ELSEVIER

Catalysis Today 75 (2002) 407–412

CATALYSIS TODAY

www.elsevier.com/locate/cattod

A catalytic NO_x reduction system using periodic steps, lean and rich operations

Tadao Nakatsuji*, Veikko Komppa

VTT Chemical Technology, P.O. Box 1401, Espoo FIN-02044, Finland

Abstract

Catalytic lean NO reduction system in periodic two steps, lean/rich operations has been investigated over Rh-based catalysts. The investigation was done using a pulse reaction. In the reaction, after H_2 or CO was pulse-injected for a moment to achieve reducing conditions, the highly dispersed Rh catalyst could catalyze NO reduction at 200–400 °C in lean conditions for 1 min. Furthermore, NO was effectively reduced over the highly dispersed Rh/β-zeolite after exposure to the gas composed of 3% of O_2, 40 ppm of SO_2 and balance of He at 300 and 400 °C for 24 h. © 2002 Published by Elsevier Science B.V.

Keywords: NO reduction system; Lean and rich operations; Rh/β-zeolite

1. Introduction

NO_x trap works well for a long period in the absence of SO_x [1–3]. However, in the presence of SO_x, the trap deteriorates drastically due to the irreversible adsorption on NO_2 adsorption sites. Therefore, periodic regeneration is mandatory. A durable NO_x reduction, using much shorter periodic two steps than those in the NO_x trap, has been proposed [4]. This NO_x reduction on the Rh catalyst works only in the much shorter rich/lean excursions, so the drawback is high fuel consumption. However, it has been confirmed that the Rh catalyst shows high durability in the presence of SO_x.

This paper presents effective NO reduction on a Rh-based catalyst in the conventional rich/lean excursions for NO_x trap without deterioration in the presence of SO_2.

2. Experimental

2.1. Catalyst preparation

γ-Alumina (GB45, 160 m^2/g; Mizusawa Chemical), ammonia-USY-zeolite ($SiO_2/Al_2O_3 = 25$, 780 m^2/g; Zeolyst) were used as catalyst supports. Some powder catalysts were prepared by immersing the support in a solution of $Rh(NO_3)_3$, followed by drying and calcining in air at 500 °C for 3 h. The other powder catalyst was prepared by ion-exchange of Rh^{+3} ion in an ammonium-zeolite. Each catalyst was sieved through 0.4–65 mm screens.

2.2. NO reduction using hydrogen or CO pulse-injection or periodic pulse-injections

NO reduction experiment was conducted at a *W/F* of 0.03–0.12 $g\,s\,cm^{-3}$ in a flow reactor system. The inlet-gas mixture for the NO reduction experiment in a lean condition contained 500 ppm of NO, 3.0% of O_2 and balance of Ar and the flow rate was 200 N ml/min. In the NO reduction experiment,

---

[*] Corresponding author. Tel.: +358-9-456-4624; fax: +358-9-456-7026.
E-mail address: tadao.nakatsuji@vtt.fi (T. Nakatsuji).

PII: S0920-5861(02)00090-1

0.46 N ml of H_2 or CO was pulse-injected with He carrier gas in 2 s into the main gas stream in order to change the gas condition from lean to rich conditions for several seconds after the outlet-NO concentration reached a constant value. The NO reduction using H_2 or CO pulse-injection usually was conducted isothermally at 500–250 °C in intervals of 50 °C. Outlet-gas concentrations of H_2, NO_2, NO, N_2O or CO_2 (in case of CO injection), N_2 or CO (in case of CO injection) and H_2O were observed with time on stream by using a quadrupole mass spectrometer (Balzers, model QUADSTAR 420). Practically, in the experiments, NO_2 and N_2O was hardly observed. A continuously pulsing reaction with an oscillation between the rich/lean conditions, at 40–60 s intervals, was carried out at 500–250 °C in 50 °C intervals. Furthermore, a catalyst was exposed to the gas composed of 500 ppm of NO, 3.0% of O_2, 40 ppm of SO_2 and balance of Ar for 24 h at 300 and 400 °C, followed by the NO_x reduction experiment using H_2 injection.

3. Results and discussion

3.1. NO reduction using a hydrogen pulse-injection

The catalysts were examined with hydrogen pulse-injection at 200–500 °C in 50 °C intervals. Relative oxygen concentration at the reactor outlet decreased rapidly after the hydrogen pulse-injection, and reached zero. Accordingly, the hydrogen pulse injection changed the reaction conditions from lean to rich conditions. Then, the concentration of zero was maintained for several seconds, and the oxygen concentration drastically increased and the water concentration increased gradually a little while later. On all examined catalysts, this phenomenon was observed at all temperatures. On the other hand, both relative concentration profiles with time for NO and N_2 depended on catalysts remarkably.

On catalysts of 0.1–0.5%Rh/β-zeolite prepared by the ion-exchange method, an NO desorption peak was observed. After the NO desorption, relative NO concentration fell rapidly and reached roughly zero. As described below, it is noted that the NO desorption peak disappeared when hydrogen injected periodically in the NO reduction using rich/lean excursions. The low concentration was maintained for 10–30 s, depending on Rh loading, and as shown in Fig. 1, during the period nitrogen was almost quantitatively formed as if NO might be decomposed into N_2 and O_2. The period was the longest on 0.5%Rh/β-zeolite and the shortest on 0.1%Rh/β-zeolite. On the other hand, on catalysts of 1.0 (not shown) and 2.0%Rh/β-zeolite and 2.0%Rh/alumina prepared by impregnation method, two NO desorption peaks were observed. In addition, the features of nitrogen formation on the 2.0%Rh/β-zeolite and 2.0%Rh/alumina were different from the others. Only two narrow steep N_2 formation peaks were observed at the same time as when NO was desorbed. It was likely that adsorbed NO was reduced with injected hydrogen and after the reduction, NO reduction did not proceed on these catalysts. In the literature [5,6], an NO-TPD (temperature programmed desorption) curve of a reduced Rh/α-alumina showed that adsorbed NO was more converted into nitrogen over reduced Rh/α-alumina than oxidized Rh/α-alumina. Furthermore, it was shown that there were different features of NO desorption and N_2 formation between oxidized and reduced Rh catalysts. Therefore, it seems that just after pulse-injecting hydrogen to the catalyst of 0.1–0.5%Rh/β-zeolite, 1.0–2.0%Rh/β-zeolite and 2.0%Rh/alumina, the catalyst is composed of reduced, reduced/oxidized (mostly reduced), oxidized rhodium (mostly oxidized), and oxidized, respectively.

Fig. 2 shows profiles of NO reduction at 250 °C on various Rh/β-zeolite with different Rh loading. Short moment after hydrogen injection, all of the NO conversions dropped to minus values, due to NO desorption. It should be noted that this phenomenon was not observed when a reductant was injected periodically in 20–60 s intervals on 0.5%Rh/β-zeolite. The conversions increased rapidly with time and reached a plateau of 90–99% of NO_x conversion in several seconds. The length of the plateau followed the order of 0.25%Rh $\approx$ 0.5%Rh $>$ 1.0%Rh $>$ 0.1%Rh. From these profiles, it is evident that NO is reduced efficiently at 250 °C in the NO reduction using Rh/β-zeolite and rich/lean excursion with hydrogen, where time span of the lean excursion is 10–30 s.

Fig. 3 shows the temperature dependence on NO reduction profile over 0.25 wt.%Rh/β-zeolite. With

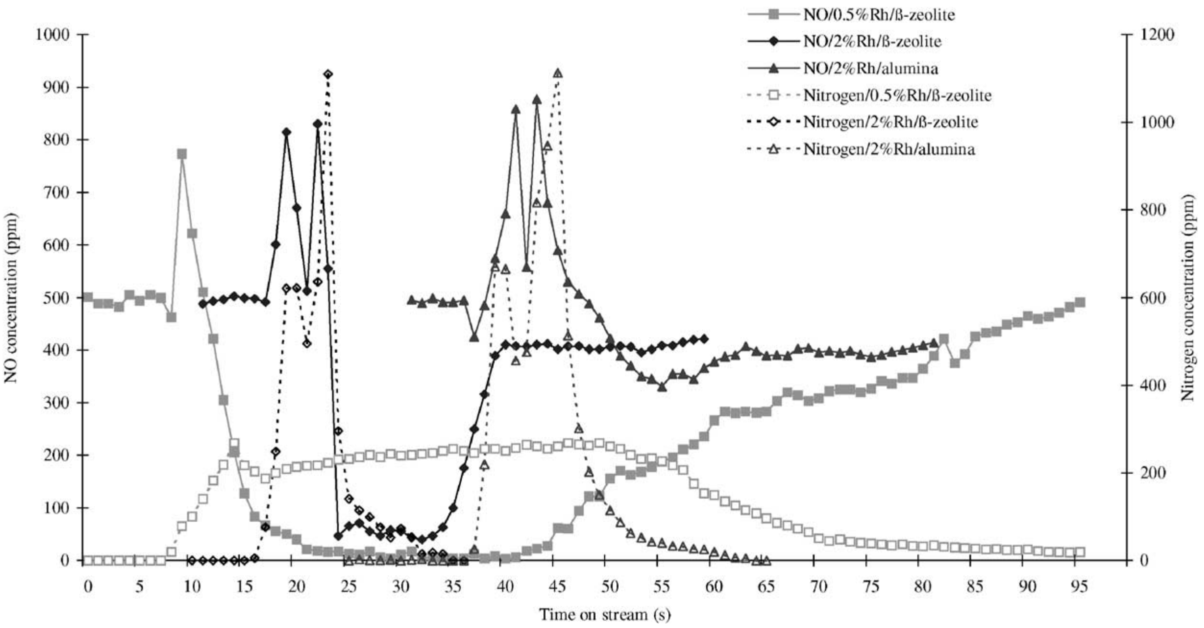

Fig. 1. Concentration profiles of NO and N_2 in NO reduction using hydrogen pulse-injection (temperature: 250 °C).

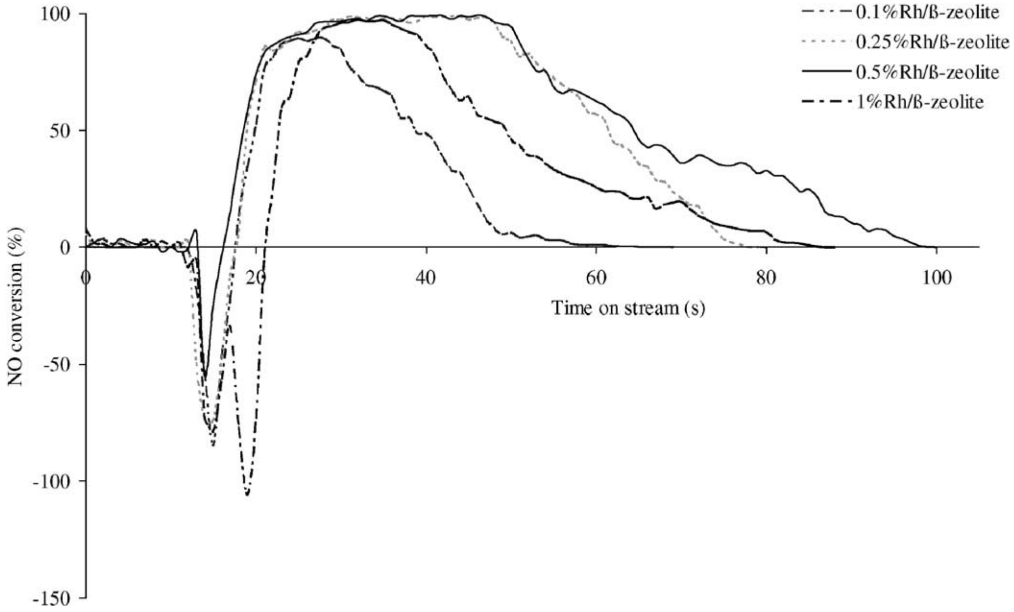

Fig. 2. NO reduction profiles at 250 °C using hydrogen as a reductant over various Rh/β-zeolites.

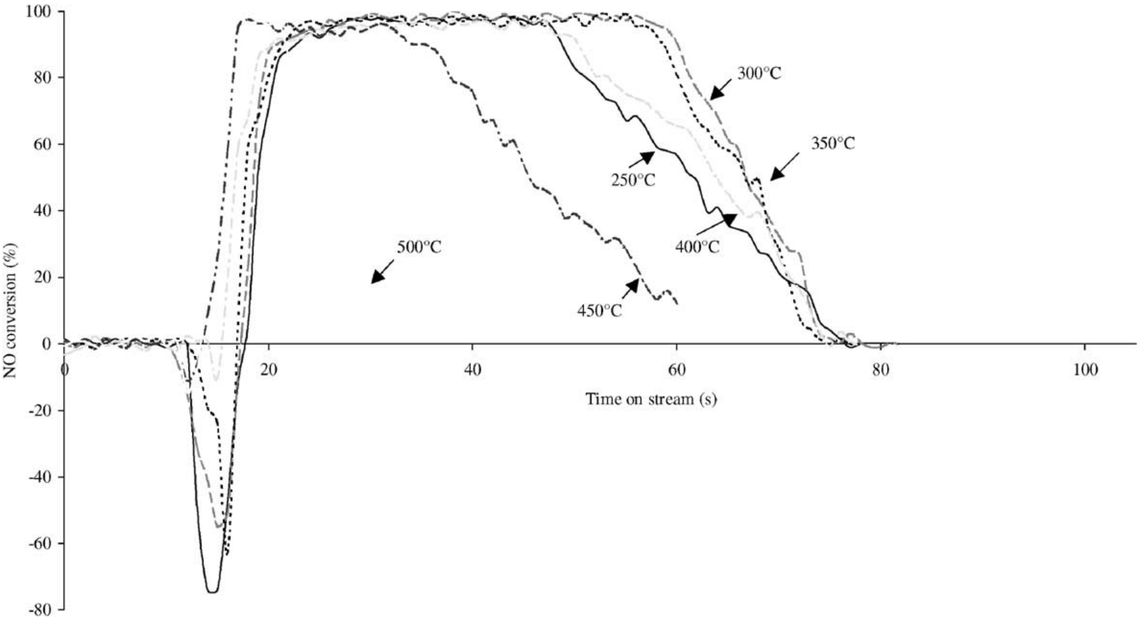

Fig. 3. Temperature dependence of NO pulse reaction using hydrogen injection on 0.25%Rh/β-zeolite.

increase in the temperature, the deterioration of the NO reduction just after hydrogen pulse injection was improved. It is most likely that the amount of NO adsorption decreased with increase in the temperature. The length of a plateau of high NO conversion followed the order of 300 °C ≈ 350 °C > 400 °C ≈ 250 °C ≫ 450 °C ≫ 500 °C. Accordingly, it is expected that at a wide temperature range from 250 to 400 °C, NO would be reduced at a high efficiency. Furthermore, it is noted that the length of a plateau of high NO conversion at 250 °C was shorter than that at 300–350 °C, and the length at the temperature above 450 °C was much shorter than that at 300–350 °C. In general, with increase in temperature, the amount of NO adsorption on Rh decreases and the oxidation velocity of Rh increases. Accordingly, it is inferred that this NO reduction after hydrogen pulse-injection does not mainly proceed from NO adsorption, but another NO reduction such as NO decomposition on reduced Rh.

3.2. NO reduction using a CO pulse-injection

0.5%Rh/β-zeolite was examined using the isothermal NO pulse reaction with CO pulse-injection at 200–500 °C in 50 °C intervals (not shown). The phenomenon was the same as that of NO reduction using hydrogen as a reductant. The length of the plateau followed the order of 300 °C ≈ 350 °C ≈ 400 °C >250 °C >450 °C >500 °C. This order was the same as it of NO reduction using H_2 pulse-injection. Accordingly, the most important thing in the NO reduction is not the kind of reductant, but which oxidized Rh is reduced by reductants.

3.3. NO_x reduction using periodic two steps, an operation in oxidizing conditions and a relatively short operation in reducing conditions

0.5%Rh/β-zeolite was examined at 250–500 °C in the NO_x reduction with pulse-injecting hydrogen in respective intervals of 40, 50 and 60 s. In the intervals of 40 s, NO_x was not detected at all and both nitrogen and water were formed continuously in the whole operation at 250–400 °C (not shown). However, in the NO_x reduction at 300 °C in the 60 s intervals, a small amount of NO was found in the outlet gas 50 s after H_2 pulse-injection. Fig. 4 shows N_2 formation profile in the NO reduction in 60 s

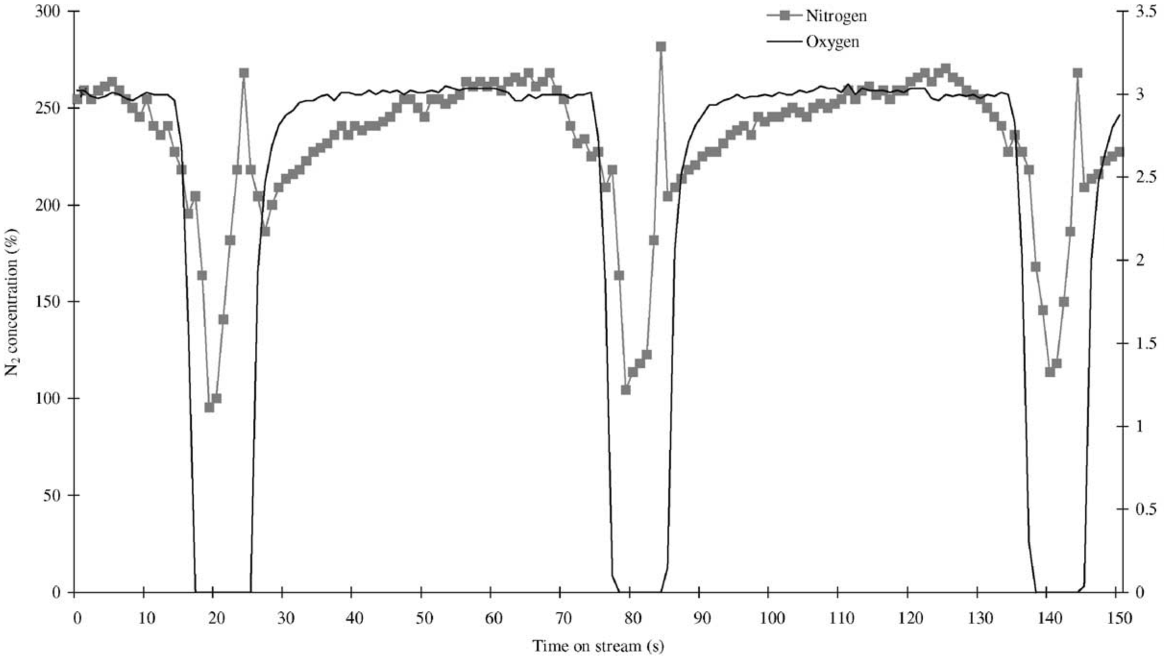

Fig. 4. Nitrogen formation profile in NO reduction using periodic hydrogen pulse-injection.

intervals. Just after the H_2 injection, N_2 concentration decreased with no deterioration of NO reduction, due to NO adsorption. Then, N_2 concentration increased, reached a plateau and finally started to decrease. It is likely that N_2 was formed qualitatively during the plateau as if NO might be decomposed into N_2 and O_2.

From the results, it is implied that in this NO reduction using the rich/lean operations, NO would be reduced as the following reaction steps over 0.25–0.5%Rh/β-zeolite. (i) NO is decomposed into N_2 and O_2 over a reduced Rh in the short lean operation. (ii) The formed oxygen mainly oxidizes the reduced Rh. (iii) The oxidized Rh is reduced with reductants in the short rich operation.

The new NO_x reduction system eliminates NO_x in a completely different reaction mechanism from NO_x storage–reduction, in other words, NO_2 adsorption on alkaline materials is not an important reaction step at all. Therefore, it is anticipated that SO_x will not deactivate Rh in the new NO_x reduction system. 0.5 wt.%Rh/β-zeolite was exposed to the gas composed of 40 ppm of SO_2, 3% of O_2 and He at 300 and 400 °C for 24 h. After the treatment, the catalyst was examined in the NO_x reduction procedure at 300 °C with pulse-injecting H_2. There was almost no difference between the both catalysts. Hence, it is anticipated that the proposed NO reduction system will have high durability in the presence of SO_x.

4. Conclusion

NO_x was effectively reduced over the 0.25–0.5%Rh/β-zeolite in lean conditions for 20–30 s after outlet-oxygen concentration reached the inlet concentration.

In the NO reduction with time spans of 40–60 and 2 s in periodic lean and rich conditions, respectively, NO was reduced at a high efficiency over 0.5 wt.%Rh/β-zeolite. Furthermore, the catalyst, which was exposed to SO_x containing gas, did not show deterioration at all. Accordingly, it is anticipated that the new NO reduction system has high durability in the presence of SO_x. The intrinsic difference in durability between the new and NO_x storage–reduction systems will attribute to the difference in the reaction mechanism of both NO reductions. In the new NO_x reduction, it is likely that NO_x will be decomposed into nitrogen and oxygen over a reduced Rh catalyst.

Acknowledgements

This work was supported with funding from the Technology Development Centre of Finland.

References

[1] N. Miyoshi, S. Matsumoto, K. Katoh, T. Tanaka, J. Harada, N. Takahashi, K. Yokota, M. Sugiura, K. Kasahara, SAE Paper 950809, 1995.
[2] S. Matsumoto, H. Watanabe, T. Tanaka, A. Isoya, K. Kasahara, Nippon Kagaku Kaishi (1996) 997.
[3] M.S. Brogan, R.J. Brisley, B. Krutzsch, N.P. Fekete, D. Voigtlander, SAE Paper 952490, 1995.
[4] T. Nakatsuji, R. Yaskawa, K. Tabata, K. Ueda, M. Niwa, Appl. Catal. B 21 (1999) 21.
[5] H. Cordatos, R.J. Gorte, Appl. Catal. B 7 (1995) 33.
[6] J. Kaspar, C. de Leitenburg, P. Fornasiero, A. Trovarelli, M. Graziani, J. Catal. 146 (1994) 136.