$Na_9[PW_5Mo_4O_{34}]$ SOLUTION AS NEW ABSORBENT FOR COMBINED REMOVAL OF SO_2 AND NO_x

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Introduction

The removal of SO_2 and NO_x from flue gas has long been a principal task for environmental protection. It is known that many methods have been developed for combined removal of SO_2 and NO_x, but each has unavoidable drawbacks to date. The ammonia reduction method requires high capital invest, moreover, leaking ammonia may cause secondary pollution. Alkaline solution absorption method is ineffective for NO removal. $CaCO_3$ containing yellow phosphorus emulsion is quite effective for simultaneous removal of SO_2 and NO_x, which may achieve conversions as 95% or higher for both, but this is achieved under successive consumption of absorbent.[1] Besides, methods concerning the use of electron beam irradiation or pulse corona, although proved to be effective, are far from practical application at present due to their very high equipment, operation and maintenance cost.[2] 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 aqueous solution of HPC, the author developed a new liquid redox method for combined removal of SO_2 and NO_x.[3] In this paper, $Na_9[PW_5Mo_4O_{34}]$, a Keggin type HPC, was synthesized for such purpose. Characteristics of desulfurization and denitrification are the subject of this paper.

Experimental

Scheme of the experiment flow sheet could be found in literature.[4] Two multiorifice plate glass absorption reactors (hole diameter: 50~70μm) 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 investigated in this study, namely $Na_9[PW_5Mo_4O_{34}]$, was synthesized and verified by ICP and IR. The feed gas stream with constant concentrations of SO_2 and NO_x, flowing at the rate of 0.5L/min, was prepared by mixing two gas streams of dilute SO_2/NO_x and pure nitrogen after passing through mass flow controllers. The SO_2 concentration was analyzed with a Dioxor II SO_2 detector. NO_x was prepared by addition of $NaNO_2$ solution drop by drop to dilute H_2SO_4 solution at a constant rate, the resultant NO_x was carried by nitrogen gas flowing at a constant rate. The NO_x concentration was analyzed by colorimetry. All other chemicals used were of reagent grade and deionized water was used throughout.

Results and Discussion

The conversions of SO_2 and NO_x increase markedly with the increase in absorbent concentration (Table 1). A favourable absorbent concentration can be recommended to be ca. 6.0×10^{-3} mol/L, corresponding to 97.6% and 90.7% for the conversions of SO_2 and NO_x respectively. The process for the removal of SO_2 tends to decrease when the absorption temperature increases from 30°C to 40°C, suggesting the effect of solubility decrease is predominant. While absorption temperature increases from 40°C to 50°C, the conversion of SO_2 shows a reverse tendency, indicating the predominant effect of the intrinsic chemical reaction between SO_2 and $Na_9[PW_5Mo_4O_{34}]$ (Table 2). As a whole, room temperature should be considered for the effective absorption of both SO_2 and NO_x.

Table 1. The Effect of Absorbent Concentration

$Na_9[PW_5Mo_4O_{34}]$, mol/L	Conversion (%)*	
	SO_2	NO_x
6.0×10^{-3}	97.6	90.7
1.2×10^{-3}	93.3	76.3
6.0×10^{-4}	65.9	44.8
1.2×10^{-4}	54.5	40.2

*$[SO_2]_{in}$=1394.2mg/m^3, $[NO_x]_{in}$=517.5 mg/m^3, T=30 °C, gas flow rate: 0.5L/min, volume of absorbent: 100mL, absorption time: 40min.

Table 2. The Effect of Absorption Temperature

T, °C	Conversion (%)*	
	SO_2	NO_x
30	93.3	76.3
40	87.2	75.4
50	88.9	70.1

*$[SO_2]_{in}$=1394.2mg/m^3, $[NO_x]_{in}$=517.5 mg/m^3; gas flow rate:0.5L/min; absorbent: 1.2×10^{-3}mol/L, 100mL; absorption time: 40min.

As to the effect of feed gas concentration, the emphasis in this study is on the role of SO_2/NO_x ratio. Hence, the feed gas SO_2 concentration was set to remain fixed whereas NO_x concentration varied. From the results listed in **Table 3**, it is apparent that the conversion of SO_2 keeps comparatively stable, regardless of the increase in NO_x concentration in the feed gas. Meanwhile, the conversion of NO_x is enhanced significantly. Accordingly, the favourable SO_2/NO_x ratio in the feed gas could be recommended as 1:1, using mg/m^3 as concentration unit.

Table 3. The Effect of Feed Gas Concentration

Feed gas conc., mol/L		Conversion (%)*	
SO_2	NO_x	SO_2	NO_x
1394.2	209.1	86.7	58.0
1394.2	517.5	85.8	70.5
1394.2	1015.5	86.0	76.8
1394.2	1394.1	86.3	77.6

* T=30 °C; gas flow rate: 0.5L/min; absorbent: 1.2×10^{-3}mol/L, 100mL; absorption time: 40min.

In order to improve the performance of the absorbent system, considering the acid property of SO_2 and NO_x to be treated, several buffering agents were added to $Na_9[PW_5Mo_4O_{34}]$ solution, which forms different absorbent systems comprising $CH_3COOH/NaOH$, NH_4Ac/HAc(Ac stands for CH_3COO^-) and NaAc/HAc in addition, respectively. Results shown in **Figure 1** prove that the desired enhancement effect exists only on the conversion of SO_2. Apparently, the removal of SO_2 was improved to a very agreeable extent, where all absorbent systems give a conversion of 100% or nearly 100%. In contrast, these buffering agents have no positive effect on the conversion of NO_x. On the contrary, the presence of them may cause more or less negative effects on the conversion of NO_x.

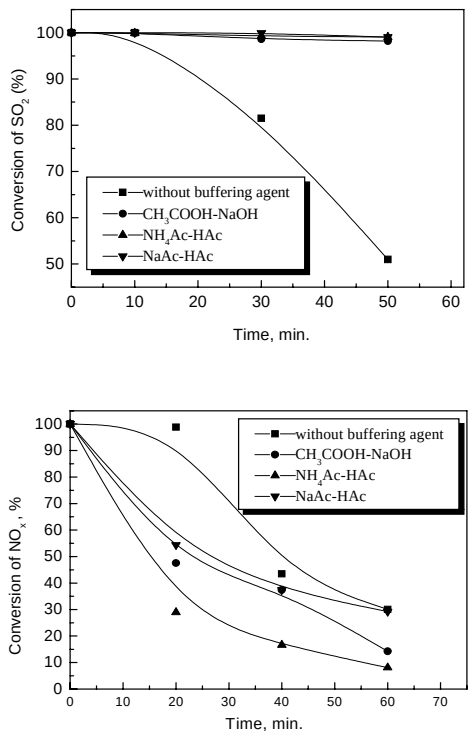

Figure 1. The effects of buffering agents on the performance of the absorbent system

Compared to NO_x, especially NO, SO_2 is quite soluble in water. Such difference can be magnified when the solution alkalinity is increased owing to the addition of buffering agents used herein. This is the reason for the marked difference between the removal of SO_2 and NO_x in the presence of buffering agents. As to the negative effect of buffering agents observed in the case of NO_x removal, it is likely that the redox property change of $Na_9[PW_5Mo_4O_{34}]$ caused by the alkalinity increase in the presence of buffering agents may be the cause. The process for combined conversion of SO_2 and NO_x can be illustrated as shown in **Figure 2**, where HPC_{re} and HPC_{ox} represent the oxidation and reduction form of HPC respectively.

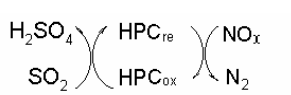

Figure 2. Principle of the process for combined removal of SO_2 and NO_x with HPC

The HPC used in this study is $Na_9[PW_5Mo_4O_{34}]$, which can be reduced from $Na_9[PW_5Mo(VI)_4O_{34}]$ to $Na_9[PW_5Mo(VI)_3Mo(V)O_{34}]$ easily. The latter can be oxidized back to the original. Thus, a sustainable process can be formed, where $Na_9[PW_5Mo_4O_{34}]$ is catalyst in nature. Such process is based on the redox property of HPC. As it is known that HPC possesses a higher redox potential in low alkalinity solution, increasing solution alkalinity is unfavorable to the conversion of both SO_2 and NO_x. Unlike NO_x, the solubility of SO_2 can be improved very considerably as solution alkalinity increases. This overwhelmes the negative effect caused by the decrease in redox potential of HPC. Hence, the results shown in **Figure 1** are the net effects.

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