Experimental Investigation of Simultaneous Removal of SO₂ and NO_x Using a Heteropoly Compound

Meiqing Yu^{1,2†}, Hongjian Zhu^{1†}, Sheng Tian³, Rui Wang^{1,2*},
Ivan V. Kozhevnikov⁴

¹ School of Environmental Science and Engineering, Shandong University, Qingdao 266237, China

² Shenzhen Research Institute of Shandong University, Shenzhen 518057, China

³ Shandong Research Institute for Chemical Technology, Qingdao University of Science & Technology, Jinan 250014, China

⁴ Department of Chemistry, The University of Liverpool, Liverpool, L69 7ZD, UK

ABSTRACT

Aiming at developing a simple, feasible method for SO₂ and NO_x removal, in this work, various doping amounts of heteropolyacid and heteropolyacid salts were prepared and used in wet absorption for simultaneous removal of SO₂ and NO. The desulfurization and denitrification performance was evaluated by investigating dynamic SO₂ and NO absorption in a simulated reactor containing a heteropoly compound (HPC) solution along with various factors influencing the reaction. The results demonstrate that this system had a high removal efficiency of SO₂ and modest NO removal. The amount of Wolfram (W) doping and the pH of the solution affecting the removal performance was studied, and a stable SO₂ removal efficiency higher than 95% was obtained for HPW₁Mo at a pH value of 5.5. In addition, the desulfurization performance of NaPWWMo with a 50% removal efficiency was higher than that of the HPWMo solution (20%) after a 60 min reaction time. A high concentration of the NaPWWMo solution and the presence of O₂ were beneficial to desulfurization at room temperature. In addition, the removal efficiency of SO₂ or NO by NaPWWMo was only affected by its own gas concentration rather than their mutual influences on each other. This work should be beneficial to the optimization leading to the development of simultaneous desulfurization and denitrification systems in practical applications.

Keywords: Polyoxometalate, SO₂, NO, Absorption, Removal efficiency

1 INTRODUCTION

All over the world, a large amount of flue gases from coal-fired power plants, oil refining and gas processing, and smelting are emitted into the atmosphere every day. Massive amounts of SO₂ and NO, as the main gas pollutants, not only do much harm to human health, but also are commonly recognized as the major contributor to acid rain and haze formation (McIlinden *et al.*, 2016; Oberschelp *et al.*, 2019; Pi *et al.*, 2020). At present, this phenomenon is particularly prominent in China because China is the largest coal producer and consumer in the world. On the other hand, the new emission standards adopted by governments at the global scale have put forward stricter requirements for limiting SO₂ and NO emissions. Thus, SO₂ and NO removal is a great concern that needs to be resolved as soon as possible. However, the development of new, efficient desulfurization and denitrification technologies is still necessary.

Commonly used SO₂ removal methods for flue gas include dry absorption and wet absorption. Activated carbon, activated coke, and zeolite have been widely used in dry absorption due to several advantages, including low cost and high operational flexibility (Karatepe *et al.*, 2008; Yan *et al.*, 2013; Rezaei *et al.*, 2015; Xu *et al.*, 2016), but the low sulfur loading process still needs further improvement. Wet flue-gas desulfurization technology (WFGD) is regarded as the most

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* **Corresponding Author:**

wangrui@sdu.edu.cn

† These authors contributed
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industrialized process, especially the lime/limestone process, because of its high efficiency and stability (Liu *et al.*, 2010; Yan *et al.*, 2013). However, the main drawbacks (high costs, complex equipment, and the formation of secondary pollutants) restrict its wider applications (Chen *et al.*, 2015; Hao *et al.*, 2017). Several denitrification technologies, including selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR), are available for NO_x removal (Zhang *et al.*, 2016). Among them, SCR with NH₃ as the reducing agent is the most widely applied method in stationary source combustion units owing to its high efficiency and selectivity (Forzatti *et al.*, 2009; Imanaka and Masui 2012). However, the presence of H₂O and SO₂ in power plant flue gas and vehicle exhaust gas causes the deposition of (NH₄)₂SO₄/NH₄HSO₄ and metal sulfates, in turn poisoning the catalyst (Han *et al.*, 2019). The separate removal of SO₂ and NO_x results in many problems; thus, a great deal of attention has been paid to developing a system for simultaneous removal of SO₂ and NO_x.

Recently, the oxidation-absorption process has been shown to have great advantages in many processes for simultaneous removal of NO_x and SO₂. Some common oxidants, including H₂O₂ (Liu *et al.*, 2011; Zhao *et al.*, 2017), Na₂S₂O₈ (Khan and Adewuyi, 2010; Xi *et al.*, 2019), O₃ (Li *et al.*, 2020), and NaClO (Mondal and Chelluboyana, 2013), show better NO_x removal efficiency using the wet method. Liu *et al.* (2019) studied the simultaneous removal of SO₂ and NO_x through a two-stage process composed of catalytic ozonation and the subsequent absorption of reaction gases by NH₃/(NH₄)₂S₂O₈. The main products were ammonium sulfate and ammonium nitrate, which can be used as fertilizers. Activated circulating fluidized bed boiler (CFB) fly ash used as a catalyst has been applied in the simultaneous removal of NO_x and SO₂, which can achieve 99% SO₂ and 92% NO_x removal efficiency at 140°C with 2 mol L⁻¹ and 5 mol L⁻¹ of H₂O₂, respectively (Cui *et al.*, 2020). Zhou *et al.* (2020) proposed a novel process that can achieve a higher NO_x and SO₂ removal efficiency and a lower nitrate concentration by using urea peroxide (CO(NH₂)₂·H₂O₂) combined with a countercurrent wet scrubber. The synergistic desulfurization and denitrification effect of the catalyst and the effect of the corona discharge on the activity of the catalyst were studied, where the desulfurization and denitrification rates on the La-Ce-V-Cu-ZSM-5 catalyst reached 97% and 83%, respectively (Qi *et al.*, 2020). In these studies, the simultaneous removal of SO₂ and NO was achieved by adding oxidants or composites. However, it is worth attempting to develop a simple, feasible method that can accomplish this goal without an oxidizing agent. The heteropoly compound (HPC) has several advantages, including versatility, favorable acidity, oxidation-reduction flexibility, and a pseudo-liquid phase feature, that have attracted significant scholarly attention and have been widely used in oil desulfurization, where it exhibits excellent activity (Zhang and Wang, 2018; Dou and Wang, 2019). In our previous work, various solid HPCs were prepared and studied initially as adsorbents used for capturing NO_x (Wang *et al.*, 2020; Zhang *et al.*, 2020).

In this study, various doped heteropoly acids and heteropoly acid salts were prepared and used in wet absorption for simultaneous removal of SO₂ and NO. The removal performance was investigated in a simulated reactor contained an HPC solution. The factors influencing the removal performance, such as the doping amount, the reaction temperature, the HPC concentration, and the NO/SO₂ concentrations, were investigated. This work should be beneficial to demonstrating the optimization potential of simultaneous desulfurization and denitrification systems for practical application.

2 EXPERIMENTAL PROCEDURE

2.1 Materials

All chemicals were of analytical reagent grade and used without further purification. H₃PMo₁₂O₄₀, H₃PW₁₂O₄₀, H₃SiW₁₂O₄₀ were purchased from Linghu Fine Chemical Factory. Na₂WO₄·2H₂O, NaH₂PO₄·2H₂O, and HCl were purchased from Sinopharm Chemical Reagent Co., Ltd., Na₂MoO₄·2H₂O was purchased from Tianjin chemical reagent factory, China.

2.2 HPC Preparation

H₃PW₁Mo₁₁O₄₀, H₃PW₃Mo₉O₄₀, and H₃PW₆Mo₆O₄₀ were prepared according to the literature (Misono *et al.*, 1982). For example, the preparation of H₃PW₁Mo₁₁O₄₀ was as follows: 26.51 g

$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and 3.29 g $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved in 100 mL of deionized water and heated to boil under magnetic stirring, after which 1.56 g of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ was added. After 30 min, a 6 mol L^{-1} HCl solution was added dropwise to reach a pH value of 1. After 5 h, the solution was cooled to approximately 60°C, ice bathed, and transferred to a separatory funnel. Small amount of 1:1 sulfuric acid and ether were added, and the solution was shaken. The solution was divided into 3 layers after standing, and the lower layer of light green oily matter was mixed polyacid etherate. The residuary ether from the obtained mixed polyacid etherate was removed in a fume hood, and a small amount of water was added. The final product was obtained after drying at 60°C overnight. The three samples were denoted as HPW_1Mo , HPW_3Mo , and HPW_6Mo , respectively.

The $\text{Na}_9[\text{PW}_5\text{Mo}_4\text{O}_{34}] \cdot 2\text{H}_2\text{O}$ was prepared as follows: 16.49 g $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, 9.97 g $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and 1.56 g $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved in 50 mL deionized water under magnetic stirring. 12 mol L^{-1} HCl solution was added dropwise until pH = 6. After 15 min, 25 mL acetone was added, and a light yellow oil was formed. The oil was washed with acetone several times until a powder was formed. The powder was filtered and recrystallized to obtain the product (denoted as NaPWWMo).

2.3 Characterizations of the Catalysts

X-ray diffraction (XRD) patterns were obtained on a Bruker D8 diffractometer using Cu $\text{K}\alpha$ radiation at a scan speed of 5° min^{-1} . Fourier transform infrared (FTIR) spectroscopy was performed on a Nicolet Avatar 370, and the spectral data were recorded in a range of 400–4000 cm^{-1} at a 4 cm^{-1} resolution. The thermogravimetric analysis (TGA) was carried out on a TGA SDT Q 600 thermogravimetric analyzer at a heating rate of $10^\circ\text{C min}^{-1}$ ranging from 25°C to 600°C under a nitrogen atmosphere.

2.4 Performance Measurement

The performance evaluation system for the simultaneous removal of NO and SO_2 using HPC solution is shown in Fig. 1. The system generated the simulated flue gas, and carried out the absorption of NO and SO_2 and detected the outlet gas. The total flow was 500 mL min^{-1} , and the simulated gases containing SO_2 , NO, 4% O_2 (when used) and balanced N_2 were metered through mass flow controllers. The flue gas was absorbed with a 100 mL HPC solution at room temperature. The inlet and outlet SO_2 and NO concentrations were continually monitored with a TH-990S SO_2 and NO gas analyzer (Wuhan Tianhong, China). The SO_2 and NO removal efficiencies were calculated as follows:

$$\text{SO}_2 \text{ removal efficiency (\%)} = \left(1 - \frac{[\text{SO}_2]_{\text{out}}}{[\text{SO}_2]_{\text{in}}} \right) \times 100\%, \quad (1)$$

$$\text{NO removal efficiency (\%)} = \left(1 - \frac{[\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \right) \times 100\%. \quad (2)$$

3 RESULTS AND DISCUSSION

3.1 XRD and FTIR

Fig. 2(a) shows the XRD pattern of HPW_1Mo and NaPWWMo . The diffraction peaks corresponded with the standard powder diffraction file (PDF) of $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 14\text{H}_2\text{O}$ (PDF: 43-0317) and $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 14\text{H}_2\text{O}$ (PDF: 50-0656) observed on HPW_1Mo , confirming a synthesized heteropolyacid with a Keggin type structure. However, for NaPWWMo , no regular PDF card corresponding to a single crystalline phase was observed, which may be because NaPWWMo consists of several substances.

To further determine the crystal structure of the catalysts, the FTIR spectra of the as-synthesized heteropoly compound were recorded. As shown in Fig. 2(b), HPW_1Mo showed obvious vibration bands at 785, 872, 965 and 1067 cm^{-1} , corresponding to the characteristic bands of heteropolyacid with a Keggin structure as reported in the previous literature (Wu *et al.*, 2000, 2005; Cheng and Wang, 2013). Consistent with the XRD results, the FTIR measurement confirmed that the solid Keggin heteropolyacid was successfully prepared. For NaPWWMo , similar to HPW_1Mo , the

Fig. 1. Schematic diagram of simultaneous desulfurization and denitrification using the experimental device.

Fig. 2. XRD patterns (a) and FTIR spectra (b) of HPW₁Mo and NaPWMo.

characteristic peaks of the Keggin heteropolyacid were also found at corresponding positions, but the peak intensity was significantly reduced.

3.2 TGA

Thermogravimetric analyses of HPW₁Mo and NaPWMo were carried out to investigate their dehydration behavior, for which the results are shown in Fig. 3. The HPW₁Mo curves in Fig. 3(a) showed three weight loss steps. Physisorbed water was evacuated below 130°C. The second weight loss step was located between 130 and 270°C, which can be regarded as structural water. Additional weight loss was observed above 300°C, which could be attributed to the decomposition of the heteropolyacids into oxides. The NaPWMo shown in Fig. 3(b) also exhibits three weight loss steps, with the second weight loss step located between 135°C and 586°C, illustrating that NaPWMo has higher thermal stability than HPW₁Mo.

3.3 The Removal Performance of HPMo, HPW, and HSiW

The absorption performance of several commonly used heteropolyacids for SO₂ and NO was evaluated, for which the results are shown in Fig. 4. As shown in Fig. 4(a), several heteropoly

Fig. 3. Thermogravimetric analyses of (a) HPW₁Mo and (b) NaPWMo.

Fig. 4. (a) Desulfurization and (b) denitrification curves for HPMo, HPW and HSiW. Reaction conditions: 630 ppm SO₂, 650 ppm NO, C_{HPC} = 6×10^{-4} M, T = 25°C.

acids had similar desulfurization performance, where it can be seen that as the absorption time increased, the desulfurization performance gradually decreased. HPMo had slightly better activity, with a removal efficiency of 66% at 15 min. Its removal efficiency dropped to 21% after the reaction proceeded for 60 min. The results for NO removal are shown in Fig. 4(b). It can be observed that the three heteropolyacids had relatively stable and similar NO absorption properties, where the removal efficiency remained at approximately 15% even after 60 min of reaction.

3.4 The Performance of HPWMo

In order to explore the effect of metal doping modifications on the performance of the absorbent, the absorption performance of HPMo doped with different amounts of W as a heteroatom was studied. As shown in Fig. 5(a), HPW₁Mo exhibits significantly improved desulfurization performance, and the SO₂ removal efficiency was as high as 90% at 15 min. As the number of doped W atoms increased, the SO₂ removal efficiency gradually declined. The order of SO₂ removal efficiency for the W-doped HPMo was as follows: HPW₁Mo > HPW₃Mo > HPW₆Mo. The NO absorption is shown in Fig. 5(b), where it can be observed that the order of NO removal efficiency was the same as that for SO₂. However, W doping had little effect on the NO removal performance of HPMo.

Fig. 5. (a) Desulfurization and (b) denitrification curves of different amounts of W doped into HPW at a pH of 2.8. Reaction conditions: 630 ppm SO₂, 650 ppm NO, C_{HPC} = 6 × 10⁻⁴ M, T = 25°C.

3.5 The Effect of pH

pH is an important factor that affects absorption reactions. Therefore, the effect of pH on the absorption performance of HPW₁Mo was studied with a comparative experiment. In this experiment, the pH of the heteropolyacid solution was adjusted to 5.5 using a NaOH solution. It can be seen in Fig. 6(a) that under a pH value of 5.5, a SO₂ removal rate higher than 95% was found on HPW₁Mo and remained stable for at least 60 min. HPW₃Mo and HPW₆Mo also showed this high removal efficiency, but their stabilization time was shorter than that of HPW₁Mo, and the absorption efficiency decreased rapidly with reaction time. As the pH value of the absorption solution increased, the desulfurization efficiency also increased. This may have been due to the fact that SO₂ as an acid gas is more easily absorbed by substances with a high pH value. In other words, the added alkaline solution can increase the absorption capacity of SO₂. On the other hand, it may also have been because the added alkaline solution can undergo an acid-base neutralization reaction with heteropoly acid to form a sodium heteropoly salt, which leads to better absorbability of SO₂. As shown in Fig. 6(b), the denitrification efficiency was not sensitive enough to the change in the pH value of the solution. A reasonable explanation for this is that due to the low solubility of NO in water, the denitrification efficiency was not as significant as the desulfurization efficiency.

Fig. 6. (a) Desulfurization and (b) denitrification curves of HPW at a pH value of 5.5. Reaction conditions: 630 ppm SO₂, 650 ppm NO, C_{HPC} = 6 × 10⁻⁴ M, T = 25°C.

3.6 The Effect of Temperature

In the former experiment, it was found that using a NaOH solution to adjust the pH can improve SO₂ absorbability. The absorption performance of the synthesized NaPWMo was studied in order to further explore the essential reason for this. The absorption experiments were carried out at different temperatures. From the Fig. 7(a), it can be found that temperature affected the absorption of SO₂ on NaPWMo solution. When the temperature increased from 25°C to 50°C, the SO₂ absorption curves displayed an obvious downward trend, implying that low temperature is beneficial to the absorption of SO₂. In addition, as the absorption time was extended, the removal efficiency at each temperature decreased. NaPWMo still had higher absorption of SO₂ at 25°C, and its removal efficiency was approximately 50% even after 60 min. By comparison, it can be seen that the desulfurization performance of NaPWMo was higher than that of the HPWMo solution with a 20% removal efficiency, but less than that of the HPWMo solution in which the pH was adjusted with NaOH. This indicated that the desulfurization performance of heteropolyacid salt may be better than that of parent heteropolyacid. For NO removal, as shown in Fig. 7(b), although NaPWMo had a good absorption capacity at 25°C, the greatest NO removal efficiency was only 13%, which was lower than that of HPWMo.

3.7 The Effect of the NaPWMo Concentration

The removal efficiency of SO₂ and NO can be greatly enhanced by an increase in the liquid-gas ratio. The effect of the NaPWMo concentration on SO₂ and NO removal efficiency was further studied, and the results are shown in Fig. 8. It can be seen in Fig. 8(a) that at a concentration of 6×10^{-3} M for the NaPWMo, the SO₂ removal efficiency achieved 95% within a reaction time of 60 min. When the concentration was 1.2×10^{-3} M, the desulfurization efficiency maintained above 90% and gradually reduced as the reaction time exceeded 45 min. Furthermore, worse desulfurization efficiency was observed with decreases in the concentration of NaPWMo. This indicated that at a higher concentration of NaPWMo, SO₂ removal efficiency was improved, and the reaction time was longer. As shown in Fig. 8(b), similarly, as the concentration of NaPWMo was increased, the NO removal efficiency also increased slightly. When the concentration of NaPWMo was 6×10^{-3} M, the removal efficiency was as high as 16% after a reaction time of 60 min.

3.8 The Effect of Gas Concentration

In order to better understand the ability of NaPWMo to remove SO₂ and NO in complex applications, the removal performance under different gas concentrations was studied. Fig. 9(a) shows the relationship between the desulfurization efficiency and the SO₂ and NO gas ratio. When the SO₂ concentration in the reaction gas was maintained at 630 ppm, as the NO concentration

Fig. 7. (a) Desulfurization and (b) denitrification curves of NaPWMo at different temperatures. Reaction conditions: 630 ppm SO₂, 650 ppm NO, $C_{\text{HPC}} = 6 \times 10^{-4}$ M.

Fig. 8. (a) Desulfurization and (b) denitrification curves of NaPWMo at different concentrations. Reaction conditions: 630 ppm SO₂, 650 ppm NO, T = 25°C.

Fig. 9. The effect of gas concentration on desulfurization and denitrification of NaPWMo. Reaction conditions: T = 25°C, C_{HPC} = 1.2 × 10⁻⁴ M.

was increased from 400 ppm to 900 ppm, the SO₂ removal efficiency barely changed, indicating that the NO concentration may have little effect on the desulfurization performance of NaPWMo. When the concentration of NO remained unchanged, the absorption performance decreased significantly with increases in the concentration of SO₂, which may have been because the high concentration of SO₂ was absorbed more easily, causing the absorption solution to quickly reach saturation and resulting in a decrease in the removal efficiency. For NO removal, as shown in Fig. 9(b), as the NO concentration increased, the NO removal efficiency also showed a downward trend when the SO₂ concentration was maintained at 630 ppm. This means that for NaPWMo, the simultaneous removal of NO and SO₂ was only limited by its own gas concentration, and they did not affect each other.

3.9 The Effect of O₂

In practical applications, some oxygen may remain in flue gas because excess air has to be introduced to ensure full combustion of the fuel. An experiment was carried out to investigate the effect of O₂ in the gas flow on desulfurization and denitrification of NaPWMo, for which the results are shown in Fig. 10. In Fig. 10(a), in the presence of 4% O₂, SO₂ removal efficiency was higher than 95% and was maintained for 45 min. However, in the absence of O₂, as the reaction

Fig. 10. The effect of O₂ on the desulfurization and denitrification of NaPWMo. Reaction conditions: 630 ppm SO₂, 650 ppm NO, T = 30°C, C_{HPC} = 2 × 10⁻³ M.

time increased, SO₂ removal efficiency gradually decreased, and the overall removal efficiency was lower than that in the presence of O₂. This implies that O₂ is an important factor affecting the removal of SO₂ by HPC solution. Based on previous reports (Rubio and Izquierdo, 1998; Raymundo-Piñero *et al.*, 2000; Xu *et al.*, 2016), when O₂ is present, SO₂ easily reacts with O₂ to form SO₃ under the action of a catalyst. SO₃ and H₂O further react to form H₂SO₄, which leads to an increase in SO₂ absorption. A similar trend also can be observed in Fig. 10(b), where the NO removal efficiency clearly increased in the presence of O₂. This may have been due to the fact that NO with low solubility was oxidized to NO₂ and then dissolved into the HPC solution (Chen *et al.*, 2020). According to the above experimental results, the optimal experimental conditions for simultaneous desulfurization and denitration of HPC can be summarized as follows: 400 ppm SO₂, 600 ppm NO, 4% O₂, T = 25°C, C_{HPC} = 6 × 10⁻³ M.

According to the experimental results, the reaction mechanism of simultaneous desulfurization and denitration on HPC could be deduced. First, SO₂ is absorbed by water to form H₂SO₃, which can further be oxidized by the HPC to H₂SO₄. Then, the reduced HPC is used to reduce NO in the presence of O₂. The reaction equation can be written as follows (taking sodium phosphomolybdate as an example):

In conclusion, HPC can remove SO₂ and NO and at the same time act as a catalytic intermediate following Eq. (6). However, in the reaction process, due to the insufficient reaction described by Eq. (5), the HPC is consistently consumed.

It is worth paying attention to the stability of HPC when attempting simultaneous desulfurization and denitration. Repeated experiments should be conducted to verify the stability and reusable ability of HPC in future work, and the accurate reaction mechanism should further be studied.

4 CONCLUSION

Heteropoly compounds were employed to simultaneously remove NO and SO₂ from flue gas.

This system had a high SO₂ removal efficiency accompanied by modest NO removal. Heteropolyacids containing P and Mo elements exhibited good removal performance. The amount of doped W and the pH of the solution affected the removal performance, where a stable SO₂ removal efficiency greater than 95% was obtained on HPW₁Mo at a pH value of 5.5. The desulfurization performance of NaPWMo was higher than that of the HPWMo solution. High concentration of the NaPWMo solution and the presence of O₂ were beneficial to desulfurization at room temperature. The removal efficiency of the SO₂ or NO in NaPWMo was only affected by its own gas concentration rather than their mutual influence on each other.

CONFLICTS OF INTEREST

There are no conflicts to declare.

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