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Decomposition of nitric oxide on metallosilicates under a large excess oxygen condition with coexistence of a low concentration cetane

Tomoyuki Inui, Shinji Iwamoto, Shinichi Kojo and Takashi Yoshida

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

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Catalytic removal of NO was conducted under the condition of large excess O_2 by using different kinds of metallosilicates having MFI structure. With coexistence of a low concentration of cetane, H-Fe-silicate, which had both acidity and redox property, exhibited the maximum performance among the catalysts tested at a fairly lower temperature range, around 350°C, and the NO was totally converted. The temperature dependence of NO conversion was consistently similar to that of cetane combustion.

Keywords: Nitric oxide decomposition; metallosilicate; H-Fe-silicate; oxygen excess condition; cetane addition

1. Introduction

The removal of NO in the exhaust gases from automobiles equipped with gasoline engines has been successfully performed by the use of the so-called three-way catalyst system [1]. As for NOx generated from the stationary sources, ammonia has been used as the reduction reagent with rather coexistence of appropriate concentration of O_2 to advance the de-NOx reaction on the supported catalyst like, for example, vanadia on titania [2]. However, under a large excess O_2 condition, the rate of reduction decreases markedly on these kinds of catalytic systems. Therefore, de-NOx from the exhaust gases of diesel engines or lean burn facilities, which involve a large excess O_2, is very important but never solved problems so far [3–7].

Most recently, some studies on the NO decomposition under the conditions of an excess oxygen with low concentration hydrocarbons comparable to NO concentration were reported using zeolitic catalysts such as the H-type zeolite [8], copper-ion-exchanged ZSM-5 [9], and Cu-incorporated zeolites [10], and some metallosilicates [11] which were prepared by the rapid crystallization method [12,13]. In our previous report [10], we found that the close correlation between the NO decomposition and the hydrocarbon combustion under a large excess oxygen condition, but key factors for exhibiting the unusual reaction are still not clear.

In the study, this reaction was investigated using some kinds of metallosilicates which had evidently different properties. As the metal, which was incorporated in the framework of the metallosilicate, the following three classes were selected.

(i) Oxides of the metals which are not easily reducible and exert strong acidities [12], i.e., Al and Ga.

(ii) Oxides of the metals which are partially reducible, i.e., Fe, Mn, and Cr.

(iii) Oxide of the metal which is easily reducible, i.e., Cu.

Protonated Fe-silicate has a fairly strong acidity but weaker than H-ZSM-5 [14]. H-Mn-silicate and H-Cr-silicate have little acidities, and H-Cu-silicate has almost no acidity.

The conversion of NO to N_2 and the combustion of added hydrocarbon (cetane) to CO_2 and CO were measured as a function of the reaction temperature using a flow type reactor. The results were discussed comparing with the characteristics of the metallosilicate catalysts.

2. Experimental

Metallosilicate catalysts were synthesized according to the intrinsic rapid crystallization method [12,13]. As the source of metal, nitrates for Al, Fe, Cr, and Mn, sulfate for Ga, and acetate for Cu were used. The crystals synthesized were heated in air at 550°C for 3.5 h to burn off the organic template, followed by ion-exchange with 1 N NH_4NO_3 solution, and calcined at 550°C in air for 3.5 h. In case of Cr-silicate it was heated in a H_2 flow instead of air to avoid the change of Cr oxide to its higher oxidation states. Contents of metals, expressed as atomic ratio of Si/metal, were 50, 20, 25, 40, 50, and 185 for metallosilicates incorporated with Al, Ga, Fe, Mn, Cr, and Cu, respectively. They were tableted and crushed to 15–24 mesh to provide the reaction.

A 0.7 ml (0.5 g) portion of the catalyst was packed into a quartz tubular reactor of 5 mm inner diameter. The reaction gas containing 1.00 vol% NO, 10.0 vol% O_2, and 1320 ppm cetane (n-$C_{16}H_{34}$) diluted with He was allowed to flow with a space velocity of 2500 h^{-1} at a temperature range from 150 to 600°C with a constant heating rate of 2.5°C/min. NO has a potential to convert N_2, NO_2, and N_2, however, N_2O usually formed only at lower NO conversion condition such as at lower reaction temperature [15,16]. The possibility to form NO_2 at higher temperature condition under coexistence of excess O_2 cannot be eliminated, however, the focus was put in this study on the NO conversion to N_2, therefore, the measurement of NO_2 was omitted for the convenience of the analysis. Many oxidation products of cetane were also possible, especially on the catalysts of H-Al-silicate and H-Ga-silicate, however, to simplify the analysis, only deep oxidation products CO and CO_2 were monitored. Consequently, N_2, O_2, and CO were analyzed by using a TCD-type gas chromatograph, Shimadzu GC 3A-PT equipped with a column MS-5A and an integrator. CO_2 formed was continuously analyzed by an infrared analyzer, Shimadzu URA-106. The conversion of NO was calculated based on the concentration of N_2 formed.

3. Results and discussion

The results of NO to N_2 conversion and cetane to CO and CO_2 conversion are shown in figs. 1–6, as a function of the reaction temperature, for protonated Al-, Ga-, Fe-, Mn-, Cr-, and Cu-silicates, respectively. In each figure open circles show the NO to N_2 conversion, open squares show the sum of CO_2 and CO formation from cetane, and closed squares show CO formation from cetane.

As shown in figs. 1 and 2, H-Al-silicate and H-Ga-silicate exhibited activity for both NO conversion and cetane combustion at above 150°C, and attained their maximum NO conversions, 54% at 350°C and 68% at 550°C, respectively. On these metallosilicates a comparable amount of CO formed besides CO_2, indicating that these kinds of metallosilicate do not have enough combustion activity for cetane. The conversion of NO had a tendency in temperature dependence similar to that of cetane, which is typically shown in fig. 2. H-Ga-silicate has a prominent performance to aromatic rich hydrocarbons. And

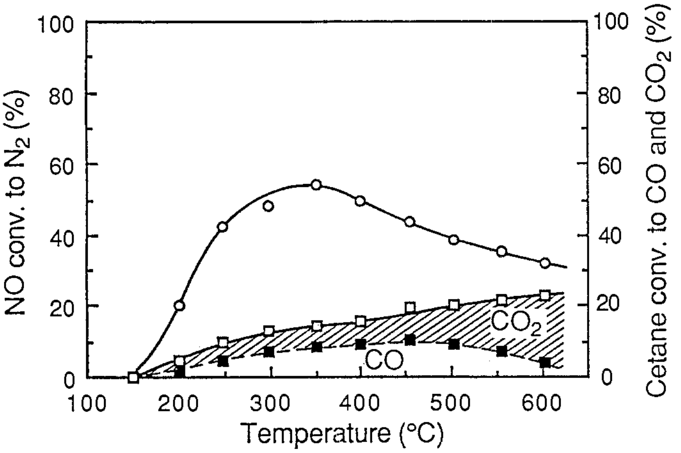

Fig. 1. Effect of temperature on the conversions of NO and cetane on H-Al-silicate. ○: NO conversion to N_2, ■: Cetane conversion to CO, □: Cetane conversion to CO and CO_2, NO 1.0%, O_2 10.0%, Cetane 1320 ppm; SV 2500 h^{-1}.

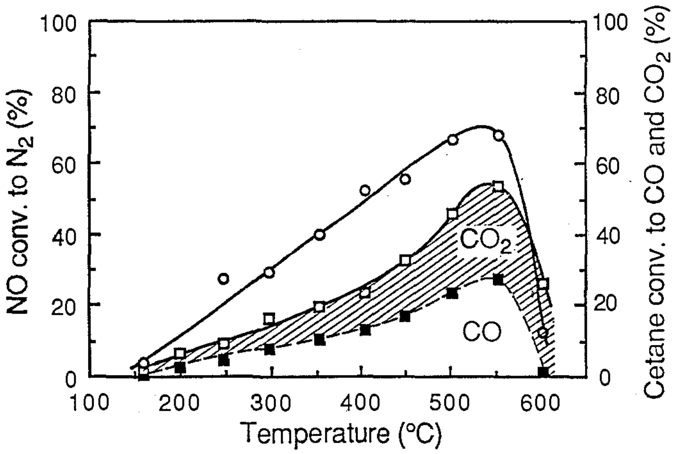

Fig. 2. Effect of temperature on the conversions of NO and cetane on H-Ga-silicate. Conditions and symbols are same as fig. 1.

especially at above 550°C [17], and these products would strongly adsorb on the catalyst surface. This would be the reason for the sharp decreases in both NO conversion and cetane conversion at above 550°C. Cetane conversion at around 470°C–560°C was beyond 100%. This would be attributed to the fact that the accumulated adsorbed intermediate species during the course of the temperature rise combusted at around this temperature range.

As for H-Fe-, H-Mn-, and H-Cr-silicates, as shown in figs. 3–5, the product of cetane combustion was mainly CO_2, except at lower temperature range below 400°C, at which a small amount of CO formed. The peaks of NO conversions showed consistently similar temperature dependence to those of cetane combustion. The peaks of NO conversions were higher than those of H-Al- and

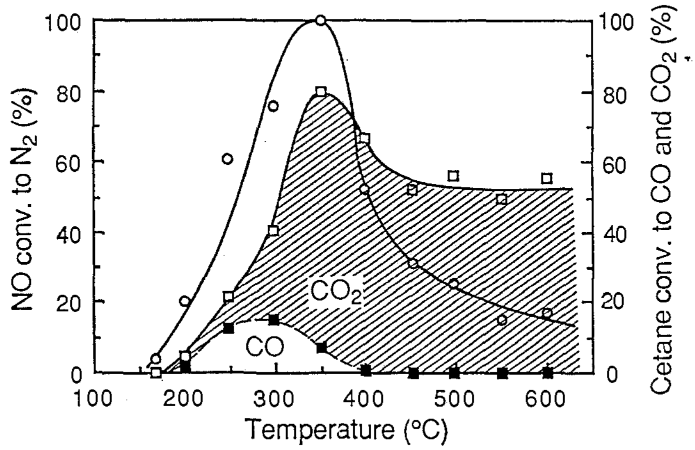

Fig. 3. Effect of temperature on the conversions of NO and cetaine on H-Fe-silicate. Conditions and symbols are same as fig. 1.

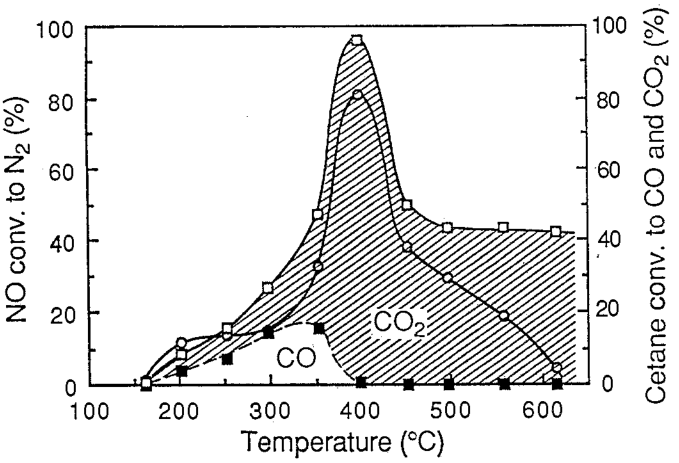

Fig. 4. Effect of temperature on the conversions of NO and cetane on H-Mn-silicate. Conditions and symbols are same as fig. 1.

H-Ga-silicates. The NO conversion in every case decreased with an increase of the reaction temperature at the higher temperature range. This must be attributed to the fact that the surface of the metal oxide part was oxidized more deeply at the higher temperature range. However, the cetane combustion could consistently progress on the oxidized catalyst surface. In every case cetane combustion attained above 100% at the medium temperature range. This would have the same reason mentioned above on the case of H-Ga-silicate.

As for H-Cu-silicate, activities of both NO conversion and cetane combustion were little as shown in fig. 6. However, reflecting the property of the Cu component, the combustion product was almost CO_2 at a whole range of the reaction temperatures. The reaction of the lower activity of H-Cu-silicate than

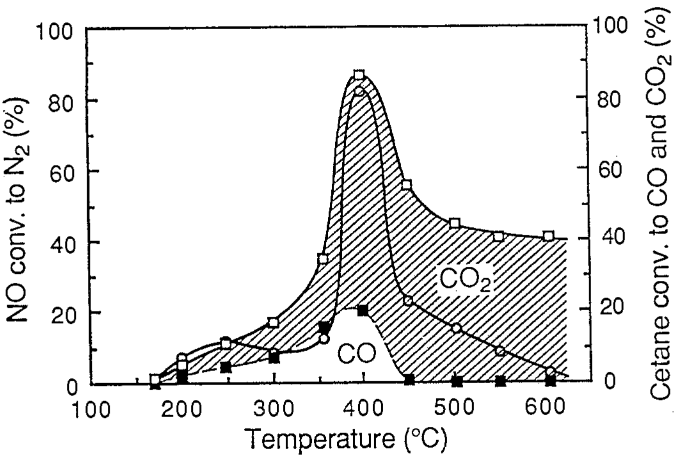

Fig. 5. Effect of temperature on the conversions of NO and cetane on H-Cr-silicate. Conditions and symbols are same as fig. 1.

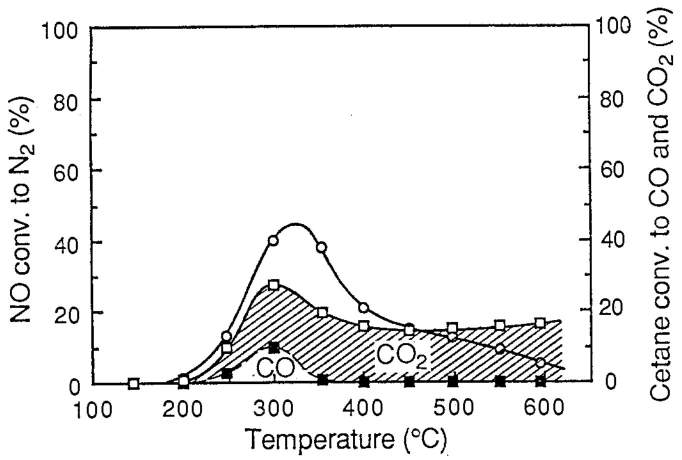

Fig. 6. Effect of temperature on the conversions of NO and cetane on H-Cu-silicate. Conditions and symbols are same as fig. 1.

of other metallosilicates would be that the content of Cu could not be increased. Therefore, the activity was limited to a lower level.

On every catalyst, the temperature dependence of the cetane combustion on metallosilicates approximately coincided with that of the NO conversion. NO conversion exhibited their maximum at the range where the cetane conversion began to increase, and after cetane conversion reached a steady line the NO conversion began to decrease. It seemed that the NO decomposition was accompanied with the combustion of cetane. This consistently agrees with the results on Cu-containing A-type zeolites [10]. We would like to propose a following reaction mechanism which we termed Microscopic Sequential Reaction mechanism, which is different from the conventional Langmuir-Hinshelwood type mechanism,

$$C_xH_y + nO_{ad}[S] \xrightarrow{k_1} C_xH_{yad}(nO_{ad}[S]) \qquad (1\text{-}1)$$

$$C_xH_{yad}(nO_{ad}[S]) + mO_{ad}[S] \xrightarrow{k_2} xCO_2 + (y/2)H_2O + (2x + y/2)[S] + [(n+m) - (2x + y/2)]O_{ad}[S] \qquad (1\text{-}2)$$

$$NO + [S] \underset{k_4}{\overset{k_3}{\rightleftarrows}} NO_{ad}[S] \qquad (2\text{-}1)$$

$$2NO_{ad}[S] \xrightarrow{k_5} N_2 + O_2 + 2[S] \qquad (2\text{-}2)$$

$$2NO_{ad}[S] \xrightarrow{k_6} N_2 + 2O_{ad}[S] \qquad (2\text{-}3)$$

$$O_2 + 2[S] \xrightarrow{k_7} 2O_{ad}[S]. \qquad (3\text{-}1)$$

The orders of acid strength and reducibility of the metal-oxide incorporated into metallosilicates are as follows, expressed with the kind of metal;

$Al \geq Ga > Fe \gg Mn, Cr > Cu$,

and

$$\mathrm{Cu} \gg \mathrm{Cr}, \mathrm{Mn} > \mathrm{Fe} \gg \mathrm{Ga} > \mathrm{Al},$$

respectively. The optimum performance for the NO conversion was thus achieved by the H-Fe-silicate catalyst, which has both a fairly strong acidity and reduction-oxidation (redox) property. The acidity and the redox properties contribute to the cracking of the cetane added and the combustion of hydrocarbons, respectively.

In conclusion, the metallosilicate, which has both properties of acidity and reducibility, is suitable for NO conversion even under coexistence of a large excess oxygen. This kind of bifunctional catalyst would have a high potential for decomposition of NO in exhaust gases from diesel engine and lean burn facilities.

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