ELSEVIER
Catalysis Today 29 (1996) 43-45
CATALYSIS TODAY

$DeNO_x$ catalyst for automotive lean-burn engine

Shin'ichi Matsumoto

Material Engineering Division 1, Toyota Motor Corporation, 1 Toyota-cho, Toyota-shi, Aichi 471, Japan

Abstract

The performance and durability of Cu-ZSM-5 were studied. Cu-ZSM-5 has fairly high NO_x reduction activity but its durability is insufficient for practical use. We developed a new $deNO_x$ catalyst. In this catalyst, we call NO_x storage reduction catalyst (NSR-catalyst), NO_x emitted from an engine at lean A/F operation is stored and this stored NO_x is reduced at stoichiometric or rich operation. This catalyst has been used on the Toyota CARINA with a lean-burn engine in Japan since 1994. This report outlines the results of our study on Cu-ZSM-5 and NSR-catalyst.

Keywords: Cu-ZSM-5; NSR catalyst

1. Introduction

From the viewpoint of environmental protection, there have been increasing demands for cleaner exhaust and better fuel economy. A lean-burn engine is one of the effective technologies for suppressing the fuel consumption of a gasoline engine. However, the lean operating conditions have been limited, because emitted NO_x under oxidizing conditions could not be purified over conventional 3-way catalysts.

2. Selective NO_x reduction catalyst

We have been investigated many catalysts for reducing NO_x in net oxidizing exhaust gas. In these catalysts, Cu-ZSM-5 has the outstanding NO_x reduction activity.

Cu-ZSM-5 was prepared by exchanging an appropriate Cu cation into ZSM-5 (Tosoh, $SiO_2/Al_2O_3 = 40$). Then, Cu-ZSM-5 was washcoated on a honeycomb substrate.

The NO_x conversion efficiency was measured by installing honeycomb catalyst in the lean-burn engine exhaust system. The NO_x conversion started around 300°C, after its maximum, approximately 40%, around 400°C and dropped substantially (Fig. 1).

Cu-ZSM-5 aged in synthesized gas exhibited a remarkable drop in NO_x conversion with an increase of aging temperature above 500°C (Fig. 2). The ^{29}Si- and ^{27}Al-NMR spectra of Cu-ZSM-5 aged at 800°C for 5 h show the dealumination of tetrahedral Al species.

The CRD pattern and Cu^{2+}-ESR spectrum of the same sample show that Cu does not agglomerate and the ZSM-5 structure does not collapse. The hydrothermal treatment above 500°C of Cu-ZSM-5 may cause the dealumination and the migration of ion-exchanged Cu^{2+} species into another sites in ZSM-5 where they are stabilized and become inactive for NO_x reduction.

SSDI 0920-5861(95)00259-6

3. NO_x storage-reduction catalyst (NSR-catalyst)

NSR-catalyst was developed recently. This catalyst consists of precious metals, alkaline-earth metals, alumina and some other metal oxides. The mechanism of NO_x reduction is shown in Fig. 3. The NO_x emitted from an engine operated in the lean-burn range is stored in the catalyst and the stored NO_x is refused into nitrogen when an engine operates in the stoichiometric or rich-burn range.

3.1. Performance of NSR-catalyst

NO_x conversion efficiency of this catalyst was measured by periodically operating a 1.8 l lean-burn engine at A/F 21 and at 14.5. This catalyst provides high NO_x conversion efficiency, specifically 90% or more at the temperature range from 300 to 450°C (Fig. 4).

Durability tests carried out in a gas containing SO demonstrated deterioration in activity. Analysis of the catalysts after testing confirmed that sulfates had formed. It is probable that, as in the case of NO_x, SO_2 in the exhaust was oxidized on the noble metal and subsequently reacted with the storage component, with resulting sulfate formation. Since sulfates are more stable than nitrates in general, once sulfates develop, NO_x storage is rendered impossible,

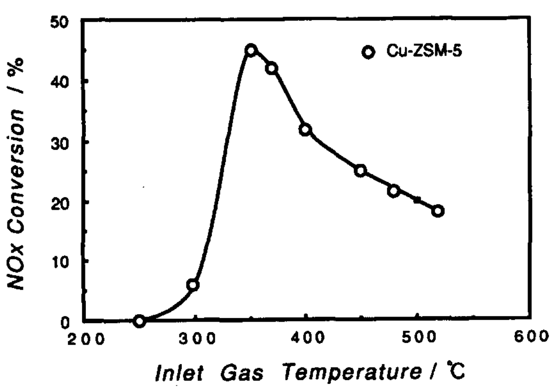

Fig. 1. Temperature dependence of NO_x conversions over Cu-ZSM-5 monolithic catalyst in engine exhaust.

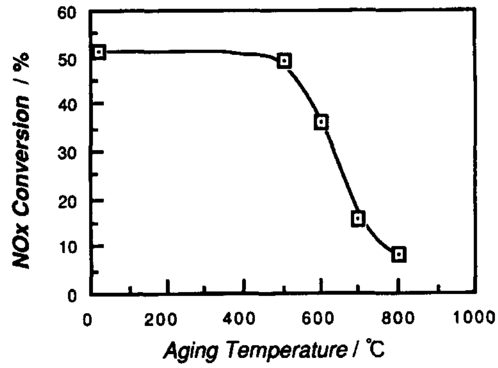

Fig. 2. Influence of aging temperature on NO_x conversions over Cu-ZSM-5 monolithic catalyst in model gas. (Aging time: 5 h).

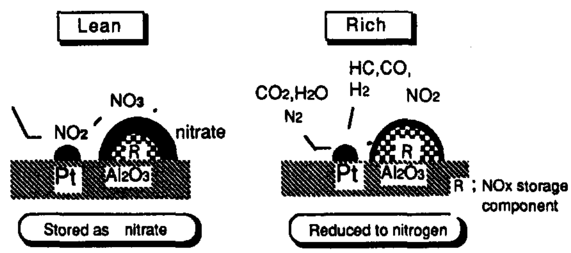

Fig. 3. NO_x storage reduction mechanism.

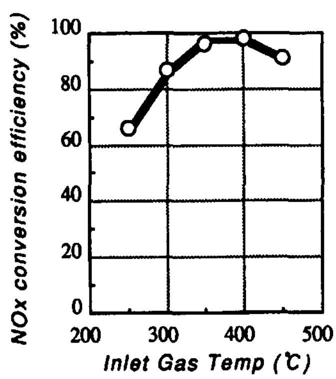

Fig. 4. NO_x conversion efficiency of NSR-catalyst on engine bench test.

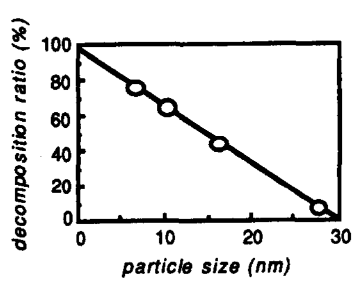

Fig. 5. Relationship between particle size and decomposition ratio of the sulfate by thermal treatment at 700°C in reducing atmosphere.

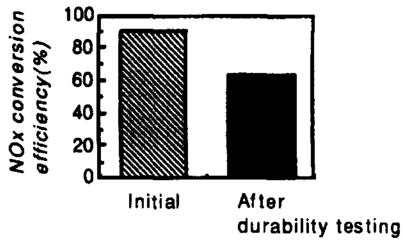

Fig. 6. NO_x conversion efficiency in Japanese 10.15 mode the developed catalyst on vehicle test Vehicle: Carina Engine: 1.6 l lean burn Catalyst: 1.7 l monolithic durability test: 100000 km-equivalent sulfur content in fuel is 30 ppm.

consequently deteriorating conversion efficiency.

However, it was found that produced sulfates decomposed, although slowly, in a range of atmosphere from that providing the stoichiometric A/F ratio to a rich atmosphere; therefore we began to search for a catalyst capable of readily decomposing sulfates during operation at the stoichiometric A/F ratio. Research on factors affecting sulfate decomposition showed that the effect of the sulfate particle size was significant. Fig. 5 presents the results of the research. The smaller the particle size, the faster the decomposition. It may be possible, therefore, to accelerate decomposition if the growth of sulfate particles can be slowed. Hence, we reviewed the chemical composition of the storage component that can inhibit the sulfate particle growth. As a result, we were able to develop a catalyst capable of both decomposing sulfates resulting from NO_x reduction when the sulfur content in the fuel is limited and providing a practical level of durability.

3.2. Vehicle test

Fig. 6 presents NO_x conversion efficiency during Japanese 10.15 mode [1] running in vehicles with the lean-burn engine. In the initial stage of testing the engine exhibited 80% or higher conversion efficiency. Even after 100000 km-equivalent durability running with Japanese regular gasoline, the catalyst retained 60% or greater NO_x conversion capacity.

[1] Measuring mode for vehicle exhaust emission.