A PRELIMINARY UNDERSTANDING OF THE GAS-LIQUID REACTION BETWEEN SO$_2$, NOX CONTANING GAS AND HETEROPOLY COMPOUND SOLUTION

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Abstract

A primary investigation on the characteristics of the gas-liquid reaction between SO$_2$, NO$_x$ from gas stream and the aqueous solution of heteropoly compound was conducted, from which the main factors affecting the process were figured out. These include the concentration and composition of the absorbent solution, temperature, the presence of O$_2$ in the gas stream, as well as the residence time of the gas in the scrubber.

Keywords: desulfurization; denitrification; flue gas; heteropoly compound.

1. Introduction

The emission of SO$_2$ and NO$_x$ from fuel combustion process has long been an environmental problem, attracting worldwide researchers. Treatment for them is an important step in controlling and preventing atmospheric pollution. Many methods have been developed to date for the separate removal of SO$_2$ and NO$_x$. SO$_2$ removal includes dry adsorption method and wet absorption method. At present, dry method has not been widely used due to its limited sulfur loading capacity. Most desulfurization processes industrialized are wet absorption methods, especially the wet Ca(OH)$_2$ slurry absorption methods with different modifications[1,2]. The wet Ca(OH)$_2$ slurry absorption method is quite effective for SO$_2$ removal, but the solid waste disposal and the high capital investment and expensive operation cost of this method is still an unresolved problem, which has already confined its application. As to the removal of NO$_x$, i.e. NO and NO$_2$, wet absorption methods using alkalis are practically ineffective, owing to the fact that NO, the predominant component of NO$_x$, is insoluble in water. In view of the oxidation property of NO$_x$, reduction methods are often considered, including the selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR)[3]. At present, both SCR and SNCR have advanced to the point of commercial application. The SCR process relies on reduction by ammonia in the presence of a catalyst to convert NO and NO$_2$ to N$_2$ and water vapor. Approximately 80%~90% NO$_x$ reduction appears feasible with SCR. The SNCR process directly reduces NO$_x$ to N$_2$ by the injection of NH$_3$ or urea without catalyst at a temperature higher than SCR. The reduction of NO$_x$ in SNCR process is around 50%~60%. Before widespread application occurs, the high investment and operation cost of SCR and SNCR, together with several technical issues of both still require resolution. These technical issues include ammonia leaking which may cause secondary pollution, by-product formation and its subsequent impact on downstream equipment, and the disposal of liquid and solid waste. 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.

In view of the reversible redox property and good chemical stability of heteropoly compound (HPC), using the aqueous solution of $H_3PMo_{12}O_{40}$ (abbr. to HPMo), a new method of simultaneous removal of SO_2 and NO_x from gas stream was developed. This method, taking HPMo solution as medium for electron transfer, enables in nature the redox reaction between SO_2 and NO_x under ambient conditions.

2. Material and Methods

Two cylinder-shaped glass gas scrubbers (i.d.: 2.5cm) with multiorifice-plate (hole diameter: 50~70μm) at the bottom of which, containing equal volume of absorbent solution, were used in series to investigate the macrokinetic behaviors of the absorbent solution. The experimental data gained are the SO_2 and NO_x concentrations in the outlet gas stream. 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 three gas streams of dilute SO_2, dilute NO_x and pure nitrogen after passing through mass flow controllers. 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. With the aid of NMR Analyzer (AMX 400, Bruker, Germany), P-31 NMR spectra were used to characterize the HPMo solution before and after using for the removal of SO_2 and NO_x. All chemicals used were of reagent grade and deionized water was used throughout.

3. Results and Discussion

During the process of SO_2 and NO_x removal by HPMo solution, HPMo undergoes two successive transformations, i.e. from HPMo(VI) to HPMo(V) as a result of the reduction by SO_2, and from HPMo(V) to HPMo(VI) resulting from the subsequent oxidation by NO_x. Ideally, for the sustainment of the whole process, it is necessary that HPMo remain unchanged after the reduction-oxidation cycle. The feasibility of such process was confirmed through comparison of the P-31 NMR spectra (D_2O as external lock, 85% H_3PO_4 as external reference) of the fresh HPMo solution (0.09619mol/L) and that with same concentration but having been used for the absorption of SO_2 and NO_x in series. The main chemical shift of the fresh HPMo emerges at -1.62ppm, with three others at 0.63ppm, 1.70ppm and -0.89ppm corresponding to H_3PO_4 and other two minor impurities. A P-31 NMR spectrum with identical shape and location was found for the used HPMo solution, indicating that, subjecting to reactions with SO_2 and NO_x, HPMo remains unchanged.

Conversions to SO_2 and NO_x can reach upto 96% and 85% respectively corresponding to the following conditions: $[SO_2]=1720$ mg/Nm^3, $NO_x/SO_2 = 1:1$(v/v); $[O_2]=10\%$(v/v); gas rate: 0.40L/min; HPMo: 120mL, 2×10^{-2}mol/L, pH=5.3; T=25°C; absorption time: 30min. The performance of HPMo solution absorbent system depends considerably on its concentration. Increasing HPMo concentration from 5×10^{-3}mol/L to 2×10^{-2}mol/L while other factors keep constant, conversions to SO_2 and NO_x can increase from 92% to 96% and from 71% to 85%, respectively. Evidently, compared to single HPMo, the absorbent system comprising ascorbic acid (abbr. to Vc) as additive is superior (Figure 1). The high efficiency of the Vc containing system lies in the coexistance of HPMo(VI) and HPMo(V), which enables the simultaneous removal of SO_2 and NO_x throughout the process. In the system of single HPMo, the HPMo(V), which is more effective for NO_x removal, is generated subsequent to the removal of SO_2. Hence, the removal efficiency of NO_x is lower. The optimal HPMo/Vc molar ratio was found to be 3: 1. The process efficiency of combined removal of SO_2 and NO_x by HPMo decreases distinctly with an increase in absorption temperature, this is due predominantly to the effect of solubility limitation caused by the temperature increase. As a whole, ambient temperature is favorable to the process.
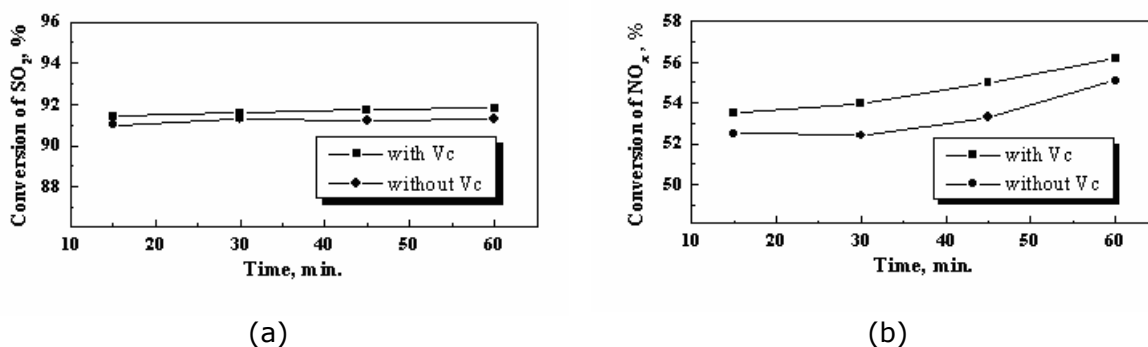
(a)　　　　　　　　　　　　　　　　(b)

Figure 1 A comparison of the conversions of SO_2 and NO_x with and without Vc in the HPMo solution

$[SO_2]$=1720 mg/Nm^3, NO_x/SO_2 = 1:1(v/v); $[O_2]$=5%(v/v); gas rate: 0.40L/min; $H_3PMo_{12}O_{40}$: 120mL, 2×10^{-3}mol/L, pH=5.5; [Vc]=10g/L; T=25°C; absorption time: 30min.

O_2 is an actual component in the flue gases. It was found 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 a mixture 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 HPMo, it is natural that a net effect in the improvement of the denitrification process should appear in the presence of O_2.

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 1, 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. 38.5s.

Table 1 The effect of residence time of the feed gas

Conversion, %*	Residence time, sec.		
	30.0	38.5	51.0
SO_2	81.8	82.7	83.0
NO_x	38.5	51.1	53.9

*$[SO_2]$=1720 mg/Nm^3, NO_x/SO_2 = 1:1(v/v); $[O_2]$=10%(v/v); HPMo: 120mL, 2×10^{-3}mol/L, pH=5.5; T=25°C; absorption time: 30min.

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