Technical Note

An Innovative Approach to Oxidative Removal of Hydrogen Sulfide Using the Solution of Peroxo Heteropolyacid

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ABSTRACT

A new method of removing H₂S using the solution of peroxo phosphomolybdic acid was developed. The results showed that the solution of peroxo phosphomolybdic acid had perfect capacity for H₂S removal. A H₂S removal efficiency of 100% for 10 h could be achieved by using two-stage absorption with an absorbent concentration of 0.02 mol L⁻¹. The effect of temperature, concentration of peroxo phosphomolybdic acid and H₂S on H₂S removal was explored. According to the results, a high absorbent concentration, low H₂S concentration and slightly excessive H₂O₂ are beneficial to H₂S removal under relatively low temperature. The absorbent showed a perfect regeneration performance, and could be reactivated simply by adding a few drops of 30% H₂O₂ solution. The X-ray photoelectron spectra showed that the H₂S was oxidized to SO₄²⁻ finally.

Keywords: Hydrogen sulfide; Oxidation; Absorption; Heteropoly acid; Regeneration.

INTRODUCTION

Due to its corrosivity, peculiar smell and toxicity for human and environment, the removal of hydrogen sulfide (H₂S) has caused concerns of numerous researchers (Wang et al., 2008; Tian et al., 2009). To date, plentiful processes have been developed for H₂S removal, and many new, effective methods will appear in the near future (Ma et al., 2009; de Angelis et al., 2010; Ko and Hsueh, 2012; Li et al., 2015).

Heteropoly acid (HPA) and heteropoly compound (HPC) have been applied for various catalytic fields based on their unique catalytic activity and redox property (Pope and Müller, 1991; Kozhevnikov, 1995; Ding and Wang, 2016). For Keggin type HPA, the coordination atom and oxygen atom are combined into MO₆ octahedron, where M is the coordination atom. With deeper research on HPA, it was found that the oxygen of MO₆ could be replaced by O₂²⁻ and generated the peroxo heteropoly acid (PHPA) (Ishii et al., 1988). Commonly, the HPA reacts with hydrogen peroxide at the ratio of 1:24, producing the corresponding peroxo species (Yadav and Mistry, 2001). The PHPA has been used in a lot of areas because of its higher catalytic activity and catalytic oxidizing ability. For example, the system of HPA/H₂O₂ has been widely employed in the field of deep-desulfurization of fuel oil (Te et al., 2001; Ying et al., 2009; Wang et al., 2010). However, there are only quite limited reports on H₂S removal using HPA (Kuznetsova and Yurchenko, 1989; Harrup and Hill, 1994; Wang, 2003; Song et al., 2011; Ma et al., 2012; Zou et al., 2013; Kim et al., 2014). Furthermore, the study on H₂S removal using PHPA has never been reported to date.

In this work, we used PHPA solution for H₂S removal for the first time. The H₂S removal performance of PHPC solution was detected by a dynamic absorption experiment. The oxidation-reduction potential of PHPA solution was measured during the absorption and regeneration process. The desulfurization product was characterized by X-ray photoelectron spectroscopy (XPS).

METHODS

All chemicals used including phosphomolybdic acid (H₃PMo₁₂O₄₀•xH₂O, HPMo), phosphotungstic acid (H₃PW₁₂O₄₀•xH₂O, HPW) and hydrogen peroxide solution (30%) were obtained from commercial sources. All chemicals were analytical reagents and were used without further purification.

The peroxo phosphomolybdic acid (PHPMo) solution and peroxo phosphotungstic acid (PHPW) solution were prepared as follows: a certain amount of HPMo or HPW was mixed with 30% H₂O₂ solution at a molar ratio of 1:24. Then the PHPA solution with required concentration was obtained by diluting with deionized water.

The XPS spectra were collected by Thermo ESCALAB...
The 250XI multifunctional imaging electron spectrometer (Thermo Fisher Scientific Corp., America). The oxidation-reduction potential of the solution was detected by platinum electrode and calomel reference electrode.

The H$_2$S absorption experiment was conducted at 25°C and atmosphere pressure. A gas mixture (N$_2$ as carrier) with a H$_2$S concentration of 1400 mg m$^{-3}$ was bubbled through the PHPA solution (20 mL) at a flow rate of 100 mL min$^{-1}$. The temperature was controlled by thermostatic water bath. The H$_2$S concentration of outlet gas was detected by a TH-990s hydrogen sulfide gas analyzer and the residual H$_2$S gas was absorbed by NaOH solution. The regeneration of absorbent was conducted by dropping slightly excessive H$_2$O$_2$ solution into the exhausted solution.

RESULTS AND DISCUSSION

The Effect of Solute on the Desulfurization Performance

The desulfurization performances of phosphomolybdic acid (HPMo) solution, peroxo phosphomolybdic acid (PHPMo) solution, phosphotungstic acid (HPW) solution, peroxo phosphotungstic acid (PHPW) solution, hydrogen peroxide solution as well as deionized water are shown in Fig. 1. As we can see, PHPMo solution showed the best desulfurization performance. The H$_2$S removal efficiency of PHPMo solution kept above 85% within 60 min. Besides, the results demonstrated that the desulfurization ability of HPA solution containing Mo is far stronger than that of HPA solution containing W. As for H$_2$O$_2$ solution, the desulfurization efficiency decreased to 20% with 30 min, indicating that single H$_2$O$_2$ solution cannot remove H$_2$S effectively. The H$_2$S removal performance of PHPMo solution showed a significant increase after the addition of H$_2$O$_2$ due to the stronger oxidative ability of PHPA. In general, the PHPMo solution showed the highest oxidation activity to H$_2$S removal.

The Effect of Other Factors on the Desulfurization Performance of PHPMo Solution

The effects of temperature, PHPMo concentration, H$_2$S concentration and the amount of H$_2$O$_2$ on H$_2$S removal are shown in Fig. 2. As shown in Fig. 2(a), the temperature showed no obvious effect on H$_2$S removal at a low range. Commonly, low temperature is in favor of H$_2$S oxidation removal because of the exothermicity of the reaction (Wang et al., 2006). However, appropriate high temperature can promote the activity of the reactants. Hence, temperature had little influence on the desulfurization performance of the absorbent in a low range. Considering that H$_2$O$_2$ is easily decomposed at high temperature, a relatively low temperature should be the first choice. The H$_2$S removal efficiency of absorbent increased with the concentration of PHPMo as shown in Fig. 2(b). According to Fig. 2(c), the H$_2$S concentration had no significant influence on H$_2$S removal in a relatively low range when the concentration varied from 650 to 1400 mg m$^{-3}$. While when the H$_2$S concentration increased to 2000 mg m$^{-3}$, the H$_2$S removal efficiency decreased obviously. The effect of the amount of H$_2$O$_2$ on H$_2$S removal under the same concentration of PHPMo is shown in Fig. 2(d). The duration with high removal efficiency was extended as the increase of H$_2$O$_2$ could supplement the consumption of peroxy anion. However, the H$_2$S removal efficiency showed no change with the increasing of the ratio of H$_2$O$_2$ and HPMo within 150 min because that the additional H$_2$O$_2$ did not elevate the concentration of PHPMo as the amount of HPMo remained unchanged. Thus it can be seen that the removal of H$_2$S is achieved by PHPMo rather than either species of HPMo or H$_2$O$_2$. However, the duration time with high removal efficiency does not extend continuously with increased H$_2$O$_2$, which could be attributed to the self-decomposition of excessive H$_2$O$_2$. In short, a relatively low temperature, high PHPMo concentration, low H$_2$S concentration and slightly excessive H$_2$O$_2$ are in favor of H$_2$S removal using PHPMo solution.
The Desulfurization Performance of PHPMo Solution under the Optimal Conditions

The desulfurization performance of PHPMo solution under the optimal conditions is shown in Fig. 3. The experiment was conducted by two-stage absorption with two absorbers (20 mL, 10 mL). As shown in Fig. 3, the H$_2$S removal efficiency kept 100% for 10 h and decreased slowly. Therefore, the PHPMo solution should be a promising desulfurizer which is efficient, cheap, clean and easy to get.

The Regeneration Performance of PHPMo Solution

The regeneration performance of PHPMo solution is shown in Fig. 4. The regeneration of absorbent was conducted by dropping slightly excessive H$_2$O$_2$ solution. The absorption-regeneration process is a two-in-one unit conducted alternately in the same reactor. We can see that the desulfurization performance showed no decrease for 5 cycles. Furthermore, the time of duration with high H$_2$S removal efficiency was extended due to the excessive H$_2$O$_2$, which is in accordance with the view we mentioned above that the removal of H$_2$S is achieved by PHPMo rather than either species of HPMo or H$_2$O$_2$. The change of oxidation-reduction potential of the absorbent is shown in Fig. 5. The oxidation-reduction potential decreased slowly with the continuous absorption process as the consumption of peroxo species, and then recovered rapidly after the addition of H$_2$O$_2$ because of the regeneration of PHPMo. In brief, PHPMo solution showed perfect regeneration performance.

Desulfurization Product Analysis

To identify the desulfurization product, the XPS spectra of S 2p before and after regeneration were collected, as shown in Fig. 6. The solid samples for XPS were obtained by vaporizing solvent of the exhausted PHPMo solution before and after regeneration. As shown in Fig. 6(a), the sulfur component of sample had various valence states before the addition of H$_2$O$_2$. After regeneration, the uppermost binding energy position of the S 2p is 168.9, which demonstrated that the major form of sulfur is SO$_4^{2-}$ (Siriwardane and Cook, 1986). To further confirm the above conclusion, the solution of BaCl$_2$ was dropwise added to the PHPMo solution after regeneration, a white precipitate formed immediately, which confirms the existence of SO$_4^{2-}$. Hence, the ultimate oxidation product of H$_2$S could be identified as SO$_4^{2-}$.

CONCLUSIONS

In this work, peroxo phosphomolybdic acid solution was
Fig. 3. The desulfurization performance of PHPMo solution under the optimal conditions [c(PHPMo) = 0.02 mol L⁻¹; c(H₂S) = 1000 mg m⁻³; 25°C; n (PHPMo)/n (H₂O₂) = 1/36; two-stage absorption (20 mL + 10 mL)].

Fig. 4. The regeneration performance of PHPMo solution.

Fig. 5. The change of oxidation-reduction potential of PHPMo solution.
used for H₂S removal for the first time. The results showed that solution of peroxo phosphomolybdic acid is a promising desulfurizer. The absorbent could achieve a H₂S removal efficiency of 100% for 10 h using two-stage absorption. The influences of temperature, concentration of peroxo phosphomolybdic acid and H₂S were explored. The results showed that a high absorbent concentration and low H₂S concentration are beneficial to H₂S removal under relatively low temperature. The absorbent showed a perfect regeneration performance, and could be recycled easily by dropping H₂O₂ solution. The XPS spectra showed that the final desulfurization product was SO₄²⁻. The peroxo phosphomolybdic acid solution is identified as a promising desulfurizer which is efficient, cheap, clean and easy to obtain.

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