Treatment of NO by a combination of MnO_2 and a CO_3^{2-} -intercalated Mg–Al layered double hydroxide

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Abstract

We examined the treatment of NO from simulated exhaust gas using a combination of MnO_2 and a CO_3^{2-} -intercalated Mg–Al layered double hydroxide ($\text{CO}_3\cdot\text{Mg}\text{--}\text{Al}$ LDH), and found that low removal efficiencies were obtained when $\text{CO}_3\cdot\text{Mg}\text{--}\text{Al}$ LDH was used in the absence of MnO_2 . The exhaust gas was circulated in a reaction tube filled with MnO_2 (first step) and $\text{CO}_3\cdot\text{Mg}\text{--}\text{Al}$ LDH (second step), and the NO_x removal efficiency of ~70% achieved at 170 °C at the beginning of the reaction decreased to 60% after 90 min. Compared to the case of only $\text{CO}_3\cdot\text{Mg}\text{--}\text{Al}$ LDH, the NO_x removal efficiency significantly increased when both MnO_2 and $\text{CO}_3\cdot\text{Mg}\text{--}\text{Al}$ LDH were employed, which was ascribed to the oxidation of NO to NO_2 over MnO_2 followed by the subsequent removal of NO_2 by $\text{CO}_3\cdot\text{Mg}\text{--}\text{Al}$ LDH.

Keywords NO · MnO_2 · CO_3^{2-} -intercalated Mg–Al layered double hydroxide · Combination

1 Introduction

NO accounts for > 95% of NO_x in the exhaust gas produced by municipal waste incineration. During catalytic denitrification [1, 22], which is the primary method of NO_x removal, NO_x is converted into H_2O and N_2 at temperatures of ≤ 400 °C. This method is also known as selective catalytic reduction (SCR). Prior to denitrification, bag filters are applied at temperatures of 150–200 °C, as low temperatures facilitate the removal of HCl and SO_x . However, as the low temperatures lead to a low catalytic activity, the exhaust gases are reheated using waste heat in the NO_x catalyst bed inlet. Given the ongoing issues posed by global warming, significant attention has been directed at increasing the energy utilization efficiency of municipal waste incineration processes, as exemplified by the increasing number of incineration facilities that function as power generation facilities and are adapted for effective thermal energy utilization. However, the increase in the catalytic denitrification efficiency is accompanied by

a decrease in the power generation efficiency, as reheating of the exhaust gas consumes energy. Interestingly, a combination treatment for the removal of HCl and SO_x based on the use of slaked lime under dry conditions [5, 15, 16, 20, 21] and NO_x removal by catalytic denitrification [1, 22] has proven to be effective for the treatment of acidic exhaust gases generated by municipal waste incineration. However, more convenient and environmentally friendly treatment processes are required.

Mg–Al layered double hydroxide (Mg–Al LDH) exhibits an anion exchange ability and comprises host layers (positively charged regular octahedral layers with the Mg^{2+} ions in $\text{Mg}(\text{OH})_2$ partially replaced by Al^{3+}), guest layers (anions compensating for the positive charge of the host layers), and interlayer water [3, 18]. Although the anion exchange ability [19] of Mg–Al LDH has been used to remove various harmful substances from aqueous solutions [6, 27], the present study focuses on the use of Mg–Al LDH for exhaust gas treatment [8, 9]. Recently, we have clarified that Mg–Al LDH intercalated with CO_3^{2-} ($\text{CO}_3\cdot\text{Mg}\text{--}\text{Al}$ LDH) is suitable

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for the individual removal of HCl [14], SO₂ [11], and NO₂ [12]. Furthermore, CO₃·Mg–Al LDH was applicable in the simultaneous removal of HCl, SO₂, and NO₂ [13], thereby indicating that it is effective for the treatment of acidic exhaust gases generated by municipal waste incineration. Although CO₃·Mg–Al LDH has been used to remove NO₂ from exhaust gases [12], whereas the removal of NO has received little attention. It is therefore possible that two-step NO removal methods featuring the use of CO₃·Mg–Al LDH and NO-oxidizing catalysts may allow the application of Mg–Al LDH in the removal of NO_x from exhaust gases produced by municipal waste incineration. In the first step, NO would be catalytically oxidized to NO₂, and subsequently, the produced NO₂ would be removed by CO₃·Mg–Al LDH.

Thus, we herein report our investigation into the MnO₂-promoted oxidation of NO, and subsequent evaluation of the efficiency of a combination of MnO₂ and CO₃·Mg–Al LDH for NO removal. MnO₂ was selected since Mn-based catalysts exhibit a high NO oxidation activity in addition to being low cost and exhibiting a minimal environmental impact. In addition, Mn complex oxides [7, 17, 24], perovskites [4, 25], and supported catalysts [23, 26] have recently been reported to exhibit high NO oxidation activities.

2 Materials and methods

2.1 Oxidation of NO over MnO₂

MnO₂ (> 85%) was purchased from Kanto Chemical Co., Inc. A reaction tube filled with MnO₂ (0.5 g) was heated to 100–350 °C, and simulated exhaust gas (150 ppm NO, 10 vol% O₂, balance N₂) was circulated through the tube for 90 min at a linear velocity of 1.0 m/min. Subsequently, the NO_x concentration was measured using a gas analyzer (testo350XL).

2.2 NO removal by MnO₂ + CO₃·Mg–Al LDH

CO₃·Mg–Al LDH was synthesized by co-precipitation [10] and contained 15.2 wt% Mg and 8.2 wt% Al (Mg:Al = 2.1:1, mol/mol). A schematic diagram of the experimental system is provided in Fig. 1. Typically, MnO₂ (0.5 g) and CO₃·Mg–Al LDH (1.0 g) were loaded onto glass wool in a 16 mm inner-diameter glass reaction tube. A nitrogen-purged tube furnace was then preheated to 110–200 °C, and simulated exhaust gas was circulated for 90 min at a linear velocity of 1.0 m/min. As a control experiment, MnO₂ (0.5 g) or CO₃·Mg–Al LDH (1.0 g) was loaded separately and used in the same experimental setup.

3 Results and discussion

3.1 Oxidation of NO over MnO₂

Figure 2 shows the effect of temperature on the efficiency of the NO to NO₂ oxidation reaction over MnO₂. The theoretical NO oxidation efficiency at equilibrium was calculated as follows [2]:

$$\log K_p = (-5749/T) + 1.75 \log T - 0.00050T + 2.839 \quad (1)$$

According to the above equation, the 100% NO oxidation efficiency expected in the range of 100–200 °C should decrease to 65% at 350 °C. In contrast, oxidation efficiencies of ~5% were observed at 100–350 °C in the absence of MnO₂, while in the presence of MnO₂, an oxidation efficiency of 24% was achieved at 100 °C. Notably, the oxidation efficiency increased upon increasing the temperature up to a maximum of 78% at 250 °C; higher temperatures resulted in a reduction in the oxidation efficiency. Thus, since the MnO₂ catalytic activity was positively correlated with the temperature, the NO oxidation efficiency

Fig. 1 Experimental apparatus for treating NO with MnO₂ and CO₃·Mg–Al LDH. (1) NO cylinder; (2) O₂ cylinder; (3) N₂ cylinder; (4) Mass flow controller; (5) Gas mixer; (6) Electric furnace; (7) Quartz tube; (8) Fiberglass; (9) NO_x analyzer.

Fig. 2 Effect of temperature on NO oxidation with and without MnO_2

Fig. 3 Variation in the NO_x removal and concentration with time on NO removal by $\text{CO}_3 \cdot \text{Mg}$ –Al LDH at 170°C

followed the same trend. However, the $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$ equilibrium shifts to the left with increasing temperature, i.e., the NO oxidation efficiency concomitantly decreases. The fact that the equilibrium oxidation efficiency could not be attained at any temperature was ascribed to the considerable stagnancy of the NO to NO_2 oxidation reaction and the insufficient contact time with MnO_2 at the selected flow velocity. We therefore considered that NO was sufficiently oxidized to NO_2 at temperatures between 150 (33%) and 200°C (69%), and this range was therefore concluded to be suitable for treatment of the incineration exhaust gas.

3.2 NO removal over $\text{MnO}_2 + \text{CO}_3 \cdot \text{Mg}$ –Al LDH

Figure 3 shows the variation in the NO removal efficiency and the NO_x concentration with time at 170°C

Fig. 4 Variation in the NO_x removal and concentration with time on NO removal by the combination of MnO_2 and $\text{CO}_3 \cdot \text{Mg}$ –Al LDH at 170°C

Fig. 5 Variation in the NO_x concentration with time on NO oxidation with MnO_2 at 170°C

for $\text{CO}_3 \cdot \text{Mg}$ –Al LDH, revealing that NO_x levels fluctuated at ~ 150 ppm, and sufficient NO removal could not be achieved under these conditions. Similarly, Fig. 4 shows the variation in the NO removal efficiency and the NO_x concentration with time at 170°C for $\text{MnO}_2 + \text{CO}_3 \cdot \text{Mg}$ –Al LDH, whereby it was apparent that the NO concentration fluctuated at ~ 40 ppm at the beginning of the reaction, and gradually increased to ~ 60 ppm at 90 min. In addition, the concentration of NO_2 increased with time to reach a value of ~ 20 ppm at 90 min. Thus, the NO_x removal efficiency of $\sim 70\%$ observed at the beginning of the reaction increased with time to reach a value of $\sim 60\%$ at 90 min. The fact that the NO_x removal efficiency increased upon the introduction of MnO_2 deserves particular attention. In the initial step, MnO_2 likely oxidized NO to NO_2 , which was then removed by $\text{CO}_3 \cdot \text{Mg}$ –Al LDH. The increase in the NO_2 concentration was ascribed to a breakthrough in the adsorption of NO_2 by $\text{CO}_3 \cdot \text{Mg}$ –Al LDH. Thus, Fig. 5 shows

the effect of time on the NO_x concentration during NO oxidation by MnO_2 at 170 °C, revealing that the NO concentration fluctuated at levels of 40–50 ppm. This finding confirmed that a fraction of the NO remained unoxidized (likely due to the rapid linear velocity), and explained the partial NO_x removal shown in Fig. 4. Moreover, Figs. 6, 7 and 8 show the time course for the NO_x removal efficiency and the NO/ NO_2 concentrations observed for the $\text{MnO}_2 + \text{CO}_3\cdot\text{Mg-Al}$ LDH system at 110, 140, and 200 °C, respectively. More specifically, no increase was observed for the NO_2 concentration at 110 or 140 °C, and both the NO_x concentration and removal efficiency were found to depend on the NO concentration. Since the efficiency of the NO oxidation reaction in this temperature range was low, the NO_2 generated by the oxidation of NO over MnO_2 was easily adsorbed by $\text{CO}_3\cdot\text{Mg-Al}$ LDH. In contrast to the case of 170 °C, the NO_2 concentration increased drastically at 200 °C, reaching a value of almost 50 ppm at 90 min, which resulted in a decrease in the NO_x removal efficiency. Indeed, the NO_x removal efficiency after 90 min at 200 °C was lower than those recorded at all other temperature examined herein. As depicted in Fig. 2, although a high NO oxidation efficiency was observed at 200 °C, $\text{CO}_3\cdot\text{Mg-Al}$ LDH was unable to effectively adsorb the generated NO_2 under these conditions.

4 Conclusions

We herein reported our examination into the treatment of NO from simulated exhaust gas using a combination of MnO_2 and a CO_3^{2-} -intercalated Mg–Al layered double hydroxide ($\text{CO}_3\cdot\text{Mg-Al}$ LDH). In the absence of MnO_2 , the NO oxidation efficiency at 100–350 °C was low, i.e., ~5%. Conversely, an oxidation efficiency of 24% was observed

Fig. 7 Variation in the NO_x removal and concentration with time on NO removal by the combination of MnO_2 and $\text{CO}_3\cdot\text{Mg-Al}$ LDH at 140 °C

in the presence of MnO_2 at 100 °C, and this value increased up to 78% at 250 °C prior to decreasing once again upon further increasing the temperature. In addition, the theoretical removal efficiency at equilibrium could not be reached due to the considerable stagnancy of the NO to NO_2 oxidation reaction, and the insufficient time of contact with MnO_2 at the chosen flow rate. For NO removal using a combination of MnO_2 and $\text{CO}_3\cdot\text{Mg-Al}$ LDH, the NO_x removal efficiency at 170 °C was ~70% at the beginning of the reaction, and this value decreased to ~60% at 90 min. In the absence of MnO_2 , NO removal was not sufficient, while for a combination of MnO_2 and $\text{CO}_3\cdot\text{Mg-Al}$ LDH, the NO_x removal efficiency exceeded that observed for $\text{CO}_3\cdot\text{Mg-Al}$ LDH alone. Initially, NO was oxidized to NO_2 over MnO_2 , and the produced NO_2 was subsequently removed by $\text{CO}_3\cdot\text{Mg-Al}$ LDH. Based on the obtained results, we concluded that NO removal by a combination

Fig. 6 Variation in the NO_x removal and concentration with time on NO removal by the combination of MnO_2 and $\text{CO}_3\cdot\text{Mg-Al}$ LDH at 110 °C

Fig. 8 Variation in the NO_x removal and concentration with time on NO removal by the combination of MnO_2 and $\text{CO}_3\cdot\text{Mg-Al}$ LDH at 200 °C

of MnO_2 and $\text{CO}_3\cdot\text{Mg-Al}$ LDH could be effectively achieved at temperatures of 140 and 170 °C. To further improve the NO_x removal efficiency, it is considered that the amounts of MnO_2 and $\text{CO}_3\cdot\text{Mg-Al}$ LDH should be increased, and the linear velocity should be decreased.

Compliance with ethical standards

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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