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On-site supply of active reductants for NO conversion through reforming reactions of hydrocarbons

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Abstract

Catalytic elimination of NO under the condition of a large excess of oxygen has been studied using MFI-type metallosilicates catalysts. In order to realize an on-site supply of active reductants, such as hydrogen and carbon monoxide, steam-reforming reaction of a hydrocarbon, *n*-octane, was investigated in conditions both with and without H_2O. With the addition of H_2O, significant amounts of H_2 and CO were recognized in the products, indicating that the steam-reforming reaction occurred even in the presence of a large excess of oxygen. Thus, in situ formed reductants were effectively consumed for NO removal, and consequently an increase in NO conversion was demonstrated. Such an increase in NO conversion in the presence of H_2O has scarcely been known and this kind of desirable effect would be suitable for the practical reaction gas condition of automobile exhaust.

Keywords: Nitrogen oxide; Steam reforming; Syngas formation; Metallosilicate; Gallium; Cobalt

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1. Introduction

Catalytic elimination of NO under the condition of a large excess of oxygen has been studied extensively, especially with the addition of an appropriate kind of hydrocarbon with a very low concentration [1–3]. It has been observed at the early stage of the study that more easily combustible reductants, such as hydrogen and carbon monoxide, had almost no effect for the NO reduction [4]. The reason for this is as follows: hydrogen and carbon monoxide are so easily combusted at the entrance part of the active catalyst bed in a flow type reactor, and on most of the catalyst bed there are no more reductants.

On the other hand, in our previous study, the reforming reaction of CH_4 with H_2O and CO_2 has been investigated using Ni-based composite catalysts for effective utilization of natural gas [5]. Since this reaction is highly endothermic, to realize the reaction with a high rate, developments of suitable methods for effective heat supply are inevitable. To overcome this problem, we investigated the effect of the on-site heat supply by adding a very small amount of oxygen in the reaction gas and confirmed a significant effect of this method [5]. Considering the basic concept of the on-site heat supply, we expected that if appropriate active molecules, such as hydrogen and carbon monoxide, are generated at the vicinity of active sites located on the whole catalyst bed, those molecules would contribute to the NO elimination, even in

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the presence of excess oxygen. In order to realize this expectation, in this study, the effect of steam reforming of added saturated hydrocarbon, *n*-octane, was examined, employing some H-type metallosilicates of MFI structure as the catalysts. Since steam-reforming reaction for the added hydrocarbon occurs at a considerably higher reaction temperature range, the catalysts which can exhibit an activity for NO elimination at high temperature were adopted in this study.

2. Experimental

MFI-type metallosilicate catalysts were prepared according to the rapid crystallization method [6] using aluminium nitrate, gallium sulfate, iron nitrate, and cobalt nitrate, as the metal sources [7,8]. The charged atomic ratios were 20, 20, 20 and 100, respectively. The as-synthesized catalysts were washed, dried, and then heated in an air stream at 540°C for 3.5 h to burn off the organic template, followed by ion exchange with 1 N NH_4NO_3 solution, and calcination at 540°C for 3.5 h. They were pressed with a tablet machine and crushed into 12–24 mesh to provide for the reaction. A 2.0-g portion of the catalyst was packed in a quartz tubular reactor. The reaction gas, composed of 1000 ppm or no NO, 1100 ppm $n\text{-}C_8H_{18}$, 10.0% O_2, 2.0% or no of H_2O, and N_2 was allowed to flow over the catalyst bed with a SV of 30 000 h^{-1} at a temperature range from 400 to 600°C. The reaction gas and the products were analyzed by a chemiluminescence NOx analyzer (Shimadzu NOA 305A) and an infrared gas analyzer (Shimadzu CGT-7000) for CO and CO_2 respectively, and gas chromatographs for H_2 and hydrocarbons.

3. Results and discussion

In the previous study [8,9], we used various metallosilicate catalysts for elimination of NO in the presence of excess oxygen and a small amount of cetane and found that the NO conversion was accompanied by the combustion of hydrocarbons and that the temperature ranges where both of the activities increased were dependent on the kind of metal element. Considering these results, in this study, MFI-metallosilicates containing Al, Ga, Fe, or Co were adopted. First as the reference reaction, the combustion of *n*-octane on the above-mentioned metallosilicates was measured both in the presence and absence of H_2O. The conversions of $n\text{-}C_8H_{18}$

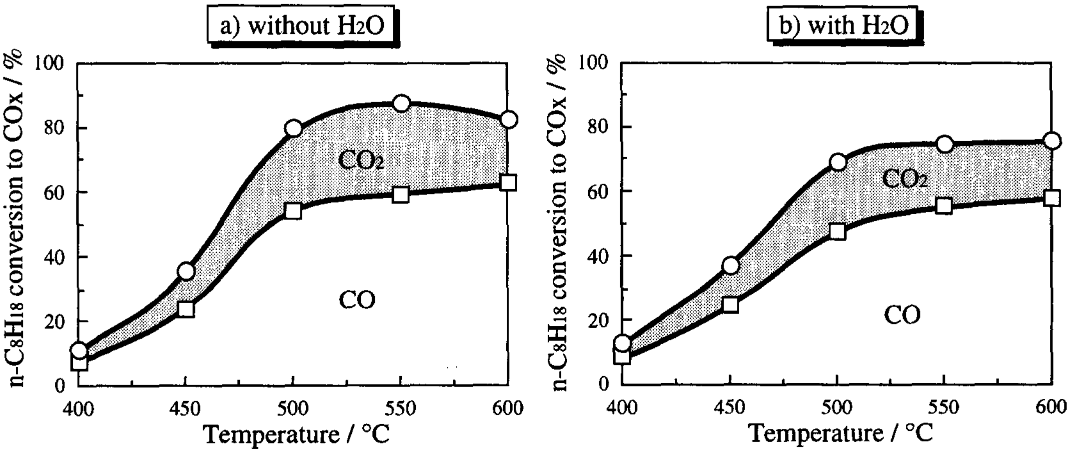

Fig. 1. Effect of H_2O addition on the combustion of *n*-octane on H–Al-silicate catalyst. $n\text{-}C_8H_{18}$ 1100 ppm; O_2 10.0%; H_2O (a) 2.0%, (b) 0%; N_2 balance, SV 30 000 h^{-1}. Catalyst: H–Al-silicate having a Si/Al = 20.

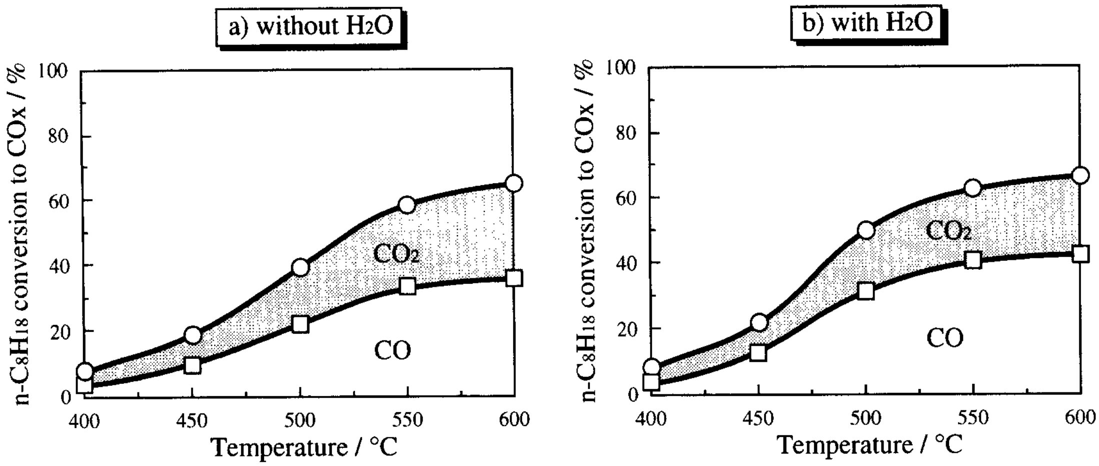

Fig. 2. Effect of H_2O addition on the combustion of *n*-octane on H–Ga-silicate catalyst. *n*-C_8H_{18} 1100 ppm; O_2 10.0%; H_2O (a) 2.0%, (b) 0%; N_2 balance, SV 30000 h^{-1}. Catalyst: H–Ga-silicate having a Si/Ga = 20.

into CO and CO_2 on H–Al-, H–Ga-, H–Fe-silicates are shown in Figs. 1–3, respectively. On H–Al-silicate, a considerable amount of CO and CO_2 formation was observed over the whole temperature range. Other products were lower hydrocarbons and aromatics, which were formed according to the acidic properties of the catalyst, and no oxygen-containing organic compounds, such as ketones or alcohols, were detected. With an addition of 2.0% of H_2O, almost the same results were obtained in octane conversion into COx. These results indicate that H–Al-silicates do not have high activity for oxidation and that the steam-reforming reaction does not occur significantly on this catalyst, which are consistent with the low redox property of the catalyst [9]. On the other hand, on H–Ga-silicate, equivalent amounts of CO and CO_2 were generated without H_2O addition, and on the addition of H_2O in the reaction gas, the generation of CO increased with an increase in reaction temperature, while CO_2 formation was

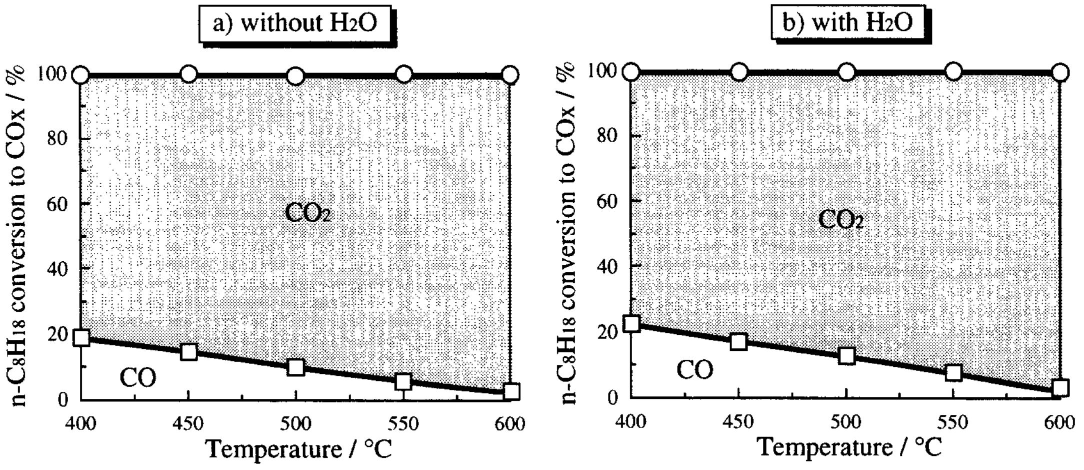

Fig. 3. Effect of H_2O addition on the combustion of *n*-octane on H–Fe-silicate catalyst. *n*-C_8H_{18} 1100 ppm; O_2 10.0%; H_2O (a) 2.0%, (b) 0%; N_2 balance, SV 30000 h^{-1}. Catalyst: H–Fe-silicate having a Si/Fe = 20.

Table 1
Comparison of amounts of H_2 and CO formed in the combustion of n-octane combustion reaction on H–Al-silicate and H–Ga-silicate

Catalyst	Temperature (°C)	Without H_2O addition H_2 (ppm)	Without H_2O addition CO (ppm)	With H_2O addition H_2 (ppm)	With H_2O addition CO (ppm)
H–Al-silicate	400	21	650	28	760
	500	51	4750	93	4190
	600	340	5530	470	5080
H–Ga-silicate	400	91	300	43	350
	500	630	1890	780	2740
	600	770	3110	1070	3750
H–Co-silicate	400	180	860	240	1080
	500	250	670	650	1630
	600	290	1340	640	1690

kept at a constant level. The amounts of H_2 and CO produced on H–Al-silicate and H–Ga-silicate are compared in Table 1 in conditions both with and without H_2O. The addition of H_2O clearly increased the formation of these products and this indicated that the steam-reforming reaction progressed in these systems, even in an oxygen-rich condition. On H–Fe-silicate, most of the added n-octane was oxidized into CO or CO_2 even at 400°C and the addition of H_2O had little effect. It might be difficult to prove if the steam-reforming reaction takes place on H–Fe-silicate similarly in the cases of H–Ga-silicate catalysts, since H_2 or CO formed on-site are rapidly oxidized on the catalyst because it has high oxidation activity, especially in the presence of excess oxygen.

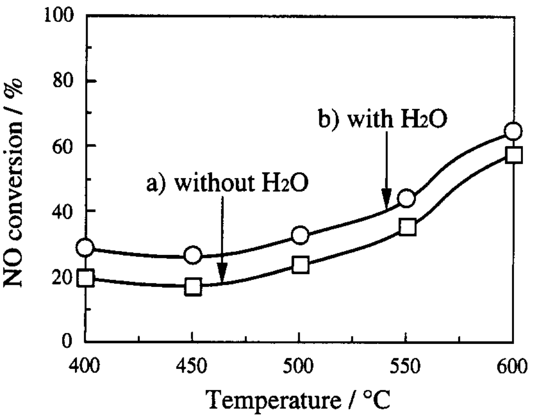

Fig. 4. Effect of H_2O addition on the NO conversion on H–Ga-silicate in excess oxygen condition. NO 1000 ppm; n-C_8H_{18} 1100 ppm; O_2 10.0%; H_2O (a) 2.0%, (b) 0%; N_2 balance, SV 30000 h^{-1}. Catalyst: H–Ga-silicate (Si/Ga = 20).

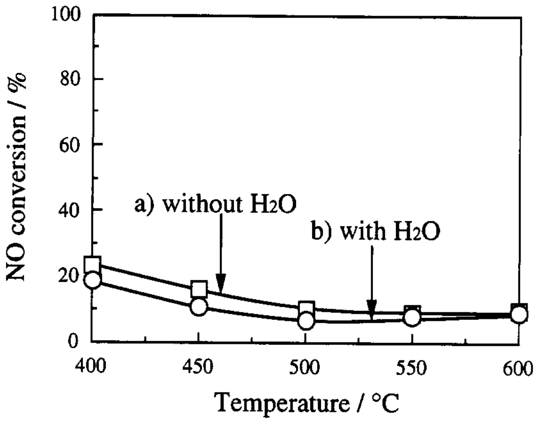

Fig. 5. Effect of H_2O addition on the NO conversion on H–Fe-silicate in excess oxygen condition. NO 1000 ppm; n-C_8H_{18} 1100 ppm; O_2 10.0%; H_2O (a) 2.0%, (b) 0%; N_2 balance, SV 30000 h^{-1}. Catalyst: H–Fe-silicate (Si/Fe = 20).

Next, the prescribed concentration of NO was added to the reaction gas in reaction conditions both with and without H_2O. The NO conversions on H–Ga-, H–Fe-, H–Co-silicates are shown in Figs. 4–6, respectively. In each case, the addition of H_2O caused an increase in NO conversions. Especially, on H–Ga-silicate the effect was demonstrated over the whole temper-

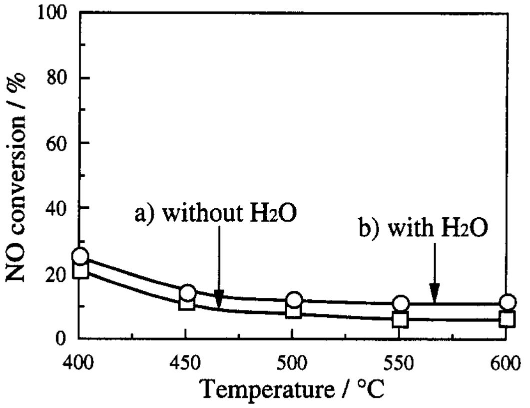

Fig. 6. Effect of H_2O addition on the NO conversion on H–Co-silicate in excess oxygen condition. NO 1000 ppm; n-C_8H_{18} 1100 ppm; O_2 10.0%; H_2O (a) 2.0%, (b) 0%; N_2 balance, SV 30000 h^{-1}. Catalyst: H–Co-silicate (Si/Co = 100).

Table 2
Comparison of amounts of H_2 and CO formed in the NO elimination in excess oxygen condition using metallosilicate catalysts

Catalyst	Temperature	Without H_2O addition		With H_2O addition	
	(°C)	H_2 (ppm)	CO (ppm)	H_2 (ppm)	CO (ppm)
H–Al-silicate	400	10	540	16	770
	500	37	2350	60	2770
	600	160	5270	25	4680
H–Ga-silicate	400	33	700	41	850
	500	450	4070	600	4140
	600	180	5330	270	5300
H–Co-silicate	400	43	870	140	1000
	500	150	1180	280	1250
	600	230	2020	270	2330

ature range. This clearly indicates that the steam reforming of *n*-octane by H_2O occurred and H_2 or CO produced on-site contributed to the increase in NO conversion. On H–Fe-silicate, the addition of H_2O resulted in only a suppression of the NO conversion at a lower temperature, around 400°C. This is explained by the fact that the addition of water merely affects the combustion of *n*-octane, and the effect of on-site supply of H_2 and CO via reforming reaction of *n*-octane is very little in the case of H–Fe-silicate, which has a considerably high activity for the combustion of *n*-octane. Therefore, when the reaction temperature is high enough, e.g., 600°C, the addition of H_2O has almost no effect, both on the combustion and NO conversion. In Table 2, the formation of H_2 and CO on these metallosilicates in the presence of NO is summarized. Formation of CO was much larger compared with the results of simple combustion experiments mentioned above. In order to confirm the activity for steam reforming of hydrocarbons on H–Ga-silicate catalyst, the reaction at 500°C was investigated varying the kind of hydrocarbon under the condition of O_2 absence. In the cases of C_3H_8 and $n\text{-}C_8H_{18}$, considerable amounts of H_2 and CO formed and those products evidently increased by the presence of H_2O in the feed gas, although in the case of CH_4, no products were detected. These results mean the kind of added hydrocarbon is quite important and that the steam reforming of higher hydrocarbons proceeds more easily on this catalyst, even at such a low temperature. Similarly, in the presence of oxygen, when a higher hydrocarbon, for example *n*-octane, as in this study, is used, the combustion does not progress completely and the formed reduced species via the steam-reforming reaction in the vicinity of the active sites contributes to the NO removal. The H_2 formation was much smaller than those of simple combustion experiments. This means that after the H_2 was formed through steam-reforming reaction it is quickly consumed in NO removal.

It is noteworthy that the increase of NO conversion under the H_2O existence condition has scarcely been known, and this rather desirable effect will fit the practical reaction gas condition of the diesel exhaust.

Acknowledgements

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References

[1] H. Hamada, Catal. Today, 22 (1994) 21.

[2] E. Kikuchi and K. Yogo, Catal. Today, 22 (1994) 73.

[3] W.X. Zhang, H. Yahiro and M. Iwamoto, J. Chem. Soc. Faraday Trans., 91 (1995) 767.

[4] M. Iwamoto, H. Yahiro, Y. Yu-u, S. Shundo and N. Mizuno, Shokubai (Catalyst), 32 (1990) 430.

[5] T. Inui, K. Saigo, Y. Fujii and K. Fujioka, Proc. Intern. Workshop Catal. Combustion, 1994.

[6] T. Inui, ACS Symp. Series, 398 (1989) 479.

[7] T. Inui, S. Iwamoto, S. Kojo and T. Yoshida, Catal. Lett., 16 (1992) 223.

[8] T. Inui, S. Shimizu and S. Iwamoto, in R. von Ballmoos, J.B. Higgins and M.M.J. Tracy (Editors), Proc. 9th Intern. Zeolite Conf., Vol. 2, Montreal, July 1992, Butterworth-Heinemann, Stoneham, 1993, p. 405.

[9] T. Inui, S. Iwamoto, S. Kojo, S. Shimizu and T. Hirabayashi, Catal. Today, 22 (1994) 41.