, 2015).

According to relevant literature reports, heteropoly compounds have been involved in various reactions as acidic and redox catalysts. Transition metal-substituted heteropoly compounds have been widely used in the field of catalytic oxidation of organic substances such as alkanes, olefins, alcohols and sulfur-containing compounds, and the catalytic oxidation desulfurization of fuel oil (Zhang *et al.*, 2016). However, for the desulfurization reaction to remove hydrogen sulfide, most

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of the catalysts used are phosphotungstates replaced by vanadium (V). Liu *et al.* (2017a) and Lütkehoff *et al.* (1995) found that the efficiency of H₂S removal of the pure phosphotungstic acid (H₃PW₁₂O₄₀) and phosphomolybdic acid (H₃PMo₁₂O₄₀) were 20% and 80%, respectively. Ma *et al.* (2014) and Wang *et al.* (2003) substituted the part elements of phosphomolybdic acid with V and W to form H₇[P₂Mo₁₇VO₆₂] $\cdot$ 39H₂O and H₃PW₁₀Mo₂O₄₀ to remove H₂S. The results showed that the efficiency of H₂S removal of them were only 85%. Few studies have used transition metal (Co, Ni, Zn, etc.) substituted phosphomolybdate to remove hydrogen sulfide in mixed gas.

In summary, we used alkaline degradation to synthesize a series of transition metal mono-substituted heteropoly compounds H₇PMo₁₁MO₃₉ (M = Co²⁺, Mn²⁺, Ni²⁺ and Zn²⁺) (HPMo₁₁M) and single-absent heteropoly compounds H₃PMo₁₁O₃₉ (HPMo₁₁). They were used to absorb hydrogen sulfide in acid gas. We used Fourier transform infrared spectroscopy (FT-IR), elemental analysis and scanning electron microscopy (SEM) to characterize and analyze the morphology and structure of HPMo₁₁M. The dynamic absorption experiment was used to test the removal and regeneration performance of HPMo₁₁M for hydrogen sulfide. At the same time, conditions optimization experiments were conducted to explore the optimal values of temperature, hydrogen sulfide concentration, heteropoly compound concentration and solution pH. Finally, based on X-ray photoelectron spectroscopy (XPS) characterization results, the desulfurization products and desulfurization mechanism were discussed.

2 EXPERIMENTAL

2.1 Materials and Reagents

Phosphomolybdic acid (H₃PMo₁₂O₄₀, Shanghai Yindian Chemical Co., Ltd., China), Cobalt acetate (Co (CH₃CO₂)₂ $\cdot$ 4H₂O), Manganous acetate (Mn (CH₃CO₂)₂ $\cdot$ 4H₂O), Nickel (II) acetate tetrahydrate (Ni (CH₃CO₂)₂ $\cdot$ 4H₂O), zinc acetate (Zn (CH₃CO₂)₂ $\cdot$ 4H₂O), sodium hydroxide (NaOH), hydrochloric acid (HCl, 36%), Barium Chloride (BaCl₂ $\cdot$ 2H₂O). All the reagents are of analytical grade and were used as received.

2.2 Preparation of HPMo₁₂, HPMo₁₁ and HPMo₁₁M (M = Co²⁺, Mn²⁺, Ni²⁺ and Zn²⁺)

The preparation process of H₃PMo₁₂O₄₀ (HPMo₁₂), H₃PMo₁₁O₃₉ (HPMo₁₁) and H₇PMo₁₁MO₃₉ (HPMo₁₁M) (M = Co²⁺, Mn²⁺, Ni²⁺ and Zn²⁺) were performed with reference to the literatures (Tourné *et al.*, 1970; Patel and Pathan, 2012):

HPMo₁₁: The pH of a solution of H₃PMo₁₂O₄₀ (1.825 g, 1 mmol) in water (20 mL) was adjusted to 4.3 using NaOH (1 M). The aqueous solution was evaporated to obtain HPMo₁₁.

HPMo₁₁M: The pH of a solution of H₃PMo₁₂O₄₀ (1.825 g, 1 mmol) in water (20 mL) was adjusted to 4.3 using NaOH (1 M). The solution was heated to 80°C by stirring. The corresponding 1 mmol transition metal acetates (Co (CH₃CO₂)₂ $\cdot$ 4H₂O, Mn (CH₃CO₂)₂ $\cdot$ 4H₂O, Ni (CH₃CO₂)₂ $\cdot$ 4H₂O, and Zn (CH₃CO₂)₂ $\cdot$ 4H₂O) were dissolved in 2 mL of hot water, and added to the above solution dropwisely. The solution was heated at 80°C with stirring for 1.5 h. After filtering, the filtrate was aged for 12 h to obtain crystals. After filtering again, it was dried at 110°C for 4 h and activated at 200°C for 3 h.

2.3 Characterization Analytical Methods

The characterization methods used for the catalysts are shown in Table 1.

Table 1. Methods for characterization and analysis of catalysts.

	Methods	Manufacturer
1	FT-IR	Thermo Fisher Scientific Corp, USA
2	ICP	Elementar Corp, Germany
3	SEM	Hitachi Limited Corp, Japan
4	XPS	Thermo Fisher Scientific Corp, USA

Fig. 1. Reaction device diagram.

2.4 H₂S Absorption and Regeneration Experiments

The H₂S absorption experiment was performed at standard atmospheric pressure. The desulfurization reagent was obtained by dissolving a certain amount of HPMo₁₁M in 50 mL of deionized water and transferring it to a cylindrical glass reactor. The mixture of N₂ and H₂S was introduced into the glass reactor at a flow rate of 100 mL min⁻¹. The H₂S concentration was detected by a TH-990s H₂S gas analyzer (Liu *et al.*, 2017). The residual H₂S gas was absorbed by NaOH solution. The temperature of the solution during the reaction was controlled by a thermostatic water bath. The effects of different operating parameters on desulfurization were studied by controlled experiments, under HPMo₁₁M concentration range of 0.0005 to 0.002 mol L⁻¹ and pH range of 1 to 9. The reaction device diagram is shown in Fig. 1. The desulfurization performance of HPMo₁₁M solutions was mainly evaluated by H₂S removal efficiency (η , %):

$$\eta = \frac{C_0 - C_t}{C_0} \quad (1)$$

where C_0 and C_t represent the inlet and outlet concentrations of H₂S, respectively.

After the reaction, the desulfurizing agent was regenerated and recovered in a water bath at 90°C with 500 mL min⁻¹ of air continuously for 6 h. The regenerated desulfurizing agent solution can continue to perform H₂S desorption experiment.

3 RESULTS AND DISCUSSION

3.1 Characterization

3.1.1 FT-IR spectrum of HPMo₁₂, HPMo₁₁, and HPMo₁₁M (M = Co²⁺, Mn²⁺, Ni²⁺ and Zn²⁺).

The Fourier transform infrared spectra (FT-IR) of HPMo₁₂, HPMo₁₁ and HPMo₁₁M (M = Co²⁺, Mn²⁺, Ni²⁺ and Zn²⁺) are shown in Fig. 2, which are consistent with the characteristic peaks of Keggin-type molybdenum heteromeric compounds (Xie *et al.*, 2008). In the FT-IR spectrum of HPMo₁₂, the characteristic peaks at 1059, 953, 881, and 747 cm⁻¹ correspond to the stretching vibration peaks of P-O_a, Mo = O_d, Mo-O_b-Mo, and Mo-O_c-Mo, respectively. After the transformation from HPMo₁₂ to HPMo₁₁, the four characteristic peaks of P-O_a, Mo = O_d, Mo-O_b-Mo and Mo-O_c-Mo changed significantly. In particular, the P-O_a bond stretching vibration peak at 1059 cm⁻¹ was split

Fig. 2. FT-IR spectra of transition metal substituted heteropoly phosphomolybdate: (a) HPMo_{12} , (b) HPMo_{11} , (c) $\text{HPMo}_{11}\text{Co}$, (d) $\text{HPMo}_{11}\text{Mn}$, (e) $\text{HPMo}_{11}\text{Ni}$, (f) $\text{HPMo}_{11}\text{Zn}$.

into two vibration absorption peaks (1077 and 1030 cm^{-1}) in the FT-IR spectrum of HPMo_{11} . This phenomenon indicates that after losing a Mo atom, the symmetry of the vibration mode of the heteroatom is reduced due to the destruction of the symmetry around it. From the FT-IR spectrum of HPMo_{11}M , it can be seen that when the transition metal is bound to HPMo_{11} , the stretching vibration peak of the P-O_a bond of HPMo_{11}M appears near the original position without splitting, indicating that the structure has been restored, that is, the symmetry around the heteroatoms is restored by the metal ions to some extent. The P-O_a bonds of HPMo_{11}M ($\text{M} = \text{Co}^{2+}$, Mn^{2+} , Ni^{2+} and Zn^{2+}) FT-IR spectra show stretching vibration peaks at 1049 , 1090 , 1097 and 1092 cm^{-1} , respectively. The stretching vibration peaks of $\text{Mo}=\text{O}_d$, $\text{Mo-O}_b\text{-Mo}$ and $\text{Mo-O}_c\text{-Mo}$ also have displacement changes. These results showed that the transition metal ions successfully replaced the Mo atom.

3.1.2 ICP of HPMo_{12} and $\text{HPMo}_{11}\text{Co}$

The contents of P, Mo, and Co in HPMo_{12} and $\text{HPMo}_{11}\text{Co}$ were determined by an inductively coupled plasma spectrometer (ICP-AES). The results of elemental analysis are shown in Table 2. The experimental values are basically consistent with the theoretical calculations, indicating that Co in $\text{HPMo}_{11}\text{Co}$ replaces a Mo.

3.1.3 Catalyst scanning electron microscope (SEM) analysis

For the morphological analysis of the HPMo_{12} and HPMo_{11}M (represented by $\text{HPMo}_{11}\text{Co}$), their SEM images are shown in Fig. 3. As can be seen in Fig. 3(a), the HPMo_{12} is a flat layer structure connected together. After the adding of transition metal cobalt (Co), the morphology becomes prismatic (as shown in Fig. 3(b)), which indicates that the transition metal Co successfully replaced Mo.

Table 2. Analytical results of elements in substituted heteropoly phosphomolybdic acid.

		P	Mo	Co
HPMo_{12}	experimental values	1	11.76	–
	theoretical calculations	1	12	–
$\text{HPMo}_{11}\text{Co}$	experimental values	1	10.86	1.2
	theoretical calculations	1	11	1

Fig. 3. SEM images of the (a) HPMo_{12} and (b) $\text{HPMo}_{11}\text{Co}$.

3.2 Optimization Experiment of H_2S Absorption Conditions

3.2.1 Effect of transition metal species on H_2S removal

The hydrogen sulfide absorption of HPMo_{12} , HPMo_{11} and HPMo_{11}M ($\text{M} = \text{Co}^{2+}$, Mn^{2+} , Ni^{2+} and Zn^{2+}) were compared under the same conditions, as shown in Fig. 4. Compared with HPMo_{12} and vacant HPMo_{11} , the heteropoly phosphomolybdate substituted by transition metal elements had better desulfurization effect and longer duration. Therefore, the focus is on the desulfurization and regeneration performance of heteropoly phosphomolybdate substituted by transition metal elements. The hydrogen sulfide absorption and regeneration results of $\text{HPMo}_{11}\text{Co}$, $\text{HPMo}_{11}\text{Mn}$, $\text{HPMo}_{11}\text{Ni}$ and $\text{HPMo}_{11}\text{Zn}$ are shown in Fig. 5. In comparison, $\text{HPMo}_{11}\text{Co}$ and $\text{HPMo}_{11}\text{Zn}$ had better removal effect on hydrogen sulfide, reaching more than 90%. Comparing the desulfurization performance after regeneration, it was found that $\text{HPMo}_{11}\text{Co}$ had the best effect. According to the comprehensive comparison of desulfurization and regenerated desulfurization effects, the desulfurization ability of heteropoly phosphomolybdate was ranked as follows: $\text{HPMo}_{12} < \text{HPMo}_{11} < \text{HPMo}_{11}\text{Zn} < \text{HPMo}_{11}\text{Ni} < \text{HPMo}_{11}\text{Mn} < \text{HPMo}_{11}\text{Co}$. Therefore, $\text{HPMo}_{11}\text{Co}$ was selected as the desulfurizer for the following condition optimization experiments in this study.

3.2.2 Effect of temperature on H_2S removal

The temperature of the desulfurizer has a significant effect on H_2S removal, and the results are shown in Fig. 6. It can be observed that the desulfurization efficiency of heteropoly

Fig. 4. Removal of H_2S in HPMo_{12} , HPMo_{11} and HPMo_{11}M ($\text{M} = \text{Co}^{2+}$, Mn^{2+} , Ni^{2+} and Zn^{2+}) ($T = 25^\circ\text{C}$, $C_{\text{HPMo}_{11}\text{Co}} = 0.001 \text{ mol L}^{-1}$, $C_{\text{H}_2\text{S}} = 1750 \text{ mg m}^{-3}$).

Fig. 5. Research on desulfurization and regeneration performance of $\text{HPMo}_{11}\text{Co}$, $\text{HPMo}_{11}\text{Mn}$, $\text{HPMo}_{11}\text{Ni}$ and $\text{HPMo}_{11}\text{Zn}$ (Absorption experiment: $T = 25^\circ\text{C}$, $C_{\text{HPMo}_{11}\text{Co}} = 0.001 \text{ mol L}^{-1}$, $C_{\text{H}_2\text{S}} = 1750 \text{ mg m}^{-3}$; Regeneration experiment: $T_{\text{air}} = 90^\circ\text{C}$).

Fig. 6. Effect of temperature on H_2S removal ($C_{\text{HPMo}_{11}\text{Co}} = 0.001 \text{ mol L}^{-1}$, $C_{\text{H}_2\text{S}} = 1750 \text{ mg m}^{-3}$).

phosphomolybdate decreased significantly with the increase of temperature within the investigated range ($25\text{--}75^\circ\text{C}$). The desulfurizer at room temperature (25°C) showed the best removal performance, and the desulfurization efficiency can be maintained above 90% within 350 min. This study also exhibited that higher temperature was not conducive to the removal of H_2S mainly in two aspects: on the one hand, the oxidation process of H_2S was exothermic, so high temperature was not conducive to the absorption process (Huang *et al.*, 2017); on the other hand, the increase of temperature tended to retard the dissolution of H_2S in aqueous solutions. Therefore, the degree of solubility played a leading role in this process. The room temperature (25°C) was selected as the best desulfurizer temperature, and subsequent experiments were carried out accordingly.

3.2.3 Effect of $\text{HPMo}_{11}\text{Co}$ concentration on H_2S removal

The effect of $\text{HPMo}_{11}\text{Co}$ concentration on desulfurization performance at 25°C is shown in Fig. 7. It can be observed that the higher the concentration of $\text{HPMo}_{11}\text{Co}$, the higher the desulfurization efficiency and the longer the reaction time. At the concentration of $0.0005 \text{ mol L}^{-1}$ for the

Fig. 7. Effect of $\text{HPMo}_{11}\text{Co}$ concentration on H_2S removal ($T = 25^\circ\text{C}$, $C_{\text{H}_2\text{S}} = 1750 \text{ mg m}^{-3}$).

$\text{HPMo}_{11}\text{Co}$, the desulfurization efficiency decreased rapidly in a short time. When the concentration was 0.001 mol L^{-1} , the time for the H_2S removal efficiency to remain above 92% was reduced to 360 min. When the concentration was $0.0015 \text{ mol L}^{-1}$, the desulfurization efficiency dropped below 50% rapidly after 400 min. At the concentration of $\text{HPMo}_{11}\text{Co}$ was 0.002 mol L^{-1} , the H_2S removal efficiency can be maintained above 92% within 400 min, and slowly decreased to less than 70% after 450 min. The desulfurization rate decreased significantly because $\text{HPMo}_{11}\text{Co}$ was consumed with the extension of the reaction time. In short, the higher the concentration of $\text{HPMo}_{11}\text{Co}$, the more favorable the desulfurization reaction. Therefore, the subsequent experiments were implemented with 0.002 mol L^{-1} of $\text{HPMo}_{11}\text{Co}$.

3.2.4 Effect of H_2S concentration on H_2S removal

The effect of different concentrations of H_2S on the desulfurization performance of $\text{HPMo}_{11}\text{Co}$ solution at 25°C was studied (Fig. 8). The results showed that the lower the H_2S concentration, the more favorable the desulfurization reaction. The desulfurization efficiency can be maintained

Fig. 8. Effect of H_2S concentration on H_2S removal ($T = 25^\circ\text{C}$, $C_{\text{HPMo}_{11}\text{Co}} = 0.002 \text{ mol L}^{-1}$).

above 90% within 350 min at most H_2S concentrations. Especially when the concentration of H_2S was 1500 mg m^{-3} , the desulfurization efficiency reached above 95% and the time lasted for 400 min. The reason for this phenomenon is that low concentration of H_2S will consume less $\text{HPMo}_{11}\text{Co}$ at the same time. The sudden drop in the desulfurization efficiency at the later stage of the reaction was due to the exhaustion of $\text{HPMo}_{11}\text{Co}$. Combined with actual conditions such as research time and gas flow rate, the subsequent experiments were implemented with H_2S concentration of 1750 mg m^{-3} .

3.2.5 Effect of desulfurizer pH on H_2S removal

The pH of desulfurizer is an important factor affecting the removal efficiency of H_2S (Zheng *et al.*, 2018). During the research, the pH of the desulfurizer was adjusted between 1 and 9 with 1 M NaOH and 1 M HCl, and the H_2S concentration was maintained at 1750 mg m^{-3} . As shown in Fig. 9, the removal efficiency of H_2S decreased rapidly at the pH value was 1 and 3. The removal efficiency of H_2S can be maintained above 90% within 360 min at the pH value was 5. When the pH value increased from 5 to 9, the removal efficiency of H_2S decreased significantly. This phenomenon may occur because the alkaline environment will destroy the structure of the heteropolyanion, while the heteropolyanion in the acidic environment can maintain a stable kegin-type structure.

Therefore, the $\text{HPMo}_{11}\text{Co}$ solution showed the best desulfurization performance under the optimal conditions (25°C , the 0.002 mol L^{-1} concentration of $\text{HPMo}_{11}\text{Co}$, the H_2S concentration of 1750 mg m^{-3} and desulfurizer pH of 5). As shown in Fig. 9, the H_2S removal efficiency remained above 90% within 360 min.

3.2.6 Absorption kinetics

The absorption kinetics of the selected optimum conditions was studied. According to the original data of pH = 5 curve in Fig. 9, the absorption curve of desulfurizer (the abscissa was time t , the ordinate was the outlet concentration C_t) was made, and it was integrated. The H_2S absorption capacity Q_t of the desulfurizer $\text{HPMo}_{11}\text{Co}$ at time t was determined by the above integration results, the H_2S flow rate, the H_2S inlet concentration C_0 , and the quality of the desulfurizer $\text{HPMo}_{11}\text{Co}$:

$$Q_t = C_0 t - \int_0^t C_t dt \quad (2)$$

Fig. 9. Effect of desulfurizer pH on H_2S removal ($T = 25^\circ\text{C}$, $C_{\text{HPMo}_{11}\text{Co}} = 0.001 \text{ mol L}^{-1}$, $C_{\text{H}_2\text{S}} = 1750 \text{ mg m}^{-3}$).

Fig. 10. Kinetic absorption and fitting curves.

Table 3. Pseudo-first-order and pseudo-second-order model parameters of HPMo₁₁Co.

Experiment (Q_e)	Pseudo-first-order model			Pseudo-second-order model		
	k_1	Q_e	R^2	k_2	Q_e	R^2
11.5	9.27×10^{-4}	32.89	0.9963	8.24×10^{-6}	60.93	0.9962

Fig. 10 showed kinetic absorption and fitting curves. It could be observed that the H₂S absorption of HPMo₁₁Co rose rapidly in a short period of time, then the growth rate gradually slowed down, and finally reached saturation. This was consistent with the curve results of the H₂S removal efficiency. The concentration of the desulfurizer in the later test decreased, resulting in the reduction of H₂S removal efficiency. Finally, the H₂S absorption of the desulfurizer reached 11.5 mol-H₂S g⁻¹-HPMo₁₁Co.

In order to further explore the relationship between the H₂S absorption capacity Q_t and the time t , pseudo-first-order (Eq. (3)) and pseudo-second-order (Eq. (4)) kinetic models were used to fit the experimental data:

$$Q_t = Q_e - Q_e e^{-k_1 \times t} \quad (3)$$

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad (4)$$

where Q_e (mol-H₂S g⁻¹-HPMo₁₁Co) is the equilibrium absorption capacity of HPMo₁₁Co; Q_t (mol-H₂S g⁻¹-HPMo₁₁Co) is the absorption capacity at different time t (min); k_1 and k_2 are the parameters of pseudo-first-order and pseudo-second-order kinetic models, respectively.

The pseudo-first-order and pseudo-second-order fitting curves of HPMo₁₁Co are displayed in Fig. 10, and the fitting constants are given in Table 3. It can be seen that the experimental data can be well described by pseudo-first-order kinetic model with the correlation coefficients ($R^2 = 0.9963$). In addition, the fitted absorption capacity of the pseudo-first-order model is 32.89 mol-H₂S g⁻¹-HPMo₁₁Co, which is closer to the experimental absorption capacity (11.5 mol-H₂S g⁻¹-HPMo₁₁Co) than that of the pseudo-second-order model (60.93 mol-H₂S g⁻¹-HPMo₁₁Co). Therefore, pseudo-first-order kinetic model is predominant in the absorption process of H₂S in HPMo₁₁Co solution.

3.3 Desulfurization Products and Desulfurization Mechanism

FT-IR spectroscopy was used to analyze functional groups of HPMo₁₁Co before and after

desulfurization and regeneration. As shown in Fig. 11, the presence of four characteristics peaks of the heteropoly acid anion after absorption and regeneration, indicating that the compound had stable Keggin-type structure.

The solid powder obtained by evaporating the $\text{HPMo}_{11}\text{Co}$ before and after absorption and regeneration was used for XPS analysis. Fig. 12 showed the XPS spectra of the Mo $3d_{5/2}$ orbital on the surface of the $\text{HPMo}_{11}\text{Co}$ compound before absorption as well as before and after regeneration. It can be seen that the valence of heteropoly compounds did not change after the whole process of absorption and regeneration, but it did not mean that Mo atoms did not participate in the reaction (Zhao *et al.*, 1996, 1998). The whole process was as follows: before absorption, the valence of Mo atom in $\text{HPMo}_{11}\text{Co}$ was +VI, and the binding energy of Mo $3d_{5/2}$ was 233.09 eV; after absorption, the binding energy of Mo $3d_{5/2}$ changed and increased by 230.72 eV, indicating that Mo became +IV valence. Whereas after high temperature air blow-off regeneration, the binding energy of Mo $3d_{5/2}$ recovered to 233.42 eV, and Mo recovered to +VI

Fig. 11. FT-IR spectra of PrPMo $\text{HPMo}_{11}\text{Co}$ before and after desulfurization and regeneration.

Fig. 12. The XPS spectra of Mo $3d_{5/2}$ in $\text{HPMo}_{11}\text{Co}$ before absorption as well as before and after regeneration.

valence. XPS spectral characterization results showed that during the absorption of H_2S , Mo (+VI) in $\text{HPMo}_{11}\text{Co}$ was reduced to Mo (+IV), and then oxidized to Mo (+VI) in the process of high-temperature air stripping.

The XPS patterns of the Co 2p orbital of the $\text{HPMo}_{11}\text{Co}$ compound surface before absorption as well as before and after regeneration are shown in Fig. 13. Before absorption, the XPS spectra of Co 2P of the sample had two absorption characteristic peaks with binding energies of 783.27 eV and 799.33 eV respectively, indicating that there are two different valence states of Co in the sample before absorption, namely Co (+II) and Co (+III). After H_2S absorption, the binding energy of Co 2p became 780.78 eV, indicating that the valence of Co in this compound was +II. After high temperature air blow-off regeneration, the XPS spectra of Co 2P of the sample recovered two absorption characteristic peaks with the binding energies of 783.32 eV and 799.04 eV, indicating that Co in the sample was oxidized and its valence state was restored. Based on the above characterization results, Co (+III) in $\text{HPMo}_{11}\text{Co}$ was reduced to Co (+II) during the absorption process, and then regenerated to Co (+III) through high-temperature air stripping (Khassin *et al.*, 2001; Le *et al.*, 2016).

The XPS spectra of the S 2p orbital of solid powder obtained by evaporating $\text{HPMo}_{11}\text{Co}$ before and after regeneration are shown in Fig. 14. Among them, a characteristic absorption peak with the binding energy of 162.32 eV illustrated that H_2S had been absorbed. At this time, the valence of the element S was -II. The characteristic absorption peak with the binding energy of 163.76 eV indicated that S (-II) had changed into S (0). The characteristic absorption peak at 169.07 eV indicated the presence of S (+VI) in the solution. After high-temperature air stripping regeneration, the characteristic absorption peak areas of S and S (+VI) increased significantly, indicating that the desulfurization product contained S elementary substance and S (+VI) (Liu *et al.*, 2017; Liu and Wang, 2017b, c). The BaCl_2 solution was added to the regenerated solution to prove that S (+VI) was SO_4^{2-} , since white precipitation was observed. The calculation of the peak areas showed that elemental sulfur S accounted for 55%, and SO_4^{2-} accounted for 45%. Therefore, the peak area ratio was 11:9, so that the molar ratio of S and SO_4^{2-} was estimated to be approximately 11:9. S was not oxidized to produce SO_4^{2-} . At the beginning, the concentration of transition metal mono-substituted heteropoly compounds ($\text{M} = \text{Co}^{2+}$, Mn^{2+} , Ni^{2+} and Zn^{2+}) was high and the oxidation was strong, which could convert hydrogen sulfide into SO_4^{2-} . As the reaction proceeded, the concentration of transition metal mono-substituted heteropoly compounds decreased and the oxidation became weak, and hydrogen sulfide could be converted into S. In addition, carbon disulfide (CS_2) is known to be a very good solvent of sulfur, which can extract elemental sulfur from desulfurization products at room temperature, so as to achieve the purpose of separating S and SO_4^{2-} .

Fig. 13. The XPS spectra of Co 2p orbitals on the surface of $\text{HPMo}_{11}\text{Co}$ compound.

Fig. 14. XPS spectra of S 2p of HPMo₁₁Co before and after regeneration.

Table 4. Surface element compositions of HPMo₁₁Co before absorption as well as before and after regeneration.

Name	Co	Mo	P	S
Before absorption	9.4%	79.7%	10.9%	0
Before regeneration	4.2%	41.6%	5.5%	48.7%
After regeneration	7.6%	66.4%	10.9%	15.1%

Table 5. Comparison with other desulfurizers for H₂S.

Desulfurizers	Efficiency of H ₂ S removal	References
H ₃ PMo ₁₂ O ₄₀	80%	Lütkehoff <i>et al.</i> (1995)
H ₃ PW ₁₂ O ₄₀	20%	Liu <i>et al.</i> (2017a)
(NH ₄) ₁₁ [Sm(PMo ₁₁ O ₃₉) ₂]	80%	Liu <i>et al.</i> (2017a)
H ₇ [P ₂ Mo ₁₇ VO ₆₂]·39H ₂ O	85%	Ma <i>et al.</i> (2014)
H ₃ PW ₁₀ Mo ₂ O ₄₀	85%	Wang <i>et al.</i> (2003)
H ₇ PMo ₁₁ CoO ₃₉	92%	This work

We used XPS to analyze surface element compositions of HPMo₁₁Co before absorption as well as before and after regeneration, including Co, Mo, P, and S elements, and calculated the relative composition content as shown in Table 4. It can be seen that the surface of HPMo₁₁Co did not contain S element before the absorption of H₂S, but after the absorption of H₂S, the content of S element on the surface of HPMo₁₁Co increased to 48.7%, and the content of S element on the surface of HPMo₁₁Co was 15.1% after regeneration. This indicated that the surface of the regenerated HPMo₁₁Co was covered by a small amount of S, leading to a decrease in the desulfurization rate after regeneration.

The absorption performance of H₇PMo₁₁CoO₃₉ for H₂S was compared with the previous desulfurizers as listed in Table 5. H₇PMo₁₁CoO₃₉ exhibited higher efficiency of H₂S removal than other desulfurizers, illustrating that the absorption performance of metal mono-substituted heteropoly compounds had been improved in this work.

4 CONCLUSION

We studied the desulfurization performance of a series of transition metal monosubstituted

heteropoly phosphomolybdate and mono-vacancy heteropoly phosphomolybdate under different reaction conditions. The major results were concluded as follows:

- (1) Multiple characterization results confirmed the successful synthesis of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{H}_7\text{PMo}_{11}\text{O}_{39}$ and $\text{H}_7\text{PMo}_{11}\text{MO}_{39}$ ($\text{M} = \text{Co}^{2+}$, Mn^{2+} , Ni^{2+} and Zn^{2+}).
- (2) $\text{H}_7\text{PMo}_{11}\text{CoO}_{39}$ had the best desulfurization performance and regeneration effect and was selected as the most suitable desulfurizer. Its solution had the best desulfurization capability at 25°C. The removal efficiency of hydrogen sulfide by the desulfurizer could reach 90% within 400 min. The higher the concentration of $\text{H}_7\text{PMo}_{11}\text{CoO}_{39}$, the higher the removal efficiency of hydrogen sulfide.
- (3) Low H_2S concentration was conducive to the progress of the desulfurization reaction. $\text{H}_7\text{PMo}_{11}\text{CoO}_{39}$ showed the highest desulfurization efficiency at pH 5. The study on the desulfurization absorption kinetics under optimal conditions showed that the process fitted into the pseudo-first-order kinetic model, and the correlation coefficient (R^2) was 0.9963.
- (4) The final products of desulfurization were S and SO_4^{2-} . $\text{H}_7\text{PMo}_{11}\text{CoO}_{39}$ played a redox role in the desulfurization process, which could convert H_2S into sulfur resources.

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REFERENCES

- Bi, L.H., Reicke, M., Kortz, U., Keita, B., Nadjo, L., Clark, R.J. (2004). First structurally characterized palladium (II)-substituted polyoxoanion: $[\text{Cs}_2\text{Na}(\text{H}_2\text{O})_{10}\text{Pd}_3(\alpha\text{-Sb}^{\text{III}}\text{W}_9\text{O}_{33})_2]^{9-}$. *Inorg. Chem.* 43, 3915–3920. <https://doi.org/10.1021/ic049736d>
- Huang, K., Zhang, X.M., Zhou, L.S., Tao, D.J., Fan, J.P. (2017). Highly efficient and selective absorption of H_2S in phenolic ionic liquids: A cooperative result of anionic strong basicity and cationic hydrogen-bond donation. *Chem. Eng. Sci.* 173, 253–263. <https://doi.org/10.1016/j.ces.2017.07.048>
- Khassin, A.A., Yurieva, T.M., Kaichev, V.V., Bukhtiyarov, V.I., Budneva, A.A., Paukshtis, E.A., Parmon, V.N. (2001). Metal-support interactions in cobalt-aluminum co-precipitated catalysts: XPS and CO adsorption studies. *J. Mol. Catal. A: Chem.* 175, 189–204. [https://doi.org/10.1016/S1381-1169\(01\)00216-3](https://doi.org/10.1016/S1381-1169(01)00216-3)
- Le, L., Zhang, X., Ma, A., Zhang, Y., Huang, H., Lin, S. (2016). Facile synthesis of Pd/PDDA-GN/ PMo_{11}Co composite and its enhanced catalytic performance for formic acid oxidation. *RSC Adv.* 6, 107370–107378. <https://doi.org/10.1039/C6RA21497E>
- Liu, X., Li, J., Wang, R. (2017a). Desulfurization and regeneration performance of heteropoly compound/ionic liquid solutions at high temperature. *Chem. Eng. J.* 316, 171–178. <https://doi.org/10.1016/j.cej.2017.01.093>
- Liu, X., Wang, R. (2017b). An innovative approach to oxidative removal of hydrogen sulfide using the solution of peroxo heteropolyacid. *Aerosol Air Qual. Res.* 17, 1341–1346. <https://doi.org/10.4209/aaqr.2016.12.0550>
- Liu, X., Wang, R. (2017c). H_2S removal by peroxo heteropoly compound/ionic liquid solution. *Fuel Process. Technol.* 160, 78–85. <https://doi.org/10.1016/j.fuproc.2017.02.024>
- Lütkehoff, S., Neumann, M., Ślebarski, A. (1995). 3d and 4d x-ray-photoelectron spectra of Pr under gradual oxidation. *Phys. Rev. B* 52, 13808. <https://doi.org/10.1103/PhysRevB.52.13808>
- Ma, Y., Wang, R. (2014). H_2S absorption capacity and regeneration performance of amine Fe-based ionic liquid. *Chem. J. Chin. Univ.* 35, 760–765. https://en.cnki.com.cn/Article_en/CJFDT01-GDXH201404017.htm (in Chinese)
- Patel, A., Pathan, S. (2012). Keggin-type cesium salt of first series transition metal-substituted phosphomolybdates: one-pot easy synthesis, structural, and spectral analysis. *J. Coord. Chem.* 65, 3122–3132. <https://doi.org/10.1080/00958972.2012.710843>

- Proust, A., Thouvenot, R., Gouzerh, P. (2008). Functionalization of polyoxometalates: Towards advanced applications in catalysis and materials science. *Chem. Commun.* 16, 1837–1852. <https://doi.org/10.1039/B715502F>
- Santos, F.M., Brandão, P., Félix, V., Nogueira, H.I., Cavaleiro, A.M. (2015). Synthesis and properties of new materials with cobalt (II), iron (III) and manganese (III)-substituted Keggin polyoxotungstates and 1-alkyl-3-methylimidazolium cations. *Polyhedron* 101, 109–117. <https://doi.org/10.1016/j.poly.2015.07.032>
- Tourné, C.M., Tourné, G.F., Malik, S., Weakley, T. (1970). Triheteropolyanions containing copper (II), manganese (II), or manganese (III). *J. Inorg. Nucl. Chem.* 32, 3875–3890. [https://doi.org/10.1016/0022-1902\(70\)80566-8](https://doi.org/10.1016/0022-1902(70)80566-8)
- Wang, R., Gao, H. (2003). Heteropoly acid as new liquid redox absorbent for low sulfur containing gas sweetening. *Macro Rev.* 16, 141–145. <https://doi.org/10.11286/jmr1988.16.141>
- Weakley, T., Malik, S. (1967). Heteropolyanions containing two different heteroatoms—I. *J. Inorg. Nucl. Chem.* 29, 2935–2944. [https://doi.org/10.1016/0022-1902\(67\)80126-X](https://doi.org/10.1016/0022-1902(67)80126-X)
- Xie, Q., Wang, X. (2008). Catalytic oxidation of cyclohexene to trans-1,2-cyclohexanediol with mono-substituted keggins-phosphomolybdic acid catalyst. *Petrchem. Technol.* 5, 18–21. http://en.cnki.com.cn/Article_en/CJFDTOTAL-SYHG200805016.htm (in Chinese)
- Zhang, Y., Wu, L., Dong, X., Wu, P., Hu, H., Xue, G. (2016). Copper (II)-substituted polyoxotungstates immobilized on amine-functionalized SBA-15: Efficient heterogeneous catalysts for liquid phase oxidative reaction. *Catal. Lett.* 146, 2468–2477. <https://doi.org/10.1007/s10562-016-1874-7>
- Zhao, Y., Bao, X., Wang, X., Zhu, Y. (1996). Removal of H₂S and recovery of sulfur from gas streams by chemical absorption using 12-molybdosilicic acid solution. *Acta Sci. Tech.* 16, 82–89. <http://www.cnki.com.cn/Article/CJFDTOTAL-HJXX601.011.htm> (in Chinese)
- Zhao, Y., Zhu, Q., Gu, G. (1998). Combined removal of SO₂, H₂S and NO_x from gas streams by chemical absorption with aqueous solution of 12-molybdophosphoric acid and its reduced species. *Water Air Soil Pollut.* 102, 157–176. <https://doi.org/10.1023/A:1004956032764>
- Zheng, W., Wu, D., Feng, X., Hu, J., Zhang, F., Wu, Y.T., Hu, X.B. (2018). Low viscous Protic ionic liquids functionalized with multiple Lewis Base for highly efficient capture of H₂S. *J. Mol. Liq.* 263, 209–217. <https://doi.org/10.1016/j.molliq.2018.04.129>