The effect of temperature on NO_x reduction by H_2 in the presence of excess oxygen on a Pt/Al_2O_3 monolithic catalyst

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ABSTRACT

This study examined the reduction of NO_x by H_2 over a Pt/Al_2O_3 catalyst coated onto a monolith as a function of temperature. The formation of N_2O began at a low temperature due to the chemisorption of NO on Pt metal and its resulting oxidation at the Pt active sites. The formation of N_2 was possible at higher temperatures because at the high temperatures, the reaction rate for N_2 formation was higher than the reaction rate for N_2O formation. The formation of NO_2 was predominant above 150 °C due to the excessive oxidation activity of the catalyst. The formation of N_2O at low temperatures and that of N_2 at high temperatures were found to be strongly related to the Pt loading and the temperature range in which the reductive activity was obtained, respectively. Therefore, both reductive conditions and an adequate reaction temperature are important factors for the selective formation of N_2 from the reduction of NO on a Pt catalyst. The temperature-dependent change in the oxidation state of Pt during the reduction of NO was also examined to determine the mechanism for the reduction of NO_x by H_2. In addition, the reaction conditions for the selective reduction of NO_x to N_2 were determined.

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1. Introduction

Lean-burn combustion was developed to reduce fuel consumption and CO_2 emissions. However, under the combustion conditions, NO_x cannot be purified sufficiently using the conventional three-way catalysts. Over the last three decades, the selective catalytic reduction (SCR) of NO_x and its underlying mechanisms have been examined extensively [1]. Ammonia and hydrocarbons are considered to be the best reducing agents in this process but hydrogen has also been reported to be a very effective reducing agent [2]. Hydrogen is one of the exhaust gases emitted by automobiles and can easily be generated by an on-board compact reformer used in a fuel cell system [3,4]. In particular, supported platinum catalysts were reported to be most active for the lean de-NO_x reaction at low temperatures where the reduction of NO by H_2 under oxygen-rich conditions was examined [5]. Costa et al. reported NO reduction with H_2 on Pt/Al_2O_3 and the effect of the Pt loading over a Pt/MgO–CeO_2 catalyst at different reaction temperatures [6,7]. Furthermore, they reported significant mechanistic isotopic studies of the H_2-SCR of NO over Pt-supported mixed-oxide and perovskite-type materials (e.g., Pt/MgO–CeO_2, Pt/La–Sr–Ce–Fe–O, Pt/La–Ce–Mn–O) using Steady State Isotopic Transient Kinetic Anal-

ysis (SSITKA) [8,9]. Recently, Efstathiou et al. have reported the significance of H_2-SCR compared to NH_3-SCR and HC-SCR considering the progressive demand for hydrogen with a growth rate of approximately 10% a year in many industrial installations [10]. In addition, the selective catalytic reduction of NO_x by CH_4 in real exhaust gas of a lean-burn gas engine was investigated [11].

Therefore, this study investigated the temperature-programmed reduction of NO_x by H_2 over a Pt/Al_2O_3 catalyst with various Pt loadings and in the presence of excess oxygen. In particular, the NO_x reduction experiments were carried using a Pt/Al_2O_3 catalyst coated onto a monolith. This is because the monolithic catalyst offers a lower pressure drop compared with the traditional catalysts used for gas-phase reactions, which obviously is quite advantageous in vehicle engine emission control.

2. Experimental

2.1. Catalyst preparation

Modern emission control catalysts utilize monolithic flow-through supports coated with a high surface area of inorganic oxides and precious metals. In this study, ceramic honeycomb (400 cells/in.^{2}, 2 cm × 2 cm × 3 cm, Ceracomb Co., Korea) was used as the monolithic support on which aluminum oxide (Al_2O_3, Aldrich Co.) had been washcoated. The washcoat was prepared with 4 g of aluminum oxide and 20 ml of alumina sol (Al_2O_3 10 wt%, AS-

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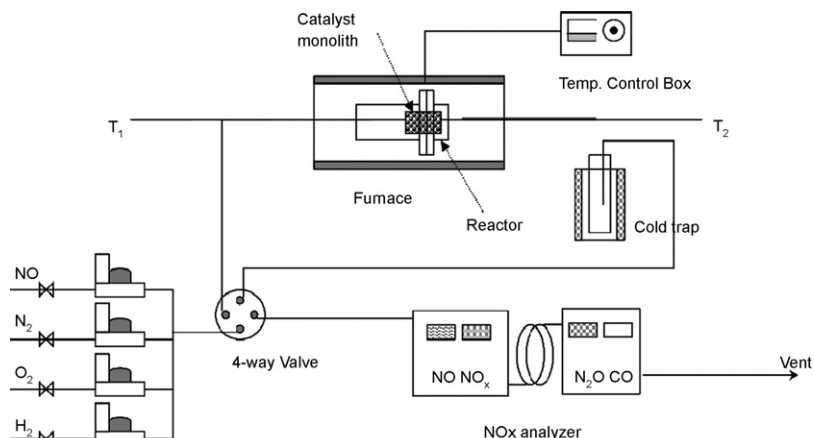E-mail address: yangji@kier.re.kr (J.-I. Yang).

Fig. 1. Schematic diagram of the experimental apparatus.

200, Nissan Chemical Co., Japan). The washcoat was applied to the monolith from water-based slurry, dried at 120 °C and calcined at 550 °C. Finally, Pt was impregnated on the alumina using an incipient wetness method from an aqueous solution of $H_2PtCl_6 \cdot xH_2O$, and its loading was controlled by adjusting the concentration of the $H_2PtCl_6 \cdot xH_2O$ aqueous solution. The catalyst was calcined at 550 °C and reduced in an N_2 stream containing H_2 (10%) at 350 °C before confirming its catalytic activity.

2.2. Catalyst characterization

The elemental platinum concentration was measured by ICP-AES (ICPS/7500, Shimadzu). The discrepancy between the intended and ICP-measured loading suggests that some of the solution had been lost during the impregnation process. The XPS spectra were recorded on a VG-ESCA2000 spectrometer with Mg Kα X-rays as the photon source (2253.6 eV). The power of the X-ray source was set to 300 W. The binding energies (BEs) were referenced to the C (1s) peak at 284.8 eV.

2.3. Experimental apparatus and methods

The activity test was carried out in a fixed-bed flow reactor system. Fig. 1 shows a schematic diagram of the reaction apparatus. Typically, the reactants gas consisted of 2000 ppm NO, 1% H_2, 5% O_2 with the balance made up of N_2 to simulate the exhaust gas from vehicles powered by lean-burn engines. The total flow rate was 2400 cm^3 (STP)/min, resulting in a GHSV of 12,000 h^{-1}. The reaction temperature was increased from 20 to 350 °C with a ramp of 5 °C/min.

On-line NO_x analyzers (ULTRAMAT 23 for NO and NO_x analysis, ULTRAMAT 6 for N_2O and CO analysis, SIEMENS Co., Germany) were used to examine the composition of the product. And, the produced N_2 concentration was calculated on the base of N-balance. The N-balance, NO_2 concentration, N_2 concentration and N_2 selectivity are defined as follows:

$$N\text{-balance}\,(\%) = \frac{\{(NO\,conc.)_{out} + (NO_2\,conc.)_{out} + 2(N_2O\,conc.)_{out}\}}{(NO\,conc.)_{in}} \times 100 \quad (1)$$

$$NO_2\,conc.\,(ppm) = (NO_x\,conc.) - (NO\,conc.) \quad (2)$$

$$N_2\,conc.\,(ppm) = \frac{\{2000 - (NO\,conc.) - (NO_2\,conc.) - 2(N_2O\,conc.)\}}{2} \quad (3)$$

$$N_2\,sel.\,(\%) = \frac{(N_2\,conc.)}{\{(N_2\,conc.) + (N_2O\,conc.)\}} \times 100 \quad (4)$$

In the above equations, we neglected an extra term in the N-balance which came from the surface adsorbed species on the catalyst because we already confirmed that the N-balance was almost equaled to 100% at the temperatures lower than 50 °C.

3. Results and discussion

3.1. Effect of temperature

The reduction of NO by H_2 in the presence of oxygen was examined over a 0.3 wt% Pt/Al_2O_3 catalyst with increasing temperature. Fig. 2 shows the temperature-programmed NO reduction by H_2 over the catalyst. There were three characteristic temperature regions with distinct catalytic activities. Only N_2O was formed in the lowest temperature region of 20–35 °C (1st region) without external heating. The formation of N_2O in this temperature range originated from the chemisorbed NO molecules on Pt metal leaving surface-oxidized Pt particles [12]. Therefore, the concentration of N_2O produced in this temperature region followed a volcano-type curve depending on the proportion of Pt oxidized by NO chemisorption. However, a small amount of N_2O was still formed in this temperature range because hydrogen continued to reduce the oxidized surface of the Pt particles, thus allowing the further adsorption of
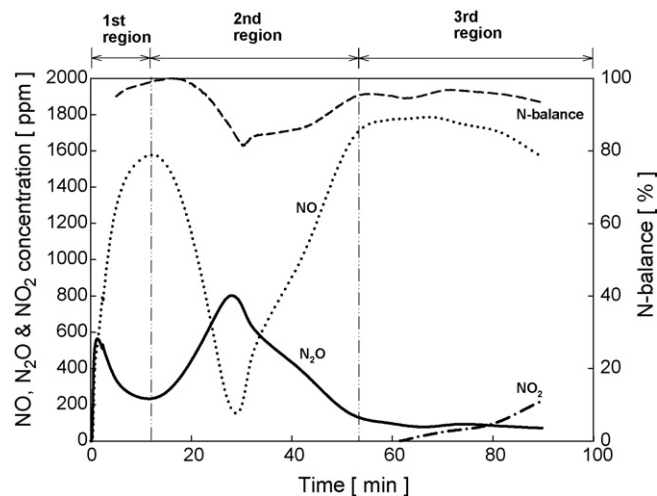

Fig. 2. Temperature-programmed NO reduction by H_2 over 0.3 wt% Pt/Al_2O_3.