Development of natural zeolite catalyst system to simultaneous reduction of greenhouse gas and nitric oxides from nitric acid manufacturing process

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Nitrous oxide (N_2O) has been well known as a powerful greenhouse gas and a precursor of stratospheric ozone depletion. It has a long lifetime of about 130 years in the atmosphere and the global warming potential (GWP) of about 310, which means 310 times more effective per kg at trapping heat than carbon dioxide. The N_2O concentration of troposphere has recently increased by an annual rate of about 0.3%/year due to emissions from anthropogenic sources [1,2].

Nitric acid industry is one of the major sources of the greenhouse gas emission. N_2O is formed as a by-product in the oxidation of ammonia on a Pt/Rh gauze catalyst. The off gas concentration of N_2O is typically between 1000 and 2000 ppm. Next to N_2O, nitric acid plants also emit NO_x (typically 100-500 ppm). In part of the existing nitric acid plants a conventional NH_3-based $DeNO_x$ system is in use. Several options are currently in development for N_2O abatement [3]. Among various pollution control technologies, a well-proven method is the selective catalytic reduction (SCR) of NO_x with NH_3 in the presence of oxygen. SCR is an optimal method for effective N_2O and NO_x removal by addition of a reducing agent to diminish the volume of off-gases and the required reactor size and to reduce the cost.

This study is to examine the activity characterization of catalyst for SCR of N_2O and NO in a single reactor under similar conditions that prevail in the tail gases of nitric acid manufacturing process. Catalytic activity of de-N_2O and NO has been observed at temperature of between 200 and 500 ℃. In addition, the chemical composition of the catalyst was analyzed by XRF and XANES.

The SCR of N_2O and NO by NH_3 and CH_4 has been studied in a flow reactor operating at atmospheric pressure. The schematic diagram of apparatus is represented in Fig. 1. The gas hourly space velocity (GHSV) is 20,000 h^{-1} and 10,000 h^{-1} for the SCR of N_2O and NO. FeHNZ (Fe ion exchanged natural zeolite) for reduction of N_2O and NO is prepared by wet ion exchange with $Fe(NO_3)_3$ onto clinoptilolite (natural zeolite) at 80 ℃ for 4 h (for detail, see Fig. 2). The chemical composition of the catalyst is examined by XRF (Shimadzu XRF-1700) and is presented in Table 1. And the shape and position of the Fe K-edge X-ray absorption near edge structure (XANES) provides information on the electronic structure and the local coordination geometry of the absorbing Fe atom. Fig. 3 and 4 reveal the XANES spectra for FeHNZ catalyst and Fe reference materials. As a result of analysis, Fe species on FeHNZ was investigated into Fe_2O_3 as shown in Fig. 3 and 4.

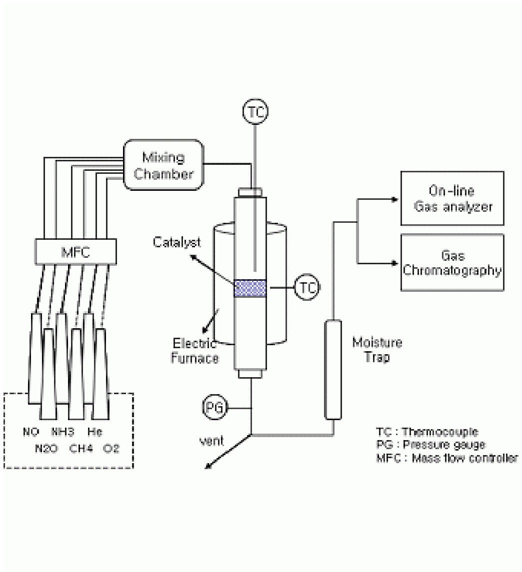


Fig. 1. Schematic diagram of apparatus for testing the catalyst.

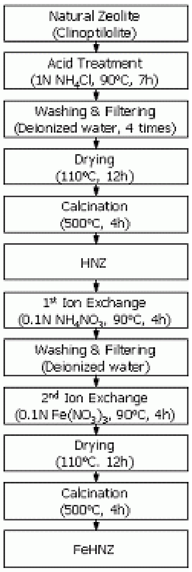


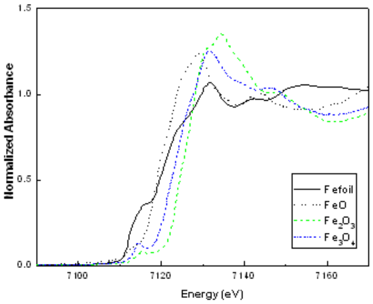
Fig. 2. Schematic flow diagram for preparing natural zeolite catalysts.

Table 1. Physicochemical Properties of Zeolite Catalysts

Catalysts	Si/Al	Fe	Mg	Ca	Na	K
HNZ* (Acid Treatment)	4.97	1.76	0.43	1.02	0.32	1.64
NH_4^+-HNZ (1st WIE**)	5.07	1.83	0.40	0.51	0.31	1.12
FeHNZ (2nd WIE**)	5.34	6.91	0.35	0.46	0.28	1.20

* NZ : Natural zeolite

** WIE : Wet Ion Exchange



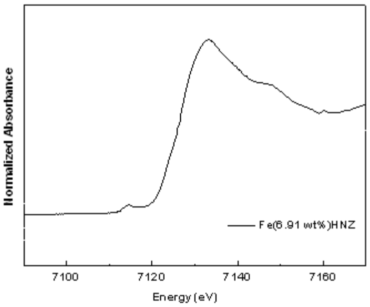


Fig. 3. Fe K-edge XANES spectra of Fe reference materials.

Fig. 4. Fe K-edge XANES spectra of FeHNZ catalyst sample.

Fe-zeolites are attractive catalysts for direct N_2O decomposition in tail-gases from chemical production and stationary combustion processes. This is due to their unique performance in the presence of tail-gas components compared to other catalytic systems based in noble metals and other transition metals, including the no inhibition by O_2 and a remarkable resistance towards deactivation by H_2O [4]. But the necessary temperatures are high (>450 ℃) for direct decomposition. However, the presence of reducing agents accelerates reducing reaction by SCR, resulting in a decreased operation temperature. So, in this study was aimed at finding an optimal condition that is able to maximize to conversion both of N_2O and NO. And the experimental conditions are given in the caption of the graphs, respectively.

Fig. 5 shows that in the presence of NH_3 and CH_4 as reducing agents, SCR profiles of N_2O and NO conversion are investigated. The conversion of N_2O is higher than 45% at above 450 ℃. NO conversion goes through a maximum at around 250 to 400 ℃ and observes steeply lower than about 50% at 500 ℃. The activity of N_2O and NO with only CH_4 is shown in Fig. 6. The conversion of N_2O is increased as the temperature is increased. But NO is represented low activity compared with using NH_3. In contrast, in presence of only NH_3 as reducing agent, the experimental result is shown in Fig. 7. While the activity of NO removal is observed a maximum conversion at 450 ℃, that of N_2O removal shows only the half.

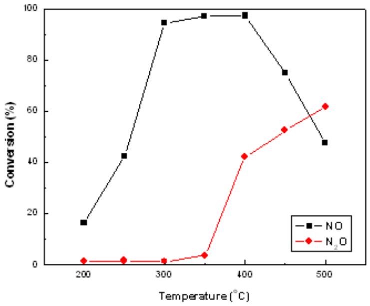


Fig. 5. SCR of N_2O (■) and NO (●) by NH_3 and CH_4 over FeHNZ catalyst : $N_2O/NO/NH_3/CH_4$ = 1/1/1/1; space velocity=20,000 h^{-1}; He balance.

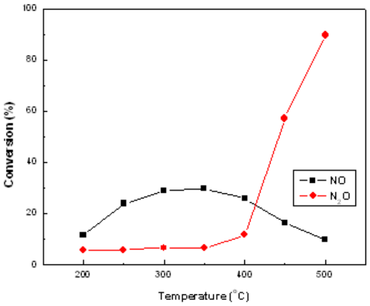


Fig. 6. SCR of N_2O (■) and NO (●) by CH_4 over FeHNZ catalyst : $N_2O/NO/CH_4$ = 1/1/2; space velocity=20,000 h^{-1}; He balance.

To optimize operating conditions in nitric acid process, Fig. 8 shows the conversions of N_2O and NO at different space velocity (10,000 h^{-1}). The conversion of N_2O is increased at low space velocity. At least 400 ℃ of reaction temperature is achieved more than 80% conversion of both N_2O and NO. N_2O conversion is also showed the maximum at 450 ℃.

As a result, conversions of N_2O and NO have been observed the maximum under the optimal conditions of 400 to 450 ℃ of reaction temperature, 10,000 h^{-1} of space velocity and NH_3 as a reducing agent. Finally, this study has been investigated simultaneous reduction of N_2O and NO from nitric acid manufacturing process using a natural zeolite (Fe ion exchanged) catalyst.

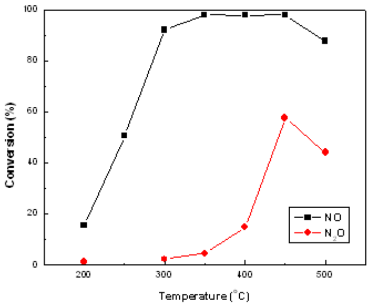


Fig. 7. SCR of N_2O (■) and NO (●) by NH_3 over FeHNZ catalyst : $N_2O/NO/NH_3$ = 1/1/2; space velocity=20,000 h^{-1}; He balance.

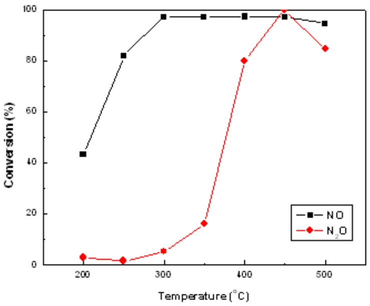


Fig. 8. SCR of N_2O (■) and NO (●) by NH_3 over FeHNZ catalyst : $N_2O/NO/NH_3$ = 1/1/2; space velocity=10,000 h^{-1}; He balance.

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Reference

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