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Evidently advantageous features of metallosilicates as the catalysts for elimination of NO in the exhaust gases containing a large excess of O_2 and H_2O

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Abstract

Effects of high temperature calcination of ion-exchanged H-ZSM-5 (Me/H-ZSM-5) and metallosilicates having MFI structure in air with and without steam on the BET-surface area and NO conversion were examined. Metallosilicates were much more stable than Me/H-ZSM-5 in both BET-surface area and catalytic performance of NO conversion in the presence of excess O_2 and a low concentration of hydrocarbons. Furthermore, in case of H-Co-silicate, catalytic properties of both hydrocarbon combustion and NO conversion were significantly increased by a high temperature calcination in air stream including steam. The reason is that Co incorporated in the framework was partly but uniformly educed by the calcination, especially with co-existence of steam, and exhibited higher catalytic activity.

Keywords: Metallosilicate; Co-silicate; Thermal stability; NO conversion

1. Introduction

Since it was found several years ago that NO can be reduced into N_2 by the addition of a low concentration of an appropriate hydrocarbon or methanol even under the condition of co-existence of O_2 [1–3], numerous studies have been done. However, the stability of the catalyst against a high temperature condition, especially with steam, remains as an impediment.

Cu/H-ZSM-5 is well known as a typically effective catalyst for de-NO_x reaction even in the presence of excess O_2 [4,5]; however, it is often pointed out that this catalyst easily deteriorates under the conditions of practical use or its equivalent reaction condition [6–8].

On the other hand, Armor et al. have reported that Co/H-ZSM-5 exhibits a significant stability [9], but reason for the stability has not been elucidated. We have already reported that the catalytic activity of H-Cu-silicate is apparently lower but its thermal stability is higher than those of Cu/ZSM-5 [10–12]. The unique and excellent performance of H-Co-silicate has also been reported as the mostly appropriate catalyst for NO elimination at around 400°C and in the presence of relatively easily combustible hydrocarbons such as propylene, *n*-octane and cetane (*n*-$C_{16}H_{34}$) [10,13]. It is noteworthy that this catalyst is largely insensitive to the existence of water vapor up to 10 vol%, and even SO_2 up to 250 ppm during the NO elimination reaction [14].

To obtain more concrete information regarding the thermal stability of H-Co-silicate, the effect of high

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temperature calcination in air with and without steam on the BET-surface area and the catalytic performances has been investigated and the results compared with those for Cu/H-ZSM-5, Co/H-ZSM-5, and metallosilicates having MFI structure. The reasons for the differences in the stability of these catalysts are discussed.

2. Experimental

2.1. *Catalyst preparation*

Metallosilicates of MFI type were prepared by the rapid crystallization method [15]. As-synthesized crystallites were washed, dried, and heated at 540°C for 3.5 h in air to remove the organic template occluded in the crystallites. They were then ion-exchanged twice with an NH_4NO_3 aqueous solution at 80°C for 1 h under the condition of continuous stirring by a magnetic stirrer, and were washed, dried, and heated again at 540°C for 3.5 h in air to prepare the protonated form. They are designated as H-Me-silicate (Me = Al, Co, Mn, or Fe). In case of Me = Al, H-Al-silicate is the same as H-ZSM-5. The charged atomic ratio of Si/Me was set at 40. The chemical compositions of the catalysts were determined by means of ICP. Except Co case, the metal ions could be incorporated into the framework approx. 87% of ions charged, however, in case of Co, 1/7 ions charged were incorporated.

Metal-ion exchanged H-ZSM-5s were prepared by ion exchange using metal acetate aqueous solution for H-ZSM-5 mentioned above. They are designated as Me/H-ZSM-5 (Me = Cu or Co). Degrees of ion-exchange determined by ICP measurement were 103% and 53% for Cu and Co, respectively. The crystallites were tabletted, crushed, and then sieved to 12–24 mesh. Thus prepared catalysts were provided to the tests of thermal or hydrothermal stability and de-NO_x reactions.

2.2. *High temperature treatments with and without steam*

The catalysts were heated with a constant heating rate of 2.5°C/min up to 800 or 1000°C, and they were maintained at each temperature for 2 h in a stream of air with or without 10 vol% of H_2O. The BET-surface area of the catalyst samples before and after the calcination was measured.

2.3. *Reaction test*

The performance of the catalysts before and after the high-temperature treatments was examined using an ordinary flow type reactor under atmospheric pressure. Two sets of reaction gas composed of 1000 ppm NO, 1000 ppm C_3H_6, 5.0% O_2, and N_2, and 1000 ppm NO, 1000 ppm n-C_8H_{18} (n-octane), 10.0% O_2 and N_2 were used, with a space velocity (SV) of 30 000 h^{-1}. The effect of reaction temperature on the catalytic performance was measured at a temperature ranging from 200 to 600°C. The reaction gas and products were analyzed by a chemiluminescence NO_x analyzer (Shimadzu NOA-305A) for NO, an infrared gas analyzer for CO and CO_2 (Shimadzu CGT-7000), and gas chromatographs equipped with integrators for other products.

3. Results and discussion

3.1. *Effect of the high temperature calcination on the BET-surface area of catalysts*

The effect of calcination on the BET-surface area is summarized in Table 1. By the 1000°C calcination in air even without steam, Cu/H-ZSM-5 showed the most evident decrease of the BET-surface area (168 m^2/g). H-ZSM-5 (i.e., H-Al-silicate), which was the same lot for the Cu ion exchange, showed a considerably low degree of the decrease (32 m^2/g) by the same calcination. Therefore, in addition to the decrease of BET-surface area owing to the dealumination, the main cause of the decrease in the BET-surface area of Cu/H-ZSM-5 is ascribed to the existence of Cu.

The ion-exchanged Cu is exposed in micropore channels of ZSM-5 [16], and easily moves and sinters because of its low melting point (1083°C), resulting in the acceleration of destroying the silicate framework and transforming into quartz phase. This phenomenon is quite similar to the well-known fact that with co-existence of a small amount of alkaline metal oxide such as Na oxide, silica gel is very easily change into

Table 1
Change in BET-surface area of catalyst (m^2/g) by high-temperature calcination in air with and without steam

Catalyst	Calcination conditions			BET-surface area reduced (m^2/g)
	540°C, 3 h	800°C, 3 h	1000°C, 2 h	
Cu/H-ZSM-5	343		179	168
Co/H-ZSM-5	333		208	125
		306[a]		27
H-Al-silicate	353		321	32
H-Co-silicate	363	344[a]	361	2
				19
			330[a]	33
H-Mn-silicate	367		356	11
H-Fe-silicate	371		357	14

[a] H_2O 10%, air 90%.

quartz phase with diminishing pores at considerably lower temperature range around 750–800°C. This was reconfirmed by the observation that Na-ZSM-5 markedly decreases its BET-surface area by a high temperature calcination.

The decrease in BET-surface of Co/ZSM-5 (125 m^2/g) was smaller than that of Cu/H-ZSM-5, however, still much larger than that of H-Al-silicate. The difference between Cu/ZSM-5 and Co/H-ZSM-5, might be ascribed to the large difference of the melting point, therefore, surface diffusivity.

On the other hand, in general, the decrease in BET-surface area of metallosilicates were much lower than those of ion-exchanged ones. In particular, in case of H-Co-silicate, almost no difference (merely 2 m^2/g) was observed, and even co-existence of steam, it showed a considerably high resistance. Largely different from H-Al-silicate, H-Co-silicate has a very weak acidity [17], and therefore, the adsorption capacity of H_2O must be very small resulting in the high resistance against hydrothermal circumstance.

3.2. *Effect of the high temperature calcination in dry air on the catalytic performance*

Catalytic reaction for NO conversion was carried out on the catalysts before and after calcination at 1000°C for 2 h in dry air. Results are shown in Figs. 1–3 for Cu/H-ZSM-5, Co/ZSM-5 and H-Co-silicate, respectively. Propylene was used as the hydrocarbon added into the reaction gas.

As shown in Fig. 1a, by the calcination, the activity of C_3H_6 combustion decreased markedly, which can

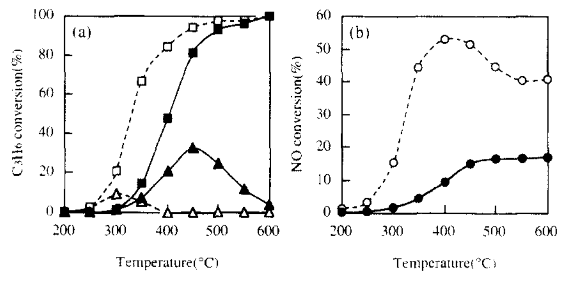

Fig. 1. Change in the activity for C_3H_6 combustion and NO conversion of a Cu/H-ZSM-5 by 1000°C calcination in air. (a) C_3H_6 combustion. Squares, C_3H_6 conversion to $CO+CO_2$; triangles, C_3H_6 conversion to CO. Open symbols, calcined at 540°C for 3.5 h; closed symbols, calcined at 1000°C for 2 h in air. Feed gas NO 1000 ppm, C_3H_6 1000 ppm, O_2 5.0%, N_2 balance, SV 30 000 h^{-1}.

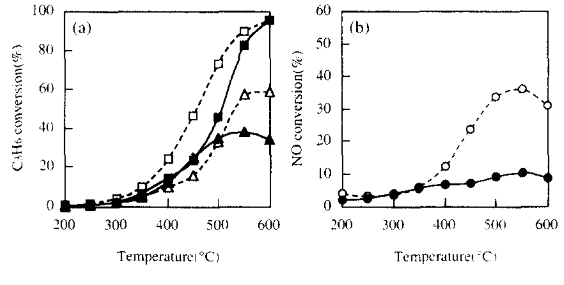

Fig. 2. Change in the activity for C_3H_6 combustion and NO conversion of a Co/H-ZSM-5 by 1000°C calcination in air. (a) C_3H_6 combustion. Squares, C_3H_6 conversion to $CO+CO_2$; triangles, C_3H_6 conversion to CO. Open symbols, calcined at 540°C for 3.5 h; closed symbols, calcined at 1000°C for 2 h in air. Feed gas NO 1000 ppm, C_3H_6 1000 ppm, O_2 5.0%, N_2 balance, SV 30 000 h^{-1}.

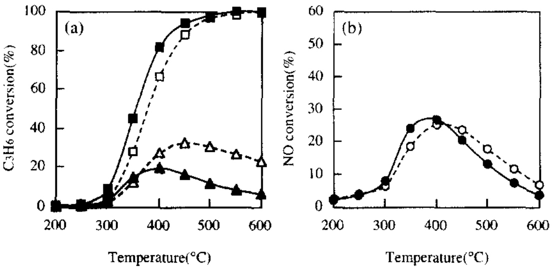

Fig. 3. Change in the activity for C_3H_6 combustion and NO conversion of a H-Co-silicate by 1000°C calcination in air. (a) C_3H_6 combustion. Squares, C_3H_6 conversion to $CO+CO_2$, triangles, C_3H_6 conversion to CO. Open symbols, calcined at 540°C for 3.5 h; closed symbols, calcined at 1000°C for 2 h in air. Feed gas NO 1000 ppm, C_3H_6 1000 ppm, O_2 5.0%, N_2 balance, SV 30 000 h^{-1}.

be estimated by both the shift of temperature dependence of combustion activity to higher temperature range and marked decrease of conversion to a partial oxidation product, CO. Reflecting the decrease in the activity of C_3H_6 combustion, NO conversion decreased very much.

The activity of propylene combustion on Co/H-ZSM-5 (Fig. 2a) was much lower than Cu/H-ZSM-5 and the effect of temperature was very insensible, however, the effect of the high temperature calcination was quite similar to each other, i.e., decrease in the combustion activity and increase in the conversion to CO. The trend of NO conversion as a function of temperature (Fig. 2b) was the same as the trend as mentioned above on the propylene combustion.

As for the H-Co-silicate catalyst before calcination, the activity of propylene combustion (Fig. 3a) was equivalent to that of Cu/H-ZSM-5, and much higher than that of Co/H-ZSM-5. It is noteworthy that although the content of Co in H-Co-silicate is about 1/3.5 of that in Co/H-ZSM-5, the activity is higher, indicating that the activity based on Co oxide component is more effectively dispersed than in Co/H-ZSM-5, due to the incorporation into the framework of MFI-type silicate matrix. The activity of NO conversion on H-Co-silicate, is about a half of that on Cu/H-ZSM-5, however, it exhibited at much lower temperature range than that of Co/H-ZSM-5, which is the general tendency that the NO conversion synchronized with the hydrocarbon combustion up to a medium temperature range, and above that temperature, the hydrocarbon combustion increases furthermore but the NO conversion decreases with the increase of the reaction temperature.

On the contrary of the tendency observed in an ion-exchanged H-ZSM-5s, in the case of H-Co-silicate, both the combustion activity and NO conversion rather increased by the high temperature calcination. The reason for this favorable change is considered as that a part of Co ingredient incorporated in the framework is educed by the calcination, however, the amount of educed Co ingredient is very small and located uniformly and isolated form each other, and as a result they exhibit a very high thermal resistance.

3.3. *Effect of the high temperature calcination in a steam-containing air on the catalytic performance*

Calcination at 800°C for 2 h was conducted for Co/H-ZSM-5 and H-Co-silicate in a 10% H_2O vapor-containing air, and the effect on the catalytic performance before and after the calcination was compared by using the same reaction gas as used in the above. The results are shown in Figs. 4 and 5, respectively.

In case of Co/H-ZSM-5, compared with the result shown in Fig. 2, the decrease in the activity of propylene combustion becomes more evident, although the effect of NO conversion was almost similar. On the contrary, as for H-Co-silicate, the activity of propylene combustion slightly decreased, however, NO conversion was rather increased at somewhat higher temperature range.

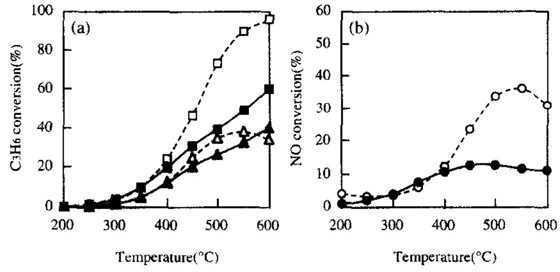

Fig. 4. Change in the activity for C_3H_6 combustion and NO conversion of a Co/H-ZSM-5 by 800°C calcination in steam-containing air. (a) C_3H_6 combustion. Squares, C_3H_6 conversion to $CO+CO_2$; triangles, C_3H_6 conversion to CO. Open symbols, calcined at 540°C for 3.5 h; closed symbols, calcined at 800°C for 2 h in 10% steam-containing air. Feed gas NO 1000 ppm, C_3H_6 1000 ppm, O_2 5.0%, N_2 balance, SV 30 000 h^{-1}.

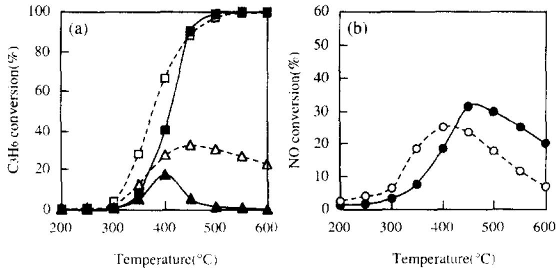

Fig. 5. Change in the activity for C_3H_6 combustion and NO conversion of a H-Co-silicate by 800°C calcination in steam-containing air. (a) C_3H_6 combustion. Square symbols, C_3H_6 conversion to CO + CO_2; triangles, C_3H_6 conversion to CO. Open symbols, calcined at 540°C for 3.5 h; closed symbols, calcined at 800°C for 2 h in 10% steam-containing air. Feed gas NO 1000 ppm, C_3H_6 1000 ppm, O_2 5.0%, N_2 balance, SV 30 000 h^{-1}.

In order to reconfirm the favorable effect of the high-temperature calcination on the catalytic performance of H-Co-silicate, the comparison was made in the more oxygen-rich reaction gas condition with the use of *n*-octane instead of propylene as the kind of hydrocarbon added, because in our previous study, the optimal performance was obtained by this gas on H-Co-silicate [11,15]. The results are shown in Figs. 6 and 7. Indeed, even on Co/H-ZSM-5 (Fig. 6), both the combustion activity and NO conversion were larger than those in the former gas condition, in which propylene was used as the added hydrocarbon, however, the effect of calcination with steam was principally same as the calcination without steam. Fig. 7a and b show the case of H-Co-silicate more evidently than the case of Fig. 5a and b, the activity of *n*-octane combustion and NO conversion were markedly enhanced by the calcination. These facts consistently support the discussion described for the result shown in Figs. 3 and 5.

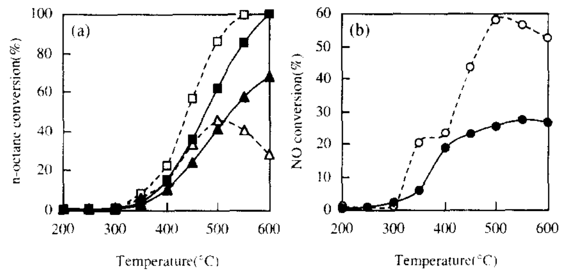

Fig. 6. Change in the activity for *n*-octane combustion and NO conversion of a Co/H-ZSM-5 by 800°C calcination in steam-containing air. (a) *n*-octane combustion. Squares, *n*-octane conversion to CO + CO_2; triangles, *n*-octane conversion to CO. Open symbols, calcined at 540°C for 3.5 h; closed symbols, calcined at 800°C for 2 h in 10% steam-containing air. Feed gas NO 1000 ppm, *n*-octane 1000 ppm, O_2 10.0%, N_2 balance, SV 30 000 h^{-1}.

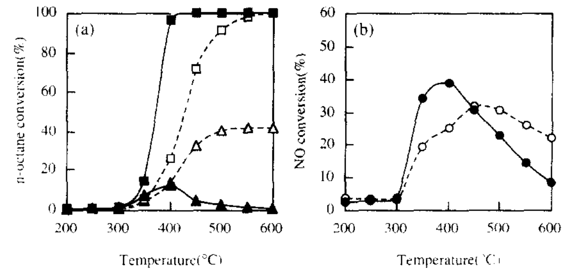

Fig. 7. Change in the activity for *n*-octane combustion and NO conversion of a H-Co-silicate by 800°C calcination in steam-containing air. (a) *n*-octane combustion. Squares, *n*-octane conversion to CO + CO_2; triangles, *n*-octane conversion to CO. Open symbols, calcined at 540°C for 3.5 h; closed symbols, calcined at 800°C for 2 h in 10% steam-containing air. Feed gas NO 1000 ppm, *n*-octane 1000 ppm, O_2 10.0%, N_2 balance, SV 30 000 h^{-1}.

Results shown in Figs. 1–7 are summarized numerically in Table 2, expressing the maximum NO conversion and the corresponding reaction temperature. As a result, the maximum NO conversion on the catalyst calcined at 1000°C for 2 h in steam-involved air was obtained by H-Co-silicate.

4. Conclusions

Thermal stability is recognized as the following order:

$$\mathrm{H-Co-silicate} \gg \mathrm{Co/H}$$
$$\mathrm{-ZSM-5} \gg \mathrm{Cu/H-ZSM-5.}$$

High temperature calcination up to 800°C in H_2O vapor involved air enhances the catalytic activity of H-Co-silicate but reduced that of Co/H-ZSM-5.

Metal oxide dispersed on the zeolitic matrix by an ion-exchange method easily sintered by a high temperature calcination, on the other hand, a part of metal incorporated into the MFI-silicate is educed from the framework uniformly but isolated by the same calcination, resulting the marked increase in the catalytic activity without occurrence of sintering.

Table 2
Maximum NO conversion obtained on various catalysts before and after high-temperature calcination with and without steam

Catalyst	Calcinated conditions			Max. NO conv. (%) (at the corresponding temp. (°C)	
	Temperature (°C)	Duration (h)	Atmosphere	Hydrocarbon added	
				C_3H_6 [a]	*n*-octane [b]
Cu/H-ZSM-5	540	3.5	air	53 (405)	—
	1000	2	air	16 (530)	—
Co/H-ZSM-5	540	3.5	air	37 (530)	58 (510)
	1000	2	air	11 (560)	—
	800	2	10% H_2O-air	13 (500)	27 (550)
H-Co-silicate	540	3.5	air	25 (410)	32 (450)
	1000	2	air	27 (380)	—
	800	2	10% H_2O-air	32 (460)	42 (370)

[a] NO 1000 ppm, C_3H_6 1000 ppm, O_2 5.0%, N_2 balance, SV 30000 h^{-1}.
[b] NO 1000 ppm, *n*-octane 1000 ppm, O_2 10.0%, N_2 balance, SV 30000 h^{-1}.

Acknowledgements

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