Desulfurization Performance of Rare Earth Mono-substituted Heteropoly Compounds

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ABSTRACT

In this study, a series of rare earth monosubstituted Dawson-type polyoxometalates were synthesized for highly effective removal of hydrogen sulfide (H2S). The unused, used and regenerated polyoxometalates were characterized by Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). The results confirmed that K17[Pr(P2Mo17O61)2] could maintain a complete Dawson-type structure even after absorption and regeneration. H2S absorption study showed that K17[Pr(P2Mo17O61)2] had the remarkable desulfurization and regeneration capabilities. Optimization experiments showed that K17[Pr(P2Mo17O61)2] under the condition of low H2S concentration or high dosage of K17[Pr(P2Mo17O61)2] had the ideal desulfurization performance. An appropriate temperature of 25°C is necessary for high removal efficiency. The optimum pH value for desulfurization is 6.8. The desulfurization product was proved to be SO42–.

Keywords: Rare earth ion; Heteropoly compounds; H2S; Desulfurization.

INTRODUCTION

Hydrogen sulfide (H2S) is a common pollutant in oil and gas production/processing, wastewater treatment plants, fossil fuel combustion, and landfill gases (Ko et al., 2015; Bamdad et al., 2018; Widiana et al., 2019). The removal of H2S from these industrial gases is very necessary owing to its highly toxic, odorous and corrosive natures (Pan et al., 2015; Beidari et al., 2017). It can be oxidized to SO2, which is one of the major sources of acid rain (Chen et al., 2017; Cheng et al., 2019). In addition, H2S can cause severe health problems for human being, affect the catalytic activity of industrial catalysts, and corrode device as well as oil-gas pipeline (Yang et al., 2006; Jiang et al., 2016; Chandran et al., 2018; Wang et al., 2019).

Nowadays, a number of methods are used for removing H2S (Widiana et al., 2017; Habeeb et al., 2018; Liu et al., 2018; Huang et al., 2019a). Desulfurization processes can be generally divided into two methods, i.e., dry and wet methods. Dry method of desulfurization is carried out by using a solid adsorbent such as activated carbons (Xie et al., 2017; Liu et al., 2019), metal oxides, molecular sieves or metal elements (Zhang et al., 2017; Cheng et al., 2018). This method is simple and easy to operate, but the adsorbents have the disadvantages of poor regenerability and high running cost (Ozkmekci et al., 2015; Tian et al., 2017; Lee et al., 2019). Whereas, the wet methods, especially those utilizing aqueous solution for catalytic and oxidative desulfurization, normally possess high removal efficiency for H2S at lower cost (Zhai et al., 2012; Liu et al., 2017a; Zhang et al., 2018). Due to its stable structure and good redox properties, heteropoly acid is an excellent catalyst for oxidative desulfurization (Ou et al., 2001; Wang et al., 2012; Choi et al., 2014; Liu et al., 2017).

Heteropoly anions, as an oxyanions, have several structures, including Keggin, Dawson, Anderson, Waugh and Silverton types. (Timofeeva et al., 2003; Ko et al., 2012). Among them, two well-know structures are Keggin-type and Dawson-type. These heteropoly compounds (HPCs) with stable structures have excellent redox properties and remarkable homogeneous and heterogeneous catalytic activity for the selective oxidation and acid catalysis reactions (Huang et al., 2019b). These two types of HPCs are often used for the oxidative dehydrogenation. To the best of our knowledge, however, there are still many restrictions on desulfurization applications of HPCs (Kozheunikov et al., 1982; Li et al., 2007). Peacock and Weakley (1997a, b) firstly reported the single-defect 2:17 series of Dawson-type HPCs with the single-substituted metal ion having large radius. Haraguchi et al. (1994) found that the size of the heteroatoms affects the occlusion angle of the unsaturated entities of the anion. They reported that the heteropolytungststate anion with a large occlusal angle could form a stable complex with tetravalent cerium. The negative charge of the Dawson structure-derived anion is greater than the Keggin structure-derived

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anion for the same heteroatom. Therefore, the tetravalent state of cerium in [CeL]^{2m-3} is more stable than that in [CeL]^{m-3}. The cerium (III) or cerium (IV) in [CeL]^{2m-3} can form a sandwich structure between two respective forms, i.e., a 8-fold coordination geometry and square oxygen atom (Haraguchi et al., 1994; Jiang et al., 2018). The above results illustrated that the HPCs with Dawson structure had the better stability and redox performance than those with Keggin structure. Luo et al. (2001) showed that Ln ions in [Ln α-P_2W_{12}O_{40}]^{17–} were trivalent and eight-coordinated, indicating that rare earth ions doped heteropoly acids had excellent redox properties. Yoshida et al. (2008) reported that heteropoly anions were stable in aqueous solution.

Herein, we synthesized a series of rare earth ion monosubstituted 2:1 double series Dawson vacancy HPCs, anions were stable in aqueous solution. The quantitates and qualitative properties of the synthesized HPCs were investigated by the dynamic absorption experiments.

**EXPERIMENTAL**

**Materials and Reagents**

Sodium molybdate (Na_2MoO_4·2H_2O, Shanghai Yindian Chemical Co., Ltd., China), phosphoric acid (H_3PO_4, 85%), TIAN JIN Fuyi Fine Chemical Co., Ltd., China), hydrochloric acid (HCl, 36%), sulfuric acid (H_2SO_4, 98%), diethyl ether (ether) was removed by adding a small amount of water into the glass reactor. The residual H_2S gas was absorbed by NaOH solution for the first time. The synthesized HPCs were characterized by Fourier transform infrared (FT-IR) spectrum and X-ray photoelectron spectroscopy (XPS) to analyze their structures and compositions. The effects of various relevant factors on the desulfurization performance of HPCs were investigated by the dynamic absorption experiments.

**EXPERIMENTAL**

**Preparation of LnPMo (Ln = Pr^3+, Gd^3+, Sm^3+, and Eu^3+)**

A series of Dawson-type HPCs (K_{17}[Pr(P_2Mo_{17}O_{61})_2], K_{17}[Gd(P_2Mo_{17}O_{61})_2], K_{17}[Sm(P_2Mo_{17}O_{61})_2], and K_{17}[Eu(P_2Mo_{17}O_{61})_2]) were synthesized. For example, the preparation process of K_{17}[Pr(P_2Mo_{17}O_{61})_2] (PrPMo) is as follows (Niu et al., 2004; Wang et al., 2006): Na_2MoO_4·2H_2O (100 g) was dissolved in 450 mL deionized water (DW), followed by the addition of 15 mL H_3PO_4 (85%) and 80 mL HCl (36%). The mixture was refluxed at 95°C for 8 h and followed by cooling at room temperature. Afterwards, NH_4Cl (100 g) was added into the mixture to get the precipitate. The obtained precipitate was dissolved in water along with adding concentrated HCl and diethyl ether. The ether was removed by adding a small amount of water into etherate. A solution of Pr(NO_3)_3 with a stoichiometric ratio of 1.5 to 2.0 was added into the above mixture. The above mixture was mixed with 50% NaAc solution with strong stirring for 2 h, and the pH of the solution was adjusted to 4. Then, KCl (25 g) was added into the solution. The solution was cooled to room temperature in an ice bath, and the resulting solution was filtered and precipitated. The resulting precipitated solution with a pH value of 3.7 was recrystallized for 3 times, and the desired product was obtained after vacuum drying process.

**Regeneration of LnPMo via an Electrolytic Cell**

Electrochemical regeneration experiment was carried out in a H-type electrolyser. The device is made up of cathode and anode cells, which are separated by a Proton Exchange Membrane with an effective cross-sectional area of 2.3 cm² (PEM, Nafion117, DuPont Co., Ltd., USA). Before the experiment, the PEM was activated by soaking the PEM in H_2O_2 solution (mass fraction of 5%) at 80°C for 1 h. After that, the PEM was rinsed with DW. The cathode and anode electrodes were made of 2 cm × 5 cm carbon paper (TGP-H-060, TORAY Co., Ltd., Japan). The power supply for the electrocatalytic cell was provided by a DC power supplied unit (IP305DE, LeDa Co., Ltd., China).

The anodic solution was obtained by transferring the absorption solution (at pH = 1) from the anode chamber. Then, cyclic voltammograms curve showed the strong redox peak, which proved the conducting nature and electrochemical regeneration property of the heteropoly compounds. The cathode solution was obtained by transferring 100 mL of NaCl (200 mM) solution into the cathode chamber. The electrochemical regeneration of the materials was initiated once the DC power supply was connected to form a closed circuit in the electrochemical cell. H_2 was detected on the surface of cathode by the portable H_2 detector (HT-4, hongchangxin Co., Ltd., China).

**Characterization**

**Analytical Methods**

The quantitates and qualitative properties of the synthesized compound were characterized by FT-IR spectroscopy (BRUKER Corp., Germany) in the range of 400 to 4000 cm⁻¹. While the elemental composition of composite materials were investigated by XPS (Thermo Fisher Scientific Corp., USA).

**H_2S Absorption Experiments**

The H_2S absorption experiment was carried out in a cylindrical glass reactor at atmospheric pressure. The reactor has a internal diameter of 28 mm and height of 250 mm. The desulfurization reagent was obtained by dissolving 0.02 mol LnPMo in 50 mL DW. The effects of different operating parameters on desulfurization were investigated by controlled experiments, under LnPMo concentration range of 0.0005 to 0.0015 mol L⁻¹ and pH range of 1 to 9. The mixture of N_2 and H_2S with flow rate of 100 mL min⁻¹ was introduced into the glass reactor. The residual H_2S gas was absorbed by NaOH solution. The H_2S concentration was detected by a TH-990s H_2S gas analyzer (Liu et al., 2017c). The desulfurization performance of LnPMo solutions was mainly evaluated by H_2S removal efficiency (η, %):

\[
\eta = \frac{C_0 - C_t}{C_0} \times 100\%
\]
where $C_0$ and $C_t$ represent the inlet and outlet concentrations of $H_2S$, respectively.

**RESULTS AND DISCUSSION**

**FT-IR Spectrum of LnPMo**

Optical characterizations of the compounds were performed by the FT-IR spectroscopy. According to the previous studies, the FT-IR spectrum of heteropolyoxymolybdates have distinctive differences between structures and their complexes with Ln (III) moieties: 900–700 cm$^{-1}$ (Mo-O-Mo bending), 1000–900 cm$^{-1}$ (Mo-O stretching), and 1100–1000 cm$^{-1}$ (P–O stretching), corresponding to the metal-oxygen oscillations (Lütkehoff et al., 1995; Wang et al., 2006). The FT-IR spectrum of the PrPMo (Fig. 1) shows the five characteristic vibration peaks corresponding to their specific regions such as 780 cm$^{-1}$ and 874 cm$^{-1}$ (Mo-O-Mo bending), 935 cm$^{-1}$ (Mo-O stretch), 1034 cm$^{-1}$ and 1066 cm$^{-1}$ (P-O stretch). These characteristic peaks suggested that PrPMo with Dawson structure was successful synthesized (Lütkehoff et al., 1995). The characteristic vibration peaks of the complex were similar to that of standard heteropolyoxymolybdate. The transfer of the praseodymium redox potential (III) is mainly due to the negative charge of the unsaturated heteropolymolybdate (Haraguchi et al., 1994).

**Effect of Lanthanide (III) Species on $H_2S$ Removal**

The effects of different lanthanide (III) species on $H_2S$ removal were investigated, and the results are shown in Fig. 2. The comprehensive ranking for the $H_2S$ removal efficiency is PrPMo > EuPMo > SmPMo > GdPMo. The aqueous solution of PrPMo showed the best desulfurization and regeneration performance. According to the previous studies, the properties of heteropoly compounds are stable at ambient temperature (Liu et al., 2017b). As shown in Fig. 3, the color of the desulfurization reagent changes from light green to dark blue, then to pale green again, suggesting that PrPMo could be effectively regenerated. Therefore, PrPMo was selected as the desulfurizer in this study.

**Effect of Temperature on $H_2S$ Removal**

The effect of temperature on $H_2S$ removal was studied to optimize the performance of the heteropoly compound in the range of 25 to 75°C (Fig. 4). It can be found that the desulfurization efficiency decreased significantly with the temperature increase. The desulfurizer at 25°C had 90% desulfurization efficiency within 200 min, and had the best removal performance. This study also showed that higher temperature was not beneficial for $H_2S$ removal. The effect of temperature lies in two aspects: on one hand, increasing temperature tends to accelerate the chemical reaction speed; on the other hand, the solubility of $H_2S$ in the aqueous solution tends to decline considerably at the same time. Besides, the oxidation of $H_2S$ is exothermic, in this regard, high temperature is also not beneficial for the desulfurization process (Huang et al., 2017). Apparently, the observed results indicated that the effect of solubility plays a predominant role in the process.

**Effect of PrPMo Concentration on $H_2S$ Removal**

Fig. 5 shows the effect of concentrations of PrPMo on desulfurization performance at 25°C. At the concentration of 0.015 mol L$^{-1}$ for the PrPMo, the $H_2S$ removal efficiency achieved 90% within 250 min. When the concentrations were 0.001 mol L$^{-1}$ and 0.0005 mol L$^{-1}$, either the desulfurization efficiency maintained above 90%, but the time span reduced to 230 min and 150 min, respectively. This revealed that higher concentration of PrPMo could achieve higher $H_2S$ removal efficiency. The desulfurization rate decreased significantly, which was due to the depletion of

![Fig. 1. FT-IR spectrum of K$_{17}$[Pr$_2$Mo$_{17}$O$_{61}$]$_2$](image-url)
Fig. 2. Effect of lanthanide (III) species on H$_2$S removal.

Fig. 3. $K_{17}[\text{Pr(P}_2\text{Mo}_{17}\text{O}_{61})_2]$ color changes before absorption, before regeneration, and after regeneration.

Fig. 4. Effect of temperature on H$_2$S removal.
PrPMo during the reaction. Thus, higher PrPMo concentration led to higher H$_2$S removal efficiency. Therefore, the subsequent experiments were performed with 0.0015 mol L$^{-1}$ of PrPMo.

**Effect of H$_2$S Concentration on H$_2$S Removal**

Concentration of H$_2$S is also an important factor affecting the H$_2$S removal efficiency of PrPMo. The effect of different concentrations of H$_2$S on the desulfurization performance of PrPMo solution at 25°C was studied (Fig. 6). The results revealed that the H$_2$S removal efficiency of PrPMo could remain over 89% within 300 min under different H$_2$S concentrations. The study showed that at lower H$_2$S concentration, the H$_2$S removal efficiency maintained above 90% for a longer time. The reason is that PrPMo was sufficient for the reaction at the early stage, but the PrPMo concentration decreased gradually, leading to the low concentration at the later stage. Thus, these results suggested that lower H$_2$S concentration was beneficial for its removal by the PrPMo solution. Considering the actual situation, the subsequent experiments were carried out with H$_2$S concentration of 2200 mg m$^{-3}$.

**Effect of pH on H$_2$S Removal**

pH plays an important role in the H$_2$S removal efficiency of the absorbent (Zheng et al., 2018). We studied this factor with the 2200 mg m$^{-3}$ of H$_2$S (Fig. 7). The results showed that H$_2$S removal efficiency increased significantly with the pH increase from 1 to 5, but it slightly decreased with the pH increase from 5 to 9. The best removal efficiency (92% within 250 min) has been achieved at pH 5. These results indicated that basic medium (higher pH value) may destroy the structure of the heteropoly acid, while the heteropoly acid in acidic medium could maintain the stable Dawson structure.

**Effect of pH Buffer Solution on H$_2$S Removal**

Since the pH of the solution is an important factor for the performance of the desulfurization agent, it is worthwhile to discuss how to keep the pH of the solution stable during the desulfurization process. In this experiment, pH buffer solution was used to maintain the pH balance of the solution during the entire reaction. The experiment was carried out with the H$_2$S concentration of 2200 mg m$^{-3}$. Shown in Fig. 8 are the experimental results. The H$_2$S removal efficiency was improved (achieved > 90%) at the pH range of 2.3 to 6.8 (acidic medium), while the removal efficiency decreased at the pH range of 6.8 to 12 (basic medium). High desulfurization efficiency can be ascribed mainly to the alkalinity effect. These results indicated that the redox potential and the alkalinity effect of the solution work jointly, with the former being predominant at pH range below 6.8. This conforms to the rationale that heteropoly compound has better redox performance at low to medium pH value. Compared with the direct adjustment of pH with HCl and NaOH, the H$_2$S removal efficiency using the pH buffer solution was significantly improved. The descriptive results of the pH changes of the solutions before and after absorption are given in Table 1.

Therefore, under the optimal conditions (25°C, the 0.0015 mol L$^{-1}$ concentration of PrPMo, the H$_2$S concentration of 2200 mg m$^{-3}$ and pH = 6.8), the PrPMo solution had the best desulfurization performance. As shown in Fig. 8, the H$_2$S removal efficiency kept 90% within 400 min, and then decreased slowly. However, the pH buffer agent reduced the concentration of H$^+$ in the solution, leading to a decrease in the rate of electrochemical regeneration. Therefore, this problem is still worth further investigation.

**Desulfurization Mechanism and Desulfurization Products**

FT-IR spectra of PrPMo before and after desulfurization and regeneration are shown in Fig. 9. The presence of four
characteristics peaks of the heteropoly acid anion after absorption and regeneration, indicating that the compound had stable Dawson structure.

The solid powder obtained by evaporating the desulfurizing agents before and after absorption and regeneration was used for XPS analysis. Fig. 10 shows the XPS spectrum of the Mo 3d5/2 orbital on the surface of the PrPMo compound before and after regeneration. Before absorption, the binding energy of Mo 3d5/2 was 233.09 eV, indicating that the valency of Mo atom in the compound was +VI. While after absorption, the Mo 3d5/2 spectra of the sample had the two characteristic peaks, i.e., Mo (+IV) at 230.72 eV and Mo (+VI) at 233.27 eV. Whereas after electrochemical regeneration, the binding energy returned to 233.42 eV, and the valency returned to Mo (+VI). The characterization results showed that Mo (+VI) in the heteropoly compounds was reduced to Mo (+IV) by H2S during the absorption process, and then was electrochemically regenerated into Mo (+VI) (Muijsers et al., 1995).

The XPS patterns of the S 2p orbitals of the compounds before and after regeneration are shown in Fig. 11. The S orbital of the heteropoly compound before regeneration existed in various valence states. The characteristic peak with the binding energy of 162.03 eV indicated that H2S gas was absorbed, and the valence of sulfur element was -II. While, the characteristic peak with the binding energy of 163.45 eV belonged to S(0) orbital. Whereas, the characteristic peak at 168.94 eV proved the presence of SO4 2-. After electrochemical regeneration, the area of characteristic peak belonging to SO4 2- was significantly increased. A white
Fig. 8. Effect of pH buffer solution on H₂S removal.

### Table 1. The pH changes of the two solutions before and after absorption.

<table>
<thead>
<tr>
<th></th>
<th>Before absorption</th>
<th>After absorption</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adjust the pH of the solution with HCl and NaOH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.36</td>
<td>+0.36</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.55</td>
<td>+0.55</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5.34</td>
<td>+0.34</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>7.60</td>
<td>+0.60</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>7.40</td>
<td>–1.60</td>
<td></td>
</tr>
<tr>
<td>Adjust the pH of the solution with a pH buffer solution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>2.43</td>
<td>+0.13</td>
<td></td>
</tr>
<tr>
<td>4.8</td>
<td>4.90</td>
<td>+0.10</td>
<td></td>
</tr>
<tr>
<td>6.8</td>
<td>6.94</td>
<td>+0.14</td>
<td></td>
</tr>
<tr>
<td>9.1</td>
<td>8.96</td>
<td>–0.04</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>9.60</td>
<td>–2.4</td>
<td></td>
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</table>

Fig. 9. FT-IR spectra of PrPMo after and before study.
precipitate can be found by adding BaCl₂ solution into the desulfurization reagent after regeneration. The above results proved that the desulfurization product was SO₄²⁻ (Baker et al., 1999).

The XPS patterns of the Pr 3d orbital of the compound before and after absorption and after electrochemical regeneration are shown in Fig. 12. XPS spectra showed the three characteristic peaks for the Pr 3d₅/₂ orbital with the absorption energies of 933.37 eV and 954.27 eV (before H₂S absorption), indicating that Pr in the PrPMo was +III state. Whereas an absorption peak with a binding energy of 975.77 eV indicated that Pr in the PrPMo was +IV state (Lutkehoff et al., 1995; Poggio-Fraccari et al., 2018). After H₂S absorption, the intensity of characteristic peak belonging to Pr (+III) was significantly reduced. But it increased again after electrochemical regeneration. In conclusion, XPS study proved that rare earth element (Pr) participated in the desulfurization reaction and played a key role in the absorption and conversion of H₂S.

Thus, the desulfurization mechanism of PrPMo can be illustrated as follows: during the absorption process, H₂S was oxidized into S and SO₄²⁻ through the redox of PrPMo. At the same time, the Mo (+VI) in PrPMo was reduced to Mo (+IV). In the electrochemical regeneration process, S in the reaction system was converted to SO₄²⁻. Furthermore, Pr was reduced from Pr (+IV) to Pr (+III) after regeneration. Mo 3d of PrPMo after regeneration exhibited a similar XPS spectrum with that before absorption, suggesting that PrPMo was successfully regenerated since Mo (+IV) was oxidized back to Mo (+VI) after electrochemical regeneration. Based on the above analysis, we inferred that PrPMo played a redox role in desulfurization.

In Table 2, we compared the PrPMo with the previous desulfurization reagents. Liu et al. (2017c) and Lütkehoff et al. (1995) found that the desulfurization efficiency of the pure phosphotungstic acid (H₃PW₁₂O₄₀) and phosphomolybdic acid (H₃PMo₁₂O₄₀) was 20% and 80%, respectively. Ma et al. (2014) and Wang et al. (2003) used V and W to substitute the part elements of phosphomolybdic acid to form...
H7[P2Mo17VO62]·39H2O and H3PW10Mo2O40, respectively, to remove H2S. The results showed that the desulfurization efficiency of them was only 85% (Wang et al., 2003; Ma et al., 2014). Thus, we found herein that the PrPMo compounds had better performance for the removal of H2S.

CONCLUSION

We investigated the desulfurization performance of a series of rare earth ion doped heteropolymolybdates under different reaction conditions. The results can be summarized as follows:

(1) FT-IR spectrum proved the successful synthesis of LnPMo (Ln = Pr3+, Gd3+, Sm3+, and Eu3+).

(2) PrPMo solution had ideal desulfurization capability at room temperature. The absorbent could achieve a H2S removal efficiency of 90% within 400 min. At higher concentration of the PrPMo, H2S removal efficiency became higher accordingly.

(3) Low H2S concentration was suitable for the desulfurization reaction. PrPMo had the highest desulfurization efficiency at pH 6.8.

(4) The final product of desulfurization was SO42−. PrPMo played a role of redox in desulfurization and could convert H2S into sulfur resources.

ACKNOWLEDGEMENTS

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REFERENCES


**Table 2.** A comprehensive study of the rare earth doped PrPMo compound for the removal of H2S gas.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Name of compound</th>
<th>Efficiency of H2S removal</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>PrPMo</td>
<td>90%</td>
<td>Fig. 2</td>
</tr>
<tr>
<td>2.</td>
<td>(NH4)11[Sm(PMo11O39)2</td>
<td>80%</td>
<td>Liu et al. (2017c)</td>
</tr>
<tr>
<td>3.</td>
<td>H3PW12O40</td>
<td>20%</td>
<td>Liu et al. (2017c)</td>
</tr>
<tr>
<td>4.</td>
<td>H3PMo12O40</td>
<td>80%</td>
<td>Lütkehoff et al. (1995)</td>
</tr>
<tr>
<td>5.</td>
<td>H7[P2Mo17VO62]·39H2O</td>
<td>85%</td>
<td>Ma et al. (2014)</td>
</tr>
<tr>
<td>6.</td>
<td>H3PW10Mo2O40</td>
<td>85%</td>
<td>Wang et al. (2003)</td>
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</tbody>
</table>

**Fig. 12.** The XPS spectra of Pr 3d of samples before absorption as well as before and after regeneration.


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