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Effect of precious metals and NOx storage materials on hydrogen reduction of stored NOx on millisecond time scale

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ABSTRACT

The effect of precious metals (PMs) and NOx storage materials (NSMs) on the reduction of stored NOx over PM/NSM/Al_2O_3 (PM = Pt, Rh, Pd; NSM = Ba, K, Na) catalysts was studied via transient reaction analysis using pulsed gases with submillisecond resolution. The time profiles of the product gases were analyzed with a high time resolution of 0.25 ms for the first 50 ms after supplying a hydrogen gas pulse.

These results were explained with a model that correlates with the spillovers of released NOx species from the NSM and the activated hydrogen on the PM. The catalyst Pt/Na/Al_2O_3 had the highest reduction rate of stored NOx among the nine catalysts examined. This performance is due to both the lowest decomposition temperature of Na and the high reactivity of hydrogen on Pt. On the other hand, the Rh-containing catalysts exhibited a lower NH_3 production capability than the Pt- and Pd-containing catalysts, and the Rh/K/Al_2O_3 catalyst had the least NH_3 production capability and the lowest reduction rate of stored NOx. The lower NH_3 production capability of Rh is caused both by the low hydrogen reactivity on Rh and the lowest reduction rate of stored NOx for Rh/K/Al_2O_3, which has the lowest surface area among the Rh-containing catalysts.

1. Introduction

To protect the global environment, a worldwide reduction in CO_2 emissions is required. High fuel-efficiency lean-burn engine technology is a promising method for alleviating the CO_2 emission problem in automotive applications. However, the emissions from lean-burn engines include NOx production under oxygen-rich conditions, and the reduction of NOx is extremely difficult under such conditions. On the basis of the considerable research conducted on various methods, a NOx storage and reduction (NSR) catalyst for automobiles was put into practical use in 1994 by the Toyota Motor Corporation [1,2].

An NSR catalyst has the ability to reduce NOx, even under oxygen-excess conditions, using two operations: first is the storage of NOx using alkali or alkali earth materials under oxygen-rich conditions, and second is the reduction of stored NOx under oxygen-poor conditions produced by a short-period, rich pulse of reducing gases. The alternate repetition of these storage and reduction operations results in the reduction of NOx to nitrogen. To develop efficient NSR techniques with low fuel cost, it is necessary to investigate the reaction mechanisms involved. It is suggested that the reduction of stored NOx is the rate limiting step in the overall NSR process at low temperature [3]. The evaluation of the rate at which stored NOx is reduced requires measurement of the time profiles of the products produced during the reduction process. However, it is difficult to measure these products because the reaction is usually very fast and the main product is gaseous nitrogen, which is also a normal emission product from engines and is used as a model gas in laboratory tests.

We previously reported the comparison results of NOx reduction processes with Pt/Ba/Al_2O_3 and Pt/K/Al_2O_3 catalysts by analyzing the NOx reduction using a temporal analysis of products (TAP) reactor [4,5]. The TAP method was developed by Gleaves et al. [6] and is widely recognized as an effective method for transient reaction analysis [7]. From our analysis, we found that the reduction rate of stored NOx using Pt/K/Al_2O_3 was faster than that using Pt/Ba/Al_2O_3, and the ratio of N_2 to NH_3 produced in the reaction was affected by different catalysts. The NOx storage process in potassium has also been studied [8–11]. Potassium-containing materials show strong potential as NOx storage materials (NSMs) and as a NOx selective-reduction catalyst [12].

Many scientists have studied the effect of precious metals (PMs) on NSR activity in order to improve the performance of NSR catalysts. In particular, Abdulhamid et al. studied the effect of different reducing agents (H_2, CO, C_3H_6, and C_3H_8) on the reduction of stored

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