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$H_4PVMo_{11}O_{40}$ SOLUTION AS A NEW ABSORBENT FOR SIMULTANEOUS REMOVAL OF SO_2 AND NO_x

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Abstract

Using the aqueous solution of $H_4PVMo_{11}O_{40}$, a Keggin type heteropoly compound, the authors developed a new liquid redox method for combined removal of SO_2 and NO_x. Factors affecting the performance of the absorbent system, including $H_4PVMo_{11}O_{40}$ concentration, absorption temperature, concentration of O_2 in the feed gas, residence time of the feed gas in solution, the addition of buffering agents, were investigated. It was indicated in the results that, using $H_4PVMo_{11}O_{40}$ only, the removal of SO_2 and NO_x from gas stream can reach up to 92% and 60% respectively. All factors investigated have marked influence on the removal of SO_2 and NO_x, whereby the favorable conditions were recommended. Experimental comparison of the absorbent system of $H_4PVMo_{11}O_{40}$ with Fe-EDTA reveals the promising performance of the new absorbent system developed.

Key words: *desulfurization, denitrification, heteropoly compound, liquid redox*

Introduction

The emission of SO_2 and NO_x from fuel combustion process has long been an environmental problem, attracting worldwide researchers. Combined SO_2/NO_x removal processes remain considered fairly complex and costly. However, emerging technologies have the potential to reduce SO_2 and NO_x emissions for less than the combined cost of conventional FGD for SO_2 control and SCR for NO_x control. Most processes are in the development stage, although some processes are commercially used on low to medium-sulphur coal-fired plants. $CaCO_3$ containing yellow phosphorus emulsion is quite effective for simultaneous removal of SO_2 and NO_x, which may achieve conversions as up to 100% for both, but this is achieved at the expense of successive consumption of absorbent[1,2]. Besides, methods concerning the use of electron beam irradiation or pulse corona, although proved to be effective, improvements are ongoing at present due to their high equipment, operation and maintenance cost[3]. Hence, development of new method, effective and economical, without causing secondary pollution, becomes quite attractive. In view of the reversible redox property and good chemical stability of heteropoly compound (HPC), using the aqueous solution of HPC, the authors developed a new liquid redox method for combined removal of SO_2 and NO_x[4,5]. In this paper, $H_4PVMo_{11}O_{40}$, a Keggin type HPC, was synthesized for such purpose. Characteristics of desulfurization and denitrification are the subject of this paper.

Material and Methods

Shown in Fig.**1** is the scheme of the experiment flow sheet. Two cylinder-shaped glass gas scrubbers (2.5cm inner diameter), each with a multiorifice-plate (hole diameter: 50~70μm) at the bottom and containing equal volume of absorbent solution, were used in series to investigate the performance of the absorbent solution. The experimental data gained are the SO_2 and NO_x concentrations in the outlet gas stream. The HPC with Keggin structure used is $H_4PVMo_{11}O_{40}$, which was prepared according to literature[6]. ICP analysis was used to determine the chemical composition of the HPC prepared, and IR spectra of which were used to confirm the Keggin structure. The feed gas stream with constant concentrations of SO_2 and NO_x, flowing at a constant rate, was prepared by mixing three gas streams of dilute SO_2, dilute NO_x and O_2 containing nitrogen gas. The original gases of SO_2, NO and NO_2 were commercial available, all with a purity of 99.97% or higher. The concentrations of SO_2 and NO_x were analyzed with TH-990S digital flue gas detector. All chemicals used were of reagent grade and deionized water was used throughout.

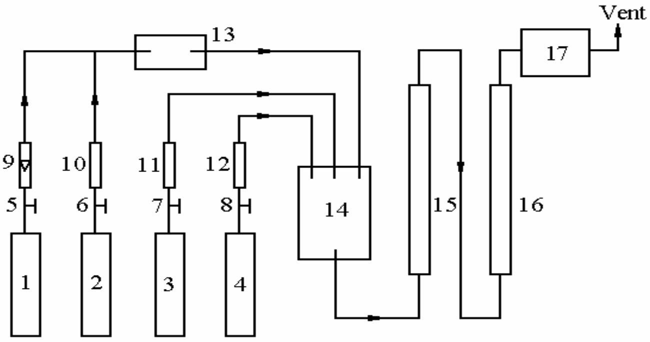

Figure 1. Scheme of the experimental flow sheet

1 N_2 vessel 2 O_2 vessel 3 SO_2 vessel 4 NO_x vessel 5-8 reductor 9,11 rotor flow meter 10,12 mass flow controller 13,14 gas mixer 15,16 multiorifice plate gas scrubber 17 flue gas analyzer

Results and Discussions

The conversions of SO_2 and NO_x increase with the increase in absorbent concentration (Table 1). A favorable absorbent concentration can be recommended to be ca. 2.0×10^{-3} mol/l, corresponding to 87.3% and 51.4% for the conversions of SO_2 and NO_x respectively. The redox reaction between SO_2, NO_x and $H_4PVMo_{11}O_{40}$ can be illustrated as follows:

$$SO_2 + 2H_2O + 2H_4PV(V)Mo_{11}O_{40} \rightarrow H_2SO_4 + 2H_5PV(IV)Mo_{11}O_{40}$$

$$2NO_2 + 8H_5PV(IV)Mo_{11}O_{40} \rightarrow N_2 + 4H_2O + 8H_4PV(V)Mo_{11}O_{40}$$

$$2NO + 4H_5PV(IV)Mo_{11}O_{40} \rightarrow N_2 + 2H_2O + 4H_4PV(V)Mo_{11}O_{40}$$

As the $H_4PVMo_{11}O_{40}$ concentration increases, the intrinsic reaction speeds of the above reactions increase accordingly. Hence the process for the removal of both SO_2 and NO_x is enhanced. In the later discussions, HPC(ox) and HPC(re) are used to refer to $H_4PV(V)Mo_{11}O_{40}$ and $H_5PV(IV)Mo_{11}O_{40}$ respectively.

Table 1 Dependence of the performance of $H_4PVMo_{11}O_{40}$ on its concentration

Conversion, %*	HPC concentration /(mmol/l)			
	10	5	2	0.5
SO_2	92.0	88.2	87.3	84.5
NO_x	60.1	55.4	51.4	47.4

$[SO_2]$ = 1740 mg/Nm^3, NO_x/SO_2 = 1:1(mol/mol); gas rate: 0.41 l/min; T=20 ^oC; HPC solution: 100 ml; absorption time: 30min.

The process of combined removal of SO_2 and NO_x by $H_4PVMo_{11}O_{40}$ is strongly influenced by absorption temperature (Table **2**). From the viewpoint of chemical reaction, the increase of absorption temperature can facilitate the chemical reaction and thus may improve the overall process when such contribution predominates. However, as temperature increases, the solubility of gases will decrease, the process of SO_2 and NO_x transfer from bulk gas stream to solution may be retarded considerably and thus slows down the overall process. From the results shown in Table **2,** the effect of solubility limitation is predominant. As a whole, ambient temperature is favorable to the effective removal of SO_2 and NO_x.

Table 2 The effect of absorption temperature

Conversion, %*	Absorption temperature, ^oC			
	20	40	60	70
SO_2	88.9	84.4	83.2	82.6
NO_x	54.7	53.0	52.5	52.3

$[SO_2]$=1740 mg/Nm^3, NO_x/SO_2 = 1:1(mol/mol); gas rate: 0.41l/min; $H_4PVMo_{11}O_{40}$: 100ml, 2×10^{-3}mol/l, pH=5.5; absorption time: 30min.

O_2 is an actual component in the flue gases. It can be seen from Table **3** that, with the increase of O_2 concentration, the removal of NO_x is enhanced considerably, but the removal of SO_2 falls distinctly. The presence of higher concentration O_2 will lower the solubility of SO_2 in solution, if such effect is predominant, the removal of SO_2 will decrease accordingly. That is the case in our experiments. The NO_x used is composed of NO_2 and NO. As NO can be easily oxidized into NO_2 by O_2, and NO_2 is quite active in the reaction with HPC(re), it is natural that a net effect in the improvement of the denitrification process as shown in Table **3** should appear.

Table 3 The influence of O_2 concentration in the feed gas

Conversion, %*	O_2 concentration, %(v/v)		
	0	5	10
SO_2	99.8	91.3	87.2
NO_x	23.6	34.0	51.3

**[SO_2]=1740 mg/Nm^3, NO_x/SO_2 = 1:1(mol/mol); gas rate: 0.41l/min; $H_4PVMo_{11}O_{40}$: 100ml, 2×10 $^{-3}$mol/l pH=5.5; T=60^oC; absorption time: 30min.*

For a gas-liquid chemical reaction, residence time of the feed gas determines the extent of the reaction and therefore requires special attention. From the results listed in Table **4**, it can be seen that the removal of NO_x is enhanced significantly as the residence time increases, however, a slight enhancement on the removal of SO_2 can be found, suggesting the absorption process for SO_2 removal is faster than the absorption process for NO_x removal. The favorable residence time of the feed gas is ca. 39.0s.

Table 4 The effect of residence time of the feed gas

Conversion, %*	Residence time, sec.		
	30.0	39.0	51.0
SO_2	82.5	83.2	83.6
NO_x	39.2	52.6	55.1

**[SO_2]=1740 mg/Nm^3, NO_x/SO_2= 1:1(mol/mol); $H_4PVMo_{11}O_{40}$: 100ml, 2×10 $^{-3}$mol/l, pH=5.5; T=60 ^oC; absorption time: 30min.*

Increasing the pH value of the buffer solution system where $H_4PVMo_{11}O_{40}$ works, the conversion of SO_2 can be increased from 97.4% to 99.8%. Whereas, the conversion of NO_x decreases from 81.0% to 73.7% (Table **5**).

As it is also known that HPC(ox) possesses a higher oxidation potential in low pH solution, and increasing solution pH is unfavorable to the redox conversion of SO_2 by HPC(ox) but favorable to the redox conversion of NO_x by HPC(re). The solubility of SO_2 can be improved very considerably as the solution alkalinity increases. This overwhelms the negative effect caused by the decrease in redox potential of HPC(ox). Hence, the results shown in Table **5** are the net effects. Theoretically, the solubility of NO_x should increase as the pH value of the solution increase, even if such effect might be slight. But owing to the solubility limitation effect, or, in another word, the stripping effect exerted by SO_2, the net process for NO_x removal may go to the negative direction. This is just what has been observed in the experiment, indicating such effect is predominant. From the results, the favorable buffer solution system can be recommended as the one with a pH value of 3.6.

Table 5 Performance of $H_4PVMo_{11}O_{40}$ in different buffer solution systems

Conversion, %*	pH value of buffer solution system		
	5.5	4.5	3.6
SO_2	99.8	98.3	97.4
NO_x	73.7	75.3	81.0

**[SO_2]=1740 mg/Nm^3, NO_x/SO_2= 1:1(mol/mol); $H_4PVMo_{11}O_{40}$: 100ml 2×10^{-3}mol/l, pH=5.5; T=60 °C; gas rate: 0.41l/min; absorption time: 30min.*

To obtain a better understanding of the new absorbent system developed, taking Fe-EDTA system as a standard, a comparison experiment was made concerning the performance of the two systems. The Fe-EDTA system, also known as the so-called chelate iron absorbent system, had reached the stage of application demonstration. From the experiment result shown in Fig.**2**, it is apparent that $H_4PVMo_{11}O_{40}$ is superior to Fe-EDTA in the removal of NO_x. As to the removal of SO_2, the performance of $H_4PVMo_{11}O_{40}$ is much better than Fe-EDTA within 120 minutes during the experiment, after which a little lower in SO_2 removal efficiency of $H_4PVMo_{11}O_{40}$ can be detected. Hence, the new absorbent system of $H_4PVMo_{11}O_{40}$ deserves further investigations to provide systematic understandings for industrial application.

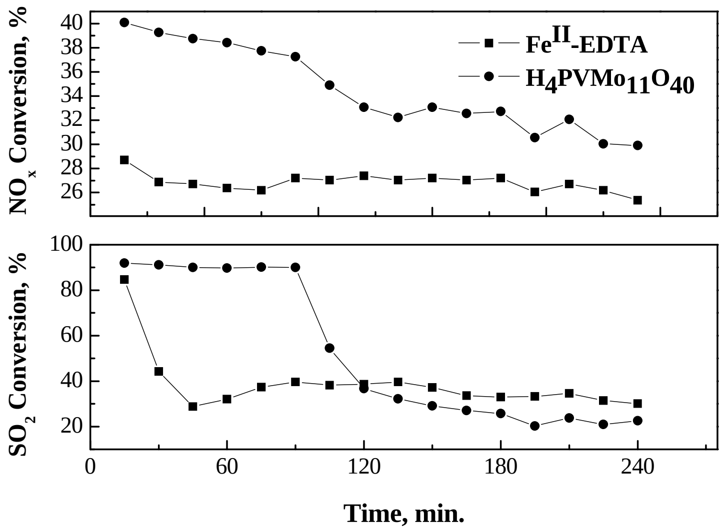

Figure 2. Comparison of the new absorbent with Fe^{II}-EDTA

$[SO_2]$=1740 mg/Nm^3; NO_x/SO_2= 1:1(mol/mol); gas rate: 0.41l/min;

$[H_4PVMo_{11}O_{40}]$=[Fe^{II}-EDTA]=2×10^{-3}mol/l, V=100 ml, T=20 °C, pH=5.5, $[O_2]$=10%.

Conclusion

1. The conversions of SO_2 and NO_x increase with the increase in $H_4PVMo_{11}O_{40}$ concentration. A favorable absorbent concentration can be recommended to be ca. 2.0×10^{-3} mol/l. The process for SO_2 removal is enhanced predominantly due to the alkalinity effect of some buffering agents used. Meanwhile, owing to the stripping effect exerted by SO_2, the NO_x removal efficiency decreases.
2. The influence of temperature attributes principally to the effect of solubility limitation. Ambient temperature is favorable to the effective removal of SO_2 and NO_x. The removal of NO_x is enhanced considerably with the increase of O_2 concentration, but the removal of SO_2 falls distinctly. This lies in the oxidation of NO by O_2 and the solubility limitation effect of O_2 on SO_2. The removal of NO_x is enhanced significantly as the residence time increases, however, a slight enhancement on the removal of SO_2 can be found, indicating the absorption process for SO_2 removal is faster than the absorption process for NO_x removal.
3. The new absorbent system of $H_4PVMo_{11}O_{40}$ was found to be superior to Fe-EDTA in the removal of NO_x, and also more effective in desulfurization than the latter during a long-time experiment as up to 120 minutes.

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