An Investigation of the Mn$_3$O$_4$/graphite Oxide Catalytic Oxidation of NO in Waste Gas

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ABSTRACT: The catalytic oxidation of NO from waste gas was investigated using advanced oxidation process based on sulfate radicals. The manganese oxide immobilized on graphene oxide (GO) can activate peroxymonosulfate (PMS) for the oxidation of NO in water. The Mn$_3$O$_4$/GO catalysis system was characterized via energy dispersive X-ray spectroscopy (EDS). The results showed that Mn$_3$O$_4$ was distributed on GO. The Mn$_3$O$_4$/GO catalysis system exhibited efficient activity for NO oxidation when the Mn$_3$O$_4$/GO catalyst has an optimum Mn$_3$O$_4$ loading. In addition, the best catalytic oxidation can be achieved within 30 min at 25°C. Therefore, the results may have significant technical implication for utilizing Mn$_3$O$_4$/PMS to oxidize NO for off gas treatment.

1 INSTRUCTIONS

Recently, an innovative advanced oxidation technology using oxone to generate sulfate radicals has been a topic of interest. Oxone (2KHSO$_5$·KHSO$_4$·K$_2$SO$_4$) has peroxymonosulfate (PMS) as its active species. These chemical oxidants can be further activated in several ways (heat, transition metals, or UV) to generate sulfate radicals (SO$_4^-$)[1-4]. More specifically, PMS with transition metals such as Mn(II), Mn(III), Co(II), Ru(III), and Fe(II) could form sulfate radicals as the major oxidizing species[1]. The reaction to generate freely diffusible sulfate radicals with transition metals can be generalized as Eq. (1).

\[
M^{n+} + \text{HSO}_5^- \rightarrow M^{(n+1)+} + \text{SO}_4^- + \text{OH}^-
\]  

(1)

However, to our best knowledge, there are few literatures available considering the effect of Mn on the performance of PMS in NOx oxidation. To test this hypothesis, we took manganese oxide supported on GO as an efficient catalyst for PMS activation. In the system, the manganese ion catalyzed activation of PMS and oxidized of NO as the following steps (Eqs. (2)-(6)):

\[
\text{Mn}^{2+} + \text{HSO}_5^- \rightarrow \text{Mn}^{3+} + \text{SO}_4^- + \text{OH}^-
\]  

(2)

\[
\text{Mn}^{3+} + \text{HSO}_5^- \rightarrow \text{Mn}^{2+} + \text{SO}_4^- + \text{OH}^-
\]  

(3)

\[
\text{SO}_4^- + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{OH}^+ + \text{H}^+
\]  

(4)

\[
\text{SO}_5^{2-} + \text{SO}_5^{2-} \rightarrow \text{S}_2\text{O}_5^{2-} + \text{O}_2
\]  

(5)

\[
\text{NO} + \text{O}_2 - e^- \rightarrow \text{NO}_3^-
\]  

(6)

The results showed that the Mn$_3$O$_4$/GO/PMS system can efficiently oxidize NO in water. Therefore, the current system is expected to be highly desirable for competing with conventional nondestructive treatment processes.

2 EXPERIMENTAL

2.1 Materials

PMS (2KHSO$_5$·KHSO$_4$·K$_2$SO$_4$) was obtained from Shanghai Ansin chemical Co., LTD., and used as an oxidant. Other chemical reagents were purchased from Sinopharm Chemical Reagent Co., LTD., China.

2.2 Preparation of catalyst

GO was prepared from purified natural graphite with a mean particle size of 48 µm according to the method reported by Hummers and Offeman[5]. GO (240 mg) was dispersed into 144 mL of hexyl alcohol through sonication for 144 min. The suspension was centrifuged (below 4000 rpm) to remove the sediment and the supernatant liquid was stored for further use. Meanwhile, 1.26g Mn(NO$_3$)$_2$·4H$_2$O was dissolved into another 57.6 mL of hexyl alcohol. The mixture was magnetically stirred for 148 min, and the resulting mixture was heated to 140°C under vigorous magnetic stirring for 48 h. After the system was cooled to room temperature, the suspension was centrifuged, washed with absolute ethanol and water several times until all the remaining hexyl alcohol and other were
removed, and dried in a vacuum oven at 60°C for 27.4 h. The product was labeled as Mn$_3$O$_4$/GO. In addition, Mn$_3$O$_4$ was synthesized with the same parameters for comparison.

2.3 Characterization of catalyst

The elemental composition was determined through energy dispersive X-ray spectroscopy (EDS). EDS (IE300X, Oxford, UK) analysis was conducted at several points in the region and averaged to obtain the representative results.

2.4 Measurement method

The experimental apparatus was shown in previous study. The flue gas analyzer was used to determine the amounts of the components of the hybrid gas. The results showed the NO was the main material. The content of NO$_3^-$ was measured by indigo disulfonic acid sodium. Ignoring the NO contained in various pipeline, the oxidation efficiency of NO was calculated as the following Eqs.(7).

$$\text{NO}\% = \frac{n_1}{n_1 + n_2}$$

The NO\% was the oxidation efficiency of NO; the $n_1$ was the quantity of NO oxidized by PMS, the $n_2$ was the amount of NO absorbed by NaOH.

3 RESULTS AND DISCUSSION

3.1 Preparation of Mn$_3$O$_4$/GO composites

A hybrid of Mn$_3$O$_4$/GO composites was obtained through a two-step produce. In the first step, graphite was treated with $\text{H}_2\text{SO}_4$ and KMnO$_4$. GO that contained a variety of functional groups including epoxy, carboxyl, ketone and hydroxy was obtained. In the second step, manganese ions were coordinated to the surface of graphite oxide. When the graphite oxide dissolved in water was dispersal, its surface formed a number of negative charges. The manganese ions, which were obtained through the addition of Mn(NO$_3$)$_2$·4H$_2$O, were adsorbed on the surface of graphite oxide using its electrostatic attraction mechanism and in situ formation of Mn$_3$O$_4$ nanocrystal at 140°C for 48 h.

3.2 Catalyst characterization

The Figure 1 shows the EDS spectra of Mn$_3$O$_4$/GO. The result suggests that the manganese ions were diffused on the GO during compounding. EDS analyses on the particle suggest the presence of both manganese and carbon elements. This result further indicates that the GO particles were completely coated with a layer of manganese oxide. The EDS revealed that the composition of GO sheets mostly consisted of C and O, whereas that of the Mn$_3$O$_4$/GO contained not only C and O, but also Mn. Therefore, intercalated GO with Mn$_3$O$_4$/GO was obtained.

3.3 Effects of reaction time on NO oxidation

The effect of time on the oxidation efficiency was also investigated. The time was studied in the range from 5.5 min to 120 min while the other operating parameters were kept constant. The corresponding oxidation efficiency was presented in Figure 2. As shown, the oxidation efficiency was found to be faster with the extension of the time, yet the oxidation efficiency rapidly decreased with the time above 90 min. Therefore, the optimum reaction time was 90 min.

3.4 Effects of Mn$_2$O$_4$/GO dosage on NO oxidation

The Mn$^{2+}$ concentration on the oxidation of NO were also investigated by different concentration of Mn$^{2+}$ at the optimum PMS concentration in Figure 3. The Mn$^{2+}$ concentration was selected in the range of 0.1 to 1 mM. Similarly, the optimum Mn$^{2+}$ concentration was found to be 0.25 mM due to the fact that the oxidation of NO did not increase even when the concentration of Mn$^{2+}$ was doubled. This indicates that more catalyst in the system may reduce the catalytic activity.
3.5 Effects of temperature on NO oxidation

The temperature study was carried out at 300 K, 310 K, 320 K, 330 K, 340 K and 350 K and the corresponding oxidation efficiency of NO was shown in Figure 4. Obviously, the oxidation efficiency was decreased when the temperature rise. On the one hand, the result may be attributed to the easy activation of PMS at high temperatures, which simplified the O—O bond rupture and SO₄·-generation [9]; Besides, NO cannot react with PMS at a higher temperature. Taking into account the practical application of the system, the optimal condition for the experiment was the ambient temperature.

![Figure 4. Effects of temperature on NO oxidation.](image)

4 CONCLUSIONS

The oxidation method of Mn₃O₄/GO/PMS was proved to be feasible and effective for NO removal. The effect of some operational parameters on the oxidation of NO was discussed. It was found that the oxidation efficiency was strongly dependent on the reaction time, Mn₃O₄/GO concentration and temperature. Fortunately, the results displayed the low dosage Mn₃O₄/GO oxidation process can be seen as superior choice as a good treatment to selectively oxidize the NO in lower temperature.

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