Removal and recovery of NO by MnO_2/Mg-Al layered double hydroxide

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INTRODUCTION

The incineration of waste generates exhaust gas containing poisonous nitrogen oxides (NO_x). At present, Selective Catalytic Reduction (SCR) process is used for NO_x removal. But treated product cannot be recycled and the high maintenance cost also become issue. Because of their capable of gas recovery and low price, CO_3・Mg-Al layered double hydroxides (LDHs) has considerable attention in recent years. From anion exchange ability, they are used as adsorbent for nitrogen dioxide (NO_2) removal, and adsorbed gases can be recovered in wet process[1)]. However, they cannot remove nitric oxide (NO) contained more than 95 percent of NOx in exhaust gas[1)]. Therefore, NO must be oxidized to NO_2 for removal. Transition metal oxides have high performances in NO oxidation. Mn based composite oxides are less expensive compared with others, and it has high activity in NO oxidation[2)]. In this study, we investigated the performance of NO treatment by MnO_2/Mg-Al LDH composite and MnO_2 + CO_3・Mg-Al LDH mixture compared with CO_3・Mg-Al LDH[3-5)]. Additionally, NO removed by MnO_2/Mg-Al LDH was examined to recover by thermal treatment.

MATERIALS AND METHODS

Preparation of MnO_2/Mg-Al LDH

CO_3・Mg-Al LDH (Mg/Al molar ratio = 2) was synthesized through co-precipitation and calcined at 500 °C for 2 h to yield Mg-Al oxide. Mg-Al oxide was added to $KMnO_4$ solution adjusted to Mn/Al molar ratios of 5 and stirred at 300 rpm and 30 °C. N_2 was bubbled into the solution throughout the procedure. After stirring for 6 h, solids were separated from the liquid and dried at 40 °C for 24 h, and MnO_2/Mg-Al LDH was obtained. MnO_2/Mg-Al LDH was analyzed by using X-ray diffraction (XRD), inductively coupled plasma-atomic emission spectrometry (ICP-AES), X-ray photoelectron spectroscopy (XPS).

NO treatment

MnO_2/Mg-Al LDH composite, MnO_2 + CO_3・Mg-Al LDH mixture, or CO_3・Mg-Al LDH were packed in reaction tube preheated to 170°C by electric tuber furnace. The mixed gas (NO: 150 ppm O_2: 10%, N_2: balance) was passed through the adsorbent for 90 min, with the flow rate adjusted by the mass flow controller (linear velocity 1.0 m/min). The residual concentrations were analyzed using a gas analyzer.

NO recovery

NO removed by MnO_2/Mg-Al LDH was recovered by thermal treatment. Firstly, desorbed temperature was analyzed via Evolved gas analysis-mass spectrometry (EGA-MS). MnO_2/Mg-Al LDH had 1.33 mmol/g of NO,

and the materials were treated at 400-600℃ using the above-mentioned apparatus.

RESULTS AND DISCUSSION

Preparation of MnO_2/Mg-Al LDH

Figure 1 and Table 1 show the XRD patterns of the MnO_2/Mg-Al LDH, and its chemical compositions. The XRD patterns indicate that LDH structure presents in the sample, while Mn species was not observed. But it contained 4.2 wt% of Mn, and basal spacing, d_{003}, was 7.6 Å. This suggests that MnO_4^- was intercalated between the LDH layers. XPS analysis indicates that 76.7% of the Mn was Mn (IV). MnO_4^-, intercalated between the LDH layers, was probably reduced to MnO_2 in the interlayer.

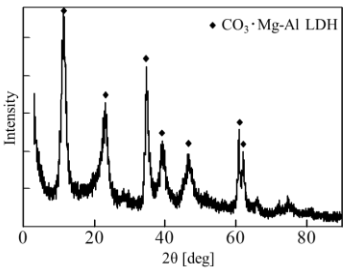

Figure 1 XRD patterns of the MnO_2/Mg-Al LDH[3)]

Table 1 Chemical compositions of MnO_2/Mg-Al LDH[4)]

Mg/Al	Mn [wt%]	Mn/Al	CO_3^{2-}/Al	OH^-/Al
1.9	4.2	0.19	0.28	0.43

NO treatment

Table 2 shows the NO removal rates of the CO_3·Mg-Al LDH, MnO_2/Mg-Al LDH, and MnO_2 + CO_3·Mg-Al LDH mixture. After 90 min, the NO removal rates of CO_3·Mg-Al LDH, MnO_2/Mg-Al LDH, and MnO_2 + CO_3·Mg-Al LDH mixture are 0%, 1.4%, and 83.9% respectively. The NO removal rates of MnO_2/Mg-Al LDH is notably higher than the others, indicating that a synergistic effect was generated when it becomes composite.

Table 2 NO removal rates of the CO_3·Mg-Al LDH, MnO_2/Mg-Al LDH, and MnO_2 + CO_3·Mg-Al LDH mixture at 90 min[5)]

	CO_3·Mg-Al LDH	MnO_2/Mg-Al LDH	MnO_2 + CO_3·Mg-Al LDH mixture
NO removal rate [%]	0	1.4	100

NO recovery

EGA-MS result of MnO_2/Mg-Al LDH after NO removal shows that NO peak was observed over 400 ℃. NO recovery at 400-600 ℃ are shown in table 3. NO recovery performed at 600 ℃ presents 100% of recovery rate that significantly higher than 500 ℃ and 400 ℃.

Table 3 NO recovery

	400℃	500℃	600℃
Recovery rate [%]	1.0	46.2	100

CONCLUSION

NO treatment by MnO_2/Mg-Al LDH composite has higher performance than CO_3·Mg-Al LDH and MnO_2 + CO_3·Mg-Al LDH mixture and denote 83.9% of removal rate. Moreover, trapped NO gas can be recovered 100 % at 600 ℃.

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